Electronic structure and spectroscopic properties of electronic states of ScC$_3$ and ScC$_3^-$

S. Roszak$^a$ and D. Majumdar
Department of Applied Science, University of California Davis, Livermore, California 94550

K. Balasubramanian$^b$
Department of Applied Science, University of California Davis, Livermore, California 94550, Chemistry and Material Science Directorate, Lawrence Livermore National Laboratory, University of California, Livermore, California 94550, and Glenn T. Seaborg Center, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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Theoretical studies on the electronic and thermodynamic properties of several electronic states are presented for the ScC$_3$ molecule and the ScC$_3^-$ anion employing state-of-the-art techniques that included up to 13 million configurations. The ground and the low-lying electronic states of these two species have been predicted to have $C_{2v}$ ring structures. On the basis of our computed results on the low-lying excited electronic states, we have suggested assignment of the observed anion photodetachment spectra of ScC$_3^-$. Thermodynamic properties of reactions involving ScC$_3$ are corrected using the computed gas-phase properties of the molecule and the partition functions. Thermodynamic functions of ScC$_3^-$ are also determined by fitting the available experimental data with thermodynamic energy cycles. The nature of bonding in the neutral and the anionic carbides has been considered. © 2002 American Institute of Physics. [DOI: 10.1063/1.1477181]

I. INTRODUCTION

Nanoclusters of transition metal carbides of several compositions are formed by the interaction of carbon with transition metals. The structures and reactivities of transition metal carbide clusters are quite important in many areas of chemistry, such as surface chemistry, catalysis, combustion chemistry, astrochemistry, solid state chemistry, and so on. The early transition metals have been found to form stable gas-phase metal-carbon ions with a stoichiometry of $M_8C_{12}^+$. These are known as metallocarbohedrenes or simply met-cars. The late transition metals are catalysts for carbon nanotube formation. Finally, the rare earth elements form endohedral fullerenes, which are quite uncharacteristic reaction products of carbon transition metal reactions. The nature of the chemical bonding between carbon and different metals is critical to gain insight into the growth mechanisms of the various metal-carbon nanomaterials.

Transition metal carbides have been studied by a number of experimental techniques such as high-temperature mass spectrometry, and photoelectron spectroscopy. While significant experimental and theoretical advances have been made to understand the formation mechanism and ground states of met-cars, experimental studies on small transition metal carbides have only been made in recent times. Our earlier high-level theoretical investigations on small transition metal carbides have pointed out that the ground and the low-lying electronic states of these carbides are multireference in nature and single reference approaches may not conclusively identify the low-lying excited states. As a result the assignments of the observed spectra of transition metal carbides using single reference techniques may not be definitive.

Theoretical studies on different transition metal carbides have shown that attachment of an electron to the neutral carbide brings about considerable change in the geometries and electronic structure of these species. Moreover, these clusters exhibit dramatic odd–even variations in properties as a function of the number of carbon atoms. The available data indicate that systematic studies are essential for the understanding of the processes, such as cluster growth or size dependence of the observed properties. Electronic structures of transition metal carbides are considerably complex due to the presence of open 3d shells of the metal atoms that give rise to a plethora of low-lying electronic states for these species. The information on the low-lying electronic states for these species is valuable to assign the observed spectra, and to provide a molecular level understanding of different nanomaterials.

Wang and Li have obtained vibrationally resolved photodetector spectra of ScC$_3^-$ and ScC$_2^-$. Vibrational structures were resolved for both the ground and the excited states. It revealed complicated low-lying excited features for these species. On the basis of their DFT studies, Wang and Li have suggested an assignment of the ground state to a doublet of unknown spatial symmetry. As would be demonstrated here, high-level computations such as the CSSCF/MRSDCI techniques yield different ground state for ScC$_3$ than the one suggested earlier. The assignments of the ob-
served spectra are suggested on the basis of our current study, and the weak bands which were observed in 355 nm spectra through the entire high binding energy (BE) side are also explained. The assignments of these weak bands were not possible using single reference theoretical studies. We have also computed the vibrational frequencies of the low-lying electronic states, which provide further evidence for the assignment of the observed spectra.

In the current study, we have also reported the computed electron affinity of ScC₃ and compared the result with experiment. The structural and electronic data are further applied to refine the thermodynamic data obtained through a high-temperature mass spectrometry technique. Atomization and dissociation energies of ScC₃⁻ anion are also computed.

II. METHODS OF CALCULATION

We have employed a variety of state-of-the-art computational techniques such as the complete active space multiconfiguration self-consistent field (CASSCF), multireference singles and doubles configuration interaction (MRSDCI), density functional theory (DFT), and Møller–Plesset second-order perturbation theory (MP2) methods. The equilibrium geometries were optimized at the DFT and CASSCF levels of theory. Vibrational frequencies were also determined for several electronic states of ScC₃. We have also computed the thermodynamic properties using the computed electronic, vibrational, and rotational properties and thus, the partition functions.

The calculations were performed using relativistic effective core potentials (RECPs) for Sc and carbon. The valence space for the scandum RECPs included 3s²3p⁶4d¹4s² shells, while the RECPs of the carbons included 2s²2p² valence shells. The most diffuse exponents in the original basis sets have been left uncontracted. This led to [7s4p2d] and [3s3p] valence basis sets for Sc and C, respectively. The Sc basis was supplemented with two s, one p, and one set of six-component 3d diffuse functions. The effect of 10-component 4f functions on Sc was tested by augmenting the Sc basis set with an f function with ξ = 0.40, but the effect was found to be rather small. The C basis included additionally the d polarization function and a set of s and p diffuse functions. The above-mentioned choice of basis sets leads to 110–120 atomic basis functions for ScC₃.

The geometry optimizations of the ring and linear structures of ScC₃ and ScC₃⁻ were carried out in C₂ᵥ symmetry (z-axis is the C₂-axis) at the CASSCF level. Other structures presented in Fig. 1 were also studied at the DFT level, and they were found to be of much higher energy. The inclusion of all of the valence orbitals of Sc and C (which correlate into 3s, 3p, 4s, and 4d orbitals of Sc and 2s, 2p orbitals of carbon) in the active space leads to a prohibitive number of configuration spin functions (CSF) at the CASSCF level. Hence, the active space was restricted by omitting three virtual orbitals from the full space. The 3s and 3p orbitals of Sc were kept inactive. The optimal active space was sought by performing several test calculations on various possible combinations of a₁, b₂, b₁, and a₂ orbitals. The combination giving the lowest energy comprises of five a₁, three b₂, two b₁, and two a₂ orbitals for the ring structure and three a₁, three b₂, three b₁, and one a₂ for the linear ScC₃ complex. The inactive set of orbitals is composed of two a₁, one b₂, and one b₁ orbitals. No excitations were allowed from the inactive orbitals, but they were allowed to relax. Fifteen (sixteen in the case of anion) electrons were distributed in all possible ways in the above active space to generate electronic states of various spin multiplicities. The above choice of the active space leads to a maximum of 47700 CSFs in the CASSCF calculations. All of the configurations of the CASSCF with coefficients >0.05 were included in the MRSDCI calculations. The MRSDCI space was quite large in that the maximum number CSFs in the MRSDCI calculations included up to 13 million configurations. The effect of unlinked quadruple clusters for the MRSDCI was estimated through a multireference Davidson correction (MRSDCI+Q) technique.

We also employed a hybrid DFT approach that utilized Becke’s three-parameter functional²⁶ with the local correlation part of Vosco et al.²⁷ and the nonlocal part of Lee et al.s²⁸ (abbreviated as B3LYP). The calculations were based on the spin-unrestricted formulation of the method. Special care was taken to locate the electronic configurations leading to the lowest energy. The DFT/B3LYP electronic configurations are also found to be the leading CASSCF configuration for most of the cases studied here. The MP2 calculations were performed using the spin-unrestricted Hartree–Fock method.²⁹ The projected values (free from contaminations due to other states) are reported. All electrons were correlated in this method.
III. RESULTS AND DISCUSSION

A. Structures of ScC₃ and ScC₃⁺ in ground and electronic excited states

The calculations of the thermodynamic functions have been performed at the DFT level by applying ideal gas, rigid rotator, and harmonic oscillator approximations. The contributions of the low-lying excited electronic states were included in the computation of partition functions and thermodynamic properties.

The reliability of the [7s4p2d] Sc basis set in our calculation has been tested by adding one ten-component 4p function in the basis set ($\zeta = 0.40$) at the DFT/B3LYP level. The $4B_1$ ring structure (Fig. 1) of ScC$_3$ was further optimized using this the [7s4p2d1f] basis set. The Sc–C$_1$, Sc–C$_2$ and C$_1$–C$_2$ bond lengths obtained in this calculation are 2.205, 2.161, and 1.319 Å respectively. In the [7s4p2d] basis set calculation, the corresponding values are 2.206, 2.163, and 1.315 Å (Table I, Sec. III A). Thus the use of the [7s4p2d] Sc basis set is quite reliable to calculate the structures of ScC$_3$ in different electronic states.

The CASSCF and MRSDCI computations were made using the GAMESS$^{31}$ program and a modified version of ALCHEMY II package$^{32}$ to include RECP's.$^{33}$ The DFT and the MP2 calculations were performed applying the GAUSSIAN 98 code.$^{34}$

### III. RESULTS AND DISCUSSION

#### A. Structures of ScC₃ and ScC₃⁺ in ground and electronic excited states

The structures of gaseous ScC$_n$ carbides have not yet been determined experimentally. The group IIIa carbides with more than two carbon atoms were studied theoretically before, and it was found that MC$_3$ (M = Y, La) carbides exhibit ring equilibrium structures.$^{17,19,36}$ A ring equilibrium geometry was also predicted for the ground state of the ScC$_3$ molecule.$^{12}$

Several geometrical arrangements for ScC$_3$ are considered here at the DFT level; these included C$_{2v}$ ring, C$_{∞v}$ linear, C$_{2v}$ top, C$_s$ bend, and nonplanar C$_{3v}$ structures (Fig. 1). The geometry optimization of nonplanar structures led to a planar equilibrium structure. Among several such structures, only the C$_{2v}$ ring and linear Sc–C–C–C isomers were found to be viable candidates for the ground and low-lying excited states of ScC$_3$. The low-lying electronic states of ScC$_3$ were further optimized at the CASSCF level. The energy separations of the low-lying electronic states were calculated at the MRSDCI and MRSDCI+Q levels (Table I).

Both the MRSDCI and the MRSDCI+Q calculations indicate that a $4B_1$ ring structure (C$_{2v}$) is the minimum energy geometry of ScC$_3$. The $2B_1$ and $2B_2$ states are very close to this state, but the $2A_2$ state is slightly higher with respect to these states. It is important to recognize that different levels of theories yield different orderings for the low-lying electronic states of ScC$_3$. Although at the CASSCF level, the $2\Pi$ state with a linear structure is the ground state, this is not the case at the MRSDCI and MRSDCI+Q levels. Consequently, although the CASSCF method appears to yield the correct geometries, the method does not yield correct energy separations, as it does not include dynamical electron correlation effects. Thus the MRSDCI method, which includes dynamical correlation effects should be considered more reliable for the energy separations. At the DFT/B3LYP level, all four C$_{2v}$ electronic states, viz., $4B_1$, $2B_2$, $2B_1$, and $2A_2$ are competing electronic states with $2A_2$ fa-

### Table I. Calculated bond lengths (Å) and energy separations (ΔE, eV) for the low-lying electronic states of the ScC₃ molecule at the DFT/B3LYP, CASSCF, MRSDCI, and MRSDCI+Q levels. Experimental energy separations of a few available states are also added for comparison.

<table>
<thead>
<tr>
<th>Structure</th>
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<th>Bond length$^b$</th>
<th>ΔE$^b$</th>
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<td>Sc–C$_2$</td>
</tr>
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<td>2.207</td>
</tr>
<tr>
<td></td>
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<td>2.228</td>
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<tr>
<td></td>
<td>$C_{∞v}$</td>
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<td></td>
<td>$2\Delta$</td>
<td>2.303</td>
<td>2.294</td>
</tr>
</tbody>
</table>

$^a$Reference 12.

$^b$The bond lengths are calculated at the CASSCF and DFT/B3LYP levels. The DFT/B3LYP values are presented within parentheses.
DFT/B3LYP calculations also, the spatial symmetry of the doublet spin state. According to our insight into these interactions will be given in Sec. IV.

The measured IR frequencies by Wang and co-workers exhibit two broad peaks (assigned as X and A) for ScC$_3$ (355 nm spectrum) with weak signals through the entire high BE side. These weak signals were attributed to the presence of several low-lying closely spaced excited electronic states of ScC$_3$. The authors have predicted from their DFT calculations a doublet state to be the ground state of ScC$_3$ without any assignment as to the spatial symmetry of the doublet spin state. According to our DFT/B3LYP calculations also, the $^2A_2$ state is the ground state, and our computed geometrical parameters of the $^2A_2$ state in Table I at the DFT level are consistent with those of Wang and Li. The next low-lying electronic state in the DFT/B3LYP calculation is $^2B_2$ and it is 0.39 eV above the ground state (Table I). The second peak of the photoelectron spectrum of ScC$_3$ appears at 0.42 eV, and could have been a candidate for this peak. But on the other hand, the MRSDCI and MRSDCI+Q results indicate that the $^2B_1$ state is the ground state, and there are two other low-lying electronic states ($^2B_1$ and $^2B_2$) within 0.2 eV of the ground state. Moreover the energy separation of the $^2A_2$ state with respect to the ground state (MRSDCI: 0.51 eV, MRSDCI+Q: 0.47 eV) is fully consistent with the second peak at 0.42 eV in the spectrum. The $^2\Pi$ (linear structure), $^4B_2$, and $^2A_1$ (ring structure) states of ScC$_3$ are higher than the $^2A_2$ state with energy separations of 0.52, 1.07, and 1.45 eV, respectively with respect to the $^2B_1$ ground state (Table I). The presence of these closely spaced electronic states that lie above the $^2A_2$ state in the MRSDCI calculation is fully consistent with the observed weak bands in the high BE region of the photoelectron spectrum. It is to be noted in this connection that the experimental energy separation (0.42 eV) is close to the first excited state of the Sc$^+$ cation (0.31 eV$^3$). This suggests that the lowest excited state of ScC$_3$ originates from the Sc$^+$ cation modified by interactions with the C$_3^-$ fragment. Further insight into these interactions will be given in Sec. IV.

The measured IR frequencies by Wang and co-workers also support our assignment. Experimentally determined symmetric stretching frequencies of the ground and the low-lying electronic states are reproduced by the MRSDCI $^4B_1$ ground state and the excited $^2A_2$ (second peak in photoelectron spectrum) state (Table II). The $^2B_2$ and $^2B_1$ states belong to the manifold of electronic states. The geometries optimized in the DFT/B3LYP and CASSCF methods agree closely. The results available from former DFT/B3LYP calculations in the extended basis set are consistent with our results for the $^2B_2$ electronic state.

The ground state of the ScC$_3^-$ anion is represented by the C$_2v$ ring structure, and the linear isomer is much higher (Table III). The electron attachment process leads to elongation of the Sc--C bonds. The computed changes in the Sc--C bond lengths are consistent with the observed Franck–Condon envelope. The ground state of the ring structure ($^3B_2$) is closely spaced with two other low-lying excited electronic states ($^2B_1$ and $^3A_2$). In fact the energy separations between the $^3B_2$ and $^3B_1$ states at the MRSDCI and MRSDCI+Q levels indicate that the two states are the competing for the ground state of ScC$_3^-$. The energies of the two states are so close that the properties of ScC$_3^-$ calculated on the basis of any of these two states would produce similar results. However since both CASSCF and MRSDCI calculations indicate the $^3B_2$ to be lower in energy, we have used this state as the ground state of ScC$_3^-$. The ScC$_3^-$ anion is 1.64 eV more stable than the neutral ScC$_3$ molecule. Our computed electron affinity (EA) values are 1.67, 1.36, 1.28, and 1.44 eV at the DFT, MP2, MRSDCI, and MRSDCI+Q, respectively and they agree well with the experimental value. The MRSDCI electron affinity for the linear isomer (1.79 eV) is overestimated. Although, it seems the linear isomer is not observed in the photoelectron spectra of ScC$_3^-$, presumably due to the low abundance of linear isomers, a feature corresponding to the linear isomer was observed in the ScC$_3^-$ spectrum with a spacing consistent with the calculated energy separation.

The calculated shift between the vertical and adiabatic electronic affinities (at the DFT/B3LYP level) for low-lying excited states (0.07–0.19 eV) is in reasonable agreement with the experimental value of 0.22 eV. Thus, the changes of the potential energy surfaces are not significant and do not

<table>
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<th>Symmetry of vibration</th>
<th>Molecule</th>
<th>Electronic states</th>
<th>Anion</th>
</tr>
</thead>
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<tr>
<td>$a_1$</td>
<td>$^4B_1$</td>
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<td></td>
</tr>
<tr>
<td>$a_1$</td>
<td>$^2B_1$</td>
<td>464</td>
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</tr>
<tr>
<td>$a_1$</td>
<td>$^2B_2$</td>
<td>602</td>
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</tr>
<tr>
<td>$a_1$</td>
<td>$^2A_2$</td>
<td>599</td>
<td></td>
</tr>
<tr>
<td>$a_1$</td>
<td>$^2B_1$</td>
<td>533</td>
<td></td>
</tr>
<tr>
<td>$a_1$</td>
<td>$^2B_2$</td>
<td>427</td>
<td></td>
</tr>
<tr>
<td>$a_1$</td>
<td>$^2A_2$</td>
<td>540</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Experimental; Ref. 12.
$^b$Calculated value in Ref. 12.
lead to drastic changes in vibrational frequencies (Table II). The zero-point vibrational energies differ by only 0.01 eV for molecular and anion ground states.

### B. Thermodynamic functions for the ground electronic states of ScC$_3$ and ScC$_3^-$

We have calculated the dissociation energy ($D_e$) of ScC$_3$ at the DFT/B3LYP, MP2, CASSCF, MRSDCI, and MRSDCI+Q levels for the following reaction:

$$\text{ScC}_3 = \text{Sc}(^2D) + \text{C}_3(^1\Sigma_g^+)$$

We used a linear geometry for C$_3$ with a C–C bond length of 1.2915 Å (optimized at the DFT/B3LYP level). The $D_e$ calculations at the DFT/B3LYP and MP2 levels are straightforward, as the techniques are size consistent. At the multireference CI level, this value is obtained by calculating the energy of the Sc...C$_3$ (in $C_{2v}$ symmetry) supermolecular system, where the fragments are separated from each other by 10 Å. The difference of energy of the supermolecular system from the equilibrium structure ($^4B_1$) gives the $D_e$ of ScC$_3$. In the actual calculation, the $D_e$ value is computed initially for the reaction:

$$\text{ScC}_3(^4B_1) = \text{Sc}(^2D) + \text{C}_3(^1\Sigma_g^+)$$

The energy difference between the ground ScC$_3$ ($^4B_1$) state and the $^2B_1$ state is taken into account to obtain the adiabatic $D_e$. The $D_e$ values computed thus at the CASSCF, MRSDCI and MRSDCI+Q levels are 335, 425, and 421 kJ/mol, respectively. The calculated $D_e$ values are reported in Table V as the enthalpy of dissociation ($\Delta H_0$). It is to be noted further that the Sc atom has a spin-orbit ground state stabilization of 168.34 cm$^{-1}$ (2 kJ/mol).$^{37}$ Thus the $D_e$ values would decrease by at most 2 kJ/mol, since the ground state of ScC$_3$ is unaffected by spin–orbit coupling in comparison to the dissociated products.

The experimental atomization energy of ScC$_3$ is deduced using second or third law methods from the measured enthalpies obtained using high temperature mass spectrometry.$^8$ The deduction of AE from the measured thermodynamic data is usually done through the third law or second law methods; this requires knowledge of the structure and spectroscopic properties of the gaseous ScC$_3$ molecule. Since no data on the electronic states of ScC$_3$ were available, the AE was estimated using empirical rules.$^8$ Furthermore, the excited states of the ScC$_3$ molecule were estimated from the excited states of Sc$_2^2$. Our present calculations indicate that these approximations are not consistent with the $ab$ initio results. The theoretical results obtained here facilitate better estimation of the Gibbs energy functions (GEF) and enthalpy ($\Delta H_0$) of the following reaction (Table IV)

$$\text{Sc}(g) + 3\text{C}(s) = \text{ScC}_3(g). \quad (1)$$

The correction of the experimental enthalpy determined by the third law could be represented as:

$$\Delta = -T(\text{GEF}_{\text{theor}} - \text{GEF}_{\text{est}}), \quad (2)$$

GEF$_{\text{est}}$ is the value estimated in the original study$^8$ and GEF$_{\text{theor}}$ is calculated with the theoretical data of gaseous ScC$_3$. In comparison to the original $\Delta H_0$ value of 355 kJ/mol, the average correction (88 kJ/mol) leads to the enthalpy of the reaction (1) as 443 kJ/mol. Using the available experimental carbon sublimation energy (711.2 kJ/mol)$^{38}$ and the atomization energy of C$_3$ (1302.8 kJ/mol)$^{39}$, we calculate the atomization and the dissociation energy values of the gaseous ScC$_3$ and report them in Table V. The correction improves the agreement between the measured and the calculated $ab$ initio enthalpies (Table V). The energy to obtain ScC$_3$ from ScC$_2$ is also determined from the experimental data and the corrected result is shown in Table V.

Although thermodynamic data are not available for the ScC$_3^-$ anion, recent works$^{11,12}$ provide electronic detachment energies of ScC$_3^-$ and ScC$_2^-$. These data enable us to estimate the thermodynamic properties of ScC$_3^-$ using a simple thermodynamic energy cycle. The atomization energy of ScC$_3^-$ defined by the reaction (3) could be calculated from the expression (4)
reaction conclusion that the enthalpy of anion cluster growth from the ab initio at the batic detachment energies are practically the same for ScC₂ and ScC₃. The dissociation energies are calculated by applying the sublimation energy of carbon and atomization energy of C₃. The dissociation energies are in good agreement with the experimental data. The Dₑ, at the MRSDCI level has been calculated using the following energy cycle: 

\[ Dₑ(\text{ScC}_3^-) = \text{IP(ScC}_3^-) + Dₑ(\text{ScC}_3^-) - \text{EA(Sc)} \]

(6)

The value calculated in this manner (530 kJ/mol) is in good agreement with the experimental data.

### C. The nature of bonding

The leading configurations of the low-lying electronic states of ScC₃ and ScC₃⁻ indicate multireference character of the electronic states of these clusters with most electronic states having coefficients less than 0.8. However, the dominant configurations for most of the electronic states in the MRSDCI wave function are the same as those in the DFT/B3LYP calculations. The only difference was found in the ²B₁ state for which the DFT/B3LYP and the MRSDCI leading electronic configurations differ. The leading configuration of the ²B₁ state in the MRSDCI wave function was found to be 6a₁1⁴b₁1⁴a₂¹, whereas in the DFT/B3LYP method, this state was found to have a single open shell (2b₁¹) configuration. The multireference nature of these

### Table IV. Gibbs energy functions, GEF=(\text{G}T-\text{H}_0)/T, and heat content functions, \( \Delta H=\text{H}_0-\text{H}_0' \) for ScC₃ and ScC₃⁻ calculated for various isomers [GEF in J/(K mol), \( \Delta H \) in kJ/mol, and temperature in K]. The calculations are based on DFT frequencies and MRSDCI+Q separation energies.

<table>
<thead>
<tr>
<th>Method</th>
<th>Structure</th>
<th>Temperature</th>
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<td></td>
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</tr>
<tr>
<td>DFT</td>
<td>C₂v</td>
<td>GEF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta H )</td>
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<td>C₄v</td>
<td>GEF</td>
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</table>

*Estimated experimental values; Ref. 7.*

### Table V. Enthalpies (\( \Delta H \)) of reactions involving gaseous ScC₃, Sc, and C₃ from experimental and theoretical studies. Energies are in kJ/mol.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
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<th>Expt corrected¹</th>
<th>Calc.</th>
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<td></td>
<td>DFT</td>
</tr>
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<td>Sc(g) + 3C(s) = ScC₃(g)</td>
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<td>2</td>
<td>ScC₃(g) = Sc(g) + 3C(g)</td>
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<td>4</td>
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<td>206</td>
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¹Reference 7.
²This work.
The leading electronic configuration of the $^4B_1$ ground state (also $^2B_2$ excited state) of the neutral ScC$_3$ is $1a_1^2...5a_1^26a_1^11b_1^2...3b_1^24b_1^1b_1^22b_2^11a_2^1$. The $^2B_2$ excited state has the dominant configuration of $1a_1^2...5a_1^21b_2^2...3b_1^22b_1^1b_1^21a_2^1$. The leading configuration of the $^2A_2$ excited state of $1a_1^2...5a_1^21b_2^2...3b_1^22b_1^1b_1^21a_2^1$, while the $^2A_1$ excited state has the $1a_1^2...5a_1^26a_1^11b_1^2...3b_1^22b_1^1b_1^21a_2^1$ leading configuration.

The electronic configuration of the ground state of the ScC$_3$ anion is $1a_1^2...5a_1^26a_1^11b_1^2...3b_1^24b_1^1b_1^22b_1^11a_2^2(^3B_2)$. The neutral electronic states produced through a simple electron detachment without rearrangement are $^2A_2$, $^2B_2$, $^2B_1$, and $^4B_1$. The two lowest states of ScC$_3$ ($^3B_1$ and $^3B_1'$) are produced by electron detachment from the $1a_2$ orbital of ScC$_3$ ($^3B_2$). The $^2B_2$ and $^2A_1$ states are produced [from ScC$_3$ ($^3B_2$)] by electron detachment from the $6a_1$ and $4b_2$ orbitals respectively, whereas the $^2A_2$ state is produced by the detachment of $6a_1^1$ electron and excitation of one $1a_2$ electron to the $4b_2$ orbital.

Figure 2 shows a few of the active orbitals of ScC$_3$ in its ground state. The compositions of these orbitals (in the MRSDCI wave function) could be expressed in a qualitative way as

$$
\Psi(5a_1) = (\text{Sc})(3d_{z^2}) + (C_1 + C_2 + C_3) \\
\times (2s + 2p_z) - (C_2 - C_3)(2p_y),
$$

$$
\Psi(6a_1) = -(\text{Sc})(4s + 4p_z + 3d_{z^2} + 2p_z) \\
+ (C_1 + C_3)(2s),
$$

$$
\Psi(3b_2) = (\text{Sc})(3d_{x^2}) - (C_1 - C_2 - C_3)(2p_y) \\
+ (C_2 - C_3)(2s + 2p_z),
$$

The compositions indicate that, except for the $2b_1$ orbital, in all the other orbitals considerable mixings of the Sc and C orbitals are found. For example, in the singly occupied $6a_1$ orbital, scandium $4s$, $4p$, and $3d_{z^2} - 2p_z$ orbitals mix with the $2s$ orbitals of C$_2$ and C$_3$. Similar mixings are also seen in singly occupied $4b_2$ and $1a_2$ orbitals. The orbital pictures presented in Fig. 2 are consistent with this. Consequently, electron donation and back donation between the Sc and C orbitals seem to be the primary mechanism for the formation of the S–C bonds. This could be better explained through the

![FIG. 2. Three-dimensional representation of the active space $5a_1$, $6a_1$, $3b_2$, $4b_2$, $2b_1$, and $1a_2$ natural molecular orbitals (MRSDCI) of ScC$_3$ ($^3B_1$). The pictures were originally drawn keeping $z$ as the vertical axis. Each MO picture is the rotated to have better visualization.](image-url)
Mulliken populations of different orbitals of Sc and C. The molecular orbitals of the excited electronic states are dominated by Sc (3d).

The gross Mulliken populations computed at the M R S D C I level of theory indicate partial ionic character of the Sc–C bonds with electron transfer from Sc to the C 3 fragment. This charge separation characteristics of Sc and C 3 fragment correlate well with the similarity of energy separations between various low-lying electronic states ( 2 B 1 :0.12 eV, 2 B 2 :0.13 eV and 2 A 2 :0.47 eV) and the lowest excited electronic state of the Sc 2 (0.31 eV) cation. The excited states of Sc atom (1.43 eV) and Sc 2+ (3.17 eV) are far from these energy separations of ScC 3 . Moreover, the charge separation found in ScC 3 and the energy separations of the excited states of ScC 2 10 and Sc 2+ were found to be comparable (0.29 versus 0.31 eV).

The Sc–C bonds are significantly ionic in higher excited states with Sc 2+C− polarity. The bond formation in the ground state ( 2 B 1 ) is accompanied by an electron donation and back donation scheme with the Sc 4s orbital donating electronic density to the carbons, and Sc 3d orbitals accepting electronic density from the carbons. The ground state Mulliken population of the Sc atom is 3 d 1.08 4 s 1.01 4 p 0.64. The Mulliken populations differ in different electronic states of ScC 3 , consistent with different electronic configurations. For example, the Mulliken populations of the 2 B 2 and 2 A 2 states are 3 d 1.78 4 s 0.35 4 p 0.39 and 3 d 1.84 4 s 0.37 4 p 0.39. The Sc Mulliken population of the 2 A 1 state is 3 d 1.27 4 s 0.40 4 p 0.52. Thus, only the 2 B 1 state has a similar charge distribution pattern to the 4 B 1 ground state, but in the other higher excited states e. g., 2 B 2 , 2 A 2 , and 2 A 1 , the charge distribution patterns on the s and d orbitals are just reverse to the 4 B 1 ground state. The overall picture of the electron donation and back donation scheme is similar. The addition of an electron to the molecule (ScC 3 ) reduces the positive charge on metal in the ground state ( 2 B 2 ) and the total excess electronic density remains on the C 3 fragment. This feature still keeps the nature of bonding in ScC 3 ionic, although this ionic character would be much less with respect to the neutral molecule.

The electron donation and back donation that we infer from the Mulliken populations can be visualized from the difference density plots of ScC 3 and ScC 3−. Figure 3 shows the difference density maps of these two molecules with respect to the separated Sc and C atoms using the C A S S C F natural orbitals in their respective ground states. The difference density plot of ScC 3 ( 4 B 1 ) shows that there is loss of electron from the 3 d orbitals of Sc and the population near s orbital region is enhanced. Moreover the overall charge around the C 3 fragment is increased with the maximum charge concentration around the s orbital regions of C 2 and C 1 . This picture clearly shows an electron donation and back donation process is operative in the ScC 3 bonds. There is depletion of electron from the Sc d orbital around the Sc…C 1 bonding region, and enhancement of C 2 and C 3 electronic density through conjugation with C 1 . The difference density picture of ScC 3− could be similarly interpreted. The difference of bonding of these two molecules is also evident from these pictures. The Sc atom shows higher concentration of negative charge in ScC 3−.

![Image](https://example.com/image.png)

**FIG. 3.** The difference electron density plots of (a) ScC 3 and (b) ScC 3− with respect to the separated Sc and C atoms. The contours are derived from the C A S S C F natural orbitals and are drawn in the yz-plane of the molecules. The separation between the contours is 0.03 electron/bohr 3 . The contours with no density are labeled with zeros, while solid lines indicate enhancement of electron density.

### IV. CONCLUSIONS

We have optimized the geometries of several low-lying electronic states of ScC 3 and ScC 3− at the D F T/B 3 L Y P and C A S S C F/M R S D C I levels. Our results have shown that due to the multireference characters of the low-lying electronic states of these molecules, the D F T/B 3 L Y P results differ from the C A S S C F/M R S D C I results even for the ground state. The C A S S C F/M R S D C I method predicts a 4 B 1 state as the ground state of ScC 3 with a ring structure, while the D F T method predicts a doublet ground state. Thus, we have suggested assignment of the observed anion photodetachment spectra using our C A S S C F/M R S D C I results. Both the D F T/B 3 L Y P and the C A S S C F/M R S D C I calculations have predicted C 2v ring structures for the ground state geometries of both ScC 3 and ScC 3−. The linear structures in different electronic states have also been optimized, but they are higher in energy. The present calculation reveals a 4 B 1 ground state for ScC 3 with a ring structure. Three other low-lying electronic states of similar structures ( 2 B 1 , 2 B 2 , and 2 A 2 ) were also found at the C S S C F/M R S D C I levels. Wang and Li 12 have observed the 355 nm spectrum of ScC 3− to be broad with weak signals throughout the high BE side. They have suggested that these peaks were probably due to closely spaced low-lying electronic states of ScC 3. The occurrence of the
low-lying $^2\Pi$, $^4B_2$, and $^2A_1$ electronic states of ScC$_3$ with energies above the $^2A_2$ state at the CASSCF/MRSDCI level (Table I) is consistent with this observation.

Thermodynamic data (Gibbs energy functions) for the ground electronic state of the ScC$_3$ molecule have been corrected using our computed structural data and energy separations of different electronic states. The corrected experimental enthalpies are in reasonable agreement with the ab initio estimates. Thermodynamic cycle has been applied to estimate the atomization energies of ScC$_3$ in combination with high temperature mass spectrometric data$^8$ and photoelectron data$^{11,12}$ The ab initio dissociation and atomization enthalpies agree well with the experimental values.

The gross Mulliken population analysis on these molecules shows that in both ScC$_3$ and ScC$_\text{3}^-$ the C$_3$ fragment hosts excess electron. This suggests significant ionic character of the Sc–C bonds in the molecule. Although the addition of an electron reduces the ionic character of Sc–C the bond, electron donation and back donation schemes can still be applied to explain the nature of bonding.

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