Electronic Structure and Thermodynamic Properties of ScC_2

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Ab initio computations using both single-reference and multireference techniques that included electron correlation effects are carried out on ScC_2. The atomization, dissociation ($Sc-C_2$) energies, and the enthalpy of formation for ScC_2 are computed. Theoretical results are in excellent agreement with available experimental data. The experimental Gibbs energy functions (GEF) are compared with theoretically computed GEF for the ground state structure.

Introduction

Gaseous rare earth and transition metal carbides have been isolated since the pioneering work of Chupka et al.[1] Subsequent to this work, a large number of metal and mixed-metal carbides have been studied,[2,3] including the extensive study of group IIIB metal carbides by Gingerich and co-workers.[2] Recent studies of metallofullerenes have raised intriguing questions on the nature and properties of the metal−carbon bond.[4,5] Although there are many experimental mass spectroscopic studies of metal carbide cations,[3,6,7] there is little insight available into the nature of metal−carbon bonding and the molecular structures of these species even for small systems.[8] Our recent theoretical studies of yttrium[9−11] and lanthanum[12] carbides have provided insight into the structure and energetics of these species. These theoretical studies also revealed that the geometries assumed in the experimental second or third law determination of thermodynamic properties are not correct. Thus, the theoretical computations provided improved thermodynamic parameters of these species through correction of the partition functions. Scandium carbides, however, have not yet been studied theoretically despite available experimental data.[13−15] Since there are no spectroscopic data available for $Sc-C_2$, molecular data are not available for these species.

The aim of this study is to determine the equilibrium structure, spectroscopic constants, and the nature of bonding of ScC_2 using high-level ab initio techniques that include electron correlation effects at both single-reference and multireference levels. The dissociation and atomization energies as well as thermodynamical functions, such as the Gibbs energy and heat content functions, were computed. Using the computed molecular structures, experimental enthalpies have been corrected for the assumed incorrect linear geometries.

Theoretical Methods and Computational Details

The calculations were performed using extensive ab initio approaches, namely, second (MP2) and fourth (MP4) order Møller−Plesset perturbation theory,[16] complete basis set (CBS) extrapolation of the MP2 energy,[17] complete active space multiconfiguration self-consistent-field (CASSCF),[18] and multireference singles and doubles configuration interaction methods (MRSDCI). Geometry searches were done at the MP2, MP4, and CASSCF levels of theory by the quasi-Newton−Raphson procedure.[19,20] The vibrational frequencies were calculated at the MP2 level.

All the calculations described here were made using the relativistic effective core potentials (RECPs) with the $3s^23p^6$-$4d^14s^2$ shells included in the valence space for scandium[21] and with $2s^22p^2$ valence shells for the carbon atoms.[22] The most diffuse exponents in the original basis sets have been left uncontracted leading to (7s4p3d) and (3p3s) valence basis sets for Sc and C, respectively. The carbon basis set was supplemented with a six-component 3d Gaussian function adopted from Dunning and Hay.[23] The above choice of basis set leads to 73 atomic basis functions for the ScC_2 cluster.

The MP2/MP4 calculations were performed using the spin-unrestricted Hartree−Fock (UHF) method.[24] All 19 electrons were correlated in these methods. The MP4 calculations were performed including single, double, triple, and quadruple excitations. The complete basis set extrapolation of MP2 energy[17] was based on an asymptotic convergence of pair natural orbitals (PNO) for pair correlation energies and pair coupling terms. Using developed asymptotic forms, the correlation energy in the complete basis set is extrapolated from finite PNO basis set calculations. A minimum of 10 PNO's for each pair has been selected in this calculation.

In the complete active space multiconfiguration self-consistent-field calculations, we included all orbitals of Sc and C that correlated into the Sc(4s), Sc(4d), and C(2p) at infinite separation. The calculations were performed in the C_{2v} group (z axis being the C_2 axis). The active space comprised six a_1, two b_1, two b_2, and two a_2 orbitals for the bent C−Sc−C structure and five a_1, three b_1, three b_2, and one a_2 orbital for the linear Sc−C−C structure. Seven electrons were distributed in all possible ways in the above active spaces. The Sc(3s) and Sc(3p) semicore and C(2s) valence orbitals were allowed to relax at the CASSCF stage, but no excitations from these orbitals were allowed. The lowest energies were obtained for the $^2A_1$ electronic state, and this state has been chosen for further studies. This choice of active space leads to 14 298 configuration spin functions (CSF) for the $^2A_1$ state. The wave function for this state is mostly single determinental. The square of the coefficient of the leading configuration (c^2) $4a_1^25a_1^22b_1^26a_1^1$ is 0.908 compared to 0.014 for the second largest configuration, $4a_1^2$-$2b_1^23b_2^25a_1^1$.

Configuration interaction calculations were carried out following the CASSCF calculations, using the first-order (FOCI) and multireference singles and doubles (MRSDCI) methods to include the higher-order electron correlation effects. The FOCI calculations included all configurations in the CASSCF and the configurations obtained by distributing six electrons in the

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TABLE 1: Calculated Geometries and Total Energies for the Symmetrical (C_{2v}) and Linear ($C_{\infty v}$) Structures of the Ground Electronic States of ScC_2[a]

method		$C_{2v}(^2A_1)$ ScC_2	$C_{\infty v}(^2\Sigma^+)$ Sc−C−C
MP2	R(Sc−C)	2.037	1.900
	R(C−C)	1.283	1.278
	∠C−Sc−C	36.1	
	E	−57.45712	−57.42372
	CBS(MP2)	−57.60343	−57.56923
MP4	R(Sc−C)	2.059	1.934
	R(C−C)	1.287	1.284
	∠C−Sc−C	36.4	
	E	−57.50822	−57.48168
CASSCF	R(Sc−C)	2.063	1.919
	R(C−C)	1.283	1.278
	∠C−Sc−C	36.2	
	E	−57.05520	−57.05037

[a] Distances in angstroms, angles in degrees, and energy in hartrees.

internal (active) and one electron in the orthogonal external spaces in all possible ways. The FOCI included up to 550 000 CSFs. All configurations in the CASSCF with coefficients >0.07 were included as reference configurations in the MRSDCI. All possible single and double excitations were allowed from these reference configurations. The MRSDCI calculations included up to 750 000 CSFs. These computations as well as Mp2 and Mp4 computations included excitations from C(2s).

On the basis of the CASSCF wave functions, it is seen that the leading configuration makes a significant contribution. However, the CASSCF method is somewhat less accurate as it includes only the zeroth-order electron correlation effects and no dynamic correlation effects. Therefore, correlation effects were also incuded based on a single-reference technique, namely, the MP2 method for computing the vibrational frequencies.

The calculations of the thermodynamic functions have been performed at the MP2 levels of theory by applying ideal gas, rigid rotor, and harmonic oscillator approximations.[25] The contributions of the low-lying excited electronic sttaes were included in the computation of the partition functions and thermodynamic properties.

The MP2, MP4, and CBS calculations were made using the Gaussian-94[26] code. The CASSCF computations were made using the GAMESS[27] program package and also a modified version of ALCHEMY II[28] to include the RECPs.[29] The MRSDCI computations were made using ALCHEMY II.

Molecular Structure of ScC_2 and the Nature of the Chemical Bond

Since the geometry of the gaseous ScC_2 is not yet determined experimentally, a previous thermodynamic estimation of the properties from experimental data had assumed ScC_2 to have an asymmetric linear structure with a Sc−C distance of 1.65 Å.[13] The available theoretical value for the Sc−C bond distance of 2.199 Å in the $ScCH_3^+$ cation[30] is significantly longer.

The ScC_2 molecule in its ground state is formed from the ^2D state of scandium and a triplet or singlet state of C_2. The geometry search was thus performed for doublet and quartet electronic states. Geometry optimizations have been performed for both the electronic states using the CASSCF level of theory, starting from different nuclear arrangements that included linear and bent structures of symmetrical and unsymmetrical geometries. Optimizations starting from symmetrical and bent unsymmetrical geometries resulted in the symmetrical C_{2v} structure. As seen from Table 1, which shows the equilibrium geometries of the bent (C_{2v}) and linear Sc−C−C structures, the $^2A_1$ electronic state with a C_{2v} structure (Table I) is found to be the ground state. Table 2 shows the optimized equilibrium geometries and energy separations of several excited electronic states of ScC_2. As evidenced from Table 2, there exist a number of low-lying excited states, especially two states close in energy to the ground state. Ten electronic states are separated by less than 2 eV from the ground state (Table 2).

TABLE 2: Optimized Geometries and Energy Separations for the Excited Electronic States of the ScC_2 Calculated within the CASSCF Approach[a]

electronic state	geometry			energy separation[b]
	R(Sc−C)	R(C−C)	∠C−Sc−C	
	C_{2v} Structure			
$^2A_2$	2.135	1.278	34.8	0.234
$^2B_2$	2.105	1.282	35.4	1.277
$^4A_1$	2.431	1.278	30.5	1.842
$^4B_1$	2.480	1.315	30.7	1.875
	$C_{\infty v}$ Structure			
$^2\Sigma^+$	1.919	1.278		0.131
$^2\Pi$	2.178	1.308		0.918
$^4\Pi$	2.245	1.237		1.673
$^4\Sigma^+$	2.289	1.244		1.747
$^4\Delta$	2.301	1.295		1.885
$^2\Delta$	2.303	1.295		1.917

[a] Distances in angstroms, angles in degrees, and energy in electronvolts. [b] Relative to the $C_{2v}(^2A_1)$ ground state.

Although at the CASSCF level the energy separation of the $^2\Sigma^+$ ($C_{\infty v}$) linear Sc−C−C structure is only 0.13 eV above the bent (C_{2v}) state, the CASSCF method does not include dynamic electron correlation effects. Therefore, higher-order FOCCI and MRSDCI computations were carried out which include electron correlation effects to a higher degree. At the FOCI level the $^2\Sigma^+$ ($C_{\infty v}$) linear Sc−C−C structure is 0.71 eV above the bent structure, while at the mRSDCI level the linear structure is 0.82 eV above the bent structure. Thus, the bent structure is unambiguously above the $C_{\infty v}$ linear structure. As noted earlier, we also carried out MP2, CBS-MP2, and MP4 computations, and the results at these levels for the linear to bent energy separations are 0.90, 0.94, and 0.72 eV, respectively. We thus conclude that the bent C_{2v} structure is decisively lower in energy compared to the $C_{\infty v}$ linear Sc−C−C structure.

The formation of ScC_2 weakens the C−C bond, which is demonstrated by the C−C bond length increase from 1.260 Å (C_2 molecule) to 1.278 Å ($C_{\infty v}$) and 1.283 Å (C_{2v}) at the MP2 level. The Sc−C bond distance of 1.900 Å in the linear structure corresponds to a double bond, while two Sc−C bonds (2.037 Å) in the C_{2v} structure are longer by 0.137 Å, thus corresponding to single bonds.

The ground state of ScC_2 is formed, as indicated by the Mulliken population analysis, by electron transfer from Sc (0.915 electron) to the C_2 fragment (Figure 1). The gross atomic populations on C (s = 1.702, p = 2.655, d = 0.100) and Sc (s = 3.059, p = 6.045, d = 0.981) indicate that the bond is formed due to the σ donation from the C_2 fragment (0.596 electron) and significant π-back-donation of 1.019 electrons from the 3d orbitals of Sc to the 2p orbitals of carbons. These ionic bonds result in an equilibrium dipole moment of 7.49 D for ScC_2. The large electron transfer within ScC_2 is consistent with the proposed[31] qualitative picture of the $Sc^{2+}(C{\equiv}C)^{2-}$ ionic bonding. The nature of Sc−C chemical bond is akin to the Y−C and La−C bonds.[9,12]

Thermodynamic Stability of ScS_2

The theoretically calculated values of atomization and dissociation ($Sc{-}C_2$) energies are compared in Table 3 with

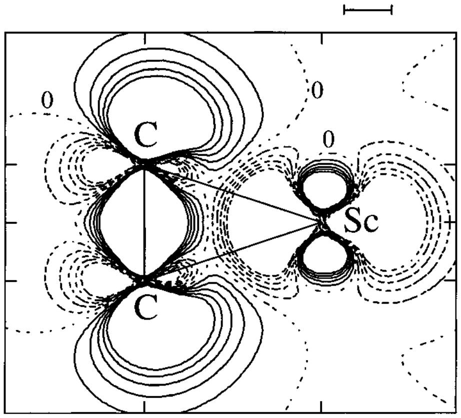

Figure 1. Electron density difference map between ScC_2 and its subunits ($Sc + C_2$) in the ScC_2 molecular plane. The map was derived from the CASSCF natural orbitals. The spacing between the contours is 0.005 electron/bohr^3. The contours with no density change are labeled with zeros, solid lines indicate enhancement of electronic density, and dotted lines indicate depletion of electronic density.

TABLE 3: Atomization Enthalpies ($\Delta H^\circ_{a,0}$) of ScC_2 and $Sc-C_2$ Dissociation Energies (D°_0)[a]

method	structure	$\Delta H^\circ_{a,0}$	D°_0
HF	C_{2v}	658	
	$C_{\infty v}$	615	
MP2[b]	C_{2v}	1183 (1164)	590 (581)
	$C_{\infty v}$	1096 (1078)	
CBS(MP2)	C_{2v}	1259 (1240)	666 (657)
	$C_{\infty v}$	1168 (1151)	
CASSCF	C_{2v}	1195 (1176)	602 (593)
	$C_{\infty v}$	1182 (1158)	
MP4	$C_{\infty v}$	1103 (1084)	
MP4	C_{2v}	1173 (1154)	580 (571)
FOCI	C_{2v}	1226 (1163)	632 (624)
FOCI	$C_{\infty v}$	1157 (1094)	
MRSDCI	C_{2v}	1242 (1223)	649 (640)
exptl		1185 ± 14[c]	592[f]
		1213 ± 21[d]	620[f]
		1155 ± 21[e]	565 ± 21[e]

[a] Results with applied zero-point vibrational energy correction are given in parentheses. Energy is in kJ/mol. [b] Projected UMP2. [c] Reference 13. [d] Reference 15. [e] Reference 14. [f] Evaluated from $\Delta H^\circ_{a,0}$ by applying heat of formation of 2C(s)=C2(g), $\Delta H^\circ_{0,f} = 829.3$ kJ/mol, and C(s)=C(g) $\Delta H^\circ_{0,f} = 709.5$ kJ/mol (ref 32).

experimental data evaluated from the third and second law methods. As seen from Table 3, the overall agreement between our computed results and experiment is excellent. The experimental results were evaluated assuming a Sc−C−C linear geometry with the Sc−C bond distance being too short. However, the agreement between the Gibbs free energy functions and heat content functions estimated with the experimental data with this incorrect geometry and the thermodynamical functions calculated form theoretical data using the correct geometry by the standard methods of statistical thermodynamics (ideal gas, rigid rotor, and harmonic oscillator approximation[25]) is surprisingly good (Table 4). The theoretical MP2 calculations for the bent C_{2v} structure gave $\nu_1 = 662$ cm^{-1} and $\nu_2 = 1388$ cm^{-1} for the deformation modes and $\nu_3 = 1120$ cm^{-1} for the unsymmetrical stretching mode. The accuracy of the MP2 level theory together with the RECPs and the basis sets was gauged using the same basis set and RECPs for Sc and a comparable basis set and RECPs for O and computing the vibrational frequency of the ScO diatomic at the MP2 level. Our computed result for the ground state of ScO is 859 cm^{-1} compared to the experimental value[33] of 964 cm^{-1}. The $C_{\infty v}$ linear Sc−C−C structure is a saddle point in the potential energy surface as this structure can be converted into a more stable bent C_{2v} structure through deformation. Therefore, the vibrational frequencies of the $C_{\infty v}$ linear Sc−C−C structure are not meaningful as this structure is not observable. We note that Haque and Gingerich have reported 1792, 761, and 534 cm^{-1} for this structure using an assumed geometry and force constants. Our computations reveal that the $C_{\infty v}$ linear Sc−C−C structure is above the C_{2v} structure and is convertible into the bent structure.

As a result of the above computations, the Gibbs energy function obtained using the third law method and the resulting atomization energy should be corrected by

$$\Delta = -T(\mathrm{GEF}_{\mathrm{exp}} - \mathrm{GEF}_{\mathrm{MP2}})$$

where $\mathrm{GEF}_{\mathrm{exp}}$ is the Gibbs energy function estimated from molecular parameters shown in Table 4 and $\mathrm{GEF}_{\mathrm{MP2}}$ is our calculated Gibbs energy function. Experimental data, especially Gibbs energy functions and equilibrium constants, are available[13] for the reaction

$$\mathrm{Sc(g)} + 2\mathrm{C(graph)} = \mathrm{ScC_2(g)}$$

Consequently, it was possible to recompute the experimental enthalpies ΔH°_0 by replacing the estimated GEF with those calculated for the computationally determined molecular structures. Enthalpies for the representative temperatures are shown in Table 5. Averaged correction leads to ΔH°_0 of 233 kJ/mol compared to an uncorrected value of 237 kJ/mol. Although the correction is not large, it is larger than the error bars (3.2 kJ/mol) estimated for the enthalpy. Other available experimental works lead to ΔH°_0 of 209[15] and 264 ± 20[14] kJ/mol. Theoretical values at various levels, namely, MP2 = 259, CASSCF = 247, MP4 = 269, FOCI = 216, and MRSDCI = 200 kJ/mol, are all reasonably close to the experimentally deduced values. The enthalpy of the reaction

$$\mathrm{M(g)} + 2\mathrm{C(graph)} = \mathrm{MC_2(g)}$$

was found to be decreasing for the M = Sc, Y, La group, as one goes down the group. The calculated ionization potential 6.4 eV (CBS-MP2) correlates well with an experimental appearance potential[13] of 7.6 ± 1 eV.

TABLE 4: Gibbs Energy Functions, GEF = $(G^\circ_T - H^\circ_0)/T$, and Heat Content Functions, $\Delta H = H^\circ_T - H^\circ_0$, Calculated by Various Methods (GEF in J/(K mol), ΔH in kJ/mol, and Temperature in K)

			temperature, K					
method	structure		298	1800	2000	2200	2400	2600
MP2	C_{2v}	GEF	−221.2	−297.1	−302.8	−307.8	−312.4	−316.7
		ΔH	10.3	88.6	100.0	111.4	122.9	134.3
	$C_{\infty v}$	GEF	−206.8	−267.5	−271.6	−275.3	−278.7	−281.9
		ΔH	9.0	68.8	77.6	86.4	95.3	104.2
exptl[a]	$C_{\infty v}$	GEF	−216.3	−296.6	−302.1	−307.2	−312.0	−316.4
		ΔH	10.8	95.2	107.4	119.2	131.9	144.2

[a] Reference 13, based on estimated structural parameters.

TABLE 5: Estimated and Theoretical Gibbs Energy Functions (in J/(K mol)), the Enthalpy Correction ($\Delta(\Delta H^\circ_0)$), and the Corrected Experimental Enthalpy (ΔH°_0) for the $Sc(g) + 2C(graph) = ScC_2(g)$ Reaction (in kJ/mol) for Selected Temperatures (in K)

	GEF			
T	est[a]	theor	$\Delta(\Delta H^\circ_0)$	ΔH°_0
2001	−302.1	−300.9	2.4	235.0
2120	−305.2	−303.8	2.9	233.6
2223	−307.7	−306.2	3.2	233.3
2297	−309.5	−307.9	3.7	234.5
2435	−312.8	−310.9	4.6	236.4
2530	−314.9	−312.8	5.2	233.3
			av 3.7 (3.5)[b]	av 233.4

[a] Linear interpolation of data from ref 13. [b] Averaged $\Delta(\Delta H^\circ_0)$ value for all temperatures given in Table 5 of ref 13.

Conclusions

The scandium−dicarbide system has been the subject of several experimental investigations[13−15] which yielded the atomization and dissociation energies of the gaseous ScC_2 molecule and the enthalpy of the reaction

$$Sc(g) + 2C(graph) = ScC_2(g)$$

We obtained the optimized geometries and energy separations for several doublet and quartet electronic states of ScC_2. This facilitated a more accurate analysis of the experimental thermodynamic data. The molecule exhibits several bound excited electronic states lying below the $Sc + C_2$ dissociation energy limit. The symmetrical C_{2v} structure in a $^2A_1$ electronic state was found to be the ground electronic state of ScC_2, although the linear Sc−C−C structure in a doublet state and a $^2A_2$ electronic state with C_{2v} symmetry were found to be close in energy.

The Sc−C bond, which was found to be highly ionic, is formed according to a σ-donation and π-back-donation scheme. The C_{2v} structure exhibits σ-donation of carbon s electrons (0.298 electron) and π-back-donation (0.655 electron) to the carbon p orbitals. The 3d orbitals of Sc take active part in the formation of the Sc−C bonds.

The calculated dissociation and atomization energies agree with the measured data. Despite the assumption of an unsymmetrical linear structure for ScC_2 for the evaluation of thermodynamic functions, the experimental results agree with the theoretically computed results. A single determinantal character of the ground state wave function leads to close agreement between the Møller−Plesset perturbation methods and multireference approaches.

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References and Notes

(1) Chupka, W. A.; Berkowitz, J.; Giese, C. F.; Inghram, M. G. *J. Phys. Chem.* **1958**, *62*, 611.
(2) Gingerich, K. A. *J. Less-Common Met.* **1985**, *110*, 41.
(3) Cassady, C. J.; McElvany, S. W. *J. Am. Chem. Soc.* **1990**, *112*, 4788.
(4) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Krato, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779.
(5) Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, *366*, 123.
(6) Shelimov, K. B.; Clemmer, D. E.; Jarrold, M. F. *J. Phys. Chem.* **1995**, *99*, 11376.
(7) Clemmer, D. E.; Jarrold, M. F. *J. Am. Chem. Soc.* **1995**, *117*, 8841.
(8) Clemmer, D. E.; Shelimov, K. B.; Jarrold, M. F. *J. Am. Chem. Soc.* **1994**, *116*, 5971.
(9) Roszak, S.; Balasubramanian, K. *Chem. Phys. Lett.* **1995**, *246*, 20.
(10) Roszak, S.; Balasubramanian, K. *J. Phys. Chem.* **1996**, *100*, 8254.
(11) Roszak, S.; Balasubramanian, K. *Chem. Phys. Lett.* **1996**, *254*, 274.
(12) Roszak, S.; Balasubramanian, K. *J. Phys. Chem.* **1996**, *100*, 11255.
(13) Haque, R.; Gingerich, K. A. *J. Chem. Phys.* **1981**, *74*, 6407.
(14) Kohl, K. A.; Stearns, C. A. *J. Chem. Phys.* **1971**, *54*, 1414.
(15) Drowart, J.; Verhaegen, G.; Smoes, S. Eleventh Annual Conference of Mass Spectrometry and Allied Topics, May 19−29, 1963, pp 329−335.
(16) Møller, C.; Plesset, M. S. *Phys. Rev.* **1943**, *46*, 618.
(17) Ochterski, J. W.; Petersson, G. A.; Montgomery, Jr., J. A. *J. Chem. Phys.* **1996**, *104*, 2598.
(18) Roos, B. O. In *Methods of Computational Molecular Physics*; Dierksen, G. F. H., Wilson, S., Eds.; Reidel: Dordrecht, 1978.
(19) Baker, J. *J. Comput. Chem.* **1985**, *7*, 385.
(20) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.
(21) Hurley, M. M.; Pacios, L. F.; Christiansen, P. A.; Ross, R. B.; Ermler, W. C. *J. Chem. Phys.* **1986**, *84*, 6840.
(22) Pacios, L. F.; Christiansen, P. A. *J. Chem. Phys.* **1985**, *82*, 2664.
(23) Dunning, Jr., T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer III, H. F., Ed.; Plenum Press: New York, 1977; p 1.
(24) Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.
(25) Davidson, N. *Statistical Mechanics*; McGraw-Hill: New York, 1962.
(26) Gaussian 94, Revision C.2: Frish, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Robb, M. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Oritz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1995.
(27) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
(28) ALCHEMY II: Lengsfield, B.; Lui, B.; Yoshimine, M. (major authors).
(29) Balasubramanian, K. *Chem. Phys. Lett.* **1986**, *127*, 585.
(30) Musaev, D. G.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 11660.
(31) Lee, J. D. *Concise Inorganic Chemistry*; Chapman and Hall: London, 1991.
(32) *JANAF Thermochemical Tables*; Dow: Midland, MI, 1961; p 1969.
(33) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; van Nostrand Reinhold: New York, 1979.