ELECTRONIC STRUCTURE AND BONDING NATURE OF THE GROUND STATE MONOCARBIDE CATIONS, ScC⁺, TiC⁺, VC⁺, AND CrC⁺

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This work is dedicated to Professors Ivan Hubač, Petr Čársky and Miroslav Urban on the occasion of their 180th = 3 × 60 birthday.

The ground states of the transition-metal diatomic carbide cations, MC⁺ (M = Sc, Ti, V, and Cr), are studied using multireference configuration interaction (MRCI) methods in conjunction with quantitative basis sets. Full potential energy curves are calculated for all four systems. When $3s^2 3p^6$ core/valence correlation contributions and scalar relativistic effects are taken into account, our best estimates for the zero-point-corrected dissociation energies of the MC⁺ series are in good agreement with relevant experimental results. For TiC⁺, the recent correlation-consistent-type basis sets for Ti of Bauschlicher are also exploited to extract complete basis set limits of selected properties. The ground states of VC⁺(X $^3\Delta$) and CrC⁺(X $^2\Delta$) are reported for the first time in the literature. For CrC⁺ an interesting competition is revealed between the $^2\Delta$ and $^4\Sigma^-$ states; although $^4\Sigma^-$ is formally the ground state at the MRCI level of theory, when core/valence and/or relativistic effects are included, the ground state of CrC⁺ becomes of $^2\Delta$ symmetry, with a calculated energy separation (a $^4\Sigma^- \leftarrow X\,^2\Delta$) of 2.3 kcal/mol.

Keywords: Ab initio calculations; Multireference configuration interaction; Transition metals; Carbides; Scandium; Titanium; Vanadium; Chromium.

Continuing our work on the elucidation of the electronic structure of diatomic metal carbides, neutral or otherwise[1], we present high level *ab initio* calculations of the series MC⁺, M = Sc, Ti, V, and Cr. In particular, we focus on the ground states of the MC⁺ species, with the purpose of obtaining accurate dissociation energies and certain spectroscopic constants, as well as to get some insight on their bonding character and trends.

Recently, we have examined by multireference variational methods, the ground and 12 excited states of ScC⁺ and TiC⁺ molecules[1a]; their ground states were found to be of $^3\Pi$(ScC⁺) and $^2\Sigma^+$(TiC⁺) symmetries. Table I col-

lects all experimental data available for the MC$^+$ series and some pertinent theoretical values.

Using extensive basis sets, variational multireference and coupled-cluster techniques, we construct potential energy curves (PEC) and we report binding energies (D_e), bond distances (r_e), harmonic frequencies (ω_e), and Mulliken charges for both VC$^+$ and CrC$^+$ species. Using the same basis sets and methods, the ScC$^+$ and TiC$^+$ cations are re-examined for reasons of comparison and uniformity.

BASIS SETS AND METHODS

For the carbon atom, the correlation-consistent basis set of quadruple-ζ quality (cc-pVQZ) 12s6p3d2f1g was used, generally contracted to [5s4p3d2f1g] [6a]. For the Sc, Ti and V, Cr metal atoms, the atomic natural-orbital (ANO) Gaussian basis sets 21s16p9d6f4g and 20s15p10d6f4g, respectively, were employed and similarly contracted to [7s6p4d3f2g] [7]. The one-electron basis set space is composed of 139 spherical Gaussian functions. In addition, the effect of one h ($l = 5$) function to the D_e and r_e values was also examined for the CrC$^+$ species. For the TiC$^+$ system only, the newly developed Ti correlation-consistent-type basis set(s) of Bauschlicher[8], 21s16p9d contracted to [7s8p6d] and augmented by a series of "polarization" sets 2f1g, 3f2g1h, and 4f3g2h1i named TZ, QZ, and 5Z, respectively, were also

TABLE I
Existing data on the ground states of the MC$^+$ systems, M = Sc, Ti, V, and Cr

Molecule	Method	D_0, kcal/mol	r_e, Å
ScC$^+$	experiment[a]	77.0 ± 1.4	
	MRCI(+Q)[b]	68.8 (71.5)/X $^3\Pi$	1.908 (1.92)
TiC$^+$	experiment[a]	93.4 ± 5.5	
	MRCI(+Q)[b]	85.2 (86.7)/X $^2\Sigma^+$	1.696 (1.70)
VC$^+$	experiment[c]	91.1 ± 0.9	
	experiment[a]	89.2 ± 3.2	
CrC$^+$	experiment[d]	66.2 ± 5.8	
	MRCI[e]	31.5/X $^4\Sigma^-$	1.735

[a] Guided-ion-beam tandem mass spectrometry, ref.[2] [b] Multireference configuration interaction (+ Davidson correction), ref.[1a] [c] Guided-ion-beam tandem mass spectrometry, ref.[3] [d] Photoionization/fragmentation by synchrotron radiation, ref.[4] [e] Ref.[5]. $D_0 = D_e - \omega_e/2$.

tested. The corresponding basis sets for C were Dunning's aug-cc-pVnZ, n = T, Q, and 5, respectively[6]. For correlated calculations including the $3s^2 3p^6$ (core) electrons of the metal atom(s), the same ANO basis sets were used throughout the Sc–Cr series. However, in the core-correlated calculations of the TiC$^+$ molecule, in conjuction with the correlation-consistent-type TZ, QZ, and 5Z bases, the latter were augmented by 1f (CTZ), 1f1g (CQZ), and 1f1g1h (C5Z) Gaussians, respectively[8]. Thus, the largest contracted basis set used in the TiC$^+$ molecule, [$7s8p6d5f4g3h1i/_{Ti}$ $7s6p5d4f3g2h/_C$] numbers 305 spherical Gaussians.

To construct potential energy curves (PEC) for all four molecules, the complete active space self-consistent field + single + double replacements (CASSCF + 1 + 2 = MRCI) method was used, in conjunction with the ANO/cc-pVQZ basis sets. The functional valence space chosen for all systems studied, ScC$^+$ to CrC$^+$, is composed of 10 orbital functions, correlating asymptotically to the valence-occupied spaces of M$^+$(4s + 3d) and C (2s + 2p) atoms. Considering the $1s^2 2s^2 2p^6 3s^2 3p^6$ and $1s^2$ electrons of M$^+$ and C as core (inactive), our zeroth-order spaces are formed by distributing 6, 7, 8, and 9 e$^-$ among 10 orbitals, giving rise to 1740, 3526, 5196, and 6996 configuration functions (CF) for the ScC$^+$(X $^3\Pi$), TiC$^+$(X $^2\Sigma^+$), VC$^+$(X $^3\Delta$), and CrC$^+$(X $^2\Delta$), respectively. It should be mentioned at this point that all our CASSCF wavefunctions obey symmetry and equivalence restrictions.

Dynamic valence correlation was obtained by single and double excitations out of the reference space(s) within the internally contracted philosophy[9] as implemented in the MOLPRO[10] suite of programs. Our largest uncontracted CI expansion (CrC$^+$) contains 66×10^6 CFs, reduced to about 1.2×10^6 internally contracted CFs.

To monitor the effect of the inner-shell of the metal, MRCI calculations including the $3s^2 3p^6$ electrons were also performed around the equilibrium distance. Our largest uncontracted CI expansion in the case of TiC$^+$/[C5Z/aug-cc-pV5Z] consists of about 3×10^9 CFs *vs* 58×10^6 of the internally contracted one. These calculations will be referred to as C-MRCI. For reasons of comparison, valence restricted coupled-cluster singles and doubles including non-iterative triples [RCCSD(T)] calculations were also done around equilibrium for the MC$^+$ series. Corresponding RCCSD(T) calculations taking into account the $3s^2 3p^6$ core electrons are referred to as C-RCCSD(T).

For TiC$^+$ only, we report complete basis set (CBS) limits of r_e and D_e values obtained by applying the mixed Gaussian/exponential formula

$$P_n = P_\infty + A e^{-(n-1)} + B e^{-(n-1)^2},$$

where P is a generic property, P_∞ its CBS limit, n the cardinal basis set number, and A, B freely adjustable parameters[11].

Relativistic effects for all four molecules are estimated at the (valence) MRCI level of theory *via* the one-electron Douglas–Kroll (DK) approximation[12] employing the DK-recontracted (aug-)cc-pVnZ basis set for C (ref.[13]) and keeping the respective ANO basis set for the M atom uncontracted. Finally, basis set superposition error (BSSE) corrections were obtained at the same level of theory by the usual counterpoise approach[14].

All our calculations were performed with the MOLPRO 2002.3 program[10].

RESULTS AND DISCUSSION

The Atoms

Table II lists total energies and first-excited state atomic energy separations (Sc^+ to Cr^+) in a series of methods and employing the ANO-[7s6p4d3f2g] basis set[7]. At the MRCI level, the absolute energy splittings are in fair agreement with the corresponding experimental values[15], the largest difference being 0.205 eV in the a ^{6}D ← a ^{6}S Cr^+ case, or 13.5%. To obtain very accurate energy separations in the transition metal atoms does not seem an easy task as the rest of Table II reveals, where core-correlation effects and relativistic effects (DK) have been included.

In Tables III and IV we report total energies, binding energies, and bond distances of the MC^+ (M = Sc, Ti, V, and Cr) ground states at different levels of theory. Table V lists similar properties of the TiC^+ molecule, but using the series of the correlation-consistent-type basis sets TZ, QZ, and 5Z of the Ti atom in conjunction with the corresponding basis sets of the C atom (*vide supra*). Potential energy curves of the four ground states are shown in Figs 1 and 2.

ScC^+. As it was found recently[1a] the ground state of ScC^+ is of $^3\Pi$ symmetry with D_e = 69.8 (D_0 = 68.8) kcal/mol and r_e = 1.908 Å. The leading CASSCF equilibrium configuration is

$$|X\,^3\Pi\rangle \approx 0.90|(\text{core})^{20}7\sigma^2\,8\sigma^1\,3\pi_x^1\,3\pi_y^2\rangle \qquad (\text{B}_1\text{ component})$$

with corresponding Mulliken populations (Sc/C)

$$4s^{0.10}\,4p_\sigma^{0.05}\,4p_\pi^{0.10}\,3d_{z^2}^{0.36}\,3d_{xz}^{0.31}\,3d_{yz}^{0.79}\,/\,2s^{1.73}\,2p_z^{0.76}\,2p_x^{0.66}\,2p_y^{1.10}\,.$$

TABLE II
Ground-state total energies E (hartree) and first-excited-state energy separations (eV) of Sc^+, Ti^+, V^+, and Cr^+ using a variety of methods and the ANO-[7s6p4d3f2g] basis set

Method	Sc^+		Ti^+		V^+		Cr^+	
	E (a^3D)	$a^1D(s^1d^1)\leftarrow$ $a^3D(s^1d^1)$	E (a^4F)	$b^4F(d^3)\leftarrow$ $a^4F(s^1d^2)$	E (a^5D)	$a^5F(s^1d^3)\leftarrow$ $a^5D(d^4)$	E (a^6S)	$a^6D(s^1d^4)\leftarrow$ $a^6S(d^5)$
NHF^a	-759.5391440	–	-848.2034008	–	-942.6707837	–	-1043.139393	–
$saSCF^b$	-759.538831	0.520	-848.202973	0.445	-942.670316	-0.151	-1043.13883	1.153
RCCSD(T)	-759.545328	–	-848.220679	0.193	-942.728225	0.394	-1043.22687	1.716
CASSCF	-759.538831	0.490	-848.202973	0.445	-942.670316	0.445	-1043.13883	1.153
MRCI	-759.543801	0.255	-848.218579	0.127	-942.725278	0.381	-1043.22423	1.727
MRCI+Q	–	–	-848.21870	0.120	-942.72636	0.398	-1043.2261	1.748
C-RCCSD(T)^c	-759.829572	–	-848.532084	0.169	-943.064637	0.470	-1043.57808	1.701
C-MRCI^c	-759.810762	0.380	-848.510815	0.065	-943.037593	0.383	-1043.54797	1.622
C-MRCI+Q^c	-759.82756	0.328	-848.52914	0.036	-943.05940	0.432	-1043.5711	1.655
C-RCCSD(T)(DK)^{c,d}	-763.424781	–	-852.919983	0.375	-948.358913	0.224	-1049.92442	1.405
C-MRCI(DK)^{c,d}	-763.401863	0.393	-852.894627	0.275	-948.327371	0.129	-1049.88976	1.321
C-MRCI+Q(DK)^{c,d}	-763.42152	0.343	-852.91580	0.250	-948.35195	0.176	-1049.9156	1.352
Experiment^e	–	0.302	–	0.107	–	0.337	–	1.522

[a] Numerical Hartree–Fock, ref.[16]; [b] Spherically averaged SCF; [c] The "core" $3s^23p^6$ electrons of the metal atom are also correlated; [d] Relativistic effects included via the Douglas–Kroll approximation; [e] Ref.[15]; +Q = the Davidson correction.

TABLE III

Total energies E (hartree), dissociation energies D_e (kcal/mol), and bond lengths r_e (Å) of the ground states of the MC^+ species (M = Sc, Ti, V, and Cr) at different levels of theory using the ANO-$[7s6p4d3f2g]_M$/cc-pVQZ$_C$ basis sets

Method	ScC$^+$ (X $^3\Pi$)			TiC$^+$ (X $^2\Sigma^+$)			VC$^+$ (X $^3\Delta$)			CrC$^+$ (X $^2\Delta$)		
	E	D_e	r_e	E	D_e	r_e	E	D_e	r_e	E	D_e	r_e
RCCSD(T)	−797.442121	69.33	1.897	−886.143235	85.50	1.679	−980.634677	75.39	1.646	−1081.07924	–	1.564
MRCI	−797.444408	71.76	1.908	−886.144803	89.31	1.695	−980.633396	79.02	1.667	−1081.07817	106.0	1.582
MRCI+Q	−797.44753	71.58	1.913	−886.14928	89.51	1.700	−980.64080	79.38	1.670	−1081.0881	106.9	1.587
MRCI(DK)^a	−801.003182	71.80	1.906	−890.492200	88.71	1.693	−985.894152	82.83	1.664	−1087.39324	105.9	1.579
MRCI+Q(DK)^a	−801.00635	71.75	1.912	−890.49671	88.93	1.698	−985.90168	83.32	1.667	−1087.4034	106.8	1.583
C-RCCSD(T)^b	−797.733135	73.58	1.859	−886.464894	91.93	1.651	−980.977048	79.13	1.642	−1081.43985	–	1.549
C-MRCI^b	−797.706781	76.63	1.869	−886.434436	94.34	1.666	−980.941494	83.02	1.648	−1081.40054	112.2	1.569
C-MRCI+Q^b	−797.73527	75.76	1.874	−886.46659	94.21	1.670	−980.98069	84.84	1.651	−1081.4431	114.7	1.573
ZPE(C-MRCI)^c	–	−1.05	–	–	−1.29	–	–	−1.31	–	–	−1.40	–
BSSE(MRCI)^d	–	−0.18	–	–	−0.26	–	–	−0.16	–	–	−0.34	–
Best value	–	75.4^e	1.867	–	92.2^e	1.664	–	85.4^e	1.645	–	111.1^e	1.566
Experiment		77.0 ± 1.4^f			93.4 ± 5.5^f			89.2 ± 3.2^f 91.1 ± 0.9^g			122.9 ± 5.8^h	

^{a} Relativistic effects included via the Douglas–Kroll approximation. ^{b} The "core" $3s^23p^6$ electrons of the metal atom are also correlated. ^{c} Zero-point energy corrections defined as $\omega_e/2$. ^{d} Basis set superposition error estimate. ^{e} D_0 (= D_e – $\omega_e/2$) value with respect to asymptotic products; see the text for details. ^{f} Ref.2 ^{g} Ref.3 ^{h} Ref.4, corrected to asymptotic Cr$^+$(a ^{4}D) + C (^{3}P) products using the experimental a ^{4}D ← a ^{6}S Cr gap (ref.15). +Q = the Davidson correction.

TABLE IV
Total energies E (hartree), dissociation energies D_e (kcal/mol), and bond lengths r_e (Å) of $TiC^+(X\ ^2\Sigma^+)$ at different levels of theory, using the sequence of increasing-size correlation-consistent-type basis sets of Bauschlicher (C)nZ for Ti, and the aug-cc-pVnZ for C, n = 3, 4, and 5 (see Table III for explanation of the acronyms)

Method	Basis set										
	(C)TZ			(C)QZ			(C)5Z			CBS^a	
	E	D_e	r_e	E	D_e	r_e	E	D_e	r_e	D_e	r_e
RCCSD(T)	−886.134857	83.79	1.684	−886.145251	86.46	1.679	−886.148752	87.50	1.677	88.0	1.676
MRCI	−886.137044	87.70	1.699	−886.146713	90.21	1.694	−886.149878	91.13	1.693	91.7	1.691
MRCI+Q	−886.14127	87.84	1.704	−886.15123	90.43	1.699	−886.15448	91.39	1.698	91.9	1.696
MRCI(DK)	−890.481389	86.00	1.698	−890.491849	88.59	1.693	−890.495391	89.65	1.692	90.1	1.690
MRCI+Q(DK)	−890.48553	86.16	1.703	−890.49634	88.81	1.698	−890.50000	89.90	1.697	90.4	1.695
C-RCCSD(T)	−886.471938	88.99	1.659	−886.511669	92.40	1.644	−886.525676	93.48	1.649	94.4	–
C-MRCI	−886.440947	91.81	1.672	−886.476448	94.73	1.666	−886.489507	95.93	1.663	96.4	1.663
C-MRCI+Q	−886.47332	91.40	1.676	−886.51172	94.62	1.670	−886.525613	95.91	1.667	96.5	1.667
ZPE(C-MRCI)	–	−1.29	–	–	−1.29	–	–	−1.29	–	–	–
Best value	–	–	–	–	–	–	–	–	–	93.5^b	1.662
Experiment^c										93.4 ± 5.5	

^{a} Complete basis set limit; see the text for details. ^{b} D_0 (= D_e − ω_e/2) value with respect to asymptotic products; see the text for details. ^{c} Ref.[2]

TABLE V
Comparison of total energies E (hartree), dissociation energies D_e (kcal/mol), bond lengths r_e (Å), and a $^4\Sigma^-$ ← $X\,^2\Delta$ energy separation T_e (kcal/mol) of the competing $^2\Delta$ and $^4\Sigma^-$ states of CrC⁺ at increasing levels of theory (see Table III for explanation of the acronyms)

Method	CrC⁺($X\,^2\Delta$)			CrC⁺(a $^4\Sigma^-$)			
	E	$D_e^{\,a}$	r_e	E	$D_e^{\,b}$	r_e	T_e
RCCSD(T)	−1081.07924	–	1.564	−1081.07689	39.98	1.627	1.47
MRCI	−1081.07817	106.0	1.582	−1081.07852	46.22	1.660	−0.22
MRCI+Q	−1081.0881	106.9	1.587	−1081.0889	47.38	1.663	−0.53
MRCI (+1h)[c]	−1081.07973	106.7	1.582	−1081.07974	46.61	1.659	−0.01
MRCI+Q (+1h)[c]	−1081.0897	107.5	1.586	−1081.0902	47.80	1.662	−0.31
MRCI(DK)	−1087.39324	105.9	1.579	−1087.39159	50.42	1.654	1.04
MRCI+Q(DK)	−1087.4034	106.8	1.583	−1087.4021	51.63	1.657	0.82
C-RCCSD(T)	−1081.43985	–	1.548	−1081.43530	44.50	1.608	2.86
C-MRCI	−1081.40054	112.2	1.569	−1081.39884	50.39	1.643	1.07
C-MRCI+Q	−1081.4431	114.7	1.573	−1081.4415	53.55	1.647	1.00
ZPE(C-MRCI)	–	−1.40	–	–	−1.26	–	–
BSSE(MRCI)	–	−0.34	–	–	−0.23	–	–
Best value	–	111.1[d]	1.566	–	53.5[d]	1.636	2.3[e]

[a] Dissociation energy with respect to Cr⁺(a ^{4}D) + C (^{3}P). [b] Dissociation energy with respect to Cr⁺(a ^{6}S) + C (^{3}P). [c] Values obtained adding one h function (exponent = 1.0) to the Cr basis set. [d] D_0 (= D_e − ω_e/2) value; see the text for details. [e] Zero-point-corrected energy separation, $T_0 = T_e − \Delta\omega_e/2$.

In accord with the above description the following valence-bond-Lewis (vbL) icon captures the bond formation (Scheme 1; see ref.[1a] for details) suggesting the formation of 3/2 π and 1/2 σ bonds. A total of 0.20 e$^-$ are transferred from Sc$^+$ to the C atom.

$$Sc^+(^3D; M = \pm1) \qquad C (^3P; M = 0) \qquad X\ ^3\Pi$$
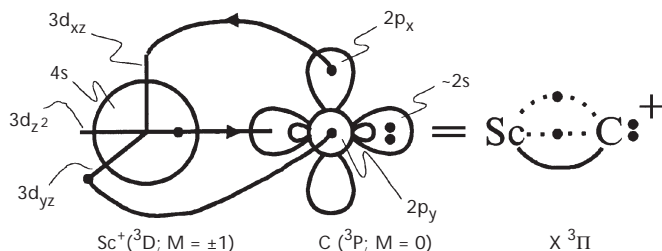
SCHEME 1

Now by increasing the Sc basis set in the present work by two g functions as compared to our previous work[1a], and performing state-specific calculations, we obtain D_e = 71.76 kcal/mol at the MRCI level. Including core-valence correlation effects, δD_e(core), due to the $3s^2 3p^6$ electrons of Sc, the MRCI D_e increases by 4.87 kcal/mol. In addition, scalar relativistic effects obtained through the DK method, δD_e(DK), and BSSE change the D_e value by +0.04 and –0.18 kcal/mol, respectively (Table III). The final MRCI bond
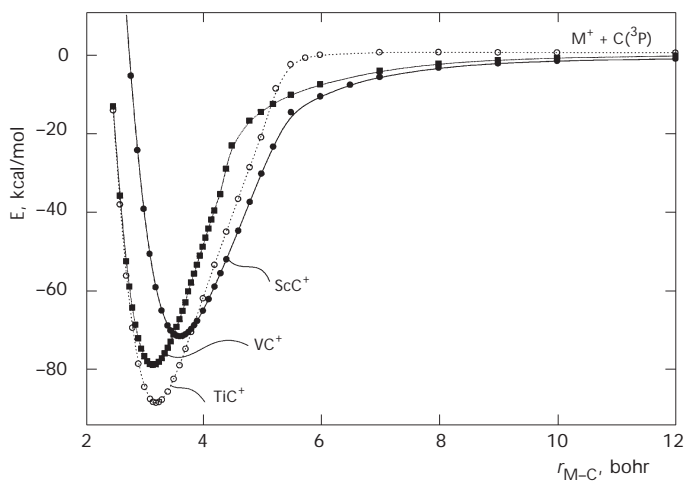
FIG. 1
Ground-state potential energy curves for ScC$^+$(X $^3\Pi$), TiC$^+$(X $^2\Sigma^+$), and VC$^+$(X $^3\Delta$) at the MRCI level of theory. Dissociation products for MC$^+$ (M = Sc, Ti, V) are: {Sc$^+$(a ^{3}D), Ti$^+$(a ^{4}F), V$^+$(a ^{5}D)} + C (^{3}P)

dissociation energy obtained is $D_e = D_e(\text{MRCI}) + \delta D_e(\text{core}) + \delta D_e(\text{DK}) + \delta D_e(\text{BSSE}) = 71.76 + 4.87 + 0.04 - 0.18 = 76.49$ kcal/mol, or $D_0 = D_e - \omega_e/2 = 75.4$ kcal/mol, as compared with the experimental value[2] of $D_0 = 77.0 \pm 1.4$ kcal/mol. The MRCI bond length (1.908 Å) is reduced by 0.002 Å when relativistic effects are included, and is reduced even further by 0.039 Å at the C-MRCI level of theory; thus, our best estimated r_e is 1.867 Å (Table III). Corresponding RCCSD(T) D_e and r_e values are smaller by 2.5–3 kcal/mol and 0.01 Å, respectively.

TiC⁺. It is known that the ground state of TiC⁺ is $^2\Sigma^+$ with $D_e = 86.4$ ($D_0 = 85.2$) kcal/mol at $r_e = 1.696$ Å [1a] (Table I). The dominant CASSCF equilibrium configuration and Mulliken distributions are

$$|\text{X}\,^2\Sigma^+\rangle \approx 0.87|(\text{core})^{20}\,7\sigma^2\,8\sigma^1\,3\pi_x^2\,3\pi_y^2\rangle$$

$$4s^{0.08}\,4p_\sigma^{0.06}\,4p_\pi^{0.06}\,3d_{z^2}^{0.61}\,3d_{xz}^{0.98}\,3d_{yz}^{0.98}\,3d_\delta^{0.04}\,/\,2s^{1.74}\,2p_z^{0.54}\,2p_x^{0.94}\,2p_y^{0.94}\,.$$

The bonding is succinctly demonstrated by the following vbL picture (Scheme 2; but for details, see ref.[1a]) suggesting that the two atoms are held together by two π and 1/2 σ bonds; overall 0.19 e⁻ are transferred from Ti⁺
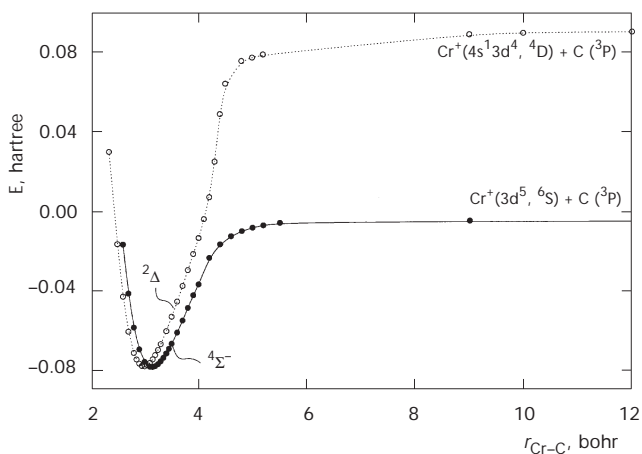

F<small>IG</small>. 2
Potential energy curves for the two competing states of CrC⁺ ($^2\Delta$, $^4\Sigma^-$) at the MRCI level of theory. Total energies have been shifted by +1081 hartree

to the C atom. From Table III we see that our final D_e value is, $D_e = D_e(\text{MRCI}) + \delta D_e(\text{core}) + \delta D_e(\text{DK}) + \delta D_e(\text{BSSE}) = 89.31 + 5.03 - 0.60 - 0.26 = 93.48$ kcal/mol, or $D_0 = D_e - \omega_e/2 = 92.2$ kcal/mol as compared with the experimental value of 93.4 ± 5.5 kcal/mol[2]. Notice that the difference of $89.31 - 86.4 = 2.9$ kcal/mol between our present and previous[1a] D_e values at the MRCI level, is due to the increase of the metal basis set by two g angular momentum functions and that the present calculations are state-specific rather than state-averaged. The corresponding bond length is $r_e = r_e(\text{MRCI}) + \delta r_e(\text{core}) + \delta r_e(\text{DK}) = 1.695 - 0.029 - 0.002 = 1.664$ Å.
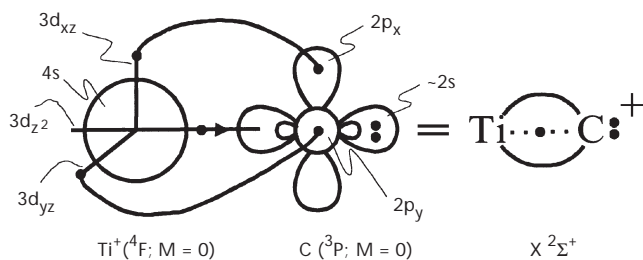
SCHEME 2

Table IV lists D_e and r_e values of the TiC$^+$ X $^2\Sigma^+$ state using the series of the Ti correlation-consistent-type basis sets of ref.[8] The CBS limits of D_e and r_e, assuming that the BSSE is practically zero, are as follows:

$D_e(\text{CBS}) = D_e(\text{MRCI/CBS}) + \delta D_e(\text{core/CBS}) + \delta D_e(\text{DK/CBS}) = 91.7 + 4.7 - 1.6 = 94.8$ kcal/mol, or $D_0(\text{CBS}) = D_e(\text{CBS}) - \omega_e/2 = 94.8 - 1.3 = 93.5$ kcal/mol;

$r_e(\text{CBS}) = r_e(\text{MRCI/CBS}) + \delta r_e(\text{core/CBS}) + \delta r_e(\text{DK/CBS}) = 1.691 - 0.028 - 0.001 = 1.662$ Å.

Notice that the extrapolation to the CBS limit alone increases the MRCI binding energy by about 2.5 kcal/mol.

VC$^+$. The ground state of VC$^+$ is "formally" of $^3\Delta$ symmetry with the first excited state ($^1\Sigma^+$) lying about 3 kcal/mol higher[17]. At infinity, the molecule is described by the product wavefunction $|^5D;M = \pm1\rangle_{V^+} \otimes |^3P;M = \pm1\rangle_C$. Moving towards the equilibrium and around 4.2 bohr, the X $^3\Delta$ state suffers an avoided crossing with a $^3\Delta$ state correlating to V$^+$(^{5}D; M = ±2) + C (^{3}P; M = 0), thus transferring its character to the X $^3\Delta$ state (Fig. 1).

The dominant equilibrium CASSCF configuration is

$$|X\,^3\Delta\rangle \approx 0.89|(\text{core})^{20}\,7\sigma^2\,8\sigma^1\,3\pi_x^2\,3\pi_y^2\,1\delta_+^1\rangle \qquad \text{(A}_1\text{ component)}$$

with the following Mulliken atomic distributions (V/C)

$$4s^{0.09} \, 4p_\sigma^{0.06} \, 4p_\pi^{0.04} \, 3d_{z^2}^{0.61} \, 3d_{xz}^{1.05} \, 3d_{yz}^{1.05} \, 3d_{x^2-y^2}^{1.0} \, / \, 2s^{1.73} \, 2p_z^{0.53} \, 2p_x^{0.90} \, 2p_y^{0.90} \; .$$

Notice that apart from the δ symmetry carrying electron of the VC^+ $X\,^3\Delta$ state, the above populations are practically identical to those of the TiC^+ $X\,^2\Sigma^+$ state (*vide supra*). Clearly the bonding comprises two π and $1/2$ σ bonds as exemplified by the vbL picture (Scheme 3).

$V^+(3d^4, \, ^5D; \, M = \pm2)$ $C\,(^3P; \, M = 0)$ $X\,^3\Delta$
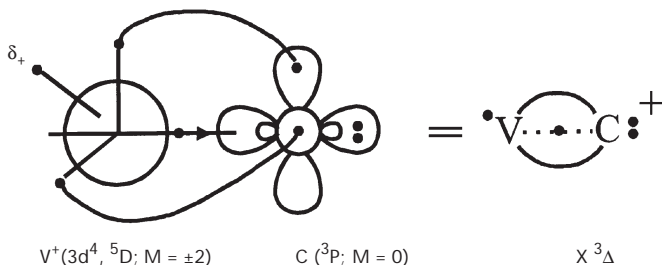
SCHEME 3

Overall, 0.1 e^- are transferred from V^+ to C. At the MRCI level of theory, D_e = 79.02 kcal/mol and r_e = 1.667 Å (Table III). Including core–valence correlation effects (*i.e.*, the V^+ $3s^2 3p^6$ e^-), Douglas–Kroll relativistic corrections, and BSSE estimates we obtain $D_e = D_e(MRCI) + \delta D_e(core) + \delta D_e(DK) + \delta D_e(BSSE)$ = 79.02 + 4.00 + 3.81 – 0.16 = 86.7 kcal/mol, or $D_0 = D_e - \omega_e/2$ = 85.4 kcal/mol, in acceptable agreement with the experimental value(s) 91.0 ± 0.9 [3] and 89.2 ± 3.2 [2] kcal/mol. Taking into account our experience with the systematic increase of the basis set in the $X\,^2\Sigma^+$ state of TiC^+, we can claim that it is reasonable to increase the D_e value of VC^+ by about 2–3 kcal/mol, *i.e.*, our estimated D_0 value becomes, D_0 = 88 kcal/mol, now in agreement with the experimental value(s).

The corresponding ground-state bond length after similar corrections is $r_e = r_e(MRCI) + \delta r_e(core) + \delta r_e(DK)$ = 1.667 – 0.019 – 0.003 = 1.645 Å.

CrC$^+$. It is natural to envisage the formation of the CrC^+ cation from the ground states of $Cr^+(a\,^6S)$ and C (^3P) according to the vbL diagram (Scheme 4) indicating two π and $1/2$ σ bonds, leading to a $^4\Sigma^-$ state. The above mechanism of bond formation is identical to the formation mechanisms of the $TiC^+(X\,^2\Sigma^+)$ and $VC^+(X\,^3\Delta)$. Indeed, the *ab initio* MCSCF + 1 + 2 calculations of Harrison[5] using a DZP basis set suggest a ground state of $^4\Sigma^-$ symmetry and a binding energy D_0 = 31.5 kcal/mol at r_e = 1.735 Å (Table I). However, although Scheme 4 captures correctly the physics of the bonding, the situation is more involved than it seems and our results indicate that the ground

state could be of $^2\Delta$ symmetry rather that $^4\Sigma^-$, albeit they are very close to each other (*vide infra*).

$$Cr^+(3d^5, \, ^6S) \qquad C \, (^3P; \, M = 0) \qquad\qquad\qquad ^4\Sigma^-$$
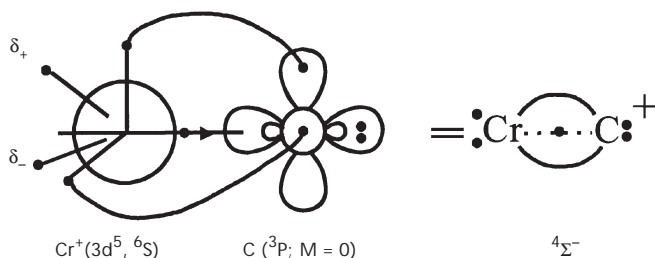
SCHEME 4

Table V lists our numerical findings and Fig. 2 presents the PECs of the $^4\Sigma^-$ and $^2\Delta$ states. The leading equilibrium CASSCF configurations of the $^4\Sigma^-$ and $^2\Delta$ states are

$$|^4\Sigma^-\rangle \approx 0.85|(core)^{20} \, 7\sigma^2 \, 8\sigma^1 \, 3\pi_x^2 \, 3\pi_y^2 \, 1\delta_+^1 \, 1\delta_-^1\rangle \, -$$
$$- \, 0.18|(core)^{20} \, 7\sigma^2 \, 8\sigma^2 \, (4\pi_x^2 \, 3\pi_y^2 + 3\pi_x^2 \, 4\pi_y^2)1\delta_+^1 \, 1\delta_-^1\rangle \, ,$$

$$|^2\Delta\rangle \approx 0.88|(core)^{20} \, 7\sigma^2 \, 8\sigma^2 \, 3\pi_x^2 \, 3\pi_y^2 \, 1\delta_+^1\rangle \, -$$
$$- \, 0.15|(core)^{20} \, 7\sigma^2 \, 8\sigma^2 \, (4\pi_x^2 \, 3\pi_y^2 + 3\pi_x^2 \, 4\pi_y^2)1\delta_+^1\rangle \qquad (A_1 \text{ component})$$

with corresponding atomic Mulliken distributions (Cr/C)

$$^4\Sigma^- : 4s^{0.09} \, 4p_\sigma^{0.07} \, 4p_\pi^{0.04} \, 3d_{z^2}^{0.68} \, 3d_{xz}^{1.05} \, 3d_{yz}^{1.05} \, 3d_{x^2-y^2}^{1.0} \, 3d_{xy}^{1.0} \, / \, 2s^{1.72} \, 2p_z^{0.45} \, 2p_x^{0.90} \, 2p_y^{0.90} \, ,$$

$$^2\Delta : 4s^{0.15} \, 4p_\sigma^{0.10} \, 4p_\pi^{0.06} \, 3d_{z^2}^{1.29} \, 3d_{xz}^{1.18} \, 3d_{yz}^{1.18} \, 3d_{x^2-y^2}^{0.5} \, 3d_{xy}^{0.5} \, / \, 2s^{1.76} \, 2p_z^{0.69} \, 2p_x^{0.77} \, 2p_y^{0.77} \, .$$

The populations of $^4\Sigma^-$ conform clearly to Scheme 4 with practically no charge transfer from the metal to the carbon atom. Now the vbL icon of the $^2\Delta$ state according to the leading CFs and the atomic populations is (Scheme 5)

$$Cr^+(3d^5, {}^4G; M = \pm 2) \quad\quad C\ ({}^3P; M = 0) \quad\quad\quad\quad {}^2\Delta$$
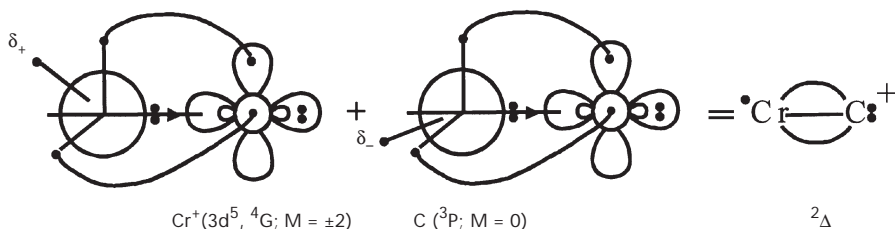
SCHEME 5

Therefore, we are dealing with a genuine triple bond with the *in situ* Cr^+ atom in the excited ^4G state, 2.544 eV above the ground ^6S state[15].

According to Fig. 2, the $^2\Delta$ state correlates to $Cr^+(4s^13d^4;\ a\ ^4D) + C\ (^3P)$. As we move towards equilibrium and at about 4.5 bohr, the $^2\Delta$ state suffers an avoided crossing with another state of the same symmetry which, we believe, correlates to $Cr^+(3d^5;\ a\ ^4G) + C\ (^3P)$, thus imparting its character to the first $^2\Delta$ state.

Now it is interesting and instructive to follow the numbers of Table V. At the MRCI level, the ground state appears to be the $^4\Sigma^-$ with the $^2\Delta$ just 0.22 kcal/mol higher, or 0.53 kcal/mol at the MRCI+Q level. Notice, however, that the RCCSD(T) method predicts the opposite, *i.e.*, the $^4\Sigma^-$ *higher* by 1.47 kcal/mol. We believe though that the RCCSD(T) results, at least at this level, are rather fortuitous because of the inability of the single-reference coupled-cluster method to describe correctly the spatial symmetry of the $^2\Delta$ state, thus lowering its energy in an artificial way. This symmetry problem does not intervene in the $^4\Sigma^-$ RCCSD(T) description. The addition of a single (11-component) h function (exponent = 1.0) in the basis set of Cr makes the two states practically degenerate, with the $^4\Sigma^-$ still being lower by a mere 0.01 (0.31) kcal/mol at the MRCI (MRCI+Q) level. Including relativistic effects through the DK method at the MRCI level, the $^2\Delta$ state is then predicted to be the lowest by 1.04 kcal/mol. At the C-MRCI level (including the $3s^23p^6$ core electrons of Cr^+), again the ground state is predicted to be of $^2\Delta$ symmetry by 1.07 kcal/mol with respect to the $^4\Sigma^-$ state. Assuming additivity of relativistic and core-correlation effects, including the zero-point energy correction ($\Delta\omega_e/2$), and BSSE corrections, our best energy separation (T_0) between the two states is 2.3 kcal/mol with the $^2\Delta$ being the ground state. Unfortunately, the whole situation is rather subtle: (i) *Adiabatically*, the $X\ ^2\Delta$ state correlates to $Cr^+(a\ ^4D) + C\ (^3P)$ with $\Delta E(a\ ^4D \leftarrow a\ ^6S) = 56.7$ kcal/mol experimentally[15], but theoretically we predict 54.9 kcal/mol at the C-MRCI(DK) level. (ii) *Diabatically*, the $X\ ^2\Delta$ state correlates to $Cr^+(a\ ^4G) + C\ (^3P)$ with $\Delta E(a\ ^4G \leftarrow a\ ^6S) = 58.7$ kcal/mol experimentally[15],

but 63.1 kcal/mol theoretically at the C-MRCI(DK) level of theory. Hypothesizing parallel shifting of the two PECs to match the experimental ΔE separations, we obtain $T_0 = 2.3 + (-1.8) = 0.5$ kcal/mol referring to adiabatic products, or $T_0 = 2.3 + 4.4 = 6.7$ kcal/mol referring to diabatic products, in either case maintaining the ordering of the two states, $X\,^2\Delta$ and a $^4\Sigma^-$.

Our best estimate for the D_0 and r_e values for the $X\,^2\Delta$ and a $^4\Sigma^-$ states are 111.1 and 53.5 kcal/mol, and 1.566 and 1.636 Å, respectively. It should be mentioned that the 111.1 kcal/mol D_0 value of the $X\,^2\Delta$ state is with respect to the adiabatic products $Cr^+(a\,^4D) + C\,(^3P)$; with respect to the ground state fragments $D_0\,(X\,^2\Delta) = 111.1 - \Delta E(^4D \leftarrow {}^6S) = 111.1 - 54.9 = 56.2$ kcal/mol employing the theoretical ΔE value. According to our previous D_0 values of the TiC^+ and VC^+ cations, it is reasonable to assume a 2 kcal/mol increase of the binding energy in the complete basis set (CBS) limit. Assuming also a parallel shifting, as before, with respect to the diabatic products $Cr^+(a\,^4G) + C\,(^3P)$, an estimated D_0 value of about 63 kcal/mol is obtained, in acceptable agreement with the recently proposed experimental value[4] $D_0 = 66.2 \pm 5.8$ kcal/mol (Table I). This agreement, perhaps, indicates the reliability of the experimental value and at the same time, the difficulty in obtaining accurate *ab initio* results even with diatomic molecules containing first-row transition metals.

SYNOPSIS AND REMARKS

In the present work, we have tried to obtain quantitative results, and to get some insight into the bonding mechanism of the ground-state metal monocarbide cations MC^+ (M = Sc, Ti, V, and Cr). To better understand the evolution of bonding, potential energy curves were constructed at the MRCI (CASSCF + 1 + 2) level of theory. Table VI condenses our best numerical values for the above MC^+ series.

In all four ground states, the C atom participates with the M = 0 component of its ^3P ground state, thus preferring the formation of two complete π bonds (with the exception of ScC^+ where it forms 3/2 π bonds) and 1/2 σ dative bond (with the exception of CrC^+ where it forms a single σ bond, but see below). In particular, the bonding in $ScC^+(X\,^3\Pi)$, $TiC^+(X\,^2\Sigma^+)$ and $VC^+(X\,^3\Delta)$ is of similar nature, maintaining 1/2 σ bond and forming 3/2 π, 2 π and 2 π bonds as we move from ScC^+ to TiC^+ to VC^+. In the case of CrC^+, although the similarly bonded $^4\Sigma^-$ state is found to be formally the ground state at the MRCI level of theory, upon allowing for core/valence correlation and/or scalar relativistic effects, the situation changes resulting in a $^2\Delta$ ground state with the $^4\Sigma^-$ just 2.3 kcal/mol higher. Contrary to the first

three cations, the X $^2\Delta$ state of CrC$^+$ correlates adiabatically to an excited state of the transition metal cation (a ^{4}D), while the *in situ* Cr$^+$ finds itself in the a ^{4}G state, thus forming a genuine triple bond with carbon. Parallel shifting with respect to the a ^{4}G state of Cr$^+$ to match the experimental energy separation gives an upper limit T_0(a $^4\Sigma^- \leftarrow$ X $^2\Delta$) = 6.7 kcal/mol.

The similarity of bonding (2 π, 1/2 σ) is reflected nicely in Table VI, where the states X $^2\Sigma^+$(TiC$^+$), X $^3\Delta$ (VC$^+$), and a $^4\Sigma^-$(CrC$^+$) have, practically, equal bond lengths; ScC$^+$, as was already mentioned, is "lacking" 1/2 π bond, resulting in a larger bond length. Notice the much shorter (by about 0.08 Å) bond length of the triply bonded CrC$^+$ X $^2\Delta$ state. The same trend is also followed in the D_0 values, the exception being the CrC$^+$ $^4\Sigma^-$ state. The latter value could be possibly rationalized considering the significantly larger ionization energy of Cr$^+$ (16.49 eV) as compared with the previous cations Sc$^+$ (12.89 eV), Ti$^+$ (13.43 eV), and V$^+$ (14.2 eV)[15].

In all four molecules, 3s^{2}3p^6 core/valence correlation effects of the M$^+$ cation were found to play a substantial role in obtaining accurate energetics and geometries. In particular, dissociation energies increase by 4–5 kcal/mol, while bond lengths shorten by 0.02–0.04 Å, although it should be stressed that the inclusion of the 3s^{2}3p^6 e$^-$ in the MRCI calculation increases significantly size-nonextensivity errors. In addition, relativistic effects estimated through the Douglas–Kroll approach were found to shorten bond lengths

TABLE VI
Summary of best calculated dissociation energies (D_0), bond distances (r_e) and harmonic frequencies (ω_e) from the present work. Experimental numbers in parenthesis

Species	Ground state and bonding	D_0, kcal/mol	r_e, Å	ω_e, cm^{-1}
ScC$^+$	X $^3\Pi$(1/2 σ, 3/2 π)	75.4 (77.0 ± 1.4)[a]	1.867	731.8
TiC$^+$	X $^2\Sigma^+$(1/2 σ, 2 π)	93.5 (93.4 ± 5.5)[a]	1.662	903.7
VC$^+$	X $^3\Delta$(1/2 σ, 2 π)	85.4[b](89.2 ± 3.2)[a]	1.645	917.2
		(91.1 ± 0.9)[c]		
CrC$^+$	X $^2\Delta$(1 σ, 2 π)	111.1[d]	1.566	976.3
		56.2[e] (66.2 ± 5.8)[f]		
	a $^4\Sigma^-$(1/2 σ, 2 π)	53.5	1.636	878.4

[a] Ref.[2] [b] "Approximate" CBS limit 88 kcal/mol; see the text. [c] Ref.[3] [d] With respect to adiabatic products. [e] With respect to ground state products; "approximate" CBS limit, including curve shifting, D_0 = 63 kcal/mol, see the text. [f] Ref.[4]

by less than 0.005 Å, while a more involved effect is observed on binding energies, 0.04, –0.60, 4.81, and –1.20 kcal/mol in $ScC^+(X\,^3\Pi)$, $TiC^+(X\,^2\Sigma^+)$, $VC^+(X\,^3\Delta)$, and $CrC^+(X\,^2\Delta)$, respectively; the corresponding effect in $CrC^+(a\,^4\Sigma^-)$ is 4.20 kcal/mol. In an effort to explain this "irregular" behavior of relativity on the dissociation energies, we note that in all MC^+ cases where the asymptote is of $4s^13d^n$ configuration (ScC^+, TiC^+, CrC^+ X-states), relativistic effects are rather small. On the other hand, for the $3d^n$ asymptotic configuration [$VC^+(X\,^3\Delta)$, $CrC^+(a\,^4\Sigma^-)$] relativistic effects are more important.

Finally, we tested the newly developed correlation-consistent-type basis sets of Bauschlicher for the Ti atom on the TiC^+ cation obtaining complete basis set values for the D_0 and r_e parameters. Upon extrapolation to the CBS limit, the D_0 value increases by about 2.5 kcal/mol with respect to the ANO-$[7s6p4d3f2g]_{Ti}$/cc-pVQZ$_C$ MRCI results, while the effect on r_e is negligible.

REFERENCES

1. a) Kerkines I. S. K., Mavridis A.: *J. Phys. Chem. A* **2000**, *104*, 11777; b) Kalemos A., Mavridis A., Harrison J. F.: *J. Phys. Chem. A* **2001**, *105*, 755; c) Kalemos A., Mavridis A.: *J. Phys. Chem. A* **2002**, *106*, 3905; d) Tzeli D., Mavridis A.: *J. Chem. Phys.* **2002**, *116*, 4901.
2. Clemmer D. E., Elkind J. L., Aristov N., Armentrout P. B.: *J. Chem. Phys.* **1991**, *95*, 3387.
3. Aristov N., Armentrout P. B.: *J. Am. Chem. Soc.* **1986**, *108*, 1806.
4. Qi F., Sheng L., Gao H., Zhang Y., Yang X., Yang S., Yu S.: *Chin. J. Chem. Phys.* **1999**, *12*, 525.
5. Harrison J. F.: *J. Phys. Chem.* **1986**, *90*, 3313.
6. a) Dunning T. H., Jr.: *J. Chem. Phys.* **1989**, *90*, 1007; b) Kendall R. A., Dunning T. H., Jr., Harrison R. J.: *J. Chem. Phys.* **1992**, *96*, 6796.
7. Bauschlicher C. W., Jr.: *Theor. Chim. Acta* **1995**, *92*, 183.
8. Bauschlicher C. W., Jr.: *Theor. Chem. Acc.* **1999**, *103*, 141.
9. a) Werner H.-J., Knowles P. J.: *J. Chem. Phys.* **1988**, *89*, 5803; b) Knowles P. J., Werner H.-J., Reinsch E. A.: *J. Chem. Phys.* **1982**, *76*, 3144; c) Werner H.-J.: *Adv. Chem. Phys.* **1987**, *LXIX*, 1.
10. *MOLPRO, A Package of ab initio Programs* designed by H.-J. Werner and P. J. Knowles; Version 2002.3, R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, P. J. Knowles, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson and H.-J. Werner.
11. Peterson K. A., Woon D. E., Dunning T. H., Jr.: *J. Chem. Phys.* **1994**, *100*, 7410.

12. a) Douglas M., Kroll N. M.: *Ann. Phys. (N. Y.)* **1974**, *82*, 89; b) Hess B. A.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1985**, *32*, 756; c) Hess B. A.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1986**, *33*, 3742.

13. de Jong W. A., Harrison R. J., Dixon D. A.: *J. Chem. Phys.* **2001**, *114*, 48.

14. a) Jansen H. B., Ros P.: *Chem. Phys. Lett.* **1969**, *3*, 140; b) Boys S. F., Bernardi F.: *Mol. Phys.* **1970**, *19*, 553.

15. Moore C. E.: *Atomic Energy Levels*, NRSDS-NBS Circular No. 35. U.S. GPO, Washington D. C. 1971.

16. Bunge C. F., Barrientos J. A., Bunge A. V., Cogordan J. A.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1992**, *46*, 3691.

17. Kerkines I. S. K., Mavridis A.: Unpublished results.