

All electron ab initio calculations on the ScTi molecule: a really hard nut to crack

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Abstract The lightest and yet completely unexplored intermetallic ScTi system has been studied by high-level ab initio methods and quantitative basis sets. We have studied in all 21 $^{2S+1}\Lambda$ states and constructed potential energy curves at the MRCI/cc-pvQZ computational level. The ground state of the system is of $^6\Delta$ symmetry with $r_e = 2.65 \text{ \AA}$ and $D_e = 32.4 \text{ kcal/mol}$ with respect to the adiabatic fragments or $D_e^0 = 10.4 \text{ kcal/mol}$ with respect to the ground state atoms while its first excited state seems to be of $^4\Delta$ symmetry with similar bonding features lying only 3 kcal/mol higher. An exceptional feature is the rather high Mulliken charge (average value of $\sim 0.5 e^-$) transferred to Sc but the small calculated dipole moments.

Keywords ScTi · Ab initio · Multireference

1 Introduction

The nine 3d-transition metal elements (M) from Sc ($Z = 21$) to Cu ($Z = 29$) comprise the most emblematic group of metals on Earth. As a matter of fact, Cu and Fe mark the dawn of human civilization, dubbed the Copper and Iron Ages, and perhaps the beginning of what we call today “Modern Chemistry.” Ironically, and despite the explosive progress in the physical sciences, we cannot

claim that we understand satisfactorily certain classes of “small” molecular systems. Prominent among them are the 3d-MM' diatomics ($M, M' = \text{Sc-Cu}$). Since the early 90 s, our research group has been engaged in an in-depth theoretical study of all 3d-M diatomics, $\text{MX}^{0,\pm}$, where $X = \text{H}$ [1–3], B [4–8], C [9–27], O [28–33], F [34–36], Al [37], P [38–40], and Cl [41] through all electron high-level ab initio calculations. One of the most interesting features of the MX species is the extremely rich variety of the binding modes entailed due to the metals' 3d electrons, which result in a remarkable density of high spin and orbital angular momenta atomic ^{2S+1}L states. This large density of states is the driving force behind the wealthy chemistry of such systems and is also the root of all computational problems encountered, which still challenge all existing state-of-the-art theoretical methods. Both features are enhanced in the 3d-dimers of either homo-(M_2) or hetero-(MM') nuclear nature due to the simultaneous presence of two capricious atoms. There are $\binom{9}{2} = 36$

3d intermetallic (MM') and nine homonuclear diatomics (M_2), a total of 45 molecules each one with a personality of its own.

In the recent past, we have carefully examined through multireference variational and single reference methods, three homonuclear and one heteronuclear diatomics, namely Sc_2 [42–47],¹ Ti_2 [48], Mn_2 [49], and TiFe [50]. Our computational and conceptual difficulties with these systems are well described in the above four references, so

Dedicated to Professor Thom Dunning and published as part of the special collection of articles celebrating his career upon his retirement.

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¹ It is interesting to follow the discussion on the ground state of Sc_2 , $^5\Sigma_u^-$ versus $^3\Sigma_u^-$, and the theoretical methods involved. The dispute was triggered by Maxtain et al. [47] who erroneously suggested that the ground state of Sc_2 is $^3\Sigma_u^-$. The controversy was settled in reference [42], see also [44].

there is no need for repetition. One thing, however, is clear: the M_2 (or MM') class is an unusual set of molecules, challenging, therefore interesting, and undisciplined to the conventional chemical wisdom. While the Cr ($4s^13d^5$, 7S) and Cu ($4s^13d^{10}$, 2S) atoms whose open structure shows a proclivity for M_2 or MM' bonding, the $4s^23d^n$ ($n = 1-3$ and $5-8$) ground state configurations of the remaining $3d$ metals with ratios of mean $4s$ and $3d$ radii $\frac{\langle r_{4s} \rangle}{\langle r_{3d} \rangle}$ ranging from 2.36 to 3.36 [51] do not allow for direct, non-van der Waals bonding [42, 48–50]. Hence, covalent interaction can only be expected from at least a $4s^2-4s^1$ distribution, i.e., an $M'-M^*$ interaction where the star (*) refers to an excited state atom.

Presently, we have examined the first that is the lightest intermetallic MM' diatomic ScTi. We are not aware of any experimental or ab initio investigation on ScTi but a DFT study by Gutsev et al. [52] who studied all ScM ($M = Sc-Zn$) dimers and their anions. Based on a [10s7p4d1f] Gaussian basis set and through the generalized gradient approximation for the exchange correlation potential, they found a $^6\Sigma^+$ ($r_e = 2.290 \text{ \AA}$, $D_e = 2.22 \text{ eV}$, $\omega_e = 272 \text{ cm}^{-1}$, $\mu = 0.57 \text{ D}$) ground state with a $^2\Sigma^+$ ($r_e = 2.065 \text{ \AA}$, $\omega_e = 382 \text{ cm}^{-1}$, $\mu = 1.07 \text{ D}$) state lying just 0.16 eV higher. An NBO analysis revealed that in both states, the Sc and Ti atoms are in situ excited in their $4s^13d^2$ and $4s^13d^3$ electronic configurations, respectively.

The interaction of the ground state fragments Sc ($4s^23d^1$, 2D) + Ti ($4s^23d^2$, 3F) results in 40 molecular states, that is, $^{2,4}(\Sigma^+[2], \Sigma^-[3], \Pi[5], \Delta[4], \Phi[3], \Gamma[2], H[1])$ doublets and quartets, expected to be of van der Waals type [42, 48, 49]. The first excited dissociation channel Sc ($4s^23d^1$, 2D) + Ti ($4s^13d^3$, 5F) located 0.806 eV higher gives rise also to 40 molecular $^{2S+1}\Lambda$ states of the same spatial symmetry as before but of quartet and sextet spin multiplicities. Finally, the interaction of two excited atoms, i.e., Sc ($4s^13d^2$, 4F) + Ti ($4s^13d^3$, 5F) at 0.806 [$\Delta E_{Ti}(^5F \leftarrow ^3F)$] + 1.427 [$\Delta E_{Sc}(^4F \leftarrow ^2D)$] = 2.233 eV [53] above the ground state fragments, results in 112 molecular $^{2S+1}\Lambda$ states of $^{2,4,6,8}(\Sigma^+[4], \Sigma^-[3], \Pi[6], \Delta[5], \Phi[4], \Gamma[3], H[2], I)$ symmetry. Between the first dissociation channel [Sc ($4s^23d^1$, 2D) + Ti ($4s^23d^2$, 3F)] and the one that combines two excited fragments [Sc ($4s^13d^2$, 4F) + Ti ($4s^13d^3$, 5F)], there are in total 17 channels producing hundreds of molecular states within an asymptotic energy range of only 2.233 eV [53].

Based on preliminary calculations at the complete active space self-consistent field (CASSCF) computational level, we decided to study states of quartet and sextet spin multiplicity with spatial symmetry ranging from Σ^+ to H ($\Lambda = 5$). For both metal atoms, the Dunning [54] correlation-consistent polarized valence quadruple zeta

(cc-pVQZ) basis set was used generally contracted to [8s7p5d3f2g1h] [55], consisting of $104 \times 2 = 208$ spherical Gaussian functions. The internally contracted (ic) variant of the multireference CISD (MRCI = CASSCF + 1 + 2) method was used in all our calculations as implemented in the MOLPRO 2010.1 code [56]. The one electron basis set was issued from state average CASSCF wave functions that in turn resulted by distributing all 7 valence electrons to 15 orbitals correlating with the $(4s + 3d) \times 2 + p'(3)$ valence space of the fragments supplemented by three p type functions to “angularly” correlate the “4s” electrons. During the CASSCF optimization, a number of states from all four irreducible representations (A_1, A_2, B_1, B_2) of the C_{2v} point group were averaged in order to assure a smooth evolution along the inter nuclear distance. For the quartet spin multiplicity, the reference space consisted of $\sim 60,000$ configuration functions (CF) giving rise to $\sim 255 \times 10^6$ CFs at the MRCI level, internally contracted to $\sim 12 \times 10^6$ CFs. For the sextet spin multiplicities, the corresponding spaces contain $\sim 17,000$ (CASSCF), $\sim 91 \times 10^6$ (MRCI), and $\sim 8 \times 10^6$ (icMRCI) CFs. Due to severe technical complications, only parts of the potential energy curves (PEC) could be calculated. No core-subvalence ($3s^23p^6$), relativistic, or spin-orbit effects were taken into account. Technical difficulties in the calculation only permitted the Davidson +Q correction to be applied to the $X^6\Delta$ ground state.

2 Results and discussion

Table 1 collects the numerical data for 21 states, while Figs. 1, 2, 3, and 4 display the corresponding PECs. In what follows, we discuss in some detail the bonding characteristics of the states studied grouped according to their symmetry.

$X^6\Delta$, $6^6\Sigma^+$, $10^6\Gamma$, $16^6\Delta$, $19^6\Delta$, $20^6\Sigma^+$, and $21^6\Gamma$.
The ground state of the ScTi system seems to be of $^6\Delta$ symmetry. Its most important equilibrium configurations at the CASSCF level are (only the seven valence electrons appear in what follows).

$$\begin{aligned} |X^6\Delta(^6A_1)\rangle \approx & 0.76 |1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 1\pi_y^1 1\delta_-^1\rangle \\ & + 0.21 |1\sigma^2 2\sigma^1 5\sigma^1 (1\pi_x^1 2\pi_y^1 - 2\pi_x^1 1\pi_y^1) 1\delta_-^1\rangle \\ & + 0.18 |1\sigma^2 2\sigma^1 5\sigma^1 1\pi_x^1 1\pi_y^1 1\delta_-^1\rangle \end{aligned}$$

with $1\sigma \approx 0.75[4s(\text{Sc})] + 0.71[4s(\text{Ti})]$, $2\sigma \approx -0.66[4s(\text{Sc})] + 0.38[4p_z(\text{Sc})] + 0.66[4s(\text{Ti})] + 0.32[4p_z(\text{Ti})]$, $3\sigma \approx 0.39[3d_{\sigma}(\text{Sc})] + 0.86[3d_{\sigma}(\text{Ti})]$, $5\sigma \approx 0.87[3d_{\sigma}(\text{Sc})] - 0.48[3d_{\sigma}(\text{Ti})]$, $1\pi \approx 0.46[3d_{\pi}(\text{Sc})] - 0.64[3d_{\pi}(\text{Ti})]$, $2\pi \approx$

Table 1 Total energies E (hartree), equilibrium distances r_e (Å), dissociation energies D_e (kcal/mol), harmonic frequencies ω_e and anharmonic corrections $\omega_e x_e$ (cm^{-1}), dipole moment μ (Debye), and energy separations T_e (kcal/mol) of 21 molecular states of $^{45}\text{Sc}^{48}\text{Ti}$ at the MRCI(+Q) level of theory

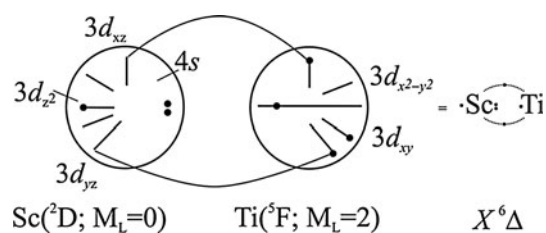
State	$-E$	r_e	D_e	ω_e	$\omega_e x_e$	μ	T_e
$X^6\Delta$	1,608.259 250 (1,608.267 82)	2.647 (2.659)	32.4 36.8	218.3 (223.2)	0.685 (3.816)	0.05	0.0 (0.0)
$2^4\Delta$	1,608.254 387	2.637	7.4	220.3	-2.458	0.65	3.05
$3^4\Pi$	1,608.246 750	2.587	2.6	159.6	-0.955	0.16	7.84
$4^4\Phi$	1,608.242 781	2.773		192.5	8.681		10.33
$5^4\Phi$	1,608.240 477	2.943		239.4	0.825		11.78
$6^6\Sigma^+$ (Local minimum)	1,608.239 6	2.96	20.1			0.10	12.3
	1,608.236 578	2.440		238.2	-0.812		
$7^4\Gamma$	1,608.239 276	2.787		196.2	3.643	0.24	12.53
$8^4\Delta$	1,608.238 994	2.927		231.8	5.292	0.27	12.71
$9^4\Pi$ (Local minimum)	1,608.238 172	2.351		300.6	0.131	-0.06	13.23
	1,608.238 054	2.708		201.8	0.994		
$10^6\Gamma$	1,608.237 719	3.005	18.9	233.1	6.845	0.09	13.51
$11^6\Pi$	1,608.237 008	2.940	18.4	180.0	3.299	0.08	13.96
12^6H	1,608.236 484	2.981	18.1	213.5	2.307	-0.14	14.29
$13^4\Sigma^+$	1,608.236 155	2.775		195.6	2.764	0.29	14.49
$14^6\Phi$	1,608.235 912	2.969	17.7	221.1	7.237	0.28	14.64
$15^6\Pi$	1,608.235 722	2.960	17.6	211.3	2.353	0.19	14.76
$16^6\Delta$	1,608.233 835	2.969	16.4	211.0	4.012	0.21	15.95
$17^6\Pi$	1,608.232 718	2.993	15.7	200.1	-3.053	0.05	16.65
$18^6\Phi$	1,608.232 450	2.985	15.6	219.0	2.935	0.01	16.82
$19^6\Delta$	1,608.230 819	2.893	14.6	239.3	5.049	0.00	17.84
$20^6\Sigma^+$	1,608.227 748	3.031	12.6	269.7	7.965		19.77
$21^6\Gamma$	1,608.226 659	2.992	11.9				20.45

$[3d_{\pi}(\text{Sc})] + [3d_{\pi}(\text{Ti})]$, $1\delta_{-} \approx [3d_{xy}(\text{Ti})]$. The MRCI Mulliken atomic distributions.

$$4s^{2.09}4p_z^{0.43}3d_{z^2}^{0.40}4p_x^{0.09}3d_{xz}^{0.40}4p_y^{0.09}3d_{yz}^{0.40}3d_{xy}^{0.05}/_{\text{Sc}}, q_{\text{Sc}} = -0.98$$

$$4s^{0.29}4p_z^{0.07}3d_{z^2}^{0.60}4p_x^{0.08}3d_{xz}^{0.47}4p_y^{0.08}3d_{yz}^{0.47}3d_{xy}^{0.94}/_{\text{Ti}}, q_{\text{Ti}} = +0.98$$

hint to an in situ Sc atom in its $4s^23d_{z^2}^1$ (^2D , $M_L = 0$) state and a Ti atom in its $4s^13d_{xz}^13d_{yz}^13d_{xy}^1$ (^5F , $M_L = \pm 2$) state, whereas the two atoms are bound together by two half π bonds due to a Ti-to-Sc charge transfer of $1e^-$, and a σ interaction of four electrons coupled into a triplet. The above bonding situation can be summarized pictorially by the following valence bond Lewis (vbl) scheme.



The MRCI(+Q) equilibrium distance and bond energy are $r_e = 2.647$ (2.659) Å and $D_e = 32.4$ (36.8) kcal/mol with respect to $\text{Sc}(4s^23d^1, ^2\text{D}) + \text{Ti}(4s^13d^3, ^5\text{F})$; see Table 1. Its MRCI (+Q) binding energy with respect to the ground state atoms is $D_e^0 = 10.4$ (15.3) kcal/mol. Its permanent electric dipole moment calculated as an expectation value is close to zero, $\mu = 0.052$ D, surprisingly small

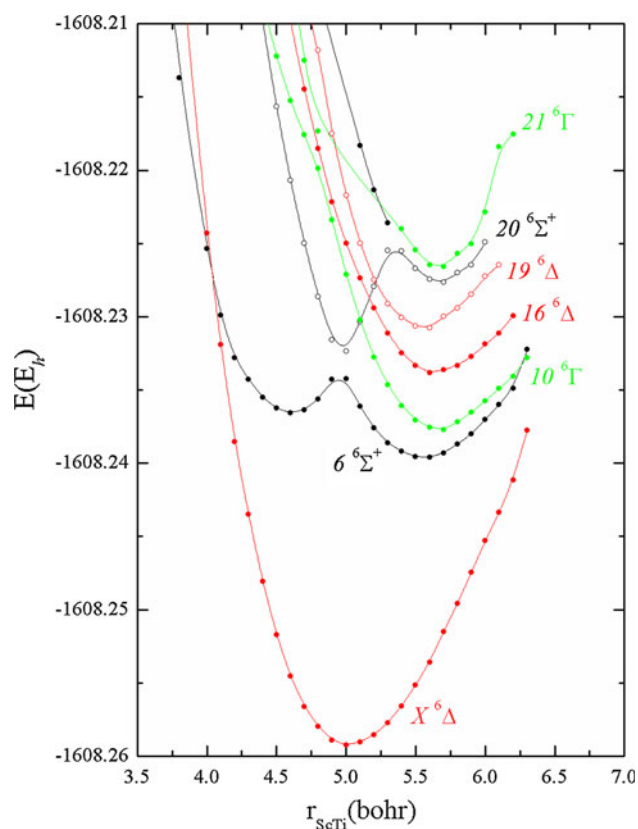


Fig. 1 MRCI/cc-pVQZ PECs of the $X^6\Delta$, $6^6\Sigma^+$, $10^6\Gamma$, $16^6\Delta$, $19^6\Delta$, $20^6\Sigma^+$, and $21^6\Gamma$ states

if one considers the $1e^-$ charge transfer from Ti to Sc. Perhaps the symmetry defining electron on the $3d_{xy}$ (Ti) orbital compensates for the centroid of charge on the Sc atom created by the charge transfer along the π -frame. It is interesting at this point to compare the ScTi $X^6\Delta$ state to the Sc₂ $X^5\Sigma_u^-$ [42] state. As was discussed in reference 42, the Sc₂ ground state results from a ground Sc ($4s^23d^1$, 2D ; $M_L = 0$) and an excited Sc* ($4s^13d^2$, 4F ; $M_L = 0$) atoms held together by a $3e^-2c$ (enter) σ interaction and two half π delocalizations due to the inversion symmetry. When a $3d_{xy}$ electron is attached to the Sc* (4F) state, the ScTi $X^6\Delta$ state is obtained with similar bonding features.

Two more states of $^6\Delta$ symmetry have been studied, namely the $16^6\Delta$ and $19^6\Delta$ ones, both dissociating adiabatically to the Sc(2D) + Ti(3F) fragments. Their equilibrium CASSCF wave functions and corresponding MRCI Mulliken populations read.

$$|16^6\Delta(^6A_1)\rangle \approx \left| 1\sigma^2 2\sigma^1 [(0.52)5\sigma^1 - (0.39)7\sigma^1] 1\pi_x^1 1\pi_y^1 1\delta_-^1 \right\rangle - 0.31 \left| 1\sigma^2 2\sigma^1 3\sigma^1 (2\pi_x^1 1\pi_y^1 - 1\pi_x^1 2\pi_y^1) 1\delta_-^1 \right\rangle$$

$$4s^{1.57} 4p_z^{0.33} 3d_{z^2}^{0.53} 4p_x^{0.11} 3d_{xz}^{0.31} 4p_y^{0.11} 3d_{yz}^{0.31} 3d_{xy}^{0.10} /_{Sc}, q_{Sc} = -0.39$$

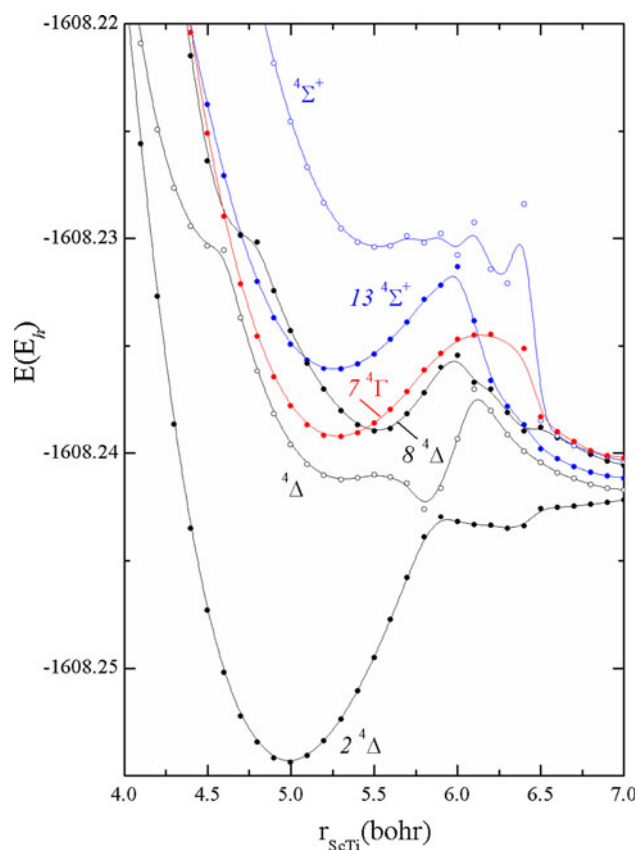


Fig. 2 MRCI/cc-pVQZ PECs of the $2^4\Delta$, $7^4\Gamma$, $8^4\Delta$, and $13^4\Sigma^+$ states

$$4s^{0.86} 4p_z^{0.13} 3d_{z^2}^{0.50} 4p_x^{0.10} 3d_{xz}^{0.50} 4p_y^{0.10} 3d_{yz}^{0.50} 3d_{xy}^{0.90} /_{Ti}, q_{Ti} = +0.39$$

and

$$|19^6\Delta(^6A_1)\rangle \approx 0.68 \left| 1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 1\pi_y^1 2\delta_-^1 \right\rangle + 0.25 \left| 1\sigma^2 2\sigma^1 3\sigma^1 (1\pi_x^1 2\pi_y^1 - 2\pi_x^1 1\pi_y^1) 2\delta_-^1 \right\rangle$$

$$4s^{1.46} 4p_z^{0.37} 3d_{z^2}^{0.20} 4p_x^{0.10} 3d_{xz}^{0.11} 4p_y^{0.10} 3d_{yz}^{0.11} 3d_{xy}^{0.86} /_{Sc}, q_{Sc} = -0.33$$

$$4s^{0.94} 4p_z^{0.13} 3d_{z^2}^{0.70} 4p_x^{0.07} 3d_{xz}^{0.68} 4p_y^{0.07} 3d_{yz}^{0.68} 3d_{xy}^{0.22} /_{Ti}, q_{Ti} = +0.33$$

The bonding character in both the $16^6\Delta$ and $19^6\Delta$ states remains the same as in the $X^6\Delta$ state; however, their orthogonality imposes a number of changes. The main CASSCF configuration of the $X^6\Delta$ state ($C_0 = 0.76$) is the $|1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 1\pi_y^1 1\delta_-^1\rangle$. In $16^6\Delta$, the 3σ orbital has been replaced by the $[(0.52)5\sigma - (0.39)7\sigma]$ orthogonal orbital ($5\sigma \approx 0.63[3d_\sigma(\text{Sc})] + 0.24[4p_z(\text{Sc})] - 0.55[3d_\sigma(\text{Ti})] - 0.26[4p_z(\text{Ti})]$ and $7\sigma \approx 0.67[3d_\sigma(\text{Sc})] - 0.53[4p_z(\text{Sc})] +$

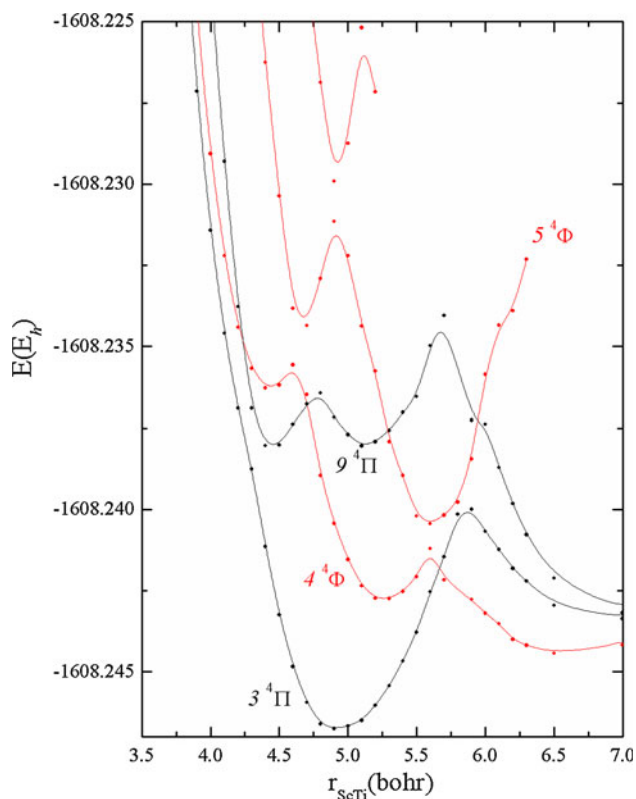


Fig. 3 MRCI/cc-pVQZ PECs of the $3\ ^4\Pi$, $4\ ^4\Phi$, $5\ ^4\Phi$, and $9\ ^4\Pi$ states

$0.32[4p_z(\text{Ti})]$, while in the $19\ ^6\Delta$ state, the $2\delta_-$ orbital is found localized on the Sc atom instead of the Ti ($X\ ^6\Delta$) one, or in other words, the transition $X\ ^6\Delta \rightarrow 19\ ^6\Delta$ is made possible through the transfer of the symmetry defining $\delta\ e^-$ from the Ti to the Sc atom.

In the $16\ ^6\Delta$ state, two half π bonds are created through the transfer of $0.40 \times 2 = 0.80\ e^-$ from Ti to Sc, while $0.43\ e^-$ are back transferred through the σ frame. The Mulliken populations reveal an in situ Sc atom in its $4s^23d^1\ (^2D; M_L = 0)$ electronic configuration as was also found in the X state, while the Ti atom defines the $\Lambda = 2$ symmetry through its $4s^13d_{xz}^13d_{yz}^13d_{xy}^1$ configuration. This character resemblance should be the product of an avoided crossing since the $16\ ^6\Delta$ state should correlate adiabatically with a different combination of fragments, see Table 1 for numerical results.

The main characteristic of the $19\ ^6\Delta$ state is the different location of the symmetry defining electron as contrasted to both the X and $16\ ^6\Delta$ states. The Mulliken populations show an in situ Sc atom in its ground $4s^23d^1\ (^2D; M_L = \pm 2)$ configuration, while the Ti atom is found in its $4s^13d_{xz}^13d_{yz}^13d_{xy}^1$ configuration, a $20\ \%|^5F\rangle + 80\ \%|^5P\rangle$ mixture. The π Ti-to-Sc migration is limited to only $0.20 \times 2 = 0.40\ e^-$, while a weak δ -bond is created through a $0.2\ e^-$ transfer from Sc to Ti. A $(4s4p_z3d_{z^2})\text{Sc}$ hybrid helps to relieve the congestion of four σ electrons. Both states appear to have similar equilibrium distances

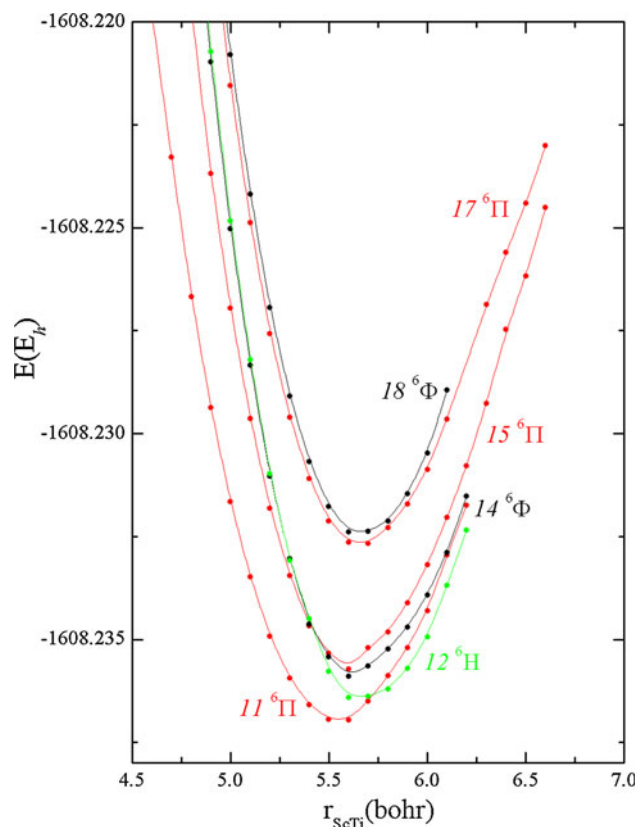


Fig. 4 MRCI/cc-pVQZ PECs of the $11\ ^6\Pi$, $12\ ^6H$, $14\ ^6\Phi$, $15\ ^6\Pi$, $17\ ^6\Pi$, and $18\ ^6\Phi$ states

and bond strengths: $r_e = 2.969$ ($16\ ^6\Delta$) and 2.893 ($19\ ^6\Delta$) Å, $D_e = 16.4$ ($16\ ^6\Delta$) and 14.6 ($19\ ^6\Delta$) kcal/mol with respect to Sc ($4s^23d^1, ^2D$) + Ti ($4s^13d^3, ^5F$).

The next states to be discussed are of $^6\Sigma^+$ and $^6\Pi$ symmetry. The $6\ ^6\Sigma^+$ state appears to have two minima of completely different electronic character, Fig. 1. The adiabatic PECs of the two $^6\Sigma^+$ states when properly rearranged define two diabatic PECs that should be considered simultaneously by a 2×2 post-Born–Oppenheimer treatment in order to extract the rovibrational levels of the system. The CASSCF equilibrium configurations of the global $6\ ^6\Sigma^+$ minimum are

$$|6\ ^6\Sigma^+\rangle_g \approx 0.54 \left| 1\sigma^2 2\sigma^1 (1\delta_+^1 1\pi_x^1 1\pi_y^1 2\delta_-^1 + 2\delta_+^1 1\pi_x^1 1\pi_y^1 1\delta_-^1) \right\rangle$$

which in connection to its MRCI atomic distributions

$$4s^{1.48} 4p_z^{0.34} 3d_{z^2}^{0.07} 3d_{x^2-y^2}^{0.44} 4p_x^{0.09} 3d_{xz}^{0.16} 4p_y^{0.09} 3d_{yz}^{0.16} 3d_{xy}^{0.47} /_{\text{Sc}},$$

$$q_{\text{Sc}} = -0.34$$

$$4s^{0.85} 4p_z^{0.13} 3d_{z^2}^{0.09} 3d_{x^2-y^2}^{0.53} 4p_x^{0.08} 3d_{xz}^{0.70} 4p_y^{0.08} 3d_{yz}^{0.70} 3d_{xy}^{0.50} /_{\text{Ti}},$$

$$q_{\text{Ti}} = +0.34$$

suggest a $|^2D, M_L = \pm 2\rangle_{\text{Sc}} \otimes |^5F, M_L = \mp 2\rangle_{\text{Ti}}$ asymptotic combination. The two atoms interact attractively by a

$3e^-2c$ σ interaction between a $(4s4p_z3d_z)_{Sc}^{1.9}$ and a $(4s4p_z3d_z)_{Ti}^{1.07}$ hybrids and a $0.25 \times 2 = 0.50 e^-$ Ti-to-Sc π migration, while two δ electrons, one at each atom, maintain the Σ character of the $1\sigma^22\sigma^11\pi_x^11\pi_y^1$ structure.

The $10^6\Gamma$ state is the orthogonal complement of the $6^6\Sigma^+$ global minimum, their only difference being a sign change “−” ($6^6\Gamma$) instead of a “+” ($6^6\Sigma^+$) in their main CASSCF configurations and with identical Mulliken populations. Their asymptotic channel is evidently the same as before but with equal M_L projections, i.e., $|^2D, M_L = \pm 2\rangle_{Sc} \otimes |^5F, M_L = \pm 2\rangle_{Ti}$, so as to result in $\Lambda = 4$.

The leading equilibrium configurations of the local $6^6\Sigma^+$ minimum are

$$|6^6\Sigma^+\rangle_i \approx \left| 1\sigma^2[(0.11)2\sigma^1 + (0.62)3\sigma^1]1\delta_+^11\pi_x^11\pi_y^11\delta_-^1 \right\rangle - 0.35 \left| 1\sigma^23\sigma^1(1\delta_+^11\pi_x^11\pi_y^12\delta_-^1 + 2\delta_+^11\pi_x^11\pi_y^11\delta_-^1) \right\rangle$$

The “0.35” component is similar to the electronic character of the global $6^6\Sigma^+$ minimum, while the “first” component results from that of the $X^6\Delta$ state by replacing a σ electron by a δ_+ one. This local minimum is a “resonant” hybrid between two structures whose main difference is the location of the δ_{\pm} electrons. In the “first” component, both are placed on Ti while in the second (“0.35”) a δ electron is on Sc and the other one on Ti.

Two more states of $6^6\Sigma^+$ and $6^6\Gamma$ symmetry separated by ~ 20 kcal/mol from the $X^6\Delta$ state have also been found. They are of intense multi configuration character that precludes an easy VB transcription of their bonding characteristics.

$2^4\Delta$, $7^4\Gamma$, $8^4\Delta$, and $13^4\Sigma^+$. The first excited state of the ScTi system is of $^4\Delta$ symmetry with bonding features practically identical to those of the $X^6\Delta$ state lying just 3 kcal/mol higher. The main CASSCF configurations read as follows

$$|2^4\Delta(^4A_1)\rangle \approx 0.56 \left| 1\sigma^22\sigma^13\bar{\sigma}^11\pi_x^11\pi_y^11\delta_-^1 \right\rangle + 0.45 \left| 1\sigma^22\sigma^13\sigma^11\bar{\pi}_x^11\pi_y^11\delta_-^1 \right\rangle + 0.32 \left| 1\sigma^22\sigma^13\sigma^11\pi_x^11\bar{\pi}_y^11\delta_-^1 \right\rangle + 0.14 \left| 1\sigma^22\sigma^13\sigma^11\pi_x^11\pi_y^11\bar{\delta}_-^1 \right\rangle.$$

All four configurations differ from the “0.76” CF of the $X^6\Delta$ state only in the way spins are coupled, both molecular orbitals and atomic distributions/charges being the same. So, it is certainly not a surprise that the $^4\Delta$ state is the first excited state of this diatomic. Both r_e (2.637 vs 2.647 (X) Å) and ω_e (220.3 vs 218.3 (X) cm^{-1}) values are quite similar, an indication of the same binding mode. The only stunning difference is the dipole moment value $\mu = 0.65$ D versus $\mu = 0.05$ D of the X state, an amazing side effect of the quartet spin multiplicity.

In Fig. 2, the adiabatic potential energy curve of a second $^4\Delta$ state is shown but with an irregular topology. This “fuzziness” will play certainly a role in the complexity of the spectrum, but offers little in the discussion of the chemical bond of the system. One of its most important characteristics is the avoided crossing with the $2^4\Delta$ state at 5.9 bohr (Fig. 2), responsible for the excited in situ Ti character. The last state of $(8)^4\Delta$ symmetry presently studied is unbound with respect to its adiabatic dissociation limit, i.e., Sc (2D) + Ti (3F), but features a potential well of 2.2 kcal/mol, sustaining some vibrational levels. Its electronic character is of extreme multiconfigurational character, thus forbidding any attempt to transcribe its bonding nature into simple vBL structures.

Two more states of quartet spin multiplicity of Γ and Σ^+ spatial symmetry have been studied. Their PECs shown in Fig. 2 reveal a parallel evolution within the minimum energy region. This is also corroborated by the similarity of the r_e (2.787 ($^4\Gamma$) versus 2.775 ($^4\Sigma^+$) Å) and ω_e (196.2 ($^4\Gamma$) versus 195.6 ($^4\Sigma^+$) cm^{-1}) values. Their main CASSCF equilibrium CFs are

$$|7^4\Gamma(^4A_1)\rangle \approx 0.38 \left| 1\sigma^22\sigma^13\sigma^11\delta_+^1(1\pi_x^2 - 1\pi_y^2) \right\rangle + 0.31 \left| 1\sigma^22\sigma^13\sigma^11\bar{\pi}_x^11\pi_y^11\delta_-^1 \right\rangle - 0.44 \left| 1\sigma^22\sigma^13\sigma^11\pi_x^11\bar{\pi}_y^11\delta_-^1 \right\rangle$$

and

$$|13^4\Sigma^+\rangle \approx 0.36 \left| 1\sigma^22\sigma^13\sigma^11\delta_+^1(1\pi_x^2 - 1\pi_y^2) \right\rangle - 0.29 \left| 1\sigma^22\sigma^13\sigma^11\bar{\pi}_x^11\pi_y^11\delta_-^1 \right\rangle + 0.42 \left| 1\sigma^22\sigma^13\sigma^11\pi_x^11\bar{\pi}_y^11\delta_-^1 \right\rangle$$

while their MRCI atomic populations (similar for both states)

$$4s^{1.75}4p_z^{0.38}3d_{z^2}^{0.28}4p_x^{0.08}3d_{xz}^{0.48}4p_y^{0.08}3d_{yz}^{0.48}/_{Sc}, q_{Sc} = -0.58$$

$$4s^{0.66}4p_z^{0.10}3d_{z^2}^{0.73}3d_{x^2-y^2}^{0.47}4p_x^{0.08}3d_{xz}^{0.39}4p_y^{0.08}3d_{yz}^{0.39}3d_{xy}^{0.52}/_{Ti}, q_{Ti} = +0.58$$

point to an excited Ti atom creating a σ and π interaction with a ground state Sc atom.

$3^4\Pi(1)$, $4^4\Phi(1)$, $5^4\Phi(2)$, and $9^4\Pi(2)$. These four quartet states correlate adiabatically with the ground state fragments Sc(2D) + Ti(3F) although it is evident from their PECs (see Fig. 3) that their minima are due to excited atomic states that interact with lower states via numerous avoided curve crossings.

The equilibrium character of the $3^4\Pi$ state is a mixture of two different structures as can be seen by its main CASSCF configurations

$$|3^4\Pi(^4B_1)\rangle \approx 0.45|1\sigma^22\sigma^13\sigma^11\pi_x^11\pi_y^2\rangle \\ + 0.41|1\sigma^22\sigma^1(1\delta_+^11\pi_x^11\pi_y^2 - 1\pi_x^21\pi_y^11\delta_-^1)\rangle.$$

The MRCI Mulliken populations are also consistent with the above structural mixture

$$4s^{2.0}4p_z^{0.49}3d_{z^2}^{0.21}4p_x^{0.09}3d_{xz}^{0.45}4p_y^{0.11}3d_{yz}^{0.62}/Sc, q_{Sc} = -1.11 \\ 4s^{0.18}4p_z^{0.08}3d_{z^2}^{0.47}3d_{x^2-y^2}^{0.22}4p_x^{0.08}3d_{xz}^{0.58}4p_y^{0.10}3d_{yz}^{0.96}3d_{xy}^{0.22}/Ti, q_{Ti} \\ = +1.11.$$

Both of the above data clearly show the difficulty to draw a simple vbL bonding scheme. Note the remarkable Ti-to-Sc charge transfer of more than one electron and $\mu = 0.16$ D.

The $4^4\Phi$ state relates to the “0.41” component of the previously discussed $3^4\Pi$ state. Its electronic character at the global minimum is $|4^4\Phi(^4B_1)\rangle_g \approx 0.49|1\sigma^22\sigma^1(1\delta_+^11\pi_x^11\pi_y^2 + 1\pi_x^21\pi_y^11\delta_-^1)\rangle$.

Its PEC presents two avoided crossings at 5.6 and 4.7 bohr with a second ($5^4\Phi$) state, where the latter avoided crossing is due to an incoming third $4^4\Phi$ state. The local minimum appears to be of the same electronic nature.

The $5^4\Phi$ state appears to have two potential minima, both of them due to avoided crossings with the $4^4\Phi$ state at the distances 5.6 and 4.7 bohr mentioned above. The main CASSCF configurations are as follows

$$|5^4\Phi(^4B_1), 5.6 \text{ bohr}\rangle \approx |1\sigma^22\sigma^1[(0.55)1\pi_x^12\pi_x^11\pi_y^1 \\ + (0.40)1\pi_x^12\pi_x^11\pi_y^1]\rangle \\ \text{and } |5^4\Phi(^4B_1), 4.7 \text{ bohr}\rangle \approx 0.54|1\sigma^23\sigma^1(1\delta_+^11\pi_x^11\pi_y^2 + 1\pi_x^2 \\ 1\pi_y^11\delta_-^1)\rangle.$$

The $9^4\Pi$ state shows two quasi-degenerate minima both of which result from avoided crossings with nearby curves of the same symmetry. The nominally global potential minimum appears at 4.4 bohr and is due to the avoided crossing with an incoming $3rd^4\Pi$ state at 4.8 bohr and with the $3^4\Pi$ state at 4.4 bohr, while the second potential minimum is due to the avoided crossing with a $3rd^4\Pi$ state at 5.7 bohr with the repulsive part of the PEC of $3^4\Pi$. Equilibrium configurations are similar at both minima, i.e.,

$$|9^4\Pi(^4B_1)\rangle_g \approx 0.49|1\sigma^23\sigma^1(1\delta_+^11\pi_x^11\pi_y^2 - 1\pi_x^21\pi_y^11\delta_-^1)\rangle \\ + 0.32|1\sigma^22\sigma^13\sigma^11\pi_x^11\pi_y^2\rangle$$

and

$$|9^4\Pi(^4B_1)\rangle_t \approx 0.55|1\sigma^22\sigma^13\sigma^11\pi_x^11\pi_y^2\rangle \\ - 0.23|1\sigma^22\sigma^1(1\delta_+^11\pi_x^11\pi_y^2 - 1\pi_x^21\pi_y^11\delta_-^1)\rangle$$

revealing a resonance between two vbL bonding schemes.

11 $^6\Pi$, 12 6H , 14 $^6\Phi$, 15 $^6\Pi$, 17 $^6\Pi$, and 18 $^6\Phi$. We have studied three $^6\Pi$ (11, 15, 17), two $^6\Phi$ (14, 18), and one 6H ($\Lambda = 5$) states all of which correlate adiabatically with Sc (2D) + Ti (5F).

The three $^6\Pi$ states are energetically close with T_e values of 13.96, 14.76, and 16.65 kcal/mol and similar equilibrium bond distances, $r_e = 2.940$ (11 $^6\Pi$), 2.960 (15 $^6\Pi$), and 2.993 (17 $^6\Pi$) Å. At their equilibrium distance, the main CASSCF configurations are

$$|11^6\Pi(^6B_1)\rangle \approx 0.49|1\sigma^22\sigma^13\sigma^1(1\delta_+^11\pi_y^12\delta_-^1 + 2\delta_+^11\pi_y^11\delta_-^1)\rangle \\ - 0.32|1\sigma^22\sigma^13\sigma^11\pi_x^1(1\delta_+^12\delta_+^1 + 1\delta_-^12\delta_-^1)\rangle$$

$$|15^6\Pi(^6B_1)\rangle \approx 0.45|1\sigma^22\sigma^1(1\delta_+^11\pi_x^11\pi_y^12\pi_y^1 - 1\pi_x^12\pi_x^11\pi_y^11\delta_-^1)\rangle$$

and

$$|17^6\Pi(^6B_1)\rangle \approx 0.48|1\sigma^22\sigma^13\sigma^11\pi_x^1(1\delta_+^12\delta_+^1 + 1\delta_-^12\delta_-^1)\rangle \\ + 0.33|1\sigma^22\sigma^13\sigma^11\pi_y^1(1\delta_+^12\delta_-^1 + 1\delta_-^12\delta_+^1)\rangle$$

They are of multi configuration nature reflected as well in the Mulliken populations; thus, a simple vbL picture cannot be drawn. Along the same lines is the nature of the $^6\Phi$ and 6H states. Their most important equilibrium CFs are

$$|14^6\Phi(^6B_1)\rangle \approx 0.54|1\sigma^22\sigma^1(1\delta_+^11\pi_x^11\pi_y^12\pi_y^1 - 1\pi_x^12\pi_x^11\pi_y^11\delta_-^1)\rangle$$

$$|18^6\Phi(^6B_1)\rangle \approx 0.32|1\sigma^22\sigma^13\sigma^15\sigma^1(1\pi_y^11\delta_-^1 - 1\delta_+^11\pi_x^1)\rangle \\ - 0.31|1\sigma^22\sigma^13\sigma^12\delta_+^1(1\pi_y^11\delta_-^1 + 1\delta_+^11\pi_x^1)\rangle \\ + 0.28|1\sigma^22\sigma^13\sigma^1(1\delta_+^11\pi_y^12\delta_-^1 + 1\pi_x^11\delta_-^12\delta_-^1)\rangle$$

and

$$|12^6H(^6B_1)\rangle \approx 0.43|1\sigma^22\sigma^13\sigma^1(1\pi_x^11\delta_-^12\delta_-^1 \\ - 1\delta_+^12\delta_+^11\pi_x^1 - 1\delta_+^11\pi_y^12\delta_-^1 + 2\delta_+^11\pi_y^11\delta_-^1)\rangle$$

thus rendering very difficult a vbL transcription of the wave functions. One major characteristic of these states is their spectroscopic similarities due to the sharing of the same configurations but with different signs.

3 Conclusions

The ScTi intermetallic diatomic molecule has been studied by high-level all electron ab initio MRCI calculations, in conjunction with correlation-consistent basis sets of

quadruple cardinality. No previous experimental or ab initio data are available in the literature. We have constructed PECs for 21 states at the MRCI/cc-pVQZ level; no core, relativistic, or other corrections have been applied. Due to severe technical difficulties, our results are of semi-quantitative nature. Our general conclusions are the following.

- (a) All 21 examined states (13 sextets and 8 quartets) are of multi reference character and exhibit weak bonding energies.
- (b) The ground state seems to be of ${}^6\Delta$ symmetry with $r_e(+Q) = 2.647$ (2.66) Å, $D_e(+Q) = 32.4$ (36.8) kcal/mol, and $\omega_e(+Q) = 218.3$ (223) cm^{-1} featuring two half π bonds and a four electron σ interaction. The first excited state is of ${}^4\Delta$ symmetry just 3 kcal/mol higher and with similar binding characteristics to that of the X ${}^6\Delta$ state. It is interesting to note that DFT (GGA) calculations predict totally different results: a ground state of ${}^6\Sigma^+$ symmetry at $r_e = 2.290$ Å and $D_e = 51.2$ kcal/mol, and an excited state (${}^2\Sigma^+$) 3.7 kcal/mol higher at $r_e = 2.065$ Å [52].
- (c) In most of the states, a $\sim 0.4 e^-$ Ti-to-Sc charge transfer is recorded. For three of the states, however, X ${}^6\Delta$, 2 ${}^4\Delta$, and 3 ${}^4\Pi$, a Mulliken Ti-to-Sc charge transfer of one electron is observed. Interestingly, the corresponding electric dipole moments are surprisingly small, that is, $\mu = 0.05$, 0.65, and 0.16 D, respectively.
- (d) In all states presently studied, the in situ Ti atom is found in its first excited 5F ($4s^13d^3$) state, a prerequisite for the development of covalent bonding between the two atoms.

References

1. Mavridis A, Harrison JF (1989) *J Chem Soc Faraday Trans II*(85):1391
2. Mavridis A, Harrison JF (1990) *J Chem Soc Faraday Trans II*(86):1625
3. Sakellaris CN, Mavridis A (2012) *J Chem Phys* 137:034309
4. Kalemoss A, Mavridis A (1998) *J Phys Chem A* 102:5982
5. Kalemoss A, Mavridis A (1999) *Adv Quantum Chem* 32:69
6. Kalemoss A, Mavridis A (1999) *J Phys Chem A* 103:3336
7. Kalemoss A, Mavridis A (2000) *J Chem Phys* 113:2270
8. Tzeli D, Mavridis A (2008) *J Chem Phys* 128:034309
9. Kerkines ISK, Mavridis A (2000) *J Phys Chem A* 104:11777
10. Kalemoss A, Mavridis A, Harrison JF (2001) *J Phys Chem A* 105:755
11. Kalemoss A, Mavridis A (2002) *J Phys Chem A* 106:3905
12. Tzeli D, Mavridis A (2002) *J Chem Phys* 116:4901
13. Kerkines ISK, Pittner J, Čárský P, Mavridis A, Hubač I (2002) *J Chem Phys* 117:9733
14. Tzeli D, Mavridis A (2003) *J Chem Phys* 118:4984
15. Kerkines ISK, Mavridis A (2003) *Collect Czech Chem Commun* 68:387
16. Tsouloucha A, Kerkines ISK, Mavridis A (2003) *J Phys Chem A* 107:6062
17. Kerkines ISK, Mavridis A (2004) *Mol Phys* 102:2451
18. Tzeli D, Mavridis A (2005) *J Chem Phys* 122:056101
19. Kalemoss A, Dunning TH Jr, Mavridis A (2005) *J Chem Phys* 123:014301
20. Kalemoss A, Dunning TH Jr, Mavridis A (2005) *J Chem Phys* 123:014302
21. Tzeli D, Mavridis A (2005) *J Phys Chem A* 109:9249
22. Kalemoss A, Dunning TH Jr, Mavridis A (2006) *J Chem Phys* 124:154308
23. Tzeli D, Mavridis A (2006) *J Phys Chem A* 110:8952
24. Tzeli D, Mavridis A (2007) *J Chem Phys* 126:194304
25. Kalemoss A, Dunning TH Jr, Mavridis A (2008) *J Chem Phys* 129:174306
26. Tzeli D, Mavridis A (2010) *J Chem Phys* 132:194312
27. Brugh DJ, Morse MD, Kalemoss A, Mavridis A (2010) *J Chem Phys* 133:034303
28. Miliordos E, Mavridis A (2007) *J Phys Chem A* 111:1953
29. Miliordos E, Mavridis A (2010) *J Phys Chem A* 114:8536
30. Sakellaris CN, Papakondylis A, Mavridis A (2010) *J Phys Chem A* 114:9333
31. Sakellaris CN, Miliordos E, Mavridis A (2011) *J Chem Phys* 134:234308
32. Sakellaris CN, Mavridis A (2012) *J Phys Chem A* 116:6935
33. Sakellaris CN, Mavridis A (2013) *J Chem Phys* 138:054308
34. Koukounas C, Kardahakis S, Mavridis A (2004) *J Chem Phys* 120:11500
35. Kardahakis S, Koukounas C, Mavridis A (2005) *J Chem Phys* 122:054312
36. Koukounas C, Mavridis A (2008) *J Phys Chem A* 112:11235
37. Tzeli D, Mavridis A (2000) *J Phys Chem A* 104:6861
38. Mavridis A, Metropoulos A (1993) *J Phys Chem* 97:10955
39. Glezakou VA, Harrison JF, Mavridis A (1996) *J Phys Chem* 100:13971
40. Tzeli D, Mavridis A (2004) *J Chem Phys* 121:2646
41. Kardahakis S, Mavridis A (2009) *J Phys Chem A* 113:6818
42. Kalemoss A, Kaplan IG, Mavridis A (2010) *J Chem Phys* 132:024309
43. Camacho C, Cimiraaglia R, Witek HA (2010) *Phys Chem Chem Phys* 12:5058
44. Camacho C, Witek HA, Cimiraaglia P (2010) *J Chem Phys* 132:224306
45. Soto J, Avila FJ, Otero JC, Arenas JF (2011) *Phys Chem Chem Phys* 13:7230
46. Camacho C, Cimiraaglia R, Witek HA (2011) *Phys Chem Chem Phys* 13:7232
47. Mxtain JM, Rezabal E, Lopez X, Ugalde JM, Gagliardi L (2008) *J Chem Phys* 128:194315
48. Kalemoss A, Mavridis A (2011) *J Chem Phys* 135:134302
49. Tzeli D, Miranda U, Kaplan IG, Mavridis A (2008) *J Chem Phys* 129:154310
50. Krechkivska O, Morse MD, Kalemoss A, Mavridis A (2012) *J Chem Phys* 137:054302
51. Bunge CE, Barrientos JA, Bunge AV (1993) *At Data Nucleic Data Tables* 53:113
52. Gutsev GL, Jena P, Rao BK, Khanna SN (2001) *J Chem Phys* 114:10738
53. Kramida A, Ralchenko Yu, Reader J, NIST ASD Team (2012). *NIST Atomic Spectra Database* (ver. 5.0), [Online]. Available: <http://physics.nist.gov/asd2013>, August 15]. National Institute of Standards and Technology, Gaithersburg, MD
54. Dunning TH Jr (1989) *J Chem Phys* 90:1007
55. Balabanov N, Peterson KA (2005) *J Chem Phys* 123:064107

56. MOLPRO is a package of ab initio programs written by Werner H-J, Knowles PJ, Knizia G, Manby FR, Schütz M, Celani P, Korona T, Lindh R, Mitrushenkov A, Rauhut G, Shamasundar KR, Adler TB, Amos RD, Bernhardsson A, Berning A, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Goll E, Hampel C, Hesselmann A, Hetzer G, Hrenar T, Jansen G, Köppl C, Liu Y, Lloyd AW, Mata RA, May AJ, McNicholas SJ, Meyer W, Mura ME, Nicklaß A, O'Neill DP, Palmieri P, Peng D, Pflüger K, Pitzer R, Reiher M, Shiozaki T, Stoll H, Stone A, Tarroni RJ, Thorsteinsson T, Wang M