

First principles investigation of chromium carbide, CrC

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We have investigated the electronic structure of 14 states of the experimentally unknown diatomic molecule chromium carbide, CrC, using standard multireference configuration interaction methods and high quality basis sets. We report potential curves, binding energies, and a number of spectroscopic parameters. The ground state of CrC, $X^3\Sigma^-$, displays triple-bond character with a binding energy of $D_e=89$ kcal/mol and an internuclear separation of $r_e=1.63$ Å. The first excited state ($1^5\Sigma^-$) lies 9.2 kcal/mol higher. All the states studied are fairly ionic, featuring an electron transfer of 0.3–0.5 e^- from the metal atom to the carbon atom. © 2005 American Institute of Physics. [DOI: 10.1063/1.1926247]

I. INTRODUCTION

The neutral diatomic chromium carbide molecule, CrC, has not been identified experimentally so far, while theoretical work is very limited and rather conflicting.^{1–4} Table I presents a complete account of the existing theoretical literature. In 1989 Shim and Gingerich¹ reported preliminary results on the $^{3,5,7,9}\Sigma^-$ states of CrC based on a complete valence configuration interaction (CI) approach with a $\text{Cr}[10s6p1d]+\text{C}[4s3p1d]$ basis set, using the molecular orbitals of the $^9\Sigma^-$ state. The ground state was found to be of $^9\Sigma^-$ symmetry, with the excited states following the order $^7\Sigma^- < ^5\Sigma^- < ^3\Sigma^-$. Three years later the same authors² reported complete potential energy curves for the $^{1,3,5,7,9}\Sigma^-$ and $^{5,7}\Pi$ states of CrC, based on complete active space self-consistent field (CASSCF) calculations with a $\text{Cr}[8s7p3d]+\text{C}[4s3p1d]$ basis set; see Table I. The ordering of the states changed dramatically as compared to their previous work:¹ the X state became a $^3\Sigma^-$ state with the sequence of the excited states following the order $^5\Sigma^- < ^7\Sigma^- < ^9\Sigma^- < ^1\Sigma^- < ^5\Pi < ^7\Pi$.

Maclagan and Scuseria³ on the basis of multireference CI, coupled cluster, and density functional (DFT) calculations, confirmed that the $^3\Sigma^-$ is the ground state with the $^5\Sigma^-$ state being the first excited state. Their results though, show an aleatory behavior without converging to specific values (Table I). Finally, in a recent DFT study of the ground states of $MC^{\pm,0}$ and $MO^{\pm,0}$ species where $M=\text{Sc–Zn}$,⁴ the ground state of CrC was determined to be of $^3\Sigma^-$ symmetry. It is interesting, however, to contrast the DFT binding energies (D_e) reported in these two works^{3,4} as a function of the empirical functional used. These ranged from 59 (UB3LYP) to 135.7 (LSDA) kcal/mol; see Table I. Obviously, the DFT approach is not the method of choice for molecular systems of the complexity of CrC. Continuing our work of clarifying

the bonding behavior of the diatomic metal carbides (neutral and cations),⁵ as well as obtaining reliable properties and energetics, we herein report high level *ab initio* multiconfigurational CI results on 14 molecular states of CrC. We have constructed full potential energy curves (PEC) of all molecular spin-spatial symmetries resulting from the two lowest asymptotic channels, i.e., $\text{Cr}(4s^13d^5;^7S)+\text{C}(2s^22p^2;^3P)\rightarrow\text{CrC}[^{5,7,9}(\Sigma^-,\Pi)]$ and $\text{Cr}(4s^13d^5;^5S)+\text{C}(2s^22p^2;^3P)\rightarrow\text{CrC}[^{3,5,7}(\Sigma^-,\Pi)]$. Due to technical difficulties, only part of the PECs were calculated for the $^3\Delta$, $^1\Gamma$, and $^3\Pi$ states, the first two of which arising from $\text{Cr}(4s^23d^4;^5D)+\text{C}(2s^22p^2;^3P)$. We also report binding energies, energy separations, dipole moments, and standard spectroscopic parameters.

II. METHODS

For the Cr atom the $20s15p10d6f4g$ atomic natural orbital basis set of Bauschlicher⁶ and for the C atom the correlation consistent basis of quadruple cardinality $12s6p3d2f1g$ (cc-pVQZ) of Dunning⁷ were employed, generally contracted to $\text{Cr}[7s6p4d3f2g]$ and $\text{C}[5s4p3d2f1g]$. This resulted in 139 spherical Gaussian functions.

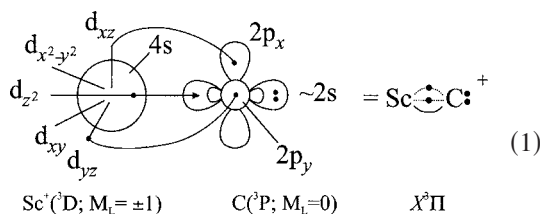
The active space of our reference wave functions consists of the valence orbitals of both atoms, i.e., $(4s+3d)_{\text{Cr}}+(2s+2p)_{\text{C}}$. The MOs used in the multireference configuration interaction method (MRCI=CASSCF+1+2) calculations were obtained from the CASSCF wave function of the $^9\Sigma^-$ state, because of severe convergence problems encountered in obtaining CASSCF functions for almost all the other states studied. The $^9\Sigma^-$ MOs were subsequently used in obtaining MRCI wave functions of the specific state; the engendering MRCI natural orbitals were then employed as the new one-electron basis for the final CI calculations. Thus, we were able to construct “smooth” PECs from infinity to equi-

librium suffering, in general, an energy loss of less than $4 mE_h$. All our MRCI calculations follow the internally contracted technique implemented in the MOLPRO package.⁸

In the present work, we have not taken into account core-valence correlation, relativistic effects, and basis set superposition errors (BSSE). From our recent study on the CrC^+ system using the same basis sets and methods,^{5(f),5(g)} it was found that the most important contribution is that of core-valence correlation. In the $X^2\Delta$ state of CrC^+ , these effects increase D_e by about 6 kcal/mol and decrease r_e by about 0.01 Å. Relativistic corrections obtained through the Douglas–Kroll approximation for the $X^2\Delta$ state of CrC^+ were not significant, while BSSE corrections reduced its D_e value by only 0.4 kcal/mol.

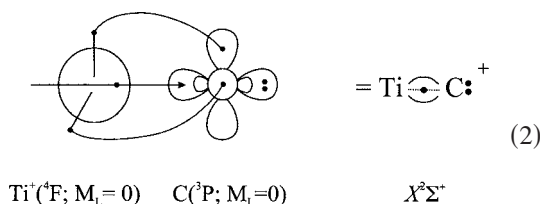
III. GENERAL MOLECULAR CONSIDERATIONS

To better understand the bonding in the neutral CrC , we begin by briefly discussing the ground electronic structures of MC and MC^+ starting from Sc^+ , whose ground state is of $^3\Pi$ symmetry.^{5(a)} Its valence-bond–Lewis (vbL) diagram



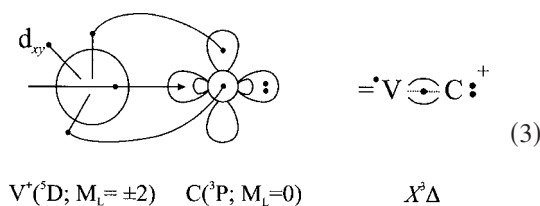
indicates a one-electron σ bond ($1/2 \sigma$), a one-electron π bond ($1/2 \pi$), and a regular π bond (π). The attachment of another electron to the σ frame results in a $(\sigma, 1/2 \pi, \pi)$ bonding configuration of $X^2\Pi$ symmetry for the neutral ScC .^{5(b)} The ScC molecule is bound by 65.5(67.0) kcal/mol at the MRCI(+ Q) level of theory.

The ground state of the next cation, TiC^+ , is of $^2\Sigma^+$ symmetry,^{5(a)} the two atoms interact attractively through a $1/2 \sigma$ bond, and two π bonds as is pictured below:



The ground state of the corresponding neutral molecule is realized by adding an electron to the σ frame and coupling the electron in that orbital into a triplet with the electron in the other σ orbital, thus generating the $X^3\Sigma^+$ of TiC .^{5(c)}

The $X^3\Delta$ state of VC^+ follows, succinctly represented by the vbL diagram^{5(g)} (3)



featuring two π bonds and a half σ bond. In line with the

ScC and TiC neutral carbides, VC has a $^2\Delta$ ground state,^{5(h)} the result of electron attachment to the σ frame of VC^+ and a corresponding $(\sigma, 2 \pi)$ bonding structure.

Now, in the CrC^+ species, the ground state is either of $^4\Sigma^-$ or $^2\Delta$ symmetry, represented graphically by Schemes (4) and (5):

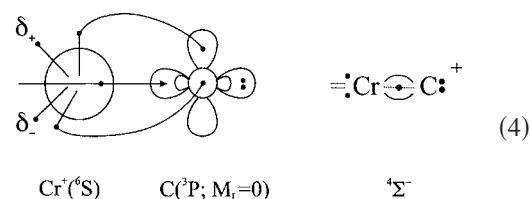


TABLE I. Existing theoretical results on various states of CrC at different methods. Bond distances r_e (Å), dissociation energies D_e (kcal/mol), harmonic frequencies ω_e (cm^{-1}), and energy gaps T_e (kcal/mol).

State	Method	r_e	D_e	ω_e	T_e
		Ref. 2			
$^3\Sigma^-$	CASSCF ^a	2.011	33.4	542	0.0
$^5\Sigma^-$		2.043		523	3.5
$^7\Sigma^-$		2.064		605	6.0
$^9\Sigma^-$		2.133		499	6.5
$^1\Sigma^-$		1.969		565	21.4
$^5\Pi$		2.106		485	33.7
$^7\Pi$		2.186		494	37.1
		Ref. 3 ^c			
$^3\Sigma^-$	LSDA	1.557	135.7	1050	0.0
	UBPW91	1.593	102.2		0.0
	UB3LYP	1.642	59.0	637	0.0
	RCCSD(T)	1.88	95.1		0.0
	UCCSD(T)	1.742	74.6		0.0
	MRCI	1.676	90.5	675	0.0
$^5\Sigma^-$	LSDA	1.623	98.0		16.3
	UBPW91	1.663	72.2		8.8
	UB3LYP	1.716	56.7	632	7.2
	RCCSD(T)	1.700	43.6		30.1
	UCCSD(T)	1.696	45.9		7.2
	MRCI	1.756	46.1	515	22.9
$^7\Sigma^-$	LSDA	1.949	33.4		80.8
	UBPW91	1.889	44.3		36.8
	UB3LYP	1.948	36.2	524	27.6
	MRCI	1.958	35.5	627	33.7
$^9\Sigma^-$	LSDA	2.073	56.7	537	57.7
	UBPW91	2.126	43.8		37.2
	UB3LYP	2.132	39.0	490	25.0
	RCCSD(T)	2.112	39.2		34.5
	UCCSD(T)	2.114	39.4		13.8
	MRCI	2.165	34.8	765	34.3
		Ref. 4 ^d			
$^3\Sigma^-$	BPW91	1.591	82.1	938	0.0
	BLYP	1.602	88.9	907	0.0
	B3LYP	1.636	66.5	638	0.0

^aCASSCF($10e^-/3\sigma 2\pi 1\delta$)/[$8s 7p 3d/4s 3p 1d/4c$].

^bThis state is the A_2 component of a $^1\Gamma$ symmetry and not of $^1\Sigma^-$ as supposed.

^c[$10s 8p 3d/4s 2p 1d/4c$].

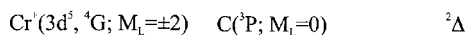
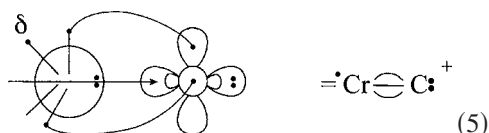
^d[$10s 7p 4d 1f/4c, 6-311+G^*/4c$].

TABLE II. Total MRCI energies E (hartree), bond distances r_e (Å), dissociation energies D_e (kcal/mol), zero point energies $G(0)$ (cm⁻¹), dipole moments μ (D), and energy gaps T_e (kcal/mol) of all CrC states presently studied in ascending energy order. Values in parenthesis refer to MRCI+Davidson correction.

State	$-E$	r_e	D_e	$G(0)$	$\langle\mu\rangle/\mu_{FF}^a$	T_e
$X^3\Sigma^-$	1081.344 56 (1081.362 0)	1.634 (1.640)	88.8 (91.3)	396.9 (395.0)	6.81/6.76	0.0 (0.0)
$1^5\Sigma^-$	1081.329 94 (1081.346 7)	1.702 (1.708)	57.5 (61.0)	369.2 (365.9)	2.22/2.85	9.2 (9.6)
$2^3\Delta$	1081.324 06 (1081.341 3)	1.605 (1.621)	76.9 (81.9)	452.2 (423.6)	2.78/2.64	12.9 (13.0)
$3^5\Pi$	1081.317 89 (1081.335 4)	1.783 (1.788)	50.0 (53.9)	336.5 (332.2)	2.37/2.77	16.7 (16.7)
$4^7\Sigma^-$	1081.307 14 (1081.324 7)	1.949 (1.935)	43.2 (47.2)	281.1 (290.7)	4.03/4.29	23.5 (23.4)
$5^1\Gamma$	1081.297 85 (1081.315 1)	1.580 (1.584)		494.3 (489.3)	6.23/6.46	29.3 (29.4)
$6^9\Sigma^-$	1081.296 52 (1081.315 4)	2.111 (2.119)	36.4 (41.1)	211.9 (227.9)	4.97/5.47	30.1 (29.2)
	1081.314 93 ^b	2.097 ^b	40.1 ^b	266.9 ^b		
$7^3\Pi$	1081.293 91 (1081.311 9)	1.848 (1.804)	57.1 (59.9)	283.1 (301.5)	2.0	31.8 (31.4)
$8^7\Pi$	1081.284 37 (1081.303 4)	2.013 (2.015)	28.9 (33.9)	265.6 (257.4)	2.55/2.67	37.8 (36.7)
$9^5\Sigma^-$	1081.278 65 (1081.301 8)	1.916 (1.910)	47.5 (53.6)	304.3 (284.5)	2.68	41.3 (37.8)
$10^7\Sigma^-$	1081.263 15 (1081.279 3)	2.124 (2.122)	37.7 (39.4)	255.8 (227.2)	2.89	51.1 (51.9)
$11^5\Pi$	1081.254 54 (1081.275 8)	1.839 (1.892)	32.4 (37.2)	349.8 (302.4)	1.00	56.5 (54.1)
$12^9\Pi$	1081.254 35 (1081.271 8)	2.128 (2.138)	10.5 (14.1)	280.7 (266.1)	0.76	56.6 (56.6)
$13^7\Pi$	1081.246 91 (1081.266 6)	2.019 (2.016)	27.7 (31.53)	270.6 (271.8)	1.17	61.3 (59.9)

^aDipole moments $\langle\mu\rangle$ are obtained as expectation values; μ_{FF} through the finite field method.

^bCCSD(T) results.



According to Kerkines and Mavridis^{5(f),5(g)} both the above structures compete for the ground state. At the MRCI level the X state appears to be of $^4\Sigma^-$ symmetry with the $^2\Delta$ being just 0.22 kcal/mol higher. Including scalar relativistic and core-valence correlation effects, the order is reversed and the $^2\Delta$ state becomes the ground state, with the $^4\Sigma^-$ state about 3 kcal/mol higher. However, independently of the X state symmetry of CrC^+ , i.e., $^4\Sigma^-$ or $^2\Delta$, it is obvious that by adding an electron to the σ frame of the $^4\Sigma^-$ state with the δ orbitals triplet coupled, or to a δ (d_{xy} or $d_{x^2-y^2}$) empty orbital of the $^2\Delta$ state also coupled into a triplet, a $^3\Sigma^-$ triplet-bonded ($\sigma, 2\pi$) state results which is the lowest state of the neutral CrC carbide (*vide infra*).

IV. RESULTS AND DISCUSSION

Table II lists the numerical results for the 14 CrC states studied, while PECs are plotted in Fig. 1.

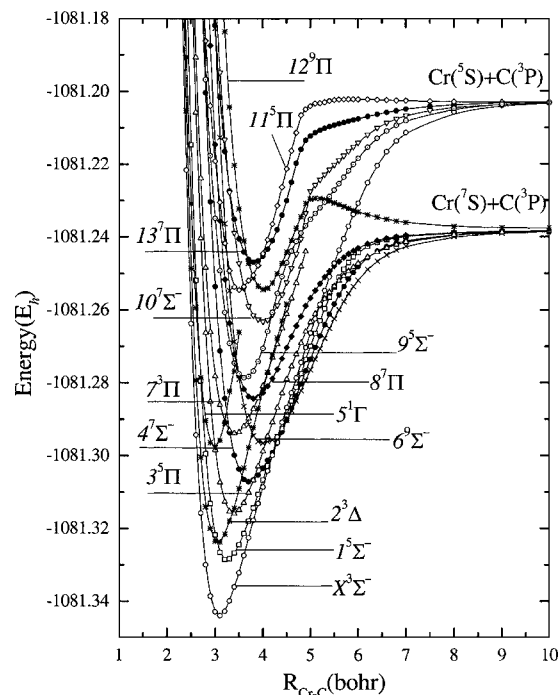


FIG. 1. Potential energy curves of 14 CrC states at the MRCI level of theory.

A. $X^3\Sigma^-$, $2^3\Delta$, and $5^1\Gamma$ states

The $X^3\Sigma^-$ state correlates adiabatically to $\text{Cr}(4s^1 3d^5; ^5S) + \text{C}(2s^2 2p^2; ^3P)$, which lies 0.963 (0.909) eV above the ground state fragments at the MRCI(+ Q) level as contrasted to the experimental splitting $\text{Cr}(^5S \leftarrow ^7S)$ of 0.941 eV.⁹ The leading CASSCF equilibrium configurations are (counting valence electrons only)

$$\begin{aligned} |X^3\Sigma^- \rangle \cong & 0.82|1\sigma^2 2\sigma^2 1\pi_x^2 1\pi_y^2 1\delta_+^1 1\delta_-^1 \rangle \\ & - 0.17|1\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2 1\delta_+^1 1\delta_-^1 \rangle \\ & - 0.16|1\sigma^2 2\sigma^2 (1\pi_x^2 2\pi_y^2 + 2\pi_x^2 1\pi_y^2) 1\delta_+^1 1\delta_-^1 \rangle \end{aligned}$$

revealing a $(\sigma, 2\pi)$ bonding configuration with two observer electrons in the symmetry defining δ_{\pm} orbitals. This particular electronic arrangement provides for the maximum number of “bonds,” minimizing at the same time the rather destabilizing character of the nonbonding electrons, thus leading naturally to the ground state.

The equilibrium Mulliken atomic distributions (Cr/C)

$$\begin{aligned} & 4s^{0.24} 3d_{z^2}^{1.15} 4p_z^{0.18} 3d_{xz}^{1.02} 4p_x^{0.04} 3d_{yz}^{1.02} 4p_y^{0.04} 3d_{x^2-y^2}^{1.0} 3d_{xy}^{1.0} \\ & 2s^{1.59} 2p_z^{0.83} 2p_x^{0.92} 2p_y^{0.92} \end{aligned}$$

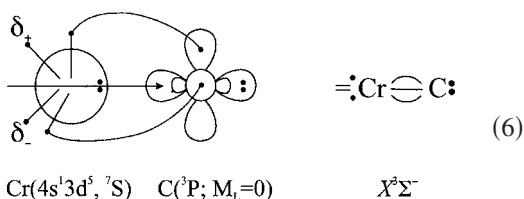
and orbital compositions

$$1\sigma \cong 0.16(4s) + 0.23(3d_{z^2}) + 0.90(2s) - 0.11(2p_z),$$

$$2\sigma \cong 0.69(4s) - 0.10(4p_z) - 0.13(2s) - 0.64(2p_z),$$

$$3\sigma \cong 0.27(4s) - 0.61(3d_{z^2}) + 0.21(4p_z) - 0.81(2p_z)$$

clearly support the following vbL picture [see also Schemes (4) and (5)]:

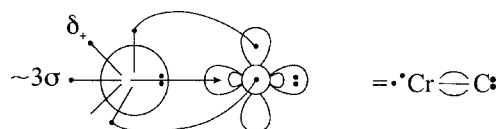


A total of $0.30e^-$ migrate from Cr to C mainly along the σ frame filling the empty $2p_z$ carbon orbital. The MRCI(+ Q) binding energy with respect to the ground state fragments equals 88.8 (91.3) kcal/mol at $r_e = 1.634$ (1.640) Å. From our past experience on the ground state of CrC^+ ,^{5(f),5(g)} core-valence correlation effects are expected to increase the binding energy as much as 6 kcal/mol and decrease the bond distance by about 0.01 Å. Therefore, our recommended D_e and r_e values for the $X^3\Sigma^-$ state of CrC are 97 kcal/mol and 1.63 Å, respectively. Due to the rather large number of active electrons the size-extensivity error amounts to 7.05(2.38) mE_h .

By moving one of the two δ_{\pm} nonbonding electrons to a σ -type orbital while retaining the $(\sigma, 2\pi)$ bonding configuration intact, the molecule is excited to a $^3\Delta$ state, correlating to the $\text{Cr}(4s^2 3d^4; ^5D)$ term, 12.9(13.0) kcal/mol above the $X^3\Sigma^-$ state at the MRCI(+ Q) level of theory. The main CASSCF equilibrium configurations and Mulliken atomic populations

$$\begin{aligned} |2^3\Delta \rangle \cong & 0.84|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2 1\delta_+^1 \rangle \\ & - 0.16|1\sigma^2 2\sigma^2 3\sigma^1 (1\pi_x^2 2\pi_y^2 + 2\pi_x^2 1\pi_y^2) 1\delta_+^1 \rangle \\ & 4s^{0.86} 3d_{z^2}^{1.25} 4p_z^{0.24} 3d_{xz}^{1.16} 4p_x^{0.03} 3d_{yz}^{1.16} 4p_y^{0.03} 3d_{x^2-y^2}^{1.0} \\ & 2s^{1.73} 2p_z^{0.90} 2p_x^{0.78} 2p_y^{0.78} \end{aligned}$$

conform to the following vbL bonding picture:



As in the $X^3\Sigma^-$ state about $0.3e^-$ are transferred from the Cr to the C atom; $0.6e^-$ are moving through the σ path filling the empty $2p_z$ C orbital, while $0.3e^-$ are moving back from C to Cr via the π frame. The 2σ (σ bond) and 3σ [see Scheme (7)] orbitals have the following atomic composition:

$$2\sigma \cong 0.70(3d_{z^2}) - 0.66(2p_z),$$

$$\begin{aligned} 3\sigma \cong & 0.66(4s) - 0.33(3d_{z^2}) - 0.24(4p_z) - 0.19(2s) \\ & - 0.27(2p_z). \end{aligned}$$

Part of the $2^3\Delta$ PEC curve is shown in Fig. 1.

With respect to the adiabatic atoms, $D_e = 76.9$ (81.9) kcal/mol at the MRCI(+ Q) level and $r_e = 1.605$ (1.621) Å. The 10 kcal/mol decrease in D_e as compared to the $X^3\Sigma^-$ state, is the result of the $\delta_{\pm}^2(X^3\Sigma^-) \rightarrow \delta^1\sigma^1(2^3\Delta)$ transition leading to a “congested” σ frame.

It is worth noting the very large difference between the dipole moment values of the $X^3\Sigma^-$ and $2^3\Delta$ states, 6.81 vs 2.89 D, respectively. This remarkable decrease stems from the $3\sigma^1$ electron distribution in the $2^3\Delta$ state, which is located primarily on the Cr atom and is polarized away from the carbon atom (see above).

Continuing the description of the triple-bonded states, we now discuss the $5^1\Gamma$ state, approximately 30 kcal/mol higher. By doubly populating a δ_{\pm} orbital of $X^3\Sigma^-$, the $5^1\Gamma$ state is obtained whose leading configurations and atomic Mulliken distributions are

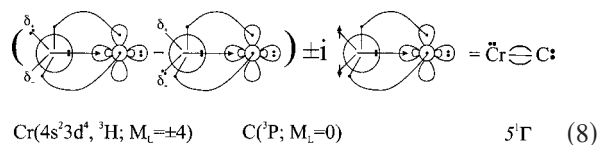
$$|5^1\Gamma(^1A_1) \rangle \cong 0.64|1\sigma^2 2\sigma^2 1\pi_x^2 1\pi_y^2 (1\delta_+^2 - 1\delta_-^2) \rangle,$$

$$|5^1\Gamma(^1A_2) \rangle \cong 0.91|1\sigma^2 2\sigma^2 1\delta_+^1 1\pi_x^2 1\pi_y^2 1\delta_-^1 \rangle$$

and

$$\begin{aligned} & 4s^{0.20} 3d_{z^2}^{1.21} 4p_z^{0.20} 3d_{xz}^{1.02} 4p_x^{0.05} 3d_{yz}^{1.02} 4p_y^{0.05} 3d_{x^2-y^2}^{1.0} \\ & 2s^{1.59} 2p_z^{0.78} 2p_x^{0.92} 2p_y^{0.92}. \end{aligned}$$

These lead to the vbL Scheme (8),



i.e., $|^1\Gamma^{\pm}\rangle = |^1A_1\rangle \pm i|^1A_2\rangle$. Note that the $5^1\Gamma$ state should cor-

relate to $\text{Cr}(4s^2 3d^4; ^3\text{H})$, 2.985 eV above the ^7S state.⁹ Because of technical problems, we were unable to complete the PEC for this state (see Fig. 1), therefore a D_e value is not reported in Table II. However, considering the experimental $\text{Cr}(^3\text{H} \leftarrow ^7\text{S})$ energy separation,⁹ the estimated bond energy is close to 106 kcal/mol, at a MRCI distance of $r_e = 1.580 \text{ \AA}$. As expected, the carbon atom carries a negative charge of $\sim 0.3e^-$.

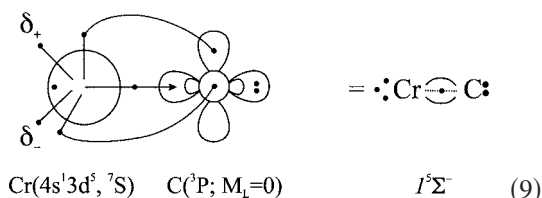
The dipole moment of the $5^1\Gamma$ state ($\mu = 6.54 \text{ D}$) is similar to that for the $X^3\Sigma^-$ state and is consistent with the previous observation made in connection with the $2^3\Delta$ state (*vide supra*).

B. $1^5\Sigma^-$, $4^7\Sigma^-$, and $6^9\Sigma^-$ states

The first excited state of CrC is of $^5\Sigma^-$ symmetry and is located 9.2 (9.6) kcal/mol above the X state at the MRCI (+Q) level of theory. It correlates to $\text{Cr}(^7\text{S}) + \text{C}(^3\text{P})$ with the following leading equilibrium CASSCF configurations:

$$|1^5\Sigma^-\rangle \cong 0.83|1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^2 1\pi_y^2 1\delta_+^1 1\delta_-^1\rangle \\ - 0.20|1\sigma^2 2\sigma^1 3\sigma^1 (1\pi_x^2 2\pi_y^2 + 2\pi_x^2 1\pi_y^2) 1\delta_+^1 1\delta_-^1\rangle.$$

In the current state the σ bond is broken, the bonding being characterized by a $1/2 \sigma$ and 2π bonds. A visual description of the bonding is provided by Scheme (9),



This picture is also in accordance with the Mulliken atomic populations

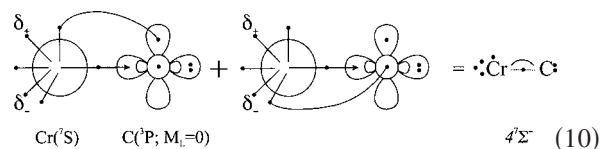
$$4s^{0.81} 3d_{z^2}^{0.69} 4p_z^{0.18} 3d_{xz}^{0.99} 4p_x^{0.03} 3d_{yz}^{0.99} 4p_y^{0.03} 3d_{x^2-y^2}^{1.0} 3d_{xy}^{1.0} / \\ 2s^{1.71} 2p_z^{0.61} 2p_x^{0.96} 2p_y^{0.96}.$$

A $1/2 \sigma$ bond is created between the $3d_{z^2} - 2p_z$ orbitals [$3\sigma \cong 0.65(3d_{z^2}) - 0.70(2p_z)$], with a concomitant transfer of about $0.3e^-$ from the metal atom to the empty $2p_z$ carbon orbital. The other σ electron is primarily located in a $4s 4p_z 3d_{z^2}$ Cr hybrid that is pointing away from the C atom. The ($1/2 \sigma, 2 \pi$) bonding is reflected in the larger bond distance (1.702 Å) and significantly smaller binding energy ($D_e = 61.0 \text{ kcal/mol}$) as contrasted to the genuinely triple bonded states; see Table II.

Breaking a π_x (or π_y) bond in the $1^5\Sigma^-$ state generates the $4^7\Sigma^-$ state. Its CASSCF wave function

$$|4^7\Sigma^-\rangle \\ \cong |1\sigma^2 2\sigma^1 1\delta_+^1 3\sigma^1 [0.55(1\pi_x^2) - 0.25(2\pi_x^2)] 1\pi_y^2 2\pi_y^1 1\delta_-^1\rangle \\ + |1\sigma^2 2\sigma^1 1\delta_+^1 3\sigma^1 [0.55(1\pi_y^2) - 0.25(2\pi_y^2)] 1\pi_x^2 2\pi_x^1 1\delta_-^1\rangle$$

with $2\sigma \cong 0.60(3d_{z^2}) - 0.22(2s) - 0.71(2p_z)$ and $3\sigma \cong 0.63(4s) - 0.43(3d_{z^2}) - 0.36(2p_z)$ supports the following diagram:



also in agreement with the atomic populations

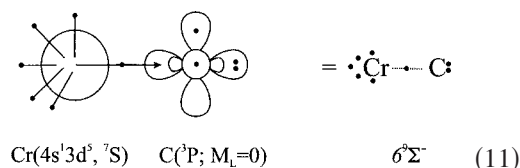
$$4s^{0.69} 3d_{z^2}^{0.69} 4p_z^{0.10} 3d_{xz}^{1.0} 4p_x^{0.06} 3d_{yz}^{1.0} 4p_y^{0.06} 3d_{x^2-y^2}^{1.0} 3d_{xy}^{1.0} / \\ 2s^{1.72} 2p_z^{0.77} 2p_x^{0.93} 2p_y^{0.93}.$$

Obviously, the two atoms interact through a $1/2 \sigma$ and a π bond, while about $1.5e^-$ are distributed in the σ frame of the metal. Overall $0.4e^-$ move from the metal to the carbon atom. The MRCI(+Q) binding energy and bond distance are 43.2 (47.2) kcal/mol and 1.949 (1.935) Å.

The rupture of the π bond of the $4^7\Sigma^-$ state, Scheme (10), leads to the high spin $6^9\Sigma^-$ state, whose wave function is dominated by the Hartree-Fock configuration $|6^9\Sigma^-\rangle \cong |1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_+^1 1\delta_-^1\rangle$ and atomic distributions

$$4s^{0.80} 3d_{z^2}^{0.47} 4p_z^{0.15} 3d_{xz}^{1.0} 4p_x^{0.04} 3d_{yz}^{1.0} 4p_y^{0.04} 3d_{x^2-y^2}^{1.0} 3d_{xy}^{1.0} / \\ 2s^{1.78} 2p_z^{0.89} 2p_x^{0.94} 2p_y^{0.94}.$$

Approximately $0.5e^-$ are transferred from the $(4s 4p_z 3d_{z^2})^{2.0}$ Cr hybrid to the empty $2p_z$ carbon orbital, creating a $1/2 \sigma$ bond worth 36.4 (41.1) kcal/mol at the MRCI(+Q) level. The corresponding RCCSD(T) value is 40.1 kcal/mol. The MRCI(+Q) and RCCSD(T) bond distance(s), one of the largest of the states studied, is 2.111 (2.119) and 2.097 Å, respectively. The bonding is succinctly shown by the vBL diagram (11),

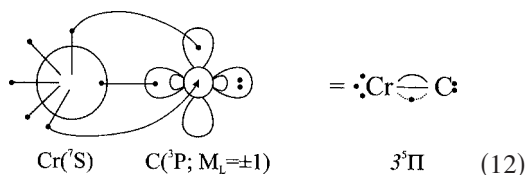


C. $3^5\Pi$, $8^7\Pi$, and $12^9\Pi$ states

States of Π symmetry are generated from the $^3\text{P}, M_L = \pm 1$ component of the carbon atom and the ^7S and ^5S terms of Cr. The lowest Π state of CrC correlates to ground state atoms and is of quintet spin symmetry, with the following leading CASSCF configurations and Mulliken atomic distributions:

$$|3^5\Pi\rangle \cong 0.79|1\sigma^2 2\sigma^2 3\sigma^1 1\delta_+^1 1\pi_x^2 1\pi_y^1 1\delta_-^1\rangle \\ - 0.21|1\sigma^2 2\sigma^2 3\sigma^1 1\delta_+^1 2\pi_x^2 1\pi_y^1 1\delta_-^1\rangle \\ 4s^{0.82} 3d_{z^2}^{1.0} 4p_z^{0.23} 3d_{xz}^{1.0} 4p_x^{0.04} 3d_{yz}^{0.62} 4p_y^{0.02} 3d_{x^2-y^2}^{1.0} 3d_{xy}^{1.0} / \\ 2s^{1.78} 2p_z^{1.10} 2p_x^{0.95} 2p_y^{0.39}.$$

The bonding, described graphically by Scheme (12),

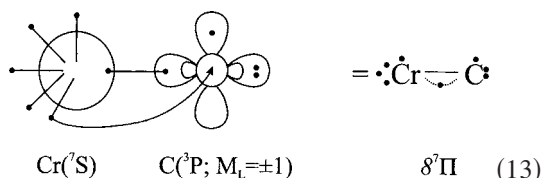


has ($\sigma, \pi_x, 1/2 \pi_y$) character, as opposed to the ($1/2 \sigma, 2 \pi$) bonding distribution of the $1^5\Sigma^-$ state (*vide supra*). Interestingly, only $0.1e^-$ move along the σ frame from C to Cr, while about $0.4e^-$ migrate to the carbon atom through the π path, resulting in a total transfer of $0.3e^-$ from Cr to C. The MRCI(+ Q) bond distance and binding energy are 1.783 (1.788) Å and 50.0 (53.9) kcal/mol. The relatively small dipole moment, 2.40 D, shows the effect of the $3\sigma^1$ charge distribution on the metal atom, the same as in the $1^5\Sigma^-$ state, Scheme (9).

The $8^7\Pi$ state can be derived from the $3^5\Pi$ by breaking the π bond. The leading equilibrium CASSCF configurations and Mulliken allotment

$$\begin{aligned}
 |8^7\Pi\rangle \cong & 0.80|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^1 2\pi_x^1 1\pi_y^1 \delta_+^1 \delta_-^1\rangle \\
 & - 0.26|1\sigma^2 2\sigma^1 3\sigma^1 4\sigma^1 1\pi_x^2 1\pi_y^1 \delta_+^1 \delta_-^1\rangle \\
 & 4s^{0.88} 3d_{z^2}^{0.93} 4p_z^{0.21} 3d_{xz}^{1.0} 4p_x^{0.07} 3d_{yz}^{0.54} 4p_y^{0.02} 3d_{x^2-y^2}^{1.0} 3d_{xy}^{1.0}/ \\
 & 2s^{1.80} 2p_z^{1.11} 2p_x^{0.92} 2p_y^{0.45}
 \end{aligned}$$

suggest that the two atoms interact attractively via a σ and $1/2 \pi$ bonds; see the diagram below



The $8^7\Pi$ state should be contrasted to the $4^7\Sigma^-$ state. The ($1/2 \sigma, \pi$) bonding structure in the $4^7\Sigma^-$ state is transformed into a ($\sigma, 1/2 \pi$) bonding configuration in the $8^7\Pi$ state, resulting to a significant binding loss of 14 kcal/mol and a bond lengthening of 0.064 Å.

By uncoupling the σ -bond electrons of the $8^7\Pi$ state, we are led to the high spin nonet $12^9\Pi$ state. Its wave function, as expected, is dominated by the Hartree-Fock configuration

$$|12^9\Pi\rangle \cong 0.95|1\sigma^2 2\sigma^1 3\sigma^1 4\sigma^1 1\pi_x^2 1\pi_x^1 1\pi_y^1 \delta_+^1 \delta_-^1\rangle$$

with

$$2\sigma \cong 0.50(4s) + 0.42(3d_{z^2}) - 0.32(2s) - 0.55(2p_z),$$

$$3\sigma \cong 0.59(4s) - 0.57(3d_{z^2}) - 0.25(4p_z) + 0.33(2p_z),$$

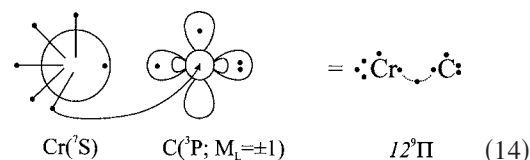
$$4\sigma \cong 0.67(3d_{z^2}) - 0.33(4p_z) + 0.61(2p_z).$$

From the Mulliken atomic population analysis

$$\begin{aligned}
 & 4s^{0.93} 3d_{z^2}^{1.01} 4p_z^{0.37} 3d_{xz}^{1.0} 4p_x^{0.05} 3d_{yz}^{0.25} 4p_y^{0.04} 3d_{x^2-y^2}^{1.0} 3d_{xy}^{1.0}/ \\
 & 2s^{1.75} 2p_z^{0.89} 2p_x^{0.93} 2p_y^{0.71}
 \end{aligned}$$

it is deduced that overall about $0.3e^-$ are transferred from the

metal atom to the carbon atom. In detail, $0.7e^-$ migrate from the Cr to the C atom via the π skeleton, while approximately $0.4e^-$ are moving back through the σ framework creating a $(4s4p_z)^{1.3}$ hybrid centered on Cr. The emerging bonding diagram



shows a weak $1/2 \pi$ interaction of 10.5 kcal/mol at $r_e = 2.128$ Å. The MRCI potential energy curve of the $12^9\Pi$ state, Fig. 1, shows a hump at $5.0 a_0$. This indicates that the interaction from $r=\infty$ to $r=5 a_0$ is dominated by the σ interaction, which is repulsive; decreasing r below $5.0 a_0$ the $1/2 \pi$ (one electron) interaction takes over resulting in a weak binding interaction.

D. $7^3\Pi, 9^5\Sigma^-, 10^7\Sigma^-, 11^5\Pi$, and $13^7\Pi$ states

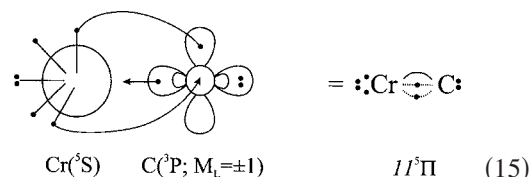
We now discuss the $7^3\Pi, 9^5\Sigma^-, 10^7\Sigma^-, 11^5\Pi$, and $13^7\Pi$ states all of which correlate to $\text{Cr}(^4\text{S})+\text{C}(^3\text{P})$; we remind the reader that the only other state which dissociates to the first excited state of Cr is the $X^3\Sigma^-$; see Fig. 1.

The $7^3\Pi$ state is similar to the previously discussed $3^5\Pi$ state, the difference being the spin coupling of the “free” electrons in the d_π and d_δ orbitals. The binding is adequately described by Scheme (12) with $D_e = 57.1$ kcal/mol at the MRCI level, not very different from that of the $3^5\Pi$ state.

The first excited state of $^5\Pi$ symmetry is $11^5\Pi$ whose leading configuration, $|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^1 \delta_+^1 \delta_-^1\rangle$, is the same as that of the $3^5\Pi$ state but with a significantly smaller coefficient, 0.59 vs 0.79. The composition of the σ valence orbitals, namely, $2\sigma \cong 0.55(4s) - 0.61(3d_{z^2}) - 0.21(4p_z)$ and $3\sigma \cong 0.22(4s) + 0.46(3d_{z^2}) - 0.75(2p_z)$, along with the atomic Mulliken distributions

$$\begin{aligned}
 & 4s^{1.03} 3d_{z^2}^{1.03} 4p_z^{0.28} 3d_{xz}^{0.97} 4p_x^{0.03} 3d_{yz}^{0.31} 4p_y^{0.02} 3d_{x^2-y^2}^{1.0} 3d_{xy}^{1.0}/ \\
 & 2s^{1.76} 2p_z^{0.90} 2p_x^{0.98} 2p_y^{0.66}
 \end{aligned}$$

point to the following bonding description:



Clearly, $0.66e^-$ are transferred from the $3d_{yz}$ to the empty $2p_y$ carbon orbital, thus creating the $1/2 \pi$ bond, with a back transfer of $0.34e^-$ through the σ frame amounting to a total migration of $0.3e^-$ from Cr to C. The MRCI(+ Q) D_e, r_e , and μ values are 32.4 (37.2) kcal/mol, 1.839 (1.892) Å, and 1.0 D.

Coupling the complete set of π bond electrons of the $11^5\Pi$ state into a triplet gives rise to the $13^7\Pi$ state, ener-

getically the highest state studied: $T_e(13^7\Pi \leftarrow 11^5\Pi) = 61.3$ kcal/mol (MRCI). The most important configurations of the $13^7\Pi$ wave function are the following:

$$|13^7\Pi\rangle \cong |1\sigma^2[(0.65)2\sigma^23\sigma^1 - (0.34)2\sigma^13\bar{\sigma}^14\sigma^1 - (0.30)3\sigma^14\sigma^2]1\delta_+^1\pi_x^12\pi_x^1\pi_y^11\delta_-^1\rangle$$

The bonding is similar to the $12^9\Pi$ state comprising a $1/2$ π attractive interaction, Scheme (14). This bonding configura-

tion is reflected in the rather low binding energy and long interatomic distance for this state, $D_e = 27.7$ kcal/mol and $r_e = 2.019$ Å.

The two remaining states, $9^5\Sigma^-$ and $10^7\Sigma^-$, correlate to $\text{Cr}(^5S) + \text{C}(^3P)$ and can be considered as arising from the $X^3\Sigma^-$ state by decoupling one and two π bonds, respectively. The most important configurations and populations of these two states

$$|9^5\Sigma^-\rangle \cong 0.43|1\sigma^22\sigma^21\delta_+^1(1\pi_x^21\pi_y^22\pi_y^1 + 1\pi_x^12\pi_x^1\pi_y^2)1\delta_-^1\rangle + 0.24|1\sigma^22\sigma^11\delta_+^13\sigma^11\pi_x^21\pi_y^21\delta_-^1\rangle + 0.26|1\sigma^22\sigma^11\delta_+^14\sigma^11\pi_x^21\pi_y^21\delta_-^1\rangle$$

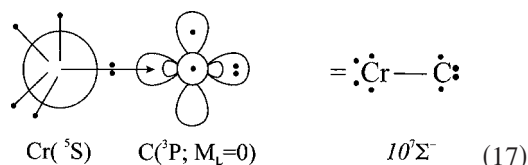
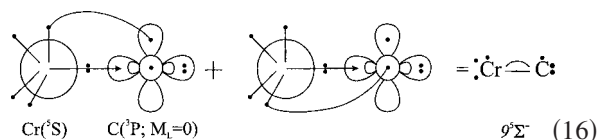
$$4s^{0.45}3d_{z^2}^{0.57}4p_z^{0.30}3d_{xz}^{1.03}4p_x^{0.04}3d_{yz}^{1.03}4p_y^{0.04}3d_{x^2-y^2}^{1.0}3d_{xy}^{1.0}/2s^{1.78}2p_z^{0.88}2p_x^{0.92}2p_y^{0.92}$$

and

$$|10^7\Sigma^-\rangle \cong 0.67|1\sigma^22\sigma^21\delta_+^11\pi_x^22\pi_x^1\pi_y^22\pi_y^11\delta_-^1\rangle - 0.34|1\sigma^22\sigma^11\delta_+^13\sigma^1(1\pi_x^21\pi_y^22\pi_y^1 + 1\pi_x^12\pi_x^1\pi_y^2)1\delta_-^1\rangle$$

$$4s^{0.60}3d_{z^2}^{0.40}4p_z^{0.34}3d_{xz}^{1.02}4p_x^{0.05}3d_{yz}^{1.02}4p_y^{0.05}3d_{x^2-y^2}^{1.0}3d_{xy}^{1.0}/2s^{1.75}2p_z^{0.86}2p_x^{0.91}2p_y^{0.91}$$

support the bonding diagrams (16) and (17).



In both the states a total of about $0.5e^-$ are transferred from Cr to C mainly through the σ framework. According to Table II, the MRCI(+ Q) dissociation energies and bond distances are $D_e = 47.5$ (53.6) kcal/mol, $r_e = 1.916$ (1.910) Å and $D_e = 37.7$ (39.4) kcal/mol, $r_e = 2.124$ (2.122) Å, respectively. The dipole moments 2.68 ($9^5\Sigma^-$) and 2.89 ($10^7\Sigma^-$) D, are surprisingly small as compared to the dipole moment of the generic $X^3\Sigma^-$ state.

V. SUMMARY AND REMARKS

The electronic structure of 14 states of the diatomic CrC have been explored by internally contracted multireference methods coupled with basis sets capable of quantitative accuracy. We report full PECs, energetics, and a number of spectroscopic parameters. The most interesting aspects of the present work are summarized below.

- (1) The ground state of the CrC is of $^3\Sigma^-$ symmetry with an estimated $D_e = 97$ kcal/mol and $r_e = 1.63$ Å with the first excited state, $^5\Sigma^-$, 9.2 kcal/mol higher.

- (2) In all states $0.3\text{--}0.5e^-$ are transferred from the Cr to the C atom, resulting in a fairly ionic molecule with a p^3 nitrogenlike carbon electron distribution.
- (3) Dipole moments obtained as expectation values range from 6.81 ($X^3\Sigma^-$) to 1.00 D ($11^5\Pi$). Note that the finite field dipole moment of the $X^3\Sigma^-$ state, $\mu_{FF} = 6.75$ D, does not differ significantly from $\langle\mu\rangle$. Of course, this numerical coincidence does not preclude large differences among $\langle\mu\rangle$ and μ_{FF} values of the excited states; see also Refs. 5(e) and 5(i).
- (4) The omission of core-correlation and relativity effects amount to a loss of about 6 kcal/mol in D_e and a bond length increase of no more than 0.01 Å according to similar calculations on $\text{CrC}^{+5(f),5(g)}$.
- (5) Nearly all states show an intense multireference character, thus excluding single reference approximate methods for such systems, if one aims for relatively reliable results.

ACKNOWLEDGMENTS

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