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The low-lying states of the scandium dimer[a)]

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A systematic investigation of low-lying states of Sc_2 using multireference perturbation theory (NEVPT2 and NEVPT3) indicates that the ground state of this system is $^5\Sigma_u^-$ with r_e=2.611 Å, ω_e=241.8 cm^{-1}, and D_e=1.78 eV. This state is closely followed by other low-lying states of Sc_2: $^3\Sigma_u^-$, $^5\Delta_u$, $^3\Pi_g$, $^1\Pi_g$, and $^1\Sigma_u^-$. Our energy ordering of the $^5\Sigma_u^-$ and $^3\Sigma_u^-$ states confirms the recent MRCI results of Kalemos *et al.* [J. Chem. Phys. **132**, 024309 (2010)] and is at variance with the earlier diffusion Monte Carlo predictions of Matxain *et al.* [J. Chem. Phys. **128**, 194315 (2008)]. An excellent agreement between the second- and third-order NEVPT results and between the computed and experimental values of ω_e (241.8 versus 238.9 cm^{-1}) for the $^5\Sigma_u^-$ state suggests high accuracy of our predictions. © *2010 American Institute of Physics*. [doi:10.1063/1.3442374]

I. INTRODUCTION

The electronic structure of bulk metals is quite well understood,[1,2] but an accurate description of small metal clusters is still far from satisfactory and constitutes a field of vigorous scientific investigations.[3–22] An example of a system that received considerable attention—both in theory and in experiment—is the scandium dimer. Even though the Sc_2 molecule is seemingly among the simplest transition metal dimers, the description of its potential energy curve (PEC) along the whole range of internuclear distances still raises a challenge to nowadays' most refined quantum chemical methods. Whereas at large internuclear distances the ground state of Sc_2 is described by the two atoms in their ^2D_g ground state, at short distances, due to the relatively low energy required to promote an atom from ^2D_g ($4s^23d^1$) to ^4F_g ($4s^13d^2$), the nature of the bond in the ground state is dominated by a $4s^24s^1$ interaction. For a long time, there seemed to be a consensus with respect to the nature of the ground state of Sc_2. However, a recent quantum diffusion Monte Carlo (DMC) study of Matxain *et al.*[8] suggested that the ground state should be classified as $^3\Sigma_u^-$ rather than $^5\Sigma_u^-$, as was previously widely accepted. We feel that an extensive study of the scandium dimer aiming at the definite characterization of the ground and low-lying excited states and their properties is timely, also in regard of the recent success of encapsulating the Sc_2 molecules inside fullerene cages.[23] The metal-fullerene interaction was found to significantly stabilize the nonisolated-pentagon fullerene isomers of C_{64}, C_{66}, C_{72}, C_{74}, and C_{82}.[24–30] It appears obvious that in-depth understanding of the stabilization mechanism must be preceded by a thorough elucidation of the electronic structure of the isolated dimer.

An excellent complete review of experimental and theoretical results on Sc_2 has been given recently by Kalemos *et al.*[31] Here, we give only an overview of the most important results that are relevant in the context of the present work. The equilibrium distance in Sc_2 is not well known; crude estimations[32] based on empirical rules locate it around 2.20–2.48 Å. In contrast, the vibrational constants of the ground state (ω_e=238.91 cm^{-1} and $\omega_e x_e$=0.93 cm^{-1}) are determined[33] very accurately from resonance Raman experiments in an argon matrix. The corresponding gas-phase harmonic frequency is expected[34] to differ only slightly (within a few wave numbers) from its matrix value. The experimental value of the dissociation energy of the scandium dimer is a subject of controversy. It was estimated in 1964 as 1.12 ± 0.22 eV by mass-spectroscopic measurements followed by the third-law thermodynamic method calculations by Drowart and co-workers.[35] In a review published two years later, Drowart[36] already quoted a different value of 1.65 ± 0.22 eV, which apparently was obtained from the same data. Further details concerning the corrected value have been given recently by Kalemos *et al.*[31] A detailed multireference theoretical study performed by Åkeby and co-workers[37,38] suggested that the presence of previously unknown low-lying electronic states of Sc_2 contributing to the molecular partition function should lower D_e to 1.05 ± 0.2 eV. In the context of this discussion, it is appropriate to mention here another attempt[39] to estimate D_e of Sc_2 using the LeRoy–Bernstein analysis[40,41] of the vibrational energy levels of the scandium dimer, which yielded a lower limit of the dissociation energy of 0.79 eV. It is important to stress that this value should just be viewed as a lower limit for the dissociation energy since the only five observed transitions in the resonance Raman progression[33] are not sufficient to show an evidence of the $\omega_e y_e$ anharmonicity in the Dunham fit, which is required for the LeRoy–Bernstein analysis to yield reasonable results.[39]

The analysis[42] of the hyperfine splitting of two ESR bands of Sc_2 trapped in solid neon matrix showed that the ground state is a quintet (S=2). It was further demonstrated

[a)]This paper is dedicated to the memory of Professor Björn O. Roos (1937–2010).
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that the observed pattern is consistent with a simulated electron spin resonance (ESR) spectrum of a $^5\Sigma$ state. It is important to stress here that the positions of the two observed perpendicular fine-structure lines in the ESR spectrum could not be reproduced for $S=1$ and $S=3$, which effectively excludes the possibility that the ground state of Sc_2 is either a triplet or a septet. An UV-vis spectrum of scandium atoms trapped in an argon matrix shows evidence of three absorptions at 15 100, 21 050, and 29 850 cm^{-1}, which were assigned to three low-lying excited states of Sc_2.[43]

Early semiempirical and HF calculations designated the $^1\Sigma_g^+$ and $^5\Delta_g$ electronic states as candidates for the ground state.[43–46] The first multireference (MCSCF/MRCI) study[47] of Sc_2 showed that the $^5\Sigma_u^-$ state with a minimum at 2.6 Å lies considerably lower than the previously investigated states. The first global PEC for the $^5\Sigma_u^-$ state was constructed by Tatewaki and co-workers[48] using an (22o, 6e) active space built from the 3*d*, 4*s*, and 4*d* atomic orbitals; state averaging was needed to assure the connected and smooth character of the curve. The electronic nature of the $^5\Sigma_u^-$ state was investigated by a number of authors.[8,31,49–51] As already pointed out, this state dissociates formally to an excited manifold of separated atoms. The electronic states arising from the lowest $^2D_g+^2D_g$ dissociation channel were found to be very closely spaced and only weakly bound.[31,52,53] Their PECs have been constructed recently by Kalemos *et al.*[31] An extensive study of low-lying states of Sc_2 was given by Åkeby and co-workers.[38] A number of DFT studies on the low-lying states of Sc_2 appeared,[51,54–60] which were mainly focused on the accurate determination of the ground state using various exchange-correlation functionals and a comparison between the lowest state in each of the spin manifolds. A compilation of spectroscopic parameters obtained with various correlated methods for covalently bound low-lying states of Sc_2 is given in Table I.

This well-established theoretical picture has been recently upset by the quantum DMC study of Sc_2 performed by Matxain *et al.*[8] This study reports single point DMC energies computed at the DFT/B3LYP equilibrium geometries for ten low-lying states of Sc_2. The symmetry of the ground state is found to be $^3\Sigma_u^-$ instead of the previously believed $^5\Sigma_u^-$. (Note that no details on the +/− symmetry of the Σ states are provided in Ref. 8.) Both states are found to be separated by only 0.17 eV (DMC). Their spectroscopic parameters are also similar. The ground character of $^3\Sigma_u^-$ is further corroborated by MRMP calculations,[61–63] which give almost identical energy spacing (0.16 eV) as DMC. It is important to stress here that these MRMP results are affected by conspicuous procedural faults, as have been shown in a recently published erratum.[64] It was demonstrated recently[65] by the present authors that MRMP and CASPT2 calculations using the chemically correct (12o, 6e) complete active space (CAS) are plagued by numerous intruder states. Intruder state removal techniques (i.e., shift techniques) produce smooth and continuous curves but simultaneously introduce unpleasant artifacts in the energy ordering of the $^3\Sigma_u^-$ and $^5\Sigma_u^-$ states. The energy ordering depends on the magnitude of the shift parameter; $^3\Sigma_u^-$ is the ground state for small values of the shift, and $^5\Sigma_u^-$ for large values. This unexpected behavior casts many a doubt on the effectiveness of MRMP and CASPT2 as an appropriate tool for the reliable investigation of the low-lying states of Sc_2. Note that the $^3\Sigma_u^-$ state was not studied using multireference methods prior to the calculations of Matxain *et al.*; previous DFT calculations[8,51,56] predicted it higher than the $^5\Sigma_u^-$ state by 0.07–0.22 eV. Also the recent MRCI calculations of Kalemos *et al.*[31] predict it higher by 0.04 eV.

The present study has two goals. First of all, we want to reaffirm that the ground state of Sc_2 is $^5\Sigma_u^-$ and that $^3\Sigma_u^-$ state is one of a few low-lying excited states of this molecule. The present results are obtained using NEVPT2[66,67] and NEVPT3,[10,68] recently developed variants of multireference perturbation theory. The particular features of NEVPT, viz., the absence of intruder states and the property of size consistence, are particularly useful in the study of a molecule such as Sc_2, where both statical and dynamical correlation energies need to be adequately accounted for. An excellent agreement between the results from the second- and third-order multireference perturbation theory combined with a large atomic basis set and including the relativistic and semicore correlation effects suggests high accuracy of our predictions. The correctness of this assignment is further corroborated by an excellent agreement between the computed and experimental values of ω_e for the $^5\Sigma_u^-$ state. The second purpose of the present study is to give a systematic account of the low-lying states of Sc_2 in order to characterize all the potential candidates for the ground state. To this end, the PEC for the ground state in each irreducible representation of the $D_{\infty h}$ point group is computed for the singlet, triplet, quintet, and septet spin manifolds ($S=0,1,2,3$) using CASSCF with the (18o, 6e) full valence active space followed by NEVPT2 corrections for the low-lying curves. We believe that the presented results are a significant contribution to the quest for finding the ground state of Sc_2.

II. COMPUTATIONAL DETAILS

The all-electron relativistic (21*s*15*p*10*d*6*f*4*g*2*h*)/[10*s*9*p*8*d*5*f*4*g*2*h*] atomic natural orbital (ANO) type basis set of Roos *et al.*[69] has been adopted for this work. The PECs of Sc_2 have been computed with the *n*-electron valence state perturbation theory (NEVPT) method.[66,68] Scalar relativistic effects have been accounted for by using the second-order Douglas–Kroll–Hess Hamiltonian.[70] Spin-orbit (SO) calculations have been performed using the full Breit–Pauli SO operator. The diagonal elements of the SO matrix have been substituted with the state-specific (18o, 6e) NEVPT2 energies; the off-diagonal elements have been calculated using the state-averaged CASSCF orbitals averaged over the six lowest-lying states ($^5\Sigma_u^-$, $^3\Sigma_u^-$, $^3\Delta_u$, $^3\Pi_g$, $^1\Pi_g$, and $^1\Sigma_u^-$) of Sc_2.

We used the full valence active space (18o, 6e) composed of the 4*s*, 3*d*, and 4*p* atomic orbitals (AOs) for this work. Two other active spaces have been tested in our calculations, the reduced valence space (12o, 6e) composed of the 4*s* and 3*d* AOs of each scandium atom and the augmented reduced valence space (14o, 6e) composed of the 4*s*, 3*d*, and $4p_z$ AOs. Dynamical correlation has been taken into account by means of the second- and third-order[10] NEVPT

TABLE I. Compilation of spectroscopic parameters computed with a variety of quantum mechanical methods for covalently bonded low-lying states of Sc_2. Bond lengths r_e are given in angstroms, harmonic frequencies ω_e in cm^{-1}, adiabatic excitation energies T_e in eV, and dissociation energies D_e in eV. Dissociation energies are determined with respect to the $^2D_g+^4F_g$ (if otherwise, see footnote).

State	Reference	Method	r_e	ω_e	T_e	D_e
$^5\Sigma_u^-$	38	IC-ACPF	2.67	186	0.00	1.87
	37	ACPF(v)+CPP(cc)	2.68	229	0.00	1.87
	47	MRCI(SD)	2.60	··· [a]	0.00	1.13
	49	MRCI(SD)	2.79	184	0.00	0.44[b]
	50	MRCI(SD)	2.69	222	0.00	1.15
	48	MRCI(SD+Q)	2.74	224	0.00	0.59[b]
	54	DFT/LSD	2.70	200	0.00	1.80
	55	DFT/BOP	2.66	··· [a]	0.00	··· [a]
	55	DFT/B3LYP	2.58	··· [a]	0.00	··· [a]
	55	DFT/B-null	2.71	··· [a]	0.00	··· [a]
	55	DFT/PW91	2.62	··· [a]	0.00	··· [a]
	55	MP2	2.39	··· [a]	0.00	··· [a]
	56	DFT/BP86	2.63	222	0.00	2.25
	57	DFT/B3LYP	2.59	263	0.00	0.50[b]
	57	DFT/B3P86	2.57	270	0.00	0.92[b]
	57	DFT/BHLYP	2.56	284	0.00	−0.71[b]
	57	DFT/BLYP	2.65	237	0.00	1.18[b]
	57	DFT/BP86	2.63	246	0.00	1.54[b]
	57	DFT/LSDA	2.57	263	0.00	2.69[b]
	51	DFT/BPW91	2.63	241	0.00	··· [a]
	58	DFT/PAW	2.58	257	0.00	2.34
	59	DFT/BP86	2.68	252	0.00	··· [a]
	60	DFT/BPW91	2.63	241	0.00	1.51[c]
	60	DFT/PW91PW91	2.62	243	0.00	1.63[c]
	60	DFT/BLYP	2.65	234	0.00	1.15[c]
	60	DFT/BP86	2.62	242	0.00	1.51[c]
	60	DFT/BPBE	2.63	241	0.00	1.53[c]
	60	DFT/PBEPBE	2.63	243	0.00	1.61[c]
	8	DFT/B3LYP	2.58	260	0.17[d]	0.93[d]
	31	MRCI(SD+Q)	2.65	224	0.00	2.08
$^3\Sigma_u^-$	56	DFT/BP86	2.64	265	··· [a]	2.03
	51	DFT/BPW91	2.61	256	0.18	··· [a]
	58	DFT/PAW	2.24	··· [a]	··· [a]	2.26
	8	DFT/B3LYP	2.57	273	0.00[d]	1.10[d]
	31	MRCI(SD+Q)	2.64	234	0.35	2.11[e]
$^1\Sigma_g^+$	50	MRCI(SD)	2.79	340	··· [a]	1.25[f]
	51	DFT/BPW91	2.27	287	0.35	··· [a]
	58	DFT/PAW	2.17	··· [a]	··· [a]	2.25
	8	DFT/B3LYP	3.16	181	0.49[d]	··· [a]
$^5\Delta_u$	38	IC-ACPF	2.84	195	0.46	1.41
	8	DFT/B3LYP	2.45	269	1.94[d]	··· [a]
$^7\Delta_g$	51	DFT/BPW91	2.50	240	0.49	··· [a]
	58	DFT/PAW	2.43	··· [a]	··· [a]	1.62
$^5\Delta_g$	38	IC-ACPF	2.43	241	0.59	2.00
	8	DFT/B3LYP	2.36	280	0.86[d]	··· [a]
$^1\Pi_g$	8	DFT/B3LYP	2.55	266	0.77[d]	··· [a]
$^3\Sigma_g^-$	54	DFT/LSD	3.25	235	··· [a]	1.00
$^5\Sigma_g^+$	8	DFT/B3LYP	2.47	240	1.56[d]	··· [a]
$^7\Delta_u$	8	DFT/B3LYP	2.45	314	1.57[d]	··· [a]

[a]Data not available.
[b]Determined with respect to the $^2D_g+^2D_g$ asymptote.
[c]The reported value is D_0.
[d]The reported value is given at the DMC//DFT/B3LYP level of theory.
[e]Uncorrected value (see Ref. 31).
[f]Determined with respect to the $^4F_g+^4F_g$ asymptote.

method. The $3s$ and $3p$ electrons have been correlated at the perturbation level in all calculations. The second-order calculations have been performed using the partially contracted formalism (PC-NEVPT2), while the third-order calculations employed both the strongly (SC-NEVPT3) and partially (PC-NEVPT3) contracted approach. It is noteworthy that this is the first time that 18 active orbitals have been used in conjunction with the NEVPT method and that the partially contracted variant of NEVPT3 has been used in quantum chemical calculations. All the calculations have been carried out

TABLE II. Excitation energies for the low-lying atomic terms of scandium in eV calculated at the CASSCF, NEVPT2, and NEVPT3 level using the (9o, 3e) full valence and (6o, 3e) reduce valence active space.

	(6o, 3e)				(9o, 3e)				
State	CASSCF	PC-NEVPT2	SC-NEVPT3	PC-NEVPT3	CASSCF	PC-NEVPT2	SC-NEVPT3	PC-NEVPT3	Expt.[a]
^2D_g	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
^4F_g	1.15	1.19	1.30	1.30	1.96	1.31	1.46	1.49	1.43
^2F_g	1.62	1.56	1.61	1.64	2.33	1.75	1.91	1.91	1.85
^4F_u	...[b]	...[b]	...[b]	...[b]	1.80	1.97	1.91	1.91	1.96
^4D_u	...[b]	...[b]	...[b]	...[b]	1.85	2.02	1.96	1.96	1.99
^2D_u	...[b]	...[b]	...[b]	...[b]	1.92	2.00	1.96	1.96	1.98

[a]Reference 73.
[b]The (6o, 3e) CAS does not permit the description of the given atomic term.

with the MOLPRO (Ref. 71) computational package in the D_{2h} point group symmetry. The proper Λ quantum number for all the studied states has been ensured by means of the LQUANT option implemented in MOLPRO.

III. RESULTS AND DISCUSSION

A. Atomic calculations

Before proceeding to the molecular calculations, we briefly inspect here the low-lying atomic terms of the scandium atom. These results help us elucidate the energy ordering of various dissociation asymptotes formally available for the molecular states. It should be clear that such information is quite crucial in obtaining accurate dissociation energies of the molecular states. Atomic calculations for the low-lying states of scandium (^2D_g, ^2D_u, ^2F_g, ^4D_u, ^4F_g, and ^4F_u) have been performed using the full and reduced valence active spaces (9o, 3e) and (6o, 3e). Note that the reduced valence CAS is capable of describing only the atomic terms of even parity: ^2D_g, ^4F_g, and ^2F_g. The calculations have been carried out in D_{2h} point group symmetry including all the appropriate components (five and seven, respectively) of the D and F terms. State-specific full-valence CASSCF calculations for the six lowest atomic terms of Sc reveal serious discrepancies with the experimental energy ordering[72] (for details, see Table II). Accounting for dynamical correlation yields the correct ordering of the states and considerably improves the energetics. The results from NEVPT3 are slightly more accurate than those from NEVPT2, especially for the terms corresponding to the $4s^23d$ and $4s3d^2$ configurations. There is only a very small deviation between the strongly and partially contracted versions of NEVPT3. Employing the full valence active space is quite crucial for obtaining accurate energetics. The mean absolute deviation for the NEVPT2 results obtained with the (9o, 3e) CAS is only 0.06 eV, while for the (6o, 3e) it is approximately five times as large (0.26 eV). A similar trend is also observed for the PC-NEVPT3 (0.04 versus 0.17 eV) and SC-NEVPT3 (0.04 versus 0.18 eV) approaches.

Special attention is given here to the ^2D_g, ^4D_u, ^4F_u, and ^4F_g atomic terms, since the ground state ($^5\Sigma_u^-$) of Sc_2 may formally originate from the $^2D_g+^4F_g$, $^2D_g+^4D_u$, or $^2D_g+^4F_u$ dissociation channels. An inspection of the $^5\Sigma_u^-$ wave function around its minimum shows almost negligible contributions from the atomic $4p$ orbitals, suggesting that the correct dissociation asymptote for $^5\Sigma_u^-$ is $^2D_g+^4F_g$. Unfortunately, the CASSCF method erroneously places the $^2D_g+^4F_u$ and $^2D_g+^4D_u$ lower than $^2D_g+^4F_g$ by 0.16 and 0.12 eV, respectively. This fact has serious consequences in the estimation of the dissociation energy. If the dissociation energy for the $^5\Sigma_u^-$ ground state is computed directly from the PEC, rather than from the separated atoms limit, a correction equivalent to the $^4F_u-^4F_g$ energy spacing must be introduced in the final result to compensate for the automatic choice of the wrong asymptote.

B. Low-lying states of Sc_2

The lowest PECs of Sc_2 for each of the $^{1,3,5,7}[\Sigma^+,\Sigma^-,\Pi,\Delta,\Phi,\Gamma]_{g,u}$ manifolds have been computed using the state-specific CASSCF method with the (18o, 6e) full valence active space. The curves, shown in Fig. 1, have been computed between 1.95 and 3.55 Å in order to designate viable candidates for the low-lying covalently bound states of the scandium dimer. As earlier anticipated,[31] the resulting curves are quite closely spaced. The dynamical correlation contribution has been estimated for each of the curve around its minimum using the NEVPT2 method. The singlet and triplet states of purely van der Waals character that were studied previously by Kalemos *et al.*[31] were omitted in this procedure. Out of the 48 studied states, the lowest six ($^5\Sigma_u^-$, $^3\Sigma_u^-$, $^5\Delta_u$, $^3\Pi_g$, $^1\Pi_g$, and $^1\Sigma_u^-$) have been further considered as possible candidates for the ground state of Sc_2.

Figure 2 shows the NEVPT2 curves for the six lowest-lying states of Sc_2. It is found that the ground state is $^5\Sigma_u^-$. This state is closely followed by $^3\Sigma_u^-$ (+0.10 eV), $^5\Delta_u$ (+0.25 eV), the two almost degenerate $^3\Pi_g$ and $^1\Pi_g$ states (+0.26 and +0.27 eV, respectively), and the $^1\Sigma_u^-$ state (+0.41 eV). The next low-lying states of Sc_2 are $^1\Sigma_g^+$, $^3\Pi_u$, $^5\Delta_g$, $^3\Delta_u$, and $^1\Delta_u$, all with minima between 0.4 and 0.5 eV higher than that of $^5\Sigma_u^-$. Our energy ordering of the $^5\Sigma_u^-$ and $^3\Sigma_u^-$ states confirms the recent MRCI results of Kalemos *et al.*[31] and contradicts the earlier DMC predictions of Matxain *et al.*[8]

Spectroscopic parameters computed for the six NEVPT2 curves presented in Fig. 2 are shown in Table III. Note that the spectroscopic parameters for all the states (except $^5\Delta_u$) are quite similar. It is important to emphasize here the excellent agreement between the computed and experimental harmonic vibrational frequency of $^5\Sigma_u^-$, which is the only spec-

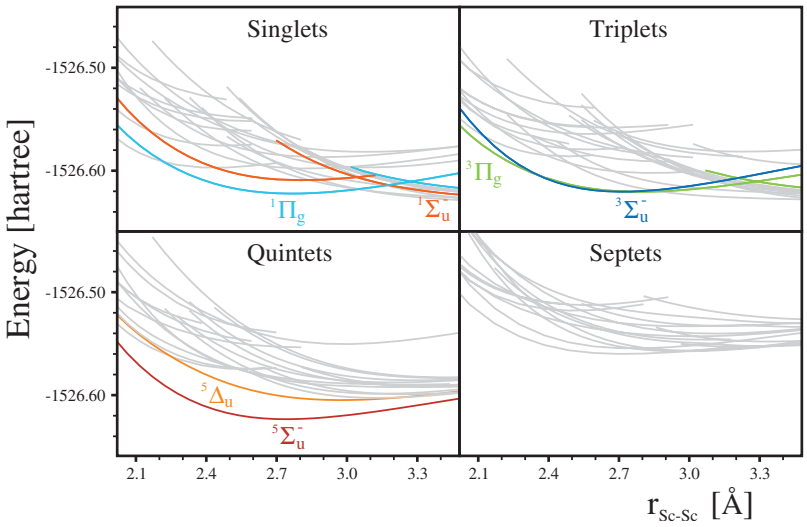

FIG. 1. The low-lying states of Sc_2 determined by the (18o, 6e) CASSCF calculations. The lowest energy state in each irreducible representation (Σ, Π, Δ, Φ, and Γ) of the $D_{\infty h}$ point group with $S=0,1,2,3$ is presented. The viable candidates for the ground state are depicted in color.

troscopic parameter known with certainty from experiment. Such a good concordance suggests that also the other spectroscopic parameters may be in good agreement with the corresponding (as yet unknown) experimental values. One of the most serious controversies concerns the dissociation energy of Sc_2. The dissociation energy computed with NEVPT2 is 1.78 eV with respect to the separated atoms ($^2D_g+^4F_g$) and 0.51 eV with respect to the ground state of the atoms ($^2D_g+^2D_g$). The analogous MRCI results recently given by Kalemos *et al.*[31] are 2.08 and 0.35 eV, respectively.

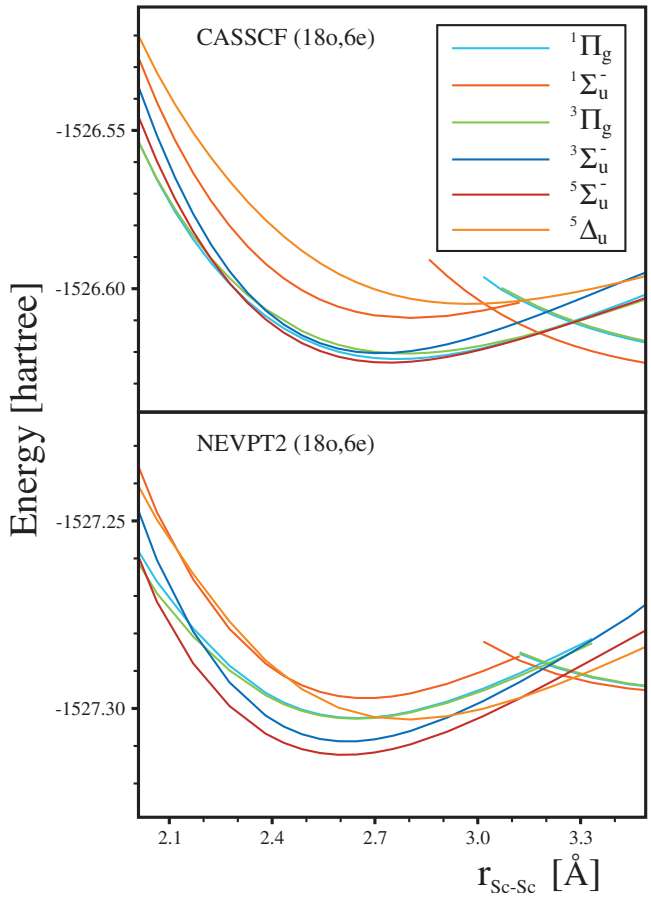

FIG. 2. A comparison of the (18o, 6e) CASSCF (upper panel) and NEVPT2 (lower panel) PECs for the six low-lying states of Sc_2.

We recall that NEVPT is a size consistent theory and the quoted results are not affected by misbehaviors at large internuclear distances (as for example in MRCI). It is important to stress that the size consistency of NEVPT follows only if the underlying CASSCF calculations are size consistent. In the case of a CASSCF wave function not providing a well balanced mixture of all the components corresponding to the atomic states at the dissociation limit, the lack of size consistency of the zeroth-order wave function breaks the size

TABLE III. Spectroscopic parameters for the five low-lying states of Sc_2 calculated at the NEVPT2 level using the (18o, 6e), (14o, 6e), and (12o, 6e) CAS. Bond lengths r_e are given in angstrom, harmonic frequencies ω_e and first anharmonicities $\omega_e x_e$ in cm^{-1}, and dissociation energies D_e in eV. Dissociation energies are determined with respect to the $^2D_g+^4F_g$ asymptote.

State	r_e	ω_e	$\omega_e x_e$	D_e
		NEVPT (18o, 6e)		
$^5\Sigma_u^-$	2.611	241.8	0.70	1.78
		238.9[a]	0.93[a]	
$^3\Sigma_u^-$	2.620	254.0	0.71	1.69
$^5\Delta_u$	2.792	212.0	0.53	1.53
$^3\Pi_g$	2.644	221.3	0.74	1.52
$^1\Pi_g$	2.645	226.9	0.71	1.52
$^1\Sigma_u^-$	2.673	235.7	0.76	1.37
		NEVPT (14o, 6e)		
$^5\Sigma_u^-$	2.588	253.9	0.83	1.72
		238.9[a]	0.93[a]	
$^3\Sigma_u^-$	2.595	265.6	0.78	1.60
$^5\Delta_u$	2.775	218.0	0.76	1.42
$^3\Pi_g$	2.592	234.7	1.26	1.56
$^1\Pi_g$	2.584	238.1	1.03	1.53
$^1\Sigma_u^-$	2.644	244.7	0.72	1.28
		NEVPT (12o, 6e)		
$^5\Sigma_u^-$	2.580	257.5	0.87	1.74
		238.9[a]	0.93[a]	
$^3\Sigma_u^-$	2.595	260.1	0.76	1.65
$^5\Delta_g$	… [b]	… [b]	… [b]	… [b]
$^3\Pi_g$	… [b]	… [b]	… [b]	… [b]
$^1\Pi_g$	… [b]	… [b]	… [b]	… [b]
$^1\Sigma_u^-$	2.637	247.0	0.78	1.34

[a]Experimental value, Ref. 33.
[b]The (12o, 6e) CAS does not permit a proper description of the electronic structure of Sc_2 for the given state.

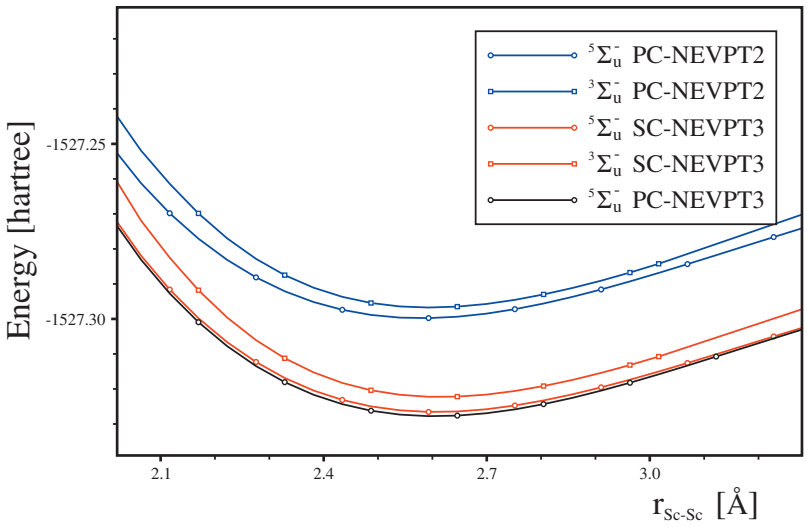

FIG. 3. A comparison of the partially contracted (PC) second-order (in blue) and strongly contracted (SC) third-order (in red) NEVPT PECs for the two lowest-lying states of the scandium dimer, $^5\Sigma_u^-$ and $^3\Sigma_u^-$. In addition, the PC third order (in black) is given for the $^5\Sigma_u^-$ state.

consistency property of NEVPT. We found that the size consistency error estimated with respect to the $^2D_g+^4F_g$ dissociation asymptote at 20.00 a.u. for the $^5\Sigma_u^-$ in the reduced valence space is as small as 0.028 eV.

Among the six lowest-lying states of Sc_2, only $^1\Pi_g$, $^3\Pi_g$, and $^5\Delta_u$ interact via the SO Hamiltonian. The energy separation between these three states is very small and therefore it is important to examine the SO splitting effects for them. Estimation of the SO coupling for $^3\Pi_g$ and $^1\Pi_g$ shows that the interaction is indeed very weak. The computed splittings at 2.59 Å with respect to the zeroth-order spin-free $^3\Pi_g$ state are -36 cm^{-1} ($\Omega=0^+$ and 0^-), -21 cm^{-1} ($\Omega=1$), $+64$ cm^{-1} ($\Omega=1$), and $+36$ cm^{-1} ($\Omega=2$). For the $^5\Delta_u$ state, the interaction is noticeably larger and causes a splitting of 206 cm^{-1} between the outermost $\Omega=0$ and $\Omega=4$ SO components of this state. As expected, none of these splittings modifies seriously the energy landscape for the low-lying states of the scandium dimer.

For some of the states, namely for those that formally dissociate to the ground state of the separated atoms, the lowest PECs consist of two crossing segments. The long-distance segment corresponds to the interaction of two $4s^23d^1$ scandium atoms, while the short-distance segment to the interaction of the $4s^23d^1$ and $4s^13d^2$ scandium atoms. Their analytical structure and consequently also the physical nature are very different. The best evidence of the dissimilarity follows from the fact that the two CASSCF solutions can be analytically continued also to metastable regions yielding the crossed, two-segment patterns observed in Fig. 1. Clearly, such a situation is not desirable for physical solutions, which should vary smoothly while passing from one region to the other. Usually, an appropriately averaged CASSCF procedure can resolve this situation. Unfortunately, it has not proved possible to achieve this result for the Sc_2 molecule. The two-segment curves presented in Fig. 1 can be thus regarded as diabatic PECs that should be coupled via an appropriate adiabatic coupling matrix element. Note that such an interaction is expected to modify the shape of these curves only in the vicinity of the crossing point owing to their very different physical nature. Actually, for our purpose, it is more convenient to analyze the diabatic curves, since the crossing point is usually shifted after accounting for the dynamical correlation. In case of adiabatic states, one would need to employ a multistate perturbation theory formalism, such as the quasidegenerate NEVPT2,[73] to recover the smooth character of PECs at the crossing region. Fortunately, for the five states analyzed here, the crossing points occur far away from their minima, thereby not influencing the final conclusions drawn from our work.

C. NEVPT3 results for the $^5\Sigma_u^-$ and $^3\Sigma_u^-$ states

The results presented in Sec. III B have been obtained using the second-order NEVPT method. In this section we extend the correlation treatment to the third order using the (12o, 6e) reduced valence space. In addition to its intrinsic value, the third-order approach is a good test to assess the efficiency and stability of the perturbation series. Actually, a large discord between the second- and third-order results would be a clear indication of the inadequacy of the zero-order wave function. So far, third-order NEVPT in its strongly contracted variant (SC-NEVPT3) has been only applied to the study of transition metal dimers for the group VI elements[6,10] (Cr_2, Mo_2, W_2, and CrMo) and for Mn_2.[11] In the present work, besides the usual strongly contracted variant, we also made use of the partially contracted NEVPT3 approach (PC-NEVPT3). We recall that in the partially contracted variant of NEVPT the whole dimensionality of the internally contracted first-order interacting space (IC-FOIS) is taken into account, whereas in the strongly contracted approach only a subspace of IC-FOIS is considered. The PC-NEVPT3 calculations are computationally more demanding than the SC-NEVPT3 ones and thus they have been performed only for the $^5\Sigma_u^-$ state, with the purpose to assess the magnitude of the differences between the two variants of NEVPT3. The resulting PECs are reported in Fig. 3 along with second-order PC-NEVPT2 ones. As can be seen, the difference between SC- and PC-NEVPT3 is very small and there is hardly any advantage in choosing the more laborious partially contracted variant. The third-order PECs for the $^5\Sigma_u^-$ and $^3\Sigma_u^-$ states run parallel to the corresponding second-order curves and are lower in energy with respect to the PC-

TABLE IV. Spectroscopic parameters for the two low-lying states of Sc_2 calculated at the NEVPT2 and NEVPT3 levels using the reduced valence (12o, 6e) active space. Bond lengths r_e are given in angstrom, harmonic frequencies ω_e and first anharmonicities $\omega_e x_e$ in cm^{-1}, and dissociation energies D_e in eV. Dissociation energies are determined with respect to the $^2D_g + {}^4F_g$ asymptote.

State	Method	r_e	ω_e	$\omega_e x_e$	D_e
$^5\Sigma_u^-$	PC-NEVPT2	2.580	257.5	0.87	1.74
	SC-NEVPT3	2.607	257.4	0.87	1.56
	PC-NEVPT3	2.605	260.3	0.87	1.61
			238.9[a]	0.93[a]	
$^3\Sigma_u^-$	PC-NEVPT2	2.595	260.1	0.76	1.65
	SC-NEVPT3	2.615	261.5	0.75	1.44

[a]Experimental value, Ref. 33.

NEVPT2 PECs, showing that the perturbation series does not suffer from oscillations. The difference in energy between the two states turns out to be slightly increased in the SC-NEVPT3 treatment with respect to PC-NEVPT2; the minimum-to-minimum energy difference changes from 0.12 eV (SC-NEVPT3) to 0.08 eV (PC-NEVPT2). These estimations using the (12o, 6e) active space embrace the 0.10 eV (PC-NEVPT2) energy spacing obtained with the (18o, 6e) CAS. The corresponding spectroscopic constants are reported in Table IV. A comparison of the (12o, 6e) NEVPT2 and NEVPT3 values shows that the harmonic vibrational frequencies are almost identical, while one can observe a small elongation in the equilibrium distance of both states, in agreement with the NEVPT2 results obtained with the full valence space (18o, 6e) and shown in Table III.

D. A comment on the applicability of reduced valence active spaces

Full-valence active space calculations for systems with a large number of configuration state functions are prohibitively expensive. Unfortunately, this is the situation for most transition metal dimers. In this respect Sc_2 is an exception; the full-valence active space calculations are not only possible, but quite robust. Therefore, Sc_2 constitutes a perfect benchmark system for verifying the applicability of reduced valence spaces in electronic structure calculations. In our previous studies[12] of Mn_2 we investigated the use of the so-called nonclosed active spaces. As stressed by Buchachenko *et al.*,[74] the nonclosed active spaces do not possess a complete set of AOs representing a particular atomic shell, and might not be appropriate for this type of calculations. For Mn_2, where the bond is of van der Waals character, a large variance in the spectroscopic parameters of the ground state was found.[12,74] It would be very interesting to investigate the applicability of reduced valence active spaces for covalently bonded transition metal dimers.

In order to evaluate the appropriateness of this particular approach, the PECs of Sc_2 shown in Fig. 4 have been computed with the traditional choice of reduced (12o, 6e) and full (18o, 6e) valence spaces along with the nonclosed (14o, 6e) active space. Spectroscopic parameters computed for the NEVPT2 PECs shown in Table III display rather small variations with the change in the active space. For instance, the largest difference in ω_e—between the (18o, 6e) and (12o, 6e) CAS for the $^5\Sigma_u^-$ state—is only 16 cm^{-1} (6.5%). Bond lengths present even smaller fluctuations. The largest difference is 0.06 Å (2.3%) and corresponds to the deviation between the (18o, 6e) and (14o, 6e) CAS for the $^1\Pi_g$ state.

The differences observed for ω_e and r_e of Sc_2 are rather small, but the most serious criticism against the nonclosed active space approach concerned the computation of the dissociation energy D_e. Since the use of nonclosed active spaces leads to an artificial symmetry breaking at the atomic level, it is expected that large discrepancies between the nonclosed and traditional active spaces can be observed. This intuitive expectation is not fully confirmed for Sc_2. It is true that the mean absolute deviation between the closed active spaces (12 orbital CAS versus 18 orbital CAS) is twice as small as the nonclosed case (14 orbital CAS versus 18 orbital CAS), but the absolute magnitude of the error is rather small in both cases: 0.04 and 0.07 eV, respectively. The largest difference detected for D_e is of the order of 0.11 eV (7.2%); it is found between the (18o, 6e) and (14o, 6e) active spaces for the $^5\Delta_u$ state. It has to be noted here that the traditional choice of active space for transition metal dimers (12o, 6e) causes much more serious problems since it does not permit a proper description of the $^3\Pi_g$, $^1\Pi_g$, and $^5\Delta_u$ states due to the

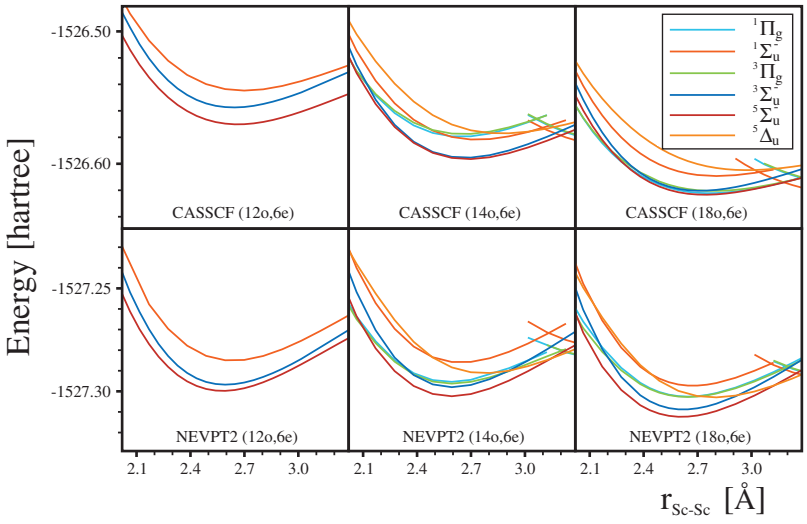

FIG. 4. PECs of the six low-lying states of the scandium dimer computed using CASSCF and NEVPT2 with the full valence (18o, 6e) CAS (right panel), augmented reduced valence (14o, 6e) CAS (middle panel), and the reduced valence (12o, 6e) CAS (left panel). Note that three states—$^3\Pi_g$, $^1\Pi_g$, and $^5\Delta_u$—cannot be described in the reduced valence space.

lack of the indispensable $4p$ AOs in the active space. Note also that in the case of other spectroscopic parameters, r_e and ω_e, the deviation between the (12o, 6e) and (18o, 6e) is actually sizably larger than between (14o, 6e) and (18o, 6e).

IV. CONCLUSION

The PECs of low-lying states of the scandium dimer have been studied with multireference perturbation theory (NEVPT2 and NEVPT3) using the full valence active space (18o, 6e) and a large $(21s15p10d6f4g2h)/[10s9p8d5f4g2h]$ ANO-type basis set. We found that the ground state of Sc_2 is $^5\Sigma_u^-$. This state is closely followed by other low-lying states: $^3\Sigma_u^-$, $^5\Delta_u$, $^3\Pi_g$, $^1\Pi_g$, and $^1\Sigma_u^-$ with energy separations of +0.10, +0.25, +0.26, +0.27, and +0.41 eV, respectively. A systematic examination of the lowest energy state in each of the $^{1,3,5,7}[\Sigma^+,\Sigma^-,\Pi,\Delta,\Phi,\Gamma]_{g,u}$ irreducible representation of the $D_{\infty h}$ point group suggests that no other state of Sc_2 can be regarded as a viable candidate for the ground state of this system. Our energy ordering of the $^5\Sigma_u^-$ and $^3\Sigma_u^-$ states bears out the recent MRCI results of Kalemos *et al.*[31] and is in contrast with the earlier DMC predictions of Matxain *et al.*[8] An excellent agreement between the second- and third-order NEVPT results and between the computed and experimental values of ω_e for the $^5\Sigma_u^-$ state indicates high accuracy of our predictions.

Another significant aspect of our work concerns the investigation of the possible reduction of the size of the active space. We found that for the low-lying states of Sc_2 the spectroscopic parameters depend only weakly on the choice of the active space with deviations of a few percent. As expected, the most accurate results are obtained with the full valence active space (18o, 6e). The traditional choice of the (12o, 6e) CAS does not permit a proper description of the electronic structure of Sc_2 in the $^3\Pi_g$, $^1\Pi_g$, and $^5\Delta_u$ states. No particular problems are detected for the nonclosed (14o, 6e) active space. These observations suggest that a strong dependence of the computed molecular parameters and potential energy surfaces on the choice of the active space may be limited to noncovalently bound species,[12,74] where the adequate description of the electronic structure requires a properly balanced composition of the active space. It can be hoped that the results shown in the present study, along with the recent surge of interest in the theoretical description of the scandium dimer, will prompt experimental groups to reinvestigate this intriguing molecule so as to remedy the current paucity of reliable experimental data on Sc_2.

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