The Sc$_2$ dimer revisited

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Thirty two states of the homonuclear neutral diatomic Sc$_2$ molecule have been studied by multireference methods using basis sets of quadruple quality. For all 30 states resulting from the ground state Sc atoms, Sc(2D$_g$)+Sc(2D$_g$), and two out of 80, X $^5\Sigma_u^-$ and 1 $^3\Sigma_u^-$, issued from the first excited channel Sc(2D$_g$)+Sc(a $^4$F$_g$), we have constructed full potential energy curves and extracted the standard spectroscopic parameters. With the exception of X $^5\Sigma_u^-$ and 1 $^3\Sigma_u^-$ which are covalently bound, the 30 states related to the ground state Sc atoms are of van der Waals nature with interaction energies of 3–5 kcal/mol at distances of 7–7.5 bohr. For the X $^5\Sigma_u^-$ state the proposed D$_g$ value is 48 kcal/mol, with respect to the adiabatic fragments and with the 1 $^3\Sigma_u^-$ state just 380 cm$^{-1}$ above it. © 2010 American Institute of Physics. [doi:10.1063/1.3290951]

I. INTRODUCTION

The scandium molecule Sc$_2$ is the simplest of all first row transition metal neutral diatomics being a six “valence” electron system. This simplicity, however, is rather deceiving given the fact that after a time period of 45 years of both experimental and theoretical work, even its ground state is not known with certainty (vide infra).

The heart of the problem is the very large number of molecular [2s$^2$1$\Delta_u^-$] states, the result of low-lying high spin and orbital angular momentum atomic Sc terms. For instance, upon the interaction of Sc(2D$_g$;4s$^2$3d$^1$) + Sc(2D$_g$;4s$^2$3d$^1$), a $^4$F$_g$ (4s$^2$3d$^2$), a $^2$F$_g$ (4s$^2$3d$^2$), z $^2$F$_u$ (4s$^4$4p$^3$3d$^1$), where a $^4$F$_g$, a $^2$F$_g$, and z $^2$F$_u$ are the first three excited states of Sc located at 1.427, 1.846, and 1.956 eV (M$_J$ averaged) above the $^2$D$_g$ term, respectively, a total of 270 molecular states are realizable.

Sc(2D$_g$;4s$^2$3d$^1$) + Sc(2D$_g$;4s$^2$3d$^1$) →
(1$\Sigma_u^+$[3], 1$\Sigma_u^-$[2], 1$\Pi_u^+$[2], 1$\Pi_u^-$[2], 1$\Delta_u^-$[2], 1$\Delta_u^+$[2], 1$\Phi_u$, 1$\Gamma_u$, 3$\Sigma_u^+$[3], 3$\Sigma_u^-$[2], 3$\Pi_u^+$[2],
3$\Pi_u^-$[2], 3$\Delta_u^-$[2], 1$\Delta_u^+$[2], 1$\Phi_u$, 3$\Phi_u$, 3$\Phi_u$, 3$\Gamma_u$) (30 states),

Sc(2D$_g$;4s$^2$3d$^1$) + Sc(a $^4$F$_g$;4s$^1$3d$^2$) →
(3$\Sigma_u^+$[3], 3$\Sigma_u^-$[3], 3$\Pi_u^+$[5], 3$\Delta_u^-$[4],
3$\Phi_u$, 3$\Gamma_u$, 3$\Phi_u$, 3$\Phi_u$, 3$\Gamma_u$) (80 states),
10.” Nevertheless the absolute entropy formula used to deduce $D_0^0$ (Ref. 2), in addition to the measured parameters pertaining to this spectroscopic thermochemical method, requires the bond length and the logarithms of the electronic and vibrational partition functions ($\ln Q_e$, $\ln Q_v$) of the diatomic species at the temperature of the experiment; see, for instance, Ref. 5. For Sc$_2$, in particular, Verhaegen et al.\textsuperscript{2} assumed a vibrational frequency of 230 cm$^{-1}$ from which a $r_e=2.70$ Å was inferred through Badger’s rule,\textsuperscript{6} turned out to be very reasonable (see below). On the contrary, the adopted “effective quantum weight of 5” for the partition functions\textsuperscript{2} should be significantly larger considering that the experiment was done at 2000 K. Because the partition functions enter the $D_0$ formula with a negative sign, an error by +1 in the $\ln Q_e$ function reduces the binding energy by RT = 4 kcal/mol. This means that the binding energy of Sc$_2$ (with respect to the ground state atoms) should be significantly smaller than 38.0 kcal/mol. In an analysis along the lines above of the Verhaegen et al.\textsuperscript{2} data by Das,\textsuperscript{7} who performed ab initio calculations on Sc$_2$, he suggests a correction to the binding energy of about −24 kcal/mol which would bring the $D_0^0=38.0$ kcal/mol to about 14 kcal/mol. The upshot of the above discussion is that the experimental binding energy of Sc$_2$ is, at least, disputable.

Eight years later Cooper et al.\textsuperscript{8} based on extended Hückel calculations predicted a $5\Sigma_g^+$ ground state with $D_e=1.25$ eV (=28.8 kcal/mol) at $r_e=2.20$ Å and $\omega_e=250$ cm$^{-1}$.

In 1976 the first optical spectrum of Sc$_2$ in frozen Ar matrices was observed, interpreted by the help of extended Hückel calculations and alluding to a ground state of $5\Delta_g$ symmetry.\textsuperscript{9}

In the first density functional theory (DFT)-local spin density approximation (LSDA) study of Sc$_2$ (and all 3d transition metal homonuclear diatomics), Harris and Jones\textsuperscript{10} calculated two states of $3\Sigma_g^-$ ($D_e=1.80$ eV, $r_e=2.70$ Å, $\omega_e=200$ cm$^{-1}$) and $3\Sigma_u^+$ ($D_e=1.00$ eV, $r_e=3.25$ Å, $\omega_e=235$ cm$^{-1}$) symmetry. They obtained $3\Sigma_u^+$ as the lowest state but finally proposed that the ground state is rather $3\Sigma_g^-$ because of a possible overestimation of the binding energy of the $3\Sigma_g^-$ state.

Based on the basis of multiconfiguration self-consistent field (MCSCF)/[6s6p3d2f] ab initio calculations, the first on Sc$_2$, Wood et al.\textsuperscript{11} reported a $3\Sigma_g^-$ ground state with $D_e=6.9$ kcal/mol with respect to Sc(2D$_g$)+Sc($^4$F$_g$) and $r_e=2.57$ Å. Additional correlation energy obtained by a limited CI gave $D_e=26.1$ (12.7) kcal/mol with respect to Sc(2D$_g$)+Sc($^4$F$_g$) and $r_e=2.6$ Å. In the same issue of Faraday Symposium, Gingerich,\textsuperscript{12} in a review article on diatomic metals and metallic clusters, cites a binding energy $D_0^0=38.0 \pm 5.0$ kcal/mol, quite different from that of Ref. 2. However, this $D_0^0$ value does not seem to be a new experimental result; it has been taken from the Gurvich et al. compilation published in 1974 (see Ref. 12), and it is perhaps the $D_0^0$ number given in Verhaegen’s Ph.D. thesis of 1965 (vide supra).

Within the restricted Hartree-Fock (HF) methodology, Wolf and Schmidtke\textsuperscript{13} studied the lowest closed-shell states of the M$_2$ series, M = Sc to Cu. For Sc$_2$, in particular, they reported bond lengths and frequencies for two $1\Sigma_g^+$ states, namely, $r_e=3.05$ and 2.22 Å, and $\omega_e=210$ and 360 cm$^{-1}$.

In a limited pseudopotential MCSCF+CI study, Das\textsuperscript{7} constructed potential energy curves (PEC) for 27 states of Sc$_2$ of $1\Sigma_g^+, 1\Sigma_u^+, 1\Sigma_g^-$, and $1\Pi_{g,u}$ symmetries dissociating to Sc(2D$_g$)+Sc($^4$F$_g$, $^2$F$_g$, $^2$F$_g$). As was already discussed, Das questions the “experimental” dissociation energy of Verhaegen et al.\textsuperscript{2,4} as well as the $X\Sigma_g^-$ state suggested by Wood et al.\textsuperscript{11} He concludes that the ground state is a vdW $1\Sigma_g^-$ state with $D_e=4$ kcal/mol, $r_e=5$ Å, and $\omega_e=61$ cm$^{-1}$.

In 1983 Walch and Bauschlicher\textsuperscript{14} examined by multi-reference CI (MRCl=MCSCF+1+2)/[8s6p4d] methods the $3\Sigma_g^-$, $1\Sigma_g^+$, $3\Sigma_u^+$, and $5\Delta_u$ states of Sc$_2$. The first three states, stemming out from the $2\Sigma_g^+$ channel, show as expected a weak interaction (=1.4 kcal/mol, $r_e=4.2$ Å). According to these authors the $3\Delta_u$ state correlates to the $2\Sigma_g^+$ state by $^{4}\Sigma_g^+(4s^44p^33d^1)$ fragments displaying a binding energy of about 18 kcal/mol with respect to $2\Sigma_g^+$ at $r_e=3.7$ Å; no ground state was proposed.

On a back-to-back article with that of Ref. 14, Knight et al.\textsuperscript{15} reported the ESR spectrum of Sc$_2$ in Ne and Ar matrices at 4 K. The observed ESR constant $\alpha$ is consistent with an electronic configuration $\ldots\sigma(3d^2\pi^2\pi^2\pi^2)$ with $S=2$;\textsuperscript{16} thus the $X$-state should be a $\Sigma_g^-$.\textsuperscript{16} Assuming a $4\sigma_g^24\pi_g^43\sigma_u^23\pi_u^43d_x^23d_y^23d_z^2\Pi_u$ configuration (vide infra and Ref. 11) it should be of negative parity and of $u$ symmetry, that is $\Sigma_u^-$.\textsuperscript{16}

Prompted by the ESR results of Ref. 15, Walch and Bauschlicher calculated a $1\Sigma_u^-$ state arising from Sc(2D$_g$)+Sc($^4$F$_g$) at the MRCl/[8s6p4d, 8s7p4d2f] level of theory.\textsuperscript{16} It was found that the $\Sigma_u^-$ is bound with respect to $2\Sigma_g^+$ channel by $D_0^0=0.44$ eV (=10.1 kcal/mol) at $r_e=2.79$ Å, and $\omega_e=184$ cm$^{-1}$. The given $D_0^0$ value includes a small differential Davidson correction (−0.03 eV), a correction for the error in the asymptotic separation (+0.26 eV), and a correction for the energy improvement due to the extended basis set (+0.09 eV).\textsuperscript{16}

A Raman study of Sc$_2$ in Ar matrices by Moskovits et al.\textsuperscript{17} revealed the vibrational parameters $\omega_e=238.91$ cm$^{-1}$ and $\omega_x=0.93$ cm$^{-1}$.

In a SCF discrete variational X$_u$ study of Sc$_2$, Fursova et al.\textsuperscript{18} proposed a $1\Sigma_g^+$ ground state at $r_e=2.21$ Å. In 1986 Jeung reported MRDCI (Ref. 19) HF pseudopotential calculations of the $5\Sigma_u^-$ and $1\Sigma_g^-$ states of Sc$_2$.\textsuperscript{20} The following spectroscopic constants are given at the MRDCI(Q) level. $5\Sigma_u^-$: $D_e=1.15$ (1.47) eV with respect to $2\Sigma_g^+$, $r_e=2.688(2704)$ Å, $\omega_e=222(209)$ cm$^{-1}$; $3\Sigma_g^+$: $D_e=1.25$ (1.99) eV with respect to $2\Sigma_g^+$, $r_e=2.281(2360)$ Å, $\omega_e=340(291)$ cm$^{-1}$, and $\Delta E(3\Sigma_g^+-5\Sigma_u^-)=11500(8100)$ cm$^{-1}$.

An analysis of the magnetic circular dichroism spectroscopy and magnetization properties of Sc$_2$ (Ref. 21) supports the ESR findings (Ref. 15) that the ground state is of $5\Sigma$ ($5\Sigma_u^-$) symmetry.

Haslett et al.\textsuperscript{22} recalculated the dissociation energies of Fe$_2$, Sc$_2$, Ti$_2$, and Mn$_2$ from previously reported mass spectrometric data and available molecular parameters using, in addition to two other methods, a LeRoy–Bernstein approach.\textsuperscript{23} Through the latter they established a
lower bound to the dissociation energy of Sc₂, $D_0^\text{D} = 0.79$ eV ($=18.2$ kcal/mol), adopting the 25.9±5 kcal/mol of Ref. 2 as an upper bound.

In 1992 Åkeby et al. published averaged coupled fair functional (ACPF) internally contracted multireference calculations for the $5\Sigma_u^-$ state employing a [8s7p5d3f] basis set. Their best results are $D_0^\text{D} = 0.77$ eV ($=17.8$ kcal/mol), $r_e = 2.673$ Å, and $\omega_v = 197$ cm$^{-1}$; with respect to Sc(4$D_g$) + Sc(4$F_g$), $D_0^\text{D} = 2.118$ eV. These numbers, however, are obtained after a series of corrections of doubtful validity.

Four years later Suzuki et al. calculated three states of $5\Sigma_u^-$ symmetry at the MRCI/DZ-Slater level. For the lowest of the three $5\Sigma_u^-$ states they report $D_0^\text{D} = 0.60$ eV ($=13.8$ kcal/mol), $r_e = 2.715$ Å, and $\omega_v = 230$ cm$^{-1}$. Curiously enough their complete active space self-consistent field (CASSCF) results are in essence identical to the MRCI ones.

From 1997 on until 2006 a series of DFT papers appeared in the literature employing a plethora of functionals. As expected, DFT results vary widely depending on the functional used. We believe that even qualitative questions concerning the existence and the nature of the possible electronic states are different.

II. COMPUTATIONAL APPROACH

For all calculated states and corresponding PECs, the correlation consistent basis set of quadruple cardinality was used, cc-pVQZ (=4Z), generally contracted to [8s7p5d3f2g1h] (Ref. 30) comprising 208 spherical Gaussians. For two states, $\Sigma_u^-$ and $\Sigma_u^+$, the quintuple cc-pV5Z (=5Z) basis similarly contracted to [9s8p6d4f3g2h1i] was employed as well.

The internally contracted variant of multireference configuration interaction approach, complete active space self-consistent field (CASSCF)+single+double replacements (CASSCF+1+2=MRCl), as implemented in the MOLPRO 2006.1 and 2008.1 codes, was used for all calculations. The CASSCF wave functions were constructed by allotting the six valence electrons (4$s^2$3$d^1$×2) to 18 orbitals [1(4$s$) +5(3$d$) +3(4$p$)] × 2 under $D_2h$ symmetry constraints. Reference wave functions comprise 17 000–40 000 configuration functions (CFS) with corresponding valence MRCI expansions ranging from 34 to 67×10$^6$ CFS internally contracted to about 1.8–3.1×10$^6$ CFS. For the $5\Sigma_u^-$ symmetry only, restricted coupled-cluster+single+doubles+quasiperturbative connected triples [RCCSD(T)] (Ref. 32) calculations were performed at both valence and core-valence level. In the latter calculations the 3$s^2$3$p^6$ semi-core electrons were taken into account in conjunction with an appropriately enlarged cc-pwCVQZ (=C4Z) basis set contracted to [10s9p7d4f3g2h]. The purpose of the CC calculations was to assess the effect of the 3$s^2$3$p^6$ electrons on D$_e$ and r$_e$ values in the $5\Sigma_u^-$ state. In addition, the effect of scalar relativistic effects on the $5\Sigma_u^-$ and $3\Sigma_u^-$ states was examined at the valence MRCI level through the second order Douglas–Kroll–Hess approach coupled with the appropriately recontracted 4Z basis set.

III. RESULTS AND DISCUSSION

Table I presents the numerical data for 30+2 states with corresponding PECs displayed in Figs. 1 and 2. Thirty states...
correlate to the ground state fragments Sc(3D_g) + Sc(3D_g), Fig. 1, while \( ^1 \Sigma^u_\pi \) and \( ^1 \Sigma^u_\sigma \) correlate to Sc(3D_g) + Sc(3F_g); see Fig. 2.

The Sc 3D_g term with a 4s 3d\(^1\) configuration and with mean radii of the 3d and 4s shells of 1.68 and 3.96 bohr, respectively,\(^{37}\) or \( r_{\text{3d}} / r_{\text{4s}} \approx 2.4\), cannot possibly form covalent bonds with another Sc 3D_g atom. A covalent interaction would be completely strangled by a repulsive Pauli wall between the 4s\(^2\) distributions long before the 3d electrons have any chance to interact covalently; see also Ref. 27.

Therefore it is expected that all 30 \( ^2 \Sigma^u \chi_{\text{sym}}^\pm \) states related to the ground state channel will be, at the most, of vdW type and this is exactly what is observed at the (valence) MRCI/4Z level. Irrespective of any symmetry and spin coupling, all states show a rather strong vdW interaction of \( \sim 3-5 \text{ kcal/mol} \) at internuclear distances of \( 3.7-4.0 \text{ Å} \), lying within an energy window \( \Delta E = 3.5 \text{ mE}_\text{h} \). In summary, from the \( ^2 \Sigma^u_\pi + ^2 \Sigma^u_\sigma \) asymptote a bundle of 30 quasidegenerate vdW states emanate, located a few kcal/mol above the \( ^2 \Sigma^u_\pi \) and \( ^3 \Sigma^u_\sigma \) states; see Table I. At interatomic distances shorter than 6 bohr, local minima are developed due to numerous avoided crossings coming in from higher dissociation channels; see Fig. 1.

The next channel, \( ^2 \Sigma^u_\pi + ^4 \Sigma^u_\pi \), gives rise to 80 triplet and quintet states (280 if the spin-orbit interaction is considered), and an accurate energy location of the lower bound states is not an easy task. The experimental results, however, point to a \( ^5 \Sigma^u_\pi \) ground state,\(^{15,21}\) whereas published theoretical DFT results\(^{26(a),26(d)}\) suggest that a \( ^5 \Sigma^u_\pi \) state is located about 0.2 eV above the \( ^5 \Sigma^u_\pi \) or even the ground state by 0.16 eV with

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### Table I. Total energies \( E_i (E_0) \), dissociation energies \( D_i (\text{kcal/mol}) \), equilibrium distances \( r_e (\text{Å}) \), harmonic and anharmonic frequencies \( \omega_c, \omega_a \chi (\text{cm}^{-1}) \), zero point energies \( ZPE (\text{cm}^{-1}) \), and \( T_e (\text{cm}^{-1}) \) of 32 states of Sc\(_2\) calculated at the MRCI(MRCI+Q)/cc-pVQZ level of theory.

<table>
<thead>
<tr>
<th>State</th>
<th>(-E_i )^a</th>
<th>( D_i )^a</th>
<th>( r_e )^a</th>
<th>( \omega_c )</th>
<th>( \omega_a \chi )</th>
<th>ZPE</th>
<th>( T_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^1 \Sigma^u_\pi )</td>
<td>1519.57061</td>
<td>49.2 [49.6]</td>
<td>2.749 [2.748]</td>
<td>224.8</td>
<td>0.69</td>
<td>112.2</td>
<td>0.0</td>
</tr>
<tr>
<td>( ^1 \Sigma^u_\alpha )</td>
<td>1519.57224</td>
<td>(49.7)[50.1]</td>
<td>(2.75)[2.75]</td>
<td>(224)</td>
<td>(0.8)</td>
<td>(112)</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Expt.\(^c\)

<table>
<thead>
<tr>
<th>State</th>
<th>(-E_i )^a</th>
<th>( D_i )^a</th>
<th>( r_e )^a</th>
<th>( \omega_c )</th>
<th>( \omega_a \chi )</th>
<th>ZPE</th>
<th>( T_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^1 \Sigma^u_\pi )</td>
<td>1519.56888</td>
<td>48.3 [48.5]</td>
<td>2.737 [2.737]</td>
<td>234.8</td>
<td>–0.29</td>
<td>118.1</td>
<td>380</td>
</tr>
<tr>
<td>( ^1 \Sigma^u_\alpha )</td>
<td>1519.57061</td>
<td>(48.7)[49.1]</td>
<td>(2.744)[2.74]</td>
<td>(234)</td>
<td>(0.6)</td>
<td>(117)</td>
<td>(351)</td>
</tr>
</tbody>
</table>

\(^a\)Numbers in square brackets have been obtained with the 5Z basis set.

\(^b\)For final (corrected) \( D_e \) and \( r_e \) values, see text.

\(^c\)Reference 17.

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bonding is shown below.

Note that the 36 inner electrons have been suppressed.

$\Sigma_w^-$ The leading MRCI equilibrium configurations and corresponding Mulliken atomic populations per Sc atom are

$$|3\Sigma_w^-(\Sigma_z)\rangle = 0.38|\sigma_g^2\sigma_u^4\pi_y^4\pi_y^1\rangle$$

$$+ 0.22(|\sigma_u^2\pi_y^4\sigma_g^4\pi_y^1\rangle$$

$$- 0.22(|\sigma_g^2\pi_y^4\sigma_u^4\pi_y^1\rangle$$

$$+ 4s^{1.22}p_z^{0.25}d_{x^2}^{0.50}d_{y^2}^{0.40}d_{z^2}^{0.12}p_x^{0.12}$$

Note that the 36 inner electrons have been suppressed.

A valence-bond-Lewis (vbL) diagram outlining the bonding is shown below.

$$3d_{x^2-y^2} 3d_{x^2-z^2} 3d_{y^2}$$

$4s \rightarrow a^4F_u$ $M_s=0$ $3d_{x^2} \sigma_g$ $1\sigma_u$ $\sigma_u^+ \sigma_u^-$

The strong attractive interaction between the $3D_g$ and $a^4F_u$ states of Sc atoms (about 50 kcal/mol; see below) is caused by a sigma bond ($1\sigma_g$ orbital), whereas one electron is moving to a $1\sigma_u$ orbital, a case of a ns$^2$–ns$^1$ interaction, with $n=4$ in the present case. Obviously the $3d_e^23d_g^1$ electrons play a rather minor role to the bonding, being screened by the 4s$^2$–4s$^1$ electron distribution. The situation is very similar to the Mn$_2$ molecule: the ground and the first excited terms of the Mn atom are $6S(4s^3d^6)$ and $6D(4s^3d^6)$, respectively, in agreement with the 36 states “covalently” bound, six of which ($1^{1}Σ_u^+,$ $1^{1}Π_{u,1},$ $1^{1}Π_{g,1}$) had been studied in Ref. 27. The lowest of those states, $1^{1}Π_{u,1}$, is bound by ~30 kcal/mol at the MRCI(+Q)/aug-cc-pVQZ level, “isovalent” to Sc$_2$ as to the 4s$^2$–4s$^1$ distributions.

In the present case the populations suggest that the 3d$_g$ electron is localized (0.5+0.5 on each atom due to the inversion symmetry), the (4s4p)$_{1.5}$ polarization facilitates the $σ$ interaction, whereas a small electron 3d$_g$–4p$_x$ delocalization strengthens the bond formation.

At the MRCI(+Q)/4Z the binding energy of Sc$_2$ with respect to Sc($3D_g$)+Sc($4^4F_u$) is $D_b=49.2(49.7)$ kcal/mol; see Table I. Observe that the $z^4F_u(4s^3d^4)$ term is the wrong asymptote, the correct one being $a^4F_u(4s^3d^3)$. This is happening because the $z^4F_u(4s^3d^4)$ channel is lowered at the HF level than the $a^4F_u(4s^3d^3)$ term, and this is preserved at the MRCI(+Q) due to its HF memory. Correcting by the MRCI(+Q)/4Z $ΔE(z^4F_u−a^4F_u)$ $= 3.44(3.60)$ kcal/mol energy difference, we obtain $D_b$.
22 $e^-$ in the CI. Therefore, to monitor the 3s 2p 6 effect we correlated and scalar relativistic effects to the $r_e$ and $D_e$ values of the 5$\Sigma_u^+$ state. It was proved technically impossible, however, to perform multireference ACPF calculations (to minimize severe size nonextensivity problems) including 22 $e^-$ in the CI. Therefore, to monitor the 3s 2p 6 effect we performed valence [RCCSD(T)/4Z] and core-valence [C–RCCSD(T)/C4Z] coupled-cluster calculations, notwithstanding the multireference character of the 5$\Sigma_u^+$ state. At the RCCSD(T)/C–RCCSD(T) level, $r_e = 2.715(2.619) \text{ Å}$ and $D_e = 39.7(39.3) \text{ kcal/mol}$. With respect to the ground state atoms, $D_e^0 = 2.7(8.4)$, or $D_e^0' = 4.7(10.4) \text{ kcal/mol}$ by adding to the $D_e^0$ the difference between the calculated and experimental $\Delta E(a^4F_g-2D_g) = 0.085 \text{ eV}$ [C–RCCSD(T)]. The CC results suggest that the 3s 2p 6 correlation energy is of no importance to the $D_e$; it reduces, however, significantly the bond length by $\Delta r = 0.069$ Å or 0.05 Å per Sc atom. Assuming transferability between MRCI and CC results, $r_e = 2.75(48.0)$ Å, $D_e = 7.3(8.0)$, and $D_e^0 = 14.6(15.1)$ Å.

We now turn to the 3$\Sigma_u^-$ state. The leading MRCI configurations are in essence identical to those of the 5$\Sigma_u^+$ state after a spin flip of the 1$\sigma_g$ electron (1$\sigma_g$ → 1$\sigma_u$). The bonding is represented as well by the vbL diagram of the 5$\Sigma_u^+$ state (vide supra). Analogously, $r_e$ and $T_e(3\Sigma_u^-\rightarrow 5\Sigma_u^-)$ values of the 3$\Sigma_u^-$ state are as follows:

\[
r_e = r_e(\text{MRCI/4Z,5Z or MRCI + DKH2/4Z})
- \Delta r(\text{core valence effects}) = 2.74 - 0.10 = 2.64 \text{ Å},
\]

\[
T_e = 380(372)(396) \text{ cm}^{-1} \text{ at the MRCI/4Z(MRCI/5Z)}
\]

[MRCI + DKH2/4Z] level,

corresponding values at the +Q level are 351(341)[365] cm$^{-1}$.

Assuming that the ground state is of 5$\Sigma_u^-$ symmetry according to the experimental evidence, our calculations imply that the 1 3$\Sigma_u^-$ state is located a mere 1 kcal/mol higher.

IV. SYNOPSIS

For the first time MRCI calculations have been performed for a total of 32 states of the Sc$_2$ molecule. All 30 states correlating to the ground state atoms, Sc(2$\Sigma_d^+$)+Sc(a$^4F_g$), are of vdW type with interaction energies of about 3–5 kcal/mol at 7–7.5 bohr, and within an energy range of no more than 3 kcal/mol.

Prompted by the ESR experimental results indicating a 5$\Sigma_u^+$ (5$\Sigma_u^+$) ground state, and the recent theoretical work by Matxain et al., who suggested a 3$\Sigma_u^-$ ground state, we calculated the 5$\Sigma_u^+$ and 3$\Sigma_u^-$ states, two out of 80 states related to the Sc(2$\Sigma_d$)+Sc(a$^4F_g$) channel. Our findings are summarized in the following numbers.

\[
3\Sigma_u^-; r_e = 2.65 \text{ Å},
D_e = 48.0 \text{ kcal/mol}, \text{ and } D_e^0 = 8.0 \text{ kcal/mol}, \text{ or } D_e^0' = 15.0 \text{ kcal/mol} \text{ by conforming to the experimental } a^4F_g \rightarrow 5D_g \text{ splitting.}
\]

It is rather certain that these 80 states correlating to the Sc(2$\Sigma_d$)+Sc(a$^4F_g$) end atoms will be crowded to a relatively narrow energy range, hence creating a very challenging molecular system either theoretically or experimentally. Finally, our numbers are in disagreement with the ones of Ref. 29 where a lower X 3$\Sigma_u^-$ state is predicted with respect to 5$\Sigma_u^+$ by 3.7 kcal/mol, $r_e(3\Sigma_u^-/5\Sigma_u^+) = 2.55/2.67 \text{ Å}$ at the CASPT2 level, and $D_e^0 = 25.4 \text{ kcal/mol}$ at the DMC level.

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31 MOLPRO, a package of ab initio programs designed by H.-J. Werner and P. J. Knowles, Version 2006.1, R. D. Amos, A. Bernhardsson, A. Berning et al.