Ultrafast excited–state dynamics of radical ions in liquid solution

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Abstract
The spectral and dynamic features of photoexcited radical ions have been studied by ultrafast spectroscopy. The excited state absorption spectrum, lifetimes and the influence of parameters like excess excitation energy, solvent or temperature on the photophysical behavior has been investigated for a series of chemically distinct systems chosen such as to span a range of chemical diversity, excited state energies (1 to 2 eV) and oxidation state (cationic or anionic). The radical ions have been generated either chemically or electrochemically in a home-built flow cell. The results reveal that the lifetime of the lowest electronic excited state, D1, is on the order of picoseconds only. Wurster’s salts, for example, have a D1 lifetime of 0.2 ps at room temperature irrespective of solvent and nitrogen substituent but influenced by temperature and, thus, fluorescence can be detected below 120 K. By contrast, temperature does not play a role for perylene radical cation whereas the solvent does. In general, the data clearly shows that the energy gap law, often invoked to explain the lack of fluorescence of radical ions, is not [...]
Ultrafast Excited-State Dynamics of Radical Ions in Liquid Solution

THÈSE
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In the evening Ambanelli would stop working and go sit in front of the house with the owner’s son because he wanted to learn to read and write.

“Let’s start with the alphabet”, said the boy who was eleven years old.

“Let’s start with the alphabet”.

“First you have A.”

“A”, said Ambanelli patiently.

“Then B.”

“Why does one come first and then the next one?” asked Ambanelli.

The owner’s son didn’t know why.

“They just put them in that order, but you can use them in whatever order you want.”

“I don’t understand why they put them in that order”, said Ambanelli.

“It’s easier”, replied the boy.

“I’d like to know whose job this was.”

“That’s how the alphabet is.”

“It doesn’t mean, then”, said Ambanelli, “that if I say B comes first and then A, anything changes?”

“No”, said the young lad.

“Right. Keep going, so.”

“Then you have C which you can pronounce in two different ways.”

“Whoever made this up must have had time to lose.”

The boy didn’t know what to say to this.

[...]

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Part I.

Introduction
1. Preface

This work is dedicated to the photophysics of radical ions in liquid solution at ambient temperature. The spectral features and dynamics have been measured using mainly transient absorption spectroscopy with femtosecond time-resolution. Such a high time-resolution, available only recently, proved to be necessary to follow the relaxation process for all the radicals studied during this work, independent of molecular structure, excited-state energy and charge.

Radicals have been the subject of many studies owing to their participation in numerous fields of chemistry,[2–4] physics,[5] biology[6,7] and technology.[8,9] Nonetheless, their excited state dynamics in liquid solution is still a largely unexplored field.

Our interest arises from the still unexplained discrepancy between the results of the seminal work by Weller and co-workers[10,11] and Marcus theory of electron transfer (ET).[12–14] The main hypotheses that have been proposed to account for this discord between experiment and theory in the case of bimolecular charge separation are the involvement of electronic excited product states, and long-range electron transfer. Despite considerable effort, there is no prove for either of them to date.

The Rehm–Weller experiment. Having evidenced that ET is an operative fluorescence quenching mechanism,[15] and having derived an equation to calculate the driving force of such a photoinduced ET, Weller and co-workers were able to experimentally access the so-called Marcus inverted region (MIR) where the rate constant for electron transfer, $k_{ET}$, had been predicted to decrease with increasing exergonicity of the reaction. The measured $k_{ET}$ did not follow the Marcus parabola (Figure 1.1) but ET remained diffusion limited instead, even at the lowest $\Delta G^0$ values attained.

Until today, no convincing observation of the MIR was published for an intermolecular charge separation reaction. Explicit observation of the MIR, on the other hand, has been published for the case of intramolecular charge recombination,[18–23] and intermolecular charge shift,[24] and intramolecular charge separation reactions.[25] This means that all but photoinduced, bimolecular charge separation reactions obey the theoretical model.

Long range electron transfer. The rate equation for electron transfer by Marcus[12,13] (eq. 1.1)$^2$ comprises two terms that depend on the distance between the reaction partners, the reorganisation energy $\lambda(r)$ and the electronic coupling $V(r)$. The distance dependence of

$^1\Delta G^0 = -E_{00} + \epsilon(E_{ox}(D) - E_{red}(A)) + C$

with the chromophore’s excitation energy $E_{00}$, the redox potential of electron donor D and acceptor A, and the Coulombic force term $C$.[16]

$^2$Containing the Boltzmann constant $k_B$, the temperature $T$, the vacuum permittivity $\epsilon$, the index of refraction $n_D$, the medium’s dielectric constant $\epsilon(0)$, and the reorganisation energy $\lambda$ which has intermolecular and solvent contributions, $\lambda_i$ and $\lambda_s$. 


Figure 1.1.: Fluorescence quenching rate constant as a function of the free energy. The experimental data by A. Rehm and D. Weller do not follow the predictions of classical Marcus theory (dashed line).[^11]

the former in the dielectric continuum model is given as $-1/r$ (eq. 1.2), the latter decreases exponentially with $r$ (eq. 1.3).

$$k_{ET} = \sqrt{\frac{\pi}{h^2 k_B T \lambda(r)}} V(r)^2 \exp \left\{ - \frac{(\Delta G^o - \lambda(r))^2}{4 k_B T \lambda(r)} \right\}$$ (1.1)

$$\lambda_s(r) = \lambda_i + \frac{e^2}{4 \pi \varepsilon} \left( \frac{1}{2a_D} + \frac{1}{2a_A} - \frac{1}{r} \right) \left( \frac{1}{n^2} + \frac{1}{\varepsilon(0)} \right)$$ (1.2)

$$V(r) = V(r_0) \cdot \exp \left\{ -\beta \frac{r - r_0}{2} \right\}$$ (1.3)

In the Marcus model, the maximum rate constant $k_{ET}$ is obtained when the free energy of the reaction is equal to $\lambda(r)$. As $\lambda(r)$ is an increasing function of the distance $r$, this condition is met at higher separation distances for more exergonic reactions, making the ET more and more remote as $\Delta G^o$ decreases. This effect, however, is counterbalanced by the exponential decrease of $V(r)$. In order to explain the data measured by Rehm and Weller, unreasonably high values for the coupling at contact distance, $V(r_0)$, have to be assumed.[^26]

The allowance of the distance dependence of $V$ and $\lambda$ is thus not sufficient to explain the lack of the MIR. From the list given above, it is evident that all systems, for which the MIR was observed, constitute particular situations in what concerns diffusion: intramolecular ET happens without diffusion, “intermolecular” charge recombination takes place within ion pairs with restricted diffusion, and the intermolecular charge shift observed by Guldi et al. benefited from the huge diffusional rate constant and the small $\lambda$ of the system chosen.
For the intramolecular case, recent progress showed that long–range ET is dominated by the exponential decay of $k_{\text{ET}}$ with $r$.\[27–30\] These studies showed furthermore that the attenuation factor ($\beta$ in eq. 1.3) is very sensitive to the conformation of the subunits that form the bridge\[29,31\] and can even lead to non-exponential distance dependence.\[27\] The $\beta$ factors for non–linked systems are so high\[32\] that remote bimolecular ET seems questionable, at least at the distances suggested by some authors.\[33\]

More reasonable values are obtained with new models for diffusion assisted reactions, which are able to explain even intricacies of the Marcus “parabola”.\[34,35\] The encounter theories\[36\] and similar models\[33,37–40\] combined with a distant dependent rate constant between the two reactants proved to be very powerful to reproduce both, charge separation and charge recombination reactions.\[34,35,41–44\] The involved data analysis and the entanglement of the parameters are drawbacks.

According to these models, highly exergonic charge separation yields two ions at remote distance, and hence charge recombination should be relatively slow. The opposite was observed for the pair perylene/tetracyanoethylene for which $\Delta G_{\text{CS}} = -2.2 \text{ eV}$ and $\Delta G_{\text{CR}} = -0.6 \text{ eV}$.\[45\] In fact, the coupling in this donor/acceptor pair was found to be so large that charge recombination occurs before the ion pair has reached equilibrium.\[46\] This is in strong disfavour of the hypothesis that electron transfer at high exergonicity leads only to remote ion pairs.

**Participation of electronic excited states.** The second hypothesis assumes the population of electronic excited states in highly exergonic ET. Figure 1.2 suggests that the lowest lying excited states of radicals are energetically accessible in the ET and the corresponding $\Delta G^\circ$ is such that the reaction is essentially barrierless, hence ultrafast.

ET to excited states was evidenced in the case of charge recombination reactions\[47–49\] and there is no evident reason why they should not participate in charge separation. Attempts to observe them with transient absorption spectroscopy, however, remained unsuccessful.\[50\] From ion yield measurements, Kikuchi et al.\[51\] argued that the ET from anthracene carboxonitriles to aminobenzenes has to occur via the radical ion’s excited state.

If the radicals are generated in an electronic excited state, the absorption of the excited state has to be small and its lifetime short so that they passed undetected. Reports published so
far and the general lack of fluorescence point towards such a fact but a comprehensive study of the excited state of radical ions in liquid r.t. solution is not available to date.

The aim of this thesis is to shed some light on the excited-state dynamics of radical ions in r.t. liquid solution. To examine their dynamics and excited state absorption spectra, their properties and behaviour under the conditions encountered in bimolecular ET studies. To this end, two ways were chosen to generate them: chemical synthesis or electrochemical in-line generation, depending on the stability of the radical ion. These two methods are considered the most versatile ones. Photoinduced generation, which has been performed in our lab earlier, is hampered by severe restrictions (namely ultrafast quenching, non–zero ion yield and suitable absorption spectra) and proved to show complex, time dependent ion–pairing effects.\textsuperscript{52} Such difficulties are not to be expected with chemical or electrochemical generation, instead, the effect of the counter–ion’s nature can be studied easily.

The structure of the text is as follows: First the basics of photophysical processes will be briefly reviewed and special attention will be paid to the peculiarities of radical ions and to non–radiative transitions which proved to be of special importance to their photophysics. Then the results for the different systems investigated will be presented after a summary of their properties known from literature. Each system is discussed separately. A general discussion in chapter 9 will point out the similarities and common findings for all the systems investigated. The description of the electrochemical flow cell used to generate some of the radical ions, experimental set–ups and data treatment are given in part 11. A list of abbreviations is given on page 211.
2. A Gallop Through Photophysics

In this chapter, a vibronically excited molecule’s fate is described in order introduce the terms and equations used in the discussion and to understand the stages of relaxation that can be observed with ultrafast spectroscopy — where Kasha’s and Vavilov’s rules\[^{53,54}\] are only the limiting case of long–time behaviour. In condensed phase the observed dynamics are strongly related to the surrounding medium, i.e. the solvent with which the molecule interacts in a specific (e.g. hydrogen bonds) or non–specific way (e.g. heat dissipation to the “bath”) and these processes shall be described briefly. No attempts are made to be exhaustive, the reader is referred to references \[^{54–56}\] and \[^{57}\] for a derivation.

There are some peculiarities when passing from closed– to open–shell systems that will be brought out in some detail in chapter 3.

2.1. Basic photophysical processes

2.1.1. Absorption of light

Light can be described either as particle (a photon) or as wave. In the latter description it consists of an electromagnetic field propagating in space with the electric and magnetic field vectors perpendicular to the propagation direction and to each other. For the case of a one–dimensional harmonic wave propagating in x–direction, the wave equation is described by eq. 2.1.\(^1\)

\[
E(x, t) = A \sin(kx - \omega t) = 1/2 E_0 e^{i(kx - \omega t)} + 1/2 E_0^* e^{-i(kx - \omega t)}
\] (2.1)

Upon interaction with this electromagnetic field, a molecule can be promoted from state 1 to state 2, this means it is excited to a state of higher energy, an excited state. Depending on the energy of the light \((E = h\nu)\) this might be, among others, a vibrational or electronic excited state. Vibrational excitation is achieved by infra–red light (IR). There are \(N = 3N - 6\) (where \(N\) is the number of atoms in the molecule) vibrational modes in a non–linear molecule. Electronic excitation takes place upon irradiation with visible and UV light, except for low–lying electronic excited states.

Absorption occurs only if the electric field of the light can interact with a transient molecular charge or current distribution characterised by the transition dipole moment \(\vec{M}\)

\(^1\)The magnetic component of light can be neglected for the purpose discussed here since interactions with it are approximately \(10^5\) times smaller than those with the electric field and even less important are higher multipoles.\[^{54}\] \(A\) is the amplitude, \((kx - \omega t)\) the phase, \(k = 2\pi/\lambda\) the wave vector, \(\omega = 2\pi\nu\) the circular frequency, \(t\) the time, \(\lambda = c/\nu\) the wavelength, and \(c\) the speed of light. \(E_0 = A/i\) is the complex amplitude and \(E_0^*\) its complex conjugate.
\[ M = \langle \Psi_1 | \hat{\mu} | \Psi_2 \rangle = \langle \theta_1 \theta_2 \rangle \langle \Phi_1 | \hat{\mu} | \Phi_2 \rangle \] 

(2.2)

with the dipole moment operator

\[ \hat{\mu} = e \cdot \hat{r} \] 

(2.3)

In eq. 2.2, the vibrational \( \theta \) and electronic \( \Phi \) wavefunction have been separated. The square of the integral \( \langle \theta_1 \theta_2 \rangle \) is called the Franck–Condon (FC) factor and is a measure of the overlap of the vibrational wavefunctions of initial and final state at the geometry of the initial state.\([54,55,57]\) The separation can be rationalised within the Born–Oppenheimer approximation and is expressed as the FC principle that states that electronic transitions are “vertical”, i.e. they happen without geometrical changes in the molecule. In a similar fashion an electron transfer reaction can be seen as “horizontal”, meaning that it happens at constant energy with only the vibrational part of the wavefunction changing.\([58]\)

The probability of the transition \( 2 \leftarrow 1 \) is governed by the Einstein coefficient for induced absorption \( B_{12} \) which is identical to \( B_{21} \), the Einstein coefficient for induced \( 2 \rightarrow 1 \) emission. Another measure for the probability of a transition is the oscillator strength \( f \) which is related to \( M \) and \( B_{12} \) and to the absorption spectrum \( \varepsilon(\tilde{\nu}) \) in the following way:\(^2\)

\[ B_{12} = \frac{2\pi}{3\hbar^2} |\langle \Psi_1 | M | \Psi_2 \rangle|^2 \] 

(2.4)

\[ f = \frac{m_e h \nu}{\pi e^2} B_{12} \] 

(2.5)

\[ k_{\text{rad}} = \frac{8\pi h \nu^3}{c^3} \cdot f_L \cdot B_{12} \] 

(2.6)

\[ = \frac{24\pi^2 \varepsilon \nu^2}{N_A e^2 c^3} \ln(10) \cdot f_L \cdot \int \varepsilon(\tilde{\nu})d\tilde{\nu} \] 

(2.7)

\[ \approx 10^4 \cdot \varepsilon_{\text{max}}^{\text{max}} \] 

(2.8)

with the Lorentz factor

\[ f_L = \left( \frac{n_D^2 + 2}{3} \right)^2 n_D \] 

(2.9)

By virtue of these equations, the radiative (also called intrinsic) rate constant \( k_{\text{rad}} \) is experimentally accessible. The rather crude approximation eq. 2.8, which relates \( k_{\text{rad}} \) to the maximum of the molar absorptivity, \( \varepsilon_{\text{max}} \),\(^3\) assumes a transition in the UV or visible part of the electromagnetic spectrum with an “ordinary” width of 3000 cm\(^{-1}\).\([60]\)

Several photophysical processes take place after electronic excitation as depicted in the Jablonski diagram in Figure 2.1. Light is emitted as fluorescence or phosphorescence; internal

\(^2\)\(m_e \) and \( e \) are the mass and charge of the electron, \( h \) Planck’s constant, \( \hbar = h/2\pi \), \( N_A \) Avogadro’s constant, \( \nu \) the central frequency of the transition, \( n_D \) the index of refraction, \( \epsilon \) the vacuum permittivity. The numeric factors take into consideration the usual unit of \( \varepsilon \).\([54,55]\)

\(^3\)Formerly called decadic molar extinction coefficient.\([59]\)
Figure 2.1.: Jablonski diagram for a closed–shell molecule. Adapted from Ref. [56].
conversion (IC) and intersystem crossing (ISC) cause a change of the electronic wavefunction; vibrational relaxation (VER) distributes the vibrational energy and dissipates it to the environment. Not shown in Figure 2.1 are solvent relaxation, quenching or other photochemical reactions feasible on the excited state potential energy surface (PES).

### 2.1.2. Fluorescence

A molecule in an electronic excited state emits light. This is due to the coupling of the excited state \( \Psi_2 \) with the ground state \( \Psi_1 \) via the electronic transition dipole moment in analogy with absorption. The overall emission efficiency, the fluorescence quantum yield \( \Phi_{flr} \), is determined by the ratio of \( k_{\text{rad}} \) and the sum of the rate constants of all processes depopulating this state (equation 2.10; quenching and photoinduced reactions are neglected). As a rule of thumb, one can identify fluorescence and ISC as the main deactivation pathways of \( S_1 \) for most aromatic organic molecules.\(^{[54,56]} \)

\[
\Phi = \frac{k_{\text{rad}}}{k_{\text{rad}} + k_{\text{IC}} + k_{\text{ISC}}} = \frac{\tau_{\text{flr}}}{\tau_{\text{rad}}} \tag{2.10}
\]

The excited state lifetime \( \tau_{\text{flr}} = 1/(k_{\text{rad}} + k_{\text{IC}} + k_{\text{ISC}}) \) is a direct experimental observable in form of the fluorescence intensity decay.\(^4\) Together with \( \Phi_{\text{flr}} \), it gives experimental access to the radiative rate constant \( k_{\text{rad}} = \tau_{\text{rad}}^{-1} \), which is identical to the Einstein coefficient for spontaneous emission, \( A_{21} \), and thus related to \( B_{12} \).

\[
k_{\text{rad}} = A_{21} = \frac{8\pi \hbar \nu^3}{c^3} \cdot f_L \cdot B_{12} \tag{2.11}
\]

Note that the ratio \( A_{21}/B_{12} \) is proportional to the cube of the transition frequency and for this reason fluorescence is unlikely at long wavelengths.\(^{[56]} \) This relation shows furthermore that a good absorber is at the same time a good emitter.

The above equations have been derived for atoms with sharp absorption lines. Strickler and Berg adapted them to the case of molecules and obtained equation 2.12 which is nowadays known as the Strickler–Berg relation.\(^{[61]} \) A summation over all the transitions is done by integration over the spectrum.

\[
k_{\text{rad}} = 2303 \frac{8\pi \hbar \nu^3}{N_A} \cdot \int \frac{F(\tilde{\nu})d\tilde{\nu}}{\tilde{\nu}^{\frac{1}{2}}} \cdot \int \frac{\varepsilon d\tilde{\nu}}{\tilde{\nu}} \tag{2.12}
\]

For the Strickler–Berg equation to be valid, the nuclear configuration of the absorbing and the emitting state have to be sufficiently similar. This assumption is not fulfilled in the presence of important solvent interaction or geometrical relaxation of the molecule. In these cases, absorption and fluorescence spectra show no mirror–image symmetry.

### 2.1.3. Non–radiative electronic transitions

Non–radiative decay of an electronic state is possible due to either IC, i.e. the isoenergetic change of the electronic wavefunction within the same spin manifold or due to ISC, the iso-
energetic change of wavefunction and spin multiplicity. IC also includes transitions to charge separated states.\cite{62}

The theory of non–radiative relaxation has been developed mainly by Robinson and Frosch,\cite{63,64} Siebrand,\cite{65–68} Freed,\cite{69–71} Bixon\cite{62} and Jortner.\cite{69,72,73} The following description follows the derivation of Freed and Jortner.\cite{69}

\begin{equation}
k_{\text{nr}}^{il \rightarrow fm} = \frac{2\pi}{\hbar} \sum_{l} \sum_{m} p(il) |V_{il, fm}|^2 \delta(E_{il} - E_{fm})
\end{equation}

Here, $\delta$ is the Dirac delta function assuring energy conservation, $p(il)$ is the probability that the system is initially in the state $\Psi_{il}$ and is assumed to be given by the Boltzmann distribution,\footnote{Which implies that thermal equilibrium has to be reached prior to IC.} i.e.

\begin{equation}
p(il) = \frac{e^{-\beta E_{il}}}{\sum_{l} e^{-\beta E_{il}}} \quad \text{with} \quad \beta = (k_B T)^{-1}
\end{equation}

and $V_{il, fm}$ are the off–diagonal matrix elements of the electronic hamiltonian, determined by the perturbation operator $V''$. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Sparse (centre) and dense manifold (right) of vibrational states. The energy gap is measured between the 0 vibrational levels of the potential energy surfaces. Adapted from Ref. [58].}
\end{figure}

Consider a two–manifold electronic system having a sparse density of vibrational states in one and a quasicontinuum of levels in the other manifold (Figure 2.2). The transition probability between the two manifolds is then given by the golden rule expression

\begin{equation}
k_{\text{nr}}^{il \rightarrow fm} = \frac{2\pi}{\hbar} \sum_{l} \sum_{m} p(il) |V_{il, fm}|^2 \delta(E_{il} - E_{fm})
\end{equation}
\[ V_{il,fm} = \langle \Psi_{il} | \hat{V}^\prime | \Psi_{fm} \rangle \] (2.15)

Such transitions, that are impossible within the framework of the Born–Oppenheimer approximation, arise from the interaction between different electronic molecular states through nuclear motion. In other words, the perturbation operator can be identified with the nuclear kinetic operator \( \hat{J}_N \).

\[
V_{if} = \sum_{k=1}^{p} \hat{J}_N^k \frac{i\hbar}{\sqrt{M_k}} \frac{\delta}{\delta Q_k^{(f)}}
\] (2.16)

\[
\hat{J}_N^k = \frac{i\hbar}{\sqrt{M_k}} \langle \Psi_i | i \frac{\delta}{\delta Q_k^{(f)}} | \Psi_f \rangle
\] (2.17)

In these equations \( Q_k^{(l)} \) is the \( k \)th reduced normal coordinate of effective mass \( M_k \). The summation over \( k \) in equation 2.16 is taken over the small number of promoting modes (\( p \ll N \)) for which \( \hat{J}_N \) is appreciable.\(^6\) The number of accepting modes, on the other hand, is large (\( \approx N \)) but this does not mean that all modes are necessarily efficient acceptors.

As a general case, the vibrations can be displaced, distorted oscillator, i.e. their origins do not coincide on the two PES and their frequencies change upon the transition. Then two limiting cases can be distinguished depending on the magnitude of the vibrational coupling strength (not to be confused with the electronic coupling strength): the weak coupling limit which corresponds to a small horizontal displacement between the two PESs and the strong coupling limit for which it is substantial. More quantitatively, the Huang–Rhys factor \( S \) (or phonon–electron coupling strength, related to the dimensionless displacement \( \Delta_m \), equation 2.19) weighted by the number \( \bar{n}_m \) of excited vibrations with frequency \( \omega_m \) at thermal equilibrium should be compared with the molecular rearrangement energy in the excited state \( E_M \) (half the Stokes shift, eq. 2.20).

\[
G = S(2\bar{n}_m + 1)
\] (2.18)

\[
S = \frac{1}{2} \sum_m \Delta_m^2
\] (2.19)

\[
E_M = \frac{1}{2} \sum_{m=1}^{N} \hbar \omega_m \Delta_m^2
\] (2.20)

In the weak coupling case \( G \ll E_M \), a condition that can be recast as \( G \leq 1 \) or \( E_M \approx \hbar \langle \omega \rangle \), i.e. the nuclear reorganisation is comparable with the energy of the mean vibrational frequency \( \langle \omega \rangle \). This is the case for IC and ISC in aromatic hydrocarbons but possibly not for heteroaromatics that undergo major geometrical changes.\(^7\) In the strong coupling limit \( G \gg 1 \) or \( E_M \gg \hbar \langle \omega \rangle \), which means that the displacement is large for at least some modes and the molecular rearrangement energy considerably exceeds the mean vibrational energy.

\(^6\)For ISC an additional spin–orbit term has to be considered.\(^{[54,67,69]}\)

\(^7\)\( N \) is the number of normal modes
This may be appropriate to the description of radiationless transitions between charge transfer states. The most important prerequisites and assumptions made in the derivation sketched above are

- The density of states in the manifold $f$ has to be a quasi–continuum. This is called the statistical limit or the large molecule case. It is in general fulfilled if the energy gap is sufficiently large, 0.5–1 eV being typically taken as limit.\cite{55,65,75} Below that, parity and symmetry will tend to reduce $k_{nr}$ and the value obtained with EGL represents an upper limit.\cite{55}
- The PESs are assumed to be harmonic. Although the true FC factors and matrix elements of $\delta/\delta Q$ are affected by anharmonicity, the harmonic approximation is supposed to give semi–quantitative results.
- $V_{if}$ is assumed to vary only slowly with the nuclear coordinates. This assumption is reasonable except near an intersection point of the PESs.

Provided additionally that $k_B T \ll \hbar \omega_i$ for all the vibrations (the low temperature limit) it can be shown\cite{69} that the frequency of the promoting mode appears in the so–called effective energy gap $\Delta E_k = \Delta E - \hbar \omega_k^{(l)}$ (which is therefore different for each mode). The result is, that the most favourable change in a promoting mode involves a single vibrational quantum.

One can then express the non–radiative rate constant as a function of molecular parameters:

$$k_{nr} = \sum_k \frac{|V_{if}|^2}{\hbar} \sqrt{\frac{2\pi}{\hbar\omega_k \Delta E_k}} e^{-S} e^{-\frac{\gamma_k \Delta E_k}{\hbar\omega_k \Delta E_k}}$$  \hspace{1cm} (2.21)

where

$$\gamma_k = \ln(2\Delta E_k/d_M \hbar \omega_M \Delta E_k^2) - 1$$  \hspace{1cm} (2.22)

The index $M$ in these equations corresponds to the group of modes of maximum frequency with nonzero displacement and $d_M$ is the degeneracy. The equation is dominated by the exponential dependence of the rate on the energy gap. It has therefore already the form of the energy gap law which predicts a linear relationship between the logarithm of the non–radiative decay rate and its energetic distance to the closest lower electronic state where the slope is a measure for the displacement,

$$\ln(k_{nr}) = \ln(m_1) - S - \frac{1}{2} \ln(\Delta E) - (\ln(\Delta E) + m_2) \frac{\Delta E}{\hbar \omega_M}$$  \hspace{1cm} (2.23)

with

$$m_1 = \frac{2\pi V^2}{\hbar \sqrt{2\pi \hbar \omega_M}}$$
$$m_2 = \ln(2/(d_M \hbar \omega_M)) - 1$$

In the case of weak coupling, the matrix elements $V_{il,fm}$ can be split into electronic and vibrational components analogous to the way done in section 2.1.2 by writing
\[ \langle \Psi_i | \hat{V}' | \Psi_f \rangle = \beta^{IC} \langle \chi_i | \chi_f \rangle \] (2.24)

Assuming that \( \beta^{IC} \) is constant and substituting into eq. 2.21, it can be reduced to give eq. 2.25 where \( \varrho_E \) is the density of states (the number of energy levels per unit energy) of the final state at the energy of the initial state. The density of states is approximately given by the number of ways of distributing \( \Delta E \) over the normal modes of vibration. Because of many low–frequency modes, the number of these overtones and combinations thereof is enormous: there are as many as 300 000 states per cm\(^{-1}\) in the \( S_1 \rightarrow T_1 \) case of benzene (that has 30 normal modes of vibration and \( \Delta E = 8500 \text{ cm}^{-1} \)).^\text{[54,55,76]}

\[ k_{ij} = \frac{2\pi}{\hbar} \beta^{IC} \langle \chi_i | \chi_f \rangle^2 \varrho_E \] (2.25)

\[ k_{ij} = k_{00} \cdot e^{-\alpha \Delta E} \] (2.26)

\( \langle \chi_i | \chi_f \rangle^2 \) is the FC factor for the transition. The expected increase of the rate constant with increasing energy gap due to the density of states is overcompensated by the unfavourable FC factor that result from the large energy gap (see Figure 2.3 left and middle). Figure 2.3 also shows nicely the importance of the relative displacement of the PES for efficient coupling.

The similarity between eqs. 2.25 and 2.2 results from the similar methods used to separate the electronic and vibrational components. For both, radiative and non–radiative transitions, the FC factors are of paramount importance.\^\text{[66,77]} The basic difference is that a radiative transition involves the electric dipole operator \( \hat{\mu} \) and takes place between vibronic states of different energy, while a non–radiative transition involves the nuclear kinetic operator \( \hat{J}_N \) and occurs between vibronic states of the same energy. A radiationless transition is horizontal and involves tunnelling.\^\text{[55]}

There also is a close relationship between IC and ET in the Marcus inverted region.\^\text{[58,78]} For a large energy gap between the “Marcus parabolas”, the lowest crossing point of the PES of reactants and products is high in energy, whereupon ET occurs via nuclear tunneling. Tunneling in the Marcus inverted region can be considered isomorphous to an intramolecular non–radiative transition in the weak coupling limit.\^\text{[58]} The rates of both types of processes are controlled by FC factors which have their origins in the differences in molecular structure between the reactants and products. The only fundamental difference might be in the specific type of electronic matrix elements that “allow” the reactions to proceed. Typically, vibronic coupling is assumed to be the predominant perturbation that causes excited–state decay while electron exchange is assumed to be dominant for ET.\^\text{[78]}

Siebrand found quantitative agreement between eq. 2.26 and the \( S_1 \rightarrow S_0 \) IC\^\text{[66]} and \( T_1 \rightarrow S_0 \) ISC\^\text{[65]} of benzenoid aromatic hydrocarbons and extracted the empirical parameters \( \alpha = 4.85 \text{ eV}^{-1} \) and \( k_{00} = 10^{13} \) and \( k_{00} = 10^5 \) for IC and ISC, respectively.\^\text{[54,66,67,8]} The energy gap law has also been successfully applied to

- the \( S_1 \rightarrow S_0 \) IC of carotenoids,\^\text{[80,81]} xanthene dyes,\^\text{[82]} azulene,\^\text{[83]} and linear polyenes.\^\text{[84]}

^\text{8}This gives a spin prohibition factor for ISC of the order of \( \approx 10^8 \), two orders of magnitude larger than what is often invoked.\^\text{[67]} Gilliespie and Lim\^\text{[79]} repeated the analysis with a larger data set and got essentially the same results, though a slightly smaller spin–prohibition factor.
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Figure 2.3.: Influence of the energy gap and relative displacement on the Franck–Condon factors of a radiationless transition. Adapted from Ref. [54].

- the $S_2 \rightarrow S_1$ IC of azulene$^{[79,83,85]}$ and aromatic thiones,$^{[86]}$
- the $D_1 \rightarrow D_0$ IC of diphenylmethyl radicals,$^{[87]}$
- ISC of fluorinated and deuterated benzenes and aniline,$^{[70,76]}$
- metal–to–ligand transfer in transition metal complexes,$^{[78,82,88–91]}$ and
- charge recombination of organic donor–acceptor complexes.$^{[92,93]}$

The group of Thomas Meyer investigated exhaustively the validity of the EGL for Os(II), Ru(II), Rh(III), and Re(I) complexes. Most polypyridyl complexes of these transition metal ions are sufficiently weak emitters that the excited state decay is governed by non–radiative processes.$^{[94]}$ They varied the MLCT state energy in a systematic fashion by either replacing ligands of the complex,$^{[78,82,95–97]}$ changing solvent polarity,$^{[90,98]}$ nature of the counter ion,$^{[89]}$ or temperature (affecting the solvent polarity — and coupling with other electronic states, see below).$^{[97,99,100]}$

In general, excellent agreement with the predictions of EGL was observed. Deviations were ascribed to the opening of an additional decay channel or to a large displacement between the initial and final state PESs.

If the state under consideration is close in energy to another one, they may mix via vibronic coupling, which will open an alternative channel for non–radiative decay. This was observed, for instance, when comparing series of transition metal complexes with varying ligands$^{[90,94,101]}$ and also invoked for organic fluorophores.$^{[102,103]}$ In the case of vibrational coupling, a strong
temperature dependence of the decay rate is superimposed on the weak temperature dependence of EGL.\cite{90,99,101}

Verhoeven, Brouwer and co–workers gave an exceptionally striking example how EGL is not obeyed.\cite{93} They studied the solvent dependence of the CR in organic dyads comprising of an aliphatic amine as electron donor and a cyano–napthalene acceptor unit.\cite{104} The rate constant for this non–radiative decay goes through a minimum at 2.5 eV. From temperature dependent measurements an activation barrier of a few kcal/mol was extracted for the alternative decay channel which the authors associated with a twist around a double bond.\cite{93}

Large displacement between the PESs leads to large FC factors (see Figure 2.3) and thereby enhances IC. The dependence of $k_{nr}$ on the displacement $\Delta_m$ (or the Huang–Rhys factor $S$) has been verified experimentally.\cite{88,94,105–107} For example, $[\text{Os(bpy)}_3]^2^+^*$ and $[\text{Os(phen)}_3]^2^+^*$ have comparable energy gaps ($\approx 1.7$ eV), but $k_{nr}$ for the bipyridine complex is approximately four times that of the phenanthroline complex in acetonitrile at 298 K.\cite{101} From a FC analysis of emission spectra, the displacement and hence the vibrational overlap is bigger for the bipyridine complex in accord with the faster relaxation. Typically, larger delocalisation of the excited electron results in smaller changes of the local C−C and C−N bonds, i.e. to smaller displacements.\cite{88}

Major structural changes necessarily imply large displacement and can lead to highly efficient excited state decay at a conical intersection (see next section). Naturally, EGL is not obeyed under such conditions since contradicting assumptions are made in its derivation.

In the theoretical development of non–radiative transitions described above, IC is treated as an intramolecular process and, in fact, IC (and ISC) can be observed in vapours at low pressure.\cite{55} The surrounding medium can be included in the treatment, acting as heat bath or directly by offering accepting modes.\cite{69,82} But since these are low frequency modes they are expected to be of little effect in agreement with experiment.\cite{9}

In the strong coupling limit the rate constant is determined by an activation energy (governed by the intersection point between the PESs) as opposed to the energy gap type behaviour in the weak coupling limit. Furthermore $k_{nr}$ is determined by a mean vibrational frequency $\langle \omega \rangle$ rather than the high frequency modes and a negligible effect of H/D substitution is expected.

To summarise the key points, the EGL in its formulation for weak coupling in the statistical limit (eq. 2.21 or 2.26)

- is valid at large effective energy gaps. For small gaps, it represents an upper limit,
- assumes Boltzmann equilibrium in the initial states so vibrational relaxation has to be much faster than the non–radiative transition,
- is not applicable when the PES couple strongly or when large frequency changes or rearrangements take place as it is to be expected for charge transfer transitions or the vicinity of state crossings.
- Deviations are also expected when anharmonicities become important.
- In the limit of a large energy gap and weak coupling, the most effective accepting modes are the highest–frequency modes. These are the C–H modes for aromatic hydrocarbons and therefore important H/D isotope effect are observed. In the strong coupling case, on the other hand, a small isotope effect is expected. Since the experimentally observed iso-

\footnote{Solvent effects might be important when they alter the energy gap, see Ref. [82]}

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tope effect does not agree with the theoretical one, Siebrand himself and others can play a major or even the dominant role as acceptor modes.

- Since the solvent is characterised by low frequency modes, IC can be treated as an intramolecular process.
- A comparison between different molecules is meaningful only, if they the non–radiative transition is governed by similar distortions (frequency shifts) and displacements (shifts in equilibrium distance).

Conical Intersections

In a diatomic molecule, the non–crossing rule prohibits two electronic states to cross unless they are of different symmetry. This is not true for polyatomic molecules but for a long time it was believed that most surface touchings are at least weakly avoided. Work in the early nineties of the last century showed, however, that (un–avoided) touchings are quite common. The regions of surface approach are referred to as funnels or as conical intersections (CI, used for real touchings).

The dimensionality of the subspace in which the two states are degenerate (the intersection subspace) is by two smaller than the number of normal modes. These two dimensions, $x_1$ and $x_2$, lift the degeneracy and span the so–called branching space. A plot of the PESs as a function of $x_1$ and $x_2$ has the shape of a double cone, hence the name CI. At the tip of the cone the states have equal energy, in its immediate vicinity, the touching is weakly avoided.

The gradient difference vector, $x_1$, is defined as $x_1 = \delta(E_1 - E_2)/\delta q$ and is the direction of maximal difference of PES slopes. The derivative coupling vector, $x_2 = \langle \Psi_1 | \delta \Psi_2 | \delta q \rangle$, is the direction of nuclear displacement that mixes the PES the best. The derivative coupling vector allows molecules to “hop” between surfaces, the gradient difference vector determines how fast it moves through the CI.

The main feature of a CI is its non-adiabatic nature, that is, the breakdown of the Born–Oppenheimer approximation which allows non–adiabatic electronic transitions to happen. An actual intersection facilitates transitions between adiabatic surfaces much more than an avoided crossing.

A CI can be on happenstance (most CIs that are relevant for reaction mechanisms fall into this category) or by symmetry. A Jahn–Teller distortion is an example where the degeneracy is a result of symmetry only.

CIs have been demonstrated in the non–radiative decay of excited states, photodissociation, isomerisation, and charge-transfer reactions and assumed to be essential for the existence of life on earth. Recently, Bearpark and co-workers have shown that the ultrafast deactivation of the cations of naphthalene and pyrene happens via two consecutive sloped $D_1/D_2$ and $D_1/D_0$ CIs.

One should bear in mind that the picture of a double cone is a bit misleading because degeneracy of the PESs is given not only at “one point”, but in all the intersection subspace. What is more, IC is very efficient in all the region on the PES around this seam and the trajectory of the wavepacket does not need to pass the tip of the cone for the surface jump to happen.

---

[108]See also the citations in Ref. [94].

[109]The authors stress that CIs are of no importance in theistic models.
Finally, it should be stressed that not the existence of a CI on the PES is important for the photophysics of a molecule (there are certainly plenty) but its accessibility.

2.1.4. Temperature dependence of photophysical processes

Matrix isolation technique has been used with great success to investigate reactive intermediates such as radicals and radical ions.\cite{118,119} The investigated compound is trapped in an organic matrix at liquid nitrogen temperature or a rare gas matrix at a few Kelvin. The question rises to what extend the temperature has an influence on photophysical processes.

First, the density of most materials increases as temperature is lowered and consequently the medium’s index of refraction, $n_D$, increases. It is via this change in the environment that the temperature can influence the radiative rate constant which, by itself, is nearly temperature independent.\cite{54,120}

The same is true for “normal” non–radiative transitions described by the energy gap law.\cite{69,121} In principle the theory of non–radiative transitions has been developed for the low temperature limit but since the energy difference between the two states is so large compared to thermal energies, room temperature still applies to the “low temperature” case.\cite{12}

Deviations from the normal behaviour can arise due to two different mechanisms. The first one invokes an increased IC for vibrationally excited states. Thermal population of these states leads therefore to a (moderate) increase in the non–radiative rate constant and the deuterium effect is small. This seems to be case for the $T_2 \rightarrow S_1$ ISC in anthracene.\cite{54}

The second mechanism invokes vibronic coupling of two electronic states, this means thermal population of another electronic state. Physically the activation energy obtained from a temperature dependent analysis corresponds then to a set of vibrational energies that mix the two electronic states most efficiently. Much stronger temperature dependence is expected in such a case.\cite{121}

If the ground state has a distribution of conformers, the equilibrium will in general shift with temperature. Such a shift can influence the photophysics of the ensemble.

Finally, photochemical reactions that need to surpass a transition state depend on vibrational energy. At low temperatures the thermal energy $k_B T$ might no suffice to overcome the barrier and the reaction is no longer feasible. Conformational and re–orientational equilibration of the environment after photoexcitation of the solute are impeded in solid phase. This is not so much a temperature but rather a matrix effect. The same is the case for diffusion in solids which does not need to be considered on the timescale of photophysical events.

It is this fixation that enables the study of unstable molecules in matrices. Care should be taken when annealing the matrix after irradiation to reduce the number of sites (i.e. solutes in spectroscopically distinct environments). Dimerisation is a rather frequent process in softened matrices, and radical cations, for instance, are known to form the so–called “dimer cation” by aggregation with a neutral parent.\cite{122}

\[12\] Unless anharmonicities become important.
2.2. Solvation

Solvation is the (dynamic) interaction of the solvent with the solute. It leads to a stabilisation of the total system (solute plus solvent; the first solvation shell contributes the most). It has to be distinguished from vibrational relaxation described in the subsequent sections, where the vibrational energy of the solute is redistributed within the molecule (IVR) or dissipated to the surrounding (VC).

In general the permanent dipole moment of the electronic ground and excited state differ from one another and the molecule exerts distinct electric fields before and after light absorption or emission.\cite{56} The solvent will react to the change that occurs during the transition quasi-instantaneously by virtue of its electron shell and on the picosecond timescale via orientational motion. The extend and rate of adaptation, which influences the molecule (its wavefunctions and hence the transition energies, rate constants, quantum yields, etc.) depend on the solvent.

Solvation has been the subject of many studies, in first place on equilibrated states, with the advent of high time resolution on non-equilibrated states.\cite{123–127}

2.2.1. Solvatochromism

A molecule’s wavefunction is not independent of the surrounding and its stabilising effect on one state with respect to another can be observed as shifts in the electronic spectra. As a result the colour of a chromophore can change with solvent if the interaction is strong.

The energy of a dipole moment in a dielectric continuum has been modelled by Onsager\cite{128} and various equations have been developed on basis of this model (see Ref. [129] or [123] for a discussion). The Debye function (eq. 2.27) represents the solvent’s polarisability, reflected in the index of refraction, $n_D$. Pure dispersion interactions between solute and solvent can be satisfactorily described by this equation.

\[
f(n_D) = \frac{(n_D)^2 - 1}{2(n_D)^2 + 1} \tag{2.27}
\]

\[
f(\varepsilon, n_D) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{(n_D)^2 - 1}{2(n_D)^2 + 1} \tag{2.28}
\]

The Lippert–Mataga function (eq. 2.28) also takes account for dipole–dipole interactions, i.e. the effect of solvent polarity ($\varepsilon$ is the static dielectric constant).\cite{125,130,131}

2.2.2. Dynamic solvation

A simple prediction for solvation dynamics can be obtained by introducing the complex frequency-dependent dielectric response $\tilde{\varepsilon}(\nu)$ which arises from the intramolecular polarisability and from the alignment of permanent molecular dipoles by an applied field against thermal motion.\cite{132} The simplest case possible is the Debye type dielectric function $\tilde{\varepsilon}(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$ which corresponds to an exponential decay in the time domain.\footnote{$\varepsilon'$ and $\varepsilon''$ stand for the real and imaginary part of $\tilde{\varepsilon}$, respectively. The imaginary part is known as the dielectric loss.}
The dielectric response is then modelled in form of equation 2.29 with the exponents $\alpha$ and $\beta$ depending on the model.\[130\] The simplest model of an ideal Debye solvent has only one relaxation time ($N=1$), $\alpha = 0$, $\beta = 1$ and the dynamics can be described by a single exponential. In the more realistic case of non-Debye behaviour, a distribution of relaxation times is assumed.\[190,134\]

\[
\hat{\varepsilon}(\nu) = \sum_{j}^{N} \frac{S_j}{1 + (j^2 \pi \nu)^{1-\alpha_j}} \beta_j + \varepsilon(\infty) \tag{2.29}
\]

As the wavelength approaches molecular dimensions, the polarisation of the solvent depends not only on time but also on the position of the responding volume element. This situation applies for example when the surrounding molecules must respond to an instantaneously created charge.\[132\] The propagating electromagnetic wave is separated in its longitudinal and transversal components which are related to one another by the dielectric permittivity at infinite and zero frequency\[135\]

\[
\tau_L / \varepsilon(\infty) = \tau_D / \varepsilon(0) \tag{2.30}
\]

In media of high static dielectric constants, $\varepsilon(0)$, one finds the longitudinal relaxation time to be much bigger than the transverse (or Debye) relaxation time, i.e. $\tau_L \ll \tau_D$. On basis of this, it has been suggested that $\tau_D$ represent the “slow” (reorientational) and $\tau_L$ the fast (inertial, libenational) motion but such an interpretation has been questioned considering that both have to represent the same, total dielectric response of the solvent.\[136\] Very crudely, $\tau_L$ correlates with the solvent viscosity in some cases, although the physical origins of these quantities are quite different.\[137\] Following Weaver’s words,\[137\] “$\tau_L$ denotes the relaxation time for an isotropic dipolar fluid in response to a sudden change in charge as will occur in ET processes. Significantly, $\tau_L$ is known to be sensitive to the solvent structure, differing by at least 50-fold (from ca. 0.2 to 10 ps at ambient temperatures) between common “Debye” solvents, i.e. those that exhibit only one dissipative relaxation in the dielectric loss spectrum.”

Experimentally, the real–time solvent dynamics can be followed by dielectric relaxation spectroscopy, time–dependent Stokes shift measurements or in form of the electron transfer (ET) rate constants, if the ET has a negligible intrinsic barrier.\[137,138\] Pioneer work in this field has been done in the groups of Marc Maroncelli and Paul Barbara.\[126,139–141\] The key points of their findings are:

- Solvation is a multi–step process spanning a wide range of timescales (i.e. $N > 1$ in eq. 2.29). The initial part happens within a few tens of femtoseconds and can account for up to 50% of the total solvation energy. Molecular dynamic simulations related this part to the motion of one single solvent molecule or the breaking of one single hydrogen bond.\[142\] Afterwards diffusive rotational motion takes place on the picosecond timescale.\[126,143\]
- The early time dependence is necessarily non-exponential.\[136,143\] Gaussian functions are frequently used.\[133\]
- Due to the long-range nature of electrostatic interactions, $\hat{\varepsilon}$ is especially sensitive to cooperative motions and very small reorientation of a few molecules can have huge impact.\[132\]
The rotational time of $\hat{\varepsilon}$, $\tau_L$, is therefore much smaller than that of individual molecules. This also leads to non-exponentiality of the early time dynamics.\cite{136}

- The dielectric continuum models work surprisingly well considering that bulk properties are used to describe a molecular process.\cite{133}

2.3. Vibrational energy relaxation

Excitation with visible or UV light promotes a molecule in general to a higher vibrational level of the excited electronic state (the transition is vibronic in nature). Since the FC factors differ largely for the many normal modes of a molecule, only some, the FC active modes, are excited in the optical transition. The same applies to non–radiative transitions which are governed by FC factors as well, as has been discussed in the last section.

The process of distributing the energy among all vibrational modes by virtue of anharmonic coupling is called intramolecular vibrational energy redistribution (IVR) and is an iso–energetic process: no energy is exchanged with the surrounding. Vibrational cooling (VC), also called vibrational energy transfer (VET), denotes the transfer of energy to the solvent. Vibrational relaxation (VER) comprises therefore of two distinct processes, IVR and VC, the former being intramolecular in nature, the latter intermolecular — in first approximation.

For a long time, it has been argued that IVR and VC are temporally well-separated processes, the former happening on the sub-picosecond, the latter on a picosecond timescale.\cite{144} This seems not to be valid for molecules in condensed phase where they take place in parallel in a multistep fashion.\cite{145,146}

2.3.1. Intramolecular vibrational energy redistribution

IVR of big molecules in condensed phase has been studied after electronic excitation with excess energy or after IC from a higher excited state.

For example, the IVR of trans–stilbene after $S_n \rightarrow S_1$ IC was estimated to happen with $\tau_{\text{IVR}} \approx 10$ fs.\cite{147} For pyrene in $n$–octane, a time constant of 400 fs was ascribed to IVR after $S_6 \leftarrow S_0$ excitation and 300 fs after $S_1 \leftarrow S_0$ excitation.\cite{148}

The bleaching dynamics of Nile Blue, Oxazine 720 and cresyl violet showed components with lifetimes of 50–100 fs and of several hundreds of femtoseconds (both insensitive to the nature of the solvent). The two time constants were ascribed to IVR to two sets of normal modes which differ in their coupling with the FC active, vibrationally excited modes.\cite{144}

Much slower IVR rate constants were deduced from the damping time of a wavepacket in perylene after $S_1 \leftarrow S_0$ excitation, amounting to 1 to 2 ps in a variety of solvents.\cite{145} Kiba et al.\cite{149} interpreted the 1–5 ps spectral changes of the $S_1 \rightarrow S_0$ emission of perylene in ketones as solvent–assisted IVR. That the solvent is not innocent to the IVR process was suggested by several authors.\cite{141,150,151} Recently, the solvent was incriminated for hindering IVR in Mn$_2$(CO)$_{10}$ which happens with time constants of 2–5 ps in all alcohol solutions investigated, except for methanol (8 ps) and butanol (12 ps).\cite{152}
2.3.2. Vibrational cooling

A frequently used probe molecule in VC studies is azulene for which cooling times from 15 to 50 ps have been reported.\cite{144,153,154} The slowest decay was observed in CCl$_4$, what agreed nicely with the model of energy dissipation via binary collisions and subsequent heat conductivity.\cite{144,153} Pigliucci pointed out that the relaxation rates reported are faster in protic, than in aprotic solvents.\cite{146}

The relaxation rate of trans–stilbene in a variety of solvents including a micellar aqueous solution was shown to correlate well with the solvent thermal diffusivity.\cite{147,155,156} Such a correlation was as well observed for merocyanine 540, having VC time constants of 2–10 ps.\cite{157}

The cooling dynamics of \textit{p}–nitroanilines studied by TA spectroscopy showed multi-phasic decay with a fast component of 1–3 and a slower one of 3–12 ps. Again, the energy dissipation was found to be faster in protic solvents. Biphasic behaviour was as well observed by Pigliucci et al.\cite{145} using perylene as probe molecule with time constants up to 5 ps.

Skhrob and co–workers\cite{158} measured the cooling rates of PAH radical cations in orthoboric acid after subpicosecond IC to the D$_0$ state and found time constants of 5 to 20 ps, depending on solute and temperature. The authors suggested that VC can be faster in a rigid matrix than in an organic liquid because the thermal conductivity of the glass is much higher and estimate characteristic times of 5–20 ps for boric acid glass.

**In summary,**

it can be said that despite considerable effort and great progress, a complete understanding of solute solvent interactions is far from being reached.\cite{141,159,160} On the contrary, things proof to be more complex than initially thought. For example, contribution of the solvent to IVR is observed, that was initially thought to be completely intramolecular. Also, the strict temporal separation of IVR and VC is questioned.\cite{146} Indeed, it seems unreasonable to assume that VC will await that the vibrational energy is equilibrated among all normal modes of the molecule.

The solvent dependence of VC is far from understood. Some groups found agreement with the thermal diffusivity or the solvent.\cite{156,157,161} Other investigations pointed to an acceleration of VC in the presence of H–bonds between the solute and the solvent molecules.\cite{145,147}

Solvent dynamics are non-exponential with the fastest stages of solvation happening within a few femtoseconds having high impact on the chromophore. The complete solvation process, in contrast, is not complete for many picoseconds (in “slow”, high–viscous solvents even several hundreds of picoseconds).
3. Radical ions

Radicals are nowadays accepted as common intermediates in all fields of chemistry, biology and physics — from organic synthesis\cite{2,162} via biochemistry\cite{7,163} to cosmology.\cite{5,164–166} The term “radical” comes from latin “radix”, root, and shows that radicals were understood as root fragments of a molecule and, indeed, they can be obtained in a homolytic bond cleavage reaction.

The idea that carbon atoms with only seven valence electrons could participate in organic reactions got broadly accepted only in the 1930s, i.e. ca. 30 years after the first report about a radical present in liquid solution at room temperature by Gomberg.\cite{167,168} He treated triphenylmethylchloride (tritychloride) with silver and obtained triphenylmethyl radical which he identified by its chemical reactivity correctly as a trivalent carbon compound. There were earlier reports on free radicals (e.g. quinhydrone in 1835,\cite{169} naphthalene radical anion in 1866,\cite{170} thianthrene radical cation in 1869,\cite{171} or Wurster’s Blue in 1879\cite{172}), but Gomberg was the first to unravel the radical nature of the compound he had. In many other cases, even after Gomberg’s publication, the radical was often mistaken for the dimer.\cite{1}

According to Roth,\cite{175} the highest influence on early radical chemistry came from W. Schlenk, A. Hantzsch and E. Weitz who advanced the reconnaissance of the correct structures and a deeper understanding of their nature.

Radical ions of medium and large polycyclic aromatic hydrocarbons (PAH) are also present in outer space\cite{165} and most likely the origin of the so-called diffuse interstellar bands (DIB), whose explanation remains a “major problem in astronomical spectroscopy.”\cite{5}

DIBs are detected in the spectra of stars that lie behind interstellar clouds. Over three hundred absorbative DIBs have been documented today. The linewidths of 2–10 cm$^{-1}$, large for astrophysical features, are explained by a short lifetime of the excited state.\cite{5} Additionally, there are emissive lines that also have been assigned to radical ions of PAHs.\cite{164,166}

3.1. Chemical stability

Radicals are in general highly reactive with only some exceptions. They undergo chemical reactions such as dimerisation, disproportionation to the neutral and the doubly charged ion, hydrogen abstraction from the solvent, and addition to molecular oxygen. Few are stable in solution and even for those that show chemical resistance, it is in most cases not thermodynamics that govern the “stability”, but rather a kinetic effect that stems from sterical hinderance and delocalisation of the radicalic site. Examples for the latter, so called persistent radicals, are the above cited triphenylmethyl radical or those radicals that serve as standards for EPR spectroscopy(see Figure 3.1). The chemical reactivity renders all work with radicals quite dif-

\footnote{Radicals, even charged ones, tend in fact to dimerise.\cite{173,174}}
3. Radical ions

Figure 3.1.: Examples for stable and persistent radicals.

Dimerisation. It might be surprising to find that many radical ions, although charged, tend to dimerise. Reversible dimerisation in solution has been demonstrated by means of UV/visible/NIR absorption (several examples are given in part II), EPR spectroscopy or by change of the magnetic properties. Dimerisation results in the formation of a σ-bonded dication in which a new single bond is formed between radical centres or of a co-facial π-complex.

Disproportionation is, as already mentioned, an important factor for radical stability. Often the doubly charged form is chemically unstable and the overall stability of the solution depends on the equilibrium between the neutral, mono and double charged oxidation state. The disproportionation constant, $K_{\text{dis}}$, can be calculated from the difference between the first and second oxidation potential (reduction potentials for radical anions).

$$K_{\text{dis}} = 10^{-\Delta E^0/0.059} \quad (3.1)$$

3.2. The electronic structure of radicals

The photophysics of molecules with an odd number of electrons shows some distinctive features with respect to the general points sketched in the last chapter. For a closed–shell system, the lowest energy transition is the one between the highest occupied molecular orbital (HOMO)
3. Radical ions

and the lowest unoccupied one (LUMO). Due to spin–selection rules, the states populated by light excitation are singlet states and for each of them exists an energetically lower lying triplet analog. In the case of molecules with an odd number of electrons, the two important spin multiplicities are doublet and quartet and the lowest excited state is a doublet unless the HOMO–LUMO energy gap is very small (as it is for example the case in biradicals).

Consider a gedankenexperiment where an electron is removed from a closed shell molecule to obtain its radical cation. The lowest–energy transitions is then the HOMO$\rightarrow$HOMO-1, no longer the LUMO$\rightarrow$HOMO transition (see Figure 3.2; often the HOMO is called SOMO to stress that it is a Singly Occupied MO). Since for a typical chromophore the energy spacing between HOMO and LUMO is larger than that within the set of bonding or anti–bonding MOs,\textsuperscript{2} new electronic transitions, lower in energy than the LUMO$\rightarrow$HOMO transition, are possible in the cation. Therefore its absorption spectrum extends far to the red and near–infrared (NIR) part of the electromagnetic spectrum. Depending on the molecule, the transition that corresponds to the LUMO$\rightarrow$HOMO transition in the neutral can be “overtaken” by many others within the manifold of binding MOs.

In a similar fashion one can obtain the radical anion by addition of an electron to the neutral parent. The lowest energy transition(s) will be between formerly unoccupied MOs (Figure 3.2) of, again, smaller energy spacing when compared to the HOMO–LUMO gap.

3.2.1. Pairing theorem

There exists a relationship between the positive and negative charged radicals of alternant hydrocarbons known as the symmetrical pairing theorem.\textsuperscript{[54,182]} It states that the bonding orbitals of the cation are paired with the anti–bonding orbitals of the radical anion. The absorption spectra of the cation and anion resemble each other closely, what is indeed found experimentally for many radical ions.\textsuperscript{[54]}

A prime example, tetracene, is presented in Figure 3.3. In this case not only the shape of radical cation and anion spectra are practically identical, additionally the transitions happen at the same energies. In general, the absorption spectra have the same aspect but are shifted one with respect to another. Shida et al. called attention to the “slight but systematic difference”.\textsuperscript{[122,183,184]}

\textsuperscript{2}This remains true although HOMO and LUMO approach each other upon ionisation. For a discussion of the changes upon ionisation, see Ref. [181].
3. Radical ions

In a similar vein to the pairing theorem, Wasielewski and co–workers\cite{185} compared the $D_n \leftrightarrow D_0$ absorption in radical anions with the $S_n \leftrightarrow S_1$ absorption of the neutral parent, i.e. the steady–state absorption of $M^{•−}$ with excited state absorption of $M$, both of which involve the LUMO of the neutral. Prerequisite for the transitions to be alike is that the surplus electron in the radical anion does not influence greatly the MOs. They found good agreement for a series of aromatic imides shown in Figure 3.7.\cite{185}

3.2.2. Quartet states

The role of quartet states for the behaviour of radicals is very distinct from the role for triplet states for closed–shell molecules. The lowest energy quartet state can be obtained only from a configuration with three unpaired electrons.\cite{186} Neglecting configuration interaction and restricting ourselves to molecules with HOMO–LUMO gaps considerably higher than the exchange energy,\cite{3} the quartet state is higher in energy than at least two excited doublet states as can be readily deduced from Figure 3.2. Then, the lowest energy excited state is the one with lower spin multiplicity, contrary to closed–shell molecules.

Furthermore, since the dipolar interaction responsible for ISC can mix doublet and quartet states (because permutation of spin variables in a three electron system gives rise to distinguishable states contrary to the two electron system that applies to the case of closed–shell

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\textsuperscript{3}Which applies to the molecules studied during this thesis.
3. Radical ions

molecules’ singlet and triplet states), the interchange between quartet and doublet states is fast. Back–ISC to the lower–lying doublet states is therefore the main deactivation process of a quartet state.\(^{75,186}\) In other words, quartet states are intermediates in the course of IC to \(D_1\) but not long lived states and hence no phosphorescence is observed for radical ions.\(^{182}\)

To the best of my knowledge the only report of \(Q\rightarrow D\) phosphorescence is the case of decacyclene radical anion. Two bands have been found in the emission spectra of decacyclene radical anion in 2–MTHF matrix at 77 K and were ascribed to \(D_2\rightarrow D_0\) fluorescence and \(Q_1\rightarrow D_0\) phosphorescence, respectively.\(^{187,188}\) As far as I understand, this assignment is based only on Pariser–Parr–Pople calculations that have not been published.

3.2.3. The Jahn–Teller effect

According to Miller and co–workers, the Jahn—Teller effect is among the oldest and most extensively studied problems in physical chemistry.\(^{108}\) It is the theorem that any nonlinear molecule in an orbitally degenerate state undergoes a geometric distortion that will lower the symmetry. The coupling of electronic and nuclear degrees of freedom in systems with near–degenerate states has been termed second order or pseudo Jahn–Teller distortion. Both, first and second order Jahn–Teller effects represent special cases of vibronic coupling.\(^{189}\)

The extend of the distortion depends on the energy separation \(\Delta E\) between the involved states in the undistorted symmetry, the coupling strength in the distorted geometry, and the size of the quadratic force constant for the symmetry–breaking normal mode in the lower energy state.\(^{115}\) The latter can be understood as the interplay between energy raise due to deformations of bond lengths and angles and the energy gain due to the electronic terms.

As emphasized by Bally and Borden,\(^{115}\) open–shell molecules are in general more prone to vibronic interactions since \(\Delta E\) is often small for these species. One should therefore never assume that a geometry of high symmetry is the most stable one in a radical ion. The vibronic interactions necessarily alter the PES, widening the lower–energy and narrowing the higher–energy PES even if the distortions are energetically unfavourable.\(^{115}\)

While the pure linear or quadratic terms of the coupling cause symmetric distortions (Figure 3.4, left), an angular dependence arises from the simultaneous presence of both. The well around the crossing of the adiabatic PESs exhibits then minima and maxima, the number of which depends on the symmetry of the undistorted molecule. Benzene radical cation is the prime example for such a case. Its 3d–PES features three minima and maxima around the moat (Figure 3.4, bottom right). Since the energy difference between them is negligible small (<10 cm\(^{-1}\)), the structure, though instantaneously \(D_{2h}\), is dynamically \(D_{6h}\).\(^{108,191}\)

External perturbations can have a significant influence on the PES, especially in the case of quadratic Jahn—Teller coupling. The dipolar interaction with the surrounding serves to deepen the quadratic Jahn—Teller well and gives rise to a “static” geometric distortion of the molecule in condensed phase.\(^{108}\) This effect is, according to Applegate et al.\(^{108}\) much of the reason for the frequent discrepancies between condensed phase and gas phase spectra of the same Jahn—Teller active molecule. The condensed phase spectra can often be ascribed to a molecule suffering a “static” Jahn—Teller distortion (enhanced by the environment), while the gas-phase results fit well with a “dynamic” model.\(^{108}\)

Owing to the non–zero spin, open–shell molecules have non–vanishing spin and electronic orbital angular momentum which possibly gives rise to significant first–order spin–orbit cou-
3. Radical ions

3.3. Photophysics of radical ions

The photophysics and –chemistry of radicals and radical ions have been extensively studied in the last decades. The electronic absorption spectra of more than 700 radical ions are compiled in the book by Tadamasa Shida,\cite{Shida2002} revealing D₁ state energies between roughly 7 and 25 kK.\footnote{\textit{kK} denotes kilokayser, 1kK = 1000 cm⁻¹.} Numerous high resolution gas phase fluorescence spectra and lifetimes are available in the literature, although it should be mentioned that the chemical diversity of open shell molecules showing fluorescence emission is quite restrained.

Instead of an attempt to survey all of them, two groups of radicals that have been very well investigated and that can be considered as well understood are described as they exemplify nicely some aspects that seem common to the photophysics of neutral and charged open–shell molecules: The participation of the D₂ state in the non–radiative decay and the impact of photochemistry. For details on different aspects of the photophysics of open–shell species,
the reader is referred to the reviews by Miller\textsuperscript{[193]} and Maier\textsuperscript{[194]} (focusing on small organic radicals in gas phase), Fox\textsuperscript{[195]} (photophysics of anions in solution), Shida\textsuperscript{[118]} or more recently Bally,\textsuperscript{[119]} and Baskir\textsuperscript{[196]} (radical ions in organic matrices), Smirnov\textsuperscript{[75]} (fluorescent radicals in matrices and gas phase), or Johnston\textsuperscript{[197]} and Haselbach\textsuperscript{[186]} (photochemistry of radicals).

3.3.1. Lack of fluorescence?

It has been noted by several authors\textsuperscript{[52,198,199]} that few radical ions show fluorescence emission in liquid solution (vide infra). Many more reports of emission of radical ions in solids and gas phase are available although these deal with a rather narrow set of molecules that vary only slightly in their chemical nature. The fluorescence quantum yields of radicals are in general much lower than that of the corresponding closed–shell parents.\textsuperscript{[186],5}

A couple of closely entangled reasons could account for this: First, since the energetically lowest lying excited state, D\textsubscript{1}, is much closer in energy to the ground state D\textsubscript{0} than S\textsubscript{1} is to S\textsubscript{0} in the neutral parent compound, IC is expected to be more efficient for the radical.\textsuperscript{[186]} Indeed, absorption spectra of radicals are characterised by transitions in the IR and NIR and the D\textsubscript{0}–D\textsubscript{1} energy gap is no bigger than 1 eV or in many cases even a fraction of that. This also makes k\textsubscript{rad} unfavourable.\textsuperscript{6} One should not forget, however, that there are several closed–shell, charged organic dyes that emit with nanosecond lifetime and appreciable quantum yields in the NIR. The IR140 laser dye, for example, has its fluorescence maximum at 850 nm in dichloroethane solution, τ\textsubscript{flr} equals 1.3 ns and the fluorescence quantum yield Φ\textsubscript{flr} to 0.19.\textsuperscript{[200,201]}

The long wavelength absorption causes that the emission is located in the NIR spectral region, where detection is difficult since suitable detectors are expensive and still rare. This contributes without doubts to the scarcity of observations.

Third, the radiative rate constant for the D\textsubscript{1}→D\textsubscript{0} transition is often very low as can be deduced from the small molar absorptivity of the lowest energy absorption. In many cases significant first–order configuration interaction between the two lowest lying transitions in the radical ions results in a weak low energy and a strong higher energy absorption band. A good example is the benzyl radical (Figure 3.5 on page 35) whose absorption spectrum shows a weak band near 450 nm that corresponds to the dipole–forbidden D\textsubscript{1}←D\textsubscript{0} transition (ε = 50 L·mol\textsuperscript{-1}·cm\textsuperscript{-1}) and a strong absorption near 300 nm.\textsuperscript{[202]} An example taken from closed–shell species where the same applies are the Q and Soret bands of porphyrins.\textsuperscript{[203]}

Another reason why fluorescence quantum yields of open–shell species are most of the time low, is that the density of electronic states is in general much higher in the radical ion than in the neutral parent. The deactivation of a vibronic excitation will pass through one ore more CIs to the ground state. The non–radiative decay of naphthalene and pyrene radical cation, for example, that happen within less than a picosecond\textsuperscript{[158,204]} has been shown\textsuperscript{[116,117]} to proceed via two CIs. Vibronic coupling with the D\textsubscript{2} state is as well at the origin of the non–radiative decay of certain benzyl type radicals that has been intensively studies in gas and solid phase.

Finally, photochemical reactions in the excited state can be important. Triphenylmethyl radicals\textsuperscript{[121,205]} and the isoelectronic triarylamine radical cations,\textsuperscript{[206]} for example, efficiently react to give a ring–closed product. Trifunac and co–workers\textsuperscript{[158,204,207,208]} claimed that electron

\textsuperscript{5}An exception to this is tetrathiafulvalene discussed in chapter 7.1.

\textsuperscript{6}As evident from eq. 2.6 on page 13.
capture from the solvent ("hole–injection"), i.e. oxidation of the solvent by the photoexcited solute, is a general mechanism for decay of photoexcited radical cations in liquid solution. The efficiency depends on the ionisation potentials of solute and solvent and can reach up to 50%.\textsuperscript{204} It is not only operative in polar solvent such as alcohols (where it is accompanied by proton transfer),\textsuperscript{204} but also in ethers\textsuperscript{204} and alkanes.\textsuperscript{207,208} In acetonitrile, this deactivation mechanism is suppressed owing to the high ionisation potential of this solvent.\textsuperscript{204}

### 3.3.2. Benzyl type radicals

Benzyl type radicals are derived from toluene. As indicated in Figure 3.5, the radicalic site is situated at the α carbon. Emission was observed in low temperature matrix experiments and for some in liquid phase at ambient temperature.\textsuperscript{193,196} The observed emission corresponds to the dipole–forbidden $D_1 \rightarrow D_0$ transition whose molar absorptivity is only $\approx 50 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ in benzyl radical and as a result of its forbidden character, the fluorescence lifetime is very long, $\tau_{flr} = 1.4 \mu s$ in 3–methylpentane at 77 K.\textsuperscript{121,202} The excited state lifetime of benzyl radical shows an unusually pronounced temperature dependence (Figure 3.6). At room temperature $\tau_{flr}$ has been estimated to 800 ps which, together with the low $k_{rad}$, makes it essentially non–emissive.\textsuperscript{121}

![Figure 3.5.: Fluorescence excitation (solid) and emission (dashed) spectrum of benzyl radical in 3–methylpentane at 77 K.\textsuperscript{209}](image)

Mixing of the close lying $^2 A_2$ and $^2 B_2$ excited states, separated by less than $\approx 700 \text{ cm}^{-1}$, has been invoked to account for the unusual absorption and fluorescence fine structure.\textsuperscript{193,202,210} Ring–substitution (contrary to α–substitution) affects this energy gap and thereby $k_{nr}$. 4–cyano substitution, for example, prolongs the room temperature lifetime from 800 ps to 58 ns.\textsuperscript{211} The mixing of $D_1$ and $D_2$ is also influenced by the solvent as has been argued by Meisel and co–workers\textsuperscript{121} on the basis of the observation that $\tau_{flr}$ is shorter in gas than in condensed phase.

The fluorescence lifetimes of benzyl type radicals span a range of 2 orders of magnitude, falling between 1 and 400 ns.\textsuperscript{197} Owing to the vibronic coupling, the excited state lifetime are sensitive to subtle changes in the substitution. Unsymmetric substitution patterns have
additionally an effect on the molar absorptivity of the longest wavelength absorption, raising $\varepsilon$ and $\Phi_{\text{flr}}$ while decreasing $\tau_{\text{flr}}$.

**Diphenylmethyl radical** absorbs almost at the same energy as benzyl radical. It is not planar and a $n\pi^*$ state is mixed to the lowest lying state of $\pi\pi^*$ type. The molar absorptivity of the $D_1\leftarrow D_0$ transition is 10 times higher than that of benzyl radical since it is less forbidden and consecutively the excited state lifetime is shorter. Substitution of the methyl hydrogen by an alkyl chain further increases $k_{\text{rad}}$ and $\Phi_{\text{flr}}$ rises from 0.3 to 0.8.[212]

The fluorescence lifetime of diphenylmethyl radical is almost independent of the temperature (430 ns in methyl–cyclohexane at 77 K,[212] 255 ns in hexane at r.t.[213], see Figure 3.6) as opposed to benzyl radical just described. This has been rationalised by a larger $D_1\leftarrow D_2$ energy gap, 3000 cm$^{-1}$. The fluorescence properties are governed by $D_1$ exclusively which manifests in a ELG behaviour when comparing differently substituted or deuterated diphenylmethyl radicals.[87]

**Triphenylmethyl radical** is very much alike diphenylmethyl radical in what concerns the nature of the frontier orbitals, $\varepsilon$, $\tau_{\text{flr}}$, or $\Phi_{\text{flr}}$. Except for a photodecomposition pathway that opens at ca. 200 K,[7] $\tau_{\text{flr}}$ is temperature independent, 240 ns.[121] Again, good mirror–image relationship between absorption and emission is found and it was concluded that the $C_3$ geometry is preserved in the excited state.

The irreversible photochemical reactions can be largely impeded by perchlorination.[216–218] The fluorescence parameters of perchloro–triphenylmethyl radical in r.t. cyclohexane are $\tau_{\text{flr}} = 7$ ns and $\Phi_{\text{flr}} = 0.02$.[205] The main deactivation pathway ($\Phi = 0.71$) remains a photochemical reaction, presumably charge separation to a state with a positive charge at the central carbon and the electron and hole at one of the aryl rings, $\text{Ar}_2\text{C}^+\text{Ar}^-\cdot$. This state decays either back to the ground state or to the photocyclisation product. “Direct” $D_1\rightarrow D_0$ IC is quite effective as well with a quantum yield of $\Phi_{\text{IC}} = 0.27$.[205]

3.3.3. Benzenoid radical cations

A considerable number of radical cations derived from benzene show luminescent properties. Fluorescence of the unsubstituted benzene radical cation, $\text{C}_6\text{H}_6^+$ is not observed in gas–phase though those of halogenobenzenes have quantum yields near unity under the same conditions.[219]

Uncertainty exists about emission from benzene radical cation in low temperature matrix that has been reported by Miller and co–workers[220] but questioned by the same author in a later review.[193] Using photoionisation spectroscopy, it was possible to detect a very long lived ($>10\mu$s) excited state at ca. 18.5 kK.[221]

Radical cations of halogenobenzenes, halogenated alkylbenzenes, alkylphenols, styryl and related compounds show emission in noble gas matrices and gas phase. The first electronic transitions fall in the 16 to 25 kK (600 to 400 nm) energy region,[8] and correspond to $\pi\pi$ transitions. The fluorescence lifetimes range from <1 ns to 50 ns (see Table 3.1 for some representative

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7 A ring–closure reaction that diminishes $\tau_{\text{flr}}$ at r.t. to less than 1 ns.[197] The quantum yield of photocyclisation is unity at r.t.[214–215]

8 Compared to $\approx 40$ kK for the neutral parent molecules.
3. Radical ions

Figure 3.6.: Temperature dependence of the inverse fluorescence lifetime of benzyl (ΦCH$_2$•), diphenyl (Φ$_2$CH•) and triphenyl (Φ$_3$C•) radical. Adapted from Ref. [121]

Table 3.1.: Examples for the fluorescence properties of benzenoid radical cations in neon matrix. Substituents not specified are hydrogens. See Ref. [75,193] for an almost complete list.

<table>
<thead>
<tr>
<th>substituent</th>
<th>$E_{00}$/ kK</th>
<th>$\tau_{flr}$/ ns</th>
<th>$\Phi_{flr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_6$</td>
<td>19.8</td>
<td>$&gt;10^4$</td>
<td></td>
</tr>
<tr>
<td>F$_6$</td>
<td>21.6</td>
<td>42</td>
<td>1.00</td>
</tr>
<tr>
<td>F$_5$</td>
<td>23.0</td>
<td>40</td>
<td>0.98</td>
</tr>
<tr>
<td>1,2,3,5–F$_4$</td>
<td>23.2</td>
<td>43</td>
<td>0.99</td>
</tr>
<tr>
<td>1,2,4,5–F$_4$</td>
<td>24.4</td>
<td>30</td>
<td>0.61</td>
</tr>
<tr>
<td>1,3,5–F$_3$</td>
<td>21.8</td>
<td>53</td>
<td>1.00</td>
</tr>
<tr>
<td>1,2,3–F$_3$</td>
<td>22.3</td>
<td>48</td>
<td>0.74</td>
</tr>
<tr>
<td>1,2,4–F$_3$</td>
<td>24.2</td>
<td>10</td>
<td>0.14</td>
</tr>
<tr>
<td>1,3–F$_2$</td>
<td>23.0</td>
<td>$&lt;5$</td>
<td>0.01</td>
</tr>
<tr>
<td>OH,F$_5$</td>
<td>22.4</td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>
### 3. Radical ions

#### X Y name

<p>| | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>N</td>
<td>N</td>
<td>phenazine</td>
</tr>
<tr>
<td>N</td>
<td>S</td>
<td>phenothiazine</td>
</tr>
<tr>
<td>S</td>
<td>S</td>
<td>thianthrene</td>
</tr>
</tbody>
</table>

Examples. Fluorescence quantum yields are in general high, up to unity, except for those benzenoide radical cations, for which the lowest excited state has σ symmetry (like it is the case for $C_6H_6^+$) in which case non-radiative relaxation becomes the main pathway.\(^{[219,222,223]}\) The state ordering is a function of nature and position of the substituents and sensitive to small changes. For example, $\Phi_{\text{flr}}$ differs by a factor of $\geq 5$ between the three trifluorotrifluorobenzene radical cation in Table 3.1.

In many cases vibrational information could be extracted from the spectra. It was noted\(^{[193,224]}\) that there are only minor changes in the vibrational frequencies when going from the neutral parent to the ground or excited state of the radical cation so the geometrical parameters are thought to change little upon oxidation or excitation.\(^{[75]}\)

The benzenoid radical cations of formal $D_{3h}$ or $D_{6h}$ symmetry are subject to Jahn–Teller distortion.\(^{[108,190,193,225]}\)

#### 3.3.4. Room temperature photophysics

It is remarkable that only a handful of reports of r.t. fluorescent of radical ions in liquid solution are available. Fluorescence was published\(^{[9]}\) for the positive radical ions of

- perylene in BF$_3$/CF$_3$CO$_2$H,\(^{[226]}\)
- tetracene in BF$_3$/CF$_3$CO$_2$H,\(^{[226]}\)
- tetramethylbenzidine in aq. dodecylsulfate,\(^{[226]}\)
- 5,10–dihydro–5–methylphenazine in iso–propanol,\(^{[227]}\)
- 5,10–dihydro–5,10–dimethylphenazine in EtOH:MeOH,\(^{[198]}\)
- N–methylphenothiazine in MeCN,\(^{[228]}\)
- thianthrene in CH$_2$Cl$_2$,\(^{[229]}\)
- two triarylamines in CH$_2$Cl$_2$,\(^{[230]}\) and
- three methoxybenzenes MeCN,\(^{[199,231]}\)

and the mono–negative radical ions of

- benzoquinone in iso–octane,\(^{[232]}\) and
- biphenyl in polyethylene glycol dimethylether.\(^{[233]}\)

The fluorescence quantum yields, where determined, had in general very low values. A r.t. fluorescence lifetime is only available for the methoxybenzene radical cations\(^{[234]}\) and benzoquinone radical anion.\(^{[232]}\)

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\(^9\)Note that the reports concerning N–methylphenothiazine and thianthrene radical cation are questionable. These and the results for perylene, tetracene, tetramethylbenzidine, and triarylamine radical cations are discussed in more detail in part II.
The lifetime of 1,3,5-trimethoxybenzene radical cation amounts to 40 ps, ca. 10 times smaller than the lifetime estimated from EGL or the Strickler–Berg relationship.\cite{234} The fluorescence properties of the radical cations of 3,5-dimethoxyphenol and 3,5-dimethoxyanilines are alike.\cite{199} Quantum chemical calculations showed that the observed fluorescence corresponds to a $D_2 \rightarrow D_0$ transition.

It is interesting to note which methoxybenzene radical cations are luminescent and for which ones the fluorescence quantum yield is below the detection limit: introduction of alkyl or acetyl substituents reduces $\Phi_{flr}$.\cite{235} Molecules with more than three aromatic hydrogens and molecules without $D_3h$ symmetry or pseudo–symmetry are non–fluorescent.\cite{231} The calculations revealed that the $D_1 \rightarrow D_2$ and $D_2 \rightarrow D_3$ energy gap greatly varies with the substitution pattern. While both energy gaps are big for the fluorescent chromophores, either $D_1$ or $D_3$ is energetically close to $D_2$ in the non–fluorescent molecules.\cite{231} 1,2-Dimethoxybenzene radical cation, however, refused to fit this explanation — having essentially the same energy levels as 1,3,5-trimethoxybenzene radical cation, it did not show any measurable fluorescence signal.\cite{231}

Hamarström and co–workers drew attention to the fact that methyl viologen radical cation did not show any ESA.\cite{236} Readily observable ESA was reported, on the other hand, for astaxanthin radical cation, a carotene derivative.\cite{238} Wachtveitel and co–workers interpreted the complex TA dynamics as $D_3 \rightarrow D_2$ IC ($\tau_1 = 100$ fs), $D_2 \rightarrow D_1$ IC ($\tau_2 = 900$ fs) and a biphasic decay of $D_1$ ($\tau_3 = 5$ ps, $\tau_4 = 40$ ps). This is not quite in agreement with the amplitude spectra (DADS), that show that the decay of the bleach is associated with $\tau_1$ while the other amplitudes have the typical
features of a vibrationally hot ground state. This suggests that the excited state lifetime of astaxanthine radical cation equals to $\tau_1$. Such an interpretation, however, is at odds with the measured fluorescence time profile at $\lambda_{\text{emi}} = 1600$ nm, which decays with $\tau_3$ and $\tau_4$,\textsuperscript{[238]} in support of Wachtveitl’s assignment.\textsuperscript{10}

**Radical anions.** Very short lifetimes were also evidenced for excited states of radical anions: GSR of the radical anions of perylene,\textsuperscript{[240]} anthraquinone,\textsuperscript{[240]} and tetraquinone\textsuperscript{[241]} took place within the IRF (15 ps).

These results are contrasted by those of Wasielewski and co–workers who studied a series of aromatic imides and diimides radical anions (Figure 3.7).\textsuperscript{[185]} The radical anions were generated electrochemically in an OTTLE cell and TA spectra recorded after excitation into the intense VIS absorption band. Lifetimes of 6–600 ps were observed (Figure 3.7). The authors noted that IC from higher excited states to $D_1$ happened within the IRF, that none of the imide and diimide radical anions showed pronounced ESA or photoionisation, and that the ESA of the neutral resembled the steady–state absorbance of the radical anion (c.f. page 30).\textsuperscript{[185]}

\textsuperscript{10}In this context the discussion about the assignment of TA bands in closed–shell carotenoids should be mentioned which was recently reviewed by Polívka and Sundström.\textsuperscript{[239]}
The N–alkyl and N–aryl compounds have essentially the same redox properties and absorption spectra, but distinct D$_1$ state lifetimes. The short lifetimes were explained by the D$_1$–D$_0$ energy gap,[185] a linear trend when plotting $\tau_{D1}$ vs. ln($E(D_1)$) is, however, not observed and especially the difference following alteration of the nitrogen substituent sticks out.

Fulleride mono anion (C$_{60}^-$) showed essentially the same GSR time constant in toluene:acetonitrile or THF solution (3.5 to 4 ps)$^{[242]}$ as in gas–phase (2.2 ps)$^{[243]}$. Meech and co–workers took this consistency as verification that the radiationless decay in C$_{60}^-$ is dominated by intramolecular relaxation, presumably via a Jahn–Teller distortion. The GSR for the dianion was much faster than for C$_{60}^-$, the former comprising a dominant recovery time of 400 fs.$^{[242]}

**Summarising** the above cited examples, the excited state lifetime of radicals and radical ions has been shown to be governed by i) $k_{rad}$ (e.g. diphenylmethyl radical); ii) vibronic coupling of D$_1$ with D$_2$ (e.g. benzenoid radical cations) which leads to complex temperature and substituent dependence of the photophysics; or iii) photochemical reactions (e.g. triphenylmethyl radical).

While many examples show nanosecond lifetimes in low temperature or gas phase experiments, the electronic excited states of most radical ions are extremely short lived in liquid solution, with excited state lifetimes on the picosecond scale and below. As discussed in chapter 2, important influences of the temperature that could explain the discrepancy between $k_{nr}$ observed in low temperature matrix and ambient temperature liquid phase experiments are only expected for vibronic coupling or photochemical reactions while $k_{rad}$ can in good approximation be considered as temperature independent.

In other words, it is $k_{nr}$ that is a function of temperature where vibrational coupling is operative, what is expected to be a general feature for radicals as discussed in chapter 3.2.3.
Part II.

Results and discussion
This chapter reports the experimental results obtained for several radical ions. They span quite a range of chemically distinct species and allowed for the study of a variety of effects. For each system under discussion a short introduction will describe its properties and put the results in the context of information available in the literature.

In the case of Wurster’s salts, a class of radical cations with extraordinary persistence, a systematic study of the influence of solvent and substitution pattern has been undertaken. Wurster’s salts are structurally related to arylamine compounds two examples of which have been included.

Perylene radical cation and tetrathiafulvalene are examples for fluorescent radical ions but whereas $\Phi_{\text{flr}}$ is close to unity for neutral perylene, it is negligibly small for neutral TTF. Both, radical cation and anion of perylene have been investigated.

Finally an example of a neutral radical, galvinoxyl, is presented. As will be shown, the excited state lifetime was found to be as short as that of the charged radicals.

Due to the general fact, that radicals have energetically lower–lying transitions than their neutral parents or the di–ions (see page 29 or the steady–state absorption spectra throughout this chapter), it was always possible to excite solely the radical ion in the time–resolved experiments.\(^{11}\) This is crucial since the electrochemical flow cell employed for the generation of some radical ions did not convert the neutral quantitatively. Even when pure salts of radical ions have been used was the sample not free of the neutral and the double charged ion owing to disproportionation reactions that are a general feature of radicals in liquid solution. The equilibrium and rate constants of the disproportionation reaction depends on the solvent.

The models for the spectral dynamics employed. The dynamics observed does in general not follow an exponential decay. This is due to the multitude of observed states and phenomena and/or the non-exponentiality of their dynamic behaviour. Multi-exponential fits can reproduce non-exponential dynamics if just the number of exponents is sufficiently high. A distribution of lifetimes caused by inhomogeneous broadening, for example, can be reproduced by a biexponential function.

In all cases presented in this thesis the measured TA time traces could be well described by a model of sequential kinetic rate equations, in which a species (state) $A$ transforms into $B$ by an exponential law. $B$ itself decays to species $C$ (and so on, if necessary).

\[
A \xrightarrow{k_{AB}} B \xrightarrow{k_{BC}} C \ldots
\]

Since such an approach is biased — it assumes that a certain model applies to the system under investigation —, a “neutral” multi-exponential fit was also performed. It corresponds to a situation where all “reactions” start in parallel and decay independently.

\[
A \xrightarrow{k_1} B
A \xrightarrow{k_2} C
\ldots
\]

\(^{11}\) with the exception of Wurster’s red that showed fluorescent decomposition products.
Part II. Results and discussion

Figure 3.8.: Three state model used to reproduce the dynamics of the TA data of Pe•+ after 800 nm excitation. The first state corresponds to the D\textsubscript{1} state that is optically populated, the second state to the vibrationally hot D\textsubscript{0} state, the last to the relaxed D\textsubscript{0} state.

To give an example, the results obtained with Pe•+ shall be anticipated at this point. The TA signal of Pe•++ in MeCN after 800 nm excitation was found to decay biexponentially with \( \tau_{a1} = 5 \text{ ps} \) and \( \tau_{a2} = 24 \text{ ps} \). The sequential model needs thus three states (see Figure 3.8) where A is the first state observed in the TA spectra, B an intermediate and C the final state (which has a zero–spectrum in TA). It will be argued on basis of the decays associated difference spectra (DADS) and species associated difference spectra (SADS, see page 182 for a discussion of these terms) that A is the D\textsubscript{1} excited state, B a vibrationally hot D\textsubscript{0} state, and C the relaxed D\textsubscript{0} state.

Throughout the text, only the lifetimes and SADS that result from such the target analysis are presented. The DADS that result from multi-exponential fits are given in the appendix, page 199 ff.
4. Wurster’s salts

Wurster’s salts are radical cations derived from \( p \)-phenylenediamine and have the general structure shown in Figure 4.1. The most stable and famous one is the tetramethyl substituted compound known as Wurster’s Blue.

Wurster’s salts have been extensively studied, apart from their excited-state properties, owing to their importance to the development of radical chemistry\(^ {175} \) and their use in photography,\(^ {9} \) photoinduced electron transfer reactions,\(^ {11,20,245,246} \) and hole transporting materials.\(^ {247–250} \)

Four Wurster’s salts have been studied in this thesis (Figure 4.1). The choice is dictated by the search for the molecular coordinate that is responsible for the excited-state decay: alteration of the alkylamino groups and isotopic substitution of the phenyl core were supposed to unravel the participation of these two entities. Alkyl groups introduced into the ring are known to strongly favour decomposition if the amino group is substituted as well,\(^ {6} \) and therefore no such sample was included.

\[
\begin{array}{cccc}
R_1^1 & R_2^2 & R_3^3 & \text{abbr.} \\
\text{Me} & \text{Me} & \text{H} & \text{WB}^{\ddagger} \\
\text{Me} & \text{Me} & \text{D} & \text{d}4\text{-WB}^{\ddagger} \\
\text{Me} & \text{H} & \text{H} & \text{WR}^{\ddagger} \\
\text{i}–\text{Pr} & \text{i}–\text{Pr} & \text{H} & \text{TiPD}^{\ddagger} \\
\end{array}
\]

Figure 4.1.: Structure formula of Wurster’s salts indicating the resonances and the abbreviations used.
4. Wurster’s salts

4.1. Antecedents

In 1879, when Casimir Wurster\(^\text{[172]}\) isolated the radical cation of N,N,N’,N’-tetramethyl-p-phenylenediamine (TMPD), nowadays commonly known as Wurster’s Blue (WB\(^\bullet\)),\(^1\) he did not know about its electronic structure and the first proposal of the existence of free radicals bearing unpaired electrons\(^\text{[168]}\) was still several years ahead.

WB\(^\bullet\) had an important role in the acceptance of radicals as persistent species and contributed significantly to the development of the corresponding terminology.\(^\text{[175,251]}\) Naturally its history is closely related to the development of electron paramagnetic resonance (EPR) where it was among the first substances for which hyperfine coupling was reported\(^\text{[252]}\) and where it serves as calibration standard.\(^\text{[253]}\) The complex EPR spectrum was published and interpreted several times\(^\text{[252,254–259]}\) and the results indicate a planar structure with two equivalent nitrogens and freely rotating methyl groups at r.t.

Electronic absorption. The intense blue color of WB\(^\bullet\) that attracted already Casimir Wurster arises from a structured absorption band peaking at 610 nm and extending down to ca. 450 nm. Polarization experiments on crystals,\(^\text{[260,261]}\) together with the independence of the Raman signal on the excitation wavelength\(^\text{[262]}\) and quantum chemical calculations\(^\text{[263]}\) suggest that this band is associated with a single electronic transition.

This transition, that has no correspondence in either the neutral nor the dicaticonic oxidation state (see Figure 4.2), puzzled scientists at the beginning of the 20\(^\text{th}\) century and its origin was debated intensively until it was established that WB\(^\bullet\) exists as monomolecular free radical in solution and the absorption does not stem from a dimer.\(^\text{[175,264,265]}\) Quantum chemical calculations agree with experiment in assigning this band to the D\(_1\)←D\(_0\) transition,\(^\text{[263,266]}\) having the transition dipole moment in the molecule’s long axis.\(^\text{[267]}\) Its position is sensitive to the number of aminoalkyl substituents (Figure 4.3).\(^\text{[6]}\)

The similarity of the UV/visible absorption spectrum of WB\(^\bullet\) and the triplet state of the neutral parent compound is remarkable (Figure 4.6). It means that not only the energies but also the Franck-Condon factors are very much alike for these two species. Such a finding is common for a couple of fluorophores like aniline\(^+\), N,N-dimethylaniline\(^+\), and some anions of polyaromatic hydrocarbons\(^\text{[261]}\) but the agreement between triplet and ion spectra is especially high for TMPD and extends even to the UV region. Cadogan and Albrecht\(^\text{[261]}\) rejected the possibility that a long lived charge separated state that decays to a short lived triplet state is the one observed in triplet-triplet absorption experiments due to the photo-chemical behaviour of the observed state towards oxygen.

A fluorescence spectrum of WB\(^\bullet\) at liquid nitrogen temperature that nicely mirror-images the absorption spectrum has been reported by Albrecht and Simpson\(^\text{[260]}\) in 1955. Fluorescence emission of WB\(^\bullet\) has also been reported in r.t. solution and on alumina surfaces but the spectral position and shape do not fit well the earlier report and the observed emission stems probably from the dimer.\(^\text{[269]}\)

\(^1\)This abbreviation is a bit misleading since the name Wurster’s Blue applies to the radical cation, not the neutral precursor (which is called Wurster’s reagent). For reasons of consistency, the charge and radical nature are nonetheless explicitly indicated. The same is true for Wurster’s red and Magic blue (vide infra).
Figure 4.2.: Absorption spectrum of N,N,N’,N’–tetramethyl–p–phenylenediamine (TMPD, top) and of N,N–dimethyl–p–phenylenediamine (DMPD, bottom) in neutral, cationic and dicationic oxidation state. Note that due to disproportionation the spectra contain contributions from other oxidation states.
4. Wurster’s salts

Figure 4.3.: Influence of amino group substitution on the absorption spectrum of Wurster’s radicals (bottom).\cite{6}

Figure 4.4.: Molecular orbitals involved in the lowest energy electronic transition of WB\(^{**}\).\cite{263}
Structure. According to X-ray, EPR, IR and Raman measurements, WB\textsuperscript{++} has a semi-quinoid, planar form in its electronic ground state. A resonant Raman study showed that the N–ring stretching frequency values are intermediate between single and double bond, indicative of a strong conjugation of the free N electrons to the electrons of the ring and thus a semi-quinoid structure. This is also in agreement with the bathochromic shift introduced upon N substitution mentioned earlier. From the resonance Raman enhancement factors, Poizat et al. concluded that the visible D\textsubscript{1}→D\textsubscript{0} transition leads to a conformational change that strongly influences the interactions of the N–alkyl groups with the system.

The Franck–Condon active vibrational mode that can be observed in the electronic absorption and emission spectra is depicted in Figure 4.5. It is a so-called 8\textsubscript{a} vibration (Wilson notation) which is an in–plane ring mode involving only ring carbons and to a little extend the aromatic hydrogens. Strong resonance enhancement factors have been found for this mode, which means its strongly coupled to the electronic transition. It is interesting to note, that TD–DFT calculations by Brédas and co–workers predict that geometry relaxation after photoexcitation is dominated by this mode and a low–frequency mode associated with the methyl groups.

Like many other radical ions, WB\textsuperscript{++} dimerises in low–temperature solution and in crystals, what leads to the changes of the absorption spectrum depicted in Figure 4.7. The dimer’s absorption spectrum shows a band at 800 nm and has a different shape in the 450 to 610 nm spectral region.

The photoelectron spectrum of TMPD shows the first peak at 6.78 eV, the second at 8.36 eV (\(\Delta E = 1.58 \text{ eV} = 12.8 \text{kK} = 790 \text{nm}\)) and the third at 8.74 eV. This places the second excited state of WB\textsuperscript{++} only 0.4 eV or 3.2 kK above D\textsubscript{1}. Owing to the state’s symmetry, the D\textsubscript{2}→D\textsubscript{0} transition is dipole forbidden and therefore not observed in optical spectroscopy.
Figure 4.6.: Comparison of the triplet–triplet absorption spectrum of TMPD with the absorption of WB$^\bullet$.\textsuperscript{[261]}

Figure 4.7.: Dimerisation of WB$^\bullet$ $8 \cdot 10^{-5}$ mol·L$^{-1}$ in EtOH:Et$_2$O when cooling from r.t. (1) to 113 K (4).\textsuperscript{[272]}
4. Wurster’s salts

Table 4.1.: Properties of Wurster’s reagents. First and second oxidation potentials $E^{1/2}$ vs. SCE (MeCN/Bu$_4$NPF$_6$)\(^{[259,276,277]}\) and ionisation potentials.\(^{[275]}\) The radical cations’ first electronic transition with molar absorptivity\(^{[259,267,278]}\) (CH$_2$Cl$_2$ except EtOH).

<table>
<thead>
<tr>
<th>cmpd</th>
<th>$E^{1/2}_1$</th>
<th>$E^{1/2}_2$</th>
<th>IP$_1$</th>
<th>IP$_2$</th>
<th>IP$_3$</th>
<th>$\lambda_{\text{abs}}^{\text{max}}$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMPD</td>
<td>115</td>
<td>703</td>
<td>6.84</td>
<td>8.36</td>
<td>8.74</td>
<td>617</td>
<td>12600</td>
</tr>
<tr>
<td>TiPD</td>
<td>105</td>
<td>700</td>
<td></td>
<td></td>
<td></td>
<td>620</td>
<td>12600</td>
</tr>
<tr>
<td>DMPD</td>
<td>205</td>
<td>755</td>
<td>7.45</td>
<td>9.00</td>
<td>9.85</td>
<td>552$^\dagger$</td>
<td>7900$^f$</td>
</tr>
</tbody>
</table>

Figure 4.8.: Crystal Structure of TiPD$^{\ast\ast}$ closo-dodecamethylcarboranate.\(^{[278]}\)

Variation of N–substitution. As mentioned before, the position of the optical transition of Wurster’s salts depends on the substitution pattern at the nitrogen (see Figure 4.3).\(^{[6]}\) The exact nature of the alkyl substituent does not play a role for the VIS absorption spectrum — it is, for example, identical for WB$^{\ast\ast}$, TiPD$^{\ast\ast}$ and even in the N,N,N’,N’–tetrabenzyl it is only red–shifted by 200 cm$^{-1}$.\(^{[259,278]}\) Note that the situation changes completely when introducing phenyl or other aromatic groups, as will be discussed in chapter 5.

EPR\(^{[259]}\) and X-ray\(^{[278,279]}\) results show that the $p$–phenylenediamine unit in TiPD$^{\ast\ast}$ is as well planar, but the $i$–propyl group is turned so that the methyl groups are arranged out of the plane and face substantial steric hindrance (Figure 4.8). This planarity is not given in the neutral parent compound: the sum of the C$_{ar}$–N–C$_{al}$ angles in crystals is 360$^\circ$ in TiPD$^{\ast\ast}$ (Figure 4.8) whereas it amounts to 341$^\circ$ in the neutral parent.\(^{[278]}\)

The redox potential of TiPD$^{\ast\ast}$ does not follow the trend of $n$–alkylamino Wurster’s salts what Grampp et al. related to the lower stability of the radical cation.\(^{[259]}\) The difference between first and second oxidation potential is almost identical for TMPD and TiPD which is in good agreement with the identical electronic transition energy (Table 4.1).

$^2$The transition energy is, on the other hand, hardly influenced by substitution at the central ring but the spectral shape is — partially due to increasing instability of the sample.\(^{[6]}\)
**Wurster’s Red.** A planar, quinoid structure is as well ascribed to Wurster’s red (WR•+) on the basis of EPR,\(^{259,280}\) IR,\(^{281}\) and Raman spectra.\(^{282}\) The C\(_{ar}\)−NH\(_2\) and C\(_{ar}\)−NMe\(_2\) bonds in WR•+Br\(^–\) crystals have distinct lengths, 1.23 Å and 1.30 Å, respectively, in contrast to the tetraalkyl congeners.\(^{283}\) The authors stress at the same time that one can not conclude that the charge is preferentially located on one of the nitrogen atoms.\(^{283}\)

The first electronic absorption of WR•+ is found at 18.0 kK, i.e. blue–shifted by 1800 cm\(^−1\) with respect to the Wurster’s salts discussed before while showing the same vibrational progression (\(\Delta\tilde{\nu} = 1640\) cm\(^−1\)) which is assigned to an 8\(\alpha\) vibration and is resonance–Raman active.\(^{282}\)

Katsumata and Kimura\(^{284}\) calculated the transition energies of WR•+ using semi–empirical quantum chemistry and found that the first electronic transition, though not symmetry forbidden, has a very small oscillator strength. It was placed at 2.36 eV (19.0 kK = 525 nm), almost the same energy as the transition that was ascribed to the first band visible in the absorption spectrum.

From the relative energy of the peaks in the photoelectron spectrum of DMPD (Table 4.1) and within Koopman’s theorem,\(^{285,286}\) the positions of electronic transitions of DMPD are expected at 12.5 kK = 800 nm, 19.3 kK = 520 nm, and 32.0 kK = 315 nm.\(^{275}\) Comparing with Figure 4.2 shows that the agreement is poor.

The first redox potential of DMPD is found at significantly higher potentials than for tetraalkyl compounds (Table 4.1). At the same time is the second oxidation potential lower, resulting in a shift of the disproportionation constant by one order of magnitude to \(K_{\text{dis}} = 10^{-9}\) (equation 3.1).

The dimerisation equilibrium of WR•+ is shifted towards the dimers when compared with WB•+.\(^{174}\) The spectral changes following dimer formation are similar, i.e. a hypsochromic shift of the absorption bands and appearance of a broad band in the red of the D\(_1\)←D\(_0\) absorption band.\(^{272}\)

### 4.2. Results

#### 4.2.1. Results for Wurster’s Blue

The absorption spectrum of WB•+ at r.t. in MeCN solution and in PMMA film at r.t. and in EtOH:MeOH = 1:1 at 85 K are shown in Figure 4.9. The spectrum recorded in MeCN is exemplary for all solvents used, the position and shape of the WB•+ visible absorption band showed only very small solvatochromic shift, 250 cm\(^−1\) between MeCN and CH\(_2\)Cl\(_2\). Major differences were noted in the UV part but they were assigned to the bands of neutral and dicationic TMPD. The concentration of these species is solvent dependent since the solvent influences the disproportionation equilibrium.

When cooling a solution of WB•+, the absorption spectrum remained essentially unchanged and perfectly resembled the r.t. spectrum with the exception of a slight red shift that took place when going from r.t. to the freezing point of the matrix, an effect that is attributed to the change of the refractive index (Figure 4.9). Further temperature decrease did not lead to any significant changes of the absorption band.

**Fluorescence.** No steady–state fluorescence could be detected for WB•+ at r.t., neither in glycerol nor in a PMMA film. As temperature was lowered below about 140 K, however, a flu-
Figure 4.9.: Absorption spectrum of WB$^{+\text{+}}$ in MeCN and PMMA solution at r.t. and in EtOH:MeOH = 1:1 at 85 K (top). Absorption spectra of WB$^{+\text{+}}$, d4–WB$^{+\text{+}}$, WR$^{+\text{+}}$ and TiPD$^{+\text{+}}$ in MeCN at r.t. (bottom).
4. Wurster’s salts

Figure 4.10.: Temperature dependent emission of WB•+. Absorption (solid black), fluorescence excitation (broken black, λem = 710 nm, 85 K) and emission (λexc = 530 nm) spectra of WB•+ in EtOH:MeOH = 1:1 at different temperatures.

A fluorescence band that was mirror-image to the absorption became apparent (Figure 4.10). The fluorescence excitation closely followed the absorption spectrum. Both, fluorescence emission and excitation spectra in the visible were found to be independent of the wavelength of excitation or emission and did not resemble the dimer absorption shown in Figure 4.7. At liquid nitrogen temperature, the fluorescence quantum yield was estimated to be of the order of 0.01. The temperature dependence of the fluorescence intensity measured in EtOH:MeOH = 1:1 glass matrix is illustrated in Figure 4.11 and was found to be identical in EtOH and in PMMA film.

Like the fluorescence quantum yield, τflr was found to be strongly temperature dependent. A signal broader than the IRF of the TCSPC5 set-up could only be found below ca. 100 K, and further lowering of the temperature lead to an increase of the lifetime, similar to that of the fluorescence intensity (see Table 4.2). At the lowest temperature investigated, namely 77 K, τflr = 660 ps was determined. The Strickler–Berg relationship gave τrad = 34 ns from the steady–state spectra. Combining this value with the measured τflr results in Φflr = 0.02, in good agreement with the experimental estimate.

The increase of τflr at lower temperature cannot simply be ascribed to the change from liquid to solid phase because i) no fluorescence signal appeared in PMMA film at r.t. and ii) in all matrices, the fluorescence signal rose at the same temperature, well below the melting point of the matrix. For example, no fluorescence was present at 150 K with pure ethanol as solvent (melting point = 159 K).

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3Unless the excitation wavelength was in the UV
4Quantum counter oxazine 725, Φ=0.11 in ethanol at 24° C. [287]
5λexc = 600 nm, FWHM of the IRF ca. 800 ps
Figure 4.11.: Temperature dependence of the relative quantum yield (integrated fluorescence) and the non–radiative rate constant of WB$^{\bullet\bullet}$ (from SPC data assuming that $\tau_{fr} = \tau_{nr}$, r.t. data from TA assuming $\tau_{D1} = \tau_{nr}$).

Table 4.2.: Fluorescence of WB$^{\bullet\bullet}$ at different temperatures T. Fluorescence lifetime $\tau_{fr}$ from fit of SPC data (except † from FU), $k_{nr}$ (calculated assuming $k_{nr} = \tau_{fr}^{-1}$), $k_{rad}$ and $\tau_{rad}$ from the Strickler–Berg equation and quantum yield $\Phi_{fr}$ from $\tau_{fr}$ and $\tau_{rad}$.

<table>
<thead>
<tr>
<th>T / K</th>
<th>$\tau_{fr}$ / ps</th>
<th>$k_{nr}$ / $10^9$ s$^{-1}$</th>
<th>$\tau_{rad}$ / ns</th>
<th>$k_{rad}$ / $10^7$ s$^{-1}$</th>
<th>$\Phi_{fr}$ · 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.21†</td>
<td>4800</td>
<td></td>
<td></td>
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<tr>
<td>140</td>
<td></td>
<td></td>
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<tr>
<td>130</td>
<td>$\leq$ 400</td>
<td>2.4</td>
<td></td>
<td></td>
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<td>110</td>
<td>$\leq$ 400</td>
<td>2.3</td>
<td>34.5</td>
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</tr>
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<td>33.6</td>
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<tr>
<td>77</td>
<td>660</td>
<td>1.5</td>
<td></td>
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</tbody>
</table>
Figure 4.12.: Room temperature fluorescence dynamics of WB$^{\bullet+}$ in MeCN at various emission wavelengths with best biexponential fit (top) and the DAS obtained in the fit (bottom).
4. Wurster’s salts

The r.t. fluorescence lifetime was measured in a few solvents using FU and in agreement with the lack of steady–state signal, ultrafast relaxation was observed. The time profiles measured at several wavelengths between 620 and 800 nm could be well accounted for with a biexponential function (see Figure 4.12). In all three solvents, the obtained time constants were around of $\tau_{f1} \approx 0.1$ ps, i.e. shorter than the IRF, and $\tau_{f2} = 0.2$ ps (Table 4.4).

The decay associated spectra, obtained as described in Ref. 288 using the low–temperature fluorescence spectra, are depicted in Figure 4.12. The spectrum associated with $\tau_{f2}$ resembled closely the low temperature fluorescence spectrum and therefore this time constant can be unambiguously ascribed to the decay time of the emitting population. On the other hand, the spectrum associated with $\tau_{f1}$ rather suggested a red shift of the emission band, with the typical feature of positive and negative amplitudes for the blue and red part of the spectrum, respectively.

**Transient absorption.** TA spectra after $D_1 \leftarrow D_0$ excitation at 610 nm of a solution of WB$^{•+}$ in water are shown in Figure 4.13. At the shortest time delay, the spectrum was dominated by two negative bands — one between 450 and 600 nm that can be assigned to the bleach of the ground state absorption, and the other above 700 nm which can be attributed to SE — and by two positive bands due to ESA — a weak one around 450 nm and a more intense one around 650 nm. The SE as well as the 450 nm ESA bands had totally vanished after about 0.5 ps, whereas the bleach of the ground state absorption had only partially decayed and the 650 nm band broadened.

The complete decay of the bleach took place on the time scale of several picoseconds. In parallel to this, the 650 nm band decayed while shifting to the blue. Additionally, small positive absorption bands located between the maxima of the bleach band around 590 nm grew and then decayed to zero. The SADS extracted from the analysis of the spectra in water are illustrated in Figure 4.13.

The smallest time constant found in the TA dynamics and which dominates the decay of the SE and the ESA at 450 nm is very close to that observed by FU and was attributed to the decay of the emitting population. As a consequence, this time constant can be considered as the lifetime of the $D_1$ state of WB$^{•+}$.

The longer lived features observed in the TA spectra can be quite unambiguously ascribed to the absorption of a hot ground state because i) there is no electronic excited state between the optically populated and the ground state, ii) its absorption is located on the red side of the ground state bleach and partially overlaps with it, as testified by the small positive feature around 590 nm, and iii) it shifts continuously to the blue while decaying to zero as can be clearly seen from the amplitude spectra (Figure 4.13).

**Solvent influence.** Such measurements were repeated in solvents of different viscosity, polarity and H-bonding ability (Table 12.1 on page 192) and almost identical TA spectra were found in all of them. Table 4.3 and Figure 4.15 show that the $D_1$ lifetime of WB$^{•+}$ is essentially the same in all solvents investigated, independently of their viscosity, dielectric constant or H-bonding ability. They show furthermore that $\tau_{a1}$ and $\tau_{a2}$ are essentially solvent-independent whereas $\tau_{a3}$ changes from one solvent to another but does not show any correlation with solvent parameters such as dielectric constant, thermal diffusivity or viscosity.
Figure 4.13.: TA spectra of WB$^+$ in H$_2$O after 610 nm excitation and SADS from the target analysis.
4. Wurster’s salts

In line with the findings of Pigliucci et al.\textsuperscript{[145]} and Kovalenko et al.\textsuperscript{[147]}, however, $\tau_{a3}$ is significantly shorter in protic ($\text{H}_2\text{O}$, MeOH, EtOH and PrOH) than in aprotic solvents. The RTIL used here is not protic but shows an influence like the protic solvents. The coulombic interaction between the ethylsulfate anion and WB$\cdot^+\text{+}$ could enhance vibrational cooling.

In order to check the influence of excess excitation energy, a measurement with the pump pulses at 530 nm instead of 610 nm was also performed. No important difference was observed, except for a ca. 10\% increase of $\tau_{a3}$ (see Table 4.3). No pronounced influence of the counter-ion was found when generating WB$^\text{++}$ in the electrochemical cell with Bu$_4$NClO$_4$ as supporting electrolyte.\textsuperscript{6} Because of the presence of neutral and dicationic form, no attempts to excite with higher excess energy were undertaken.

4.2.2. Results for deuterated Wurster’s Blue

The spectra obtained with deuterated Wurster’s Blue, d$4$–WB$\cdot^+\text{+}$, were virtually identical to those of WB$^\text{++}$ (Figs. 4.9 and 4.16). The electronic absorption and fluorescence spectra showed identical band position and shape\textsuperscript{7}, no solvatochromic shift was present, no fluorescence was detected at r.t. in solution or a PMMA film but below $\approx$120 K in EtOH:MeOH = 1:1.

Unexpectedly, also the dynamic behaviour was very close to WB$^\text{++}$. The r.t. fluorescence decay was found to be biexponential (see Table 4.4) and the TA dynamics were triphasic (Table 4.3).

\textsuperscript{6}Proving at the same time the interchangeability of both these generation methods.
\textsuperscript{7}The change in vibrational frequency of the FC active mode from 1630 to 1610 cm$^{-1}$ was not observed.\textsuperscript{[262,266]}

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Figure 4.14.: Dynamic traces of the TA signal of WB$^\text{++}$ in $\text{H}_2\text{O}$ at selected wavelengths.
Table 4.3.: Lifetimes (in ps) obtained in the target analysis of the TA data of Wurster’s salts. †$\lambda_{\text{exc}} = 550$ nm. ‡ electrochemical generation with 0.1 mol-L$^{-1}$ Bu$_4$NPF$_6$ in MeCN.

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\tau_{a1}$</th>
<th>$\tau_{a2}$</th>
<th>$\tau_{a3}$</th>
<th>$\tau_{a1}$</th>
<th>$\tau_{a2}$</th>
<th>$\tau_{a3}$</th>
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<tbody>
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<td>WB$^{*+}$</td>
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<td>3.0</td>
<td>0.24</td>
<td>0.29</td>
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</tr>
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</tr>
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<tr>
<td>$\text{D}_2\text{O}$</td>
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<tr>
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<td>0.25</td>
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<td>PrCN</td>
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<tr>
<td>PhCN</td>
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<td>0.80</td>
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<tr>
<td>TiPD$^{*+}$</td>
<td>0.11</td>
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<td>5.7</td>
<td>0.10</td>
<td>1.3</td>
<td>10.9</td>
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<tr>
<td>WR$^{*+}$</td>
<td>0.11</td>
<td>0.10</td>
<td>5.7</td>
<td>0.11</td>
<td>1.3</td>
<td>10.9</td>
</tr>
</tbody>
</table>

Table 4.4.: Lifetimes (in ps) obtained in the bi-exponential fit of the FU data of Wurster’s salts. † Triple-exponential decay with $\tau_{f3} = 1.5$ ps that stems presumably from a degradation product (see text); ‡ ascribed to a photodegradation product.

<table>
<thead>
<tr>
<th>cmp</th>
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<td></td>
<td>$\tau_{f1}$</td>
<td>$\tau_{f2}$</td>
<td>$\tau_{f1}$</td>
</tr>
<tr>
<td>WB$^{*+}$</td>
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<td>0.10</td>
</tr>
<tr>
<td>d4–WB$^{*+}$</td>
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<td>0.22</td>
<td>0.10</td>
</tr>
<tr>
<td>TiPD$^{*+}$</td>
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<td>0.10</td>
<td>0.12</td>
</tr>
<tr>
<td>WR$^{*+}$</td>
<td>0.10</td>
<td>0.20</td>
<td>0.11</td>
</tr>
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</table>
Figure 4.15.: Solvent effect on the TA dynamics of Wurster’s salts: $\text{WB}^{\bullet+}$ downright triangles, $d4-\text{WB}^{\bullet+}$ upright triangles, $\text{TiPD}^{\bullet+}$ diamonds, $\text{WR}^{\bullet+}$ circles.
Figure 4.16.: Low-temperature fluorescence emission (solid lines) and excitation spectra (dotted lines) of d4–WB$^{++}$ in EtOH:MeOH = 1:1 at different temperatures.

Figure 4.17.: Fluorescence decay of Wurster’s salts in r.t. MeCN. $\lambda_{emi}$ corresponds to the 2nd vibronic peak.
Table 4.5.: Effect of isotopic substitution in the phenyl ring of WB•+ on the excited-state relaxation dynamics. \( r_n = \tau_{an}(\text{D})/\tau_{an}(\text{H}). \)

<table>
<thead>
<tr>
<th>solvent</th>
<th>( r_1 )</th>
<th>( r_2 )</th>
<th>( r_3 )</th>
</tr>
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<tbody>
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<td>1.3</td>
<td>1.3</td>
</tr>
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<td>EtOH</td>
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</tr>
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</tr>
<tr>
<td>D(_2)O</td>
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<td>0.8</td>
</tr>
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<td>MeCN</td>
<td>0.9</td>
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<td>1.0</td>
</tr>
<tr>
<td>PhCN</td>
<td>1.1</td>
<td>1.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Transient absorption.** As in the case of WB•+, \( \tau_{a1} \) and \( \tau_{a2} \) obtained in the target analysis of TA data of d\(_4\)-WB•+ proved to be independent of the solvent with average values of \( \overline{\tau}_{a1} = 0.26 \text{ ps} \) and \( \overline{\tau}_{a2} = 0.27 \text{ ps} \), indistinguishable from the averages found for WB•+. \( \tau_{a3} \) varied between ca. 2 and 7 ps with protic solvents having shorter lifetimes than aprotic solvents (Figure 4.15). Inspection of the DAS and SADS suggested to assign \( \tau_{f1} \) to a solvent induced shift, \( \tau_{f2} \) and \( \tau_{a1} \) to an excited-state decay and \( \tau_{a2} \) and \( \tau_{a3} \) to VER, just as for WB•+.

\( \tau_{f1} \) and \( \tau_{f2} \) in MeCN and D\(_2\)O were within experimental error identical for light and heavy WB•+ (Table 4.4). The situation was similar for the TA data. As can be seen in Table 4.5, no significant isotope effect can be extracted for \( \tau_{a1} \) and \( \tau_{a2} \). The isotope ratios are rather close to one and since \( \tau_{a1} \) and \( \tau_{a2} \) are close to the IRF of the set-up, the small differences can hardly be regarded as significant. For \( \tau_{a3} \) the lifetime differences are bigger but no clear trend shows up: while a decrease in lifetime upon deuteration is obtained in EtOH, H\(_2\)O and D\(_2\)O, the opposite is the case in MeOH and PhCN.

4.2.3. Results for TiPD•+

As shown in Figure 4.9, the absorption spectrum of TiPD•+ is very similar to that of WB•+ but slightly red-shifted and broader. The deviations are bigger in the UV where the neutral parent compounds absorb in line with bigger structural differences between the neutrals than between the mono-cations.\(^{[278]}\) The two peaks of the visible absorption band are found at 619 and 574 nm, respectively, that is 1270 cm\(^{-1}\) apart from one another.

**Low-temperature behaviour.** Cooling a solution of TiPD•+ in EtOH:MeOH = 1:1 gave the absorption spectrum shown in Figure 4.19. At low temperatures new absorption bands appeared at 240 and 740 nm that are most likely associated with the dimer. The apparent rise of the UV absorbance is mainly due to imperfection of the background subtraction,\(^8\) the slight red-shift (300 cm\(^{-1}\)) and accentuation that are similar to what has been observed with WB•+ are ascribed to the change from liquid to solid phase. The vibrational spacing measured at 80 K is 1430 cm\(^{-1}\), i.e. it approaches the energy spacing in WB•+ spectra.

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\(^8\) Differences in the glass quality between the sample and pure solvent that cause different amount of diffraction.
Figure 4.18.: TA spectra after 610 nm excitation and SADS of d4-WB*+ in r.t. MeCN.
Figure 4.19.: Absorption spectrum of TiPD$^{••}$ at 300 and 80 K in EtOH:MeOH = 1:1. The reason for the differences in the UV is probably an imperfect background subtraction. Note the additional absorption band in the red of the radical cation’s band assigned to the dimer.

Figure 4.20.: Room temperature fluorescence dynamics of TiPD$^{••}$ in MeCN with best fit (traces are horizontally displaced).
In contrast to the other Wurster’s salts, no measurable fluorescence signal resulted from excitation in the 500 to 600 nm spectral region, even at 80 K.\(^9\)

The r.t. fluorescence decay has been measured in MeCN and D\(_2\)O and the results are shown in Figures 4.20 and 4.17 and Table 4.4. A mono–exponential function describes the fluorescence dynamics in MeCN satisfactorily;\(^10\) the lifetime extracted is shorter than the IRF. In D\(_2\)O an additional, longer lifetime was found. This lifetime, however, might be associated with a photoproduct of TiPD\(^{•+}\) since the sample degraded\(^11\) in D\(_2\)O while it was stable in MeCN where this lifetime was not present. The DAS obtained in the fit of the FU data shows that the importance of the slower fluorescence decay component increases with wavelength (which also means measurement time).

The TA spectra have essentially the same shape as described for WB\(^{•+}\) but in none of the solvents used for TiPD\(^{•+}\) was SE observed — even at the earliest time delays accessible, the spectra showed the ESA that in the case of WB\(^{•+}\) build up in the red part of the spectrum during the first picoseconds (Figure 4.21). The three time constants that describe the temporal evolution of the TA spectra are summarised in Table 4.3. The average lifetimes of the first two components are a bit shorter than that of WB\(^{•+}\), namely 0.17 and 0.23 ps. The SADS, that are very similar to those of WB\(^{•+}\), suggest that \(\tau_a1\) is associated with an excited-state decay, whereas \(\tau_a2\) and \(\tau_a3\) describe the relaxation of a vibrationally hot ground state.

### 4.2.4. Results for Wurster’s Red

As shown in Figures. 4.2 and 4.9, the absorption spectrum of WR\(^{•+}\) is located at shorter wavelengths than those of the tetraalkyl derivatives. The shape is identical and again it is only the radical cation that shows absorption in the visible part of the spectrum. The sample stability is inferior when compared to the other Wurster’s salts.

Upon cooling a solution of WR\(^{•+}\) in EtOH:MeOH = 1:1, the sample underwent similar changes as observed for TiPD\(^{•+}\). The low–temperature fluorescence emission and excitation spectra depended on excitation and emission wavelength, respectively. Additionally to a band that could be ascribed to WR\(^{•+}\) on the basis of its spectral position and shape (Figure 4.22), there was a longer wavelength emission whose fluorescence excitation spectrum peaks at 590 nm. This band did not resemble the broad dimer spectrum and might come from a decomposition product of WR\(^{•+}\).

The r.t. fluorescence decay in MeCN was triphasic with \(\tau_f1<0.1\) ps, \(\tau_f2=0.2\) ps and \(\tau_f3=1.5\) ps. The relative amplitude of \(\tau_f3\), however, increased with laser irradiation time of the sample and was therefore ascribed to a decomposition product. The other two lifetimes, \(\tau_f1\) and \(\tau_f2\), were close to the values obtained for the other Wurster’s salts, though shorter (Figure 4.17). Contrary to before, the DAS depicted in Figure 4.22 did not indicate that the process underlying \(\tau_f1\) lead to a spectral shift. Both amplitudes had similar shape but \(A_1\) is approximately 10 times bigger than \(A_2\) and contributes therefore the main part of the excited-state decay.

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\(^9\) Tentative measurements at 12 K did not show any luminescence either.

\(^10\) The data is slightly better reproduced with a biexponential function. Both the lifetimes obtained from such a fit are shorter than the IRF.

\(^11\) The absorbance decreased to half its initial value.
Figure 4.21.: TA spectra of TiPD$^{\ast\ast}$ in MeCN after 610 nm excitation and SADS. Note the absence of SE and the change of the bleach signal with $\tau_{a1}$. 
Figure 4.22.: Fluorescence emission and excitation spectra of WR$^{\ast +}$ in EtOH:MeOH = 1:1 at 80 K (top) and DAS of the r.t. fluorescence decay in MeCN measured by FU.
A thorough study of the exact nature of the fluorescence decay is impeded by the presence of other emissive products and the stability of WR$^{•+}$ samples.

Example TA spectra of WR$^{•+}$ are shown in Figure 4.23. The spectra measured with WR$^{•+}$ were completely consistent with those of WB$^{•+}$: at early pump–probe time delays they showed a bleach (450–550 nm), SE (>600 nm) and ESA at 400–450 nm. The SE and ESA decayed within less than a picosecond and were replaced by ESA at $\lambda$>600 nm. This ESA decayed on the same time scale as the bleach while shifting to the blue. Comparing the SADS in Figure 4.23 with Figure 4.13 the main difference is that in the case of WR$^{•+}$ the intensity of the bleach signal decreases partially already with $\tau_{a1}$ whereas no change of the bleach is associated with $\tau_{a1}$ in the case of WB$^{•+}$.

Both, FU and TA measurements, indicate thus that the excited-state decay of WR$^{•+}$ at r.t. happens on a shorter time scale than that of WB$^{•+}$.

4.3. Discussion

All Wurster’s salts investigated show ultrafast non–radiative excited-state decay after D$_1$←D$_0$ excitation at r.t. The solvent has no measurable influence on the time constants associated with the D$_1$ population decay ($\tau_{a2}$ in Table 4.4 and $\tau_{a3}$ in Table 4.3) or on the position of the electronic transition. An excess energy of 1600 cm$^{-1}$ (TA measurement) to 3600 cm$^{-1}$ (FU measurements) or change of the counter–ion (PF$_6^-$ instead of ClO$_4^-$) does not influence the excited-state lifetime WB$^{•+}$ significantly either.

The excited-state decay slows down as temperature decreases and for all but TiPD$^{•+}$ a steady–state fluorescence signal was detected that was ascribed to the radical. For WB$^{•+}$ the threshold temperature below which fluorescence could be observed was determined to be $\approx$120 K, independent of the solvent, for d4–WB$^{•+}$ and WR$^{•+}$ it is estimated to be the same.

Given an excited-state lifetime of only 200 fs, VER of the hot ground state should most certainly act as the bottleneck in the transition from the D$_1$ to the thermally equilibrated ground state. As discussed on page 26, vibrational relaxation in liquids is known to take place over several time scales. The TA spectra point to a biphasic decay of the hot ground state population, with $\tau_{a2}$ and $\tau_{a3}$. Each of these time constants cannot be precisely ascribed to a well-defined step of vibrational relaxation and this biphasic decay most probably reflects a distribution of time constants accounting for the various pathways for the dissipation of vibrational energy.

All these experimental findings, namely an ultrafast non-radiative deactivation despite a relatively large energy gap (2 eV) and a non–Arrhenius temperature dependence of the fluorescence quantum yield with a rather well–defined threshold temperature, point to the presence of a CI connecting the D$_1$ and the D$_0$ PESs located slightly above the minimum of the D$_1$ surface. The apparent insensitivity of the rate constant responsible for the D$_1$ decay to solvent viscosity indicates that it does not involve an intramolecular mode with large amplitude motion, as it is for example the case for triphenylmethane dyes.$^{[289]}$ This indicates either the existence of a nearly planar CI slightly higher in energy than the fluorescent state or, alternatively, the existence of a nearly planar transition state associated with a small barrier leading to a deeper well (with respect to D$_1$) containing a CI.
Figure 4.23.: TA spectra of WR$^{*+}$ in MeOH after 550 nm excitation and corresponding SADS.
Computational results for Wurster’s Blue. Computational investigations performed by E. Laricheva and M. Olivucci point to the second mechanism. The D1 PES of WB•+ was explored by CASPT2/CASSCF/6-31G*/Amber calculations. The FC D1 state which is populated by photoexcitation has the quinoid ground state geometry but the unpaired electron and positive charge located at the phenyl ring. Upon relaxation of the D1 state, the quinoid character is lost, as shown in Figure 4.24. The C_ar−N bonds lengthen and the phenyl bonds equalise to reach aromatic character. This goes along with a slight twist of one of the NMe2 groups and at a twist angle of 10°, a local minimum D1 min is found. A further twist of the NMe2 group leads to a D0/D1 CI that is located 3500–5000 cm⁻¹ below FC D1. In a methanol solvent box, the path from FC D1 to the CI features a small barrier (<1000 cm⁻¹) at ≈20° torsional angle (Figure 4.24). The coupled increase of the bond stretch and C-N twisting on the path from D1 min to the D1/D0 CI induces the unpaired electron to localise on the twisting NMe2 group. Upon decay at the D1/D0 CI, the charge goes back to the phenyl ring and during the D0 relaxation moves first to the in–plane (conjugated) NMe2 group and, after planarisation of the twisted NMe2 group, to the original D0 min symmetric distribution.

The D1←D0 absorption transition is hence associated with a hole transfer from the NMe2 groups to the central phenyl ring and the D1 population decay with a hole transfer to the rotating NMe2 group and back to the phenyl ring and the conjugated NMe2 group. The decay is characterised by a charge transfer process.

It is interesting to note that the gradient derivative vector that results from the CASPT2//CASSCF calculations (Figure 4.25) is identical with the FC active vibrational mode (Figure 4.5) and with the vibration that Brédas and co–workers associated with the relaxation of the excited state.

The CASPT2//CASSCF calculations in a methanol solvent box placed the D2 state 6500 cm⁻¹ above D1 min and located a D1/D2 CI 4500 cm⁻¹ above D1 min. TD–DFT results gave an energy difference of only 2100 cm⁻¹ and photoelectron spectroscopy 3200 cm⁻¹, considerably closer to D1. Photoelectron spectroscopy, however, measures ionisation potentials at the geometry of neutral TMPD whose structure differs considerably from that of WB•+. This is presumably at the origin of the poor agreement between the energy of the D1←D0 transition which is found at 16.3 kK in electronic absorption and predicted at 12.8 kK from photoelectron spectroscopy.

The CASPT2//CASSCF//Amber calculations predict furthermore that the solvent cavity is sufficiently large to exert no friction to the rotating NMe2 group and hence no dependency of the D1 lifetime on the solvent viscosity is to be expected.

The quantum chemical results can thus model the experimental results: At r.t. an ultrafast decay of D1 WB•+ is observed in all solvents. At low temperatures the small barrier comes into play and makes fluorescence a competing process. They concur as well with the fact that isotopic substitution of the aromatic hydrogen atoms had no significant effect on the excited-state lifetime since they are not involved in the vibrational modes along which the CI is reached.

Yet, a considerable effect on the D1 lifetime is expected when replacing the methyl groups with bulky i–propyl groups. The solvent cage might allow for an unrestricted twist of the former but certainly not of the latter. In opposition to the this expectation, the experimentally observed D1 lifetime of TiPD• at r.t. is shorter and even at temperatures where the other Wurster’s salts showed fluorescence signal, no emission was observed for TiPD•+.
The TICT model. A twisting dimethylamino group has also been invoked to explain the dual fluorescence of N,N–dimethylaminobenzonitrile (DMABN) and related compounds and is under debate since decades.\textsuperscript{[291–293]} Two models oppose each other, the twisted intramolecular charge transfer (TICT) and the planar ICT (PICT) model. The former identifies the coordinate for the CT reaction with the torsion of the NMe\textsubscript{2} group and a pronounced viscosity effect is expected. The PICT model associates the CT state with a structure showing a quinoid ring and a planar NMe\textsubscript{2} group.\textsuperscript{12} A minor influence of viscosity is predicted on the basis of the PICT model since it does not involve large amplitude motions.

The CT reaction in DMABN is known to happen with a time constant of $\tau_{\text{CT}} = 4$ ps in MeCN at r.t.\textsuperscript{[145,298–300]} It can, however, not be taken as the ‘pure’ rotational time of the NMe\textsubscript{2} group, since different time constants have been found for molecules that differ in the acceptor unit. For example, the CT rate constant equals 0.9 ps for DMAE\textsubscript{301} and amounts to 27 ps for penta-
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Figure 4.25.: Branching plane vectors of the $D_1/D_0$ CI of WB$^+$. $x_1$ is the gradient difference and $X_2$ the derivative coupling vector.\(^{290}\)

cyano–N,N–dimethylaniline\(^{302}\) (see Figure 4.26). The CT rate constant is rather a complex function of solvent polarity (affecting strongly the relative energy of the excited states) and relaxation time.

It has been shown that the CT rate constant increases with increasing steric demand of the alkylamino group.\(^{296,303,304}\) Some examples are shown in Figure 4.26. A pretwist (i.e. a non–zero torsional angle in the ground state) was invoked to explain this behaviour\(^{292,301}\) in spite of the fact that these molecules do not show any pretwist.\(^{292,294,13}\)

CT emission was also found for N,N–di–iso–propylaminobenzonitrile in solution\(^{296}\) and, surprisingly, in crystals.\(^{304}\) By time–resolved X–ray spectroscopy it was shown that the molecule planarises in the excited state, decreasing the torsional angle from 14° to 10° again contradicting the pretwist hypothesis (and TICT model).\(^{295}\)

The biggest equilibrium torsional angle is found in the di–$t$–butyl compound DTABN in which the dialkylamino group is essentially orthogonal in the electronic ground state and for which the CT happens within 60 fs in MeCN solution. Its CT rate constant is therefore higher than that of DMABN, contrary to the other alkylaminobenzonitriles.

Computational methods favour in general the TICT over the PICT model.\(^{300,305}\) Recent quantum chemical results\(^{306–308}\) however, combine structural characteristics of the TICT and

\(^{13}\)Even the authors that proposed the pretwist have to admit that there “is no evidence for a pretwist”.\(^{292}\)

Astonishingly this found only place as footnote in their 134 pages review (Ref. [292]). Presumably due to limited space.
the PICT model in the calculated CT geometry that were supposed to be contradictory, namely a twisted NMe$_2$ group and quinoidal character of the ring.

A TICT has also been proposed for a series of (neutral) \( p \)-phenylenediamines with aromatic acceptor units.$^{[276]}$ The spectral changes (fluorescence and time-resolved absorption) that were assigned to a rotation of the arylamino group (where not sterically hindered) were said to happen on the picosecond time scale. For example, a time constant of 1.6 ps was extracted from the TA dynamics of N,N',N'-trimethyl-N-phenyl-\( p \)-phenylenediamine.$^{[276],14}$ Similarly was the rise of \( k_{nr} \) with temperature and/or lower viscosity in oxazine dyes that carry a neutral and a cationic NMe$_2$ group interpreted as less hinderance of rotational motion of the NMe$_2$ group.$^{[309,310]}$ Also in this case the data revealed that, in fact, things were more complicated since i) compounds carrying piperidino groups decayed faster than their dimethyl analogues$^{[309]}$ and ii) different solvents with very similar viscosity showed very different fluorescence lifetimes.$^{[287]}$

\[14\] It should be mentioned that the incompleteness and inconsistency of the data presented does not allow to certify the proposed interpretation.
4. Wurster’s salts

Criticism on the TICT hypothesis for Wurster’s salts. The insensitivity even to extremely high viscosity casts doubts on the mechanism suggested by ourselves — the RTIL has $\eta = 120$ cP and no slow down was observed. It should be stressed that the TA measurements monitor not just the decay of the fluorescent state but rather the population of the vibrationally hot GS, i.e. the arrival of the wavepacket on the ground state surface and that this process is apparently solvent insensitive. The transition state calculated is close to the FC $D_1$ and the $D_1$ min states, and the FU data might therefore not reflect correctly the solvent dependence. The TA measurements, however, do as they monitor the total of the decay.

The excited-state decay time of TiPD$^••^+$ is incompatible with a model involving a twist. The rotational frequency of the NMe$_2$ group in N,N–dimethylaniline was estimated to be around 50 cm$^{-1}$, corresponding to a period of 670 fs. This frequency represents rather a lower limit for the rotational frequency of the NMe$_2$ group in electronically excited state of Wurster’s salts because of the higher bond order in the ground state and therefore higher frequencies are anticipated.

The data for neutral compounds — DMABN derivatives and $p$–phenylenediamines — show that a simple relation between steric demand of the supposedly twisting group and the ICT time constant does not exist. This has been explained by a ‘pretwist’. There is no reason to expect a ‘pretwist’ in TiPD$^••^+$: crystal and EPR data and the similarity of the electronic absorption coefficient show that it has the same planar structure as WB$^••^+$. It is puzzling that compounds which are quinoid and planar in their electronic ground state, reach the proposed 70 (liquid) to 90$^\circ$ (gas phase) twisted structure faster than molecules that have a freely rotating dialkylamino group.

Four reasons can be suggested to account for the discrepancy:

- First, the excited-state decay of TiPD$^••^+$ might obey a different mechanism than WB$^••^+$. A new decay channel might open when $D_2$ approaches $D_1$. This is in fact the case for DIABN where the $S_2$–$S_1$ energy gap is smaller than for DMABN. It can be seen from Figure 4.24 that $D_2$ approaches $D_1$ when the WB$^••^+$ when the calculations mimic the solvent. According to photoelectron spectra there is a higher excited state of WB$^••^+$ 0.4 eV (3100 cm$^{-1}$) above $D_1$ at the geometry of the neutral precursor. It is difficult to estimate at which energy it appears in WB$^••^+$.

- Second, the calculations might overestimate the torsional angle necessary for the PES jump to take place. Efficient coupling might be possible at smaller angles. The solvent had a remarkable effect on this coordinate in the ab inito calculations, placing the CI at a torsional angle of 70$^\circ$ whereas it was found at 90$^\circ$ in gas–phase. Robb and co–workers pointed out that the PES jump of DMABN can take place at various torsion angles of the NMe$_2$ group along the extended CI seam.

- Third, the participation of the torsion in the $D_1$ decay might be an artefact. In the ab initio calculations the $D_1$ PES profile was scanned along selected coordinates only because of the high computational cost of numerical CASPT2 gradients. The result depends thus on the ‘educated guess’. There is without doubt a CI that can be reached upon this coordinate but the experimental data presented here are insufficient to tell that the molecule actually follows it.

- Finally, the apparent equality might be due to limited time-resolution of our set–up that might hide the differences. The time constants are close to the IRF width, and,
as discussed in section 11, we cannot observe the initial part of the dynamics. Yet, if the lifetime were really much shorter in low–viscous solvents, no fluorescence could have been detected by the fluorescence up–conversion set–up which has essentially the same time–resolution. That even extreme cases like TiPD•⁺ and the RTIL have extremely short lifetimes, shows that the effect cannot be pronounced, meaning that the overall conclusions are correct.
5. Triarylamine and Tetraarylbenzidine

This chapter concentrates on the radical cations of two triarylamines, namely tris(4-bromo-phenyl)amine and N,N’-diphenyl-N,N’-dixylylbenzidine. These radical cations have a planar structure around the nitrogen center,\(^1\) just like Wurster’s salts. From a structural point of view, one might consider the N,N,N’,N’-tetraarylbenzidines either as bis(triarylamine)s or as Wurster’s salt with an extended bridge.\(^2\)

As discussed earlier, the number of alkyl substituents influences the D\(_{1}\)←D\(_{0}\) transition energy of Wurster’s salt. The exact nature, on the other hand, does not play a role — even a benzyl group does not shift the absorption band significantly.\(^{[259]}\) If, however, R = phenyl or methoxyphenyl, the transition energy is lowered by 4.2 and 6.8 kK, respectively, the band shape becomes a distorted Gaussian without visible vibrational progression and the transition energy depends on the solvent.\(^{[277,316–319]}\) The D\(_{1}\)←D\(_{0}\) transition in WB\(^{•+}\) can be characterised as transferring the hole from the amino centres to the central phenyl ring whereupon the quinoid character is lost and aromaticity is regained.\(^{[263,290]}\) The same applies to N,N,N’,N’-tetraphenyl-p-phenylenediamine (structure (1) in Figure 5.1 with R = C\(_{6}\)H\(_{5}\)) but the contribution from the peripheral rings is higher and charge is transferred from them to the central phenyl ring in the optical transition.\(^{[319,320]}\)

The HOMO of N,N,N’,N’-tetraarylbenzidine radical cations is delocalised over the central benzidine (including the nitrogens) and the HOMO-1 is delocalised over the whole molecule. The D\(_{1}\)←D\(_{0}\) transition can be regarded as charge redistribution from the peripheral aryl to the benzine system.\(^{[320–322]}\)

The lowest-energy transition in triarylamine radical cations, is a \(\pi\pi\) transition with minor charge transfer character.\(^{[323]}\)

For all three classes of compounds, this lowest-energy transition has gained incredible attention in the last years when triarylamines were found to be almost ideal systems to study inter-valence charge transfer: their IVCT absorption shows vibrational structure, has high molar absorptivity, is well separated from other transitions, and the inner reorganisation energy upon oxidation is very small which places them at the border line between Robin–Day class II and III compounds.\(^{[317]}\)

This interest is not purely academic. Molecules of the polyarylamine family are widely used in Xerox machines,\(^{[324]}\) hole transporting and light emitting materials,\(^{[325–327]}\) have good two-photon–absorption cross sections,\(^{[328,329]}\) and hyperpolarisabilities.\(^{[330]}\)

Various neutral triarylamines are commercially available as they are used as mild oxidising agents in organic chemistry. The radical cation, which is de facto the reagent, is prepared in situ by oxidation with [NO]\(^{+}\), Ag\(^{+}\) or electrochemical means.\(^{[331,332]}\)

\(^1\)The neutral precursors have a pyramidal geometry around the nitrogen.

\(^2\)In fact they can be synthesised by oxidation of triarylamines followed by dimerisation.\(^{[314,315]}\)
5. Triarylamine and Tetraarylbenzidine

5.1. Magic Blue

5.1.1. Antecedents of Magic Blue

Tris(4–bromophenyl)ammonium hexachloroantimonate salt (MB$^+$SbCl$_6^-$) carries the name Magic Blue and its solution definitively has a wonderful blue colour. The crystal structure of MB$^+$ (Figure 5.2) shows the three–bladed propeller structure typical for triarylamines. It is remarkable that in the case of MB, the neutral and the oxidised form have within experimental error identical crystal structures including bond lengths and the twist angle of the bromophenyl groups.\cite{333} For most triarylamines, especially those with aryl moieties carrying an electron–donating group, the C–N bonds shorten and one aryl group aligns with the central plane upon oxidation indicating an increasing quinoid character.\cite{321,333,334}

In case of MB$^+$ the C–N bond length is 1.41 Å, and the torsional angle is $37^\circ$. This geometry is close to that of triphenylamine radical cation but significantly different from neutral triphenylamine.\cite{333,334}

EPR\cite{335} and DFT calculations\cite{336} indicate that the unpaired electron of MB$^+$ is largely localised at the phenyl rings (2/3 of the spin density) especially at the 4–position. This is in line with the higher chemical reactivity of triarylamine radical cations that are unsubstituted at this position.\cite{314} In contrast to that, ab initio calculations locate 60% of the spin density on the nitrogen.\cite{337}

Electron absorption. A thorough study of the UV/visible properties of methyl–, chloro– and methoxy–substituted triarylamines has been done by Lambert and co–workers.\cite{323} The absorption spectra of triarylamine radical cations shown in Figure 5.3 are characterised by an intense absorption band around 350 nm and a less intense one around 700 nm. The authors explained the shape of the NIR band as superposition of two electronic transitions: the degenerate HOMO-1 splits if the $C_3$ symmetry is lifted and two energetically close–lying transitions result that can be regarded as HOMO$^+$–HOMO-1 and HOMO$^-$–HOMO-2 transitions. This symmetry breaking happens as well in symmetrical triarylamines by twisting one of the aryl groups in the central NC$_3$–plane under the influence of the solvent and facilitated by a Jahn–Teller distortion of the excited state (Figure 5.4).
Figure 5.2.: Crystal structure of MB$^{**}$SbCl$_6^-$ showing the propeller structure typical for triarylamines.\cite{333}

Figure 5.3.: Absorption spectrum of MB$^{**}$ClO$_4^-$ in CH$_2$Cl$_2$. Adapted from Ref. [338].
A different interpretation has been given recently by Nelsen and co-workers, who assigned the 630 nm band to a transition from the non-bonding, aryl-based HOMO-3 and HOMO-4 to the HOMO.\textsuperscript{339} Thereby the positive charge is transferred from the nitrogen $p$ orbital to the $p$-bromophenyl moiety. In the framework of their TD-DFT calculations (B3LYP/6-31G* $D_{3h}$ symmetry), the intense absorption band at 350 nm was identified as the $D_7 \leftarrow D_0$ transition. The oscillator strength for the $D_n \leftarrow D_0$ bands with $n=4-6$ were small, $D_3 \leftarrow D_0$ calculated at 530 nm was comparable to $D_2 \leftarrow D_0$.\textsuperscript{339}

The molar absorptivity of the $D_1 \leftarrow D_0$ transition of MB$^\ast$ is $\approx 33,000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ in CH$_2$Cl$_2$ and amounts to $38,000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ in MeCN.\textsuperscript{338,340} Amthor et al. deduced from the small influence of the solvent polarity (c.f. Figure 5.6) on the NIR and UV absorption bands that they have minor CT character.\textsuperscript{338}

**Fluorescence.** MB$^\ast$ and its anisyl analogue are luminescent in r.t. liquid solution as could be shown by Breslin and Fox.\textsuperscript{239} The main deactivation pathway of the $D_1$ state is internal conversion but photocyclisation ($\Phi_{\text{cycl}}=2.1 \cdot 10^{-4}$) and fluorescence ($\Phi_{fl} \approx 10^{-5}$) are slightly competitive. Apart from photocyclisation\textsuperscript{206}, MB$^\ast$ shows other photochemical reactions with oxygen and the solvent leading to permanent bleach of the solution when exposed to light. In methanol, for example, a methoxylation of one of the rings takes place.\textsuperscript{331} Light plays a crucial role for the stability of MB$^\ast$ samples.\textsuperscript{338,341}

The fluorescence spectrum of MB$^\ast$ obeys the mirror–image relationship and on basis of the Strickler–Berg equation (eq. 2.12) $k_{\text{rad}}$ equals 14 ns. Together with the fluorescence quan-
5. Triarylamine and Tetraarylbenzidine

Figure 5.5.: Combined triarylamine/triarylmethyl NIR emitters from Lambert’s group.\cite{201}

tum yield this gives \(\approx 150\) fs as estimated lifetime of \(D_1\), 3 orders of magnitude smaller than \(\tau_{nr} = 300\) ps calculated with the EGL (eq. 2.26).

Resonance Raman data obtained after excitation in vicinity of the \(D_1\) \(\rightarrow\) \(D_0\) transition is dominated by vibrations corresponding to in–plane ring rocking and ring breathing modes and a out–of–plane aryl–H bend, as expected for a weakening of the N–Ar bonds when populating an orbital that is anti–bonding between them.\cite{339} In accord with assigning the band at 630 nm to a different electronic transition (with distinct resonance enhancement factors), the Resonance Raman excitation profiles of these ring rocking and breathing modes are close to zero with the laser at 570 or 650 nm.\cite{339}

The first oxidation wave of MB in MeCN at \(E_{1/2} = 1.01\) V vs. SCE is fully reversible, the second one at 1.78 V vs. SCE is irreversible.\cite{342} For a series of differently substituted triarylamines it was found that \(E_{1/2}\) correlates well with \(\lambda_{\text{abs}}^{\text{max}}\) of the radical cation, but not of the neutral (for which the absorption band was hardly influenced by the substitution).\cite{332,342}

An interesting triarylamine has been synthesised recently by Lambert and co–workers.\cite{201} It combines a perfluoro–triphenylmethyl radical with the triarylamine moiety (see Figure 5.5, the substituent \(R\) fine–tunes the properties) to give radicalic NIR emitters with r.t. fluorescence quantum yields up to 40 % and lifetimes from 2 to 20 ns in cyclohexane. The optical transition corresponds to a charge transfer between the amine and the triarylmethyl as could be evidenced by TA measurements. A twist between the two central aromatic rings slows the back electron transfer down so that fluorescence becomes competitive.\cite{201,343,344}

5.1.2. Results for Magic Blue

Measurements with MB\(^{+}\) could only be performed in deaerated\(^3\) MeCN, and \(\text{CH}_2\text{Cl}_2\), all other solutions\(^4\) were unstable and turned immediately colourless.

The absorption and emission spectra in MeCN and \(\text{CH}_2\text{Cl}_2\) are depicted in Figure 5.6. Several absorption bands are apparent in the visible and NIR (c.f. Figure 5.3). Note that the shift of the electronic transition energies correlates with the refractive index \(n_D\), not the dielectric constant \(\varepsilon(0)\). The Stokes shift is noticeable, even in the low polar \(\text{CH}_2\text{Cl}_2\) but

\(^3\)1 hour argon purging
\(^4\)MeOH, EtOH, 2–PrOH, THF, DMSO, EtCN, PhCN, Ecoeng 212 (RTIL); all used as received. Very slow degradation can as well be observed in MeCN.
mirror–image relationship between absorption and fluorescence is observed, which is a sign of minor structural changes — at least on the lifetime of the fluorescent state and in so far as they affect the FC active vibrational modes.

A biexponential fluorescence decay ($\tau_1 = 400 \text{ ps (64\%)}$ and $\tau_2 = 2.7 \text{ ns (36\%)}$) was recorded after 395 nm excitation of a $3 \cdot 10^{-5}$ mol·L$^{-1}$ solution of MB$^+$ in MeCN using a 540 nm longpass filter in the emission path. Such a long lifetime is unexpected. No signal was detected with a 780 nm bandpass filter.\(^5\) Probably the sensitivity of the SPC’s PMT is insufficient at 780 nm. Even when using only $\tau_1$ and $k_{\text{rad}}$ estimated from the absorption, a fluorescence quantum yield on the order of several percent is calculated, in contradiction to that measured by Breslin and Fox.\(^{230}\)

Fluorescence up–conversion measurements with an excitation wavelength in the visible spectral range were not possible due to difficulties to filter the excitation pulse.

\(^5\)10 nm FHWM, 40% transmission at 780 nm
Figure 5.7.: TA spectra of MB$^{+\circ}$ in MeCN after 700 nm excitation and the corresponding SADS obtained in the target analysis.
Table 5.2.: Lifetimes obtained from the TA data of MB$^{\bullet\bullet}$, solvent dielectric constant $\varepsilon(0)$ and viscosity $\eta$ at 25$^\circ$C.

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\lambda_{\text{exc}}$ / nm</th>
<th>$\tau_1$ / ps</th>
<th>$\tau_2$ / ps</th>
<th>$\tau_3$ / ps</th>
<th>$\varepsilon(0)$</th>
<th>$\eta$ / cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>700</td>
<td>0.6</td>
<td>1.6</td>
<td>14.5</td>
<td>35.9</td>
<td>0.341</td>
</tr>
<tr>
<td>MeCN</td>
<td>760</td>
<td>0.5</td>
<td>1.4</td>
<td>17.2</td>
<td>35.9</td>
<td>0.341</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>700</td>
<td>1.0</td>
<td>2.1</td>
<td>21.3</td>
<td>8.9</td>
<td>0.411</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>760</td>
<td>0.7</td>
<td>2.3</td>
<td>25.5</td>
<td>8.9</td>
<td>0.411</td>
</tr>
</tbody>
</table>

**Transient absorption.** TA spectra of MB$^{\bullet\bullet}$ were measured upon 760 nm (10 nm FWHM) and 700 nm (100 nm FWHM) excitation$^6$ in MeCN and CH$_2$Cl$_2$. The 700 nm pulse covers both, the $D_1\leftarrow D_0$ and $D_2\leftarrow D_0$ transition, the 760 nm pump is at the red edge of the $D_1\leftarrow D_0$ absorption band.

Figure 5.7 shows the TA spectra of MB$^{\bullet\bullet}$ in MeCN after 700 nm excitation. At short pump–probe time delays they consisted of the bleach and ESA peaking at 550 nm. From the position, this ESA could be ascribed to the $D_4\leftarrow D_1$ absorption band. The discrepancy between the scaled, inverted steady–state absorption spectrum and the bleach for the 350 nm absorption might be due to $D_5\leftarrow D_1$ ESA (calculated at 340 nm) or chromatic aberration. The latter might also be the reason or contribute to the apparent shift between the maxima of steady–state absorption and TA bleach. It could be as well owing to $D_4\leftarrow D_2$ ESA that should be found at 700 nm.

No pronounced SE was present in the TA spectra despite the favourable value of $k_{\text{rad}}$. This might be due to $D_3\leftarrow D_1$ ESA (that should be centred at 750 nm), decay of the optically populated state within the IRF, and/or experimental problems at these wavelengths.

The spectral changes that happened with increasing time delay can be described as a decay of negative signal at the red edge of the spectrum and a slight decrease of the $D_4\leftarrow D_1$ ESA while the bleach signal did, at first, not decay and increasingly matched the steady–state spectrum. In a second step, the bleach decayed in large parts together with the main part of the $D_4\leftarrow D_1$ ESA. At the same time two ESA bands rose, located slightly red–shifted of the steady–state absorption bands. These bands decayed finally together with the rest of the bleach signal. At very long time delays only signal between 700 and 800 nm remained that was most likely a distortion from the pump and not permanent bleach since there was no bleach signal at 350 nm and only little photodegradation was found when comparing the steady–state absorption spectra before and after the TA measurement.

Qualitatively identical spectra have been obtained in CH$_2$Cl$_2$. In both the solvents, the dynamics of the TA signal could be well reproduced by a scheme with 3 consecutive reactions (Table 5.2). The amplitude associated with $\tau_{a1}$ reflects the small changes of the $D_4\leftarrow D_1$ ESA and the bleach, $\tau_{a2}$ the decay of these two bands with a concomitant rise of the two ESA bands at 400 and 750 nm and $\tau_{a3}$ the decay of these two with the remainder of the bleach. Since the $D_4\leftarrow D_1$ ESA decayed with $\tau_{a2}$, this lifetime was associated with the population of a hot

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$^6$The 760 nm pulses were obtained by tuning the Spitfire laser, the 700 nm pulses from the NOPA which gives extremely broad spectra in this wavelength region.
Figure 5.8.: TA spectra of MB\(^{\ast\ast}\) in MeCN after 760 nm excitation and the corresponding SADS obtained in the target analysis.
ground state and $\tau_{a3}$ with subsequent VER. Both of them were significantly longer in CH$_2$Cl$_2$ than in MeCN.

As for the shortest time constant, several phenomena can be at the origin of $\tau_{a1}$. First, it can be solvation or structural relaxation of D$_1$. The Stokes shift of MB$^{•+}$ is several hundreds of wavenumbers indicating a non-negligible stabilisation of the excited state after excitation. The effect of such changes on the TA spectrum is hard to predict since they can both, augment and diminish the energy gap between two states causing hypso- and bathochromic shifts and might additionally affect the FC factors. The intramolecular changes must be such that do not affect the FC active modes (in-plane ring rocking and ring breathing modes), given the good mirror-image relationship of absorption and fluorescence.

Second, it can be D$_2$→D$_1$ IC but this is expected to be ultrafast, much faster than $\tau_{a1}$, owing to the small D$_2$–D$_1$ energy gap. Such a process should be reflected in the TA spectra as a decrease of the D$_4$←D$_2$ ESA (700 nm) and increase of the D$_4$←D$_1$ ESA (550 nm, see Figure 5.9), D$_3$←D$_1$ ESA and D$_1$→D$_0$ SE (both at 750 nm). The last two contributions might cancel each other and therefore not be observed. A rise at 550 nm on the timescale of $\tau_{a1}$ is not present in the spectra.

Non-exponential dynamics of the process underlying $\tau_{a2}$ might give rise to an apparently biexponential behaviour. The “real” amplitude would then be the sum of $A_1$ and $A_2$ which is not to different from $A_2$ alone.

**Red edge excitation.** When exciting at 760 nm, an initial increase of the bleach signal that went along with the decay of its red edge described above was clearly observed (Figure 5.8). In other respects the spectra and spectral dynamics were identical to those described before. The lifetimes obtained in the target analysis were close to the ones obtained when pumping at 700 nm (Table 5.2). Again was the fact that the D$_4$←D$_1$ ESA vanished with $\tau_{a2}$ taken as
prove that this lifetime is associated with the D₁ lifetime and the SADS that correspond to \( \tau_{a3} \) suggested an assignment to VER.

In this measurement, \( \tau_{a1} \) might reflect solvent or structural relaxation of D₁ (as discussed before), cross phase modulation, or spectral diffusion.

The DADS of \( \tau_{a1} \) extracted from the TA data after 700 and 760 nm excitation (\( A₁ \) in Figure 14.4 on page 202 of the appendix) have the same shape which speaks in favour of assigning the time constants to a similar process, such as solvent or structural reorganisation.

Cross phase modulation (XPM) leads to a uniformly positive signal in the whole spectral range. Its tail distorts the early spectra especially in the case of low absorbance differences and high pump energies — the latter has been the case for the 760 nm excitation. The amplitude assigned to \( \tau_{a1} \) (Figure 14.4) is significantly bigger than the XPM signal recorded with pure solvent and the spectral changes are not uniform across the spectrum. This interpretation is therefore disregarded.

Finally, the observed spectral dynamics might correspond to the re-establishment of a Boltzmann–distribution of MB•+ in the ground state after selective excitation on the red edge of the absorption band — similar to dynamic hole–burning spectroscopy. Only a sub–population will be deplete upon 760 nm excitation and the increase of the bleach blue edge would then reflect the first phases of homogeneous broadening (spectral diffusion). This interpretation accounts for the positive sign (intensitivation of the bleach) of the amplitude after 760 nm excitation.

5.1.3. Discussion

The pico– and nanosecond fluorescence lifetimes measured upon 395 nm excitation are not assigned to MB•+ but rather to a product that formed (photo)chemically in the solution, given the incompability with the measured fluorescence quantum yield. Since neither the excitation nor the observation wavelength could be adjusted to selectively excite and observe MB•+, it is not astonishing that fluorescence from another, presumably closed–shell product, was detected.

The TA dynamics of MB•+ were found to be triphasic. While the second and third time constant can be unambiguously ascribed to D₁ state decay and VER, respectively, the origin of \( \tau₁ \) is not clear.

The most likely explanation is structural reorganisation coupled with solvation. From the big Stokes shift (700 cm⁻¹ in CH₂Cl₂), an important stabilisation of the excited state after excitation is expected, much too big to be explained by reorientation of the solvent alone. The insensitivity of the DADS to solvent and \( \lambda_{exc} \) also speaks in favour of this interpretation although this is not a strong argument (vide infra).

The question is the extend of structural reorganisation that happens with \( \tau_{a1} \), i.e. how distinct is “species” \( A₂ \) from \( A₁ \)? From the Strickler–Berg relation and the experimental value of \( \Phi_{flr} \), a lifetime of \( \approx 200 \text{fs} \) was estimated for the fluorescent state, which is reasonably close to \( \tau_{a1} \). In such a case, \( A₂ \) is a non–emissive state. Alternatively, the structural changes do not affect \( k_{rad} \), nor the FC active vibrations (in–plane ring rocking and ring breathing modes) greatly and \( A₂ \) is as well fluorescent and contributes most to the steady–state spectrum. We will come back to this having had a look on alternative interpretations and a look at similar molecules.
The similarity of $A_1$ in the DADS might as well be fortuitous and $\tau_{a1}$ might reflect different processes after 700 and 760 nm excitation, $D_2\rightarrow D_1$ IC in the former case, spectral diffusion in the latter. Given that the value of $\tau_{a1}$ and $\tau_{a2}$ are not very different form one another, the fit amplitudes have considerable uncertainties. While the TA spectra after 760 nm clearly show the intensification of the bleach, it is not directly apparent in the data after 700 nm spectra, but appears in the DADS. A non-exponential spectral evolution could be at the origin of $\tau_{a1}$, meaning that it has no meaning by itself.

The excited-state lifetime, $\tau_{a2}$, is not affected by the excitation wavelength. On the other hand, an important solvent effect was found showing a 50% slow down of the excited-state decay in $\text{CH}_2\text{Cl}_2$ when compared to MeCN. Since MB$^{•+}$ was only stable in two solvents, $\tau_{a2}$ cannot be related to solvent properties.

The fast electronic relaxation of the structurally similar Malachite Green dye (MG) is caused by a twist of the phenylamino groups.\cite{289,345–347} The $S_1$ lifetime serves as indicator of local viscosity changing from 0.1 ps in low viscosity solvents like MeOH\cite{345} to 0.6 ps in water\cite{347} and 1.2 ns in PMMA film at ambient temperature.\cite{348} Fita et al.\cite{347} examined the viscosity dependence of MG in water/glycerol mixtures and observed TA spectra and dynamics that are astonishingly close to what is observed for MB$^{•+}$ here — the fastest decay (0.3 ps) which showed an intensification of bleach and ESA, was associated with minor structural reorganisation and librational motion of solute and solvent. The slower TA decay showed the well known twist (0.6–2 ps in the viscosity range explored) and back-twist/VER (2–7 ps) of MG. The fluorescence vanishes upon rotation of the phenyl group and a CI is reached at a twist angle $10^\circ$.\footnote{An angle of 70$^\circ$ was suggested in chapter 4 to reach the CI in WB$^{•+}$.} Just like for MB$^{•+}$, SE gives only very weak contributions to the TA spectrum of MG.

Assuming that a twist is involved in the excited state decay of MB$^{•+}$, the time constants should increase with solvent viscosity, which is indeed the case.\footnote{Being stable only in 2 solvents, there was a 50% chance...} The dynamics of a rotational motion are expected to show non-exponential behaviour, which might explain the origin of $\tau_{a1}$. The decay can happen via a $D_1/D_0$ CI like in MG, or maybe with participation of the $D_2$ state which is situated 2200 cm$^{-1}$ above the $D_1$ state at the ground state equilibrium geometry. In the diphenylmethyl radical, this energy gap amounts to 3000 cm$^{-1}$ and no state mixing is observed whereas in benzyl radical ($\Delta E = 450$ cm$^{-1}$) mixing is very efficient.\cite{121}

The triphenylmethyl radicals introduced on page 36 are iso–electronic with MB$^{•+}$ but have, in contrast to MB$^{•+}$ and MG, nanosecond lifetimes in liquid solution. In clear contrast to triphenylmethyl radical, photocyclisation was shown to be extremely inefficient for MB$^{•+}$, the main relaxation of $D_1$ being IC.\cite{206} The photostable perchlorotriphenylmethyl radical has a high quantum yield for a reaction that was surmised to be a charge separation yielding $\text{Ar}_2\text{C}^+–\text{Ar}^-$.\cite{205} Such a reaction is expected to be faster in more polar solvents, in agreement with the changes of $\tau_{a2}$ for MB$^{•+}$.\footnote{Again it was a 50% chance.}

The most likely explanations for the decay mechanism seem therefore a twist leading to a CI in analogy with MG or a symmetry lifting charge separation in analogy with perchlorotriphenylmethyl radical. Variation of solvent viscosity and polarity should help to distinguish between them but were impeded by the chemical instability of the samples.
5.2. DMTPD$^{•+}$

5.2.1. Antecedent of DMTPD$^{•+}$

Combining two triarylamine centres of different oxidation state in one molecule gives a series of mixed valence compounds that are a welcome playground to study intervalence electron transfer.$^{[180,316,320,349–353]}$

The ortho–methyl groups in N,N’–diphenyl–N,N’–bis(2,4–dimethylphenyl)–(1,1’–biphenyl)–4,4’–diamine radical cation (DMTPD$^{•+}$, (2) in Figure 5.1 with $R = C_6H_5$ and $R' = 2,4$–dimethylphenyl) improve solubility and crystallinity of the product. Crystals show that one of the peripheral aryl groups is almost orthogonal and the other one aligned with central rings. The benzidine rings that are twisted against each other in the neutral parent, are almost co–planar.$^{[321]}$

Figure 5.11 depicts the spectral changes upon oxidation of the neutral parent to the radical cation and subsequently to the dication. The neutral parent has only UV absorption bands, the radical cation bands at 350, 472 and 1327 nm, and the dication a strong NIR absorption at 750 nm.

The electronic structure of DMTPD$^{•+}$ is thus quite peculiar: $D_1$ is low in energy, only 7500 cm$^{-1}$ (0.9 eV) above the ground state. The closest lying excited states are situated 13.0 kK (1.6 eV) and 21.0 kK (2.6 eV) above $D_1$. The lifetime of $D_1$, $D_2$ and $D_3$ are estimated to be 8 ps, 240 ps and 13 ps, respectively, by the EGL (eq. 2.26 with these energy gaps.$^{10}$ TD–DFT calculations assign $D_1$←$D_0$ to a HOMO←HOMO-1 and $D_2$←$D_0$ to a LUMO←HOMO transition.$^{[321]}$ These orbitals are depicted in Figure 5.11.

$^{10}$The values for $D_1$ and $D_3$ can only be taken as rough estimates since the energy gaps are at the limit of applicability of the EGL.
Figure 5.11.: Spectral changes upon oxidation of DMTPD to its radical cation (top) and subsequent oxidation of the latter to the dication (bottom) (0.1mol·L⁻¹ Bu₄NBF₄ in CH₂Cl₂). [321]
5. Triarylimine and Tetraarylbenzidine

Figure 5.12.: Frontier orbitals calculated with TD—DFT. The 1260 nm band of the radical cation can be described as HOMO←HOMO-1 (β spin), the 472 nm transition as LUMO←HOMO (α spin) transition.

Based on its shape and position, Low et al. [321] ascribed the 750 nm absorption band of DMTPD$^{2+}$ to the $\pi\pi$ transition typical for triarylimine radical cations. It is remarkable that in biphenyl systems such as DMTPD, the $D_2←D_0$ transition of the monocation is at substantially higher energy than $D_1←D_0$ transition of the dication,[321,336] whereas they are at identical energies in molecules with a bigger bridge, where the molar absorptivity of this band rises in the second oxidation as the number of chromophores doubles.[317]

In Raman experiments of DMTPD$^•^+\,$, a broad signal centred at 590 nm was observed after 514 nm excitation and attributed to emission from the upper excited state. The occurrence of $D_2$ emission was explained by the sensitivity of the Raman set-up and the big $D_2-D_1$ energy gap.[354] The resonance Raman factors showed that the 472 nm excitation involves a significant change of the electron density on the outer aryl rings.[354]

Contrary to what is usually observed, the molar absorptivity of tetraarylbenzidines depends tremendously on the solvent: Values between 16 700 (EtCN) and 30 800 L/mol-cm (CHCl$_3$) have been reported for DMTPD$^{2+}$. For CH$_2$Cl$_2$ a molar absorptivity of $\varepsilon = 24 600$ L·mol$^{-1}$·cm$^{-1}$ is given for the $D_1←D_0$ absorption which translates to $k_{rad} = 1/(30 \text{ ns})$. [321]

\[11\text{In contradiction to this interpretation is the observation that the dication is EPR silent. The authors invoked antiferromagnetic coupling to explain this discrepancy.}[321]\]
Low et al.\cite{321} emphasise the small solvatochromic shift of DMTPD\(\bullet^+\), especially if compared to the tetrakis(4–anisyl) analogue. The spectral position does not seem to correlate with the molar absorptivity. From inspection of the molecular orbitals, the authors assigned the solvent interaction to the peripheral ring systems.\cite{321}

N,N,N’,N’–Tetramethylbenzidine, that absorbs at 2 kK higher energy than DMTPD\(\bullet^+\), was shown to be luminiscent at r.t. in micellar solution and on alumina surfaces.\cite{226,355} The fluorescence maximum is situated in the NIR spectral region, \(\lambda_{flr} = 1100\) nm, 800 cm\(^{-1}\) below the absorption maximum. The fluorescence lifetime was shorter than the IRF, i.e. <2 ns.\cite{226}

5.2.2. Results for DMTPD\(\bullet^+\)

The steady–state absorption spectrum of DMTPD\(\bullet^+\) in MeCN is shown in Figure 5.13. The lowest–energy transition in MeCN and EtCN was found at 1260 nm, 600 cm\(^{-1}\) blue–shifted with respect to the position in CH\(_2\)Cl\(_2\) in agreement with the literature data that indicates small solvent dependence of the transition energy.\cite{321} The VIS absorption did not show solvent–induced shifts.

No steady–state fluorescence signal of DMTPD\(\bullet^+\) was detected between 500 and 700 nm in MeCN solution and a PMMA film that would not have shown up equally with pure solvent or undoped film. The \(D_2\rightarrow D_0\) fluorescence decay after 480 nm excitation was measured using fluorescence up–conversion between 520 and 590 nm and lifetimes around 50 fs were found.

**Transient absorption.** The TA spectra of DMTPD\(\bullet^+\) recorded after \(D_2\rightarrow D_0\) excitation in MeCN solution at \(\lambda_{exc} = 500\) nm are given in Figure 5.14. At early pump–probe time delays, they consisted of ESA at \(\lambda<410\) nm and \(\lambda>515\) nm and the bleach signal in-between these. In
Figure 5.14.: TA spectra of DMTPD$^{\bullet\bullet}$ in MeCN after 500 nm excitation and SADS obtained in the target analysis. The SADS around the pump were obtained by including this spectral region in the fit with a zero weighting factor.
Table 5.3.: TA lifetimes of DMTPD•+ in various solvents. Solvent dielectric constant $\varepsilon(0)$ and viscosity $\eta$ at 25°C, and longitudinal relaxation time $\tau_L$.\cite{356–358}

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\varepsilon(0)$</th>
<th>$\eta$ / cP</th>
<th>$\tau_L$ / ps</th>
<th>$\tau_{a1}$ / ps</th>
<th>$\tau_{a2}$ / ps</th>
<th>$\tau_{a3}$ / ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>35.9</td>
<td>0.341</td>
<td>0.21</td>
<td>0.3</td>
<td>1.2</td>
<td>15.0</td>
</tr>
<tr>
<td>EtCN</td>
<td>28.3</td>
<td>0.405</td>
<td>0.25</td>
<td>0.6</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>8.9</td>
<td>0.411</td>
<td>2.07</td>
<td>0.9</td>
<td></td>
<td>14.2</td>
</tr>
</tbody>
</table>

fact, the negative band was narrower than the steady–state absorption band. Within the first picosecond the ESA vanished except for a rather narrow band at 520 nm and the bleach signal apparently shifted to the blue while decaying in large parts. Afterwards, the 520 nm ESA and the bleach signal decayed completely on the picosecond time scale.

A target analysis of the TA data gave the SADS depicted in Figure 5.14. They show that the decay of the ESA present at early time delays happens with a time constant of 0.3 ps. One notes that the decay of the negative signal is restricted to the spectral region of the steady–state absorption and that no stimulated emission is observable.

The second component of the fit is associated with a further decay of the bleach and the decay of an ESA in the red of the bleach. Finally, the amplitude of $\tau_{a3}$ is similar to the one of $\tau_{a2}$ except for its position — it is located further in the blue.

The TA spectra and SADS obtained in the other two solvents, CH$_2$Cl$_2$ and EtCN, are very similar (Figure 5.15). The lifetimes of the target analysis are summarised in Table 5.3. The main difference to MeCN is, that $\tau_{a1}$ is longer and that the second part of the decay can be well reproduced with a single-exponential instead of a biexponential function.

5.2.3. Discussion

The fluorescence signal of D$_2$ after D$_2$←D$_0$ excitation decayed within the IRF, i.e. in less than 200 fs. According to the EGL, D$_2$ should have a lifetime of 240 ps. The IC process of D$_2$ is not influenced by a rigid environment and no fluorescence was therefore detected in a PMMA film. Like in WB•+, the density of electronic states is rather low and nonetheless subpicosecond internal conversion was observed. If the electronic configuration of the D$_2$ state involves only the LUMO and HOMO orbitals, as Low et al. found in TD–DFT calculations, there is no corresponding quartet state that might mediate its decay.

The state observed in the early TA spectra of DMTPD•+ is not the optically populated FC D$_2$ state and presumably not a relaxed D$_2$ state either. The FC D$_2$ state decays within the IRF of the TA set–up and consequently no SE is present in the TA spectra in the 500–600 nm spectral region. The state responsible for the TA signal at early pump–probe time delays might be a lower lying excited state or a dark D$_2$ state obtained by structural rearrangements of DMTPD•+.

The inverse rate constant $\tau_{a1}$ is ascribed to GSR, populating a vibrationally excited state with typical absorption bands at slightly lower transition energies than the relaxed ground state (Figure 5.14). This lifetime is strongly solvent dependent, but not related to solvent viscosity (see Table 5.3). It roughly correlates with the viscosity and the longitudinal relaxation time of the solvent.
Figure 5.15.: SADS of DMTPD$^{\ast\ast}$ in EtCN (top) and CH$_2$Cl$_2$ (bottom).
Table 5.4.: Comparison of aromatic amine radical cations. (a): $D_0 - D_1$ and $D_1 - D_2$ energy gap, (b): $D_1$ lifetime calculated with the EGL (eq 2.26, the value for DMTPD$^{*+}$ is at the limit of the theory), (c): measured excited-state lifetime in MeCN and CH$_2$Cl$_2$, (d): solvatochromic shift of the $D_1 \leftarrow D_0$ absorption band in these two solvents.

<table>
<thead>
<tr>
<th></th>
<th>WB$^{*+}$</th>
<th>MB$^{*+}$</th>
<th>DMTPD$^{*+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E(D_1-\text{D}_0)$ / eV$^{(a)}$</td>
<td>2.0</td>
<td>1.8</td>
<td>0.9</td>
</tr>
<tr>
<td>$\Delta E(D_2-\text{D}_1)$ / eV$^{(a)}$</td>
<td>1.1</td>
<td>0.3</td>
<td>1.6</td>
</tr>
<tr>
<td>$\tau_{nr}$(EGL) / ps$^{(b)}$</td>
<td>1600</td>
<td>300</td>
<td>$\approx$8$^\dagger$</td>
</tr>
<tr>
<td>$\tau_{D1}$(MeCN) / ps$^{(c)}$</td>
<td>0.2</td>
<td>1.6</td>
<td>0.3</td>
</tr>
<tr>
<td>$\tau_{D1}$(CH$_2$Cl$_2$) / ps$^{(c)}$</td>
<td>0.2</td>
<td>2.1</td>
<td>0.9</td>
</tr>
<tr>
<td>$\Delta \nu$ / cm$^{-1}$$^{(d)}$</td>
<td>250</td>
<td>500</td>
<td>500</td>
</tr>
</tbody>
</table>

In MeCN a biphasic VER follows the 300 fs IC, whereas it is well described by a monoexponential function in EtCN and CH$_2$Cl$_2$. This is presumably due to the slower IC rate in these solvents, which hides the fast component of VER.

5.3. Comparison of aromatic amine radical cations

Table 5.4 compares Wurster's Blue with Magic Blue and DMTPD$^{*+}$. For all of them, excited-state lifetimes in the picosecond and subpicosecond range were determined experimentally. It is evident that in all cases the excited-state lifetime is much shorter than predicted by the energy gap law (eq. 2.21 with the $S_1 \rightarrow S_0$ IC determined by Siebrand): 1, 2 and 4 orders of magnitude smaller for DMTPD$^{*+}$, MB$^{*+}$ and WB$^{*+}$, respectively. This difference stems from the EGL that predicts a picosecond lifetime for DMTPD$^{*+}$ but a nanosecond lifetime for WB$^{*+}$.

Whereas no solvent dependence was observed for the excited state lifetime of WB$^{*+}$, the other two aromatic amine radical cations are susceptible to the solvent, though to a very different extend. The slow down when exchanging MeCN for CH$_2$Cl$_2$ is 30% for MB$^{*+}$, contrasted by 200% in DMTPD$^{*+}$. The solvatochromic shifts of the absorption bands in MB$^{*+}$ and DMTPD$^{*+}$ are comparable to one another, practically no shift was observed for WB$^{*+}$. In the former two molecules the shift is related to the solvent index of refraction.

The three compounds are structurally kindred having planar nitrogen centres and their vibrational frequencies are close to one another: the highest energy vibrations apparent in the IR spectrum are the $8a$ for WB$^{*+}$, C=C skeleton vibrations in MB$^{*+}$, and ring stretches in DMTPD$^{*+}$, all situated between 1600 and 1650 cm$^{-1}$. Slightly lower in energy, namely at about 1500 cm$^{-1}$ are Me deformation and combination vibrations. The highest energy vibrations, which, according to the reasoning in chapter 2.1.3 should dominate the IC, are the aromatic CH stretch vibrations at ca. 3000 cm$^{-1}$. It was found experimentally and computationally that the corresponding absorptions are one order of magnitude weaker in the IR spectrum of radical cations of small and medium size PAHs compared to the bands of the neutrals. The intensity of the CH vibrations is directly proportional to the charge at the hydrogens.
Given this similarities in vibrations, it should be possible to compare these compounds in the framework of the EGL, eq. 2.21, if the displacement is similar. It is evident that the $D_1$ lifetime is not related to the state’s energy — the shortest lifetime is found for the, $WB^{*+}$, the compound with the highest $D_1$ state energy; very close lifetimes are found for $WB^{*+}$ and $DMTPD^{*+}$ although their $D_1$ state energies differ by more than 1 eV.

In other words, the EGL is not able to explain the trend observed among these radical cations — either the displacement is significantly different from one compound to the other, or the IC mechanism involves strong coupling or a CI. In the preceding chapter, the $D_1$ state decay of $WB^{*+}$ has been ascribed to a CI, although the reaction coordinate could not be determined unequivocally. The similarity of the TA spectral dynamics of $MB^{*+}$ with those of malachite green might be due to a common decay mechanism of the excited state. The chemical instability of $MB^{*+}$ in most solvents prevented thorough studies, measurements in low–temperature matrices or PMMA films. An alternative explanation of the excited state decay includes charge separation as invoked in the case of triphenylmethyl radical.

Proximity of a higher lying excited state is evidenced in the absorption spectra of $MB^{*+}$ but not anticipated for the other two, yet, the longest $D_1$ state lifetime being related to this compound (Table 5.4).

\[12^{\text{See the discussion about the photoelectron spectra of TMPD above.}}\]
6. Aromatic Hydrocarbons

Large aromatic hydrocarbons are interesting model systems in the framework of this thesis because the perturbation of the electronic system with ionisation is expected to be small. The molecular system remains planar in the charged species and does not suffer major rearrangements. As a consequence, the vibrational frequencies are essentially identical in the neutral and the radical ion.\cite{193,368,369}

The two examples chosen are distinct from most other aromatic hydrocarbons because the radical cations of both, perylene (Pe) and tetracene (Te) are reportedly fluorescent. Several studies revealed various of their properties, especially of Pe$^{\bullet+}$ (vide infra).

The high density of electronic states in Pe$^{\bullet+}$ throughout the visible part of the spectrum makes it an interesting candidate to test the effect of excitation energy on the excited-state lifetime. A CI between a higher excited and the ground state may offer a non–radiative decay channel that circumvents D$_1$. This has been shown to be the case for benzoid radical cations and suggested for methoxybenzenes (see page 28). A D$_n > 1$/D$_0$ CI would manifest in excitation wavelength dependent fluorescence quantum yield and GSR rate constant.

6.1. Perylene

Every textbook on photophysics will dedicate a large part to polycyclic aromatic hydrocarbons. Among them, perylene (Pe) has an outstandingly high fluorescence quantum yield, close to unity.\cite{370,371} Therefore, Pe and its derivatives\cite{1} have been used extensively as fluorescent probe in studies of phenomena as diverse as electron and energy transfer,\cite{15,20,41,44,372–376} IC and ISC\cite{67,377} or vibrational energy relaxation.\cite{145,378–380}

The x–ray structure\cite{381} and gas–phase electron diffraction pattern\cite{382} of Pe show that the central ring (ring B in Figure 6.2) is not really aromatic: The 6a–6b bond is with 1.48 Å longer by 8 pm than an average aromatic bond. Pe might thus be considered as two interacting naphthalene units. This conclusion has also been drawn from analysis of the electronic spectra.\cite{383}

Perylene’s S$_1$ state is 2.85 eV (23.1 kK, MeCN solution) above S$_0$, has a lifetime of 5.5 ns in polar and slightly longer in non–polar solvents or in EPA matrix at 77 K.\cite{371,384–386} A Stokes shift of 250 cm$^{-1}$ is measured in MeCN solution. The index of refraction accounts for the solvatochromic shift of absorption and emission, indicating that it is related to dispersion interactions solely.\cite{145}

The triplet state, located ca. 10.0 kK below S$_1$, is populated with a quantum yield of only 1% and has a lifetime of 5 ms in PMMA at 298 K.\cite{77,371}

\^One of the most important ones is perylenediimide (PDI).
Both, absorption and fluorescence show vibrational progression with 1450 cm\(^{-1}\) spacing, the average frequency of the totally symmetric CC vibrations.\(^{[387]}\) Even in Ar matrix experiments a few modes of symmetric CC and CH vibrations suffice to explain the vibronic pattern.\(^{[387–389]}\)

The polarisation of the lowest–energy absorption and the emission band is parallel to the long molecular axis.\(^{[391,392]}\) The \(S_2\) state is dark in absorption, calculated at 27.3 kK (366 nm) and was observed by two–photon excitation spectroscopy (Figure 6.3).\(^{[390]}\) Its transition dipole moment is aligned along the short molecular axis.

The initial fluorescence anisotropy of Pe, \(r_0\), is smaller than 0.4, the value expected for parallel orientation of absorption and emission transition dipole moments.\(^{[393,394]}\) Initially ascribed to ultrafast free rotational motion in the solvent cavity,\(^{[393]}\) this was recently explained by vibrational relaxation.\(^{[145]}\) When measured in the blue part of the fluorescence spectrum, the initial anisotropy amounts in fact to 0.4 and decays with a time constant of 300 fs due to VER to the lower value that had been observed in earlier experiments. This shows that the transition dipole moment of absorption incorporates some short axis contributions due to vibronic coupling between the two lowest lying excited states.\(^{[145,391,392]}\)

**Butterfly vibrational mode.** The laser induced fluorescence excitation spectrum of Pe in a free jet shows a progression with 94 to 98 cm\(^{-1}\). It was ascribed to an overtone of the ungerade butterfly mode depicted in Figure 6.2 which can be viewed as torsion of the two naphthalene parts of the molecule around the 6a–6b and 12a–12b bonds (Figure 6.2) with a fundamental frequency of 49 cm\(^{-1}\).\(^{[395–397]}\) Analysis of a wavepacket observed by time resolved fluorescence of Pe in several solvents showed that the butterfly mode is Franck–Condon active.\(^{[145]}\)
Figure 6.3.: Two–photon excitation spectrum of Pe compared to the “conventional” one–photon absorption.\textsuperscript{390} No fluorescence was observed with irradiation energies below 13.0 kK.

This mode is strongly perturbed by aggregation, as expected for a low frequency mode (which usually couple strongly with lattice modes).\textsuperscript{396,398}

From the frequency shifts of this mode between the ground and first excited electronic state, it was concluded that the molecule is more rigid in the excited state,\textsuperscript{396} although not all modes behave the same way.\textsuperscript{395}

Others\textsuperscript{399} identified the observed frequency of 94 cm\textsuperscript{-1} to the fundamental frequency of the butterfly mode and argued from this high value and the good performance of the harmonic approximation that perylene is relatively rigid.

IC and VER of Pe. IC of Pe was studied in the electronic ground and excited state. Sato and co–workers looked at the early fluorescence dynamics of Pe in a series of ketone solvents after 388 nm excitation (2800 cm\textsuperscript{-1} excess energy) and found triphasic behaviour with $\tau_1 \approx$ IRF (200 fs), $\tau_2 = 0.6$ to 1 ps (rather insensitive to the solvent) and $\tau_3 = 2$ to 4 ps.\textsuperscript{149} The latter two
were ascribed to “solvent–assisted IVR”. No slower VER rate constants were reported.\textsuperscript{149}

The group of Blanchard studied VER of Pe and MePe in various solvents with single wavelength TA spectroscopy exciting the 0–0 $S_1 \leftarrow S_0$ transition.\textsuperscript{380} They found VC time constants of 10 to 50 ps in ketones and less than 5 ps in aldehydes.\textsuperscript{380} Much faster VER times, namely 0.2 to 3 ps were reported by Pigliucci et al. after 400 nm excitation (2000 cm$^{-1}$ excess energy) in a wide range of chemically distinct solvents.\textsuperscript{145}

The narrowing and rise of Pe SE and ESA after 266 nm excitation (14 000 cm$^{-1}$ “excess energy”) is shown in Figure 6.4. It follows biphasic dynamics with $\tau_{a1} = 3$ ps and $\tau_{a2} = 20$ ps. From the small spectral changes with increasing pump–probe time delay it is argued that IC is faster than the IRF (1 ps) and the observed dynamics are due to IVR and VC. In fact, both time constants are very similar to the time constants reported for these processes in Pe.\textsuperscript{145,380}

**Perdeuteration.** The effect of isotopic substitution on the fluorescence quantum yield and lifetime of Pe is negligible.\textsuperscript{371,386} The triplet state lifetime, on the other hand, increases from

\footnote{The term intends to show the involvement of the solvent in the IVR process. A clear distinction between solvent–assisted IVR and VC taking place in parallel with IVR cannot be made.}
6 to 14 ms in PMMA at 298 K\textsuperscript{[77]} (this gives a kinetic isotope effect of 2.3 for the \(T_1 \rightarrow S_0\) ISC) in good agreement with what is expected from EGL.\textsuperscript{[67]}

The oxidation potentials of h12–Pe and d12–Pe are virtually identical.\textsuperscript{[400]}

**Methylperylenes.** Depending on the position of the methyl substituent, a spectral red– or blue–shift can be observed in the electronic spectra.\textsuperscript{[385,401]} 2– and 3–methylperylene (MePe) are essentially planar and absorption and emission spectra are red–shifted by 100 cm\(^{-1}\) and 300 cm\(^{-1}\), respectively, from the band position in Pe. In contrast, 1–MePe is non–planar and the electronic absorption 350 cm\(^{-1}\) higher in energy than that of Pe.\textsuperscript{[385,401]} The Stokes shift of 1–MePe is approximately twice as large as that of Pe or the other MePe derivatives. The effect of the methyl group on the fluorescence quantum yield is minor for all three positions.\textsuperscript{[385]}

A distorted geometry of 1–MePe is invoked for this effect in 1–MePe and presumably also at the origin of its shorter retention time in chromatography as compared to Pe or other alkylated perylenes, all of which elute later.\textsuperscript{[401]} A bit contradictory is the result that the rotational time constants of Pe and 1–MePe could not be distinguished.\textsuperscript{[380]}

The twist angle between the two naphthalene moieties in MePe has been calculated to amount 23° on the molecule’s side carrying the methyl group and 14° on the opposite side.\textsuperscript{[402]} It is surprising to find that such important distortions lead to minor effects in the electronic spectra which have an identical shape and are displaced by a relatively small amount of energy only.

Interestingly, the weak fluorescence of 1–bromoperylene (\(\Phi_{flr} = 0.05\)) is not due to an increase in triplet yield, \(\Phi_{ISC}\), but in \(\Phi_{IC}\) which rises to 0.88.\textsuperscript{[385]} At the same time \(\Phi_{IC}\) of 1–MePe is essentially as small as that of unsubstituted Pe.\textsuperscript{[385]} This discrepancy has been tentatively explained by i) the longer C–Br bond as compared to the C–Me bond leading to enhanced encumbrance with the facing naphthalene subunit and therefore a more distorted structure,\textsuperscript{3} and/or ii) by the unequal effect of Br and Me on the vibronic coupling between \(S_1\) and \(S_2\) through both, a shift of the relative state energies and the capability of the CBr and CMe vibrations to mediate it.\textsuperscript{[385]}

### 6.1.1. Antecedents of perylene radical cation

The oxidation and reduction potential of Pe are at 1.0 and -1.67 V vs. SCE in MeCN and DMF, respectively.\textsuperscript{[371,403,404]}

The electronic absorption spectrum of Pe\(^{**}\) depicted in Figures 6.5 and 6.7 shows several transitions. The \(D_1 \leftrightarrow D_0\) transition that appears only weakly in the absorption spectrum at 794 nm in liquid Ne is allowed and has a molar absorptivity of \(\varepsilon = 2000\) L·mol\(^{-1}\)·cm\(^{-1}\). As indicated in Figure 6.5, there is a high density of electronic states and the dominant band at 535 nm is the \(D_5 \leftrightarrow D_0\) transition.\textsuperscript{5} It can be described as a two electron four orbital transition — configuration interaction mixes the HOMO\(\rightarrow\)HOMO-1 and LUMO\(\rightarrow\)HOMO transitions.\textsuperscript{[383]} The other combination is the \(D_2 \leftrightarrow D_0\) transition at 733 nm.

\textsuperscript{3}The absorption spectrum of 1–BrPe is in fact further blue–shifted and the Stokes shift larger than that of 1–MePe

\textsuperscript{4}The *Handbook of photochemistry* reports 0.85 V for the oxidation.\textsuperscript{[371,405]}

\textsuperscript{5}Note that the quantum chemical calculations disagree about the state ordering.\textsuperscript{[406,407]} Throughout this text, the labels of Hirata et al.\textsuperscript{[408]} are applied.

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\textsuperscript{[77]}\textsuperscript{[67]}\textsuperscript{[385]}\textsuperscript{[401]}\textsuperscript{[380]}\textsuperscript{[385]}\textsuperscript{[400]}\textsuperscript{[371]}\textsuperscript{[403]}\textsuperscript{[404]}\textsuperscript{[371]}\textsuperscript{[405]}\textsuperscript{[406]}\textsuperscript{[407]}\textsuperscript{[408]}

Figure 6.5.: Absorption spectrum of Pe$^{•+}$ in Ne at 4K after photolysis at 10.2 eV. The bands denoted with an asterisk are assigned to Pe$^{•-}$; curly brackets indicate the electronic origins, the double arrows at the top results of quantum chemical calculations. Adapted from Ref. 406

Impressive agreement was found between the photoelectron spectrum, the absorption spectrum of the radical cation and quantum chemical calculations, although this agreement stems partially from incorrect assignments, namely the identification of non–Koopmans’ states with photoelectron peaks.\cite{387,408–410} The peak positions of the photoelectron spectrum of perylene are 1.55 (800 nm), 1.68 (740 nm), 1.8 (690 nm), 1.9 (650 nm) and 2.3 eV (540 nm) above the ionisation threshold at 7.0 eV.\cite{409} Except for the peak at 7.0 + 1.8 eV all of them have a counterpart in the absorption spectrum (Figure 6.5). Calculations suggest that this transition (D$_5$←D$_0$) is invisible owing to its small transition dipole moment.\cite{408} The peak at 1.68 eV is presumably a vibrational band of the 1.55 eV peak ($\Delta \nu = 1050 \text{ cm}^{-1}$) since the D$_2$←D$_0$ transition, that happens to appear at the same energy, is described either as pure or as configuration interaction mixed LUMO←HOMO transition (vide infra). The good agreement of the 2.3 eV photoelectron and absorption band cannot be explained that straightforward. Theoretical results by different groups\cite{388,407,408} attribute important configuration interaction and participation of virtual orbitals to this electronic transition (D$_3$←D$_0$) which should therefore appear largely shifted in the photoelectron spectrum.\cite{285}
Emission. Chillier et al. observed \( D_1 \rightarrow D_0 \) fluorescence of \( \text{Pe}^{\bullet +} \) in liquid Ne after \( D_5 \leftarrow D_0 \) (\( \lambda_{\text{exc}} = 535 \text{ nm} \)) and \( D_2 \leftarrow D_0 \) (\( \lambda_{\text{exc}} = 731 \text{ nm} \)) excitation. The same fluorescence signal was observed in micellar liquid solution and on \( \gamma - \text{Al}_2 \text{O}_3 \) or SiO\(_2\) : Al\(_2\)O\(_3\) surfaces at ambient temperature. Attempts to observe \( \text{Pe}^{\bullet +} \) emission in the gas phase were unsuccessful and the authors supposed that this might be either due to a low stability of \( \text{Pe}^{\bullet +} \) or an increase of \( k_{\text{nr}} \) in gas phase.

No emission in the visible was found by Chillier et al. and Gumy et al. Based on the spectral position of the emission of \( \text{PeClO}_4 \) crystals (500 to 600 nm), it should be probably ascribed to neutral perylene, not to \( \text{Pe}^{\bullet +} \).

Vibrational analysis of the NIR emission showed that it can be almost entirely assigned to symmetric vibrations (CC stretch and a combination of CC stretch and CH out–of–plane) and that the cation preserves the \( D_{2h} \) symmetry of the neutral parent molecule. The energy change of the vibrations upon oxidation of \( \text{Pe} \) is very small, the IR bands shift by less than 80 cm. Table 6.1 lists the transition energies of selected absorption bands and the emission of \( \text{Pe}^{\bullet +} \). The solvent dependence of the \( D_5 \leftarrow D_0 \) and \( D_2 \leftarrow D_0 \) transitions is evident from this Table. Owing to its low oscillator strength, it is more difficult to draw conclusions for the \( D_1 \leftarrow D_0 \) transition. From the high resolution liquid Ne and Ar spectra a hypsochromic shift of \( \approx 40 \text{ cm}^{-1} \) in absorption and emission appears, which means it shifts with an opposite sign as the \( D_5 \) and \( D_2 \) bands. In other media the bandshifts seem to be parallel but the spectral resolution of this data might not suffice to draw clear conclusions.

The protonated form of \( \text{Pe} \), \( \text{PeH}^{+} \), which forms in \( \text{H}_2\text{SO}_4 \) in the presence of oxygen (and is spontaneously oxidised and deprotonated) has an absorption maximum at 500 nm and emission between 550 nm and 700 nm with \( \tau_{\text{flr}} = 5.7 \text{ ns} \). This emission has been observed in orthoboric acid, \( \text{H}_3\text{BO}_3 \), and in hexane after multiphoton ionisation of \( \text{Pe} \).

Dimerisation of \( \text{Pe}^{\bullet +} \) leads to the typical spectral behaviour: the appearance of a new IR absorption band (\( \lambda_{\text{abs}}^{\text{max}} = 1000 \text{ nm} \) in the case of \( \text{Pe}_2^{2+} \) in \( \text{H}_2\text{SO}_4 \)) and a blue–shift of the monomer bands (Figure 6.7).

Time resolved measurements. The excited-state dynamics of \( \text{Pe}^{\bullet +} \) were examined using TA and TG spectroscopy in MeCN, orthoboric acid (\( \text{H}_3\text{BO}_3 \)), and \( \text{H}_2\text{SO}_4 \). They revealed excited-state lifetimes of 3 to 100 ps, depending on solvent and temperature (see Table 6.2). For example, the GSR of \( \text{Pe}^{\bullet +} \) in MeCN after 532 nm excitation was measured to be ca. 3 ps. Significantly longer excited-state lifetimes are reported for liquid \( \text{H}_2\text{SO}_4 \) (20 – 30 ps) and solid \( \text{H}_3\text{BO}_3 \) r.t. solution (20 – 35 ps), and even longer ones in organic glasses at 77 K (80 – 100 ps) (Table 6.2).

The discrepancy between the values reported for MeCN solution can probably be put down to the fact that Shkrob et al. determined the D\(_1\) lifetime indirectly from a quenching experiment whereas Vauthey and co–workers measured it directly in a pump–pump–probe experiment.\(^6\)

\(^6\) \( \text{Pe}^{\bullet +} \) as generated in MeCN by a bimolecular PET reaction with 1,4-dicyanobenzene after 400 nm excitation of \( \text{Pe}^0 \). If \( \text{Pe}^{\bullet +} \) was then excited by 530 nm laser pulse 1 ns after the 400 nm pulse, the GSR of \( \text{Pe}^{\bullet +} \) could be probed at 530 nm by a third laser pulse. The authors showed that the excited state dynamics of \( \text{Pe}^{\bullet +} \) depend on pairing with the 1,4-dicyanobenzene radical anion.\(^5\)
Figure 6.6: Fluorescence spectrum of Pe$^{*+}$ in BF$_3$·H$_2$O–CF$_3$CO$_2$H solution at 298 K (top)\cite{226} and in Ar matrix at 10 K (bottom).\cite{406} Bands marked with an asterisk are artefacts from the excitation laser.
Table 6.1.: Selected absorption bands (in nm) of Pe** in different environments.

<table>
<thead>
<tr>
<th>solvent</th>
<th>T / K</th>
<th>(\lambda_{D_5\rightarrow D_0})</th>
<th>(\lambda_{D_2\rightarrow D_0})</th>
<th>(\lambda_{D_1\rightarrow D_0})</th>
<th>(\lambda_{D_1\rightarrow D_0})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>4</td>
<td>525.1</td>
<td>723</td>
<td>794.1</td>
<td>794.3</td>
<td>[414]</td>
</tr>
<tr>
<td>Ne</td>
<td>4</td>
<td>525.3</td>
<td>723</td>
<td>794</td>
<td>[388]</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>4</td>
<td></td>
<td></td>
<td>791.2</td>
<td>792.2</td>
<td>[414]</td>
</tr>
<tr>
<td>Ar</td>
<td>10</td>
<td>535</td>
<td>731.2</td>
<td>790</td>
<td>792</td>
<td>[406]</td>
</tr>
<tr>
<td>Ar</td>
<td>12</td>
<td>534.1</td>
<td>734.5</td>
<td>791.2</td>
<td>[387]</td>
<td></td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>298</td>
<td>538</td>
<td>733</td>
<td>768</td>
<td>[173]</td>
<td></td>
</tr>
<tr>
<td>H(_3)BO(_3)</td>
<td>298</td>
<td>542</td>
<td>736</td>
<td>765</td>
<td>[415]</td>
<td></td>
</tr>
<tr>
<td>SbCl(_3)</td>
<td>350</td>
<td>554</td>
<td></td>
<td></td>
<td></td>
<td>[416]</td>
</tr>
<tr>
<td>CF(_3)COOH</td>
<td>298</td>
<td></td>
<td>≈800</td>
<td></td>
<td>[411]</td>
<td></td>
</tr>
<tr>
<td>CF(_3)COOH</td>
<td>298</td>
<td>530</td>
<td>730</td>
<td>770</td>
<td>≈810</td>
<td>[226]</td>
</tr>
<tr>
<td>SiO(_2)·Al(_2)O(_3)</td>
<td>298</td>
<td>550</td>
<td>730</td>
<td>810</td>
<td>≈820</td>
<td>[226]</td>
</tr>
<tr>
<td>(\gamma)-Al(_2)O(_3)</td>
<td>298</td>
<td>540</td>
<td>740</td>
<td>810</td>
<td>≈820</td>
<td>[226]</td>
</tr>
<tr>
<td>alumina</td>
<td>298</td>
<td>≈540</td>
<td>≈810</td>
<td></td>
<td></td>
<td>[411]</td>
</tr>
<tr>
<td>2-BuCl</td>
<td>77</td>
<td>540</td>
<td>730</td>
<td>770</td>
<td></td>
<td>[417]</td>
</tr>
</tbody>
</table>
Pe•+* proves thus to be rather long lived when compared to the radical cations of other PAHs that have usually sub-picosecond lifetimes.\textsuperscript{158,241} The energy gap law predicts an excited-state lifetime of 200 ps, substantially longer than what has been measured, even in frozen matrices. The radiative rate constant, $k_r$, is very small due to the rather small molar absorptivity and the low transition frequency of the $D_1 \leftarrow D_0$ absorption band.

Considering that Zhao et al.\textsuperscript{158} observed identical relaxation rates at 15 and 298 K, the differences in Table 6.2 should be ascribed to a solvent effect. The fastest relaxation is observed in MeCN, a low viscosity solvent with fast and ultrafast dynamic relaxation.\textsuperscript{133,138,356} Much higher viscosity and slower solvent dynamics\textsuperscript{356,420} are present in $\text{H}_2\text{SO}_4$ where the lifetime of Pe•+* is much longer. Zhao et al.\textsuperscript{158} state that vibrational energy transfer from solute to solvent in $\text{H}_3\text{BO}_3$ glass takes place in 5 – 20 ps, making it comparable to organic solvents. The slowest excited state relaxation is reported in the low-polar solid matrices freon and iso-pentane.

Brodard et al.\textsuperscript{241} found that deuteration of either Pe•+ or sulfuric acid prolongs the excited-state lifetime of the solute, the effects being approximately additive. The lifetime of $\text{d}12$–Pe•+* in $\text{H}_2\text{SO}_4$ and $\text{D}_2\text{SO}_4$ were found to be 32 and 38 ps, respectively, compared to 26 and 30 ps for $\text{h}12$–Pe•+*.\textsuperscript{241} This gives a kinetic isotope factor of 1.25 for the solute and 1.17 for the solvent. The factor 1.25 is in excellent agreement with what has been determined by Siebrand and co-workers in their work on the energy gap law (EGL, eq. 2.21), where an H/D isotope effect of 1.5 is expected theoretically, but a factor of 1.3 was determined experimentally.\textsuperscript{67}\textsuperscript{7}

\textsuperscript{7}The discrepancy between theoretical and experimental value was ascribed to the participation of C=C vibrations in the ISC.\textsuperscript{67}
Table 6.2.: excited-state lifetime of $\text{Pe}^{+}$ in various solvents at different temperatures

<table>
<thead>
<tr>
<th>solvent</th>
<th>T / K</th>
<th>$\tau$ / ps</th>
<th>method</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>298</td>
<td>$\approx$ 3</td>
<td>TA$^{[52]}$</td>
</tr>
<tr>
<td>MeCN</td>
<td>298</td>
<td>35</td>
<td>quenching$^{[204]}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>298</td>
<td>26</td>
<td>TG$^{[241]}$</td>
</tr>
<tr>
<td>$\text{D}_2\text{SO}_4$</td>
<td>298</td>
<td>30</td>
<td>TG$^{[241]}$</td>
</tr>
<tr>
<td>$\text{H}_3\text{BO}_3$</td>
<td>298</td>
<td>35</td>
<td>TG$^{[240]}$</td>
</tr>
<tr>
<td>$\text{H}_3\text{BO}_3$</td>
<td>298</td>
<td>19</td>
<td>TG$^{[158]}$</td>
</tr>
<tr>
<td>$\text{H}_3\text{BO}_3$</td>
<td>15</td>
<td>19</td>
<td>TG$^{[158]}$</td>
</tr>
<tr>
<td>freon</td>
<td>77</td>
<td>100</td>
<td>TG$^{[241]}$</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>77</td>
<td>83</td>
<td>TG$^{[241]}$</td>
</tr>
</tbody>
</table>

Quantum chemical calculations for $\text{Pe}^{+}$. Recent theoretical results by Bearpark and co-workers showed that $\text{Pe}^{+}$ has no planar conical intersection that is easily accessible, as opposed to other PAH radical ions.$^{[407]}$ In this study, the lowest energy excited states of $\text{Pe}^{+}$ were explored using the molecular mechanics/valence bond (MMVB), RASSCF and TD–DFT protocols.

The geometry of $\text{Pe}^{+}$ was constrained to planarity since the authors did not expect important influence of out-of-plane deformations. This is surprising since even for neutral Pe, the out-of-plane butterfly motion can be observed in the ultrafast fluorescence dynamics$^{[145]}$ (see above), the Jahn–Teller effect discussed in chapter 3.2.3 leads to an enhancement of vibronic coupling, and Negri et al.$^{[421]}$ explicitly invoked “resonance vibronic coupling between $D_1$ and $D_3$ by the 1013 cm$^{-1}$ mode of $b_{1g}$ symmetry as the most probable source of the doublet structure of the origin observed for the $D_3\leftrightarrow D_0$ transition of perylene radical cation.” In fact, the $D_3$ state was not included at all in the analysis by Tokmachev et al. because of its different symmetry, an argument that holds strictly only in the case of the constrained geometry employed.$^{[407]}$

Within this framework, the authors of the calculations found two almost degenerate excited states, $D_1(B_{3g})$ and $D_1(B_{2g})$, connected by a CI. The relaxation from the FC excited state to either of the two minima is characterised by small geometrical changes. The charge distribution of these two states, however, differs significantly. Only an unreasonably distorted geometry in which the 1–2 and 6a–6b bonds (Figure 6.2) are more than 1.55 Å long leads to CIs between $D_0$ and $D_1$, one of $D_{2v}$ and another one of $C_{2v}$ symmetry. They are so high in energy — 1.8 and 1.2 eV, respectively — that they are not expected to play a role for the photophysics of $\text{Pe}^{+}$.$^{[407]}$

6.1.2. Antecedents of perylene radical anion

For Schiedt and Weinkauf,$^{[422]}$ perylene radical anion ($\text{Pe}^{--}$) is a prime example for a molecule that does not change its molecular structure upon electron capture.

The highest spin densities of $\text{Pe}^{--}$ are found at carbon atoms number 3 and 1 (Figure 6.2).$^{[424]}$ Disproportionation into the neutral and the dianion was found to be important in Et$_2$O so-
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Figure 6.8.: Absorption of Pe•− in DMF/Bu₄NBF₄ generated electrochemically at r.t. [423]

Figure 6.9.: Absorption spectrum of Pe•− in MTHF at 77 K. [184]
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Table 6.3.: Calculated electronic transitions of Pe•− with non-zero oscillator strengths \(f\) and state assignment.\(^{[388]}\)

<table>
<thead>
<tr>
<th>(E / \text{eV} )</th>
<th>(E / \text{nm} )</th>
<th>(f)</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.39</td>
<td>890</td>
<td>0.0040</td>
<td>(^2B_{1u} \leftarrow ^2B_{3g})</td>
</tr>
<tr>
<td>1.61</td>
<td>770</td>
<td>0.0025</td>
<td>(^2A_{u} \leftarrow ^2B_{3g})</td>
</tr>
<tr>
<td>1.64</td>
<td>757</td>
<td>0.0347</td>
<td>(^2B_{1u} \leftarrow ^2B_{3g})</td>
</tr>
<tr>
<td>1.73</td>
<td>718</td>
<td>0.0028</td>
<td>(^2B_{2u} \leftarrow ^2B_{3g})</td>
</tr>
<tr>
<td>2.26</td>
<td>549</td>
<td>0.3328</td>
<td>(^2A_{u} \leftarrow ^2B_{3g})</td>
</tr>
</tbody>
</table>

This seems not to be the case for the electrochemical generation\(^{[423]}\) in DMF shown in Figure 6.1.2 where the spectral feature of neutral and dianion (\(\lambda_{\text{abs}}^{\text{max}} = 552\, \text{nm}, \varepsilon = 32\,000\, \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}\) in Et\(_2\)O)\(^{[425]}\) are clearly absent.

The electronic spectrum of Pe•− recorded in low temperature matrix is shown in Figure 6.9. The transition energies are in general lower for the anion than those of the cation but the pairing theorem is fairly well fulfilled for perylene (see also Figure 6.15), showing that the energy spacing and Franck–Condon factors in the bonding and antibonding manifold of MOs are close to one another.

The first absorption band is situated at 1000 nm (10.0 kK = 1.2 eV) and the most intense at 580 nm (17.3 kK = 2.1 eV, \(\varepsilon = 56\,000\, \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}\) in DMF\(^{[423]}\)). Several vibronic transitions are resolved in MTHF\(^{[184]}\) and Ar matrix\(^{[388]}\) experiments. Table 6.3 compiles the allowed transitions calculated at the TD–DFT level of theory. According to these computations,\(^{[388]}\) the transition with high molar absorptivity is subject of the same configuration interaction as has been discussed for the cation.

An interesting result from this calculations is that the D\(_1–D_2\) energy gap amounts to 1800 cm\(^{-1}\). Experimentally, the second transition is found 1200 cm\(^{-1}\) above the first one, the third one 1900 cm\(^{-1}\). These gaps are still in the range of vibrational energies and the authors do not attempt to correlate certain features of the experimental spectrum with the calculated transitions.

The dominant absorption band is considerably blue shifted in Ar matrix with respect to (liquid and solid) organic solutions. While it peaks at 556 nm in Ar, it is found at 578±2 nm in THF\(^{[426]}\), MTHF,\(^{[184]}\) DMSO,\(^{[427]}\) and MeCN.\(^{[423,426]}\)

**Time resolved measurements.** The excited state lifetime of Pe•− in MeCN was found to be less than 15 ps, the width of the IRF.\(^{[240]}\) The radical anion was obtained by photoinduced (\(\lambda_{\text{exc}} = 355\, \text{nm}\)) ET of Pe with N,N–dimethylaniline and monitored at 532 or 545 nm by TG spectroscopy after 532 nm excitation. In these experiments, the GSR was incomplete owing to electron photoejection from the radical anion.\(^{[240]}\)

The radical anions of perylene dicarboximide (PMI) and perylene tetracarboxydiimide (PDI, structures (3) and (4), respectively, in Figure 3.7 on page 40) have excited state lifetimes of 530 and 145 ps, respectively.\(^{[185]}\) In agreement with EGL, the diimide that has the lower situated
Table 6.4.: Energy of the absorption maximum of $\text{Pe}^{\bullet+}$ in various solvents. $f(n_D)$ is the Debye (eq. 2.27), $f(\varepsilon, n_D)$ the Lippert–Mataga function (eq. 2.28).

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\lambda_{\text{abs}}^{\text{max}}$ / nm</th>
<th>$\tilde{\nu}_{\text{abs}}^{\text{max}}$ / kK</th>
<th>$f(n_D)$</th>
<th>$f(\varepsilon, n_D)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>537</td>
<td>18.6</td>
<td>0.348</td>
<td>0.611</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>543</td>
<td>18.4</td>
<td>0.404</td>
<td>0.436</td>
</tr>
<tr>
<td>THF</td>
<td>544</td>
<td>18.4</td>
<td>0.394</td>
<td>0.421</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>539</td>
<td>18.6</td>
<td>0.403</td>
<td>0.582</td>
</tr>
</tbody>
</table>

D$_1$ state, has a shorter D$_1$ lifetime.$^8$ Including the other imides and diimides measured by these authors, no correlation is apparent.$^{[185]}$

**Perylene radical ions.** Before coming to the experimental results, let us summarise what is known about perylene and its ions. The structure, that is not much perturbed upon ionisation, can be illustrated as two naphthalenes connected by almost single bonds. These two halves of the molecule can vibrate in a butterfly motion which is Franck–Condon active. The other FC active modes are symmetric vibrations. IC in the excited state manifold is fast in neutral and also present (though maybe not quantitative) in the radical cation since only D$_1\to$D$_0$ emission is observed. The D$_1$ state lifetime of the radical ions was determined to be of a few up to 100 picoseconds, depending on the solvent and deuteration. Substitution distorts the geometry if situated at C1 leading to efficient IC while hardly influencing the shape of the UV/visible spectra.

### 6.1.3. Results for perylene radical cation

Perylene has been oxidised electrochemically in MeCN, CH$_2$Cl$_2$ and THF solution. The steady–state spectra are shown in Figure 6.10 together with spectra of Pe in H$_2$SO$_4$. A slight solvent induced shift (200 cm$^{-1}$ from MeCN to CH$_2$Cl$_2$) but no dimerisation were apparent (c.f. Figure 6.7). A plot of the D$_5\leftrightarrow$D$_0$ transition energy vs. the Debye function (eq. 2.27) or the Lippert–Mataga function (eq. 2.28) revealed no linear correlation, though a rough correlation with the latter (Table 6.4). No spectral shift was induced by replacing the supporting electrolyte Bu$_4$NPF$_6$ by Bu$_4$NClO$_4$.

The TA spectra of $\text{Pe}^{\bullet+}$ in MeCN$^9$ after 540 nm excitation (Figure 6.11) comprised of a strong bleach signal at the position of the D$_5\leftrightarrow$D$_0$ and D$_2\leftrightarrow$D$_0$ absorption bands and of ESA in the blue part of the spectrum. The spectral width of the bleach signal was close to that of the steady–state absorption, i.e. no feature of either D$_5\to$D$_0$ nor D$_2\to$D$_0$ SE could be deduced from the TA spectra. The ESA peaking at 390 nm was present only at very early time delays. As it vanished, another ESA band rose situated at the red edge of the bleach at 540 nm. This new ESA continuously shifted to the blue while it decayed on the same timescale as the bleach signal. The time traces could be accounted for with a biexponential function.

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$^8$Although this correlation is lost when taking into account the number of CH bonds, see page 19

$^9$electrochemical generation with 0.1 mol·L$^{-1}$ Bu$_4$NPF$_6$
Figure 6.10.: Absorption spectra of Pe$^{•+}$ in different solvents (top, all except for H$_2$SO$_4$ containing 0.1 mol·L$^{-1}$ Bu$_4$NPF$_6$) and spectra of Pe$^{•+}$, d12-Pe$^{•+}$, and MePe$^{•+}$ in MeCN/Bu$_4$NPF$_6$ (bottom). The distortions between 350 and 450 nm are due to neutral Pe, the shoulder at 503 nm in H$_2$SO$_4$ stems from Pe$_2^{•+}$ (c.f. Figure 6.7).
The SADS depicted in Figure 6.11 indicated that \( \tau_{a1} = 5 \text{ ps} \) represents the decay of the excited-state population and \( \tau_{a2} = 24 \text{ ps} \) the decay of a hot ground state population. Qualitatively identical TA spectra have been recorded after 540 nm excitation in MeCN/Bu4NCIO4, CH2Cl2/Bu4NPF6, THF/Bu4NPF6, as well as in MeCN/Bu4NPF6 after 800 nm excitation. It is noteworthy that the relative intensity of the ESA band around 550 nm that was ascribed to a hot ground state was approximately the same when using Bu4NCIO4 and after 800 nm excitation and slightly smaller only in CH2Cl2 but it seems smaller in the TA spectra (Figure 6.12) due to the convolution of rise and decay.

The lifetimes obtained from the target analysis are collected in Table 6.5. An additional lifetime of ca. 1 ps was necessary to describe the dynamics after 800 nm excitation (Table 6.5). The SADS suggested that it stems from XPM. Due to the inefficiency of the electrochemical generation of Pe•+ in THF (see the steady–state spectrum, Figure 6.10), the signal intensity was very low and only a rough estimate of the lifetime could be extracted from the dynamic traces. The lifetime of Pe•++ in THF was close to that in MeCN.

Superimposing the dynamic traces showing the decay of the ESA at 400 nm (Figure 6.14), no slowing down could be evidenced when comparing \( \tau_{a1} \) measured after 800 nm with that after 540 nm excitation. The numerical difference in Table 6.5 is within the estimated uncertainty with the current design of the electrochemical flow–through system (25%).

On the other hand, the longer excited-state lifetime in CH2Cl2 solution (see Table 6.5 and Figure 6.14) is significant — \( \tau_{a1} \) more than doubled when comparing to MeCN but the overall behaviour remained the same.

A complete change of dynamics was observed in H2SO4 where the ESA persisted much longer than in the other solvents. Target analysis associated a time constant of 18 ps to the decay of this band and an additional, shorter time constant with a cooling process (Figure 6.13). This cooling was not observed in H2SO4 after 800 nm excitation, presumably due to the lower TA signal (only 5% of the signal after 540 nm excitation). Close inspection of the TA spectra showed that the red edge of the bleach decayed faster than the blue indicating that a hot ground state was populated in this case as well, though maybe to a minor extend or simply not spectrally resolved.

### 6.1.4. Results for d12–Pe•+ and MePe•+

The bottom panel of Figure 6.10 shows the steady–state spectra of the radical cations of perdeuterated perylene (d12–Pe•+) and 3–methylperylene (MePe•+). The absorption spectrum of the former showed no difference with the isotopically unlabelled compound, the electronic transitions of the latter were red–shifted by 280 cm\(^{-1}\) with respect to the bands of Pe•+ — compared to a shift of 275 cm\(^{-1}\) for the neutrals in MeCN solutions.

The TA spectra of d12–Pe•+ and MePe•+ in MeCN/Bu4NPF6 were indistinguishable from those of Pe•+ in the same solvent (except for the red shift of MePe•+). The spectral dynamics were the same as for Pe•+ within experimental error (Table 6.5). A graphical comparison of the excited-state lifetime hinted on a minor slow down of the relaxation for MePe•+ but an exact answer cannot be given with the current data (Figure 6.14).

---

10 The result of the fit is not affected if \( \tau_{a1} \) is fixed to 0.2 ps, the width of the IRF, or freely optimised. The results in Table 6.5 show the unconstrained fit.

11 Note the presence of XPM in the spectra after 800 nm excitation.
Figure 6.11.: TA spectra of Pe•⁺ in MeCN/\text{Bu}_4\text{NPF}_6 at various time delays after 540 nm excitation and SADS.
Figure 6.12.: TA spectra of Pe\(^{•+}\) in MeCN/\(\text{Bu}_4\text{NPF}_6\) at various time delays after 800 nm excitation and in \(\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NPF}_6\) after 540 nm excitation.
Figure 6.13.: TA spectra of Pe•+ in H₂SO₄ at various time delays after 540 nm excitation and SADS.
Figure 6.14.: Dynamics of the TA signal of \( \text{Pe}^{*+} \) (ESA at 400 nm) in different solvents (top, \( \lambda_{\text{exc}} = 540 \text{ nm} \)) and of \( \text{Pe}^{*+}, \text{d12-Pe}^{*+} \) and \( \text{MePe}^{*+} \) in MeCN (bottom).
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Table 6.5.: Lifetimes extracted from the target analysis of TA data of Pe•+, d12–Pe•+ and MePe•+ (error ±25%). Electrochemical generation with (a) 0.1 mol·L⁻¹ Bu₄NPF₆ or (b) Bu₄NClO₄ supporting electrolyte except for H₂SO₄ solution where it forms spontaneously. (c) 4 µJ, (d) 10 µJ pump power, † fixed.

<table>
<thead>
<tr>
<th>cmpd</th>
<th>solvent</th>
<th>λexc / nm</th>
<th>τa₀ / ps</th>
<th>τa₁ / ps</th>
<th>τa₂ / ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pe•+</td>
<td>MeCN</td>
<td>540</td>
<td>5.0</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Pe•+</td>
<td>MeCN</td>
<td>540</td>
<td>5.5</td>
<td>23</td>
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</tr>
<tr>
<td>Pe•+</td>
<td>MeCN</td>
<td>800(c)</td>
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<td>6.0</td>
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<tr>
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<td>800(d)</td>
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<td>6.0</td>
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<tr>
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<td>MeCN</td>
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<tr>
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<td>MeCN</td>
<td>800</td>
<td>6.9</td>
<td>21</td>
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</tr>
<tr>
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<td>MeCN</td>
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<td>0.3</td>
<td>5.5</td>
<td>17</td>
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</tbody>
</table>

6.1.5. Results for perylene radical anion

The steady–state absorption spectrum of Pe•− generated electrochemically in MeCN/Bu₄NPF₆ solution is shown in Figure 6.15. It reproduces the low temperature matrix isolation[184,388] and r.t. DMF solution spectra published.[423] The electrochemical conversion efficiency was ca. 90%.

TA spectra after 800 nm excitation (Dₓ←D₀) are shown in Figure 6.16. At early time delays they showed ESA in all the spectral region of our TA set–up except for negative bands at the position of dominant absorption features, i.e. at 580, 680 and above 720 nm. This ESA decayed monotonically within some picoseconds. The dynamics around 590 nm could be described as a rising and decaying signal. The spectral features of this ESA were typical of a vibrationally hot ground state.

Target analysis required three exponentials to describe the evolution of the TA spectra (Table 6.5). The SADS of the first two species were identical except for a vertical displacement (Figure 6.16)¹² and the lifetime τa₁ was thus ascribed to XPM. The second lifetime, τa₂, was associated with the rise of the 590 nm ESA and contributed to the decay of the bleach. All TA signal decayed to zero with τa₃, no bleach signal persisted.

6.1.6. Discussion

The results presented above show that the excited-state lifetime of perylene radical cation strongly depends on the environment but within experimental error not (or only to a minor

¹²The DADS is a horizontal line, see page 206.
extent) on the excitation wavelength (Table 6.5). The GSR time constant in MeCN is in good agreement with the value published by Pages et al.,[52] the measurement in H$_2$SO$_4$ presented here gives a slightly shorter value than observed by Brodard et al.,[241] presumably due to the improved time resolution.

The decay of D$_1$ is followed by cooling with $\approx$ 24 ps in MeCN, 21 ps in CH$_2$Cl$_2$, and 6 ps in H$_2$SO$_4$. The time constant in MeCN agrees well with that ascribed to VER of neutral Pe after 266 nm excitation or of azulene after ultrafast S$_1\rightarrow$S$_0$ IC,[428] but is much slower than those of VER of polar solutes in the same solvent.[147,429] Zhao et al. observed no such cooling for Pe$^{•+}$ in H$_3$BO$_3$ although it was present in the case of shorter lived PAH radical cations.[158]

**Excitation wavelength dependence.** The TA spectra of Pe$^{•+}$ at early time delays after 540 nm excitation (D$_5\rightarrow$D$_0$) are identical to those after 800 nm excitation (red edge of the D$_1\rightarrow$D$_0$ transition) and the spectral dynamics can be described by the same function. The first signal observed in the TA spectra is therefore ascribed to the same electronic state, namely D$_1$. This means that D$_5\rightarrow$D$_1$ IC happens within the IRF ($\tau_{D_5\rightarrow D_1}$ $\ll$ 200 fs) as it is the case in neutral Pe after 266 nm excitation. Efficient IC to D$_1$ is in agreement with the finding that excitation to higher excited states of Pe$^{•+}$ leads only to D$_1\rightarrow$D$_0$ fluorescence[406,414] although the fluorescence quantum yield was not determined in these studies and a lower fluorescence quantum yield could have been expected for shorter wavelength excitation.

The same holds for MePe$^{•+}$ for which no significant difference could be evidenced in the GSR rate upon change of excitation wavelength. The lifetime difference, if any, has to be rather small and a definitive answer has to await the improvements of the electrochemical flow–through cell discussed in chapter 11.5.

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Figure 6.15.: Absorption spectrum of Pe$^{•+}$ and Pe$^{••}$ in MeCN (electrochemical generation, 0.1 mol·L$^{-1}$ Bu$_4$NPF$_6$) and the neutral parent in MeCN.
Figure 6.16.: TA spectra of Pe\textsuperscript{•−} in MeCN after 800 nm excitation and SADS from the target analysis.
For both, Pe\textsuperscript{•+} and MePe\textsuperscript{•+}, GSR mediated by a CI between higher lying excited states and the ground state, if existing, can obviously not compete with IC to D\textsubscript{1}, at least not on large scale. If the rate constant for D\textsubscript{n>1}→D\textsubscript{0} IC was much higher than that of D\textsubscript{n>1}→D\textsubscript{1} IC, the TA signal after 540 nm excitation should be negligible. If they were comparable in magnitude, a fraction of the bleach should decay within the IRF, which is not observed experimentally either.

As anticipated\cite{407} the D\textsubscript{0}/D\textsubscript{1} CI found by quantum chemical methods and located 9800 cm\textsuperscript{-1} (1.2 eV) above the D\textsubscript{1} relaxed state does not intervene in the decay process of Pe\textsuperscript{•+}, not even after 540 nm excitation which represents an excess energy of 6000 cm\textsuperscript{-1} (0.7 eV).

If there is no CI connecting D\textsubscript{1} and D\textsubscript{0}, the non–radiative decay of Pe\textsuperscript{•+} should follow the EGL which estimates\cite{407} the D\textsubscript{1} lifetime to 200 ps, 50 times longer than what is observed. Additionally no important influence of the solvent would be expected in such a case, contrary to what has been observed.

**Environmental influences.** The solvatochromic shift of Pe\textsuperscript{•+} is minor and the aspect of the electronic absorption spectrum is unaltered by the environment and supporting electrolyte.

In contrast to that stands the big diapason of lifetimes for the GSR of Pe\textsuperscript{•+} (Table 6.2 and 6.5) in different solvents. The excited-state lifetime of Pe\textsuperscript{•+} after 540 nm excitation is 5 ps in MeCN and THF, twice longer in CH\textsubscript{2}Cl\textsubscript{2} and almost 4 times longer in H\textsubscript{2}SO\textsubscript{4}. Even longer excited state lifetimes have been reported in iso–pentane (83 ps) and freon (100 ps) glasses.\cite{241} The prolongation cannot be ascribed to viscosity since the lifetime in solid H\textsubscript{3}BO\textsubscript{3} is on the same order of magnitude as CH\textsubscript{2}Cl\textsubscript{2} or H\textsubscript{2}SO\textsubscript{4}, much shorter than in freon or iso–pentane.

Table 6.6 compiles the excited state lifetime of Pe radical ions and the solvent longitudinal relaxation time \(\tau_L\). To the best of my knowledge, \(\tau_L\) is not available for the solid matrices but it seems reasonable to expect that it is slower than for liquid solution, and slower in a less polar medium. A rough correlation between \(\tau_L\) and \(\tau_{D1}\) can be deduced from Table 6.6. Such a correlation is meaningful if the D\textsubscript{1}→D\textsubscript{0} IC has substantial charge transfer character.

The longitudinal relaxation time is proportional to viscosity, but such a correlation would not explain the differences in the different solid matrices.

**Structure.** Brodard et al. found a 25% slow down of the GSR of Pe\textsuperscript{•+} upon perdeuteration in H\textsubscript{2}SO\textsubscript{4}.\cite{241} The value for Pe\textsuperscript{•+} decay in MeCN extracted from the TA data (\(\tau_{a1}\) in Table 6.5) would be in perfect agreement but this difference is just at the limit of the uncertainty of the current set–up and a definitive answer cannot be given.

The same holds for MePe\textsuperscript{•+} — within experimental error, there is neither a slow down nor an acceleration of the the non–radiative D\textsubscript{1} decay, hence the geometrical distortion by the methyl group is small as anticipated from the electronic spectra and theoretical results.\cite{402} From the similarity of the vibronic pattern of the fluorescence spectra of neutral and cationic Pe, Chiller et al.\cite{406} concluded, that Pe maintains its D\textsubscript{2h} symmetry upon oxidation. If the out–of–plane butterfly vibration contributes to the excited state decay of these radical cations, its amplitude has to be small.

\textsuperscript{13}(Equation 2.21) with the S\textsubscript{1}→S\textsubscript{0} parameters by Siebrand.
6. Aromatic Hydrocarbons

Table 6.6.: Comparison of the excited state lifetime of Pe radical ions with solvent longitudinal relaxation time $\tau_L$ and viscosity $\eta$.\cite{137,356,420}

<table>
<thead>
<tr>
<th>ion</th>
<th>solvent</th>
<th>$\tau_{D1}$/ ps</th>
<th>$\tau_L$/ ps</th>
<th>$\eta$/ cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pe•+</td>
<td>MeCN</td>
<td>5</td>
<td>0.3</td>
<td>0.34</td>
</tr>
<tr>
<td>Pe•+</td>
<td>THF</td>
<td>6</td>
<td>0.8</td>
<td>0.46</td>
</tr>
<tr>
<td>Pe•+</td>
<td>CH$_2$Cl$_2$</td>
<td>12</td>
<td>2.2</td>
<td>0.41</td>
</tr>
<tr>
<td>Pe•+</td>
<td>H$_2$SO$_4$</td>
<td>18</td>
<td>400</td>
<td>23.6</td>
</tr>
<tr>
<td>Pe•+</td>
<td>H$_3$BO$_3$</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pe•+</td>
<td>iso-pentane</td>
<td>83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pe•+</td>
<td>freon</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pe•−</td>
<td>MeCN</td>
<td>5</td>
<td>0.3</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Perylene radical anion. The excited-state decay of Pe•− in MeCN was found to be 5 ps, i.e. one order of magnitude faster than given by the EGL and practically identical to perylene radical cation despite a different $D_1$ state energy and a bigger energy gap between $D_1$ and $D_2$ (while $D_2$ is at least 1100 cm$^{-1}$ above $D_1$ in Pe•−, this gap amounts only to 300 cm$^{-1}$ in Pe•+). Both these differences do not seem to affect the $D_1$ lifetime.

Wasielewski and co–workers\cite{185} found good agreement between the ESA of neutral PMI and PDI, (structures (3) and (4) in Figure 3.7 on page 40) and the ground state absorption of the corresponding radical anions, i.e. the $S_n\rightarrow S_1$ and the $D_n\rightarrow D_0$ transitions are alike. This was attributed to the similarities in the electronic configuration.

Figure 6.17 shows the case of perylene. The shape of the intense absorption band at 580 nm of Pe•− and the ESA band at 700 nm of neutral Pe resemble each other but, contrary to the small shifts reported by Gosztola et al., the energy difference between the two transitions is substantial, namely 2900 cm$^{-1}$ ($=0.35$ eV). Surprisingly, the steady–state absorption of PDI•− (Figure 6.18) is closer to Pe $S_n\rightarrow S_1$ ESA than Pe•− $D_n\rightarrow D_0$ absorption. While the steady state absorption of PMI•− resembles closely that of Pe•−, strong absorption band of PDI•− is red–shifted. This shift does not correlate with that in the neutral parent compounds.

The TA signal of Pe•−, PMI•− and PDI•− have in common a small to negligible ESA (Figures 6.16 and 6.19).

The excited-state lifetime of PMI•− and PDI•− were determined to be 530 and 150 ps, respectively at $D_1$–$D_0$ energy gaps of 12.2kK ($=1.5$ eV) and 10.5kK ($=1.3$ eV), respectively.\cite{185} Despite the comparable $D_1$ energies, their $D_1$ lifetimes are 50 to 100 times longer that that of Pe•−. It should be mentioned that both, PMI•− and PDI•−, are longer lived than the 50 ps calculated from EGL using the parameters obtained by Siebrand for the $S_1$–$S_0$ IC of PAHs.

Conclusions. Pe radical ions show $D_n\rightarrow D_1$ IC in $\ll$200 fs, the $D_1$ state itself has a lifetime that depends strongly on the environment. EGL and calculations with constrained $D_{2h}$ symmetry are unable to explain the dynamics.\textsuperscript{14} It is suggested that the lifetime correlates with the longitudinal solvent relaxation time. This implies that the IC has substantial charge transfer

\textsuperscript{14}While naphthalene\cite{117} and pyrene\cite{116} show planar CIs.
Figure 6.17.: Comparison of the ground state absorption of \( \text{Pe}^{0+} \) with the TA signal (ESA, SE and bleach) of neutral perylene in MeCN.

Figure 6.18.: Absorption spectrum of PDI (see Figure 3.7) in neutral, anionic and dianionic oxidation state.\cite{185}
Figure 6.19.: TA signal of PMI•− 50 ps after 590 nm excitation (dashed) and of PDI•− 24 ps after 705 nm excitation.\cite{185}

character, presumably among the naphthalene moieties whose decoupling will be strongly influenced by the butterfly vibration which has been shown to be excited in the vibronic transition of neutral perylene. This explanation might also account for the identical lifetimes of radical cation and anion — although of course different MOs would be involved in the intramolecular charge transfer.

Alternatively a Jahn–Teller distortion of first or second order\cite{115,189,191} might be responsible for stating mixing. Both, the D$_2$ and D$_3$ state are close in energy to D$_1$, indeed.

The comparably longer lifetime of PMI•+• and PDI•+• might then be understood as a symmetry lowering avoiding the Jahn–Teller distortion or a localisation of the charge on the diimide unit(s).

6.2. Tetracene radical cation

Tetracene (Te) is a cata–condensed PAH. Its S$_1$ state energy is a bit lower than that of perylene, 21.0 kK in MeCN. The fluorescence quantum yield is $\Phi_{flr} = 0.17$ while most of the S$_1$ state population decays to the triplet state, $\Phi_{ISC} = 0.67$ with a time constant $\tau_{flr} = 6.4$ ns.\cite{371} The Stokes shift is small, 250 cm$^{-1}$ in MeCN.

The redox potentials of Te are close to those of Pe, namely at 1.0 and -1.58 V vs. SCE for oxidation in MeCN and reduction in DMF solution, respectively.\cite{371,403,430,15}

\footnote{The *Handbook of Photochemistry* reports 0.77 V for the oxidation.\cite{371,405}}
Figure 6.20.: Absorption spectrum of Te•+ in 2–BuCl.[184]

Figure 6.21.: Emission ($\lambda_{\text{exc}} = 390\,\text{nm}$) of tetracene radical cation in BF$_3$·H$_2$O – CF$_3$COOH.[226].
6. Aromatic Hydrocarbons

6.2.1. Antecedents of tetracene radical cation

The lowest energy transition in Te•+ is situated at 876 nm (11.5 kK = 1.4 eV) in Ar matrix\(^{[361,431]}\) and virtually the same in 2–BuCl\(^{[184]}\) (Figure 6.20) and H\(_2\)SO\(_4\).\(^{[173]}\) From calculations\(^{[431]}\) it is a ππ\(^*\) type HOMO→HOMO-1 transition. The second electronic transition, a LUMO→HOMO transition, is located at 745 nm,\(^{[431]}\) 2000 cm\(^{-1}\) (0.25 eV) above D\(_1\).

It was found that the CC and CH in–plane vibrations are enforced in Te•+ compared to neutral Te, while the CH out–of–plane vibrations are 11 times weaker.\(^{[361]}\) The latter are very strong in the neutral parent compound.

Figure 6.21 shows the emission spectrum of tetracene radical cation measured in BF\(_3\)·H\(_2\)O/CF\(_3\)CO\(_2\)H mixtures by Pankasem et al.\(^{[226]}\) Like for perylene, the emission is located in the NIR spectral region, just below the lowest lying absorption band. The emission spectrum shows vibrational structure with bands at 910 nm (11 000 cm\(^{-1}\)) and 1030 nm (\(\Delta \nu = 1280 \text{ cm}^{-1}\)) in reasonable agreement with either the 1000 cm\(^{-1}\) or the 1400 cm\(^{-1}\) vibrational regression found in absorption.\(^{[431]}\)

Vauthey and co–workers published the TG spectrum and dynamics of Te•++ in r.t. H\(_2\)SO\(_4\) and D\(_2\)SO\(_4\). The spectrum depicted in Figure 6.22 shows a strong bleach signal\(^{16}\) centred at 745 nm and weaker signals at 663 and 610 nm. The GSR can be reproduced with an exponential decay of 26 ps in H\(_2\)SO\(_4\) and 30 ps in D\(_2\)SO\(_4\).\(^{[241]}\) With D\(_1\) located at 11.0 kK, eq. 2.21 predicts \(\tau_{D1} = 75 \text{ ps}\). Like for perylene, the measured lifetime is shorter than that predicted by the EGL.

Dimerisation of Te•+ leads to similar spectral changes as has been observed for Pe•++.\(^{[173]}\) TeH\(^+\) has an absorption maximum at 460 nm.\(^{[432]}\)

The pairing theorem\(^{[54]}\) is especially well fulfilled in the case of Te radical ions (Figure 3.3 on page 31).

\(^{16}\)TG spectra do not contain information on the sign.
6.2.2. Results for tetracene radical cation

Tetracene radical cation has been obtained in $\text{H}_2\text{SO}_4$. Attempts to oxidise it chemically in MeCN were unsuccessful, presumably due to water impurities. It is remarkable that $\text{Pe}^{*+}$, whose reduction potential is very close to that of $\text{Te}^{*+}$, is sufficiently stable under similar conditions, while only follow-up products could be detected when oxidising a solution of Te in MeCN/Bu$_4$NPF$_6$ under experimentally identical conditions.

The absorption spectrum in r.t. $\text{H}_2\text{SO}_4$ was practically identical with the one in 2–BuCl matrix spectrum by Shida$^{[184]}$ except for a broadening of the bands.

The TA spectra after 800 nm excitation are shown in Figure 6.23. The spectra consisted of ESA all over the observation window except for bleach signal at the position of dominant absorption bands, i.e. at 393, 680 and 750 nm. While most of the ESA decayed monotonically without spectral shifts, the ESA band around 400 nm rose while shifting to the blue in a first step and then decayed continuing the shift. The dynamics could be reproduced with a biexponential function or target analysis with three species (the last one being the relaxed ground state, hence with zero amplitude). The second species had the amplitude spectrum of a hot ground state. The lifetimes were $\tau_{a1} = 22.9$ ps and $\tau_{a2} = 4.2$ ps.

6.2.3. Discussion

The TA spectrum of $\text{Te}^{*+}$ after 800 nm agrees well with the TG spectrum published.$^{[241]}$ The 650 nm that was ascribed to ESA$^{[241]}$ stems in fact from bleach. Comparing the steady–state absorption with the early TA spectra shows that $\text{Te}^{*+*}$ absorbs in all the visible spectral region. Peaks are to be expected around 390 and 460 nm, in the other part of the spectrum, the molar absorptivity of the $\text{D}_n^{*-}\text{D}_1$ absorption is just slightly higher than that of the $\text{D}_n^{*-}\text{D}_0$ absorption.

From the TA spectral dynamics, only one intermediate state between the photoexcited and the relaxed ground state can be evidenced. This state is assumed to be a hot ground state, based on the amplitude spectrum $A_2$ in Figure 6.23. IC to $\text{D}_1$ happens within the laser pulse, subsequent $\text{D}_1^{*-}\text{D}_0$ with $\tau_{\text{D}1} = 22.9$ ps. This value is very close to the lifetime of $\text{Pe}^{*+*}$ in $\text{H}_2\text{SO}_4$ and the good agreement is taken as indication that also in this case the solvent dictates the GSR rate constant. Again, it is shorter than what it is expected from EGL. The $\text{D}_2^{*-}\text{D}_1$ energy gap seems to be of no importance either, since it amounts to 2000 cm$^{-1}$ in $\text{Te}^{*+}$, 1000 cm$^{-1}$ in $\text{Pe}^{*-}$ and 300 cm$^{-1}$ in $\text{Pe}^{*+}$.

The time constant ascribed to VER of the hot ground state is a bit shorter for $\text{Te}^{*+}$ in $\text{H}_2\text{SO}_4$ than for $\text{Pe}^{*+}$ in the same solvent.
Figure 6.23.: TA spectra of Te•+ in H$_2$SO$_4$ after 800 nm excitation and SADS from the target analysis.
7. Heterocycles

The radical cations of three heterocycles are presented in this section, tetrathiafulvalene (TTF), thianthrene (TH) and N–methylphenothiazine (MePTZ). All three radical cations are stable, the neutral molecules being excellent electron donors.

Figure 7.1.: Structure formula and side view on neutral TTF, TH and MePTZ. The dihedral angles are largely exaggerated in the sketch.

They share a non–planar molecular structure in the neutral oxidation state illustrated in Figure 7.1. As Hosoya et al.\cite{433} pointed out, anthracene derivatives having the carbons in the 9 and 10 position replaced by heteroatoms are planar if the heteroatoms are second row elements, whereas they are non–planar if any of the heteroatoms is sulfur, selen or tellur. This effect was ascribed to the $d$ orbitals of the latter elements.\cite{433,434} The geometries are by no means rigid but very flexible with low barriers for inversion by a butterfly vibrational mode.

7.1. Tetrathiafulvalene

7.1.1. Antecedents of Tetrathiafulvalene

Tetrathiafulvalene (TTF) has gained great attention after the observation of the metal–like conductivity of TTF·TCNQ crystals.\cite{1} It is widely used in studies of electron transfer processes due to the outstanding stability of the radical cation, TTF’s low oxidation potential ($E_{1/2}^1 = 0.34 \text{ V}, E_{1/2}^2 = 0.78 \text{ V}$ vs. SCE\cite{439}), and reasonably easy synthesis of derivatives containing

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\footnote{The “undisputed champion”\cite{435} in terms of conductivity is bis(ethylenedithio)TTF (BDET–TTF, see Figure 7.4).\cite{436–438}}
Figure 7.2.: Absorption spectra of TTF\(^0\) (dotted), TTF\(^\bullet\) (dashed) and TTF\(^{2+}\) (solid line) in MeCN at r.t.\(^{[439]}\) The inset shows the emission spectrum of TTF\(^{2+}\) (\(\lambda_{\text{exc}} = 352\) nm).

a more or less unperturbed TTF subunit.\(^{[438]}\) Due to these favourable properties it has been employed in various “switchable systems” whose fluorescence is controlled by the redox state of TTF: the neutral TTF is an efficient electron donor, thus a potential fluorescence quencher while the oxidised form is not.\(^2\) This strategy has also been exploited for sensing of, e.g., fluorescent metal ions.\(^{[441]}\)

**Structure of TTF.** Only the central S\(_2\)C=CS\(_2\) of TTF\(^0\) is planar whereas the HC=CH groups are lying on the same side, out of plane (see Figure 7.1). The bent angle was determined to be 13.5±4° by electron diffraction in the gas–phase\(^{[442]}\) while crystal structures show almost planar structures with the rings bent in opposite directions.\(^{[443]}\)\(^3\)

In the liquid phase, the most stable conformer of TTF\(^0\) is a boat-like structure\(^{[442]}\) but it is expected to be extremely floppy having a practically negligible inversion barrier for the change from \(C_{2v}\) to \(D_{2h}\) symmetry.\(^{[446]}\) In quantum chemical calculations TTF planarises in the electronic excited state.\(^{[446,447]}\)

\(^2\)See, for example, \([438]\) and \([440]\) and references therein

\(^3\)Derivatives of TTF with bent crystal structures have also been synthesised.\(^{[444,445]}\)
Electronic spectroscopy of TTF. The longest wavelength absorption of TTF$^0$ that can be observed experimentally is the very weak band at 450 nm ($\varepsilon = 230 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). From samples in stretched polyethylene films, it was concluded that the transition dipole moment has components in both, the molecular long and short axis. The next transition is found 0.6 eV (5000 cm$^{-1}$) higher in energy with a slightly higher molar absorptivity (Table 7.1 and Figure 7.2) and the transition dipole moment aligned along the short molecular axis. Two close lying transitions polarised along the long axis of the molecule are responsible for the peculiar shape of the band around 300 nm (Figure 7.7).

Controversy exists about the assignment of these electronic transitions. The lowest–energy band has been ascribed to i) $\pi\sigma^*$, $\pi\pi^*$, ii) $n\pi^*$, iii) forbidden $\pi\pi^*$, and iv) $\pi^3\pi^*$ transitions.

The HOMO of TTF$^0$ has $\pi$ symmetry, the LUMO $\sigma$ symmetry (Figure 7.3) — although it should be borne in mind that the molecule is not planar what renders this nomination approximative. Based on Extended Hückel, MINDO/3, ab initio Hartree–Fock–Slater, CNDO/S, and TD–DFT calculations, the 450 nm band has been ascribed to a transition between them, calculated at similar energies and with low oscillator strengths, as expected for a $\pi\sigma^*$ transition.

A different interpretation invokes two forbidden $\pi\pi^*$ transitions that are weakly vibrationally allowed. The Pariser–Parr–Pople calculations performed were in agreement with experiment in what concerns the polarisation axes and ionisation energies (compared with the photoelectron spectrum).

A singlet–triplet absorption of $\pi$ symmetry — enhanced by spin–orbit coupling of the sulfur atoms — was invoked on the basis of Xα and MS–CASPT2 results. The polarisation axis of these two transitions are oriented along the short and long molecule axis, respectively, matching the experimental results by Gleiter et al. These calculations, however, locate also the $\pi\sigma^*$ transitions at the energy of the observed transition.

As Fabian et al. pointed out, all the computational methods find more or less the same transitions, and it is just a question of the authors’ preference which one to assign to the ones observed. In other words, the density of states is exceptionally high for TTF$^0$ (see Table 7.1) and includes several Rydberg states.

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4It is surprising to find that most of the calculations, even recent ones, have been performed restricting the geometry to $D_{2h}$ symmetry.
Better consensus is found concerning the higher energy bands that are commonly ascribed to $\pi\pi^*$ transitions, with a $\pi\sigma^*$ transition contributing to a minor extent. TTF$^0$ is non–fluorescent\textsuperscript{[439]} and owing to the negligible oscillator strength of the lowest–energy transition, the estimated radiative lifetime of S$_1$ is on the order of microseconds.\textsuperscript{[446]}

To the best of my knowledge, no experimental excited-state lifetime has been reported. Weak emission of BEDT–TTF samples has been reported,\textsuperscript{[460,461]} though questioned later on.\textsuperscript{[244]} In contrast to the neutral form, the radical cation and the dication are aromatic in the Hückel sense having one and two 1,3–dithiolium cations with 6 $\pi$ electrons, respectively.\textsuperscript{[462]}

The dication fluoresces weakly ($\Phi=0.04$, $\tau < 1$ ns) with the fluorescence maximum located at 488 nm (inset in Figure 7.2).\textsuperscript{[439]}

In crystals, TTF$^\cdot$+ adopts a planar structure of $D_{2h}$ symmetry.\textsuperscript{[463–465]} Compared to TTF$^0$ the central C=C bond is significantly elongated and the adjacent C–S bonds are significantly shortened in TTF$^\cdot$+. The length of these bonds is used as a direct indicator for the charge transfer character of the TTF salt.\textsuperscript{[463]}

The lowest energy absorption of TTF$^\cdot$+ is found at 580 nm. From Table 7.2 it can be seen that it is the low dipole moment transition that results from first order configuration interaction of the HOMO$\leftarrow$HOMO-1 and LUMO$^+$+4$\leftarrow$HOMO transitions. The other combination is responsible for the prominent band at 430 nm (2.9 eV). The second band observed in the absorption spectrum of TTF$^\cdot$+, the shoulder located at 2.51 eV (i.e. 0.35 eV = 2800 cm$^{-1}$) above D$_1$, is, according to MS–CASPT2\textsuperscript{[457]} and TD–DTF\textsuperscript{[453]} calculations, the D$_2$–D$_0$ transition. Both these methods find another state, D$_2$, close in energy to D$_1$, although the assignment of the electronic transition differs between them (Table 7.2). In summary, the computational results indicate that the density of electronic states is high for both, neutral and mono–cationic TTF. In fact, even higher than expected from the experimental absorption spectrum.

TTF$^\cdot$+ Emission. In the light of these findings, it is surprising that emission of radical cations of TTF and two of its derivatives, 4,4’–dimethyl–5,5’–diphenyl–TTF (DMDP–TTF) and bis(4,5–dihydronaphtho-[1,2d])–TTF (BDHN–TTF, see Figure 7.4), has been reported by the group of Armin Schweig.\textsuperscript{[244]} After ionisation of the neutral parent compound by $\gamma$–irradiation in a freon matrix or by UV–irradiation in either methylcyclopentane/iso–pentane or 2–BuCl/CH$_2$Cl$_2$ solution, fluorescence emission and excitation spectra have been recorded at 77 K. The fluorescence excitation spectra published closely resembled the absorption spectra (except for TTF$^\cdot$+, see Figure 7.5) ruling out the possibility of emission from the dimer. No fluorescence of the corresponding halide or perchlorate salts was observed in r.t. liquid or low temperature solid solution.\textsuperscript{5}

The maximum of emission of TTF$^\cdot$+ was found at 740 nm (1.68 eV) yielding a surprisingly large Stokes shift of 3400 cm$^{-1}$. This Stokes shift is considerably higher than the one found for BDHN–TTF$^\cdot$+ or DMDP–TTF$^\cdot$+.\textsuperscript{[244]} Such a large Stokes shift (4100 cm$^{-1}$) was also found by CASSCF/CASPT2 calculations when optimising the excited state geometry restricting the molecule to planar.\textsuperscript{[457]}

For DMDP–TTF$^\cdot$+ the fluorescence lifetime could be measured and a value of 1 ns was found.\textsuperscript{[244]} It is remarkable that the experimental value is close to the value of $k_{nr} = (0.6 \text{ ns})^{-1}$ obtained in the framework of EGL when treating DMDP–TTF$^\cdot$+ as a PAH.

\textsuperscript{5}Cooling these solutions apparently leads to dimerisation.
Table 7.1.: Electronic state energies of TTF$^0$ in eV. *(a)* Experimental value in cyclohexane,$^{[450]}$ with molar absorptivity $\varepsilon$ in L·mol$^{-1}$·cm$^{-1}$, *(b)* CASCF/MS–CASPT2 $D_2h$ symmetry,$^{[457]}$ *(c)* B3P86/aug-cc-pVDZ $C_2v$ symmetry,$^{[447]}$ *(d)* B3P86/aug-cc-pVQZ $C_{2v}$ symmetry,$^{[453]}$ † forbidden.

<table>
<thead>
<tr>
<th>$\Delta E$</th>
<th>$\log(\varepsilon)$</th>
<th>MS–CASPT2 ($D_{2h}$)$^{(b)}$</th>
<th>TD–DFT$^{(c)}$</th>
<th>TD–DFT$^{(d)}$</th>
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<tr>
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<td>$1A_g$</td>
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<td>1.92</td>
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Table 7.2.: Electronic state energies of TTF$^+$ in eV. (a)in MeCN$^{[450]}$ with molar absorptivity$^{[278,458,459]} \varepsilon$ in L·mol$^{-1}$·cm$^{-1}$, (b)CASSCF/MS–CASPT2 $D_{2h}$ symmetry,$^{[457]}$ (c)B3P86/6–311G(2d,p),$^{[453]}$ (d)LNDO/S–PERTCI $D_{2h}$ symmetry,$^{[244]}$ (e)MOs contributing most to the excitation: H = HOMO, L = LUMO, †forbidden.

<table>
<thead>
<tr>
<th>$\Delta E$ (eV)</th>
<th>$\Delta E$ lg($\varepsilon$)</th>
<th>$\Delta E$ MS–CASPT2(b)</th>
<th>$\Delta E$ TD–DFT(c)</th>
<th>$\Delta E$ LNDO/S(d)</th>
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<td>state config(e)</td>
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<td></td>
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<td>2.58 0.000 $\pi^*$$\rightarrow$H</td>
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</tr>
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<tr>
<td></td>
<td></td>
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<td>L$\rightarrow$H</td>
<td>3.27 0.300 $\pi^*$$\rightarrow$H</td>
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<td></td>
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<td>L$\rightarrow$H</td>
<td>3.58 0.300 $\pi^*$$\rightarrow$H</td>
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<td>H$\rightarrow$H-2</td>
<td>3.76 0.191 H$\rightarrow$H-2</td>
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Figure 7.4.: Structure formulas of the TTF derivatives whose fluorescence was studied by Schweig and co–workers.

Figure 7.5.: Absorption, fluorescence emission (dashed, $\lambda_{\text{exc}} = 439\,\text{nm}$) and excitation ($\lambda_{\text{emi}} = 725\,\text{nm}$) spectra of TTF$^{+}$ in $\gamma$–irradiated freon glass at 77 K. Adapted from Ref. [244].
The photoelectron spectrum of TTF shows relatively few peaks whose positions are 6.83, 8.69 ($\Delta E = 1.86 \text{ eV} = 670 \text{ nm}$), 9.76 ($\Delta E = 2.93 \text{ eV} = 425 \text{ nm}$), 10.18 ($\Delta E = 3.35 \text{ eV} = 380 \text{ nm}$), and 10.56 eV ($\Delta E = 3.73 \text{ eV} = 333 \text{ nm}$). Controversy exists about their assignment and at this point it should be only mentioned that the agreement with the absorption spectrum of TTF$^{\bullet\bullet}$ is minor except if one accepts to assign them to non–Koopman’s transitions. The discrepancy reflects probably the importance of the geometrical changes between neutral and oxidised TTF.

Dimerisation. Dimers of TTF$^{\bullet\bullet}$ in solution are only stable below ambient temperature. (TTF$^{\bullet\bullet}$)$_2$ is characterised by a strong absorption band at 730 nm (Figure 7.6) and the lack of EPR signal. Formation of mixed valence dimers, (TTF$_2$)$^{\bullet\bullet}$, has been observed in non–polar solvents or in polar solvents at rather high concentrations. They show a very broad intervalence charge transfer absorption band with a maximum in the NIR spectral region (1700 to 2100 nm, depending on the solvent) extending down to the 580 nm absorption of TTF$^{\bullet\bullet}$.

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6See Ref. [457] for a discussion.
7.1.2. Results for Tetrathiafulvalene

Since no excited-state lifetime of TTF\(^0\) seems to be reported in literature, attempts to measure it with TA after 266 nm excitation in MeCN solution were undertaken but failed due to ionisation of the sample. No signal was obtained upon 400 nm excitation. Also, attempts to observe emission at r.t. or liquid nitrogen temperature in EtOH:MeOH = 1:1 glasses were without success.

TTF\(^{•+}\) was generated electrochemically in MeCN/\(\text{Bu}_4\text{NPF}_6\) solution. The SS spectrum shown in Figure 7.7 resembles the literature spectra with maxima of the VIS absorption at 580 and 435 nm. The lowest–energy transition of the dication was located at 355 nm. Note that all the bands present in the absorption spectrum could be ascribed to the monomeric TTF\(^{•+}\) — no dimerisation was evident from the absorption spectrum. Furthermore it is noteworthy that the bands of TTF\(^0\) recorded in MeCN are at identical spectral positions as in cyclohexane or hexane solution.\([448]\)

The excited-state dynamics of TTF\(^{•+}\) was studied after 580 nm, i.e. D\(_1\)←D\(_0\), excitation. The TA spectra (Figure 7.8) were comprised of the two dominating absorption bands in form of a bleach signal and two distinct ESA bands: the first one was present at the earliest time delays and covered all the VIS region. It was clearly observed as positive signal above ca. 600 nm and below 380 nm and indicated by the discrepancy between TA and steady–state signal in the spectral region where a bleach signal was to be expected. The second ESA around 450 nm rose with time and decayed while shifting to the blue. Such a shift was also present around 610 nm.
Figure 7.8.: TA spectra and the scaled SS absorption spectrum of TTF$^{*+}$ after 580 nm excitation and SADS from the target analysis.
The evolution of the TA spectra could be reproduced with a triple-exponential function. The DADS related with the fastest component shows a major decay of the 600–800 nm ESA and a rise of the signal around 500 nm while the bleach signal at 430 nm remains practically unchanged. With \( \tau_{a2} \), the ESA band in the 450–550 nm region develops while the 430 nm bleach band decays partially. The SADS associated with \( \tau_{a3} \) has typical features of a hot ground state in agreement with the blue shift of the TA band mentioned before.

7.2. Thianthrene

Thianthrene (TH) is an electron rich heterocycle having 16 \( \pi \) electrons, hence no Kekulé aromaticity. The stable radical cation TH\(^{\bullet+} \) is a common oxidising agent in organic synthesis.\(^{[331]} \) The oxidation potential (\( E_1 = 1.25 \) V vs. SCE in MeCN/\( \text{Bu}_4\text{NPF}_6 \)) varies a bit with the solvent.\(^{[467]} \) The second oxidation wave at \( E_2 = 1.7 \) V is irreversible.\(^{[468]} \)

Crystal structures of TH\(^0 \) show that the molecule is bent around an axis connecting the two sulfur atoms while the benzene rings are planar (see Figure 7.9). The dihedral angle between the benzene rings was determined to be 128°.\(^{[468,469]} \)

In benzene solution, the dipole moment was determined to be \( \mu = 1.4 \) D.\(^{[470–472]} \) From this value it follows that the dihedral angle is bigger in solution (142°) than in crystals.\(^{[470]} \) The molecule is floppy and the inversion barrier is 4–7 kcal/mol,\(^{[469,470,473]} \) what is small but substantially bigger than for TTF or phenothiazine.\(^{[472]} \) From dipole relaxation studies, a time constant of \( \approx 50 \) ps was associated with the butterfly motion, although it could not be unequivocally separated from reorientational motion.\(^{[472,474]} \)

TH\(^0 \) absorbs in the UV spectral region (see Figure 7.11) with the maximum at 255 nm and a shoulder at 293 nm (34.0 kK = 4.2 eV). The apparent Stokes shift is huge, \( \Delta \tilde{\nu} = 11300 \) cm\(^{-1} \) since the maximum of fluorescence emission appears at 430 nm (23.3 kK = 2.9 eV). Quantum chemical calculations at the PM3 level of theory located several electronic transitions with low oscillator strength below the longest wavelength visible absorption band.\(^{[468]} \) The lowest energy absorption band is calculated at 24.5 kK (3.0 eV = 410 nm) in good agreement with the onset of the fluorescence. These calculations associate a strong contribution of the sulfur \( \sigma \)-orbitals to the electronic transitions.
Almost the entire $S_1$ state population decays to the triplet state, $\Phi_{\text{ISC}} = 0.94$, fluorescence is weak, $\Phi_{\text{flr}} = 0.04$. The phosphorescence peaks at 480 nm with a lifetime of $\tau_{\text{phos}} = 40 \text{ ms}$ in EPA. The fluorescence lifetime was determined to be 4.7 ns.

7.2.1. Antecedents of thianthrene radical cation

According to Nishinaga and Komatsu, TH$^{•+}$ is one of the first radicals described in literature, namely in 1869 when it was obtained in $\text{H}_2\text{SO}_4$. Its solutions are purple, owing to VIS absorption bands which are absent in the neutral and dication. The absorption spectrum in 2–BuCl at liquid nitrogen temperature (Figure 7.10) shows the lowest energy transition at 1070 nm (9.4 kK = 1.1 eV) and an intense band at 554 nm (540 nm in MeCN, 546 nm in $\text{H}_2\text{SO}_4$, $\varepsilon = 8500 \text{ L mol}^{-1} \text{ cm}^{-1}$). Further bands are observed at 920 and 810 nm (Figure 7.10).

The $D_1 \leftrightarrow D_0$ transition was characterised as a HOMO$\rightarrow$HOMO-1 transition by PM3 calculations. The authors ascribed the second electronic transition, calculated at 640 nm to the shoulder observed at 833 nm and the 550 nm absorption band was designated as $D_3 \leftrightarrow D_0$.

The photoelectron spectrum of TH shows in addition to the bands located 1.36, 1.51 and 2.26 eV above the ionisation threshold (IP$_1 = 7.94$ eV) — corresponding to transition energies of 910, 822, and 549 nm, respectively, in astonishingly good agreement with the measured absorption bands — a peak at 8.43 eV ($= \text{IP}_1 + 0.49 \text{ eV} \approx 3.9 \text{ kK}$). That peak of the photoelectron spectrum would correspond to an IR transition at 2550 nm. No such transition was found in the before-mentioned PM3 calculations.

Disagreement exists about whether or not to call the structure of TH$^{•+}$ folded or planar and how important the structural changes upon oxidation are. From the similarities of the IR and resonance Raman frequencies of TH and TH$^{•+}\text{ClO}_4^-$ in KBr pellets and TH$^{•+}$ in MeCN
solution,[480] it was concluded that the molecule is folded in both oxidation states. The CSC ring stretch and CS stretch vibrations change by 20 and 10 cm\(^{-1}\), respectively, much less than the shifts observed in MePTZ (vide infra). The authors note, however, that the CC stretch and CH in–plane frequencies change significantly.[479] A non–planar structure was also deduced from EPR results,[481] and ab initio calculations.[482]

More recent TD–DFT calculations, on the other hand, find that oxidation induces major structural changes and that TH\(^{+}\) is essentially flat.[483,484] The radical cation has been crystallised as AlCl\(_4\),[468] BF\(_4\),[485] and ClO\(_4\) salts.[478] TH-AlCl\(_4\) crystals are almost planar, the dihedral angle is \(\theta = 174^\circ\).[468]

Although sulfur compounds are known to form 2–centre–3–electron \(\sigma\) bonds, the dimers of TH\(^{+}\) are presumably \(\pi\) dimers in which the aromatic systems are coplanar.[177,486]

The excited-state lifetime of TH\(^{+}\) has been determined by Vauthey and co–workers using transient grating spectroscopy.[241] In r.t. H\(_2\)SO\(_4\) the excited-state lifetime was found to be 25 ps after D\(_3\leftarrow\)D\(_0\) excitation, independent of deuteration of the sulfuric acid. Almost the same GSR rate constant was recorded in \(i\)-pentane/BuCl at 77 K. The authors reasoned that IC is the main deactivation pathway of TH\(^{+}\).[487]

The fluorescence quenching of electrochemically generated \(^7\)TH\(^{+}\) has been reported by the group of Eriksen.[487] The fluorescence maximum and lifetime are 580 nm and 4.7 ns, respectively,[487] the latter being in clear disagreement with the non–radiative measurements just mentioned. The position of the emission ascribed to TH\(^{+}\) is reasonable considering the maximum of absorption at 550 nm, although in such a case it would be emission from a higher excited state, which is not expected to have a nanosecond lifetime. It is likely that Eriksen and co–workers observed emission from a secondary product of the electrochemical generation, just as it was the case for anthraquinone radical anion generated in the same manner.[230]

### 7.2.2. Results for thianthrene

The steady–state spectra of neutral and cationic TH are compared in Figure 7.11. Note the huge apparent Stokes shift discussed earlier. The band around 360 nm in the irradiated matrix shown in Figure 7.10 is absent in H\(_2\)SO\(_4\) solution.

The TA spectra of TH\(^0\) after 266 nm excitation in MeCN are given in Figure 7.12. The two ESA bands that were present at short pump probe time delays shifted slightly and rose a bit in intensity. On a much longer timescale, an ESA at 480 nm grew in at expense of the former two. The time constants associated with these processes are 6 and 6200 ps, respectively. The long lifetime is in agreement with the fluorescence lifetime reported, the short one reflects either geometrical or vibrational relaxation. The spectral changes are not very pronounced, though comparable with those observed for oligo(phenylethynyl) compounds[488] that are known to undergo structural changes after photoexcitation.[489–491]

The TA spectra of TH\(^{+}\) in H\(_2\)SO\(_4\) after 540 nm excitation (D\(_3\leftarrow\)D\(_0\)) are depicted in Figure 7.13. Directly after excitation, the TA spectra showed weak ESA in the blue and red spectral region in addition to the bleach signal between 480 and ca. 550 nm. While the ESA in the blue part decayed, the other one rose and shifted to the blue, then diminished together with the bleach. No SE is apparent in the spectra, even at the earliest pump–probe time delays.

\(^7\)CH\(_2\)Cl\(_2\) : (CF\(_3\)CO\(_2\))\(_2\)O : CF\(_3\)CO\(_2\)H = 45 : 5 : 1, Bu\(_4\)NI supporting electrolyte, potentiostatic generation with \(E = 1.2\) V vs. SCE
Target analysis gave the SADS depicted in the bottom panel of Figure 7.13. From these, the first species was identified with an electronic excited state, the second with a hot ground state. The lifetime of 1.5 ps reflects thus the excited state decay populating the hot ground state.

In an alternative interpretation, already the first spectra observed in the TA measurement correspond to a hot ground state, i.e. that IC to the D₀ state happens within the IRF, either by intermediacy of D₁ or directly D₂→D₀. The ESA band around 600 nm and the fact that this band shift, rather than decays (in contrast to the clear isosbestic point at 458 nm), speak in favour of this interpretation. On the other hand, the shape of the ESA in the 360-460 nm spectral region but more importantly the presence of the just mentioned isosbestic point are aspects in favour of assigning the SADS A₁ to an electronic excited state.

Electrochemical generation of TH⁺⁺ in MeCN/Bu₄NPF₆ had a poor yield (<25%) and only a rough estimate of the excited state lifetime could be extracted from the TA spectra. This was obtained by integration over the total of the bleach signal and reflects therefore GSR without the possibility of differentiating between electronic and vibrational excited states. The lifetime was on the order of 12 ps.

7.3. N–Methylphenothiazine

Phenothiazine (PTZ) is frequently used as electron donor in studies on intramolecular ET.⁴⁹,⁴⁹²-⁴⁹⁸ Compared to the triphenylamines discussed in chapter 5, it has significantly higher reorganisation energies.⁴⁹² The geometrical changes after one electron oxidation are at the origin of this.
Figure 7.12.: TA spectra of TH$^0$ in MeCN after 266 nm excitation and SADS from the target analysis.
Figure 7.13.: TA spectra of TH$^{*+}$ in H$_2$SO$_4$ after 540 nm excitation and SADS from target analysis. The lack of overlap between bleach and steady-state absorption might be ascribed to superimposed ESA.
Several of its derivatives have tranquillising effects. The ease of oxidation \((E_1 = 0.71 \text{ V vs. SCE in CH}_2\text{Cl}_2)\)\(^{[278,499]}\) might be responsible for the pharmacological activity. The absorption spectrum of MePTZ is similar to that of TH (Figure 7.15). The most eye-catching difference is that the transition at the low energy side of the intense 250 nm band \((\varepsilon = 40 \text{ 000 L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})\)\(^{[278,499]}\) has a clear maximum \((306 \text{ nm}, \varepsilon = 5100 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})\)\(^{[500]}\) whereas it only appears as shoulder in the case of TH. The fluorescence maximum is found at 452 nm, if it is found at all since \(\Phi_{\text{flr}}=0.008\) while \(\Phi_{\text{ISC}}\) is close to unity.\(^{[500,501]}\) Again, the apparent Stokes shift is large, \(\Delta \nu = 10.1 \text{ kK}\) because the emitting state is overlooked owing to its low absorptivity.

Three transitions of \(\pi\)–symmetry polarised along the two in–plane molecular axes were attributed to the longest–wavelength absorption band of \(\text{PTZ}^0\) by calculations in the framework of the Pariser–Parr–Pople model.\(^{[502]}\) The polarisation of the phosphorescence varies indeed within this absorption band.\(^{[502]}\)

### 7.3.1. Antecedents of N–methylphenothiazine radical cation

While neutral MePTZ is strongly bent \((\theta = 144^\circ)\),\(^{[503–505]}\) the radical cation attains an essentially planar structure \((\theta = 172^\circ)\). This was the outcome of EPR,\(^{[505]}\) IR and Raman,\(^{[506,507]}\) and x–ray studies,\(^{[508]}\) and was reproduced by quantum chemical calculations.\(^{[502,507,509]}\) A difference of 128 cm\(^{-1}\) was observed between the CNC skeletal deformation vibration of neutral and cationic MePTZ.\(^{[506]}\) Significant shifts upon radical formation are also present in the CSC skeletal deformation and ring stretch vibrations (60 and 20 cm\(^{-1}\), respectively). The sign of the changes is consistent with a lessening of the fold, i.e. an increase in dihedral angle.\(^{[506]}\)

The absorption spectrum of PTZ\(^*+\) in a low–temperature matrix is shown in Figure 7.14. The absorption spectrum of the N–methyl derivative is essentially the same with the maxima of absorption \((\log \varepsilon)\) at 439 nm (3.55), 474 nm (3.63), 492 nm (3.80), 511 nm (3.96), 760 nm (3.08), and 830 nm (3.06).\(^{[228,278,500,511]}\) As one can see, the absorption spectrum extends down to the NIR region with a high density of states all over the visible region although some might reflect vibrational progression.

The photoelectron spectrum of MePTZ shows peaks at 7.15, 8.23, 9.06, and 9.25 eV and, based on the shape, they were ascribed to ionisations of lone pair orbitals, where the lone pair is situated at the N and S atom for the first and second ionisation, respectively.\(^{[499]}\) There is no agreement between the energy spacing of the photoelectron spectrum (8.7 kK, 15.4 kK, and 16.9 kK) and the electronic absorption spectrum of the radical cation (12.0 kK, 13.5 kK, 14.9 kK, 19.2 kK, 20.0 kK, see Figure 7.14), as expected for a molecule that undergoes major structural rearrangements upon oxidation.

Taking nevertheless the \(D_1–D_2\) energy gap of 6.7 kK from the photoelectron spectrum, the most likely origin of the absorption of MePTZ\(^*+\) at 760 nm is a vibrational progression of the 830 nm transition with a vibrational spacing of 1100 cm\(^{-1}\), and not a distinct electronic transition which would then be located at 530 nm, reasonably close the absorption band at 511 nm.

\(^8\)This peak is in my opinion not due to MePTZ\(^*+\) but a side product.\(^{[498,510]}\)
Not at all interested in the fluorescence itself, Shine and Zhao\cite{228} reported the emission of MePTZ\textsuperscript{•+} in their publication on its photochemical reaction with acetylenes. They synthesised MePTZ\textsuperscript{•+} as the perchlorate salt by oxidation with iodine,\cite{512} recorded the room temperature fluorescence spectrum in the MeCN solution and found $\lambda_{\text{flr}}^{\text{max}} = 600$ nm ($E_{00} = 18.0$ kK, Stokes shift $\Delta \tilde{\nu} = 2900$ cm\textsuperscript{-1}) and $\Phi_{\text{flr}} = 3 \cdot 10^{-4}$.

Since the absorption spectrum of MePTZ\textsuperscript{•+} extends to the infrared region, the observed emission would correspond to a transition from a higher excited state. The transition dipole moment of the 511 nm band is quite high and translates to $k_{\text{rad}} \approx 10^8$ s\textsuperscript{-1} (equation 2.8). Assuming that the EGL can be used\cite{9} and taking the band observed at 830 nm as the closest electronic state ($\Delta E = 0.9$ eV), $k_{\text{nr}}$ is calculated to be (8 ps)$^{-1}$ for the state observed at 511 nm in absorption. This yields $\Phi_{\text{flr}} = 8 \cdot 10^{-4}$ for emission from this state.

### 7.3.2. Results for N–methylphenothiazine

The steady–state spectra of MePTZ in both oxidation states are depicted in Figure 7.15. The discrepancy between the absorption and excitation spectra (intensity normalised at 310 nm) stems from the poor correction function of the fluorescence spectrometer in this wavelength region.

The TA spectra of MePTZ\textsuperscript{0} after 266 nm excitation showed, just as those of TH\textsuperscript{0}, minor spectral changes in the first picoseconds. The ESA signal at 380 and 660 nm shifted a bit to the blue and grew in intensity with $\tau_{\text{a1}} = 8.2$ ps. On a nanosecond timescale, $\tau_{\text{a2}} = 1500$ ps, these two bands were replaced by an ESA centred at 460 nm. The latter lifetime and the band position are in accord with the reported fluorescence lifetime\cite{500} of 1.9 ns and triplet–triplet

\footnote{The energy gap of 0.9 eV is at the limit of applicability and the $\alpha$–value for PAHs is taken.}
Figure 7.15.: Absorption, fluorescence excitation and emission spectrum of MePTZ\textsuperscript{0} in MeCN and absorption of MePTZ\textsuperscript{•+} in H\textsubscript{2}SO\textsubscript{4}. The poor agreement between absorption and excitation spectra in the UV is presumably due to the correction function (c.f. page 177).

absorption of MePTZ.\textsuperscript{[50]} Hence, the dynamics observed could be assigned to geometrical or vibrational relaxation of the S\textsubscript{1} state and subsequent ISC to T\textsubscript{1}.

With the S\textsubscript{1} state of MePTZ\textsuperscript{0} at 415 nm (24.1 kK = 3.0 eV) and S\textsubscript{3} at 254 nm (39.4 kK = 4.9 eV) the S\textsubscript{3}←S\textsubscript{1} ESA should show up at 660 nm, exactly were a band is observed. In a centrosymmetric compound the transition S\textsubscript{n}←S\textsubscript{0} is forbidden if both, S\textsubscript{n}←S\textsubscript{0} and S\textsubscript{1}←S\textsubscript{0} are allowed. The fact, that this transition is observed speaks in favour of a non–planar structure. Given furthermore that its shape does not change appreciably with time, geometrical relaxation after photoexcitation of MePTZ\textsuperscript{0} has to be either faster than the IRF, small, or of little importance for the FC factors of this ESA band.

MePTZ\textsuperscript{•+} excited state dynamics were measured in H\textsubscript{2}SO\textsubscript{4} after 510 nm excitation. The spectra are shown in Figure 7.17 together with the amplitude extracted from a mono-exponential fit.\textsuperscript{10} The decay of the ESA band in the blue part of the spectrum clearly follows this lifetime, which means it reflects the excited state decay, not a cooling process of D\textsubscript{0}. It could be in principle hot ground state absorption of the broad steady–state band between 300 and 350 nm but the relative intensity with respect to the bleach signal at 510 nm is much too high, ruling this interpretation out.

\textsuperscript{10}The unusually strong noise on the data prevented a detailed analysis.
Figure 7.16.: TA spectra of MePTZ° in MeCN after 266 nm excitation and SADS from the target analysis.
Figure 7.17.: TA spectra of MePTZ$^{•+}$ in H$_2$SO$_4$ after 510 nm excitation and SADS from the target analysis.
7.4. Discussion

The radical cations of the three compounds discussed in this section have vastly different D$_1$ state energies, 2.1 eV for TTF\(^{•+}\) (1.7 eV in emission),\(^{[244,457]}\) 1.5 eV for MePTZ\(^{•+}\), and 0.5 eV for TH\(^{•+}\). Nonetheless the lifetimes associated with their D$_1$ state are in the picosecond range for all of them.

The neutral parent compounds TH\(^0\) and MePTZ\(^0\) show minor spectral changes in the first picoseconds after photoexcitation. From the data collected, it can not be deduced, whether or not the structure changes in the excited state. The time constants $\tau_{a1}$ extracted from the TA spectra of TH is substantially larger than that estimated for its butterfly motion (50 ps) but similar to $\tau_{a1}$ of MePTZ which is expected to be rather flat and have a much smaller inversion barrier. It is therefore likely that $\tau_{a1}$ is dominated by other processes than the butterfly vibration. Also, the good agreement between the photoelectron and the ion’s absorption spectrum do not speak in favour of major structural changes, at least none that affect the FC factors.

ISC in TH\(^0\) and MePTZ\(^0\) is not ultrafast,\(^{11}\) but owing to the low radiative rate constant of S$_1$, $\Phi_{ISC}$ approaches unity. In TTF\(^0\) ISC might be ultrafast and explain the absence of fluorescence, but the lack of phosphorescence emission in rigid glasses is puzzling and leaves the question about the nature of the lowest lying absorption band unanswered.

**Tetrathiafulvalene radical cation.** The radiative rate constant of TTF\(^{•+}\) determined from the absorption spectrum\(^{12}\) and eq. 2.6 amounts to $k_{rad} \approx (33\,\text{ns})^{-1}$, the non–radiative with $\Delta E=2.14\,\text{eV}$ (the absorption maximum) and eq. 2.26, $k_{nr} = (3\,\text{ns})^{-1}$. A fluorescence quantum yield around 0.05 results from these values. Taking the fluorescence maximum reported by Zimmer et al.\(^{[244]}\) as the D$_0$–D$_1$ energy gap (1.7 eV), the estimated fluorescence quantum yield drops to 0.01. Such a high fluorescence quantum yield is in contradiction with the statement that TTF\(^{•+}\) proved to be non–emissive at r.t.\(^{[244,439]}\) and shows thus that EGL is not applicable to TTF\(^{•+}\) or that there is a lower lying excited state that is not found by absorption spectroscopy and quantum chemistry. The band at 1.86 eV in the photoelectron spectrum is lower in energy than the lowest energy absorption, yet, it might be shifted due to structural changes between neutral and cation, and does not necessarily indicate a different electronic state.

The measured excited-state lifetime of 0.8 ps and the radiative rate constant of $(33\,\text{ns})^{-1}$, give $\Phi_{flr} \approx 2 \cdot 10^{-5}$. This seems a better estimate than the value based on the non–radiative rate constant calculated with the EGL. Fluorescence emission with such a low quantum yield can in principle be detected using a good spectrometer though this is at the detection limit and no r.t. fluorescence was, in fact, observed by Schweig’s group from liquid solution.

Admittedly, good agreement between the measured lifetime and the estimate from EGL was found for DMDP–TTF\(^{•+}\) in solid solution where the measured D$_1$ lifetime amounted to 1 ns.\(^{[244]}\) This contrasts the apparent “failure” of EGL for TTF\(^{•+}\) at r.t.

The optical density of the ESA of TTF\(^{•+}\) is rather strong and has essentially the same molar absorptivity as the D$_1$←D$_0$ transition — though broad and without distinct features.

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\(^{11}\)Contrary to thioxanthon where $\tau_{ISC} = 125\,\text{ps}$ in MeCN and 5 ps in cyclohexane solution.\(^{[513]}\)

\(^{12}\)Due to partial overlap with the D$_2$←D$_0$ absorption, the value is only an approximation
It should be stressed that there is no SE in the wavelength range of the reported fluorescence, i.e. between 600 and 800 nm with a maximum at 700 nm (see Figure 7.5), nor does the shape of the ESA hint on a superimposed SE. It might be, that structural changes happening within the IRF lead to a state with a low oscillator strength for the D\(D_0\)–D\(D_1\) transition. This would extend the scheme proposed before to a 4 level scheme with a relaxed, non–emissive D\(D_1\) state and the vibrationally excited D\(D_0\) state apart from the D\(D_0\) and the Franck–Condon D\(D_1\) state. In such a case, the fluorescence lifetime would be even shorter than 0.8 ps and the quantum yield even lower than 2 \(\cdot 10^{-5}\), explaining why Schweig and co–workers could not observe emission of r.t. samples. The geometrical relaxation responsible for the decay of the Franck–Condon D\(D_1\) state (either to a dark excited or the ground state) might be inhibited in the low temperature matrix, therefore emission was observed in such cases.\[244\] Alternatively, the lack of emission at ambient temperature might be due to an activated process, e.g. vibronic coupling and not a matrix effect. The proof or rejection of the involvement of a dark excited state has to await FU measurements.

**Thianthrene radical cation.** The excited state lifetime of TH\(+\) is \(\leq 1.5\) ps in H\(\text{}_2\text{SO}_4\) which is much shorter than the decay measured for other radical cations in this solvent: Pe\(+\) and MePTZ\(+\) have D\(D_1\) lifetimes of tens of picoseconds H\(\text{}_2\text{SO}_4\) and for the former this is longer when compared to MeCN solution.

The GSR of TH\(+\) in MeCN was determined to be \(\approx 12\) ps, but this reflects presumably rather vibrational relaxation since the time constant compares favourably with the VER time constant of DMTPD\(+\) or MB\(+\) in MeCN. It is, on the other hand, shorter than that measured with the more rigid Pe\(+\), MePe\(+\), Pe\(+\)\(^{-}\), or Te\(+\) in MeCN.

The discrepancy with the lifetime reported in literature (25 ps in H\(\text{}_2\text{SO}_4\) at r.t.)\[241\] can be attributed to the insufficient time resolution of the set–up used at that time. Another problem was the single wavelength detection that cannot distinguish between the different stages of relaxation. A slow down of the GSR to 33 ps, as observed by Brodard et al.\[241\] in \(i\)–pentane/BuCl glass, might be due to a change of VER rather than of IC.

The absence of SE and of long lived excited states, contradict the results of Eriksen et al.\[487\] who reported emission of TH\(+\) with a fluorescence lifetime of several nanoseconds, but in accord with Brodard et al. who did not detect emission of TH\(+\) in orthoboric acid.\[241\]

**N–Methylphenothiazine radical cation.** Despite the similarity of TH and MePTZ in both oxidation states — structurally as well as in what concerns the electronic spectra (absorption and emission in singlet and triplet manifold) —, their excited state dynamics in H\(\text{}_2\text{SO}_4\) differ by one order of magnitude.

Assuming that \(\tau_{a1}\) represent the lifetime of the state of MePTZ\(^{+}\) which absorbs at 510 nm, a fluorescence quantum yield of \(\approx 10^{-3}\) is obtained with \(k_{rad}\) taken as before. This is close to the experimental value by Shine and Zhao who measured \(\Phi_{fl}=3\cdot10^{-4}\) for MeCN solution.\[228\] Yet, looking at the absorption spectrum it is hard to believe that MePTZ\(^{+}\) emits at 600 nm, the wavelength reported by these authors. The absorption of MePTZ\(^{+}\) is non–zero in this wavelength region and the shape suggests rather that several electronic states are responsible for the observed absorption. It seems more likely that the state populated by the pump laser
decays within the IRF to D$_1$ and that $\tau_{a1}$ reflects the electronic relaxation of this state. In such a case, no emission could be observed at 600 nm.

Due to the low quality of the spectra a detailed analysis of the decay, entangling IC and VER is not possible, but the presence of ESA at 400 nm even after several picoseconds speaks for assigning $\tau_{a1}$ to IC, not to VER. With this value, the excited state lifetime of MePTZ$^{•+}$ in H$_2$SO$_4$ is close to that of the PAHs, but not to TH$^{•+}$. 
8. Galvinoxyl

Contrary to the radicals presented so far, galvinoxyl (G*) is a neutral radical and was chosen to study the influence of charge on the excited-state dynamics. It has a high density of states in the visible part of the spectrum down to 1.4 eV. This is, however, not the D_1 state which is observed at 0.7 eV in the photoelectron spectrum. Given this reasonably large D_2–D_1 energy gap and the not too small oscillator strength of the D_2→D_0 transition, it might be possible to detected fluorescence with the equipment available in our laboratory. The structure of the molecule shown in Figure 8.1 suggests that a twist of the two phenyl groups with respect to each other happen in the excited state and lead to non–radiative deactivation.

G* serves as EPR standard and as radical scavenger/antioxidant and has therefore biological applications.\(^\text{514–516}\) It makes part of the phenoxy radicals and is structurally similar to the diphenylmethyl radical (Figure 8.1).

A large variety of phenoxy radicals are stable\(^\text{517,518}\) and the 2,4,6–tris(t–butyl)phenoxy radical is reported to be fluorescent in r.t. benzene solution.\(^\text{519}\).\(^1\) The lowest energy transition of 2,4,6–tris(t–butyl)phenoxy radical at 1120 nm (8.9 kK, 1 eV) is of nπ character and optically forbidden (\(\varepsilon \approx 250 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\)).\(^\text{520}\)

The lowest–energy transition of diphenylmethyl radicals is found at 520 nm (19.0 kK = 2.4 eV) with a small molar absorptivity, 370 L·mol\(^{-1}\)·cm\(^{-1}\).\(^\text{212}\) The phenyl groups are twisted out of planarity and a σπ state is admixed to the lowest lying state of ππ type.\(^\text{75}\)

Diphenylmethyl radical shows r.t. fluorescence emission in a variety of solvents.\(^\text{87,213,521,522}\) The fluorescence properties are governed by the lowest lying excited state exclusively\(^2\) which manifests in an energy gap law behaviour when comparing differently substituted diphenylmethyl radicals and a strong influence of deuteration on the fluorescence lifetime.\(^\text{121}\) Contrary to other benzyl type radicals, the fluorescence lifetime of diphenylmethyl radical is almost independent of temperature (290 ns in methyl–cyclohexane at 77 K,\(^\text{212,214}\) 255 ns in hexane at r.t.\(^\text{87,213,521,522}\)). This long lifetime can be explained by the forbidden character of the D_1→D_0 transition. Substitution of the methyl hydrogen by an alkyl chain reduces the fluorescence lifetime to 130 ns and increases the quantum yield from 0.3 to 0.8 since it introduces sterical constraints which make the transition less forbidden and hence lead to an increase in \(k_{\text{rad}}\).\(^\text{212}\)

\(^1\)Although the result is questionable owing to the poor agreement between the absorption, fluorescence emission and excitation spectra and the fact that the emission is observed at shorter wavelengths than the D_1→D_0 absorption.

\(^2\)In contrast to the other benzyl type radicals where D_1 couples strongly with the energetically close lying D_2 state.\(^\text{210}\) The magnitude of this vibronic coupling is influenced by temperature.\(^\text{121}\) The D_1–D_2 energy gap in diphenylmethyl radicals can be diminished by substitution on the phenyl rings and the fluorescence lifetimes of the resulting compounds is shorter as \(k_{\text{rad}}\) increases.\(^\text{87}\)
8. Galvinoxyl

Figure 8.1.: Structure formula of galvinoxyl (left), diphenylmethyl (centre) and 2,4,6–tris(t–butyl)phenoxyl radical (right).

8.1. Antecedents of galvinoxyl

Galvinoxyl (G•) has a $C_2$ rotational symmetry axis in crystals. The observed $C_{ar}-CH-C_{ar}$ bond angle at the methine carbon is 134 degrees, and the angle between the phenyl groups’ plane is 12 degrees. Overall, the molecule does not deviate greatly from planarity. The two C–O bonds have an equal length of 1.27 Å. This geometry implies delocalisation of the unpaired electron throughout the conjugated system. The same conclusion was drawn from IR data and TD–DFT calculations. The absorption spectrum of G• is rich in features (see Figure 8.4). The lowest energy transition is located at 860 nm (11.7 kK = 1.4 eV) and has a molar absorptivity of only 3300 L·mol$^{-1}$·cm$^{-1}$. This transition has $\pi\pi^*$ character, in contrast to the lowest energy transition in phenoxyl radicals mentioned earlier. It is the dipole forbidden combination of the HOMO→HOMO-1 and LUMO→HOMO transitions — the dipole allowed combination is the one at 428 nm with $\varepsilon \approx 200 000$ L·mol$^{-1}$·cm$^{-1}$ (Table 8.1). The molar absorptivity of the latter transition is strongly influenced by substitution at the methine carbon atom.

The second excited state is very close in energy to the first one, only 1350 cm$^{-1}$ (0.2 eV) above it. Quantum chemical calculations associate it with a $n\pi$ transition and locate the $n$ orbitals involved at the oxygen atoms (Figure 8.2). Another $n\pi$ type excitation is calculated at 2.44 eV (510 nm) where the absorption spectrum shows a weak, broad band ranging from ca. 450 to 600 nm (Figure 8.4).

The photoelectron spectrum of galvinoxyl radical [sic] shows a high density of states (Figure 8.3), especially above 10 eV. The first ionisation potential at 7.5 eV is substantially lower than that of simpler phenoxyl radicals as a result of the delocalisation of the unpaired electron. The next ionisation potentials are 0.7 and 1.2 eV above IP$_1$. The authors interpret the first peak as ionisation of the HOMO (orbital 4$a_2$ in Figure 8.2) and the succeeding peaks as ionisation of the oxygen $n$ orbitals (14$b_1$ and 15$a_1$ in Figure 8.2) on basis of DFT calculations. The energy gap between HOMO and these orbitals should therefore be unusually small, 0.7 eV. This is in sharp contradiction with the calculations by Degtyarev et al. mentioned earlier in the context of the electronic transitions. From the photoelectron spectrum, one could expect emission only below 0.7 eV (1800 nm).

The fluorescence of diphenylmethyl radical is quenched by galvinoxyl at a rate constant of $8 \cdot 10^9$ L·mol$^{-1}$·s$^{-1}$ in benzene solution. The quenching mechanism remained unclear since all of electron transfer, Förster–type energy transfer, and Dexter–type energy transfer are feasible. No fluorescence of G• was detected, nor was the presence of ions evidenced. The authors estimated that at least the first two mechanisms are operative.
Figure 8.2.: Molecular orbitals of G*: Relative energies\(^{[527]}\) and isoelectronic density representation.\(^{[528]}\)

Table 8.1.: Calculated\(^{[527]}\) and experimental electronic transitions in G*. Calculated transition energy \(E\), oscillator strength \(f\), character of the transition and MOs involved (c.f. Figure 8.2) with configuration interaction coefficient \(c_{\text{CI}}\), experimental transition energy \(E_{\text{exp}}\) (wavelength / nm in parentheses) and molar absorptivity \(\varepsilon\).

<table>
<thead>
<tr>
<th>(E) / eV</th>
<th>(f)</th>
<th>(S)</th>
<th>(c_{\text{CI}})</th>
<th>(E_{\text{exp}}) / eV</th>
<th>(\varepsilon) / L·mol(^{-1})·cm(^{-1})</th>
</tr>
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<tbody>
<tr>
<td>1.38</td>
<td>(4.0 \cdot 10^{-4})</td>
<td>(\pi\pi^*)</td>
<td>(4a_2 \leftarrow 4b_2)</td>
<td>0.703</td>
<td>1.45 (860)</td>
</tr>
<tr>
<td>2.24</td>
<td>(1.9 \cdot 10^{-7})</td>
<td>(n\pi)</td>
<td>(4a_2 \leftarrow 14b_1)</td>
<td>0.916</td>
<td>1.62 (770)</td>
</tr>
<tr>
<td>2.44</td>
<td>0.00</td>
<td>(n\pi)</td>
<td>(4a_2 \leftarrow 15a_1)</td>
<td>0.892</td>
<td>—</td>
</tr>
<tr>
<td>3.25</td>
<td>0.51</td>
<td>(\pi\pi^*)</td>
<td>(4a_2 \leftarrow 4b_2)</td>
<td>0.709</td>
<td>2.92 (425)</td>
</tr>
<tr>
<td>3.57</td>
<td>(1.9 \cdot 10^{-4})</td>
<td>(\pi\pi^*)</td>
<td>(4a_2 \leftarrow 3a_2)</td>
<td>0.811</td>
<td>3.08 (403)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(5a_3 \leftarrow 4a_2)</td>
<td>0.566</td>
<td></td>
</tr>
</tbody>
</table>
The half-wave potentials for oxidation and reduction of G\textsuperscript{•} are at 0.07 and -2.2 V vs. SCE,\textsuperscript{3} respectively.\textsuperscript{[531]} The disproportionation constant \( K_{\text{dis}} \) calculated from these standard redox potentials using equation 3.1 amounts to \( K_{\text{dis}} = 10^{-38} \), indicating the stability of this radical.

The disproportionation of G\textsuperscript{•} is enhanced by UV light, though. Irradiation with 270–380 nm light was shown to increase the sample’s absorbance at 580 and 560 nm — bands that were ascribed to the anion (\( \varepsilon_{580} = 120 \text{,}000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \)) and cation (\( \varepsilon_{560} = 53 \text{,}000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \)) both in EtOH), respectively.\textsuperscript{[530,532]} These two closed shell products are fluorescent with \( \lambda_{\text{flr}} = 600 \) and 570 nm, respectively.\textsuperscript{[530]} The cation G\textsuperscript{+} is instable and gets quickly reduced to yield the corresponding phenol, GH.\textsuperscript{[530]} The phenol absorbs at 399 nm with a much lower molar absorptivity, \( \varepsilon = 3300 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \).

The photochemistry of G\textsuperscript{•} was also studied by Kuzmin et al.\textsuperscript{[533]} After UV excitation (260–380 nm) in hexane or propanol solution, a transient species with absorption at 560 nm and a lifetime of roughly 10 \( \mu \)s was observed and ascribed to the excited state of G\textsuperscript{•}. The authors observed permanent photobleaching due to formation of phenols (via hydrogen abstraction from the solvent) that was suppressed in the presence of oxygen.\textsuperscript{[533]}

At the photon fluxes used in the last two studies, visible light (\( \lambda > 400 \text{ nm} \)) did not cause photochemical reactions.\textsuperscript{[530,533]}

### 8.2. Results for galvinoxyl

Galvinoxyl (G\textsuperscript{•}) was studied in a variety of solvents, namely MeCN, CH\textsubscript{2}Cl\textsubscript{2}, cyclohexane, toluene, MeOH, and EtOH and in a PMMA film. In water and glycerol it was not soluble. All solutions except for MeCN were pale yellow. MeCN solutions had an intense violet colour that stems from an additional absorption band centred at 580 nm which was ascribed to the

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\( ^3 \)MeCN solution, 0.1 mol\cdot L\textsuperscript{-1} Bu\textsubscript{4}NClO\textsubscript{4}
galvinoxylat anion $G^-$ owing to its spectral position and shape.\textsuperscript{530} The same spectrum is obtained in basic EtOH solution (Figure 8.4).

The most likely explanation for this behaviour is a disproportionation reaction whose equilibrium is (unexpectedly) shifted towards the ionic forms in MeCN and (as expected) in basic EtOH. The cation is subsequently transformed to the phenol\textsuperscript{530} whose absorption band is weak and overlaps with that of $G^*$, therefore it could not be identified unequivocally in the spectra. Oxygen did not have an important influence on the absorbance at 580 nm.

The absorption spectra in other solvents agreed with literature data. No absorption band of $G^*$ could be found between 900 and 3000 nm (not shown) although the presence of an electronic state at 0.7 eV (1800 nm)\textsuperscript{528} is evident in the photoelectron spectrum. As mentioned earlier, there is a high density of states with low molar absorptivity between ca. 600 nm and the intense absorption band at 428 nm. Position and shape of the latter band are sensitive to the solvent, unlike the 860 nm transition. The 428 nm band broadens with increasing solvent polarity and especially proticity. In toluene and CH$_2$Cl$_2$ the band appears red-shifted by 300 cm$^{-1}$. In the least polar solvent used, cyclohexane, on the other hand, it is situated at the same wavelength as in the polar MeCN. Excluding cyclohexane, the band position roughly correlates with the solvent refractive index or dielectric constant. Most likely is the measured spectrum a superposition of galvinoxyl in neutral, oxidised, reduced, and/or protonated form, all having different spectra and molar absorptivity. This also manifests in the spectral divergence that can be best seen around 400 nm in the bottom of Figure 8.4.

This indicates that with the pump wavelength used in the time-resolved experiments, $\lambda_{\text{exc}} = 400$ nm, not only $G^*$ but also other species present might be excited.

No steady-state fluorescence signal originating from the D$_2$ state could be detected between 870 and 1100 nm in r.t. solution, in PMMA film or in EtOH:MeOH = 1:1 at 77 K.\textsuperscript{4} Attempts to measure the D$_4$ state lifetime after 400 nm excitation of r.t. samples by FU were not successful due to rapid and complete decomposition of the samples. This decomposition took just some seconds of laser irradiation. The cyclohexane sample showed the best stability but no reliable lifetime could be extracted.

No important sample degradation was observed during the TA measurements upon 400 nm excitation and although it was more pronounced than with other samples, the lifetimes are expected to be accurate to 10%. The TA spectra of $G^*$ in MeCN and MeOH are depicted in Figure 8.5. At early time delays, the spectra showed the bleach signal and a broad ESA that covered the whole spectrum and had a maximum around 600 nm. In most solvents this ESA decayed to zero in less than a picosecond. In MeCN, the decay took place on a slightly longer timescale and in toluene a significant ESA persisted over all the time window exploited.

As the pump–probe time delay increased, a rather narrow ESA around 440 nm rose at extend of the broad ESA present at early time delays. In the end, the bleach signal and the 440 nm ESA decayed on a picosecond timescale. A small fraction of the bleach and a broad, weak ESA signal with a maximum around 580 nm (see the residuals in Figure 8.6) were found in all solvents but MeCN even at very long time delays (2 ns). This is the wavelength at which galvinoxylat, $G^-$, absorbs.

\textsuperscript{4}The low temperature samples showed in fact fluorescence with maxima at 500 and 550 nm but the shape of the excitation spectrum did not coincide with the absorption spectrum of $G^*$. 
Figure 8.4.: Absorption spectra of G\(^\ast\) in different solvents. Note the weak absorbance between 430 and 600 nm (top) and the solvent effect on the prominent 430 nm band (bottom).
Table 8.2.: Lifetimes extracted from TA data of $G^\bullet$ after 400 nm excitation

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\tau_{a1}$ / ps</th>
<th>$\tau_{a2}$ / ps</th>
<th>$\tau_{a3}$ / ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>0.18</td>
<td>1.2</td>
<td>5.1</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.26</td>
<td>1.2</td>
<td>4.1</td>
</tr>
<tr>
<td>EtOH</td>
<td>0.19</td>
<td>1.3</td>
<td>4.6</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>0.46</td>
<td>1.2</td>
<td>6.5</td>
</tr>
<tr>
<td>toluene</td>
<td>0.15</td>
<td>1.3</td>
<td>4.6</td>
</tr>
</tbody>
</table>

A target analysis with 3 successive reactions was able to reproduce the dynamics satisfactorily. The lifetimes are compiled in Table 8.2 and the SADS are shown in Figure 8.2. The SADS corresponding to $\tau_{a1}$ shows the bleach and the broad ESA, the SADS of $\tau_{a2}$ has no more broad ESA (except for MeCN and toluene) but the one at 440 nm. The SADS of $\tau_{a3}$ is similar to that of $\tau_{a2}$ with exception of the position of the ESA signal and the optical density of this ESA and the bleach. The SADS in the bottom panel show the residual TA signal whose decays cannot be observed with our set-up. No SE can be evidenced from any of the spectra or SADS.

8.3. Discussion

No fluorescence of $G^\bullet$ D$_1$ state was observed, even at 77 K or in a PMMA film, indicating that its decay is not governed by a large amplitude motion, identical to the results for Wurster’s salts and DMTPD$^*$$^\dagger$.

The experiment gives no evidence for SE from the bright D$_4$→D$_0$ state, thus of appreciable D$_4$ population 0.3 ps after the excitation pulse. This lack of SE in the TA signal shows that IC from the initially populated D$_4$ state to a lower lying excited state is faster than our IRF and not observed with the TA set-up. On basis of the SADS, $\tau_{a1}$ is associated with the population of the hot electronic ground state since it is associated with the decay of ESA but not with recovery of the bleach signal. The excited state lifetime is thus on the same order of magnitude as the IRF of the TA set-up.

The other time constants, $\tau_{a2}$ and $\tau_{a3}$, are assigned to VER of the hot ground state owing to the spectral features that are interpreted as hot ground state absorption. The SADS of $\tau_{a1}$ in cyclohexane shows already an important contribution of the hot ground state absorption around 440 nm although the lifetime associated with the excited-state decay is considerably longer in this solvent. Presumably the lifetime is in fact shorter but the data treatment, that ignores the early time delays and therefore fits only the tail of the (very fast) decay, is unable to reproduce this component accurately. It is interesting to note that $\tau_{a2}$ and $\tau_{a3}$ do not differ much in cyclohexane from the other solvents, meaning that VER is not affected by faster IC.

The trend that the time constant ascribed to VER, $\tau_{a3}$, is shorter in protic than in aprotic solvents as it has been found for Wurster’s salts, neutral perylene$^{[145]}$ and nitroanilines,$^{[147]}$ is as well observed for $G^\bullet$. Toluene is an exception since $\tau_{a3}$ in this solvent is as short as in EtOH. The spectra in toluene are presumably contaminated by signal from the solvent and maybe galvinoxyl in other oxidation states and this might affect the lifetimes extracted from the TA
Figure 8.5.: TA spectra of $\text{G}^*$ in MeCN (top) and MeOH (bottom) after 400 nm excitation. The lack of bleach signal at 580 nm shows that $\text{G}^-$ does not contribute to the TA signal.
Figure 8.6.: SADS extracted from the target analysis in different solvents. The amplitudes are scaled to the initial intensity of the bleach signal.
data. This is also congruent with the fact that the TA spectra in toluene have a different aspect (Figure 8.6).

Another similarity with Wurster’s salts is that $\tau_{a2}$ is solvent independent and not even affected by solvent proticity. This suggests an intramolecular process, like IVR or conformational changes. For $G^\cdot \tau_{a2}$ is considerably longer and amounts on average to 1.2 ps compared to 0.3 ps for $WB^\cdot \tau$. This rather high value casts doubts on assigning it to IVR, which is expected to happen on a shorter time scale in large molecules. Conformational changes are restricted to small amplitude motions since a more pronounced influence of the solvent is expected otherwise and since the measurements in PMMA films do not hint on the participation of important twists in the non–radiative decay. The real nature of the process underlying $\tau_{a2}$ cannot be deduced from the TA data.

It is surprising to find photobleaching for $G^\cdot$ despite the short excited-state lifetime. The fact that degradation was very fast and quantitative in the FU (that runs at 82 MHz repetition rate) but much slower in the TA set–up (that runs at 1 kHz repetition rate) suggests that the decomposition involves a photoproduct which degrades when being (re–)excited. This assumption is also in accord with the residual TA signal at long pump–probe time delays. As mentioned earlier the long lived signal absorbs at the same wavelength as galvinoxylat, $G^-$. Hence, the photoexcited neutral radical captures an electron from the solvent. Such a process has been studied, among others, by Shkrob et al. and termed “hole injection”. The efficiency of hole injection was found to be proportional to the liquid ionisation potential (IP$_{\text{liq}}$) of the solvent and this is also observed here for $G^\cdot$: the ESA at 580 nm is highest in the alcohols and cyclohexane, solvents of rather low IP$_{\text{liq}}$, and absent in MeCN or H$_2$SO$_4$, both of which are high IP$_{\text{liq}}$ solvents.

It should be mentioned, however, that the shape of the residual signal is not identical with the SS absorption of $G^-$ and that the ratio of ESA to bleach does not reflect the molar absorptivity of $G^\cdot$ and $G^-$ (both around 200 000 L·mol$^{-1}$·cm$^{-1}$). It is reasonable to assume contributions from other species to the long term TA signal since the pump laser wavelength is suitable to excite also other compounds. At the same time, the similarity of the bleach signal with the steady–state absorption spectrum ensures that the main features observed in TA can be attributed to the radical.

Toluene is somewhat special. It is a low IP$_{\text{liq}}$ solvent, and the early TA spectra suggest the presence of $G^-$ which persist over the entire temporal observation window. Most of the broad and rather intense ESA, however, should be ascribed to other products, contribution of the solvent, or maybe solvent–galvinoxyl adducts.

Kuzmin et al. observed presumably $G^-$, not the excited state of $G^\cdot$ in their flash photolysis experiments. This interpretation bases on the facts that the observed species absorbs rather close to the absorption maximum of $G^-$, that the intermediated was only observed in deoxygenated samples, and that the lifetime recorded, 10$\mu$s, is far too long for a $\pi\pi^*$ excited state at 0.7 eV.

\textsuperscript{5}At least to reach a non–radiative state.
9. Conclusions

In this chapter, conclusions about the excited state dynamics of radical ions shall be drawn by comparison of the different systems presented in detail above. The influence of excitation wavelength or of the environment on the excited state dynamics will be discussed. Table 9.1 compiles the lifetimes associated with the excited-state decay together with those calculated based of the energy gap law (EGL) using Siebrand’s parameters and the \( D_1 \) state energy.\(^\text{[66]} \)

A graphical representation of the dependence of the \( D_1 \) lifetime on the state’s energy is given in Figure 9.1. It will be argued that the EGL is not applicable to the radical ions investigated during this thesis and presumably not to radical ions in general.

9.1. Excited state lifetime

9.1.1. Excitation wavelength dependence

In all systems investigated, the state responsible for the initial TA signal is assigned to the \( D_1 \) state based on the following arguments.

First, in the case of the Wurster’s salts as well as \( \text{MB}^+, \text{Pe}^+, \) and \( \text{TTF}^+ \) the photoprepared state is \( D_1 \). No quartet state is anticipated below \( D_1 \) for the reasons given in chapter 3 and the features of the TA signal do not resemble a vibrationally hot ground state.

Second, the spectral features of the ensuing state (corresponding to the SADS termed \( A_2 \)),\(^1 \) on the other hand, are typical of a vibrationally hot electronic ground state, hence the preceding state has to be an electronic excited state.

Third, even at the shortest time delays accessible, identical TA spectra are obtained when varying the excitation wavelength, i.e. when the photoprepared state is a higher excited state (\( D_2 \) for \( \text{MB}^+ \) and \( D_3 \) for \( \text{Pe}^+ \)).

Fourth, no SE of the photoprepared higher state is present in the TA spectra of \( \text{DMTPD}^+ \), \( \text{Pe}^+, \text{Pe}^-, \text{TH}^+, \) or \( \text{G}^+ \). A \( D_2 \) state lifetime of \(<50 \text{ fs} \) is found by fluorescence up-conversion experiments for \( \text{DMTPD}^+ \), in accord with this. Tentative fluorescence measurements for \( \text{G}^+ \) also showed a very short lifetime for the photoprepared \( D_{n>5} \) state.

Finally, the density of states between the photoprepared \( D_n \) and the \( D_1 \) state is very high in the case of \( \text{Pe}^-, \text{Te}^+ \) and \( \text{MePTZ}^+ \) and efficient \( D_n \rightarrow D_1 \) is anticipated unless there is an extremely efficient decay pathway that circumvents \( D_1 \), i.e. \( D_m \rightarrow D_0 \) IC (where \( n \geq m > 1 \)) competes successfully with \( D_n \rightarrow D_1 \) IC. If the latter was operative, the initial TA spectra would show participation of the hot \( D_0 \) state and/or an excitation wavelength effect on the GSR rate should have been observed — depending on the ratio of the rate constants of these two IC channels. None of this is evident from the TA spectra. In fact, no effect of excitation wavelength on the excited-state lifetime is observed for \( \text{WB}^+ \) (excess vibrational energy), \( \text{Pe}^+ \) (excitation

\(^1 \)\( A_3 \) in the case of \( \text{MB}^+ \).
9. Conclusions

to D₁ or to D₅), and MB⁺⁺ (excitation to D₁ or to D₁ and D₂), in agreement with fast IC to D₁ which is therefore assumed to be by far the most efficient relaxation of higher electronic states. More reliable, quantitative conclusions could be drawn from excitation wavelength dependent fluorescence quantum yield studies that have not been performed.

As a matter of fact, an appreciable D₂–D₁ energy gap is present in DMTPD⁺⁺ (0.7 eV), TH⁺⁺ (0.9 eV), and G⁺ (0.5 eV) all of which have been excited to a higher excited state in the TA measurements. Since the D₂ state lifetime of DMTPD⁺⁺ determined by fluorescence upconversion does not coincide with the GSR rate, it is concluded that the ESA in the early TA spectra stem from D₁ while D₂ is too short lived to be apparent in the TA spectra. For the other two radicals, there is no direct evidence for the involvement of D₁. At this point, the difference in their early ESA shall be pointed out: While TH⁺⁺ shows ESA only in vicinity of the 540 nm D₂←D₀ absorption, both, DMTPD⁺⁺ and G⁺, have an ESA all over the spectral observation window (Figures 7.13, 5.14 and 8.5). Therefore, one can be quite confident ascribing the origin of the ESA in the latter two to an electronic excited state while the electronic ground state of thianthrene radical cation might be populated within the IRF, as discussed in section 7.2.2. Hence, the τD₁ value in Table 9.1 might reflect VER, not IC.

Thus, for all molecules (with the possible exception of TH⁺⁺), IC to the lowest lying excited state happens in ≪200 fs. This is in agreement with most data available in the literature.[158,185] Notable exemptions from this are di- and trimethoxybenzene radical cations[199,231] (D₂ − D₁ ≥ 1.2 eV) and tetraquinone radical anion[241] (D₂ − D₁ = 1.3 eV) which show D₂ fluorescence.[199,231,241]

9.1.2. Influence of the environment

The effects of counter-ions on electronic transitions of open-shell charged chromophores are well documented.[195,540–543] Absorption bands of radical ions are known to shift with nature and degree of association with the counter-ion.[195,542,544] The presence of ion pairs in low polarity r.t. solvents was evidenced by absorption and EPR spectroscopy.[195,540,544]

Fluorescence emission of cyclooctatetraene radical anion in 2–methyltetrahydrofuran matrix is only observed when it is paired with potassium, rubidium and cesium, but not for the sodium ion pair or the free radical anion.[542] Several factors have been suggested to account for this behaviour: i) decreased rigidity or non-planarity of some of the ion pairs contrary to others, ii) the relative position of the 4E₃g quartet and the lowest doublet state, and iii) differences in the ability to undergo a charge-transfer from COT•− to the metal in some of the ion pairs.[542]

By contrast, the nature of the counter-ion did not show an influence on the r.t. spectra and dynamics of WB⁺⁺ and Pe⁺⁺ in MeCN solution. In the case of WR⁺⁺, the counter-ion might account for the blue-shift of the electronic transitions observed upon cooling of an EtOH:MeOH solution.

For all radical ions studied here, the solvatochromic shift of the absorption band is small, at most 500 cm⁻¹.

No influence of the nature of the solvent on the dynamics of the electronic relaxation is found for Wurster’s salts. Yet, a slowing down by a factor of 2–3 when going from MeCN to CH₂Cl₂ is observed for the other amine radical cations and for Pe⁺⁺. No clear trend can be extracted for G⁺, presumably due to an insufficient time resolution.
9. Conclusions

Table 9.1: Selected measured and calculated† (eq. 2.26 with $\alpha = 4.87$-eV$^{-1}$, $k_{00} = 10^{13}$) excited-state lifetimes and excited state energies. $\Delta E_{12} = E_{D2} - E_{D1}$, (a) experimental from electronic absorption, (b) experimental from photoelectron spectrum, (c) calculated gas phase values, (d) for (Ph)$_3$N from Ref. [537] and [323], (e) might reflect VER, not IC.

<table>
<thead>
<tr>
<th>solute</th>
<th>solvent</th>
<th>$E_{D1}^{(a)}$ / eV</th>
<th>$E_{D1}^{(b)}$ / eV</th>
<th>$E_{D1}^{(c)}$ / eV</th>
<th>$\Delta E_{12}^{(a)}$ / eV</th>
<th>$\Delta E_{12}^{(b)}$ / eV</th>
<th>$\Delta E_{12}^{(c)}$ / eV</th>
<th>$\tau_{D1}$ / ps</th>
<th>$\tau_{EGL}$ / ps</th>
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<tbody>
<tr>
<td>WB$^{**}$</td>
<td>MeCN</td>
<td>2.0</td>
<td>1.5$^{[275]}$</td>
<td>2.1$^{[290]}$</td>
<td>1.1</td>
<td>0.4$^{[275]}$</td>
<td>0.7$^{[290]}$</td>
<td>0.2</td>
<td>1600</td>
</tr>
<tr>
<td>d4-WB$^{**}$</td>
<td>MeCN</td>
<td>2.0</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td>1600</td>
</tr>
<tr>
<td>TiPD$^{**}$</td>
<td>MeCN</td>
<td>2.0</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td>1600</td>
</tr>
<tr>
<td>WR$^{**}$</td>
<td>MeCN</td>
<td>2.2</td>
<td>1.6$^{[275]}$</td>
<td>2.4$^{[284]}$</td>
<td>0.9</td>
<td>0.9$^{[275]}$</td>
<td>&lt;0.1$^{[284]}$</td>
<td>&lt;0.2</td>
<td>7000</td>
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<tr>
<td>MB$^{**}$</td>
<td>MeCN</td>
<td>1.7</td>
<td>1.8$^{(d)}$</td>
<td>1.9$^{(d)}$</td>
<td>0.3</td>
<td>0.4$^{(d)}$</td>
<td>0.1$^{(d)}$</td>
<td>1.6</td>
<td>400</td>
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<td>DMTPD$^{**}$</td>
<td>MeCN</td>
<td>0.9</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
<td>8</td>
</tr>
<tr>
<td>Pe$^{*}$</td>
<td>MeCN</td>
<td>1.6</td>
<td>1.6$^{[409]}$</td>
<td>1.6$^{[388]}$</td>
<td>0.15</td>
<td>0.1$^{[409]}$</td>
<td>&lt;0.1$^{[388]}$</td>
<td>5</td>
<td>200</td>
</tr>
<tr>
<td>Po$^{*}$</td>
<td>MeCN</td>
<td>1.0</td>
<td>1.4$^{[388]}$</td>
<td></td>
<td>0.15</td>
<td>0.2$^{[388]}$</td>
<td></td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>Pe$^{*}$</td>
<td>H$_2$SO$_4$</td>
<td>1.6</td>
<td>1.6$^{[409]}$</td>
<td>1.6$^{[388]}$</td>
<td>0.15</td>
<td>0.1$^{[409]}$</td>
<td>&lt;0.1$^{[388]}$</td>
<td>18</td>
<td>200</td>
</tr>
<tr>
<td>Te$^{*}$</td>
<td>H$_2$SO$_4$</td>
<td>1.4</td>
<td>1.4$^{[538]}$</td>
<td>1.6$^{[538]}$</td>
<td>0.2</td>
<td>0.2$^{[538]}$</td>
<td>&lt;0.1</td>
<td>23</td>
<td>90</td>
</tr>
<tr>
<td>TTF$^{**}$</td>
<td>MeCN</td>
<td>2.1</td>
<td>1.9$^{[449]}$</td>
<td>2.2$^{[457]}$</td>
<td>0.4</td>
<td>1.1$^{[449]}$</td>
<td>0.2$^{[457]}$</td>
<td>0.8</td>
<td>2600</td>
</tr>
<tr>
<td>TH$^{**}$</td>
<td>H$_2$SO$_4$</td>
<td>1.1</td>
<td>0.5$^{[471]}$</td>
<td>1.2$^{[468]}$</td>
<td>0.3</td>
<td>0.9$^{[471]}$</td>
<td>0.8$^{[468]}$</td>
<td>1.5$^{(e)}$</td>
<td>20</td>
</tr>
<tr>
<td>MePTZ$^{**}$</td>
<td>H$_2$SO$_4$</td>
<td>1.5</td>
<td>1.1$^{[499]}$</td>
<td></td>
<td>0.9</td>
<td>0.8$^{[499]}$</td>
<td></td>
<td>26</td>
<td>150</td>
</tr>
<tr>
<td>G$^{*}$</td>
<td>MeCN</td>
<td>1.5</td>
<td>0.7$^{[528]}$</td>
<td>0.7$^{[528]}$</td>
<td>0.2</td>
<td>0.5$^{[528]}$</td>
<td>0.4$^{[528]}$</td>
<td>&lt;0.2</td>
<td>150</td>
</tr>
</tbody>
</table>
The largest slow down caused by change of solvent is observed for Pe\textsuperscript{•+} in H\textsubscript{2}SO\textsubscript{4}. The decay of Te\textsuperscript{•+} and MePTZ\textsuperscript{•+} in H\textsubscript{2}SO\textsubscript{4} happens on the same timescale but a comparison with MeCN solution is not possible for these ions because the experiments in MeCN were unsuccessful. Not all the compounds show “slow” IC in H\textsubscript{2}SO\textsubscript{4}, though. TH\textsuperscript{•+} decays in \(\leq 1.5\) ps, at least ten times faster than the others.

Temperature is a crucial factor for the excited-state decay of Wurster’s salts. The D\textsubscript{1} lifetime of 660 ps at liquid nitrogen temperature drops to 0.2 ps at ambient temperature. That this is a purely thermal and not a matrix effect has been proven by variation of the matrix (in all of them the onset of the fluorescence is at the same temperature, \(\approx 120\) K) and the lack of emission in a r.t. PMMA film. Solid samples of G\textsuperscript{*} and DMTPD\textsuperscript{•+} are also non–emissive. However, only fluorescence from a higher excited state of these two open–shell species would have been accessible in the observation window of our fluorescence spectrometer.

9.1.3. Relation with the D\textsubscript{1} state energy

Throughout the preceding chapters and for the \(\tau\text{EGL}\) values given in Table 9.1, it was assumed that the \(k_{00}\) and \(\alpha\) values found for the S\textsubscript{1}→S\textsubscript{0} IC of PAHs\textsuperscript{[54,65]} are reasonable estimates for D\textsubscript{1}→D\textsubscript{0} IC of the molecules investigated in this work. This seems sound in first place since all compounds investigated are medium size aromatic organic molecules and have aromatic CH and CC bonds that are expected to play the role of the dominant acceptor modes for the electronic energy (see chapter 2.1.3). It neglects, however, differences in frequency distortions and displacement. To illustrate this, Siebrand’s \(\alpha\) and \(k_{00}\) parameters cannot explain the slow D\textsubscript{1}→D\textsubscript{0} IC of diphenyl radical (measured lifetime 255 ns,\textsuperscript{[213]} calculated 10 ns) or perylene dicarboxyimide radical anion (PMI\textsuperscript{•−}, measured 530 ps,\textsuperscript{[185]} calculated 50 ps), both of which are polycyclic aromatic molecules.

Less restrained than to rely on Siebrand’s S\textsubscript{1}→S\textsubscript{0} values is a simple relation of \(k_{nr}\) with the D\textsubscript{1} state energy. According to eq. 2.23, a plot of ln(\(k_{nr}\)) versus \(E_{D1}\) is linear if the frequency distortion and PES displacement associated with the IC are similar in all the systems under investigation. Since for all the data present in Table 9.1 the D\textsubscript{1} lifetimes are much shorter than \(1/k_{rad}\), it is possible to approximate \(k_{nr} \approx 1/\tau_{D1}\). Figure 9.1 shows a plot of ln(\(1/\tau_{D1}\)) against the energy of the D\textsubscript{1} state. The grey arrow on the left of Figure 9.1 indicates the width of the IRF, and the measured D\textsubscript{1} lifetimes of G\textsuperscript{*}, WR\textsuperscript{•+} and TiPD\textsuperscript{•+} are most likely limited by the instrument. Figure 9.1 speaks also in favour of assigning the shortest lifetime, \(\tau_{a1}\), of TH\textsuperscript{•+} to VER, not IC, the latter being presumably faster than the IRF.

Figure 9.1 shows first the expected decrease of \(k_{nr}\) with \(E_{D1}\), but at ca. \(E_{D1} = 1.5\) eV, the opposite trend is observed and \(k_{nr}\) increases with increasing D\textsubscript{1} state energy.

Even when only chemically similar compounds are compared, \textit{no} correlation between ln(\(k_{nr}\)) and \(E_{D1}\) is observed: picking, for example, the nitrogen based radical ions (number 1 through 6, c.f. Table 9.1), or the PAHs (number 7 through 10) the same “parabolic” behaviour is obtained. The members of the pairs Pe\textsuperscript{••}/Pe\textsuperscript{•−} or Wurster’s salts/DMTPD\textsuperscript{•+} have the same D\textsubscript{1} lifetime although the energy of their first exited states differs greatly. The energetically intermediate MB\textsuperscript{•+} and Te\textsuperscript{•+} have much longer excited state lifetimes.

The slow down observed for Pe\textsuperscript{•+} upon change of solvent is not accounted for by the EGL unless the energy gap is altered significantly by the solvent or solvent vibrations promote the
IC. The solvatochromic shift of the $D_1 \rightarrow D_0$ transition in the solvents is small and the latter seems unlikely since solvent modes are usually poor acceptor modes.

Another extreme is to compare the radical anion of perylene with those of its dicarboximide (PMI$^{*−}$) and tetracarboxydiimide (PDI$^{*−}$), which all three of which have very similar $D_1$ state energies while the lifetimes differ by two orders of magnitude.

Clearly, the EGL in its formulation of weak coupling is not capable of describing the trend observed. In order to obtain a minimum as in Figure 9.1, the following conditions\(^2\) have to be fulfilled for the derivatives of $\ln(k_{nr})$ with respect to $E_{D1} = \Delta E$.

\[
\frac{d\ln(k_{nr})}{d\Delta E} = \frac{-1}{2\Delta E} - \frac{1 + m_1}{\hbar \omega_M} \ln(\Delta E) = 0 \tag{9.1}
\]

\[
\frac{d^2\ln(k_{nr})}{d^2\Delta E} = \frac{\hbar \omega_M - 2\Delta E}{2\Delta E^2 \hbar \omega_M} < 0 \tag{9.2}
\]

where

\[
m_1 = \ln\left(\frac{2}{(d_M \hbar \omega_M \Delta^2_M)}\right) - 1
\]

The inequality 9.2 is only fulfilled if $\hbar \omega_M > 2\Delta E$, i.e. for unreasonably large vibrational frequencies.

\(^2\)See page 17 for a definition of the symbols.
As outlined in chapter 2.1.3, the EGL is only applicable for i) sufficiently large energy gaps, ii) thermally equilibrated states, iii) harmonic PESs, iv) small nuclear displacement in the course of the transition, and v) weak coupling between the PESs.

The first of these conditions is valid for all radicals except \( \mathbf{G}^\bullet \) and \( \mathbf{TH}^{\bullet+} \). Condition ii) is certainly not fulfilled, and in an approach that goes beyond the one derived in section 2.1.3, non–radiative rate constants for each vibrational level have to be calculated.\(^{[70,545–547]}\) Such a treatment does not lead to substantially different results unless the anharmonic coupling of the excited vibrational modes is large.

For the data presented here, the most likely reason for the “failure” of EGL seem to be the assumptions that the PESs are harmonic and couple only weakly and/or that the nuclear displacement between the PES is minor. The importance of the displacement for the coupling has been pointed out several times.\(^{[70,94,548,549]}\) Strong coupling is necessary for an ultrafast decay, and this is what is observed.

Finally, if the decay of the radical ions was simply governed by the \( \mathrm{D}_1–\mathrm{D}_0 \) energy gap, there is no evident reason why they should behave different from closed–shell NIR emitters at comparable density of states. Numerous closed–shell compounds, however, are emissive at these \( \mathrm{S}_1 \) state energies with lifetimes of hundreds of picoseconds. Examples are the oxazine and carbocyanine dyes or nile blue.\(^{[550]}\)

In light of all this, it is questionable to argue with the small \( \mathrm{D}_1 \) state energy to explain the lack of fluorescence of radical ions. The energy gap is not the determining factor and can not account for the IC rates observed.

9.1.4. Proximity of higher excited states

The importance of higher excited states arises through vibronic coupling that is in presence of higher symmetry elements enhanced by the second order Jahn–Teller effect. For benzenoid radical cations the decay of \( \mathrm{D}_1 \) is governed by the proximity of \( \mathrm{D}_2 \), as described in chapter 3. For di– and trimethoxybenzyl type radical cations it was argued that only those with a sufficiently large separation between the emitting \( \mathrm{D}_2 \) state and the neighbouring states show fluorescence emission.\(^{[231]}\)

In section 2.1.3 examples were given where the opening of an additional decay channel invalidates the EGL. Parabolic EGL plots such as the one in Figure 9.1 have in fact already been observed.\(^{[93,102]}\) Both cases concern a charge separated state whose energy was influenced by the polarity of the solvent. The increase of \( k_{\text{nr}} \) with \( \Delta E \) was ascribed to an additional decay channel whose importance increases when the emissive charge separated state is close to another electronic excited state.\(^{[93,102]}\)

Table 9.1 includes the energy gap between the lowest excited states. Clearly the \( \mathrm{D}_2–\mathrm{D}_1 \) energy gap is uncorrelated with the \( \mathrm{D}_1 \) state lifetime: \( \mathbf{Pe}^{\bullet+} \), which has among the longest lifetimes, has the smallest \( \mathrm{D}_2–\mathrm{D}_1 \) energy gap. Likewise \( \mathbf{G}^\bullet \) has no close lying excited state that might explain its fast decay.\(^{4}\)

\(^3\)Contrary to Figure 9.1, these cases compare thus only one chemical system. Other examples where non–linear EGL plots were obtained (see the References in section 2.1.3) do not cover such a broad range of excited state energies.

\(^4\)Owing to their small \( \mathrm{D}_1–\mathrm{D}_0 \) gaps the EGL is not applicable for \( \mathbf{G}^\bullet \) and \( \mathbf{TH}^{\bullet+} \) and the calculated lifetimes should reflect lower \([\text{sic}]\) limits.
If vibronic coupling is responsible for the non-radiative decay, the thermal energy at ambient temperature suffices for highly efficient coupling and additional vibrational energy has no effect. The observation of fluorescence at low temperatures in Wurster’s salts is not due to reduced vibrational coupling but a small barrier on the D\(_1\) PES.

9.1.5. Fluorescence

Six of the radical ions studied in this work are reportedly fluorescent, four of them even at room temperature: WB\(^{++}\), TTF\(^{++}\), MB\(^{++}\), Pe\(^{++}\), Te\(^{++}\) and TH\(^{++}\). Among these radical ions, WB\(^{++}\) has the shortest D\(_1\) lifetime and after MB\(^{++}\) the second highest molar absorptivity. SE is unequivocally observed in the TA spectra of WB\(^{++}\), d4–WB\(^{++}\) and WR\(^{++}\) only. In the case of MB\(^{++}\) and Pe\(^{++}\), the lack of SE signal might be due experimental problems in the corresponding wavelength region (NIR), although the complete absence is astonishing. The SE of Te\(^{++}\) is out of the spectral window of the probe pulse.

A superimposed ESA can always prevent the observation of SE. In the case of MB\(^{++}\), an ESA band is indeed expected at the respective wavelengths. The value for the fluorescence quantum yield \(\Phi_{flr}\) reported in Ref. [230] hint on the fluorescent state decaying with \(\tau_{a1}\), not with \(\tau_{a2}\) and that \(A_2\) reflects a non-emissive excited state which does not possess a SE band. The experimental uncertainty of \(\Phi_{flr}\) is, however, too big to be sure about this assignment and to exclude emission from \(A_2\).

The quantum yield calculated for TTF\(^{++}\) on basis of \(\tau_{D1} = 0.8\) ps and the radiative rate constant are very low, in agreement with the observation\([244]\) that TTF\(^{++}\) is non-emissive in r.t. solution. It should be mentioned that the simplicity of the spectral dynamics does not quite agree with the enormous Stokes shift found experimentally\([244]\) and theoretically\([457]\) what might mean that such changes are not present or too fast to be resolved with the set-up used.

All Wurster’s salts except for TiPD\(^{++}\) are fluorescent at liquid nitrogen temperature with a quantum yield of \(\Phi_{flr} \approx 0.01\). Due to the increase of the non-radiative rate constant with temperature, they can be considered as non-fluorescent at ambient temperature having \(\Phi_{flr} < 10^{-5}\).

A r.t. fluorescence quantum yield of \(\Phi_{flr} \approx 10^{-5}\) can be estimated for Pe\(^{++}\) from the lifetime \(\tau_{D1} = 5\) ps and the radiative rate constant for the D\(_1\)\(\rightarrow\)D\(_0\) absorption. Whether or not the fluorescence quantum yield increases at low temperature has not been investigated.

As discussed in detail in chapter 7.4, it is not likely that the fluorescence observed\([487]\) from a r.t. solution of TH\(^{++}\) stems from TH\(^{++}\). It is interesting to note that for TTF with 14 π electrons, the fluorescence quantum yield seems to increase as aromaticity is increased in the first and especially the second oxidation step, while in the case of TH the 16 π electron neutral is a better fluorophore than the radical ion.

9.1.6. Speculations about the relaxation mechanism.

Given the extremely short lifetimes and the fact that the EGL cannot account for them, it is likely that CIs are involved in the excited-state decay of the radical ions studied here. In the case of those radicals having higher symmetry elements, first and second order Jahn–Teller will
strongly favor state mixing. The rigidity of radical ions deduced from vibrational spectroscopy reflects the situation for the electronic ground, not the excited state.

**Aromatic amines.** Quantum chemical results for WB$^{••}$ found a CI upon twist of one of the NMe$_2$ groups, yet the insensitivity of the D$_1$ lifetime to friction raises the question, if there is no CI on the PES accessible without large amplitude motion. The FC active 8α mode seems a likely candidate since this state was associated with the relaxation of the excited state.\[263\] This would also account for the lack of deuterium effect because the aromatic hydrogens hardly participate in this vibration.

According to the CASPT2 calculations, however, no CI can be reached on this coordinate without a significant twist.\[290\] Clearly, such a twist cannot be involved in the decay of TiPD$^{••}$. But the energetic situation is not necessarily the same in the methyl and iso–propyl derivative and different mechanisms could apply in the two cases. The same is true for DMTPD$^{••}$ where the electronic situation is different and the solvent has a measurable influence on the decay rate. Comparing the D$_0$ and D$_1$ state of DMTPD$^{••}$ shows that the excited state has a higher electron density at the central benzidine core which stems from the peripheral aryl rings. The D$_1$→D$_0$ IC has to include the charge recombination and it is therefore not surprising to find that it is solvent dependent.

The TA spectra of MB$^{••}$ show contributions that might be ascribed to minor structural reorganisation of the photoexcited state or to a twist of one of the phenyl groups (τ$_{a1}$ in Table 5.2), in analogy to what is known for malachite green. Indeed, the TA spectra of malachite green are very similar to those of MB$^{••}$. From the data given here, no conclusion can be drawn about the importance of viscosity that might indicate large amplitude motion in the course of the decay. Another possible IC pathway of MB$^{••}$ is charge separation between two aryl rings like it has been proposed for the IC of triphenylmethyl radical.

**Polycyclic aromatics.** No accessible CI was found in a symmetry–restricted computational investigation of Pe$^{••}$.\[407\] Deformation, for example in a butterfly type motion, could mix D$_1$ with D$_3$ or maybe directly with D$_0$. The relaxation seems to have substantial charge transfer character since the lifetime correlates with the longitudinal solvent relaxation time, τ$_L$, although this might be fortuitous since τ$_L$ is correlated with many other solvent properties, e.g. the viscosity.\[137\] The absorption bands have measurable solvatochromic shifts indicating a CT character of the transition, yet the shifts are small.

Despite the differences in excited state energies, Pe$^{••−}$ has virtually the same lifetime as Pe$^{•••}$ which points to a similarity of the decay mechanism. The D$_1$→D$_0$ IC of Te$^{••}$ and MePTZ$^{••}$ might as well be controlled by an ET since they have virtually the same excited-state lifetime in H$_2$SO$_4$ as Pe$^{••}$ does.

Owing to the high density of electronic states of G$^*$ down to 0.7 eV, it is not surprising to find ultrafast electronic relaxation. The microsecond lifetime assigned to G$^{••}$ in earlier reports\[536\] rather reflects the chemical reactivity of the corresponding anion obtained by photolysis.

**Heterocycles.** The sulfur containing radical ions of TTF and TH are the two “outliers” in Figure 9.1. If this originates from peculiarities associated with the sulfur atoms or results from an insufficient time–resolution remains unclear. TH$^{••}$ has the lowest D$_1$ state of all molecules
studied in this work (but a quite important \(D_2-D_1\) energy gap) while that of TTF\(^{**}\) is among the highest ones, yet, both of them show ultrafast electronic relaxation.

### 9.2. Vibrational energy relaxation

Before discussing the observations concerning VER made in the dynamics of the radicals studied here, it should be reminded that VER is comprised of both, IVR and VC, as discussed in chapter 2.3. Furthermore intramolecular structural changes may contribute to the spectral changes assigned to VER in this work. As argued in the introduction, IVR and VC are not temporally separated, independent processes as has been assumed until recently and no attempts to model them have been undertaken as this would go beyond the scope of this work. Some observations shall nonetheless be highlighted in the following paragraphs.

Only in the case of MB\(^{**}\) structural and/or solvent reorganisation significantly alter the TA spectrum of the \(D_1\) state and the evolution of the early TA spectra has, in this case, been ascribed to such a process (vide infra). In all other cases, the VER dynamics take place on the ground state PES.

The fact that no VER of \(D_1\) was observed\(^5\) is explained by the small excess energy (Wurster’s salts, MB\(^{**}\), TTF\(^{**}\)) or with the short \(D_1\) state lifetime (DMTPD\(^{**}\), \(TH^{**}\), \(G^{*}\), \(Pe^{*\pm}/MeCN\)). Most radicals have lifetimes shorter or at best in the range of typical VER times so the spectral contributions of VER are buried in the amplitude of the excited-state decay. In \(H_2SO_4\) solution, \(Pe^{*+}\) and \(Te^{*+}\) have considerably longer lifetimes but from the spectral features in the SADS (Figures 6.13, 6.23) it is clear that the observed VER takes place in the ground state.

Given the lack of pronounced peaks in the ESA, it might simply be that the VER of \(D_1\) cannot be extracted from the TA data.

The VER of the electronic ground state can be reproduced by mono– or biexponential functions. The respective time constants for MeCN, \(CH_2Cl_2\) and \(H_2SO_4\) solutions are summarised in Table 9.2.

The short component of VER in Wurster’s salts and galvinoxyl, \(\tau_{a2}\), is remarkably insensitive to the solvent (see also Table 4.3 and 8.2). Most likely it reflects IVR in Wurster’s salts. In galvinoxyl it is much longer, 1.2 ps, which casts doubts on such an assignment. Several groups reported IVR lifetimes in this range, although they showed solvent dependence.\(^{[145,149,151]}\)

For other solutes, such as MB\(^{**}\) or DMTPD\(^{**}\), \(\tau_{a2}\) varies with the solvent. In MB\(^{**}\) \(\tau_{a2}\) might be related to structural changes which, if large amplitude motion is involved, are expected to be a function of the solvent. In DMTPD\(^{**}\), the short component of VER is only observed in MeCN where \(D_1\rightarrow D_0\) IC is the fastest. In chapter 5.2.3 it was argued that it cannot be observed in the other solvents due to the slower population of the hot ground state. In \(H_2SO_4\), however, the hot ground state of the radical cations of PAHs and TH is populated with even slower rate constants, but VER with a lifetime that is four times shorter than that of IC contributes to the observed TA dynamics.

The slowest part of VC is in the range \(5 < \tau_{a3} < 24\) ps and \(7 < \tau_{a3} < 21\) ps in MeCN and \(CH_2Cl_2\), respectively. It depends as much on the solvent as on the solute. For example, VC of WB\(^{**}\) in MeCN takes place with \(\tau_{a3} = 5\) ps, while it amounts to 15 ps for DMTPD\(^{**}\) and 24 ps for \(Pe^{**}\) and \(Pe^{*-}\). The relation of \(D_1\) state energies of these compounds is

\(^5\)As is has been, for example, in \(Pe^0\) after 266 nm excitation, Figure 6.4.
Table 9.2: Lifetimes associated with VER. (a): Solvation and/or relaxation in D1, (b): absent, (c) might reflect IC.

<table>
<thead>
<tr>
<th>solute</th>
<th>$E_{exc}$/eV</th>
<th>$E_{D1}$/eV</th>
<th>$\tau_{a2}$/ps</th>
<th>$\tau_{a3}$/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MeCN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WB**+</td>
<td>2.0</td>
<td>2.0</td>
<td>0.3</td>
<td>4.9</td>
</tr>
<tr>
<td>WB**+</td>
<td>2.3</td>
<td>2.0</td>
<td>0.3</td>
<td>5.9</td>
</tr>
<tr>
<td>d4–WB**+</td>
<td>2.0</td>
<td>2.0</td>
<td>0.3</td>
<td>4.7</td>
</tr>
<tr>
<td>TiPD**+</td>
<td>2.0</td>
<td>2.0</td>
<td>0.2</td>
<td>5.6</td>
</tr>
<tr>
<td>WR**+</td>
<td>2.3</td>
<td>2.3</td>
<td>0.8</td>
<td>8.5</td>
</tr>
<tr>
<td>MB**+</td>
<td>1.8</td>
<td>1.7</td>
<td>0.6(a)</td>
<td>14.5</td>
</tr>
<tr>
<td>DMTPD**+</td>
<td>2.5</td>
<td>1.0</td>
<td>1.2</td>
<td>15.0</td>
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</tr>
<tr>
<td>Pe**–</td>
<td>1.6</td>
<td>1.0</td>
<td>24</td>
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<td>2.1</td>
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<td>3.1</td>
<td>0.7</td>
<td>1.2</td>
<td>5.1</td>
</tr>
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<td><strong>CH$_2$Cl$_2$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>2.0</td>
<td>2.0</td>
<td>0.3</td>
<td>6.9</td>
</tr>
<tr>
<td>WR**+</td>
<td>2.3</td>
<td>2.3</td>
<td>1.3</td>
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<tr>
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</tr>
<tr>
<td>Pe**+</td>
<td>2.3</td>
<td>1.6</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td><strong>H$_2$SO$_4$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pe**+</td>
<td>2.3</td>
<td>1.6</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Pe**+</td>
<td>1.6</td>
<td>1.6</td>
<td>(b)</td>
<td></td>
</tr>
<tr>
<td>Te**+</td>
<td>1.6</td>
<td>1.4</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>TH**+</td>
<td>2.3</td>
<td>0.5</td>
<td>1.5(c)</td>
<td>8</td>
</tr>
</tbody>
</table>
WB$^\bullet$ > DMTPD$^\bullet$ + $\approx$ Pe$^\bullet$ > Pe$^\bullet$-. An excess energy of 0.3 eV leads to a 10% increase of $\tau_{a3}$ in WB$^\bullet$; 0.6 eV have no significant effect in Pe$^\bullet$ and Pe$^\bullet$-.

Similar differences with changing solute are observed in CH$_2$Cl$_2$ as shown in Table 9.2.

9.3. Synopsis

During this thesis, the excited-state dynamics of several radical ions has been investigated. Although distinct with respect to structure (aromatic amines and phenols, polycyclic aromatic hydrocarbons or heterocycles), oxidation state (cationic, anionic or neutral), excited-state energy (from 1 to 2 eV), and environment (r.t. liquid and solid solution or low temperature glasses), all of them showed ultrafast excited-state decay with lifetimes in the picosecond range and below.

Generalisations why this is the case cannot be made and the data collected is rather a warning not to do so — simplifying assumptions and conclusions from similarity of structure or energies clearly fail completely in several cases.

Obviously, the often invoked energy gap between the first excited and the ground state seems to play no role for their short $D_1$ state lifetime and this argument should not be put forward. Rather are conical intersections whose access is facilitated by the Jahn–Teller effect involved in the excited state decay.

In what concerns the possibility to observe excited states of radical ions in photoinduced electron transfer reactions — the question that initiated this work —, the results hint on that they can easily pass unseen in TA data containing contributions from numerous species. The excited state lifetimes are very short in MeCN solution which makes it difficult to achieve appreciable concentrations of M$^\bullet$; the ESA of radical ions is small and unstructured what would make it hard to unequivocally sort it out from the TA signal of the (other) products of the ET; and stimulated emission, that, just like ESA, would unequivocally prove the involvement of the radical ions’ excited state was only observed in the TA spectra of some Wurster’s salts.

Absence of SE is especially surprising in the case of TTF$^\bullet$+ and MB$^\bullet$+ because they have high molar absorptivity for the longest wavelength absorption.

TTF$^\bullet$+ has a quite strong ESA signal but unfortunately in the blue part of the spectrum where contributions from other species are very likely and, like observed in all cases, its ESA is unstructured. Additionally its first excited state is very high in energy so that it cannot be reached in most ET reactions. With respect to the latter criterion, the other compounds are preferable but none of them seems to own high molar absorptivity for $D_2$←$D_1$ ESA. The highest values are found for the ESA of Te$^\bullet$+ around 350 nm and of MePTZ$^\bullet$+ around 400 nm which amount to roughly half the intensity of the bleach signal.

Hence, experimental evidence for the participation of the radical ions’ excited state is without doubt difficult. This is, of course, neither proof nor refutation of the hypothesis and the question remains thus open.
9. Conclusions

9.4. Perspectives

The main tools used for this work are a home-built electrochemical flow cell and a transient absorption set-up both of which have been substantially improved but certainly not to a point where there is nothing left to do for successors. Apart from further improvements of the electrochemical cell, it will be necessary to systematically investigate what has been shown for a set of open-shell organic ions in the present work. The incompleteness of data prevents detailed analysis of effects like VER or to pin down the mechanism that governs the ultrafast $D_1 \rightarrow D_0$ IC. The latter was attempted in the case of Wurster’s salts which were studied quite thoroughly but the results showed that simple models and reasoning by analogy are tenuous. Also in the case of $\text{Pe}^{\bullet+}$, subject of many studies, an unequivocal assignment cannot be drawn. The importance of vibronic coupling might be deduced from temperature dependent measurements.

No attempts to model VER were made in this work, yet, radical ions might offer good candidates for such investigations since they show ultrafast IC during which a substantial amount of electronic energy is converted into vibrational energy, similar to what is the case for azulene which has been intensively used for studies of VER.

The question that initiated this work remains open: Do excited states participate in bimolecular photoinduced charge separation reactions? The data collected shows that, indeed, it would be extremely difficult to observe them in the course of such a reaction.

With the low ESA signal observed for the radical ions and the absence of SE in almost all cases, it is not sure that efforts to monitor the formation and decay of radical ions’ excited states in ET reactions will succeed. More luck might be given to infrared-TA measurements since absorption bands in the IR spectral region are usually less overlapping and unequivocal identification may be possible there. To this end, their spectra and dynamics will have to be characterised just as exemplified for the visible spectral region in this work.

Hammarström and co-workers suggested to look for the ESA of the hot ground state rather than to try to catch the excited state.[236] The strong point of this idea are that the spectral position and dynamics of the hot ground state are known or can be measured in a way like done during this thesis. Yet, the presence of the radical ion’s hot ground state is no proof for the intervention of its electronic excited state. ET, just as IC, is a non-radiative transition converting electronic into vibrational energy. Only a quantitative measure of the vibrational energy could evidence the exact pathway. In the case of ET populating the excited state of one of the ions, this ion will carry most of the energy whereas the energy will be more evenly distributed among the two ions if this is not the case. Very recent results with IR spectroscopy indicate that unequal distribution is in fact the case in the ET between $\text{MePe}$ and tetracyanoethylene.[551]

Even spontaneous fluorescence might be detectable in favourable cases, in particular for those radical ions that have a reasonable $k_{\text{rad}}$, such as the Wurster’s salts, $\text{MB}^{\bullet+}$ or the radical anions of perylene dicarboximide and tetracarboxydiimides investigated by Wasielewski and co-workers.[185] Such experiments are currently under way.
10. Résumé de la thèse en français

Cette thèse a pour sujet la photophysique d’ions radicaux en solution à température ambiante. Ces ions ont été générés soit chimiquement soit électrochimiquement. Dans ce dernier cas, une cellule électrochimique à flux, adaptée à la spectroscopie ultra rapide, a été mise au point et a prouvé être un outil versatile pour la génération d’ions radicaux.

Les spectres, ainsi que les dynamiques, ont été mesurés en utilisant principalement la spectroscopie d’absorption transitoire ayant une résolution de l’ordre de la femtoseconde. Une telle résolution, accessible seulement récemment avec des systèmes de lasers pulsés, s’est révélée indispensable pour suivre les processus de relaxation des radicaux étudiés durant ce travail de thèse, indépendamment de la structure moléculaire (amines aromatiques et phénols, hydrocarbures aromatiques polycycliques ou hétérocycliques), de l’énergie de l’état excité (de 1 à 2 eV), de la charge (cationique, anionique ou neutre) et, dans de nombreux cas, de l’environnement. Par exemple, les fameux sels de Wurster (p-phénylénediamines) ont un temps de vie à l’état excité de 0,2 ps à température ambiante, quelque soit le solvant. Par contre, ce temps de vie varie fortement avec la température, augmentant ainsi de 650 ps à la température de l’azote liquide.

En conséquence, la fluorescence est observée en dessous d’un seuil de température d’environ 120 K, mais pas dans une matrice rigide à température ambiante. Le contraire est trouvé pour les hydrocarbures aromatiques polycycliques. Ainsi, pour le radical cation du pérylène, des effets de solvants importants ont été mis en évidence, le temps de vie à l’état excité variant pour ce dernier de 5 ps dans l’acétone à 25 ps dans l’acide sulfurique. Une comparaison avec les données de la littérature montre que dans ce cas, la température n’a pas d’influence. Nos résultats suggèrent en effet que le processus de conversion interne est concomitant avec un transfert de charge majeur.

Les données montrent clairement que la loi d’écart d’énergie (energy gap law), mettant en relation la constante de vitesse de relaxation non radiative et la différence d’énergie avec le niveau d’énergie plus proche, qui est souvent invoquée pour expliquer l’absence de fluorescence des ions radicaux en phase liquide, ne peut pas être considérée dans les cas étudié ici. Par contre, des intersections coniques sont clairement impliquées et leur accessibilité est influencées par des effets subtils tels que la nature des substituents, la flexibilité structurale ou encore l’environnement.

Il a été prouvé que l’absorption à l’état excité des ions radicaux a généralement des coefficients d’extinction très faibles et par conséquent la présence d’ions excité est peut-être passée inaperçue dans les études de réactions de transfert d’électron intermoléculaire.
Part III.

Experimental
11. Experimental set–ups

In this section the experimental set–ups used throughout this thesis are described. Special attention is paid to the transient absorption (TA) set–up that has been substantially improved and to the electrochemical flow cell that has been re–developed on the basis of examples from literature. The key points of the data treatment are described together with their shortcomings. For the radicals that have been employed as salts, the synthesis is briefly described.

11.1. Steady–state

The steady–state absorption spectra have been recorded on a Cary 50 (Varian) one–path UV/visible spectrophotometer. Fluorescence emission and excitation spectra were collected on a Cary Eclipse (Varian), corrected for the wavelength dependent sensitivity of the spectrometer and transformed in the transition dipole representation when plotted against an energy scale. Because of the poor sensitivity of the spectrometer, the emission and excitation slits were typically 5 nm but up to 20 nm when little or no fluorescence was expected (e.g. the room temperature measurements in PMMA films).

The photosensitivity of the Cary Eclipse spectrometer drops rapidly above 800 nm and therefore the fluorescence spectra of Magic Blue were recorded on a Fluoromax (Jobin-Yvon) spectrometer. NIR absorption spectra of galvinoxyl were recorded on a Cary 5000 spectrometer (Varian).

Low temperature measurements have been collected in a Optistat DN cryostat by Oxford Instruments cooled by liquid nitrogen.

Where the electrochemical oxidation was not quantitative, the absorption spectrum of the radical was obtained by subtracting the spectrum of the neutral multiplied by an arbitrary value such that the resulting spectrum was smooth.

11.2. Single photon counting

The time-correlated single photon counting (TCSPC) unit was the same as described in Ref. [553]. The fluorescence was detected at 90 degrees with the analyser polariser at magic angle. The IRF had a FHWM of ≈200 ps. The data was analysed by iterative convolution of the IRF (measured using a LUDOX light scatterer) with a trial function, namely a mono– or biexponential function.

For the measurements of Wurster’s Blue the excitation source was a Picoquant PLS600 LED generating 596 nm pulses. The IRF of the set–up when using this LED had a FWHM of 800 ps. Due to the low count rate and the high level of scattered light in this measurement (caused by reflections on the cryostat windows and defects in the low-temperature matrix), the following function was used to reproduced the kinetics:
11. Experimental set–ups

\[ I_{\text{flr}}(t) = I_{\text{IRF}}(t) \otimes A_1 \cdot \exp(-t/\tau_{\text{flr}}) + A_2 \cdot I_{\text{scatter}}(t) \]  

(11.1)

where \( \otimes \) represents a convolution. The free fit parameters, \( A_1, \tau_{\text{flr}} \) and \( A_2 \) where optimized in a least square fit algorithm (Matlab, The Mathworks), whereas \( I_{\text{scatter}}(t) \) was taken as the response of the pure solvent.

11.3. Fluorescence up–conversion

Valuable information can be obtained from fluorescence since i) in most cases the emissive state can be unequivocally identified, ii) the signal to noise is superior to TA and iii) the time-resolution is better than for our TA set–up (vide infra).

The fluorescence up–conversion technique (FU) is a method to measure fluorescence decays with femtosecond time-resolution. The idea underlying this technique is to gate the spontaneous fluorescence using a laser pulse. This is done by delaying the gate pulse with respect to the excitation pulse. The fluorescence that coincides temporally with the gate pulse in a non–linear crystal will give UV light via sum–frequency generation and this UV light is in fact the measured signal. In other words, instead of gating the detector itself, one, in a way, gates the emitted light. Femtosecond time-resolution can easily be obtained thereby, the width of the response function will depend essentially on the width of the gate pulse.\(^1\)

If measuring the fluorescence decay at several wavelengths and analysing the results in a global way, decay associated spectra (DAS) are obtained.\(^2\) These DAS hint on the process that underlies each rate constant. It can be shown\(^{[554]}\) that a band shift (e.g. due to a dynamic Stokes shift) is related to a DAS with positive sign in the blue and negative in the red part of the spectrum, a band narrowing (e.g. due to vibrational cooling) has a dispersion shaped DAS, and a population decay has an amplitude spectrum that is identical with the steady–state fluorescence spectrum.

Since FU has been used to a minor extend in this thesis, it will not be described in detailed here, for more information, especially on our set–up, see, e.g., Ref. [555] and [556].

Briefly, the output of a MaiTai laser (Spectra Physics, tuneable between 690 and 1050 nm, 120fs FWHM, 82 MHz repetition frequency) is split into two parts, one serves as gate pulse, the other is frequency doubled and serves as pump pulse between 350 and 500 nm. The pump energy at the sample is typically 50 \( \mu \)J-cm\(^{-2} \). The sample that is contained in a 1 mm thick rotating cell has an absorbance of ca. 0.4 (except for the DMTPD\(^{+} \) samples where it was 0.75) at the excitation wavelength. Sample stability is verified by the steady–state absorption spectrum taken before and after the experiment.

The FU data was analysed in a global way (linked lifetimes) by multi-exponential decay laws convolved with a Gaussian representing the IRF (IGOR Pro, Wavemetrics, see page 195 for the coding). Decay associated spectra (DAS) were obtained in the way described in Ref. 288.

\(^1\) And geometrical factors of the set–up
\(^2\) The amplitudes have to be related to the steady–state signal intensity at the respective wavelength, which is, by its nature, the time-integrated signal. For the samples that fluoresce only at low temperatures, it is assumed that the emitting state/species is identical in the ambient temperature FU and low temperature steady–state measurement.
11. Transient absorption

TA spectroscopy is a pump–probe technique based on the same ideas as the flash photolysis method invented by George Porter, Nobel prize winner in 1967.\textsuperscript{557} Instead of a flash lamp, a second laser pulse is used as probe beam which improves sensitivity and time resolution. The theory of femtosecond pump–probe spectroscopy has been developed mainly by Mukamel.\textsuperscript{558} The approach to use a spectrally broadened probe (called “supercontinuum” or “white light continuum” (wlc)) beam was put on solid feet in a series of papers by Ernsting and co–workers.\textsuperscript{559,560} They showed\textsuperscript{559} that the signal recorded using a chirped wlc pulse can be treated analogous to that of a non–chirped (“single” wavelength) pulse.

In practice the TA signal is measured as a difference signal, just as any absorption signal, but the “reference” beam is one that passes a sample that has not been perturbed by the pump beam. One subtracts therefore the absorption of the sample in the ground state from the one in (any of) the excited state(s). Hence, the absorption spectrum of the ground state will show up as negative signal in the TA spectrum since this state has been depleted by the pump pulse and the sample shows less absorbance at the respective wavelengths. This so–called bleach signal provides information about the ground state recovery. Note the difference to fluorescence spectroscopy that is sensitive only to emitting states and cannot answer the question at which point the ground state is recovered. Further contributions to the TA spectrum come from stimulated emission (SE) and excited state absorption. These three contributions make up the sequential (resonant) signal.\textsuperscript{560}

Additional signals are present while pump and probe beam overlap temporally in the sample: the coherent signal of the sample, cross phase modulation (XPM) generated in the cuvette windows and the solvent, and stimulated Raman signal.\textsuperscript{560} The XPM and the solvent Raman signal can in principle be subtracted when measuring the TA signal of the pure solvent\textsuperscript{561} but it is questionable if this can be done in a reliable way because i) XPM is a 3rd order non–linear effect and absorbance of the pump light by the solute changes its intensity and shape and ii) the precision of our translational stage is ca. 3 fs which means that the “pure” XPM is in general shifted to other wavelengths with respect to the solute’s measurement.

Dobryakov et al.\textsuperscript{560} showed that the coherent signal (stemming from mixed order of the pump–pump–probe interactions with the sample) contains the same information as the sequential signal and can be used for data–interpretation. Their data treatment has as a key step “singular value decomposition (SVD) with tricks.”\textsuperscript{562–564} This allows to access the total of the sequential signal from time zero onwards. It bears, however, the risk to suppress spectral features by the personal choice of “important” over “not important” vectors (the latter being ascribed to noise).\textsuperscript{565} This is especially critical since SVD is known not to reproduce well spectral shifts.\textsuperscript{566}

Therefore we prefer not to use SVD and to neglect all data with significant pump–probe overlap, i.e. from time zero onwards until the width of the IRF (both are determined by measuring either the XPM or the OKE signal of pure solvent).\textsuperscript{3} This exclusion of data has three obvious disadvantages: First, we lose information on processes happening with lifetimes faster than or close to the IRF width, i.e. $\approx 200$ fs. Second, we cannot convolve the dynamics

\textsuperscript{3}Note that the OKE signal is temporally broader than the XPM because of the nuclear response. Only the electronic response is taken into consideration.
with an IRF which renders our lifetimes inaccurate if they approach the IRF width — not to talk about their amplitudes.\(^{[567]}\) Third, the choice of the starting point is arbitrary and can slightly influence the lifetimes obtained.

### The transient absorption set-up

The set-up used for the femto-second TA experiments uses laser pulses from a 1kHz Ti:sapphire stretched-pulse amplifier (Spitfire, Spectra Physics). The seed beam for this amplifier comes from a Ti:sapphire oscillator (Tsunami, Spectra Physics) and the pump beam from a Nd:YVd\(_2\)O\(_4\) laser (Empower, Spectra Physics). The pulses that exit the Spitfire are centred at 800 nm and have about 150 fs pulse width (FWHM). This beam is split into two parts used as pump and probe.

The pump beam can be either the fundamental of the Spitfire (800 nm, typically 4–10 µJ), its frequency double (400 nm, 1–3 µJ, generated in a 1 mm BBO crystal), its frequency triple (266 nm, typically 1 µJ, generated by frequency mixing of the fundamental with 400 nm light in a 0.1 mm BBO crystal) or the output of a home-built non-collinear optical parametric amplifier (NOPA, 500–700 nm, 1–2 µJ). This NOPA, that has been constructed in the beginning of this thesis, is a copy of the commercial NOPA Clark system by Riedle\(^{[568,569]}\) except for the frequency doubling crystal (BiBO instead of BBO) and unimportant geometrical differences. After the NOPA, the laser beam passes a compressor with SF10 prisms\(^{[570]}\) and the autocorrelation measured at the sample position is typically 60–100 fs.

The pump beam is chopped at half the laser frequency and the polarisation is set to magic angle with respect to the probe beam. It is focused onto the sample with 500 to 600 nm lenses (800/400 nm and NOPA excitation, respectively) or a 500 mm focal length curved mirror (266 nm excitation). The focal point is not in, but behind the sample and the beam diameter at the sample is 300–500 µm. The pump beam diameter at the sample is thus typically 3 times bigger than the probe beam in order to minimise the effect of beam walk-off.

This walk-off that arises when moving the retro reflector on the translational stage and that is inherent to all pump–probe spectroscopic techniques, contaminates the kinetics extracted from the spectra. The time window accessible is 2 ns wide.

The probe beam is obtained by focusing 1 µJ of the Spitfire’s output in a 3 mm CaF\(_2\) window where it gets spectrally broadened so that the probe comprises light in the spectral range from 350 to 800 nm and is thus called “white light continuum” (wlc).\(^4\)

The remaining fundamental (\(\approx 99\%\) of the incident light) is filtered by a 800 nm mirror having an anti-reflection coating for the visible (HR800HT400–720nm) and is recollimated by a quartz lens. The intensity of the wlc above 700 nm could be improved by detuning HR800HT400–720nm filter and installation of a CuSO\(_4\) solution after the sample. Unfortunately it is impossible to avoid the pronounced shape at 720 nm (Figure 11.1). Due to the steep edges of the wlc in this wavelength range, small fluctuations create quite an important,

\(^4\)Initially the wlc was generated by focusing the fundamental of the Spitfire into a 10 mm cuvette of water/heavy water. The remaining fundamental was filtered by a C3C23 colour filter. The wlc obtained in this way has quite a big chirp and is restricted to a rather small wavelength range due to the filter. Better results (less chirp, better conversion efficiency (both, in the centre but especially at the borders giving thus a flatter spectrum), improved stability) were obtained with the combination of a 3 mm thick sapphire or 3 mm calcium fluoride window and a HR800HT400–720nm filter.
11. Experimental set-ups

Figure 11.1.: White light continuum in the latest version of the TA set-up

erroneous TA signal that is superimposed on the sample response. This, however, effects only
the shape but not the sign or overall intensity of the spectra.

It has been pointed out several times\cite{571–573} that the polarisation of the wlc can be rotated
from the polarisation axis of the incident light or that the wlc can be depolarised. A wire grid
polariser rectifies the polarisation after the CaF$_2$ window.

The wlc is divided into two parts that are monitored by two spectrographs. One beam passes
the sample (signal beam), the other one is used to correct for shot to shot fluctuations of the
wlc (reference beam).\cite{574} The wlc beam diameter at the sample is ca. 60 µm. The quartz lens
focusing the wlc in the sample is a source of chromatic aberration. The chromatic aberration
causes distorted TA spectra and deteriorates reproducibility (since the spectrum depends on
the exact pump–probe overlap). Attempts to meliorate the focusing by a combination of a
collimating quartz lens and a focusing CaF$_2$ lens had only minor impact. The transmissive
optics will therefore be replaced by reflective optics. Note that the generation of the wlc in
the CaF$_2$ window cannot be assumed to happen at one point and that different colours are
generated at different positions which will always cause some chromatic aberration. A thinner
CaF$_2$ window is preferable considering this aspect.

Important improvements were achieved by replacing the Oriel Multispec 77400–M spectro-
graphs equipped with a single line CCD by Andor SR163 equipped with a back–thinned FFT–
CCD array (Hamamatsu S7030-906), both assembled by Entwicklungsbüro Stresing, Germany.
A Kodak Wratten filter (Red No. 25) removes the 2nd order reflection of the gratings. The
multi–line CCD in the new set–up helped to improve the S/N ration and reproducibility and
to reduce the acquisition time by a factor of more than 5. This was crucial for the molecules
presented in this thesis. 500 TA spectra (i.e. 1000 laser shots) are on average sufficient to get
a root mean square error of less than 0.1 mOD.
The sample is contained in a quartz cell of 1 mm pathlength with 1.2 mm windows and continuously stirred by nitrogen bubbling. At high viscosities sample mixing was achieved with a L-shaped teflon stirrer. When the 266 nm pump was used, cell windows of only 0.6 mm thickness were used in order to reduce the temporal broadening of the pump in the sample cell.

The cuvette used in combination with the electrochemical flow cell has two 2 mm thick quartz windows and an optical pathlength of 1 mm.

The time resolution of the set-up is estimated to be 200–300 fs, the width of the electronic OKE signal.

**TA data treatment**

**Chirp correction.** Owing to the chirp of the wlc light that stems from the creation process itself and the lenses that focus it into the sample cell, time zero differs for every colour contained in the wlc. The TA data has to be corrected for this chirp prior to further processing. This was done via interpolation along the time-axis.

It has been shown\(^{[559]}\) that the cross phase modulation (XPM) can be used to properly describe the chirp of the white light continuum. Unfortunately the signal obtained in the sample cell having 3.5 mm width\(^5\) deviates more and more from the perfect dispersion shape as the wavelength difference between pump and probe increases. This is an intrinsic problem that stems from the increasing group velocity difference. A way to circumvent this which is frequently used, is to replace the cell with a thin quartz plate but this means that the TA measurement is not made under identical conditions as the determination of the chirp. The same is true when the pump-probe overlap is determined via the non-linear response of a crystal placed at the sample position.

We, like others,\(^{[575]}\) found the optical Kerr effect (OKE) to give the same result as the XPM but maintaining quite well its shape over the whole spectrum. Except for a substantial broadening (again due to differences in group velocity between pump and the respective part of the probe beam), they are all Gaussian with the same sign which makes it easy to determine the centre of the intensity vs. time-delay signal in an automated fashion.

**Data fitting.** In order to get information about the temporal evolution of the TA signal, two approaches to extract dynamic information were employed. Either dynamic traces every 10 nm all over the spectrum were selected and fit globally (lifetimes linked, IGOR Pro, Wavemetrics) or the total of the spectrum was fit with only the lifetimes as free fit parameters, while the amplitudes are calculated (this has been named “matrix construction algorithm”\(^{[576]}\)). The procedure is described in references [576,577] and [513], the coding is printed on page 195.

Multi-exponential fit functions (global analysis in a narrower sense of the meaning) or a model of successive exponential transformation reactions (target analysis) were used to reproduce the data. The former approach yields so-called decay associated difference spectra (DADS) that represent the spectral changes of the TA spectrum which occur with the associated lifetime. The latter give species associated difference spectra (SADS) that represent the TA spectrum of a species decaying with the associated lifetime. It should be stressed that the term “species” here does not mean chemically distinct molecules but rather a distinguishable TA signal (that

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\(^5\)Two windows of 1.2 mm each and 1 mm optical pathlength.
might stem from a variety of chemical “species”). Furthermore it should be reminded that, as the name says, it is a species associated difference spectrum, comprising of ESA, SE and bleach.

The scheme of the target analysis is given on page 43. It yields a series of coupled differential equations. For the example of three species (A, B and C) they read (square brackets indicate concentrations, $t$ the time, $k$ rate constants):

$$\frac{d[A]}{dt} = -k_{AB}[A(t)]$$
$$\frac{d[B]}{dt} = k_{AB}[A(t)] - k_{BC}[B](t)$$
$$\frac{d[C]}{dt} = k_{CD}[B](t)$$

which gives

$$[A](t) = [A]_0 e^{-k_{AB}t}$$
$$[B](t) = [A]_0 \frac{k_{AB}}{k_{BC} - k_{AB}} (e^{-k_{AB}t} - e^{-k_{BC}t})$$
$$[C](t) = [A]_0 \left(1 - \frac{k_{BC}}{k_{BC} - k_{AB}} e^{-k_{AB}t} + \frac{k_{AB}}{k_{BC} - k_{AB}} e^{-k_{BC}t}\right)$$

**Interpretation of TA data.** TA spectroscopy — as any electronic spectroscopy — is sensitive to the molecule’s state (its wavefunction) and environment and since it is a time–resolved method, dynamic changes can be unravelled. For example, dynamic solvation of a perturbed molecule leads to spectral shifts, as does the change of the vibrational wavefunction in the course of VER.

From the spectral position, the sign and the time behaviour, one can assign the (in most cases overlapping) bands to certain states. For example, the diminution of the stimulated emission is a clear indication of depopulation of the emitting state, whereas the diminution of the bleach is a clear indication of ground state recovery (GSR) and these two processes do not need to coincide if an intermediate state is involved in the excited state dynamics. A global analysis of the data is clearly more powerful yielding DADS or SADS (vide infra).

TA spectra of vibrationally excited $p$–nitroaniline and trans–stilbene were recorded by Kovalenko et al.\cite{147} These samples undergo ultrafast IC back to the electronic ground state and the electronic energy is “damped” into molecular vibrations. By subtracting the contribution of the bleach, they obtained the absorption spectrum of the “hot” molecules which are, as expected, shifted to lower energies compared to that of the relaxed molecule and compare well with steady–state spectra obtained from heated samples.\cite{147,6}

\footnote{These spectra are not identical since the solvent is “cold” after photopreparation of the “hot” solute while it is “hot” in the case of thermal preparation.}
Criticism on the data treatment. The data treatment has some weak points that have their origin in experimental reasons or in the fit procedure. They are summarised here to draw the readers attention to the limits of the results.

- As stated earlier, the TA data recorded during pump–probe overlap are neglected. In the case of very short lifetimes, the most important part of the decay is thereby deleted, and it is assumed that a tail fit gives reasonable values for lifetimes that approach the IRF with which the dynamic trace is convolved.

- Coherent artefacts are sometimes pronounced in the TA spectra at early pump–probe time delays. This is mainly the case after 800nm excitation due to the higher pump intensity and the broader pulses. The NOPA pulses are compressed, the 400 nm pulses are shortened in the doubling process but the 800 nm pulses represent directly the Spitfire output (≈150 fs), slightly broadened by the transmissive optics. This causes an additional signal with flat amplitude \( \tau_{XPM} \) 200 fs to 1 ps — since only the tail of the signal is fit, this lifetime has a big uncertainty.

- Both ways used to reproduce the TA data, multi-exponential decays and target analysis, are based on the assumption that an exponential function can satisfactorily reproduce the dynamic behaviour. Such an assumption, however, is not fully valid for ultrafast conversion where thermal equilibrium is not reached. Kinetic rate equations are not really appropriate for processes happening far from equilibrium. Multi-exponential decay of a optically populated state can also arise from inhomogeneities or equilibra. Deviation from simple sequential rate equations are also observed in the presence of back–reactions or branching. Finally, spectral shifts are not well reproduced by exponential functions. In their series of papers on time dependent Stokes shift, Maroncelli and co–workers needed between two and four exponents to properly describe the solvation dynamics. This originates partially in the complex processes that underlie solvation. Owing to lack of a reliable model for excited state or solvation dynamics, the simple sequential model and multi-exponential fits are taken as the least biased choice. Also, since it is the most common approach, it ensures a certain comparability with results published by other groups.

11.5. In–line electrochemical radical ion generation

In order to examine radicals that are not easily obtained as salts, a home–built electrochemical flow cell was used to generate them in–line. This section describes the designs and modes of application that have been examined. In order to make these choices traceable, the design of some exemplary spectro–electrochemical cells is briefly reviewed after the definition of the basic electrochemical terms.

Some terms from electrochemistry

In an electrochemical reaction, a molecule M is either oxidised to yield the cation \( M^{\bullet+} \) or reduced to the anion \( M^{\bullet -} \). The reaction “partner” is the electrode (or the electrons in the electrode) that has a variable oxidation potential, depending on the voltage applied. For a
discussion of the processes that happen in the course of such a reaction inside an electrochemical cell, let us consider the case of oxidation.

With each molecule $M$ that is oxidised, a positively charged ion is created at the working electrode (WE) and an electron is transferred to the counter electrode (CE). In first place, this will cause a polarisation layer to build up at the CE which "stores" the charge just like a capacitor. The two capacitor plates are in this case the CE and its double layer. In a typical electrochemical cell used for analytical purposes, e.g. for cyclovoltammetry, the surface of the CE is much bigger than that of the WE and this double layer can account for all the charge difference between the electrodes built up during the measurement. If this is not or no longer the case, the potential of the CE will rise until a reduction reaction will take place at the CE, releasing electrons to the solution.

The flux of electrons from WE to CE (for an oxidation reaction) is counter–balanced by a flux of ions in the solution. To facilitate the electrochemical reaction, a good ion mobility is necessary. This is given for low–viscous, polar solvents containing high concentrations of salts. For organic solvents like MeCN or CH$_2$Cl$_2$ organic salts are most frequently used. The redox potentials depend on the supporting electrolyte and its concentration,[331] too low concentration increases the ohmic drop of the cell.[579]

Since the potential between two electrodes cannot be measured precisely if a current flows between them,[579] most electrochemical systems contain a third electrode, the reference electrode (RE). The potential measured between WE and RE is then specific of the type of RE used. Instead of a RE with well defined potential (e.g. the Ag/AgCl electrode), one can use so–called pseudo–reference electrodes whose potential depends strongly on the environment. Such a pseudo–RE can in the simplest case be a metal wire (Ag is most frequently used). As long as temperature and sample composition stay constant, the potential of the pseudo–RE is constant as well. It can then be calibrated with an internal standard, e.g. the ferrocene/ferrocinium couple.[580]

The potential of an electrode through which current flows is different from that at equilibrium by a amount called overpotential. Among the factors contributing to the overpotential are i) the activation energy for the transfer of an electron in the redox reaction step (“charge transfer” or “activation overpotential”), ii) a chemical reaction step preceding or ensuing the redox reaction, e.g. the loss of the hydration shell or a ligand (“reaction overpotential”), and iii) mass transport to the electrode (“diffusion” or “concentration overpotential”).

Diffusion near the electrode or, in the case of absence of convection, in all the electrochemical cell can limit the current and therefore the overall performance of the cell. Increased electrode surface and convection help to optimise the mass transport to and away from the electrode.

It is straightforward to calculate the charge required to oxidise or reduce a certain amount of substance and therefore the necessary current in a flow cell.\(^8\)

$$I = \frac{Q}{t} = \frac{F \cdot n}{t} = F \cdot c \cdot v$$  \hspace{1cm} (11.2)
$$F = e \cdot N_A$$  \hspace{1cm} (11.3)

\(^7\)And experimental parameters such as cell design.

\(^8\)I denotes current, $Q$ charge, $t$ time, $F$ the Faraday constant, $n$ mole of molecules, $c$ the molar concentration, $v$ the flow rate, $e$ the elementary charge, and $N_A$ Avogadro’s constant.
Instead of controlling the current flowing between electrodes, it is possible to control the potential between electrodes. This refers to galvanostatic (amperostatic) and potentiostatic mode, respectively.

**Spectroelectrochemistry**

Spectroelectrochemistry is the combination of an electrochemical cell with spectrophotometric detection. Typical spectroscopic methods in spectroelectrochemistry include UV/visible/IR absorption, fluorescence emission, Raman, EPR, or, though less commonly, NMR and X-ray absorption.\[^{581}\] Various cell designs have been invented throughout the years reflecting the variety of spectroscopic methods.\[^{582–585}\] Most of them are incompatible with ultrafast spectroscopy owing to a too long optical pathlength or the lack of controlled sample renewal during the experiment. Further difficulties arise from the difference in concentrations between a “pure” electrochemical and a spectroelectrochemical analysis and from the time window of observation — solutes that are stable on the timescale of a cyclovoltammetric (CV) experiment (typical sweep rates 100 mV/s) can undergo irreversible secondary reactions on the much slower timescale of the spectrometric detection, which is, depending on the cell design and technique, between 10 s and minutes.\[^{581}\]

Short optical pathlengths of variable length can be obtained, for example, in so-called optically transparent thin layer electrochemical cells (OTTLE).\[^{581,586}\] In a typical design the working electrode is a metal grid and the light beam passes through one of the grid’s holes. Mass transport of the solute from the electrode surface to the observation area is given by diffusion. The thin cell design assures it to take place rather quickly while it minimises diffusion of side products that might be formed at the CE to the observation window. In a variant the metal grid is replaced by a transparent electrode such as an ITO electrode.

This type of cell has proven very versatile but sample renewal in the observation window is determined by diffusion which is critical for laser spectroscopy. For example, Gosztola et al.\[^{185}\] observed rapid photodegradation of benzenedicarboximide radical anions upon laser irradiation even at pump energies of only 100 nJ per pulse. The radical anions of other imides\[^{185}\] and $C_{60}$ fullerene\[^{242}\] proved to be sufficiently photostable for the TA experiment. Hammarström and co–workers move the OTTLE cell vertically to minimise photodegradation.\[^{236}\]

Sample renewal between consecutive laser shots is ensured in flow–through systems where the ion generation happens in–line. The cell designed by the group of Okazaki is shown in Figure 11.2.\[^{480,587}\] The WE consists of carbon wool tightly filled in the glass diaphragm. Carbon wool provides a huge, homogeneous surface for the electrochemical reaction to take place and proved to be superior to other carbon fibres which, when compressed, caused too high a pressure against the solution’s flow. The load of carbon wool is crucial for efficiency.\[^{587}\]

The separator is a microporous glass diaphragm tube of 50 Å pore size. A Pt wire wound around the diaphragm serves as CE.\[^{480}\]

In a later version of the cell, a RE was introduced, though in the outer compartment.\[^{587}\]

The design is such that the solution flows through the inner compartment, then the cuvette and finally the outer compartment so that both electrodes are constantly flushed, thereby probably avoiding the built–up of a concentration overpotential (vide infra). In their experiment, they see dimerisation of thianthrene radical cation at 0.3 to 1 mmol·L$^{-1}$ in MeCN.\[^{480}\]
A similar cell was presented by Pedersen and co-workers.\textsuperscript{[423,589]} WE (carbon fibre or felt) and CE (gold foil) are separated by a porous ceramics (porosity not given). The solution is only passed from the reservoir through the inner compartment and then the cuvette connected by 1.6 mm teflon tubings by a HPLC pump.

Pedersen showed that this cell can reduce a variety of organic molecules quantitatively to the corresponding radical anions.\textsuperscript{[423]} He runs the cell without reference electrode in a galvanostatic mode, where the current was controlled such as to get maximum yield of the anion. It was noted that this current was much higher than what was expected from the flow rate and equation 11.3, presumably due to presence of oxygen.

A variant of the cell in which the CE is made of carbon felt, the contact wires are from tungsten instead of platinum and the electrodes are separated by porous teflon instead of a ceramics has been used in the group of Günter Grampp for EPR spectroscopy.\textsuperscript{[589]}
The home-built flow cell

The electrochemical flow system used during this work is in principle the same as the one published by Pedersen [588] and Grampp [589]. The cell has cylindrical shape with the solution passing the innermost part where the WE is placed. This electrode is made of a carbon fibre contacted by a tungsten wire. The CE that is located in the outer part of the cell is made of flexible graphite, the separator between WE and CE either of a MACOR ceramics (Morgan Technical ceramics) or porous teflon (Bola). Several porosities have been tested and 5 micron proofed to have a reasonable electrical resistance while not allowing for too fast diffusion of ions from the outer to the inner compartment. With respect to the latter problem, the non-porous MACOR ceramics is advantageous but it makes the electrical resistance between WE and CE very high (≥ 20 kΩ) and causes high overpotentials. No anions could be obtained with the MACOR ceramics, presumably due to this overpotential.

The shortcomings of the cell as published by Pedersen are i) the rather small surface of the CE, ii) the big volumes (1.6 mm tubings and flow rates of 10 mL/min), iii) the teflon tubings, iv) the lack of a RE. The following attempts to improve it were undertaken (causing other difficulties).

ad i) The electrochemical reaction at the WE has to be counterbalanced at the CE, either by the formation of a charged double layer, or by a redox reaction. For both of them a big electrode surface is favourable. Mladenova et al. [589] used a carbon felt instead of the gold foil proposed by Pedersen, increasing the surfaces of the CE with respect to that of the WE. Still, since the outer compartment is not stirred, it is prone to concentration gradients at the CE that build up in the course of the experiment and become the rate limiting reaction step, reducing the performance of the cell.

No success was granted to the idea to continuously flow the solution in the outer compartment in a close circle. Such tests were undertaken using a peristaltic pump and the teflon spacer (5 micron porosity). The pressure difference between inner and outer
compartment, however, caused an exchange of solution between them or flow in either one or the other direction. No stable working conditions could be found this way.

**ad ii)** Connecting tubes of 1.6 mm diameter need flow rates and hence sample volumes to ensure a short time between ion generation and spectrometric experiment. A TA experiment takes between half an hour and an hour,\(^9\) additional time is needed for optimising the parameters first and for the electrode potentials to stabilise so the whole experiment necessitates an prohibitive amount of MeCN (toxic) and supporting electrolyte (expensive). In order to reduce the volumes, the teflon tubings were replaced by capillary PEEK tubings connecting the reservoir with the electrochemical cell and the latter with the cuvette assuring a fast transport of the ions generated in the electrochemical cell to the cuvette (less than 1 second at a flow rate of 2 mL/min).

**ad iii)** Oxygen can penetrate through teflon and interfere by reaction with the radicals. PEEK, on the other hand, is impermeable to oxygen.\(^10\)

**ad iv)** We introduced a RE to have control over the potential of the WE. In galvanostatic mode (used by Pedersen and Grampp), it is crucial to control the flow rate precisely. A drop in flux will cause oxidation to the dication (or reduction to the dianion), an increase in flux will cause minor yield of the radical ion. A potentiostatic mode is not sensitive to variations in the flow rate, the current would simply adjust. Since no pump allowing for small flux was available, the flow was regulated by pressure of nitrogen or simply by gravitation. Both ways lead to sizeable fluctuations of flow rate and consequently of radical ion concentration. These fluctuations added an error on the dynamics of the TA measurements.

Therefore a Pt–wire was introduced in the inner compartment of the cell as a pseudo–RE. Tungsten wires contacting the electrodes have the advantage over platinum to be electrochemically more inert. They tend, however, to break at the endings. This can cause very high local electric fields at the sharp edges formed and render the potential measured between WE and CE meaningless. For this reason they were used as contacts only, not for the RE.

In the end, the potentiostatic mode suffered from a drop in efficiency, presumably due to an increasing concentration overpotential at the CE.\(^11\) The yield dropped to ca. 50% after some tens of minutes and the fluctuations in concentration of the radical ions added an uncertainty in the lifetimes extracted from the TA analysis. This could be evidenced by consecutive scans which had variations of up to 25% in the lifetimes. The concentration overpotential might be reduced by circulating the solution in the outer compartment. As stated earlier, the design of the cell and choice of materials were not compatible with stirring of the outer compartment.

The inner diameter of the cell determines the surface of the WE and the amount of dead volume. While the former should be large, the latter should be zero. At the same time it

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\(^9\)With the old set–up at least 3 hours

\(^10\)Otherwise the surface to volume ratio of the capillaries would render them counter–productive.

\(^11\)In the case of amperostatic mode, the voltage increases as the overpotential increases, causing finally oxidation of the solvent. In potentiostatic mode the current drops to the diffusion limited value.
11. Experimental set–ups

influences the distance of the WE and CE. Diameters from 3 to 6 mm were tested and better results were obtained with larger diameters. Most of the time, a cell with 5 mm inner diameter was employed. Tight loading with carbon fibre helps to decrease the dead volume.

**Improvements planned.** Although only a re–development, there remains plenty of space for improvement of the electrochemical flow cell. The following are foreseen or were recently achieved.

- A precise control of the flow rate will be possible with a micropump purchased lately. This should ensure a constant ion concentration and diminish the experimental error of the lifetimes from currently 25% to estimated 10%.
- A precise control of the current will be possible with an *Autolab* amperostat available in the house now. The *BASi* potentiostat used so far can then serve for what it is best at — collecting dust. This means that we attain to the system of Pedersen: galvanostatic mode with controlled flux. Although the idea of potentiostatic mode should be buried, the RE added to the design is not useless as it allows to measure the potential of the WE.
- Thorough drying of the inert gas is crucial for the stability of the radical ion solution. The fact that this was not done properly is most likely the reason for the poor yield of $\text{Te}^{\bullet+}$ and the failure to obtain any other radical anion than $\text{Pe}^{\bullet-}$. Water is known to reduce the electrochemical window (the potential range usable for experiments) in the reduction half.$^{[500]}$
  For anions, DMF or a mixture of 1,4–dioxane/MeCN are better solvents, having stabilising effects. Dioxane/MeCN mixtures have been successfully used in electrochemiluminescence (ECL) measurements and deliver higher yields of ECL most likely due to a higher anions stability.$^{[590,591]}$
- The teflon separators are easily machinable contrary to ceramic separators. Since teflon is non–polar and not wetted by the polar electrolyte solution, rather big pores are necessary before reasonable ion mobility between the electrodes is achieved. In the case of teflon this is given when there are channels through the teflon, in ceramics the pores are only connected by microchannels. A low–porous ceramics, when wet, has superior electric conductivity. Unfortunately our work shop cannot process them.
- Convection in the CE compartment is necessary to avoid concentration overpotentials, but possible only when using ceramic separators. The high ohmic drop that the ceramics cause will remain a problem and ask for optimisation of the cell design.
12. Substances and solvents

All substances were purchased from Fluka/Aldrich except for the RTIL 1-ethyl-3-methylimidazolium ethylsulfate (ECOENG 212, Solvent Innovation) and deuterated water (Armar Chemicals) and the acetonitrile for electrochemical measurements (Roth, Rotidry). The solvents were of analytical grade and used as received except for some experiments were they were argon saturated. Sulfuric acid (Fluka) was p.a. grade (95–97 %). The polymethylmethacrylat (PMMA) was purchased from Kremer pigmente. Perylene, and tetracene were sublimed prior to use. The abbreviations used for the solvents and some of their properties are collected in Table 12.1.

**Polymer matrix experiments.** Polymer films have been prepared from CH$_2$Cl$_2$ solutions of poly(methylmethacrylat) (PMMA). The CH$_2$Cl$_2$ slowly evaporated from the petri-dish to leave films of ca. 100 µm thickness.

The films were were placed in the fluorimeter and SPC unit with an angle of ca. 45 degrees with respect to excitation light. In order to proof that in this way it is possible to detect fluorescence, a PMMA film of malachite green (MG) was prepared. MG is known to have efficient non-radiative relaxation associated with large amplitude motion.\[347,594\] The steady-state and time-resolved fluorescence of a PMMA film doped with MG are shown in Figure 12.1.

The PMMA showed a broadened fluorescence spectrum and a biphasic fluorescence decay with $\tau_1 = 0.4$ ns (67 %) and $\tau_2 = 1.3$ ns (33 %). Note that the spectral broadening is not present in the absorption (Figure 12.1). The biphasic decay has been explained by sites with distinct microviscosity.[348]

**Synthesis**

DMTPD$^{+}$SbCl$_6$ was prepared by Paul Low’s group (University Durham, United Kingdom).[321] 3-Methylpyrene was synthesized by Jean–Luc Roulin according to a procedure reported before[595] and purified by column chromatography.[596]

The perchlorate salts of WB$^{+}$ClO$_4^-$ and WR$^{+}$ClO$_4^-$ were prepared according to literature procedures.[6,597] WR$^{+}$ClO$_4^-$, d4–WB$^{+}$ClO$_4^-$ and TiPD$^{+}$ClO$_4^-$ were prepared by Dr. Philipp Buchgraber.

d4–TMPD$^0$ was prepared following a procedure of Giumanini et al.[598] A slurry of d4–p–phenylenediamine (735 mg) and NaBH$_4$ (2.99 g) in THF (25 mL) was added dropwise to a solution of aqueous formaldehyde (4.2 mL, 40%), H$_2$SO$_4$ (3 mol·L$^{-1}$, 10 mL) and THF (25 mL) at -10° to avoid vigorous reaction. After addition of half of the slurry, the reaction mixture was acidified again by addition of H$_2$SO$_4$ (3 mol·L$^{-1}$, 10 mL). After complete addition, the reaction mixture was immediately basified by addition of NaOH and extracted with Et$_2$O. The combined organic phases were washed with brine, dried (Na$_2$SO$_4$) and concentrated to
Table 12.1: Solvent properties: index of refraction $n_D$, dielectric constant $\varepsilon$, viscosity $\eta$, heat capacity $C_p$, thermal diffusivity $\lambda_{th}$ in W·K$^{-1}$·m$^{-1}$, permittivity at infinite frequency $\varepsilon(\infty)$, dielectric relaxation time $\tau_D$, longitudinal relaxation time $\tau_L$, Stokes shift times$^{[133]}$. All values at 25°C.

<table>
<thead>
<tr>
<th>solvent</th>
<th>abbr.</th>
<th>$n_D$</th>
<th>$\varepsilon(0)$</th>
<th>$\eta$ / cP</th>
<th>$C_p$ / J·K$^{-1}$·mol$^{-1}$</th>
<th>$\lambda_{th}$ / ps</th>
<th>$\varepsilon(\infty)$ / ps</th>
<th>$\tau_D$ / ps</th>
<th>$\tau_L$ / ps</th>
<th>$\tau_e$ / ps</th>
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<tbody>
<tr>
<td>acetonitrile</td>
<td>MeCN</td>
<td>1.800</td>
<td>35.9</td>
<td>0.36</td>
<td>91.4</td>
<td>0.1877</td>
<td>3.51</td>
<td>3.2</td>
<td>0.2</td>
<td>0.15</td>
</tr>
<tr>
<td>propionitrile</td>
<td>EtCN</td>
<td>1.364</td>
<td>29.3</td>
<td>0.43</td>
<td>119.7</td>
<td>0.1677</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>butyronitrile</td>
<td>PrCN</td>
<td>1.382</td>
<td>24.8</td>
<td>0.55</td>
<td>155.8</td>
<td>0.1673</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>benzonitrile</td>
<td>PhCN</td>
<td>2.328</td>
<td>25.2</td>
<td>1.34</td>
<td>190.3</td>
<td>4.5</td>
<td>37.9</td>
<td>5</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>methanol</td>
<td>MeOH</td>
<td>1.760</td>
<td>32.7</td>
<td>0.59</td>
<td>81.5</td>
<td>0.1999</td>
<td>2.79</td>
<td>53</td>
<td>2.75</td>
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<td>ethanol</td>
<td>EtOH</td>
<td>1.359</td>
<td>24.6</td>
<td>1.19</td>
<td>112.3</td>
<td>0.168</td>
<td>2.69</td>
<td>143</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>1-propanol</td>
<td>1–PrOH</td>
<td>1.384</td>
<td>20.5</td>
<td>2.19</td>
<td>143.8</td>
<td>0.154</td>
<td>2.44</td>
<td>430</td>
<td>5.3</td>
<td>18</td>
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<tr>
<td>tetrahydrofuran</td>
<td>THF</td>
<td>1.405</td>
<td>7.58</td>
<td>0.46</td>
<td>123.9</td>
<td>0.1200</td>
<td>2.18</td>
<td>2.9</td>
<td>2.87</td>
<td>0.70</td>
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<tr>
<td>dichloromethane</td>
<td>CH$_2$Cl$_2$</td>
<td>2.020</td>
<td>8.93</td>
<td>0.41</td>
<td>177</td>
<td>0.1390</td>
<td>1.98</td>
<td>8</td>
<td>2.2</td>
<td>0.38</td>
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<td>chloroform</td>
<td>CHCl$_3$</td>
<td>2.082</td>
<td>4.79</td>
<td>0.57</td>
<td>117</td>
<td>0.1175</td>
<td>2.08</td>
<td>7.4</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>cyclohexane</td>
<td>cy</td>
<td>1.424</td>
<td>2.0</td>
<td>0.90</td>
<td>156</td>
<td>0.1234</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>water</td>
<td>H$_2$O</td>
<td>1.333</td>
<td>78.3</td>
<td>1.00</td>
<td>75.4</td>
<td>0.606</td>
<td>4.49</td>
<td>9.5</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>heavy water</td>
<td>D$_2$O</td>
<td>1.328</td>
<td>78.1</td>
<td>1.21</td>
<td>84.5</td>
<td>0.596</td>
<td>12.3</td>
<td>0.5</td>
<td></td>
<td></td>
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<tr>
<td>sulfuric acid</td>
<td>H$_2$SO$_4$</td>
<td>1.418</td>
<td>100</td>
<td>23.55</td>
<td>7.2</td>
<td>480</td>
<td>400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>orthoboric acid</td>
<td>H$_3$BO$_3$</td>
<td>1.385</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ionic liquid†</td>
<td>RTIL</td>
<td>1.481</td>
<td>27.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>120.40</td>
</tr>
</tbody>
</table>
provide the crude product as grayish white solid (920 mg). The product was oxidised with bromine to yield the radical cation, d4–WB•+.[6,597]

N,N,N’,N’-tetra-iso-propyl-p-phenylenediamine: Isopropyl iodide (21 mL) was added to a solution of freshly sublimated p-phenylenediamine (1.04 g) in dry toluene (6.0 mL). NaNH2 (1.75 g) was added in portions and the suspension was stirred for 2 h at ambient temperature and then refluxed for ca 2 d. 1H NMR of the reaction mixture indicated no change in conversion. Additional isopropyl iodide (21 ml) and NaNH2 (1.7 g) were added and the mixture was refluxed for another 24 h, without any change in conversion. For work-up, all volatiles were removed under reduced pressure, and the brown residue was filtrated over a pad of basic aluminium oxide and eluted with toluene. The brown residue obtained (1.46 g) after evaporation of the solvent was purified by kugelrohr distillation, yielding and off-white waxy solid (ca. 80% pure by 1H NMR). Attempts to recrystallise from toluene or ethanol failed. FC (basic aluminium oxide, toluene) yielded the pure (>95% 1H NMR) product as the second more polar fraction (indicated by the blue color of the radical cation on the TLC plate) as white crystalline solid (140 mg) unoptimized yield. The product was oxidised with bromine to yield the radical cation, TiPD•+. [6,597]

**Oxidation with sulfuric acid.** Several aromatic hydrocarbons can be transformed in the corresponding radical cation by strong acidic oxidising agents like concentrated sulfuric acid or trifluoroacetic acid/BF3 mixtures. In the former SO3 may act as the electron acceptor, in the latter and others presumably molecular oxygen.[432]
In such media, an equilibrium exists between the monocationic and the protonated form.\cite{418,599} Brodard et al.\cite{241} observed that the protonated form of tetracene spontaneously vanishes after some hours leaving a solution of the cationic form of tetracene only. Perylene as well dissolves first as the proton complex in H$_2$SO$_4$ if oxygen is present.\cite{432}

Concentrated sulfuric acid is, however, not a chemically well defined environment but rather a mixture of species including SO$_3^-$, HSO$_3^-$, H$_3$SO$_4^+$, HSO$_4^-$, H$_2$O, and H$_3$O$^+$. This makes an interpretation of solvent effects impossible.
13. Code

This section presents the code used for the data analysis, namely the mono– and biexponential function convoluted with a Gaussian function used for the analysis of the FU data (Conv1 and Conv2) and the implementation of the target analysis in IGOR (Wavemetrics) and Matlab (The Mathworks).

**Multi-exponential decay laws convoluted with a Gaussian**

Function Conv1(w,t) : FitFunc
Wave w
Variable t

//CurveFitDialog/ Independent Variables 1
//CurveFitDialog/ t
//CurveFitDialog/ Coefficients 5
//CurveFitDialog/ w[0] = t0
//CurveFitDialog/ w[1] = w
//CurveFitDialog/ w[3] = tau1
//CurveFitDialog/ w[4] = bg

variable result = 0
result = w[4]+0.5*w[2]*exp(-(t-w[0])/w[3])*exp(w[1]^2/(4*w[3]^2))
result *= (1+erf((t-w[0]-(w[1]^2/(2*w[3])))/w[1]))
return result
End

Function Conv2(w,t) : FitFunc
Wave w
Variable t

//CurveFitDialog/ Independent Variables 1
//CurveFitDialog/ t
//CurveFitDialog/ Coefficients 7
//CurveFitDialog/ w[0] = t0
//CurveFitDialog/ w[1] = w
//CurveFitDialog/ w[3] = tau1
//CurveFitDialog/ w[5] = tau2
//CurveFitDialog/ w[6] = y0

variable result1, result2
result1 = 0.5*w[2]*exp(-(t-w[0])/w[3])*exp(w[1]^2/(4*w[3]^2))
result1 *= (1+erf((t-w[0])-(w[1]^2/(2*w[3])))/w[1]))
result2 += 0.5*w[4]*exp(-(t-w[0])/w[5])*exp(w[1]^2/(4*w[5]^2))
result2 *= (1+erf((t-w[0])-(w[1]^2/(2*w[5])))/w[1]))
return w[6] + result1 + result2
End

Target analysis

Function AtoB(w,t) : FitFunc
Wave w
Variable t

//CurveFitDialog/ Independent Variables 1
//CurveFitDialog/ t
//CurveFitDialog/ Coefficients 3
//CurveFitDialog/ w[0] = A1
//CurveFitDialog/ w[1] = A2
//CurveFitDialog/ w[2] = k1

return w[0] * exp(-w[2]*t) + w[1] * (1-exp(-w[2]*t))
End

Function AuptoC(w,t) : FitFunc
Wave w
Variable t

//CurveFitDialog/ Independent Variables 1
//CurveFitDialog/ t
//CurveFitDialog/ Coefficients 5
//CurveFitDialog/ w[0] = A1
//CurveFitDialog/ w[1] = A2
//CurveFitDialog/ w[3] = k1
//CurveFitDialog/ w[4] = k2

variable concA, concB, concC
concA = exp(-w[3]*t);
concB = w[3]/(w[3]-w[4])*(exp(-w[4]*t)-exp(-w[3]*t))
concC = 1 - concB - concA;
End

Function AuptoD(w,t) : FitFunc
Wave w
Variable t

//CurveFitDialog/ Independent Variables 1
//CurveFitDialog/ t
//CurveFitDialog/ Coefficients 7
variable concA, concB, concC, concD
concA = exp(-w[4]*t);
concB = w[4]/(w[4]-w[5])*(exp(-w[5]*t)-concA)
concC = (w[4]-w[5])*exp(-w[6]*t) + (w[5]-w[6])*exp(-w[4]*t)
concC += (w[6]-w[4])*exp(-w[5]*t)
concC *= (w[4]*w[5])/((w[4]-w[5])*(w[4]-w[6])*(w[5]-w[6]))
concD = 1 - concA - concB - concC

return w[0]*concA+w[1]*concB+w[2]*concC+w[3]*concD
End

Implementation in Matlab[576,577]

• File E3.m
  function E3=E3(tau, time);
  E3=[exp(-time/tau(1)); exp(-time/tau(2)); exp(-time/tau(3))];

• File chi3.m
  function chi3=chi3(tau, data, time, FitOptions)
  E = E3(tau, time);
  A_rec = A*E'*inv(E*E')*E;
  chi3 = trace((A_rec-A)'*(A_rec-A));

• Find the minimum and calculate DADS, reconstructed spectra and residuals
  tau = fminsearch(@chi3, initial_guess, '', ...
                  data.spectra, data.time, FitOptions);
  E = E3(tau, data.time)
  DADS = data.spectra*E'*inv(E*E');
  A_rec = DADS * E;
  residuals = A - A_rec;
Part IV.

Appendix
The following Figures show the decay associated difference spectra (DADS) obtained in multi-exponential fits of the TA dynamics.

Figure 14.1.: DADS of Te\textsuperscript{2+} in H\textsubscript{2}SO\textsubscript{4} after 800 nm excitation.
Figure 14.2.: DADS of WB\(^{\ast \ast}\) in H\(_2\)O (top) and d4–WB\(^{\ast \ast}\) in MeCN (bottom) after 610 nm excitation
14. Decay associated difference spectra (DADS)

Figure 14.3.: DADS of TiPD$^+$ in MeCN after 610 nm (top) and WR$^+$ in MeOH after 550 nm excitation.
Figure 14.4.: DADS of MB$^{+}$ in MeCN after 700 nm (top) and 760 nm excitation (bottom).
Figure 14.5.: DADS of DMTPD\(\textsuperscript{++}\) in MeCN (top) and CH\(_2\)Cl\(_2\) (bottom) after 500 nm excitation.
Figure 14.6.: DADS of Pe in MeCN after 266 nm excitation (top) and of Pe$^{*+}$ in MeCN/Bu$_4$NPF$_6$ after 540 nm excitation (bottom).
Figure 14.7.: DADS of Pe$^{+\ddagger}$ in MeCN/Bu$_4$NPF$_6$ after 800 nm excitation (top) and in CH$_2$Cl$_2$/Bu$_4$NPF$_6$ after 540 nm excitation (bottom).
Figure 14.8.: DADS of Pe$^{•+}$ in H$_2$SO$_4$ after 540 nm excitation (top) and of Pe$^{•−}$ in MeCN after 800 nm excitation (bottom).
Figure 14.9.: DADS of TTF$^{\ddagger}$ after 580 nm excitation (top) and of MePTZ$^0$ in MeCN after 266 nm excitation (bottom).
Figure 14.10.: DADS of TH in MeCN after 266 nm excitation (top) and of TH$^+$ in H$_2$SO$_4$ after 540 nm excitation (bottom).
Figure 14.11.: DADS of $G^\bullet$ in MeCN (top) and MeOH (bottom) after 400 nm excitation.
Figure 14.12.: DADS of G in MeCN (top) and MeOH (bottom) after 400 nm excitation.
15. Abbreviations

List of abbreviations. See page 192 for solvents.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
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<tr>
<td>ΔA</td>
<td>absorbance difference</td>
</tr>
<tr>
<td>Φ_{flr}</td>
<td>fluorescence quantum yield</td>
</tr>
<tr>
<td>ar</td>
<td>aromatic</td>
</tr>
<tr>
<td>al</td>
<td>aliphatic</td>
</tr>
<tr>
<td>CE</td>
<td>counter electrode (auxiliary electrode)</td>
</tr>
<tr>
<td>CI</td>
<td>conical intersection</td>
</tr>
<tr>
<td>CNDO</td>
<td>complete neglect of differential overlap</td>
</tr>
<tr>
<td>d4–WB++</td>
<td>2,3,5,6-tetradutero-N,N,N',N'-tetramethyl-p-phenylenediamine</td>
</tr>
<tr>
<td>WR++</td>
<td>N,N',-dimethyl-p-phenylenediamine, Wurster’s red</td>
</tr>
<tr>
<td>DADS</td>
<td>decay associated difference spectrum</td>
</tr>
<tr>
<td>DAS</td>
<td>decay associated (amplitude) spectrum</td>
</tr>
<tr>
<td>EGL</td>
<td>energy gap law</td>
</tr>
<tr>
<td>ESA</td>
<td>excited state absorption</td>
</tr>
<tr>
<td>FC</td>
<td>Franck–Condon</td>
</tr>
<tr>
<td>FU</td>
<td>fluorescence up-conversion</td>
</tr>
<tr>
<td>GSR</td>
<td>ground state recovery</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>IC</td>
<td>internal conversion</td>
</tr>
<tr>
<td>IRF</td>
<td>instrument response function</td>
</tr>
<tr>
<td>IVR</td>
<td>intramolecular vibrational energy redistribution</td>
</tr>
<tr>
<td>i–Pr</td>
<td>2-propyl</td>
</tr>
<tr>
<td>k_{rad}</td>
<td>radiative rate constant</td>
</tr>
<tr>
<td>k_{nr}</td>
<td>non-radiative rate constant</td>
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<tr>
<td>kK</td>
<td>kilokayser, 1kK = 1000 cm⁻¹</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MB++</td>
<td>tris(4-bromophenyl)ammonium hexachloroantimonate</td>
</tr>
<tr>
<td>MePTZ</td>
<td>N-methylphenothiazine</td>
</tr>
<tr>
<td>MTHF</td>
<td>2-methyltetrahydrofuran</td>
</tr>
<tr>
<td>NIR</td>
<td>near infra red</td>
</tr>
<tr>
<td>OTTLE</td>
<td>optically transparent thin layer electrochemical cell</td>
</tr>
<tr>
<td>PAH</td>
<td>polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>Pe</td>
<td>perylene</td>
</tr>
<tr>
<td>PES</td>
<td>potential energy surface</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly-methylmethacrylat</td>
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<tr>
<td>RE</td>
<td>reference electrode</td>
</tr>
<tr>
<td>r.t.</td>
<td>room temperature</td>
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</table>
RTIL  room temperature ionic liquid
SADS  species associated difference spectra
SE  stimulated emission
SOMO  singly occupied molecular orbital
SS  steady–state
TA  transient absorption spectroscopy
TD–DFT  time dependent density functional theory
Te  tetracene
TG  transient grating spectroscopy
TH  thianthrene
THF  tetrahydrofuran
TiPD\textsuperscript{±}  N,N,N',N’–tetraisopropyl–p–phenylenediamine
TTF  tetraphthalfulvalene
UV  ultraviolet
VC  vibrational cooling
VER  vibrational Energy Relaxation
VET  vibrational Energy Transfer
VIS  visible light/spectral region
WB\textsuperscript{±}  N,N,N',N’–tetramethyl–p–phenylenediamine, Wurster’s blue
WE  working electrode
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16. Bibliography


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16. Bibliography


16. Bibliography


