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Reference

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Quantum Monte Carlo study of the ground state and low-lying excited states of the scandium dimer

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A large set of electronic states of scandium dimer has been calculated using high-level theoretical methods such as quantum diffusion Monte Carlo (DMC), complete active space perturbation theory as implemented in GAMESS-US, coupled-cluster singles, doubles, and triples, and density functional theory (DFT). The $\Sigma_u^+$ and $\Sigma_u^-$ states are calculated to be close in energy in all cases, but whereas DFT predicts the $\Sigma_u^+$ state to be the ground state by 0.08 eV, DMC and CASPT2 calculations predict the $\Sigma_u^-$ to be more stable by 0.17 and 0.16 eV, respectively. The experimental data available are in agreement with the calculated frequencies and dissociation energies of both states, and therefore we conclude that the correct ground state of scandium dimer is the $\Sigma_u^-$ state, which breaks with the assumption of a $\Sigma_u^+$ ground state for scandium dimer, believed throughout the past decades. © 2008 American Institute of Physics. [DOI: 10.1063/1.2920480]

I. INTRODUCTION

Scandium dimer is one of the least known first row transition metal dimers in spite of the numerous experimental and theoretical works carried out in order to determine the ground state and characterize its properties.1,2 A clear example of this is the absence of a sound experimental value for the bond length, although an empirical estimation was derived from Badger’s rule by Weisshaar, 2.29 Å, nearly two decades ago. Unfortunately, as discussed by the author,3 Badger’s rule does not work accurately for transition metals, and the error can be as large as ±0.35 Å.

The dissociation energy has also been a matter of discrepancy. It was first evaluated by Verhaegen et al.4 in 1964, using mass spectrometry techniques, $\approx 1.30$ eV. This value was then revised by Gingerich,5 who set it at 1.65 eV. A few years later, in 1984, based on resonance Raman experiments, Moskovits et al.6 measured a dissociation energy of 1.1 ± 0.2 eV. Finally, in 1989, Haslett et al.7 reevaluated the dissociation energy for a number transition metal dimers, including scandium. They obtained very different results depending on the experimental method employed, ranging from 1.13 eV using a thermodynamically determined third-law value, to 0.79 eV obtained from a LeRoy–Berstein calculation on resonance Raman data. These authors claimed that 0.79 eV should be understood as a lower bound instead of an accurate value. According to the experimental data available, it seems reasonable to assume that the dissociation energy ranges from 0.80 to 1.15 eV.

The vibrational frequency, however, is well accepted. It was measured by Moskovits et al.6 $\omega_2=238.91$ cm$^{-1}$.

The only experimental assignment of the electronic ground state of Sc$_2$ is based on the ESR measurements of Knight et al.,8 who proposed a $\Sigma_u^-$ ground state. However, this proposal did not come from direct observation, but was made in such a way to obtain agreement with the prediction of a previous theoretical calculations by Harris et al.9 They performed local spin density calculations on the first row transition metal dimers, and for Sc$_2$ they predicted a $\Sigma_u^-$ ground state with $1\sigma^2_11\sigma^1_1\pi^2_2\sigma^1_2$ configuration. The $\Sigma_u^-$ state was also claimed to be the ground state by Walch et al.10 on the basis of some CASSCF/CI(SD) calculations. According to their calculations, the $1\sigma^2_11\sigma^1_1\pi^2_2\sigma^1_2$ was indeed the dominant configuration of the $\Sigma_u^-$ state. This combination of experimental and theoretical works seemed to set on firm grounds that the ground state of the scandium dimer was a $\Sigma_u^-$ state, and not a $\Delta_g$ state as predicted by Busby et al.11

In a related work, Knight et al.12 experimentally determined that the ground electronic state of the dimer cation, Sc$_2^+$, was the $\Sigma_u^-$ state, which is in agreement with the removal of the electron from the $1\sigma_g$ of the $\Sigma_u^-$ ground state’s dominant configuration of Sc$_2$. Therefore, it became widely accepted that the ground state of scandium dimer was a $\Sigma_u^-$ state. However, a number of its properties, such as the bond length and dissociation energy, along with the nature of the low-lying excited states remained unclear. A handful of theoretical works have appeared in the literature reporting such properties. Harris et al.9 predicted a bond length of 2.70 Å and a harmonic frequency of 200 cm$^{-1}$. Åkeby et al. using high-level CASSCF and IC-ACPF calculations,13,14 predicted the bond length to be in the range of 2.5–2.8 Å, and a dissociation energy of 1.04 eV. Recall that in order to accurately estimate the dissociation energy, one must accurately reproduce the $2D^4F \rightarrow 4F$ transition energy of the scandium atom, known to be 1.44 eV, since the ground state dissociates to the $2D^4F$ asymptote. The dissociation energy calculated by Åkeby et al. is accurate enough and agrees with the experimental val-
ues of Moskovits and Haslett. The calculated frequencies of 261 cm\(^{-1}\) at the CASSCF level and 286 cm\(^{-1}\) at IC-ACPF level are in reasonably good agreement with the experimental value.

However, according to the CASSCF results, a \(^1\Pi_u\) state was found to be more stable than the \(^5\Sigma_u^+\) by 0.295 eV and a low-lying \(^3\Sigma_u^+\) excited state by 0.291 eV. The IC-ACPF method, on the other hand, predicted the \(^5\Sigma_u^+\) to be more stable than the \(^1\Pi_u\) by 0.391 eV. The authors attributed this discrepancy to the fact that CASSCF does not correctly describe the state ordering because of the inability to treat dynamical electron correlation, which was better accounted for by the IC-ACPF method. Suzuki et al. performed multireference configuration interaction calculations of the \(^5\Sigma_u^+\) state, predicting frequencies in very good agreement with experimental (230 versus 239 cm\(^{-1}\)) and a bond length of 2.8 Å in agreement with that of Åkeby et al. However, they severely underestimated the dissociation energy, predicting a value of 0.6 eV.

Several approximate density functionals have also been used to evaluate the properties of the scandium dimer. In general, these studies predicted bond lengths in the range of 2.55–2.70 Å and frequencies that are in good agreement with the corresponding experimental marks. The calculated ionization energy of Sc was also in agreement with the experimental value of 6.56 eV. However, the dissociation energy of Sc\(_2\), along with the \(^2D–^2F\) energy difference of the scandium atom, was in all cases badly underestimated. In those cases where different electronic states were studied, the predicted ground state was the \(^5\Sigma_u^+\) state. However, it is worth noting that Papai and Castro, using B3LYP, found an open shell \(^3\Sigma_u^+\), with an electronic configuration of \(1\sigma^4_2\,^3\sigma^2_1\,^1\pi^2_5\,(1\pi^2_5\,^2\sigma^1_1)\), only 0.22 eV higher in energy. Similarly, Gutsev et al. using BPW91, found at least three states of the scandium dimer thermodynamically stable, being the \(^5\Sigma_u^+\) described earlier by Papai and Castro the lowest-lying excited state only 0.18 eV higher than the \(^5\Sigma_u^+\) state, and interestingly, with very similar properties: \(R_1=2.61\) Å, \(\omega_c=256\) cm\(^{-1}\) for the triplet and \(R_1=2.63\) Å, \(\omega_c=241\) cm\(^{-1}\) for the quintet. In addition to these similarities, the electronic state resulting from the ionization of the 1\(\sigma^2_1\) orbital of the \(^5\Sigma_u^+\) and the \(^5\Sigma_u^+\) states is the same, i.e., the \(^5\Sigma_u^+\) state experimentally found by Knight et al. for the dimer cation.

The \(^5\Sigma_u^+\) triplet state was not considered in the high-level multiconfigurational calculations performed by Åkeby et al., and therefore the only information available on this state is the one provided by the DFT calculations. Given the very similar physical properties of this state with respect to those of the \(^5\Sigma_u^+\) assumed ground state and the small energy difference between the two states, it seems worthy to explore further this triplet state at higher levels of theory. Recall that \(^3\Sigma_u^+\) state is also compatible with the established experimental evidences pointing to the \(^2D–^2F\) dissociation asymptote and the formation of the \(^3\Sigma_u^+\) ground state of Sc\(_2\) by ejection of the electron from the 1\(\sigma^2_1\) orbital of the Sc\(_2\) dominant configuration’s ground state.

In this work, we will examine the properties of both the \(^5\Sigma_u^+\) and the \(^3\Sigma_u^+\) states of Sc\(_2\) and a selected number of other singlet, triplet, quintet, and septet states with the diffusion quantum Monte Carlo method, which is known to be very efficient and reliable to recover substantial large portions of the electron correlation.

Additionally, some properties of the scandium atom, such as the first excitation energy, i.e., the energy difference between the \(^2D\) and \(^4F\) states and the ionization energy (IE) has also been calculated and confronted to accurately measure experimental values. This constitutes a further check to the accuracy of the methods used throughout this study.

II. METHODS

Preliminary geometry optimizations and harmonic frequency calculations have been carried out at the B3LYP (Refs. 24 and 25) level of theory. This functional was combined with the triple zeta quality basis set, given by Schäfer et al. supplemented with one diffuse \(s\) function, two sets of \(p\) functions optimized by Wachters for the excited states, one set of diffuse pure angular momentum \(d\) function, optimized by Hay, and three sets of uncontracted pure angular momentum \(f\) functions, including both tight and diffuse exponents, as recommended by Ragavachari and Trucks. This basis set is denoted as TZVP+G(3df, 2p). This basis set has been claimed to be accurate for transition metals.

Quantum diffusion Monte Carlo (DMC) calculations were performed at the previously optimized geometries. For the DMC calculations, the trial wave functions used in this work are written as a product of a Slater determinant and a recently developed Jastrow factor, which is the sum of homogeneous, isotropic electron-electron terms \(u\), isotropic electron-nucleus terms \(\chi\) centered on the nuclei, and isotropic electron-electron-nucleus terms \(f\), also centered on the nuclei. The determinantal part was calculated at the UHF level of theory, combined with the relativistic Stuttgart pseudopotentials and basis sets (ECP10MD), motivated by their earlier successful performance in DMC calculations in a number of transition metal containing systems. The Jastrow factor, containing up to 51 parameters, was optimized using variance minimization techniques. The DMC method is one of the quantum Monte Carlo implementations that, together with the variational Monte Carlo method, is becoming widely used nowadays. Briefly, in DMC, the imaginary-time Schrödinger equation is used to evolve an ensemble of electronic configurations toward the ground state. Exact imaginary-time evolution would lead to the exact fermion ground-state wave function, provided it has a nonzero overlap with the initial fermion state. However, the stochastic evolution is never exact, and the solution converges to the bosonic ground state. The fermionic symmetry is maintained by the fixed-node approximation, in which the nodal surface of the wave function is constrained to be equal that of a guiding wave function. The fixed-node DMC energy provides a variational upper bound on the ground-state energy with an error that is second order in the error in the nodal surface.

CCSD(T) and CASPT2 calculations were carried out for the scandium’s ground and low-lying excited states and the lowest-lying two states of its dimer. For both the CCSD(T) and CASPT2 calculations, the TZVP-G(3df, 2p) basis set
described above were used. CCSD(T) is a coupled-cluster method, which uses single and double excitations from the Hartree–Fock determinant, and includes triple excitations noniteratively. Finally, CASPT2 applies second-order perturbation theory on a multiconfigurational wave function generated with the orbitals of the active space. For the scandium dimer calculations, the active space was chosen to be that shown in Fig. 1, which makes a total of six electrons in 18 molecular orbitals. The effect of the highest six orbitals has been observed to be negligible, and therefore a final active space of six electrons in 12 orbitals was chosen.

All the B3LYP, UHF, and CCSD(T) calculations were carried out using the GAUSSIAN03 package, the DMC calculations with the CASINO program and, CASPT2 calculations were carried out using GAMESS-US.

III. RESULTS

Before turning our attention to the characterization of the electronic structure and physical properties of the ground and low-lying states of the scandium dimer, we wish to estimate the energy gap and the ionization energy of the scandium atom, for which precise experimental data are available. This will serve as initial check to the accuracy of our selected theoretical procedures.

A. The 2D-4F energy gap and the IE of the scandium atom

Table I shows the relative energies between the lowest two electronic states of scandium atom (2D-4F) and the IE for the scandium atom calculated at the B3LYP, CCSDT, CASPT2, and DMC levels of theory along with their corresponding experimental data.

Experiments show the 4F state to be 1.43 eV higher in energy than the 2D state. As one may observe, B3LYP clearly yields incorrect results; it underestimates ΔE by about 0.5 eV. However, the B3LYP results presented here substantially improve earlier ones by Papai and Castro, who calculated the 4F only 0.60 eV above the 2D ground state. This improvement is due to the use of a larger basis set. Our calculated value of 0.94 eV for the 2D-4F energy gap constitutes a substantial improvement toward a better matching with the experimental mark. Remarkably, CCSD(T) calculations overestimate the experimental 2D-4F energy gap by ~0.17 eV. This failure can tentatively be ascribed to the multiconfigurational character of states investigated. Indeed, the T1 diagnostics of the 2D and 4F yield 0.026 and 0.019, respectively. The critical estimated value for the multiconfigurational character is 0.02. Multiconfiguration based methods, such as CASPT2, remarkably perform better. Thus, observe that the CASPT2 and DMC estimate for the scandi-

![Fig. 1. Scheme of the molecular orbitals included in the active space for the CASPT2 calculations.](image)
um’s $^2D$–$^2F$ energy gap are 1.39 eV and 1.52 eV, only 0.04 eV and 0.09 eV from the experimental mark, respectively. The experimental value for the IE was determined to be 6.56 eV.\textsuperscript{57} B3LYP exactly predicts this value, but this success must be ascribed to a lucky cancellation of errors rather than to a high accuracy. CCSD(T), on the other hand, understimates the IE by 0.22 eV, predicting a value of 6.34 eV. DMC and CASPT2 behave much better, with errors of about 0.1 eV.

Taking into account these results, we can conclude that DMC results are as confident as CASPT2 results and both accurately predict the calculated properties of scandium atom.

### B. Ground state and excited states of scandium dimer

We have characterized ten electron states of the scandium dimer. Namely, two septets, four quintets, three triplets, and four singlets. Table II shows the dominant electronic configuration of the considered states.

<table>
<thead>
<tr>
<th>State</th>
<th>Dominant Configuration</th>
<th>$R_e$</th>
<th>$\omega_e$</th>
<th>$\Delta E$</th>
<th>$D_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma_g^+$</td>
<td>$\sigma(4s)(3d)\pi^2(1)\delta^2(1)\sigma(4s)\pi^2(1)$</td>
<td>2.447</td>
<td>255.3</td>
<td>1.57 ± 0.01</td>
<td>…</td>
</tr>
<tr>
<td>$^3\Sigma_g^+$</td>
<td>$\sigma(4s)(3d)\pi^2(1)\delta^2(1)\pi(4s)\pi^2(1)$</td>
<td>2.311</td>
<td>314.4</td>
<td>2.46 ± 0.01</td>
<td>…</td>
</tr>
<tr>
<td>$^5\Sigma_u^-$</td>
<td>$\sigma(4s)(3d)\pi^2(1)\delta^2(1)\pi(4s)\pi^2(1)$</td>
<td>2.582</td>
<td>259.9</td>
<td>0.17 ± 0.01</td>
<td>0.93</td>
</tr>
<tr>
<td>$^3\Sigma_g^+$</td>
<td>$\sigma(4s)(3d)\pi^2(1)\delta^2(1)\pi(4s)\pi^2(1)$</td>
<td>2.363</td>
<td>280.5</td>
<td>0.86 ± 0.01</td>
<td>…</td>
</tr>
<tr>
<td>$^3\Sigma_u^+$</td>
<td>$\sigma(4s)(3d)\pi^2(1)\delta^2(1)\pi(4s)\pi^2(1)$</td>
<td>2.466</td>
<td>239.6</td>
<td>1.66 ± 0.01</td>
<td>…</td>
</tr>
<tr>
<td>$^3\Sigma_u^-$</td>
<td>$\sigma(4s)(3d)\pi^2(1)\delta^2(1)\pi(4s)\pi^2(1)$</td>
<td>2.451</td>
<td>268.7</td>
<td>1.94 ± 0.01</td>
<td>…</td>
</tr>
<tr>
<td>$^1\Sigma_u^-$</td>
<td>$\sigma(4s)(3d)\pi^2(1)\delta^2(1)\pi(4s)\pi^2(1)$</td>
<td>2.570</td>
<td>273.3</td>
<td>0.00 ± 0.01</td>
<td>1.10</td>
</tr>
<tr>
<td>$^3\Sigma_u^+$</td>
<td>$\sigma(4s)(3d)\pi^2(1)\delta^2(1)\pi(4s)\pi^2(1)$</td>
<td>2.356</td>
<td>320.2</td>
<td>2.55 ± 0.01</td>
<td>…</td>
</tr>
</tbody>
</table>

The next excited states appear to be the calculated singlets, followed by the rest of quintets, septets, and triplets.

The predicted ground state’s properties must correctly reproduce the well-established experimental values, which are a vibrational frequency of $\omega$ = 238.9 cm\(^{-1}\) (Ref. 6) and a dissociation energy $D_r$ = 0.79–1.13 eV.\textsuperscript{7} For bond lengths, direct measurements are not available, and the indirect extrapolation pointed out a bond length of 2.5 Å. The previously assumed ground state, the $^5\Sigma_u^-$ state, is calculated to have a vibrational frequency of 259.9 cm\(^{-1}\), a dissociation energy of 0.93 eV, and a bond length of 2.58 Å, which are in agreement with the experimental values. However, the $^3\Sigma_u^-$ candidate also fulfills these requirements, being the frequency 273.3 cm\(^{-1}\), the dissociation energy 1.1 eV, and a bond length of 2.57 Å.

In order to further discriminate between both states and check the DMC results, CCSD(T) and CASPT2 calculations have been carried out on the two states under consideration, namely, $^3\Sigma_u^-$ and $^5\Sigma_u^-$. CCSD(T) calculations have been carried out with the T1 diagnostic\textsuperscript{55} to check if a multiconfigurational treatment is necessary. The energy difference between these two states is decreased to 0.03 eV at this level of theory, but for both states, T1 ∼ 0.04, which mean that multiconfigurational calculations are required for the proper description of these states. Therefore, CASPT2 geometry optimizations have been carried out for both states, and the predicted equilibrium structures are very similar to the B3LYP ones, as one can note in Fig. 2. The CASPT2 results confirm the DMC prediction that the $^3\Sigma_u^-$ state is more stable by 0.16 eV. According to these results, we predict the $^3\Sigma_u^-$ state to be the ground state of scandium dimer, and not the $^5\Sigma_u^-$ as was previously believed.

### IV. CONCLUSIONS

A large set of different electronic states of scandium dimer has been studied using B3LYP, DMC, CCSD(T), and CASPT2. B3LYP predicted a $^5\Sigma_u^-$ state as the ground state, in agreement with previous studies. However, high-level methods such as DMC and CASPT2 predict a $^3\Sigma_u^-$ to be more stable than the $^5\Sigma_u^-$ by around 0.15 eV. This triplet state is an
open shell triplet, with very similar bond length, frequency, and dissociation energy to the $^3\Sigma_g^+$ state. Both states have the same orbital occupancy, the only difference is that while in the quintet state the $\sigma_u$ orbital has an electron with alpha spin, in the triplet this electron has a beta spin. Our calculations show that the ground state of scandium dimer is the $^3\Sigma_g^+$ state, and not the $^3\Sigma_u^+$ state as was thought. New experiments would be interesting in order to confirm our prediction.

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