**Ab initio** study of the electronic structure of manganese carbide

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We report electronic structure calculations on 13 states of the experimentally unknown manganese carbide (MnC) using standard multireference configuration interaction (MRCI) methods coupled with high quality basis sets. For all states considered we have constructed full potential energy curves and calculated zero point energies. The X state, correlating to ground state atoms, is of $^4\Sigma^-$ symmetry featuring three bonds, with a recommended dissociation energy of $D_0=70.0$ kcal/mol and $r_e=1.640$ Å. The first and second excited states, which also correlate to ground state atoms, are of $^6\Sigma^-$ and $^8\Sigma^-$ symmetry, respectively, and lie 17.7 and 28.2 kcal/mol above the X state at the MRCI level of theory. © 2006 American Institute of Physics. [DOI: 10.1063/1.2181972]

I. INTRODUCTION

Aiming towards a comprehensive characterization of the electronic structure of the 3d-transition metal diatomic carbides and their cations $MC$ and $MC^+$, $M=$Sc, $\text{Ti}$ [Ref. 1(d)], (Sc$^+$), Fe$^+$, Cr$^+$, V$^+$, Ni$^+$, Co$^+$, Mn$^+$, and Zn$^+$, $X=$Zn, $\text{Fe}$ [Refs. 1(h), 1(i)], (Fe$^+$), (Ni$^+$), and (Co$^+$), we report high level ab initio results for the ground and several excited states of manganese carbide (MnC). The existing theoretical literature on MnC is exhausted to a single article by Gutev et al., who studied the ground states of all $MC^0,\pm$ and $MO^0,\pm$ species ($M=$Sc–Zn) using density functional theory (DFT). They identified the X state of MnC as of $^4\Sigma^-$ symmetry with $r_e=1.606–1.699$ Å, dissociation energy $D_0=3.07–4.65$ eV, and dipole moment $\mu_e=2.75–3.00$ D, depending on the functional used. As far as we know no experimental data are available for MnC.

A state of $^4\Sigma^-$ symmetry results naturally from the interaction of the ground state atoms as pictured clearly in valence-bond-Lewis (vbL) diagram 1.

![Diagram 1](image1.png)

The above diagram conforms also to the bonding pattern of the X states of both VC [Ref. 1(e)] and CrC [Ref. 1(g)] carbides. The $X^3\Sigma^-$ state of CrC arises by adding an electron to the $\delta$ orbital of the $X^2\Delta$ state of VC, while the $^8\Sigma^-$ state of MnC is obtained by adding an electron to a $\sigma$ orbital of the $X^3\Sigma^-$ state of CrC. It is interesting to note at this point that

the $X^3\Delta$ state of FeC [Ref. 1(h)] can be formed from the $X^4\Sigma^-$ state of MnC by adding one electron to one of the singly occupied $\delta$ (or $\delta_\perp$) orbitals. By doubly occupying the remaining $d_\delta$ orbital we obtain the $X^2\Sigma^+$ state of CoC [Ref. 1(l)] while a double occupancy of the last singly occupied orbital of $\sigma$ type gives rise to the $X^4\Sigma^+$ of NiC.\(^2\)

In the present work we examine by multireference variational methods all molecular states correlating to the Mn($^8S$)+[C($^3P$), C($^1D$)] atom limit, three states which correlate to the Mn($^8P$)+C($^3P$) limit, and one state related to the Mn($^6P$)+C($^3P$) limit, i.e., a total of 13 molecular states. Full potential energy curves (PEC) have been constructed for all states studied and standard spectroscopic constants have been calculated from the computed adiabatic potential energy curves.

II. METHODS

For the Mn atom the newly developed correlation consistent cc-pVQZ (22s18p11d3/2g1h) and cc-pwCVQZ (24s20p13d4/3g3h) basis sets of Balabanov and Peterson\(^4\) were employed; for the C atom the regular cc-pVQZ (12s6p3d2/1g) set by Dunning\(^5\) was used. Both sets were generally contracted to \[8s7p5d3f2g1h/(10s9p7d4f3g2h)\] /\[5s4p3d2f1g\] for the valence (core-valence) calculations. The zeroth-order wave functions are of the complete active space self-consistent-field (CASSCF) type and are formed by distributing the 11 valence electrons among 13 orbitals correlating to the (4s, 4p, 3d) atomic orbitals of Mn and the (2s, 2p) orbitals of C.

Additional electron correlation was introduced by including single+double excitations out of the zeroth-order space [CASSCF+1+2=multipreference configuration interaction (MRCI)]. The size of the CI expansions range from ~344×10\(^6\) ($^8\Sigma^-$ and $^8\Pi$ states) to ~1.4×10\(^8\) configurations (for all the remaining states), internally contracted to about 3.8×10\(^6\) ($^6\Sigma^-$ and $^6\Pi$ states) and 17–38×10\(^6\) configura-
tions. For the $X^4\Sigma^-$ state, scalar relativistic effects were taken into account through the second-order Douglas-Kroll-Hess (DKH2) approximation by using the suggested contracted basis sets for both atoms. For all calculations the ground state fragments: Mn $^6S(4s^23d^5)$ and C $^3P(2s^22p^2)$ states along with energy splittings \( \Delta E(\text{eV}) \) of the Mn $^3D$, $^3P$, and $^3P$ and C $^3D$ terms, respectively, using a variety of electronic structure methods.

### Table I

<table>
<thead>
<tr>
<th>Method</th>
<th>$E(^6S)$</th>
<th>$\Delta E(^3D-^6S)$</th>
<th>$\Delta E(^3P-^6S)$</th>
<th>$\Delta E(^3P-^3D)$</th>
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<tbody>
<tr>
<td>CISD</td>
<td>115.003693</td>
<td>2.403</td>
<td>1.947</td>
<td>2.754</td>
</tr>
<tr>
<td>CISD+Q</td>
<td>115.013751</td>
<td>2.384</td>
<td>2.135</td>
<td>2.905</td>
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<tr>
<td>CISD+DKH</td>
<td>115.513129</td>
<td>2.612</td>
<td>2.006</td>
<td>2.838</td>
</tr>
<tr>
<td>CISD+DKH+Q</td>
<td>115.522382</td>
<td>2.585</td>
<td>2.195</td>
<td>2.987</td>
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<tr>
<td>C-CISD</td>
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<tr>
<td>C-CISD+Q</td>
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<td>1.972</td>
<td>2.821</td>
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<tr>
<td>C-CISD+DKH+Q</td>
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<tr>
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<td>2.315</td>
<td>2.041</td>
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<td>115.10860</td>
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<td>MRCI+DKH</td>
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<td>MRCI+DKH+Q</td>
<td>115.52392</td>
<td>2.532</td>
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<td>C-MRCIb</td>
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<td>C-MRCI+Qb</td>
<td>115.44325</td>
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<tr>
<td>C-MRCI+DKHb</td>
<td>115.923006</td>
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<tr>
<td>C-MRCI+DKH+Qb</td>
<td>115.953419</td>
<td>2.458</td>
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</tr>
<tr>
<td>Expt.</td>
<td>—</td>
<td>2.145</td>
<td>2.303</td>
<td>3.074</td>
</tr>
</tbody>
</table>

$^a$Q and DKH refers to Davidson correction and second-order Douglas-Kroll-Hess scalar relativistic corrections, respectively. MRCI(Mn)=CASSCF(4e-4s, 4p, 3d)+1+2, MRCI(C)=CASSCF(4e-7s, 2p)+1+2.

$^b$The $3s^23p^6$ semeicon electrons of Mn are included in the CI procedure.

### III. RESULTS AND DISCUSSION

Table I presents total energies and splittings of the low-lying atomic states of the Mn and C atoms in a variety of methods. Note that the Mn $^3P$ state is calculated in reverse order than the experimental findings with respect to the $^3D$ term at all levels of theory. Table II summarizes our numerical results, whereas potential energy curves for all states are displayed in Fig. 1.

### A. $X^4\Sigma^-$, $1^6\Sigma^-$, and $2^8\Sigma^-$ states

The ground state is of $^4\Sigma^-$ symmetry and dissociates to the ground state fragments: Mn($4s^23d^5$, $^6S$) + C($2s^22p^2$, $^3P$; $M_L$=0). The two atoms are held together by a $\sigma$ and two $\pi$ bonds while the electrons in the three non-bonding ("spectator"), singly occupied orbitals, two of $\delta$=$(3d_{z^2}-\gamma^2, 3d_{xy})$ and one of $\sigma$ symmetry, define the spin and spatial symmetries of the molecule. The electronic arrangement can be synopsized by the vbL diagram.

The configuration with the largest coefficient at equilibrium is $\mid X^4\Sigma^- \rangle$ = 0.70[(core)$^{20}1\alpha^22\sigma^23\sigma^11\delta_1^11\pi_2^11\delta_2^1$] with corresponding Mulliken CASSCF atomic distributions (Mn/C),

$$
\begin{align*}
4s^{0.84} & 4p_z^{0.38} 3d_{z^2}^{1.14} 4p_x^{0.03} 3d_{xz}^{1.14} 4p_y^{0.03} 3d_{yz}^{1.14} 3d_{xy}^{1.0} 3d_{x^2-y^2}^{1.0} \\
& /2s^{1.74} 2p_z^{0.82} 2p_x^{0.82} 2p_y^{0.82} 
\end{align*}
$$

The above imply the formation of a $\sigma$-dative bond by the transfer of about 0.7 $e^-$ from the 4s4p$\sigma$ hybrid of Mn to the initially empty 2p$\sigma$ C orbital, whereas the formation of two $\pi$ bonds gives rise to a transfer of 0.4 $e^-$ from C to Mn; in total, about 0.3 $e^-$ migrate from Mn to C. A dissociation energy of $D_0=64.58(66.7)$ kcal/mol and equilibrium distance of $r_g$ = 1.686(1.681) Å are obtained at the MRCI(+Q) level of theory. Correcting for the zero point energy [$G(0)$] and basis set superposition error (BSSE), we obtain

$$
D_q(+Q) = D_q(+Q) - G(0)(+Q) + BSSE(+Q) = 64.58(66.7) - 0.86(0.90) - 0.39(0.42) = 63.33(65.4) \text{ kcal/mol.}
$$

Including scalar relativistic effects through the DKH2 approximation, we obtain $D_q(+\text{rel}(+Q))=63.82(65.9)$ kcal/mol at $r_g=1.683(1.678)$ Å. Correcting for $G(0)$ and BSSE, we predict
**TABLE II.** Total MRCI energies $E_r$(hartree), bond distances $r_e$(Å), dissociation energies $D_e$(kcal/mol), zero point energies $G(0)$(cm$^{-1}$), dipole moments $\mu$(D), and energy gaps $T_r$(kcal/mol) of all MnC states presently studied, in ascending energy order. values in parenthesis refer to MRCI+Davidson correction.

<table>
<thead>
<tr>
<th>State</th>
<th>$-E_r$</th>
<th>$r_e$</th>
<th>$D_e$</th>
<th>$G(0)$</th>
<th>$\langle\mu\rangle/\mu_{pe}^*$</th>
<th>$T_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^4\Sigma^-$</td>
<td>1187.893 01</td>
<td>1.686</td>
<td>64.58</td>
<td>299.80</td>
<td>1.96/2.35</td>
<td>0.0</td>
</tr>
<tr>
<td>(1187.907 4)</td>
<td>(1.681)</td>
<td>(66.7)</td>
<td>(313.6)</td>
<td>(0.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1^4\Sigma^+$</td>
<td>1187.864 76</td>
<td>1.965</td>
<td>46.85</td>
<td>256.24</td>
<td>2.29/2.65</td>
<td>17.73</td>
</tr>
<tr>
<td>(1187.878 0)</td>
<td>(1.948)</td>
<td>(48.2)</td>
<td>(256.4)</td>
<td>(18.5)</td>
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<td></td>
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<tr>
<td>$2^4\Sigma^-$</td>
<td>1187.848 00</td>
<td>2.093</td>
<td>36.33</td>
<td>255.43</td>
<td>2.45/2.75</td>
<td>28.25</td>
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<td>(1187.860 1)</td>
<td>(2.086)</td>
<td>(37.0)</td>
<td>(256.2)</td>
<td>(29.7)</td>
<td></td>
<td></td>
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<tr>
<td>$3^4\Sigma^-$</td>
<td>1187.824 55</td>
<td>2.006</td>
<td>68.74</td>
<td>282.03</td>
<td>1.68/2.05</td>
<td>42.96</td>
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<tr>
<td>(1187.838 11)</td>
<td>(1.995)</td>
<td>(72.0)</td>
<td>(284.2)</td>
<td>(43.5)</td>
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<td>$4^4\Pi$</td>
<td>1187.823 68</td>
<td>1.617</td>
<td>21.21</td>
<td>430.12</td>
<td>4.86/5.21</td>
<td>43.50</td>
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<tr>
<td>(1187.841 3)</td>
<td>(1.618)</td>
<td>(25.2)</td>
<td>(435.2)</td>
<td>(41.5)</td>
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<tr>
<td>$5^6\Delta$</td>
<td>1187.817 76</td>
<td>1.929</td>
<td>47.35</td>
<td>218.44</td>
<td>2.99/3.29</td>
<td>47.22</td>
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<tr>
<td>(1187.833 3)</td>
<td>(1.910)</td>
<td>(49.5)</td>
<td>(228.7)</td>
<td>(46.2)</td>
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<td></td>
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<tr>
<td>$6^6\Pi$</td>
<td>1187.809 72</td>
<td>1.738</td>
<td>12.90</td>
<td>351.99</td>
<td>3.0</td>
<td>52.27</td>
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<tr>
<td>(1187.828 2)</td>
<td>(1.734)</td>
<td>(17.1)</td>
<td>(391.5)</td>
<td>(49.7)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Local minimum

| | | | | | | |
| 1187.805 3 | 2.147 | | | | 214.16 |
| (1187.821 4) | (2.132) | | | | 339.2 |
| 7^4\Pi | 1187.805 36 | 1.792 | 78.46 | 533.03 | 1.98 | 55.0 |
| (1187.816 5) | (2.274) | (9.6) | (179.9) | (57.1) |
| 8^4\Pi | 1187.802 98 | 2.271 | 8.22 | 191.67 | 2.22/2.23 | 56.49 |
| (1187.815 2) | (1.931) | (36.2) | (233.4) | (59.6) |
| 9^6\Sigma^+ | 1187.798 03 | 1.952 | 34.74 | 230.61 | 3.06/3.38 | 59.60 |
| (1187.812 5) | (1.931) | (36.2) | (233.4) | (59.6) |
| 10^4\Pi | 1187.787 71 | 1.930 | 29.17 | 567.94 | 2.85 | 66.08 |
| (1187.805 1) | (1.934) | (31.9) | (461.5) | (64.2) |

Local minimum

| | | | | | | |
| 1187.786 54 | 2.171 | | | | 252.77 |
| 11^4\Pi | 1187.782 25 | 2.021 | 44.87 | 478.14 | 1.7 | 69.51 |
| (1187.799 7) | (2.012) | (48.7) | (448.5) | (67.6) |
| 12^4\Pi | 1187.775 48 | 2.015 | 40.53 | 421.58 | 3.57/4.07 | 73.75 |
| (1187.791 9) | (2.015) | (43.8) | (427.6) | (72.5) |

^* Dipole moments ($\mu$) are obtained as expectation values; $\mu_{pe}$ through the finite field method.

$D_0(\pm Q) = D_e + \text{rel}(\pm Q) - G(0)_{\text{rel}}(\pm Q) + \text{BSSE}(\pm Q)$

$D_0(\pm Q) = 63.82(65.9) - 0.87(0.93) - 0.39(0.42)$

$D_0(\pm Q) = 62.56(64.6)$ kcal/mol.

In order to perform corresponding MRCI calculations but including the semeicore Mn(3s$^2$3p$^6$) electrons, we were forced, because of the extremely large number of ensuing configurations, to remove the three Mn(4p) orbitals from the active space of the zeroth-order (CASSCF) reference function. Within this space our valence MRCI+$Q$ results are $D_e=65.91(66.5)$ kcal/mol at $r_e=1.671(1.667)$ Å as contrasted with $D_e=64.58(66.7)$ kcal/mol and $r_e=1.686(1.681)$ Å. Including core-valence correlation effects we get $D_e=67.66(71.8)$ kcal/mol and $r_e=1.648(1.641)$ Å. Further correcting now for relativity, $G(0)$ and BSSE, we obtain

$D_0(\pm Q) = D_e + \text{rel}(\pm Q) - G(0)_{\text{rel}}(\pm Q) + \text{BSSE}(\pm Q)$

$D_0(\pm Q) = 68.18(71.3) - 1.06(1.17) - 0.39(0.42)$

$D_0(\pm Q) = 66.73(69.7)$ kcal/mol

and $r_e=1.647(1.639)$ Å. Therefore, our “best” $r_e$ and $D_0$ values for the $X^4\Sigma^-$ state of MnC are 1.640 Å and 70 kcal/mol, respectively, an increase of less than 5 kcal/mol as compared with the plain MRCI $D_0$ value.

The first excited state of MnC is of $^6\Sigma^-$ symmetry and lies 17.73(18.5) kcal/mol above the $X$ state at the MRCI($+Q$) level. The interpretation of the wave function’s character at equilibrium is rather difficult due to its dispersion over many CFs. For instance, the sum of the square of the first ten variational coefficients of the leading CFs does not exceed 0.72, the first three of which are given below:

$|1^6\Sigma^-> \approx -0.38|1\alpha^22\alpha^33\alpha^11\delta_1^0$

$\times (1\pi_1^01\pi_2^02\pi_1^1 + 1\pi_1^12\pi_1^01\pi_2^01\delta_1^0)$

$+ 0.28|1\alpha^22\alpha^33\alpha^11\delta_1^04\alpha^11\pi_1^11\delta_1^0$.

However, closer examination and comparison to the $X^4\Sigma^-$ state reveal a simple and quite interesting bonding pattern described by the following structure:

$$X^4\Sigma^-$$

\[
\text{Mn} \equiv C: \longrightarrow \{ \text{Mn} \equiv C: \quad + \quad \text{Mn} \equiv C: \}
\]
The 1 $6\Sigma^-$ state can be described as a “mixture” of two major double bonded structures: a $(\sigma, \pi)$ and $(\pi, \pi)$ one at the expense of a $\pi$ and $\sigma$ bond, respectively, of the $X$ $6\Sigma^-$ state.

The second excited state, which also correlates to the ground state fragments, Mn($^6S$)+C($^3P$; $M_L$ = 0), lies $T\bar{E}$ $= 28.25 (29.7)$ kcal/mol higher and is a high spin octet state $8\Sigma^-$. The main CASSCF equilibrium configurations for this state,

$$|2^{8}\Sigma^-\rangle \approx 0.56 |1\sigma^2\sigma^2\alpha^1\delta^1\pi^4_1\pi^2_1\pi^1_1\pi^1_1\delta^1\rangle + 0.38 |1\sigma^2\sigma^2\alpha^1\delta^2\alpha^1\delta^1\pi^1_1\pi^1_1\pi^1_1\pi^1_1\delta^1\rangle + 1\pi^1_1\pi^1_1\pi^1_1\delta^1\rangle,$$

appear rather puzzling vis-à-vis the interpretation of the chemical bond, but when considered along with those of the $X$ $4\Sigma^-$ and $1$ $6\Sigma^-$ states they reveal a rather “simple” bonding picture visualized by the following Lewis structures.

$$\{ \Phi_{\text{Mn}-\text{C}} \rightarrow \Phi_{\text{Mn}-\text{C}}^* \} \rightarrow \{ \Phi_{\text{Mn}-\text{C}} \rightarrow \Phi_{\text{Mn}-\text{C}}^* \}$$

This state is characterized as a $\sigma$ and $\pi$ bonded system and can be derived directly from the $1$ $6\Sigma^-$ state by breaking a $\pi$ bond from its $(\sigma, \pi)$ and $(\pi, \pi)$ major components. The parental state $X$ $4\Sigma^-$, a $(\sigma, \pi, \pi)$ bonded structure, becomes sequentially a $(\sigma, \pi)/(\pi, \pi)$ state ($1$ $4\Sigma^-$), and finally a $\sigma^*/\pi$ system state ($2$ $3\Sigma^-$). Moving from $X$ $4\Sigma^-$ through $1$ $6\Sigma^-$ to $2$ $3\Sigma^-$, the binding energies decrease monotonically followed by a “logical” increase of the corresponding bond distances: $D_r = 64.58 (66.7)$, 46.85 (48.2), and 36.33 (37.0) kcal/mol, and $r_e = 1.686 (1.681)$, 1.965 (1.948), and 2.093 (2.086) Å, respectively, at the MRCI(+Q) level of theory.

**B. $3$ $6\Sigma^-$ state**

The next state in ascending energy order is (formally) of $6\Sigma^-$ symmetry lying 42.96 (43.5) kcal/mol above the $X$ state. It is practically degenerate with a rival state of $4^2\Pi$ symmetry at 43.50 (41.5) kcal/mol with respect to the ground state. The intense multiconfigurational character of the $3$ $6\Sigma^-$, as evidenced by a dispersion of the MRCI coefficients over many configurations, prohibits any discussion of its bonding features, and consequently no simple vbL structures can be drawn.

The binding energy with respect to the dissociation channel Mn($4s^44p^3d^5$; $^3P$)+C($^3P$) is $D_r = 68.74 (72.0)$ kcal/mol with $r_e = 2.006 (1.995)$ Å at the MRCI(+Q) level of theory. However, it should be noted at this point that Mn($^6P$)+C($^3P$) is not the adiabatic dissociation limit Mn($^6D$)+C($^3P$), which lies below the Mn($^6P$)+C($^3P$) channel with an experimental energy splitting of $\Delta E(8^6P-6^6D) = 0.158$ eV. This “anomaly” is due to the better description of the Mn($^6P$) state than the Mn($4s^43d^5$; $^6D$) one at all levels of calculation, therefore predicting the $5^2P$ state lower than the $6^2D$ by 0.378 eV at the MRCI level. Thus, with respect to the $6^2D$ dissociation energy should be increased by about 0.378 eV or $D_r = 77.5$ kcal/mol. Although our wave function does not conform to the correct dissociation limit, we believe that it behaves reasonably well around equilibrium and includes the necessary ingredients for a balanced and physically acceptable description.

**C. $4^4\Pi$ and $7^4\Pi$ states**

These two $4^4\Pi$ states interact at $-3.4$ bohr as depicted nicely in Fig. 1. The $4^4\Pi$ curve stems from the ground state atoms maintaining this character up to 3.5 bohr where an avoided crossing with the incoming $7^4\Pi$ state is realized. The most characteristic feature of this interaction is the introduction of $4p$ metallic character through the Mn($4s^44p^3d^5$; $^6P$) as evidenced by its $7^4\Pi$ dissociation path, i.e., Mn($^6P$)+C($^3P$). The leading configuration of the $4^4\Pi$ state, along with its Mulliken CASSCF atomic distributions, is

$$|4^4\Pi \rangle \approx 0.74 |1\sigma^2\sigma^2\alpha^1\delta^1\pi^4_1\pi^2_1\pi^1_1\pi^1_1\delta^1\rangle + 0.26 |1\sigma^2\sigma^2\alpha^1\delta^2\alpha^1\delta^1\pi^1_1\pi^1_1\pi^1_1\pi^1_1\delta^1\rangle.$$

This clearly indicates that the Mn atom is in the excited $6P$ state. Notice, that the minimum of the $7^4\Pi$ is located at the avoided crossing with the $4^4\Pi$ state. A second avoided crossing at 2.75 bohr is observed between the $7^4\Pi$ and another $\Pi$ not presently studied.
D. 5 6Δ and 9 6Σ* states

Both states correlate to Mn(4s23d56S)+C(2s22p21D). Due to the spherical symmetry of the metal atom the Λ = 2 or 0+ symmetry of the titled states is the result of the different vector components of the C atom,

\[ |1D; M_L = \pm 2>_{\Lambda_1} = \frac{1}{\sqrt{2}}(2s^2(2p_x^2 - 2p_y^2)) \]

and

\[ |1D; M_L = 0> = \frac{1}{\sqrt{6}}(2s^22p_x^2 - 2s^22p_y^2 - 2s^22p_z^2) \]

At equilibrium they share the same binding characteristics conforming to the main configurations and CASCCF Mulliken populations,

\[ |5 6Δ \rangle \equiv 0.43|1σ^22σ^21δ^13σ^1(1π_x^21π_y^1 - π_x^11π_y^2)1δ^1 \rangle 
\]

\[ 4s_{0.93}p_{0.23}d_{0.05}p_{0.15}d_{0.04}p_{0.15}d_{0.04}d_{1.0} \]

\[ /2s_{1.82}2p_{0.95}2p_{0.80}2p_{0.80}2p_{0.80} \]

and

\[ |9 6Σ^+ \rangle \equiv 0.44|1σ^22σ^21δ^23σ^2 \times (1π_x^21π_y^1 + 1π_x^11π_y^2)1δ^1 \rangle 
\]

\[ 4s_{0.91}p_{0.23}d_{0.04}p_{0.18}d_{0.04}p_{0.18}d_{0.04}d_{1.0} \]

\[ /2s_{1.80}2p_{0.95}2p_{0.81}2p_{0.82} \]

The associated vbL diagram is shown below.

\[
\text{Mn}^{(S)} \quad \text{C}^{(D, M_L = \pm 2 \text{ or 0})}
\]

The two atoms interact attractively through a single σ bond and not via a σ and π as perhaps conveyed misleadingly by the CASCCF configurations. The \( D_{ei}(\text{kcal/mol}) \) and \( r_e(\text{Å}) \) values are 47.35 (49.5), 34.74 (36.2) and 1.929 (1.910), 1.952 (1.931) for the 5 6Δ and 9 6Σ* states, respectively, at the MRCI (+Q) level. The almost identical dipole moments, 2.99 (5 6Δ) and 3.06 (9 6Σ*) D, are also indicative of their similar electronic distributions.

Following the evolution of the bond formation along the potential energy curves of both states, it is easily inferred that in the case of the 5 6Δ state, the character at infinity is maintained along the potential curve, while in the case of the 9 6Σ* the repulsive \( 2s^22p^2 \) component of the C(1D; \( M_L = 0 \)) term is gradually decreased up to around 6.2 bohrs projected in the hump of its potential energy curve (Fig. 1). By reasons of symmetry this “unclogging” interaction should be provided by a 6Σ* state resulting from the C(1S) atomic state.

E. 6 11II, 10 6II, and 11 6II states

These states are discussed together because of their interwoven behavior for several regions of the Mn–C distance. The 6 11II results from the interaction of the ground state atoms, Mn(6S)+C(3P), whereas the 10 6II state correlates to Mn(6S)+C(1D). The 11 6II is expected to dissociate adiabatically to Mn(4s23d56S)+C(3P), but due to its poor description at all levels of theory, this channel lies above the experimentally higher Mn(4s24p3d56P) atomic term, which also gives rise to 6II states. Consequently, and incorrectly, this state arises from the Mn(6S)+C(3P) separated atom limit. We believe, however, that close to equilibrium the natural content of the wave functions is adequately described.

Notwithstanding the intense multiconfigurational, and rather blurry character of these sextet II states, we will try to comment upon their most important features. The local minimum (l) of the 6 11II state is dominated by a configuration that reflects its character at infinity, i.e.,

\[ |6 11II \rangle_l \equiv 0.48|1σ^22σ^23σ^14σ^1π_x^21π_y^11δ^1 \rangle , \]

and

\[ 4s_{1.05}p_{0.41}d_{0.03}p_{0.09}d_{0.04}p_{0.02}d_{1.0}d_{1.0}d_{1.0}d_{1.0} \]

\[ /2s_{1.87}2p_{0.87}2p_{0.21}2p_{0.21} \]

while its global minimum (g), past an avoided crossing at around 3.7 bohrs, is dominated by the character of the third 6II (11 6II) state that carries the memory of the Mn(4s24p3d56S; 8P; \( M_L = \pm 1 \)) atomic term,

\[ |6 11II \rangle_g \equiv 0.72|1σ^22σ^23σ^1δ^11π_x^1π_y^21π_y^11δ^1 \rangle , \]

and

\[ 4s_{0.78}p_{0.17}d_{0.93}p_{0.03}d_{1.0}p_{0.41}d_{1.9}d_{1.0}d_{1.0}d_{1.0}d_{1.0}d_{1.0} \]

\[ /2s_{1.69}2p_{0.48}2p_{0.82}2p_{0.13} \]

The 10 6II and 11 6II states are more entangled as evidenced by the potential energy curves of Fig. 1 and, consequently, their character is difficult to be analyzed. The local (l) minimum of the 10 6II state is

\[ |10 6II \rangle_l \equiv 0.48|1σ^22σ^23σ^1δ^11π_x^1π_y^11π_y^11δ^1 \rangle + 0.41|1σ^22σ^23σ^1δ^14σ^1π_x^1π_y^11δ^1 \rangle 
\]

\[ - 0.29|1σ^22σ^23σ^1δ^14σ^1π_x^1π_y^11δ^1 \rangle 
\]

\[ - 0.23|1σ^22σ^23σ^1δ^11π_x^1π_y^11δ^1 \rangle , \]

whereas its global (g) minimum is situated very close to an avoided crossing with the higher located 11 6II state, and is a mixture of different bonding schemes:

\[ |10 6II \rangle_g \equiv 0.44|1σ^22σ^23σ^1δ^14σ^1π_x^1π_y^11δ^1 \rangle + 0.40|1σ^22σ^23σ^1δ^11π_x^1π_y^11δ^1 \rangle 
\]

\[ - 0.24|1σ^22σ^23σ^1δ^14σ^1π_x^1π_y^11δ^1 \rangle + 0.21|1σ^22σ^23σ^1δ^11π_x^1π_y^11δ^1 \rangle . \]

This makes its “chemical” interpretation unwieldy. The last avoided crossing with the 11 6II state is located around 3.1 bohr; past this point the two curves interchange their bonding character.

The case of the 11 6II state is further complicated by the fact that its minimum is situated on the avoided crossing
with the previously discussed $^{6}\mathrm{II}$. Its major components at the minimum convey a rather “fuzzy” situation,

\[
|^{11}\mathrm{II}\rangle \approx 0.54|\sigma^2 \sigma^2 \sigma^2 1 \delta^2 \pi^2 1 \pi^2 1 \delta^2 \rangle \\
+ 0.29|\sigma^2 \sigma^2 \sigma^2 1 \delta^2 4 \delta^2 1 \pi^2 1 \pi^2 1 \delta^2 \rangle \\
- 0.22|\sigma^2 \sigma^2 \sigma^2 1 \delta^2 4 \delta^2 1 \pi^2 1 \pi^2 1 \delta^2 \rangle \\
- 0.22|\sigma^2 \sigma^2 \sigma^2 1 \delta^2 4 \delta^2 1 \pi^2 1 \pi^2 1 \delta^2 \rangle.
\]

**F. $^{8}\mathrm{II}$ and $^{12}\mathrm{II}$ states**

The $^{8}\mathrm{II}$ state dissociates to ground state fragments, i.e., Mn(6S) + C(3P) $; M_L = \pm 1$. Its equilibrium CASSCF configuration

\[
|^{8}\mathrm{II}\rangle \approx 0.95|\sigma^2 \sigma^2 \sigma^2 1 \delta^2 4 \delta^2 1 \pi^2 1 \pi^2 1 \delta^2 \rangle
\]

reflects its parental character, which is, however, lost after an avoided crossing at around 3.8 bohr with the $^{12}\mathrm{II}$ state. By comparing the $^{8}\mathrm{II}$ with the main configuration of the $|^{6}\mathrm{II}\rangle$ state, we observe that it results from the latter by breaking a $\pi$ bond.

The $^{12}\mathrm{II}$ state, the highest of all states studied here, dissociates to Mn(6P) + C(3P), although its correct adiabatic limit is Mn(6D) + C(3P). The $^{8}\mathrm{P}$ atomic term introduces 4p metallic character, which is evident both in its equilibrium configurations and in the $^{8}\mathrm{II}$ state after the avoided crossing. The minimum, in the region of the interaction with the $^{8}\mathrm{II}$ state, is a mixture of both bonding schemes,

\[
|^{12}\mathrm{II}\rangle \approx 0.55|\sigma^2 \sigma^2 \delta^2 \pi^2 1 \pi^2 1 \pi^2 1 \delta^2 \rangle \\
- 0.49|\sigma^2 \sigma^2 \delta^2 \pi^2 1 \pi^2 1 \pi^2 1 \delta^2 \rangle,
\]

hampering a chemical interpretation along the traditional path.

**IV. SUMMARY**

We have reported, for the first time, high level *ab initio* results on 13 states of the experimentally unknown MnC. Most of the molecular states have intense multiconfigurational character, thus rendering MRCI the only suitable method to treat such complicated cases. The X state is of $^{3}\Sigma^{-}$ symmetry featuring three bonds: a $\sigma$ and two $\pi$ bonds with a suggested $D=70.0$ kcal/mol at $r_c = 1.640$ Å. All of states studied here are bound with respect to their dissociation limits and cover an energy range of 74 kcal/mol. Dipole moments have been calculated both as expectation values ($\langle \mu \rangle$) and by the finite field method ($\mu_{FF}$); in all examined states $|\mu_{FF}| > |\langle \mu \rangle|$ by 0.3–0.4 D, and according to our experience [see also Refs. 1(i) and 1(j)], $\mu_{FF}$ values are to be trusted more than the $\langle \mu \rangle$ ones.


6. H.-J. Werner, P. J. Knowles, R. D. Amos et al., MULTIFRO, a package of *ab initio* programs, version 2002.6 (Birmingham, UK, 2002).