A very short uranium-uranium bond: The predicted metastable U22+

GAGLIARDI, Laura, PYYKKÖ, Pekka, ROOS, Björn O.

Abstract
Quantum chemical calculations, based on multiconfigurational wave functions and including relativistic effects, show that the U22+ system has a large number of low-lying electronic states with S of 0 to 2 and ranging from zero to ten. These states share a very small bond length of about 2.30, compared to 2.43 in neutral U2. The Coulomb explosion to 2 U+ lowers the energy by only 1.6 eV and is separated by a broad barrier.

Reference

DOI : 10.1039/b505593h
A very short uranium–uranium bond: The predicted metastable $\text{U}_2^{2+}$

Laura Gagliardi, a,a Pekka Pyynkö b and Björn O. Roos c

a Dipartimento di Chimica Fisica “F. Accascina”, Università degli Studi di Palermo, Viale delle Scienze - Parco d’Orléans II, I-90128 Palermo, Italy. E-mail: laura.gagliardi@unipa.it
b Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 University of Helsinki, Finland
c Department of Theoretical Chemistry, Chemical Center, P.O.B. 124, S-221 00 Lund, Sweden

Received 21st April 2005, Accepted 6th May 2005
First published as an Advance Article on the web 13th May 2005

Quantum chemical calculations, based on multiconfigurational wave functions and including relativistic effects, show that the $\text{U}_2^{2+}$ system has a large number of low-lying electronic states with $S$ of 0 to 2 and $A$ ranging from zero to ten. These states share a very small bond length of about 2.30 Å, compared to 2.43 Å in neutral $\text{U}_2$. The Coulomb explosion to $\text{U}^+$ lowers the energy by only 1.6 eV and is separated by a broad barrier.

1. Introduction
Uranium metal has a high atomization energy of 533(8) kJ mol$^{-1}$ and an experimental dissociation energy of 218(21) kJ mol$^{-1}$ has been reported for the neutral diatomic $\text{U}_2$ molecule from mass-spectrometric measurements. A recent quantum chemical calculation on $\text{U}_2$ yielded a bond length of 2.43 Å and revealed a very complicated fivefold chemical bond with a total spin $S$ of 3 and a total orbital angular momentum $A$ of 11. This study took into account electron correlation using a multiconfigurational wave function and relativistic effects. (Earlier, more approximate calculations on neutral $\text{U}_2$ are quoted there.) This analysis is interesting, given the virtual absence of well-defined uranium–uranium, or more generally, actinide–actinide bonds, especially multiple bonds, in molecular inorganic or organometallic chemistry.

If two of the twelve valence electrons of $\text{U}_2$ are removed, some simplification of the electronic structure could be expected. Indeed, preliminary DFT or CAS calculations suggested for $\text{U}_2^{2+}$ a singlet, predominantly $(\sigma_u)^2(\pi_u)^2(\delta_u)^4$ state with bond lengths, as short as 2.15 Å.

On the experimental side it is interesting to note that a mass-spectrometric study using an Au–$\text{U}$ liquid-alloy ion source for uranium with 20% $^{235}\text{U}$ and 80% $^{238}\text{U}$ showed no fingerprint for the mixed diatomic dication with a total spin $S$ of 3 and a total orbital angular momentum $A$ of 11. This study took into account electron correlation using a multiconfigurational wave function and relativistic effects. ( Earlier, more approximate calculations on neutral $\text{U}_2$ are quoted there.) This analysis is interesting, given the virtual absence of well-defined uranium–uranium, or more generally, actinide–actinide bonds, especially multiple bonds, in molecular inorganic or organometallic chemistry.

If two of the twelve valence electrons of $\text{U}_2$ are removed, some simplification of the electronic structure could be expected. Indeed, preliminary DFT or CAS calculations suggested for $\text{U}_2^{2+}$ a singlet, predominantly $(\sigma_u)^2(\pi_u)^2(\delta_u)^4$ state with bond lengths, as short as 2.15 Å.

We report here the results of a study on the $\text{U}_2^{2+}$ species, at a comparable level as that used for $\text{U}_2$. No other earlier work seems to exist on $\text{U}_2^{2+}$.

2. Results and discussion
The spin-free potential energy curves around equilibrium for the lowest electronic states of $\text{U}_2^{2+}$ are reported in Fig. 1. The region near equilibrium has been enlarged (Fig. 2) in order to explore the various electronic states. The most stable spin-free electronic state was found to be a singlet state and to have a total orbital angular momentum, $A$, equal to 10 atomic units, (a $^1\text{N}_g$ state). The equilibrium bond distance is 2.30 Å without the inclusion of spin–orbit coupling and the harmonic vibrational frequency is 300 cm$^{-1}$. A triple-bond covalent radius of 1.18 Å has recently been proposed for uranium. For a triple $\text{U}$–$\text{U}$ bond this would give 2.36 Å, close enough to the calculated 2.30 Å.

Inspection of the wave function for the lowest electronic states reveals a triple bond, corresponding to the electron configuration $(\sigma_u)^2(\pi_u)^2$. The molecular orbitals are reported in Fig. 3. The $\sigma$ orbital is a hybrid comprising $7s$, 6$d$, and 5$f$ atomic orbitals and the $\pi$ orbital is mainly 6$d$ in character. The next four electrons, which were active in the calculations, occupy the $5f\delta$ and $5f\phi$ orbitals. They are essentially non-bonding in all the low-lying electronic states. Thus, the electronic structure corresponds to a triple bond plus two localized $5f$ electrons on each of the uranium ions. This is different from the neutral molecule $\text{U}_2$, where the 6$d$ orbitals take a more active part in the formation of the chemical bond. Ionization will stabilize $5f$ more than $6d$ and the weaker bond in $\text{U}_2^{2+}$ will favor the electronic configuration of the $\text{U}^+$ ion, which is $5f^27s^27p$. This explains the high angular momentum preferred by the non-bonding $5f$ electrons.

The total spin of the four unpaired electrons in the molecule can be 0, 1, or 2. With an angular momentum on each atom of 5, one obtains $A = 0, 5,$ or 10 in the molecule. Which of these
combinations will give the lowest energy, is difficult to predict and the calculations show that all combinations have low energy. The predicted ground state has \( S = 0 \) and \( A = 10 \). Thus the two atomic open shells add their local angular momenta, while the coupling between them is antiferromagnetic. In the neutral molecule on the other hand, a ferromagnetic coupling occurs between the open-shell electrons. This is due to the formation of two 6d one-electron bonds. Exchange stabilization then favors parallel spin for all the six open shell electrons. This mechanism does not work here, because all four open-shell electrons are localized, with one triplet-coupled pair of electrons on each atom. Antiferromagnetic coupling between the two atoms will then be favored because it leads to some additional, but weak binding.

In our previous study on neutral \( \text{U}_2^{3+} \) the inclusion of spin–orbit coupling did not have any effect on the equilibrium bond distance. We have thus not recalculated the equilibrium bond distance including spin–orbit coupling, but only estimated spin–orbit effects at the 2.328 Å interatomic distance. Inspection of Fig. 2 shows that at this bond distance the first spin-free excited state of \( \Sigma^+_g \) type lies 279 cm\(^{-1}\) above the ground state \( 1\Sigma^+_g \) and it is degenerate with the first triplet excited state. The first quintet state (triangle left in Fig. 2) lies 1682 cm\(^{-1}\) above the ground state. The inclusion of spin–orbit coupling gives a ground state \( \Omega = 0^+_g \), arising from the combination of a triplet, singlet and quintet state, all with \( A = 0 \).

The \( \text{U}_2^{2+} \) system is metastable and lies 1.59 eV higher in energy than two \( \text{U}^{3+} \) ions. Calculations for larger distances need an active space which is outside the limits of present technology because all valence electrons have to be active (see Method section for details). Studies of the curve-crossing region, including SO splitting are therefore not possible. A rough estimate for the curve-crossing from the ground-state singlet curve to the point-charge-like long-distance Coulomb explosion is shown in Fig. 4. It is high enough and far enough, not to form a likely danger for the metastability of the predicted \( \text{U}_2^{2+} \) species.

A potential future problem is the study of neutral molecules with a similar bonding system, a possible candidate being FUUF.

3. Method and details of the calculations

The quantum chemical calculations were performed using the software MOLCAS-6.0.\(^7\) The complete active space (CAS) SCF method\(^8\) was used to generate molecular orbitals and reference functions for subsequent multiconfigurational second order perturbation calculations of the dynamic correlation energy (CASPT2).\(^9\)\(^-\)\(^11\)

The choice of the active space is crucial for the method. The valence electronic configuration of the uranium atom is \( 5f^2(6d)^{10}(7s)^2 \). In the \( \text{U}_2 \) case there are thus twelve valence electrons available for bonding. It was shown\(^7\) that three normal electron pair bonds, involving six of the twelve valence electrons are formed by hybrid atomic orbitals dominated by 7s and 6d character. They were thus kept doubly occupied in the CASSCF calculations. The remaining six electrons were allowed to freely occupy the remaining 5f and 6d orbitals. Four electrons were allowed to occupy the same orbitals in \( \text{U}_2^{2+} \). Electronic states of singlet, triplet and quintet type were then calculated.

Relativistic all electron atomic basis sets of atomic natural orbital (ANO) type were used. A primitive set of 27\(e\)24\(p\)18\(d\)14\(f\)6\(g\)3\(h\) functions was contracted to 9\(s\)8\(p\)6\(d\)5\(f\)2\(g\)1\(h\). The relativistic effects which need to be included in the treatment of an atom as heavy as uranium were taken into account using the second-order Douglas–Kroll-Hess Hamiltonian. The scalar part of this Hamiltonian was used in the generation of the CASSCF wavefunction. Spin–orbit (SO) coupling was included by allowing the CASSCF wavefunctions to mix under the influence of the SO Hamiltonian. The method has been described in detail in a recent article.\(^12\)

Calculations were performed for a number of points around the equilibrium bond distance. The binding energy was estimated by a calculation on the uranium monocation, \( \text{U}^{2+} \), which was performed with the same basis set used for \( \text{U}_2^{2+} \) and with the valence orbitals active.

![Fig. 2](image)

An enlarged version of Fig. 1 for bond distances near equilibrium.

![Fig. 3](image)

The valence molecular orbitals forming the chemical bond in \( \text{U}_2^{2+} \). The orbital label is given below each orbital together with the number of electrons occupying this orbital or pair of orbitals in the case of degeneracy.

![Fig. 4](image)

A Morse-potential fit to the calculated ground-state potential curve and its crossing with an 1/\(R\) estimate for the Coulomb explosion to two \( \text{U}^{2+} \) ions. The dissociation limit is the abscissa.
Acknowledgements

This work was supported by Ministero dell’Iniziativa, dell’Università e della Ricerca, The Academy of Finland, grants 200903 and 206102, and the Swedish Foundation for Strategic Research (SSF).

References