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Theoretical Investigation of Scandium Carbide, ScC

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The electronic structure of the diatomic carbide ScC has been investigated by ab initio multireference methods in conjunction with large basis sets. The ground state has been determined to be of $^2\Pi$ symmetry with D_e = 65.5 kcal/mol and R_e = 1.988 Å. Eight more states have been examined within an energy range of about 1 eV, with the first excited state ($^4\Pi$) being 1.2 kcal/mol higher.

Introduction

The purpose of the present work is to report quantitative ab initio calculations on the carbide ScC, the simplest of the first row transition metal diatomic carbides. The computational difficulties encountered in transition metal containing molecules do not need to be overemphasized. This is probably the reason that, despite their intrinsic interest, both practical and academic, the literature on the (neutral) carbides cannot be considered as either rich or informative. In Table 1 we have tried to collect the existing data concerning dissociation energies (D_e), and bond lengths (R_e) for the (proposed) ground states of the series MC, M = Sc, Ti, V, Cr, Fe, Co, Ni, and Cu. A glance at the Table 1 convinces that almost nothing can be considered as certain, not even the ground-state symmetries. Note for instance, the difference in D_e between experiment and theory on ScC (X-state $^2\Pi$, vide infra), the large discrepancies on the D_e TiC values, particularly among the density functional results, or the interplay between $^3\Sigma^-$ and $^9\Sigma^-$ states as to which one is the ground state of CrC.

In an effort to obtain reliable results, we have performed multiconfigurational valence CISD calculations on ScC combined with large basis sets. In particular, we employed the complete active space SCF (CASSCF) + singles + doubles excitations (MRCI) approach, coupled with the ANO-$[7s6p4d3f]_{Sc}$, aug-cc-pVQZ (with no *g* functions)-$[6s5p4d3f]_C$ basis sets of Bauschlicher[22] and Dunning,[23] respectively. Our reference space is composed of 13 orbital functions $(4s+4p_{x,y,z}+3d_{\sigma,\pi,\delta})_{Sc} + (2s+2p_{x,y,z})_C$, with seven valence (active) electrons, $(4s3d)^3_{Sc}/(2s2p)^4_C$. We have studied nine molecular states, namely $X^2\Pi$, $^4\Pi(2)$, $^2\Sigma^-$, $^2\Sigma^+(2)$, $^4\Delta(2)$, and $^2\Delta$, eight of which trace their lineage to the ground state of the metal, $^2D(4s^23d)$ and the ground carbon ^3P state and one (a $^2\Sigma^+$), which correlates to the C ^1D atomic state.

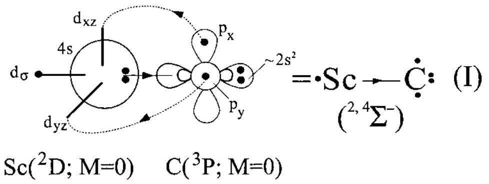
Table 2 lists the states studied and their symmetries under C_{2v} constraints, the number of CASSCF, and MRCI configuration functions (CF), and the number of the internally contracted (ic)[24] MRCI CFs used. The CASSCF wave functions display pure axial symmetry, i.e., $|\Lambda|$ = 0, 1, and 2. Based on our previous experience on the similar systems ScC^+ and TiC^+ [25] where the basis set superposition errors are 0.15 and 0.27 kcal/mol (X-states), respectively, no such correction was considered as necessary. All calculations were performed with the MOLPRO suite of codes.[26]

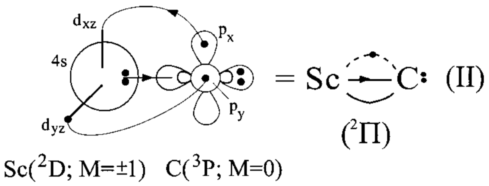
Atomic States

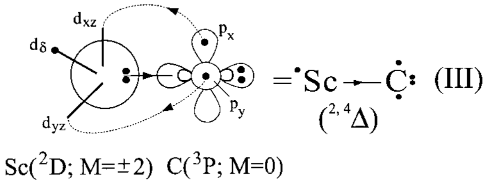
Table 3 reports total energies of the Sc $^2D(4s^23d)$ and $^4F(4s3d^2)$ and of the C $^3P(2s^22p^2)$ and $^1D(2s^22p^2)$ spectroscopic terms, in different methodologies, as well as corresponding energy splittings. As evidenced from the $\Delta E(C; {}^1D \leftarrow {}^3P)$ energy splitting (MRCI value 1.262 eV vs the experimental value of 1.260 eV [28]), the C atom is properly described by the chosen basis set. For the Sc atom the (valence) MRCI value of the $^4F \leftarrow {}^2D$ separation (1.630 eV) differs by 0.203 eV (or 14%) from the experimental value of 1.427 eV,[28] probably due to core-valence (differential) effects.

Insights

It is of interest to examine what one expects to be the structure of the ground and also of some low-lying states, by employing "simple" valence bond Lewis (vbL) icons. Starting from the ground-state atoms and disregarding the carbon M = ±1 component due to its repulsive interaction with the $4s^2$ metal electron distribution, the following diagrams can be drawn.







The next lowest atomic state is that of the C atom, $^1D(2s^2$-

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TABLE 1: Theoretical and Experimental Results on Dissociation Energies D_e(kcal/mol), and Bond Lengths R_e(Å) of Suggested Ground (X) States of First Row Transition Metal Neutral Monocarbides, MC

molecule	X-state	D_e	R_e	method
ScC		105 ± 5[a]		Exp[a,b]
	$^4\Pi$	37.6	1.889	MRDCI[c]
TiC	$^3\Sigma^+$	69.6	1.75	MRCI[d]
	$^3\Sigma^+$	65.0	1.733	MRCI[e]
	$^3\Sigma^+$	70.3	1.703	CCSD(T)[f]
	$^3\Sigma^+$	83	1.668	B3LYP[f]
	$^1\Sigma^+$	145	1.602	LSDA[f]
	$^1\Sigma^+$	112	1.641	BPW91[f]
	^{3}(?)	148.6	1.679	LDA[g]
VC	$^2\Sigma^+$			Exp[h]
	$^2\Delta$			Exp[i]
	$^2\Delta$	156.1	1.577	LDF[j]
CrC	$^3\Sigma^-$	33.4	2.01	CASSCF[k]
	$^9\Sigma^-$	27.2	2.13	Valence CI[l]
	$^3\Sigma^-$	69.2	1.676	MRCI[m]
	$^9\Sigma^-$	37.8	2.113	UCCSD[m]
	$^3\Sigma^-$	53.3	1.742	UCCSD(T)[m]
	$^9\Sigma^-$	37.6	2.112	RCCSD[m]
	$^3\Sigma^-$	>73.8	>1.88	RCCSD(T)[m]
	$^3\Sigma^-$	114.4	1.577	LSDA[m]
	$^3\Sigma^-$	80.9	1.593	UBPW91[m]
	$^3\Sigma^-$	63.9	1.642	UB3LYP[m]
FeC	$^1\Sigma^+$		1.5049	MP4//SCF[n]
	^{3}(?)	143	1.54	LDA[o]
	^{3}(?)	114	1.57	DFT(NL)[o]
	^{3}(?)	95.5	1.92	MP4[o]
	^{3}(?)	155.6	1.565	LDA/BP[g]
	$^3\Delta$		1.596	Exp[p]
	$^3\Delta$	89.9 ± 6.9[q]	1.5962134(1)	Exp[q]
	$^3\Delta$	79.3	1.607	MRCI[r]
CoC	$^2\Sigma^+$		1.5612	Exp[s]
	$^2\Sigma^+$		1.5601	Exp[t]
NiC	$^1\Sigma^+$	23	1.80	GVB[u]
	$^1\Sigma^+$	75	1.699	MRCI[v]
	^{1}(?)	141.5	1.624	LDA[g]
	$^1\Sigma^+$		1.631	Exp[w]
	$^1\Sigma^+$	63.4	1.640	MRCI[x]
CuC	^{2}(?)	90.3	1.799	LDA[g]

[a] Reference 1; it refers to D_o. [b] High-temperature Knudsen effusion mass spectrometry. [c] Reference 2, multireference CI/[3s2p3d/2s2p], pseudopotential approach; the D_e=37.6 kcal/mol is with respect to the ground-state atoms. [d] CASSCF-contracted CISD/[5s4p3d1f/3s2p1d], ref 3. [e] CASSCF+1+2/[10s8p3d/4s2p1d], ref 4. [f] Reference 4. [g] Reference 5. [h] Electron spin resonance, ref 6. [i] ESR, ref 7. [j] Reference 8. [k] Reference 9; D_e with respect to adiabatic products, Cr(^{5}S)+C(^{3}P); [8s7p3d/4s3p1d] basis set. [l] D_e with respect to the ground-state atoms, Cr(^{7}S)+C(^{3}P); CI within the valence space including 4 CFs, ref 9. [m] Reference 10; [10s8p3d/4s2p1d] basis set; D_e with respect to Cr(^{7}S)+C(^{3}P). [n] Reference 11. [o] Reference 12; [5s3p3d/3s2p1d] basis set. [p] Rotational spectroscopy, ref 13, 14. [q] Reference 15, two photon ionization spectroscopy; the dissociation energy refers to D_o and is obtained from the equation $D_o(\mathrm{FeC}) = \mathrm{IE}(\mathrm{FeC}) - \mathrm{IE}(\mathrm{Fe}) + D_o(\mathrm{FeC}^+)$, where IE stands for the ionization energy, and neglecting the IE(FeC) uncertainty of 2.1 kcal/mol $D_o(\mathrm{FeC}^+) = 94.5 \pm 6.9$ kcal/mol, ref 16. [r] Reference 17; CASSCF+1+2/[7s6p4d3f/cc-pVTZ]. [s] Laser-induced fluorescence spectroscopy, ref 18. [t] Laser ablation rotational spectroscopy, ref 19. [u] Generalized valence bond, ref 19. [v] Multireference contracted CI approach/pseudopotential description of the Ni atom, ref 20. [w] As quoted in ref 21. [x] Reference 21, [8s6p3d1f/4s3p1d] basis set.

TABLE 2: Number of CASSCF and MRCI(*ic*MRCI) Configuration Functions along with Their Symmetry Symbol under C_{2v} Constraints of the ScC 9 States Studied

state	#CASSCF	#MRCI(*ic*MRCI)	C_{2v} symmetry
$X^2\Pi$	26 026	48 531 973 (1 932 038)	$^2B_1$
$1^4\Pi$	19 537	43 030 490 (1 635 337)	$^4B_1$
$2^2\Sigma^-$	25 854	48 520 098 (1 942 354)	$^2A_2$
$3^2\Sigma^+$	26 198	48 543 890 (1 974 259)	$^2A_1$
$4^4\Delta$	19 385	42 988 816 (1 673 592)	$^4A_1$
$5^2\Delta$	26 198	48 543 890 (1 942 268)	$^2A_1$
$6^4\Delta$	19 385	42 988 816 (1 673 592)	$^4A_1$
$7^2\Sigma^+$	26 198	48 543 890 (1 974 259)	$^2A_1$
$8^4\Pi$	19 537	43 030 490 (1 644 562)	$^4B_1$

TABLE 3: Energies E(hartree) of the Sc ^{2}D(4s^{2}3d) and ^{4}F(4s3d^2) and of the C ^{3}P(2s^{2}2p^2) and ^{1}D(2s^{2}2p^2) Atomic States and Corresponding Energy Splittings ΔE (eV) in Different Methodologies

	Sc		
method	^{2}D(4s^{2}3d)	^{4}F(4s3d^2)	$\Delta E(^4\mathrm{F} \leftarrow {}^2\mathrm{D})$
NHF[a]	−759.735 718	−759.698 786	1.005
sa-SCF[b]	−759.735 546	−759.698 546	1.007
CISD	−759.776 378	−759.718 082	1.586
CISD+Q	−759.780 6	−759.718 6	1.69
CISD(11 e$^-$)[c]	−760.015 864	−759.971 285	1.213
sa-CASSCF[b,d]	−759.766 283		1.843[e]
MRCI	−759. 777 985		1.630[f]
MRCI+Q	−759.778 2		1.62
MRCI(11 e$^-$)[c]	−760. 029 572		1.586
Exp[g]			1.427

	C		
	^{3}P(2s^{2}2p^2)	^{1}D(2s^{2}2p^2)	ΔE(^{1}D←^{3}P)
NHF[a]	−37.688 619		
sa-SCF[b]	−37.688 256	−37.630 985	1.558
CISD	−37.783 523	−37.736 845	1.270
CISD+Q	−37.788 7	−37.743 1	1.24
sa-CASSCF[b,h]	−37.705 611	−37.647 775	1.574
MRCI	−37.785 224	−37.738 853	1.262
MRCI+Q	−37.788 2	−37.742 8	1.24
Exp[g]			1.260

[a] Numerical Hartree−Fock, ref 27. [b] Spherically averaged SCF or CASSCF. [c] The 3s^{2}3p^6 “core” e$^-$ are included in the CI treatment. [d] The active space is comprised of the 4s, 4p, and 3d orbitals. [e] Calculated as the energy difference $E_{\mathrm{sa-SCF}}(^4F) - E_{\mathrm{sa-CASSCF}}(^2\mathrm{D})$. [f] Calculated as the energy difference $\mathrm{E}_{\mathrm{CISD}}(^4\mathrm{F}) - \mathrm{E}_{\mathrm{MRCI}}(^2\mathrm{D})$. [g] Experimental results, averaged over M_J, ref 28. [h] The active space is comprised of the 2s, and 2p orbitals.

2p^2), 1.26 eV [28] above the ground ^{3}P state. However, none of the three components, M = 0, ±1, ±2

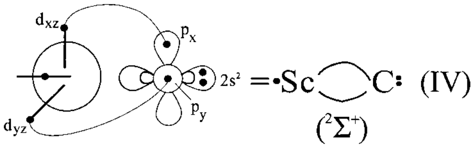
$$|^1\mathrm{D};\, \mathrm{M}=0\rangle = \frac{1}{\sqrt{6}}\left(2|2\mathrm{p}_z^2\rangle - |2\mathrm{p}_x^2\rangle - |2\mathrm{p}_y^2\rangle\right)$$

$$|^1\mathrm{D};\, \mathrm{M}=\pm1\rangle = \frac{1}{\sqrt{2}}\left(|2\mathrm{p}_0 2\bar{\mathrm{p}}_{\pm1}\rangle - |2\bar{\mathrm{p}}_0 2\mathrm{p}_{\pm1}\rangle\right)$$

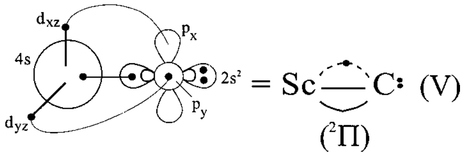
$$|^1\mathrm{D};\, \mathrm{M}=\pm2\rangle = \begin{cases} |2\mathrm{p}_{+1}^2\rangle = \dfrac{1}{\sqrt{2}}\left[\left(|2\mathrm{p}_x^2\rangle - |2\mathrm{p}_y^2\rangle\right) + i\left(|2\mathrm{p}_x 2\bar{\mathrm{p}}_y\rangle - |2\bar{\mathrm{p}}_x 2\mathrm{p}_y\rangle\right)\right] \\ |2\mathrm{p}_{-1}^2\rangle = \dfrac{1}{\sqrt{2}}\left[\left(|2\mathrm{p}_x^2\rangle - |2\mathrm{p}_y^2\rangle\right) - i\left(|2\mathrm{p}_x 2\bar{\mathrm{p}}_y\rangle - |2\bar{\mathrm{p}}_x 2\mathrm{p}_y\rangle\right)\right] \end{cases}$$

are suitable for chemical binding.

We consider next the Sc(^{4}F) interacting with the ground C ^{3}P state, the former being 1.43 eV[28] above the ground ^{2}D state. The most promising binding schemes are



Sc(~^{4}F; M= 0) C(^{3}P; M=0)



Sc(~^{4}F; M= 0) C(^{3}P; M=±1)

Note the similarity between bonding schemes (II) and (V) and

TABLE 4: Absolute Energies E(hartree), Dissociation Energies D_e(kcal/mol), Bond Lengths R_e(Å), Dipole Moments μ(D), Harmonic Frequencies and Anharmonic Corrections ω_e, $\omega_e\chi_e$ (cm^{-1}), Energy Separations T_e(kcal/mol) and Adiabatic Fragments of the Nine States Examined of the ScC Molecule

method[a]	$-E$[b]	D_e[c]	R_e	μ	ω_e, $\omega_e\chi_e$	T_e
Sc(^{2}D; M = ±2) + C(^{3}P; M = ∓1) → ScC(X$^2\Pi$)						
CASSCF	.567 81	60.0	2.064			
MRCI	.665 28	65.5	1.988	3.267	607, 5.6	0.0
MRCI+Q	.671 9	67	1.973		690	
Sc(^{2}D; M = ±2) + C(^{3}P; M = ∓1) → ScC(1$^4\Pi$)						
CASSCF	.567 27	59.6	1.958		580	
MRCI	.663 39	64.3	1.931	3.281	708, 11.0	1.2
MRCI+Q	.668 9	65	1.937		694	
Sc(^{2}D; M = 0) + C(^{3}P; M = 0) → ScC(2$^2\Sigma^-$)						
CASSCF	.563 41	57.3	2.117			
MRCI	.654 87	59.0	2.051	3.492	563, 2.6	6.5
MRCI+Q	.661 4	60	2.050		593	
Sc(^{2}D; M = ±1) + C(^{3}P; M =∓1) → ScC(3$^2\Sigma^+$)						
CASSCF	.570 32	62.0	1.824		800	
MRCI	.653 75	58.2	1.823	5.936	759, 12.3	7.2
MRCI+Q	.658 2	58	1.827		744	
Sc(^{2}D; M = ±2) + C(^{3}P; M = 0) → ScC(4$^4\Delta$)						
CASSCF	.562 66	58.4	2.273		515	
MRCI	.647 59	54.8	2.218	2.880	511, 11.5	11.1
MRCI+Q	.651 6	54	2.207		524	
Sc(^{2}D; M = ±2) + C(^{3}P; M = 0) → ScC(5$^2\Delta$)						
CASSCF	.577 08	66.3	2.276		448	
MRCI	.646 26	53.5	2.243	3.084	532, 3.2	11.9
MRCI+Q	.649 4	53	2.250		505	
Sc(^{2}D; M = ±1) + C(^{3}P; M = ±1) → ScC(6$^4\Delta$)						
CASSCF	.545 89	47.9	2.264		504	
MRCI	.633 54	45.8	2.208	2.314	516, 7.9	19.9
MRCI+Q	.638 8	46	2.200		538	
Sc(^{2}D; M = 0) + C(^{1}D; M = 0) → ScC(7$^2\Sigma^+$)						
CASSCF	.547 47	83.8	1.772		854	
MRCI	.629 54	71.2	1.822	6.183	731, 18.2	22.4
MRCI+Q	.634 0	71	1.834		695	
Sc(^{2}D; M = 0) + C(^{3}P; M = ±1) → ScC(8$^4\Pi$)						
CASSCF	.532 11	37.7	2.328		544	
MRCI	.623 97	39.9	2.282	3.532		25.9
MRCI+Q	.630 5	41	2.268			

[a] The state average technique has been used for the MCSCF optimization, ref 29; +Q refers to the multireference analogue of the Davidson correction, ref 30. [b] Energy values shifted by 797 hartree. [c] D_e with respect to the adiabatic products.

the expected interaction between these two states. Assuming that electron transfer from C to Sc is chemically counterintuitive, we conclude that the best candidate for the ground ScC state is described by scheme (II), $^2\Pi$. We also anticipate that the $^2\Sigma^+$ state with two π bonds and one-half σ bond, should be very close to the ground state.

Numerical Findings and Discussion

Table 4 lists total energies (E), binding energies (D_e), bond lengths (R_e), dipole moments (μ), harmonic frequencies (ω_e), and anharmonic corrections ($\omega_e x_e$), energy separations (T_e), and adiabatic reaction products of all nine states considered at the CASSCF, MRCI, and +Q (multireference Davidson correction)[30] levels of theory. Figure 1 shows potential energy curves (PEC); numbers in front of the term symbol refer to the absolute energy ordering with respect to the ground (X) state.

X$^2\Pi$. In accord with our previous discussion, the ground state is indeed of $^2\Pi$ symmetry with the following leading CASSCF configurations (CF):

$$|X^2\Pi\rangle \sim -0.72|1\sigma^2 2\sigma^2 1\pi_x^1 1\pi_y^2\rangle + 0.42|1\sigma^2 3\sigma^2 1\pi_x^1 1\pi_y^2\rangle - 0.28|1\sigma^2 2\sigma^1 3\sigma^1 1\bar{\pi}_x^1 1\pi_y^2\rangle$$

and Mulliken atomic distributions (Sc/C)

$$4s^{1.02}4p_x^{0.03}4p_y^{0.07}4p_z^{0.24}3d_{z^2}^{0.23}3d_{xz}^{0.22}3d_{yz}^{0.83}/2s^{1.66}2p_x^{0.75}2p_y^{1.08}2p_z^{0.82}$$

Taking into account the populations at infinity,

$$4s^{1.83}4p_x^{0.06}4p_y^{0.06}4p_z^{0.06}3d_{x^2-y^2}^{0.50}3d_{xy}^{0.50}/2s^{1.96}2p_x^{0.52}2p_y^{0.52}2p_z^{1.0}$$

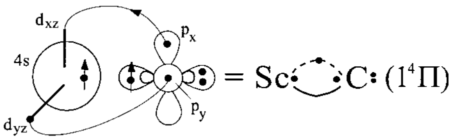
we observe the formation of a π_y bond (0.83 + 1.08 = 1.91 e$^-$), of a half π_x bond (0.22 + 0.75 = 0.97 e$^-$), and of a σ dative bond originating from the 4s^2 metal pair, in complete agreement with the bonding scheme (II). However, note the character change from Sc(^{2}D; M = ±2) + C(^{3}P; M = ∓1) at infinity (Table 4) to Sc(^{2}D; M = ±1) + C(^{3}P; M = 0) at equilibrium due to an avoided crossing, permitting the dative σ bond from Sc to the empty carbon 2p$_z$ (M = 0) orbital. In total, 0.35 (0.41) e$^-$ are transferred from Sc to C at the CASSCF (MRCI) level. On the basis of the MRCI Mulliken charges and bond length, we calculate a dipole moment of μ = 0.41 e$^-$ × 3.7284 bohr × 2.54177 D/a.u. = 3.89 D in reasonable agreement with the calculated value of 3.267 D. At R_e = 1.988 Å we obtain a D_e = 65.5(67) kcal/mol at the MRCI(+Q) level, as compared to an experimental (upper limit) value of 105 ± 5 kcal/mol (Table 1), certainly in error if it is given with respect to the ground-state atoms.

1$^4\Pi$. A spin flip in the σ frame of the X$^2\Pi$ state leads to the 1$^4\Pi$ state just 1.2 kcal/mol above the X-state, Table 4. The leading CASSCF equilibrium CFs and Mulliken populations reflect a character change from M = (±2, ∓1) → (±1, 0),

$$|1^4\Pi\rangle \sim 0.92|1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 1\pi_y^2\rangle - 0.21|1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 2\pi_y^2\rangle$$

$$4s^{1.03}4p_x^{0.03}4p_y^{0.04}4p_z^{0.24}3d_{z^2}^{0.30}3d_{xz}^{0.23}3d_{yz}^{0.81}/2s^{1.61}2p_x^{0.74}2p_y^{1.12}2p_z^{0.79}$$

in striking similarity with those of the X$^2\Pi$ state. The bonding can be exemplified by the following vbL diagram, suggesting 3/2 π bonds:



Along the σ and π_y frames 0.36 and 0.2 e$^-$ are transferred from Sc to C, respectively, while via the π_x frame 0.23 e$^-$ are moving from C to Sc. It should be mentioned at this point that the only previous theoretical investigation of ScC by Jeung and Koutecký,[2] predicts the 1$^4\Pi$ to be the ground state (D_e = 37.6 kcal/mol), while our X$^2\Pi$ state is their second excited state with an energy gap of 2000 cm^{-1} = 5.7 kcal/mol. The small 1$^4\Pi$ ← X$^2\Pi$ energy splitting and their computational approach justify the above discrepancies. It is fair to report however that, as they say, it is difficult to identify the ground state due to the complexity, and the near degeneracy of (their) first four states.

2$^2\Sigma^-$. As is evidenced from the CASSCF equilibrium CFs

$$|2^2\Sigma^-\rangle \sim 0.74|1\sigma^2 2\sigma^2 3\sigma^1 1\bar{\pi}_x^1 1\pi_y^1\rangle + 0.43|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1 1\bar{\pi}_y^1\rangle$$

and the Mulliken distributions

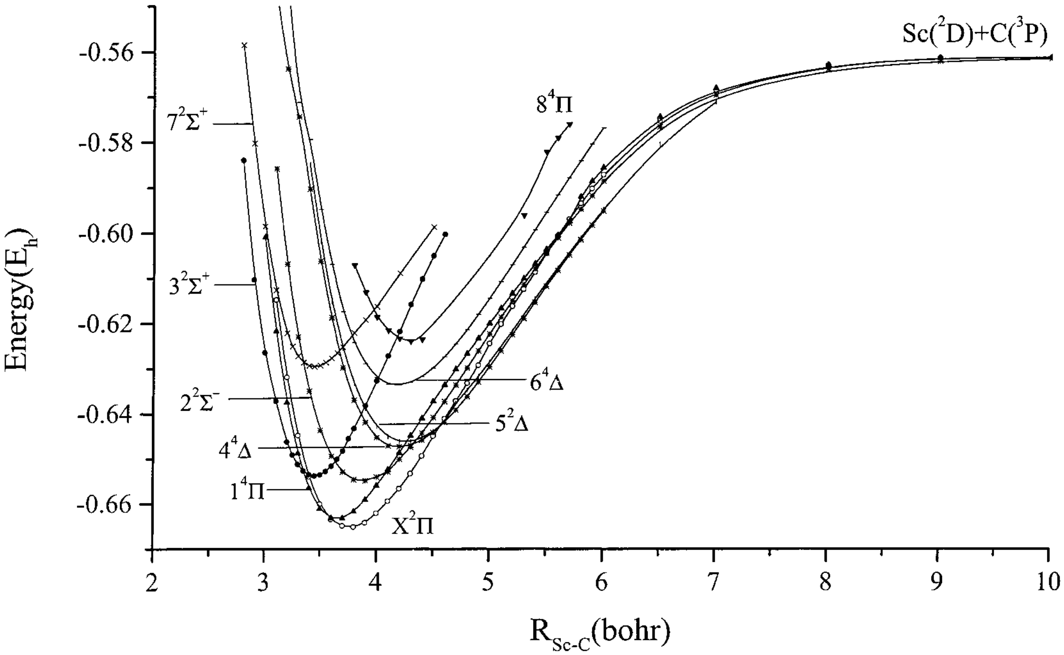


Figure 1. Potential energy curves of ScC at the MRCI level of theory.

$$4s^{1.02}4p_x^{0.03}4p_y^{0.03}4p_z^{0.26}3d_{z^2}^{0.96}3d_{xz}^{0.10}3d_{yz}^{0.10}/2s^{1.77}2p_x^{0.86}2p_y^{0.86}2p_z^{0.95}$$

the $|^2\text{D}; \text{M} = 0\rangle \otimes |^3\text{P}; \text{M} = 0\rangle$ asymptotic character is maintained along the reaction channel. This means that the empty $2p_z$ of C at infinity, is filled with ~1 e^-, 0.7 of which originating from the $4s^2$ Sc distribution. The bonding is described clearly by scheme (I) of the previous section, with a σ bond worth 59 kcal/mol at $R_e = 2.051$ Å. A net charge of 0.5 e^- is transferred from the metal to the carbon atom, resulting in a dipole moment of 3.49 D.

$3^2\Sigma^+$, $7^2\Sigma^+$. As it is seen from Table 4 the $3^2\Sigma^+$ state correlates to Sc(^{2}D; M = ±1) + C(^{3}P; M = ∓1), but at equilibrium the in situ metal finds itself in the $4s^1 3d_\pi^2$ (~$|^4\text{F}$; M = 0⟩) distribution, with a corresponding $\text{M} = \mp 1 \rightarrow 0$ change of the C atom, so that the Σ character is maintained. The dominant CASSCF equilibrium CFs and Mulliken distributions

$$|3^2\Sigma^+\rangle \sim 0.65|1\sigma^2 2\sigma^1 1\pi_x^2 1\pi_y^2\rangle - 0.64|1\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2\rangle$$

$$4s^{0.76}4p_x^{0.07}4p_y^{0.07}4p_z^{0.22}3d_{z^2}^{0.20}3d_{xz}^{0.69}3d_{yz}^{0.69}/2s^{1.55}2p_x^{1.20}2p_y^{1.20}2p_z^{0.31}$$

suggest that the two atoms are held together by two π bonds, with a σ density of 1.18 e^- localized on the metal hybrid $4s4p_z$-$3d_{z^2}$, implying a small electron transfer along the σ skeleton from C to Sc. Scheme (IV) describes the interaction pictorially, but admittedly the situation along the σ frame is rather vague. At $R_e = 1.823$ Å we predict $D_e = 58.2$ kcal/mol at the MRCI level, but the intrinsic bond strength, i.e., with respect to the *diabatic* fragments Sc(^{4}F; M = 0) + C(^{3}P; M = 0) is 58.2 + $\Delta E(^4\text{F} \leftarrow {}^2\text{D})$ = 95.8 kcal/mol.

The $7^2\Sigma^+$ is the only state which correlates to the first excited state of the C atom, namely $|^1\text{D}(2s^2 2p^2); \text{M} = 0\rangle$, 1.26 eV above the ground ^{3}P state (Table 3). Moving from infinity to equilibrium, a character change occurs, the in situ atoms being in the "states" Sc(^{4}F; M = 0) + C(^{3}P; M = 0) as in the previously described $3^2\Sigma^+$ state. The examination of the leading configurations and corresponding populations of the $7^2\Sigma^+$ state reveals its similarity to the $3^2\Sigma^+$ state, and, of course, the same bonding mechanism. Owing to severe technical problems, we were unable to extend the PECs of the $3^2\Sigma^+$, $7^2\Sigma^+$ and $4^4\Delta$, $5^2\Delta$, $6^4\Delta$, and $8^4\Pi$ states beyond 5 or 6 bohr, as shown in Figure 1. From Table 4 we read that $D_e = 71.2$ kcal/mol with respect to the adiabatic fragments, but the intrinsic bond strength, i.e., with respect to Sc(^{4}F)+C(^{3}P) is $71.2 + \Delta E(^4\text{F} \leftarrow {}^2\text{D})_{\text{Sc}} - \Delta E(^1\text{D} \leftarrow {}^3\text{P})_{\text{C}}$ = 79.7 kcal/mol. Note that both $^2\Sigma^+$ states have the smallest bond lengths ($R_e = 1.822$ Å), and the largest dipole moments, $\mu = 5.94(3^2\Sigma^+)$, $6.18(7^2\Sigma^+)$ D of all states studied.

$4^4\Delta$, $6^4\Delta$. Both states at equilibrium have the same character Sc(^{2}D; M= ± 2)+C(^{3}P; M = 0), as revealed from the dominant CFs and corresponding Mulliken densities,

$$|4^4\Delta\rangle \sim 0.65|1\sigma^2 2\sigma^2 1\pi_x^1 1\pi_y^1 1\delta_-^1\rangle - 0.39|1\sigma^2 3\sigma^2 1\pi_x^1 1\pi_y^1 1\delta_-^1\rangle + 0.34|1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 1\pi_y^1 1\bar{\delta}_-^1\rangle + 0.28|1\sigma^2 2\sigma^1 3\bar{\sigma}^1 1\pi_x^1 1\pi_y^1 1\delta_-^1\rangle + 0.31|1\sigma^2 2\sigma^1 3\sigma^1 (1\pi_x^1 1\bar{\pi}_y^1 + 1\bar{\pi}_x^1 1\pi_y^1) 1\delta_-^1\rangle$$

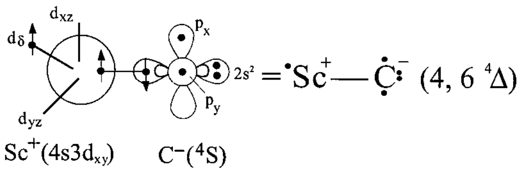
$$4s^{1.04}4p_x^{0.03}4p_y^{0.03}4p_z^{0.22}3d_{z^2}^{0.11}3d_{xz}^{0.06}3d_{yz}^{0.06}3d_{xy}^{1.0}/2s^{1.76}2p_x^{0.91}2p_y^{0.91}2p_z^{0.84}$$

and

$$|6^4\Delta\rangle \sim 0.80|1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 1\pi_y^1 1\bar{\delta}_-^1\rangle - 0.35|1\sigma^2 2\sigma^1 3\bar{\sigma}^1 1\pi_x^1 1\pi_y^1 1\delta_-^1\rangle$$

$$4s^{1.0}4p_x^{0.03}4p_y^{0.03}4p_z^{0.25}3d_{z^2}^{0.12}3d_{xz}^{0.06}3d_{yz}^{0.06}3d_{xy}^{1.0}/2s^{1.75}2p_x^{0.91}2p_y^{0.91}2p_z^{0.85}$$

Observe the, practically, identical Mulliken densities between the two states. For both states about 0.6 e^- are transferred from Sc to C via the σ frame with the synchronous formation of two hybrids: a $(4s4p_z3d_{z^2})^{1.4}$ on the metal, and a $(2s2p_z)^{2.7}$ on the C atom; 0.1 e^- return to the metal via the π route. The bonding picture is given in scheme (III) of the Insights section. The single σ bond that keeps the two atoms together has a strength of 54.8 and 45.8 kcal/mol for the $4^4\Delta$ and $6^4\Delta$ states, respectively with similar bond lengths, Table 4. Based on the large charge transfer from Sc to C, ~0.5 e^-, an alternative bonding picture can be envisaged, namely



We believe that both pictures are needed (in "resonance") for a better description and/or understanding of the bonding in the $^4\Delta$ states.

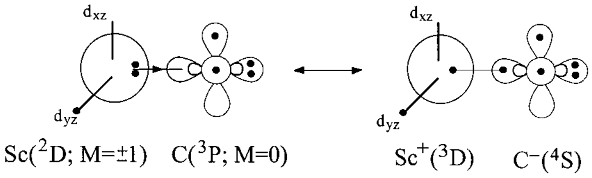
$5^2\Delta$. A spin flip along the π frame of the $4^4\Delta$ state leads to the $5^2\Delta$ state, accompanied by an energy loss of about 1 kcal/mol and a bond length increase of 0.025 Å, Table 4. The bonding character remains the same represented fairly well by scheme (III); about 0.5 e^- are transferred from Sc to the C atom.

$8^4\Pi$. At the CASSCF level the $8^4\Pi$ state is described by the following CFs and populations:

$$|8^4\Pi\rangle \sim -0.64|1\sigma^2 2\sigma^2 1\pi_x^1 1\pi_y^1 2\pi_y^1\rangle + 0.36|1\sigma^2 3\sigma^2 1\pi_x^1 1\pi_y^1 2\pi_y^1\rangle + 0.31|1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 1\pi_y^2\rangle - 0.28|1\sigma^2(2\sigma^1 3\bar{\sigma}^1 + 2\bar{\sigma}^1 3\sigma^1)1\pi_x^1 1\pi_y^1 2\pi_y^1\rangle$$

$$4s^{1.06}4p_x^{0.02}4p_y^{0.02}4p_z^{0.22}3d_{z^2}^{0.11}3d_{xz}^{0.08}3d_{yz}^{1.0}/2s^{1.77}2p_x^{0.89}2p_y^{0.97}2p_z^{0.82}$$

Note the character change from M = (0, ±1) at infinity (Table 4) to M = (±1, 0) at equilibrium. The above data coupled with the large charge transfer from Sc to C, ~0.5 e^-, converge to the following "resonant" bonding icon with a single σ bond of



an energy content of 40 kcal/mol at $R_e = 2.282$ Å.

Summary and Remarks

The salient findings of the present report on ScC can be synopsized as follows. We feel confident that the ground state of ScC is a $^2\Pi$ state with the first excited state of $^4\Pi$ symmetry 1.2 kcal/mol higher. On the basis of our experience on similar systems, we anticipate that our binding energy is underestimated by no more than 7%, leading to an estimated "true" D_e of 70 kcal/mol, in disagreement with the experimental (but upper limit) value of 105 ± 5 kcal/mol.[1] In all states studied a charge transfer of 0.4−0.5 e^- is observed from the metal center to the carbon atom. Finally, we understand that for states correlating adiabatically to Sc(^{2}D) + C(^{3}P; M = ±1), a character change to C(^{3}P; M = 0) is induced, thus avoiding the repulsive Sc $4s^2$ confrontation.

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