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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 $Sc(^2D_g)+Sc(a\ ^4F_g)$, 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_e 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 $|^{2S+1}\Lambda_{g,u}^{\pm}\rangle$ states, the result of low-lying high spin and orbital angular momentum atomic Sc terms.[1] For instance, upon the interaction of $Sc(^2D_g;4s^23d^1)+Sc[^2D_g(4s^23d^1),\ a\ ^4F_g(4s^13d^2),\ a\ ^2F_g(4s^13d^2),\ z\ ^4F_u(4s^14p^13d^1)]$, where $a\ ^4F_g$, $a\ ^2F_g$, and $z\ ^4F_u$ are the first three excited states of Sc located at 1.427, 1.846, and 1.956 eV (M_J averaged) above the ^2D_g term,[1] respectively, a total of 270 molecular states are realizable,

$$Sc(^2D_g;4s^23d^1)+Sc(^2D_g;4s^23d^1)\rightarrow (^1\Sigma_g^+[3],{}^1\Sigma_u^-[2],{}^1\Pi_g[2],{}^1\Pi_u[2],{}^1\Delta_g[2],{}^1\Delta_u,{}^1\Phi_g,{}^1\Phi_u,{}^1\Gamma_g,{}^3\Sigma_u^+[3],{}^3\Sigma_g^-[2],{}^3\Pi_u[2],{}^3\Pi_g[2],{}^3\Delta_u[2],{}^1\Delta_g,{}^3\Phi_u,{}^3\Phi_g,{}^3\Gamma_u)\quad (30\ \text{states}),$$

$$Sc(^2D_g;4s^23d^1)+Sc(a\ ^4F_g;4s^13d^2)\rightarrow (^{3,5}\Sigma_{g,u}^+[2],{}^{3,5}\Sigma_{g,u}^-[3],{}^{3,5}\Pi_{g,u}[5],{}^{3,5}\Delta_g[4],{}^{3,5}\Phi_{g,u}[3],{}^{3,5}\Gamma_{g,u}[2],{}^{3,5}H_{g,u})\quad (80\ \text{states}),$$

$$Sc(^2D_g;4s^23d^1)+Sc(a\ ^2F_g;4s^13d^2)\rightarrow (^{1,3}\Sigma_{g,u}^+[2],{}^{1,3}\Sigma_{g,u}^-[3],{}^{1,3}\Pi_{g,u}[5],{}^{1,3}\Delta_{g,u}[4],{}^{1,3}\Phi_{g,u}[3],{}^{1,3}\Gamma_{g,u}[2],{}^{1,3}H_{g,u})\quad (80\ \text{states}),$$

$$Sc(^2D_g;4s^23d^1)+Sc(z\ ^4F_u;4s^14p^13d^1)\rightarrow (^{3,5}\Sigma_{g,u}^+[3],{}^{3,5}\Sigma_{g,u}^-[2],{}^{3,5}\Pi_{g,u}[5],{}^{3,5}\Delta_{g,u}[4],{}^{3,5}\Phi_{g,u}[3],{}^{3,5}\Gamma_{g,u}[2],{}^{3,5}H_{g,u})\quad (80\ \text{states}).$$

Considering as well the spin-orbit interaction we would be enmeshed in a computational nightmare. This is the reason that even our best *ab initio* state-of-the-art quantum mechanical methods combined with current computer technology are not powerful enough to tackle satisfactorily this kind of problems.

The electronic configuration of the ground state of $Sc(^2D_g)$ precludes any strong bonding interaction other than van der Waals (vdW) (*vide infra*), therefore well bound states should stem from the next dissociation channels, e.g., $Sc(^2D_g)+Sc(a\ ^4F_g)$.

In what follows we outline in chronological order the existing literature on Sc_2. The very first study published in 1964 was a mass spectrometric absolute entropy method determination of the dissociation energy, $D_0^0 = 25.9 \pm 5$ kcal/mol, with respect to ground state atoms.[2] As to the experimental dissociation energy of Sc_2, however, the situation is more complex. In the Huber–Herzberg compilation of 1979 (Ref. 3), a D_0^0 value of 1.65 ± 0.10 eV ($=38.0 \pm 2.3$ kcal/mol) is cited referring to Verhaegen's Ph.D. thesis as quoted by Drowart.[4] Obviously, the question naturally arises as to which number is correct. In a personal communication with Professor Verhaegen we have been advised to consider the higher value as the most appropriate, the reason being an "overestimation of the Sc_2 vapor pressure in the original experiments, probably up to a factor of

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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.*[2] assumed a vibrational frequency of 230 cm^{-1} from which a $r_e=2.70$ Å was inferred through Badger's rule,[6] turned out to be very reasonable (see below). On the contrary, the adopted "effective quantum weight of 5" for the partition functions[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.*[2] data by Das,[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.*[8] based on extended Hückel calculations predicted a $^1\Sigma_g^+$ 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.[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[10] calculated two states of $^5\Sigma_u^-$($D_e=1.80$ eV, $r_e=2.70$ Å, $\omega_e=200$ cm^{-1}) and $^3\Sigma_g^-$($D_e=1.00$ eV, $r_e=3.25$ Å, $\omega_e=235$ cm^{-1}) symmetry. They obtained $^5\Sigma_u^-$ 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 $^5\Sigma_u^-$ state.

On the basis of multiconfiguration self-consistent field (MCSCF)/[6s3p2d] *ab initio* calculations, the first on Sc_2, Wood *et al.*[11] reported a $^5\Sigma_u^-$ ground state with $D_e=6.9$ kcal/mol with respect to $Sc(^2D_g)+Sc(a\ ^4F_g)$ 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 $^2D_g+a\ ^4F_g(^2D_g+^2D_g)$ at $r_e=2.6$ Å. In the same issue of Faraday Symposia, Gingerich,[12] in a review article on diatomic metals and metallic clusters, cites a binding energy $D_0^0=38.0\pm5.0$ 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[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[7] constructed potential energy curves (PEC) for 27 states of Sc_2 of $^{1,3}\Sigma_{g,u}^+$, $^{1,3}\Sigma_{g,u}^-$, and $^{1,3}\Pi_{g,u}$ symmetries dissociating to $Sc(^2D_g)+Sc(^2D_g,\ a\ ^4F_g,\ a\ ^2F_g)$. As was already discussed, Das questions the "experimental" dissociation energy of Verhaegen *et al.*,[2,4] as well as the $X\ ^5\Sigma_u^-$ state suggested by Wood *et al.*[11] He concludes that the ground state is a vdW $^1\Sigma_g^+$ state with $D\approx4$ kcal/mol, $r_e\approx5$ Å, and $\omega_e\approx61$ cm^{-1}.

In 1983 Walch and Bauschlicher[14] examined by multireference CI (MRCI=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 $^2D_g+^2D_g$ channel, show as expected a weak interaction (≈1.4 kcal/mol, $r_e\approx4.2$ Å). According to these authors the $^5\Delta_u$ state correlates to the $^2D_g+z\ ^4F_u(4s^14p^13d^1)$ fragments displaying a binding energy of about 18 kcal/mol with respect to $^2D_g+z\ ^4F_u$ at $r_e\approx3.7$ Å; no ground state was proposed.

On a back-to-back article with that of Ref. 14, Knight *et al.*[15] reported the ESR spectrum of Sc_2 in Ne and Ar matrices at 4 K. The observed ESR constant A is consistent with an electronic configuration "$\cdots\sigma_s^1\sigma_d^1\pi_d^2$ with S=2," thus the *X*-state should be a $^5\Sigma$.[15] Assuming a $4s\sigma_g^2 4s\sigma_u^1 3d_{z^2}\sigma_g^1 3d_{xz}\pi_u^1 3d_{yz}\pi_u^1$ configuration (*vide infra* and Ref. 11) it should be of negative parity and of *u* symmetry, that is $^5\Sigma_u^-$.

Prompted by the ESR results of Ref. 15, Walch and Bauschlicher calculated a $^5\Sigma_u^-$ state arising from $Sc(^2D_g)+Sc(a\ ^4F_g)$ at the MRCI/[8s6p4d, 8s7p4d2f] level of theory.[16] It was found that the $^5\Sigma_u^-$ is bound with respect to $^2D_g+^2D_g$ channel by $D_e^0=0.44$ eV (=10.1 kcal/mol) at $r_e=2.79$ Å, and $\omega_e=184$ cm^{-1}. The given D_e^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).[16]

A Raman study of Sc_2 in Ar matrices by Moskovits *et al.*[17] revealed the vibrational parameters $\omega_e=238.91$ cm^{-1} and $\omega_e x_e=0.93$ cm^{-1}.

In a SCF discrete variational X_a study of Sc_2, Fursova *et al.*[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.[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 $^2D_g+a\ ^4F_g$, $r_e=2.688(2.704)$ Å, $\omega_e=222(209)$ cm^{-1}; $^1\Sigma_g^+$: $D_e=1.25$ (1.99) eV with respect to $a\ ^4F_g+a\ ^4F_g$, $r_e=2.281(2.360)$ Å, $\omega_e=340(291)$ cm^{-1}, and $\Delta E(^1\Sigma_g^+\leftarrow{}^5\Sigma_u^-)=11\,500(8100)$ cm^{-1}.

An analysis of the magnetic circular dichroism spectrum 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.*[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.[23] Through the latter they established a lower bound to the dissociation energy of Sc$_2$, D_e^0=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.*[24] 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_e^0= 0.77 eV (= 17.8 kcal/mol), r_e=2.673 Å, and ω_e=197 cm^{-1}; with respect to Sc(^2D_g)+Sc($a\ ^4F_g$), D_e=2.118 eV. These numbers, however, are obtained after a series of corrections of doubtful validity.

Four years later Suzuki *et al.*[25] 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_e^0=0.60 eV (=13.8 kcal/mol), r_e=2.715 Å, and ω_e=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.[26] As expected, DFT results vary wildly depending on the functional used. We believe that even qualitative results are questionable, at least for the time being, for this kind of molecular systems at the DFT level; see also Ref. 27 on the Mn$_2$ molecule and the general analysis[28] of the problems arising in DFT for the states with definite total spin. For instance, Furche and Perdew,[26(g)] and Zhao and Truhlar[26(h)] investigated six (LSD, BP86, PBE, TPSS, B3LYP, and TPSSh) and seven (TPSS, B3LYP, TPSSh, M05, BLYP, MPWLYP1M, and BP97-2) functionals, respectively. For the $^5\Sigma_u^-$ state of Sc$_2$ calculated D_e^0 values range from 0.50 (B3LYP) to 2.37 [Ref. 26(g)] and 0.50 (B3LYP) to 1.40 (TPSS) eV [Ref. 26(h)].

Finally the most recent work on Sc$_2$ published in 2008 is that of Matxain *et al.*[29] These workers examined ten states singlets, triplets, quintets, and septets ($^1\Sigma_g$, $^1\Pi_g$; $^3\Sigma_u$, $^3\Sigma_g$; $^5\Sigma_u$, $^5\Sigma_g$; $^5\Delta_u$, $^5\Delta_g$; $^7\Sigma_g$, $^7\Delta_u$), reporting r_e and ω_e values at the DFT(B3LYP)/TZVP+G(3df,2p) level; for some reason parities of the Σ states are not given. At the DFT equilibrium distances diffusion Monte Carlo (DMC) single point calculations were performed using the relativistic Stuttgart pseudopotentials and basis sets (ECP10MDF), thus obtaining T_e values for the above states. According to DMC the ground state is of $^3\Sigma_u$ symmetry with the $^5\Sigma_u$ lying at 0.17 eV (=3.9 kcal/mol) higher.[29] In addition, DMC D_e values are given for the $X\ ^3\Sigma_u$ (1.10 eV) and $^5\Sigma_u$ (0.93 eV) states, but without clarification as to the asymptotic channels. This particular ordering of the $^3\Sigma_u$ and $^5\Sigma_u$ states has been corroborated by CASPT2/TZVP+G(3df,2p) calculations. At this level of theory $T_e(^5\Sigma_u \leftarrow X\ ^3\Sigma_u)$=0.16 eV, $r_e(^5\Sigma_u) \approx 2.55$ Å, $r_e(^3\Sigma_u) \approx 2.67$ Å, and $E(^5\Sigma_u) = -1519.490\ E_h$, as deduced from Fig. 2 of Ref. 29. No dissociation energies of the $^5\Sigma_u$ and $^3\Sigma_u$ states are given at the CASPT2 level.[29]

The question arises now as to what we really know for the Sc$_2$ molecule since 1964 when the first experimental work was published.[2] According to the previous exposition the theoretical results are conflicting, nevertheless it appears to favor a $^5\Sigma_u^-$ symmetry for the ground state, disputed, however, by the recent theoretical work of Matxain *et al.*[29] Recall, however, that the $^5\Sigma_u^-$ state which correlates to Sc(^2D_g)+Sc($a\ ^4F_g$) is one of 80 possible $|^{2S+1}\Lambda_{g,u}^{\pm}\rangle$ states sprouting out from this channel (*vide supra*). Our most solid information right now is only a $^5\Sigma$ ($^5\Sigma_u^-$) symmetry for the ground state as inferred from ESR spectra[15] and magnetic measurements,[21] and two frequencies ω_e=238.91 cm^{-1}, $\omega_e x_e$=0.93 cm^{-1} from Raman vibrational spectroscopy.[17] From these frequencies an approximate dissociation energy can be obtained through the relation $D_e \approx \omega_e^2/4\omega_e x_e$ =44 kcal/mol with respect to Sc(^2D_g)+Sc($a\ ^4F_g$), or $D_e^0 \approx 44 - \Delta E[\mathrm{Sc}(a\ ^4F_g) \leftarrow \mathrm{Sc}(^2D_g)] = 44 - 32.9$[1], or $D_e^0 \approx 11$ kcal/mol with respect to Sc(^2D_g)+Sc(^2D_g).

From the above analysis on the status of Sc$_2$, it is clear that a more systematic and appropriate theoretical approach is needed with the hope to obtain some definitive answers. To this end, we have performed mainly MRCI calculations on 32 states of Sc$_2$ using large correlation consistent basis sets. Section II gives some technical details followed by Sec. III, on results and discussion, whereas a short summary is presented in Sec. IV.

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, $^5\Sigma_u^-$ and $^3\Sigma_u^-$, the quintuple cc-pV5Z(=5Z) basis similarly contracted to [9s8p6d4f3g2h1i] was employed as well.[30]

The internally contracted variant of multireference configuration interaction approach, complete active space self-consistent field (CASSCF)+single+double replacements (CASSCF+1+2=MRCI), as implemented in the MOLPRO 2006.1 and 2008.1 codes, was used for all calculations.[31] The CASSCF wave functions were constructed by allotting the six valence electrons (4s^{2}3d^1×2) to 18 orbitals [1(4s)+5(3d)+3(4p)]×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+singles+doubles+quasiperturbative connected triples [RCCSD(T)] (Ref. 32) calculations were performed at both valence and core-valence level. In the latter calculations the 3s^{2}3p^6 semi-core electrons were taken into account in conjunction with an appropriately enlarged cc-pwCVQZ(=C4Z) basis set contracted to [10s9p7d4f3g2h].[33] The purpose of the CC calculations was to assess the effect of the 3s^{2}3p^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[34,35] coupled with the appropriately recontracted 4Z basis set.[33,36]

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

TABLE I. Total energies $E_e(E_h)$, dissociation energies D_e(kcal/mol), equilibrium distances r_e(Å), harmonic and anharmonic frequencies ω_e, $\omega_e x_e$(cm^{-1}), zero point energies ZPE(cm^{-1}), and T_e(cm^{-1}) of 32 states of Sc_2 calculated at the MRCI(MRCI+Q)/cc-pVQZ level of theory.

State	$-E_e$ [a]	D_e [a]	r_e [a]	ω_e	$\omega_e x_e$	ZPE	T_e
[Channel Sc(^2D_g)+Sc($a\ ^4F_g$)][b]							
$X\ ^5\Sigma_u^-$	1519.570 61	49.2 [49.6]	2.749 [2.748]	224.8	0.69	112.2	0.0
	(1519.5722)	(49.7)[50.1]	(2.75)[2.75]	(224)	(0.8)	(112)	0.0
Expt.[c]				238.91	0.93		
1 $^3\Sigma_u^-$	1519.568 88	48.3 [48.5]	2.737 [2.737]	234.8	−0.29	118.1	380
	(1519.5706)	(48.7) [49.1]	(2.744) [2.74]	(234)	(0.6)	(117)	(351)
[Channel Sc(^2D_g)+Sc(^2D_g)]							
2 $^3\Sigma_g^-$	1519.566 33	5.40	3.450	93.4	3.72	45.6	939
3 $^3\Pi_u$	1519.565 57	5.08	3.467	81.3	1.68	40.2	1106
4 $^1\Delta_g$	1519.565 12	4.87	3.609	76.2	0.61	37.9	1205
5 $^3\Gamma_u$	1519.564 74	4.29	3.931	81.7	1.09	40.7	1288
6 $^1\Sigma_u^-$	1519.564 63	4.26	3.935	79.8	0.80	39.6	1312
7 $^1\Pi_u$	1519.564 57	4.40	3.709	61.7	−0.16	32.3	1326
8 $^3\Sigma_g^-$	1519.564 56	4.63	3.872	94.9	1.54	47.0	1328
9 $^3\Sigma_u^+$	1519.564 56	4.29	3.935	82.9	1.24	41.1	1328
10 $^1\Sigma_g^+$	1519.564 41	4.42	3.703	69.2	0.54	36.6	1361
11 $^3\Phi_u$	1519.564 35	4.22	3.821	77.3	0.96	38.4	1374
12 $^3\Pi_u$	1519.564 33	4.30	3.817	82.3	1.00	40.8	1378
13 $^1\Phi_u$	1519.564 25	4.23	3.858	79.1	0.99	39.3	1396
14 $^1\Pi_g$	1519.564 14	4.13	3.875	79.7	1.14	39.8	1420
15 $^1\Phi_g$	1519.564 10	4.14	3.886	81.3	2.74	39.8	1429
16 $^3\Phi_g$	1519.564 10	4.17	3.874	79.0	1.11	39.2	1429
17 $^1\Gamma_g$	1519.564 08	4.20	3.950	73.2	0.34	36.9	1433
18 $^1\Pi_u$	1519.564 04	4.10	3.804	93.6	5.54	44.2	1442
19 $^3\Pi_g$	1519.564 03	4.00	3.884	78.5	1.13	38.7	1444
20 $^1\Sigma_g^+$	1519.563 91	4.11	3.935	69.9	0.90	34.7	1470
21 $^3\Delta_g$	1519.563 85	3.89	3.862	76.6	1.18	37.9	1484
22 $^1\Sigma_g^+$	1519.563 54	3.88	3.828	100.8	2.72	49.4	1552
23 $^1\Sigma_u^-$	1519.563 47	3.98	3.849	76.4	1.10	37.9	1567
24 $^3\Delta_u$	1519.563 40	3.61	3.934	73.5	1.08	36.5	1582
25 $^3\Delta_u$	1519.563 36	3.87	3.934	74.0	1.24	36.6	1591
26 $^1\Delta_u$	1519.563 35	3.82	3.943	74.7	1.32	37.0	1593
27 $^1\Delta_g$	1519.563 14	3.62	3.914	69.9	0.27	35.3	1639
28 $^3\Sigma_u^+$	1519.562 95	3.36	3.905	74.8	1.06	37.1	1681
29 $^1\Pi_g$	1519.562 76	3.30	3.953	70.5	2.98	34.2	1723
30 $^3\Pi_g$	1519.562 62	3.24	3.953	70.0	1.36	34.6	1754
31 $^3\Sigma_u^+$	1519.561 76	2.87	4.044	59.8	1.20	29.6	1942

[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.

correlate to the ground state fragments Sc(^2D_g)+Sc(^2D_g), Fig. 1, while $X\ ^5\Sigma_u^-$ and 1 $^3\Sigma_u^-$ correlate to Sc(^2D_g)+Sc(^4F_g); see Fig. 2.

The Sc ^2D_g term with a $4s^23d^1$ configuration and with mean radii of the 3d and 4s shells of 1.68 and 3.96 bohr, respectively,[37] or $\langle r_{4s}\rangle/\langle r_{3d}\rangle \approx 2.4$, cannot possibly form covalent bonds with another Sc ^2D_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 $|^{2S+1}\Lambda_{g,u}^{\pm}\rangle$ 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 ~3–5 kcal/mol at internuclear distances of 3.7–4.0 Å, lying within an energy window $\Delta E \approx 3.5$ mE_h. In summary, from the $^2D_g+^2D_g$ asymptote a bundle of 30 quasidegenerate vdW states emanate, located a few kcal/mol above the $^5\Sigma_u^-$ and $^3\Sigma_u^-$ 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, $^2D_g+a\ ^4F_g$, 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 $^5\Sigma_u^-$ ground state,[15,21] whereas published theoretical DFT results[26(a),26(d)] suggest that a $^3\Sigma_u^-$ state is located about 0.2 eV above the $^5\Sigma_u^-$, or even the ground state by 0.16 eV with

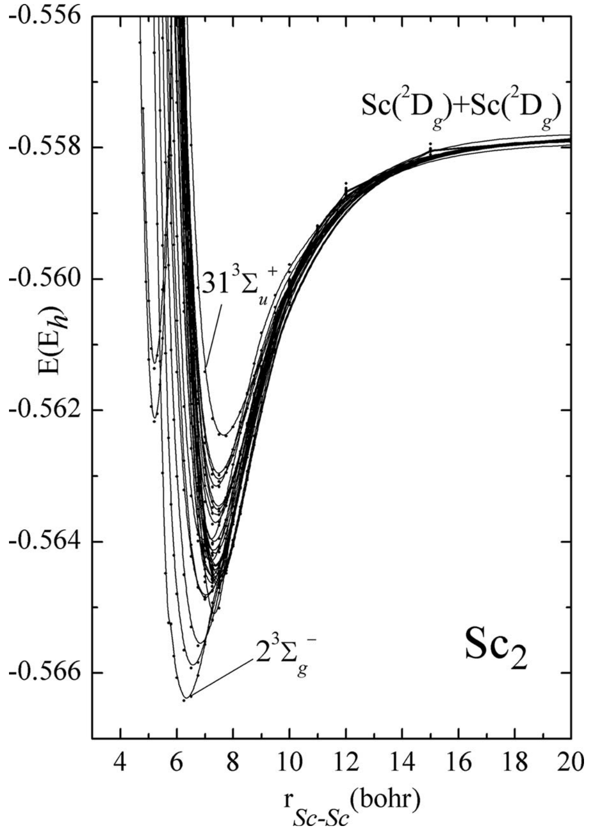


FIG. 1. MRCI/4Z PECs of all 30 vdW states issued from Sc(^2D_g) + Sc(^2D_g). Starting with 2 $^3\Sigma_g^-$, the ordering of the PECs follows strictly the one given in Table I. Energies have been shifted by +1519.0 E_h.

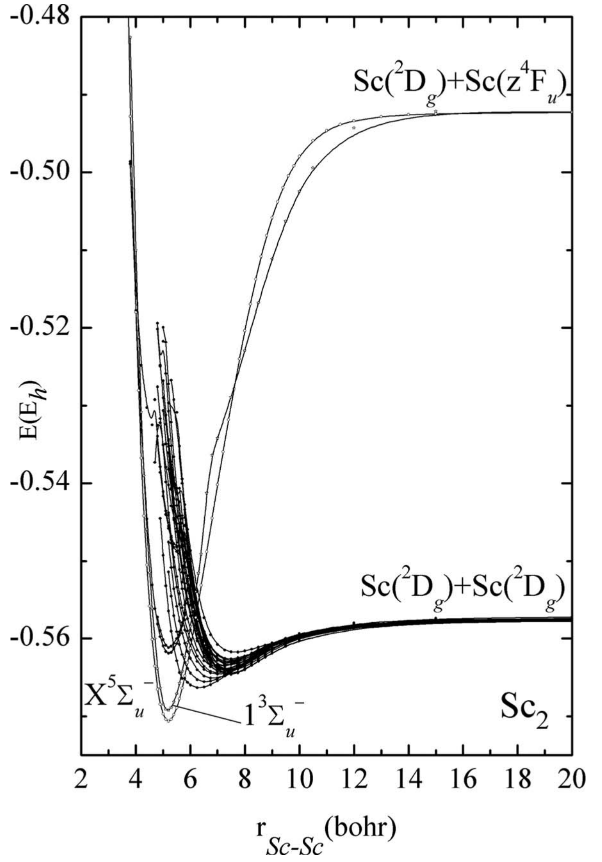


FIG. 2. MRCI/4Z PECs of all 32 states studied in the present work. Energies have been shifted by +1519.0 E_h.

respect to the $^5\Sigma_u^-$ according to DMC and CASPT2 calculations.[29] This is the reason of selecting, in addition to the obvious choice of the $^5\Sigma_u^-$ state, the $^3\Sigma_u^-$ to be investigated presently.

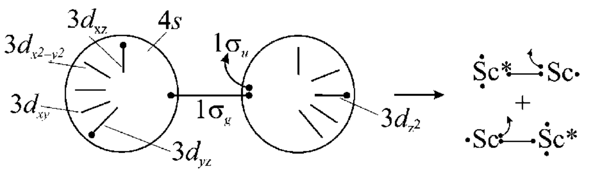
$^5\Sigma_u^-$. The leading MRCI equilibrium configurations and corresponding Mulliken atomic populations per Sc atom are

$$\begin{aligned}|{}^5\Sigma_u^-\rangle \approx\, & 0.83|1\sigma_g^2 2\sigma_g^1 1\sigma_u^1 1\pi_{x,u}^1 1\pi_{y,u}^1\rangle \\ & + 0.24(|1\sigma_g^2 1\pi_{x,u}^1 1\sigma_u^1 2\sigma_u^1 1\pi_{y,g}^1\rangle \\ & - |1\sigma_g^2 1\pi_{y,u}^1 1\sigma_u^1 2\sigma_u^1 1\pi_{x,g}^1\rangle)\end{aligned}$$

$$4s^{1.22}4p_z^{0.25}3d_{z^2}^{0.50}3d_{xz}^{0.40}3d_{yz}^{0.40}4p_x^{0.12}4p_y^{0.12}.$$

Note that the 36 inner electrons have been suppressed.

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



The strong attractive interaction between the ^2D_g and $a\ ^4F_g$ 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 $3d_\pi^2 3d_\sigma^1$ 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:[27] the ground and the first excited terms of the Mn atom are $^6S(4s^2 3d^5)$ and $^6D(4s^1 3d^6)$, respectively, ^6D being located 2.145 eV higher.[1] A total of six $^{1,3,5,7,9,11}\Sigma^+$ of g or u alternating symmetries of vdW nature are related to the $Mn(^6S)+Mn(^6S)$ channel, completely analogous to the 30 vdW Sc_2 states. On the other hand the $^6S+{}^6D$ channel gives rise to 36 states "covalently" bound, six of which ($^{11}\Sigma_{g,u}^+$, $^{11}\Pi_{g,u}$, $^{11}\Delta_{g,u}$) had been studied in Ref. 27. The lowest of those states, $^{11}\Pi_u$, 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 $3d_{z^2}$ electron is localized (0.5+0.5 on each atom due to the inversion symmetry), the $(4s4p_z)^{1.5}$ polarization facilitates the σ interaction, whereas a small electron $3d_\pi-4p_\pi$ delocalization strengthens the bond formation.

At the MRCI(+Q)/4Z the binding energy of Sc_2 with respect to $Sc(^2D_g)+Sc(z\ ^4F_u)$ is D_e=49.2(49.7) kcal/mol; see Table I. Observe that the $z\ ^4F_u(4s^1 4p^1 3d^1)$ term is the wrong asymptote, the correct one being $a\ ^4F_g(4s^1 3d^2)$. This is happening because the $z\ ^4F_u(4s^1 4p^1 3d^1)$ is calculated lower at the HF level than the $a\ ^4F_g(4s^1 3d^2)$ term, and this is preserved at the MRCI(+Q) due to its HF memory. Correcting by the MRCI(+Q)/4Z $\Delta E(z\ ^4F_u - a\ ^4F_g)$ = 3.44 (3.60) kcal/mol energy difference, we obtain D_e

$=45.8$ (46.1) kcal/mol with respect to the correct asymptote, Sc(^2D_g)+Sc($a\ ^4F_g$). Increasing the basis set to 5Z, D_e hardly changes; see also Table I.

With respect to ground state Sc atoms, the above given D_e should be reduced by the MRCI(+Q)/4Z $\Delta E(a\ ^4F_g - a\ ^2D_g) = 1.627(1.619)$ eV, thus $D_e^0 = 45.8(46.1) - 37.5(37.3) = 8.3(8.8)$ kcal/mol. Had the experimental $\Delta E = 1.427$ eV value has been used, $D_e^{0'} = 12.9(13.2)$ kcal/mol would have been obtained.

The question now arises as to the effect of core ($3s^2 3p^6$) correlation 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 $3s^2 3p^6$ 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, $r_e = 2.715(2.619)$ Å and $D_e = 39.7(39.3)$ kcal/mol. With respect to the ground state atoms, $D_e^0 = 2.7(8.4)$, or $D_e^{0'} = 4.7(10.4)$ kcal/mol by adding to the D_e^0 the difference between the calculated and experimental $\Delta E(a\ ^4F_g - ^2D_g) = 0.085$ eV [C-RCCSD(T)]. The CC results suggest that the $3s^2 3p^6$ correlation energy is of no importance to the D_e; it reduces, however, significantly the bond length by $\delta r_e = 0.096$ Å or 0.05 Å per Sc atom. Assuming transferability between MRCI and CC results, $r_e = 2.75(\text{MRCI}) - 0.10 = 2.65$ Å. Valence scalar relativistic effects (MRCI+DKH2(+Q)/4Z) leave the bond distance practically invariant, but affect slightly the dissociation energy, namely (in kcal/mol), $D_e = 47.5(48.0)$, $D_e^0 = 7.3(8.0)$, and $D_e^{0'} = 14.6(15.1)$.

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 $1\sigma_u$ electron ($1\sigma_u \rightarrow 1\bar{\sigma}_u$). The bonding is represented as well by the vbL diagram of the $^5\Sigma_u^-$ state (*vide supra*). Analogously, r_e and $T_e(^3\Sigma_u^- \leftarrow {}^5\Sigma_u^-)$ values of the $^3\Sigma_u^-$ state are as follows:

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

$$T_e = 380(372)[396] \text{ cm}^{-1} \text{ at the MRCI/4Z(MRCI/5Z) [MRCI + DKH2/4Z] level,}$$

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(^2D_g)+Sc(^2D_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 $^5\Sigma$ ($^5\Sigma_u^-$) ground state,[15] and the recent theoretical work by Matxain *et al.*[29] 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(^2D_g)+Sc($a\ ^4F_g$) channel. Our findings are summarized in the following numbers.

$^5\Sigma_u^-$: $r_e = 2.65$ Å, $D_e = 48.0$ kcal/mol, and $D_e^0 = 8.0$ kcal/mol, or $D_e^{0'} = 15.0$ kcal/mol by conforming to the experimental $a\ ^4F_g - ^2D_g$ splitting.

$$^3\Sigma_u^-: r_e = 2.64 \text{ Å}, \quad T_e(^3\Sigma_u^- \leftarrow {}^5\Sigma_u^-) \approx 1.0 \text{ kcal/mol}.$$

It is rather certain that these 80 states correlating to the Sc(^2D_g)+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, $r_e(^5\Sigma_u/^3\Sigma_u) = 2.55/2.67$ Å at the CASPT2 level, and $D_e^0 = 25.4$ kcal/mol at the DMC level.

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