A density functional study of Sc$_2$ and Sc$_3$

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Abstract

Density functional theory, using a gradient-corrected exchange–correlation functional, has been applied to determine the equilibrium properties of various spin states of the Sc$_2$ and Sc$_3$ molecules. The ground state of Sc$_2$ is predicted to be $^5\Sigma_u^-$ with $R_e = 2.64$ Å, $\omega = 222$ cm$^{-1}$ and $D_e = 0.92$ eV, followed by the $^3\Sigma_u^-$ and $^1\Sigma_g^+$ states. The equilibrium structure of the $^2A_1'$ ground state of Sc$_3$ is found to have $D_{3h}$ symmetry with a bond length of 2.83 Å. The calculated harmonic frequencies are 272 cm$^{-1}$ ($\alpha''$) and 153 cm$^{-1}$ ($\epsilon'$), while the atomization energy is 2.49 eV. Several low-lying excited states of Sc$_3$ are found to lie about 0.2 eV above the ground state. The predicted ground states of Sc$_2$ and Sc$_3$ and their vibrational frequencies are in accordance with the findings of ESR and resonance Raman studies. © 1997 Elsevier Science B.V.

1. Introduction

It is now well understood that the adequate treatment of both dynamical and near degeneracy correlation is absolutely required to provide reliable theoretical predictions for the physical properties of small transition metal clusters [1]. Among post-Hartree–Fock correlation techniques, multireference configuration interaction (MRCI) calculations have proved to be the most successful. Numerous transition metal dimers and trimers have been investigated using the complete active space multiconfiguration self-consistent field (CAS-MCSCF) method followed by MRCI calculations, and several equilibrium structures corresponding to different electronic states have been located for these systems (see, for instance, recent works by Balasubramanian and co-workers [2–4] and references therein). These calculations, however, often include millions of configuration spin functions and the cost of the computations becomes prohibitive for larger clusters. Given its single determinantal formalism and the availability of gradient-corrected exchange–correlation functionals, density functional theory (DFT) offers a feasible alternative in this field. DFT has already been applied to the late transition metal clusters [5–8], and the calculated structural, electronic and magnetic properties have generally been in line with experiment.

In this Letter we report the results for the simplest transition metal dimer and trimer, the Sc$_2$ and Sc$_3$ molecules, obtained by using a level of DFT that has recently been applied to several transition metal- monoligand systems [9]. “Simple” here refers only to the number of valence electrons, since the electronic structure of these clusters is far from simple (see later in the discussion). Both Sc$_2$ and Sc$_3$ are relatively well characterized experimentally: their ground states have been determined from ESR measurements [10,11], their vibrational frequencies are known from resonance Raman experiments [12], and for Sc$_2$ the disso-
cation energy has also been estimated [13,14]. Theoretically, a number of studies have been reported on Sc$_2$ [1,15–19], of which the investigations by Åkeby et al. [18,19] represent the most demanding works. These authors first examined the effect of core (3p) correlation on the ground state properties of Sc$_2$ using an MRCI treatment with large basis sets [18] and then calculated the equilibrium properties for several low-lying excited states using the average coupled pair functional (ACPF) method [19]. The Sc$_3$ molecule, on the other hand, has been the subject of only a few theoretical studies [20,21]. Walch and Bauschlicher carried out CASSCF calculations followed by contracted CI calculations and found that the ground state of Sc$_3$ is $^2A_2''$, which is different from what was suggested in the ESR study [11]. Although their calculated equilibrium geometry for the $^2A_2''$ state was close to the experimentally deduced equilateral triangle, their predicted symmetric stretching frequency did not agree with the Raman data.

In our work we have determined the lowest lying electronic states for various spin multiplicities ($2S + 1 = 1, 3$ and $5$) of Sc$_2$ and for doublet and quartet Sc$_3$. We have calculated the equilibrium geometries, vibrational frequencies and dissociation energies for each state and made a comparison with experiment and previous theoretical results. We will show in this Letter that the results obtained with the present functional and basis set are all consistent with the available experimental data. The nature of the bonding in Sc$_2$ and Sc$_3$ will also be discussed.

2. Computational method

The calculations were carried out using the Gaussian94/DFT [22] software package. All properties of the investigated clusters were obtained at the nonlocal level of theory, using the BP86 exchange–correlation functional, i.e. using Becke’s [23] nonlocal corrections to the local spin density and Perdew’s [24] gradient-corrected correlation functional. The all-electron basis set developed by Godbout et al. [25] was used for the Sc atom with a (63321/5211/41) contraction of Cartesian Gaussian functions.

The integration grid was the default fine grid in the program, which includes about 7000 grid points per atom. The geometries were optimized using the Berny algorithm [22] from various arbitrarily chosen initial geometries. The harmonic vibrational frequencies were obtained from the analytical second energy derivatives. The total energies for the equilibrium geometries of the investigated systems are given in Table 1.

3. Results and discussion

3.1. The Sc atom

The key element in the theoretical determination of bond dissociation energies for transition metal clusters is the accurate description of the transition metal atomic states, in particular, the $s^2d^n ightarrow s^1d^{n+1}$ transfer energies. It has been well documented in previous systematic studies that in DFT calculations the atomic configuration with higher d-occupations ($s^1d^{n+1}$) is always favoured energetically with respect to $s^2d^n$. The mean error for the $s^2d^n ightarrow s^1d^{n+1}$ separation is about 1 eV when using the local spin density approximation [1], which can be reduced to approximately 0.5 eV with gradient-corrected functionals [26,27]. The calculated adiabatic corrected dissociation energies may inherit this error as well if the cluster dissociates into fragments including excited state atom(s). However, as shown for several transition metal-ligand systems [28,29], one can still get reliable dissociation energies if they are calculated with respect to the proper asymptotic limit and corrected with the experimental

<table>
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<tr>
<th>State Orbit occupation</th>
<th>Total energy ($E_h$)</th>
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<tr>
<td>Sc $^2D$ $s^2d^1$</td>
<td>-760.5940</td>
</tr>
<tr>
<td>$^4F$ $s^1d^2$</td>
<td>-760.5682</td>
</tr>
<tr>
<td>Sc$_2$ $^1\Sigma^+_u$</td>
<td>-1521.2297</td>
</tr>
<tr>
<td>$^1\Sigma^+_g$</td>
<td>-1521.2367</td>
</tr>
<tr>
<td>$^3\Pi$</td>
<td>-1521.2204</td>
</tr>
<tr>
<td>Sc$<em>3$ $^2A</em>{1g}$</td>
<td>-2281.9197</td>
</tr>
<tr>
<td>$^2A_{2g}$</td>
<td>-2281.9116</td>
</tr>
<tr>
<td>$^2B_{2g}$</td>
<td>-2281.9139</td>
</tr>
<tr>
<td>$^4B_1$</td>
<td>-2281.9133</td>
</tr>
<tr>
<td>$^4B_2$</td>
<td>-2281.9118</td>
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</table>
In order to estimate the error at the present level of theory, we have calculated the total energies of the 2D ground state Sc atom arising from the s^2d^1 configuration and the lowest lying state (4F) derived from the s^1d^2 configuration. Nonspherical charge densities, i.e. integer occupation numbers, were used in these calculations, and for each configuration we considered only the pure state determinant corresponding to the maximal \( M_L \) quantum number: \( M_L = 2 \) for s^2d^1 (2D) and \( M_L = 3 \) for s^1d^2 (4F), i.e. the \( d_{xy} \) orbital was occupied in the former, while \( d_{xy} \) and \( d_{xz} \) were occupied with parallel spins in the later case.

From Table 1 we get the s^2d^1 \( \rightarrow \) s^1d^2 excitation energy to be 0.70 eV. Since the experimental splitting is 1.33 eV [30], the present method underestimates the s^2d^1 \( \rightarrow \) s^1d^2 excitation energy by 0.63 eV. This error, which is remarkably close to those found with two other gradient-corrected functionals by Kutzler and Painter (0.61 eV) [26] and Russo et al. (0.64 eV) [27], will be taken into account to correct the calculated dissociation energies.

### 3.2. The Sc\(_2\) dimer

Our calculations show that the lowest singlet, triplet and quintet states for Sc\(_2\) are \( ^1\Sigma_g^+ \), \( ^3\Sigma_u^- \) and \( ^5\Sigma_u^- \) arising from the \( 1\sigma_g^2 \pi_u^4 \), \( 1\sigma_g^2 \pi_u^2 \tau_u^{2(1)} \) \( 2\sigma_g^{1(1)} \) \( 1\sigma_u^{1(1)} \) and \( 1\sigma_g^2 \pi_u^{2(1)} \) \( 2\sigma_g^{1(1)} \) \( 1\sigma_u^{1(1)} \) electron configurations, respectively. The predicted equilibrium properties for these states are given in Table 2 and the energies and occupations of the Kohn-Sham orbitals are depicted in Fig. 1.

In line with the results of the matrix isolation ESR study by Knight et al. [10], the ground state of the Sc\(_2\) molecule is predicted to be \( ^3\Sigma_u^- \). Based on the calculated dissociation energies the \( ^3\Sigma_u^- \) and \( ^1\Sigma_g^+ \) states lie 0.22 and 1.04 eV higher than the ground state. Note that the same ordering is obtained if the total energies of these states are compared; however, the energy separation between the singlet and the higher spin states is far smaller in this case. Although we have not derived full potential energy curves for these states, the electron configuration of the Sc atoms (Table 2), the nature of individual molecular orbitals (see later in this section), as well as the calculated bond orders (3.0, 2.2 and 2.3 for the singlet, triplet and quintet states, respectively) suggest that the \( ^1\Sigma_g^+ \) state dissociates to two excited state Sc atoms (4F-+4F), while the other two states correlate to mixed asymptotes (2D-+4F).

The experimental dissociation energy of Sc\(_2\) was first determined to be 1.13±0.2 eV using a thermodynamical third-law method [13], which was later modified to 1.03 eV based on an improved Sc\(_2\) partition function derived by Åkeby and Pettersson [19]. A different method, the LeRoy-Bernstein analysis of resonance Raman data, gave a much lower value \( (D_e = 0.79 \text{ eV}) \) for the Sc\(_2\) dissociation energy [14], but as pointed out by the authors, this should be considered as a lower bound rather than an accurate value. The present method gives \( D_e = 0.92 \text{ eV} \), which is slightly lower than the modified third-law value, but is still within the error bar of the experiment. The calculated dissociation energy also compares reasonably well with the best ACPF estimate of Åkeby et al. [18] which is 0.77 eV. The observed vibrational frequency (238.9 cm\(^{-1}\)) is fairly well reproduced also, getting \( \omega_e = 222 \text{ cm}^{-1} \) for the ground state Sc\(_2\).

As already noted in previous studies [16,17], the bonding in \( ^3\Sigma_u^- \) can be described as a single two-electron \( \sigma \) bond due to the bonding overlap of 4s orbitals \( (1\sigma_g) \) combined with three one-electron d–d...
Table 2
Calculated properties for various states of Sc2

| State      | Dissociation asymptote | \( R_e (\text{Å}) \) | \( \omega_e \text{ (cm}^{-1}\) | \( D_e \text{ (eV)} \) | Atomic populations  \\
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<tr>
<td>( ^1\Sigma_g^+ )</td>
<td>( \text{Sc(4F)}^1 + \text{Sc(4F)}^1 )</td>
<td>2.308</td>
<td>324</td>
<td>-0.12 (2.54)</td>
<td>4s10d8s3d19s1d4p0.11</td>
</tr>
<tr>
<td>( ^3\Sigma_u^- )</td>
<td>( \text{Sc(4F)}^1 + \text{Sc(2D)}^1 )</td>
<td>2.642</td>
<td>265</td>
<td>0.70 (2.03)</td>
<td>4s11d10d13d4p0.23</td>
</tr>
<tr>
<td>( ^5\Sigma_u^- )</td>
<td>( \text{Sc(4F)}^1 + \text{Sc(2D)}^1 )</td>
<td>2.635</td>
<td>222</td>
<td>0.92 (2.25)</td>
<td>4s13d3s1d4p0.19</td>
</tr>
</tbody>
</table>

\( a \) Dissociation energies calculated with respect to the dissociation asymptotes and corrected with the experimental \( s^2d^1 \rightarrow s^1d^2 \) splitting (1.33 eV). The uncorrected values are given in parentheses.

\( b \) From gross Mulliken populations.

The \(^3\Sigma_u^-\) state can be derived from the ground state by flipping the spin of the \( 1\sigma_u \) electron. It appears that the loss of the s–d exchange energy has only a minor effect on the molecular properties. The \(^3\Sigma_u^-\) state is only 0.12 eV less stable than the ground state and its \( R_e \) and \( \omega_e \) are quite similar to those of the \(^3\Sigma_g^-\) state.

It is interesting to mention that none of the previous studies predict \(^3\Sigma_u^-\) to be the lowest triplet state. For instance, Åkeby and Pettersson [19] found the \(^3\Sigma_g^-\) \((1\sigma_g^2 1\sigma_u^2 1\pi_u^2 2(11))\) state to be the closest to the \(^3\Sigma_u^-\) state, although they point out that they did not intend to give a complete coverage of the excited states. We predict the \(^3\Sigma_u^-\) state to lie 0.44 eV above the \(^3\Sigma_u^-\) state with \( R_e = 2.99 \text{ Å} \) and \( \omega_e = 197 \text{ cm}^{-1} \), however, it is likely that in the present approach, the \(^3\Sigma_u^-\) state is overestimated with respect to \(^3\Sigma_g^-\), because we find a significant quintet contamination in the \(^3\Sigma_u^-\) state \( (\langle S^2 \rangle = 3.05)\), while the \(^3\Sigma_g^-\) state is calculated to be a pure triplet \( (\langle S^2 \rangle = 2.03)\).

The nature of bonding in the \(^1\Sigma_g^+\) state is very different from that in the higher spin states. As seen from Fig. 1, the bonding involves one \( \sigma \) bond \((1\sigma_g)\) and two \( \pi \) bonds \((1\pi_u)\) formed by spin-pairing of the two excited state \( s^1d^2 \) \( (4F) \) Sc atoms. Because of the lack of \( \sigma \)-repulsion in this state, the two Sc atoms can get so close that the bonding overlap between the \( 3d\pi \) orbitals becomes important. Consequently, the equilibrium bond length of \(^1\Sigma_g^+\) is far shorter and the vibrational frequency is higher than those of the \(^3\Sigma_u^-\) and \(^5\Sigma_u^-\) states. In spite of the fact that this state is strongly bound relative to the \( ^4\text{F} + ^4\text{F} \) dissociation asymptote, it is about 1 eV less stable than the ground state molecule, and it is actually unbound with respect to the ground state Sc atoms. Another \(^1\Sigma_g^+\) state of Sc2 can be derived from the \(^2\text{D} + ^2\text{D}\) asymptote, but as shown in previous works [16,19], this state has a large \( R_e \) and a shallow potential with low \( \omega_e \). The \(^1\Sigma_g^+\) state arising from the two \( ^4\text{F} \) state Sc atoms has been investigated by Jeung [17]. Our calculated \( R_e \) and \( \omega_e \) are in between his MRCI results obtained without and with Davidson correction.

3.3. The Sc3 trimer

We have carried out geometry optimizations for various doublet and quartet states of Sc3. The calculated properties for these states are given in Table 3.

In contrast to the CASSCF/CCI results [20,21], we find the \(^2A_1\) state to be the ground state. The \(^2A_2''\) and \(^2E\) states lie about 0.2 eV higher in energy. The \(^2A_1\) and \(^2A_2''\) states have \( D_{3h} \) equilibrium structure, whereas the \(^2E\) state undergoes Jahn–Teller distortion and splits into two components \((^2B_2 \text{ and } ^2A_1)\). The equilibrium geometry of the \(^2B_2\) component stays...
close to an equilateral triangle (with an apex angle of 57.1°) and the Jahn–Teller stabilization energy is only 0.08 eV. For the \(^2A_1\) component we were unable to optimize the geometry, because the \(^2A_1\) excited state always collapsed to the ground state in the SCF procedure. The quartet electronic states (\(^4B_1\) and \(^4B_2\)) have also been found to lie about 0.2 eV above the ground state. They both have a \(C_2v\) structure, but only a slight distortion from the equilateral triangle structure is obtained for the \(^4B_1\) state.

The equilibrium Sc–Sc bond length in the ground state molecule is 2.83 Å. For the \(^2A_2''\) state, this distance is calculated to be 2.86 Å, which is approximately 0.2 Å shorter than that obtained by Walch and Bauschlicher for the same state [20]. About the same difference in the DFT and CASSCF/CCI bond lengths are seen for the \(^2E'\) state as well. We find that the lowest lying quartet state (\(^4B_1\)) has an 0.07 Å longer, while the \(^4B_2\) state has an 0.07 Å shorter \(R_e\) than the ground state.

The calculated vibrational frequencies for the symmetric and the degenerate stretching-bending modes of the ground state \(Sc_3\) are 272 and 153 cm\(^{-1}\). These are in good agreement with those observed in the resonance Raman study [12], but in spite of this agreement, we can not definitely conclude that the two bands observed at 248 and 150 cm\(^{-1}\) in the Raman spectra are due to the \(^2A_1'\) state \(Sc_3\). Although the assignment to the \(^2B_2\) and \(^4B_2\) states can be ruled out (the resonance Raman experiments suggest a \(D_{3h}\) structure with degenerate low frequency modes), the predicted frequencies for the \(^2A_2''\) and \(^4B_1\) states also match quite closely with the observed data. We also note that our calculated frequency for the symmetric stretching mode of the \(^2A_2''\) state (255 cm\(^{-1}\)) is much lower than that predicted by Walch and Bauschlicher (513 cm\(^{-1}\)) [20].

The electron configuration of the Sc atoms in the ground state of \(Sc_3\) is \(4s^{1.19}3d^{1.50}4p^{0.31}\), indicating that similarly to the ground state \(Sc_2\) molecule, the \(^2A_1'\) state \(Sc_3\) dissociates to mixed state atoms. The low population of the \(4s\) orbitals and the nature of the bonding in \(Sc_3\) (spin paired \(d\) electrons) suggest that the ground state trimer correlates to an \(sd^2\) \((4F)\) Sc atom and \(5\Sigma_u^+ Sc_2\) molecule, i.e. it is derived from two excited state and one ground state Sc atoms (\(2^4F+2^D\)). Assuming this dissociation path, the atomization energy of \(Sc_3\) is calculated to be 2.49 eV. Thus we find that \(Sc_3\) is thermodynamically far more stable than was predicted in the previous theoretical study [20], in which the ground state of \(Sc_3\) was found to be bound by about 1.0 eV with respect to the ground state Sc atoms. Since the atomic electron configurations in the investigated excited states are similar to that in the ground state molecule, they can probably be derived from the same \((2^4F+2^D)\) atomic asymptotes. Consequently, the stability order for the states considered here is the same as obtained from the total energies.
4. Concluding remarks

The main goal of the present work was to provide DFT predictions for the ground states and equilibrium properties of Sc$_2$ and Sc$_3$ and compare them with available experimental data. Although the presented results are encouraging, much more work must be done before general conclusions can be drawn about the applicability of the methodology for the family of transition metal clusters. In this testing phase, when other functionals and basis sets ought to be considered on trial, perhaps the greatest challenge concerns the calculation of reliable dissociation energies, for which not only technical, but also conceptual problems arising for open shell systems in DFT have to be overcome [32-34]. The fact that different formally degenerate pure state single determinants belonging to the same atomic state yield total energies that differ by tenths of an eV (see Ref. [26]) means that the calculated atomic excitation energies are uncertain within this energy interval. On the other hand, we also saw that the empirical corrections applied in the calculation of dissociation energies bring the predicted values reasonably close to experiment and alter the relative stability of states with different dissociation asymptotes. It is therefore recommended to use the corrected dissociation energies to establish the relative ordering in the stability of close lying states rather than compare their total energies.

Acknowledgements

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