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Density Functional Study of the Photodissociation of Mn$_2$(CO)$_{10}$

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Potential energy curves (PECs) have been calculated for a number of excited states of Mn$_2$(CO)$_{10}$, along the Mn−Mn bond dissociation coordinate and along Mn−CO$_{ax}$ and Mn−CO$_{eq}$ coordinates, in order to understand why irradiation into the $\sigma$ → $\pi^*$ band does not only lead to Mn−Mn bond breaking but also to Mn−CO dissociation. Mn−Mn bond homolysis can straightforwardly occur along the dissociative $\sigma$ → $\sigma^*$ $^3B_2$ PEC. The $\sigma$ → $\sigma^*$ excited state is not itself Mn−CO dissociative. CO dissociation occurs since PECs that correspond at equilibrium geometry to d$_{\pi}$ → $\sigma^*$ $^1E_1$ excited states (nearly degenerate with the $\sigma$ → $\sigma^*$ excited state) are Mn−CO$_{ax}$ dissociative (both $^1E_1$ and $^3E_1$, $^1E_2$ in C$_4v$) or Mn−CO$_{eq}$ dissociative (only just, and only the b$^2A'$ component (in C$_h$) of $^3E_1$). The Mn−CO dissociative characteristic has been traced to the precipitous lowering of the initially high-lying Mn−CO $\sigma$-antibonding (3d$_{eg}$-like) orbitals upon Mn−CO bond lengthening, making them considerably lower than $\sigma^*$ in Mn$_2$(CO)$_{9}$. Excitations to these orbitals (the ligand-field (LF) excitations) are at high energy in Mn$_2$(CO)$_{10}$, much higher than the $\sigma$ → $\sigma^*$ and d$_{\pi}$ → $\sigma^*$ excitations. However, the energy of these LF excited states very rapidly goes down upon Mn−CO bond lengthening, they cross the $\sigma$ → $\sigma^*$ and d$_{\pi}$ → $\sigma^*$ excited states, and the energy lowering of the LF excitation energy in Mn$_2$(CO)$_{10}$ with respect to the lowest excitation energies in Mn$_2$(CO)$_{10}$ to $^3B_2$ $\sigma$ → $\sigma^*$ and $^1E_1$ d$_{\pi}$ → $\sigma^*$, provides the energy for the Mn−CO bond breaking.

\[ \text{Mn}_2(\text{CO})_{10} \xrightarrow{hv} 2\text{Mn(CO)}_5 \]  

on the excitation wavelength. Generally it was found that low-energy excitation favors metal−metal bond homolysis, while higher energy excitation leads mostly to the generation of Mn$_{10}$−(CO)$_9$. Kobayashi et al. have measured the quantum yields of processes 1 and 2, $Y_1$ and $Y_2$, at different excitation wavelengths. They obtained a ratio $R = Y_1/Y_2$ of 0.19, 0.43, and 1.1 at $\lambda_{ex} = 266$, 337, and 355 nm, respectively.

Gas-phase photodissociation studies of Mn$_2$(CO)$_{10}$ are consistent with the photochemistry of the molecule in solution. Excitation at 350 nm of Mn$_2$(CO)$_{10}$ in the gas-phase produces Mn−Mn bond homolysis and CO loss, while excitation at 248 and 193 nm only leads to CO loss. In spite of the intense experimental work on the photochemistry of Mn$_2$(CO)$_{10}$ developed during the past decade, thanks to the availability of very sophisticated identification techniques, the mechanism of the primary photochemical processes is far from being understood. Whether Mn−Mn and Mn−CO cleavage originate from the same or from different excited states and why the relative quantum yields of the photoproducts depend on the excitation wavelength is still crucial questions concerning the photochemistry of Mn$_2$(CO)$_{10}$ that are basically unanswered. With the aim of locating the possible photoactive excited states of Mn$_2$(CO)$_{10}$, we have recently investigated the nature of the excited states involved in the electronic spectrum of this compound and their corresponding excitation energies. A significant point to arise from our calculations is that only two transitions, i.e., d$_{\pi}$ → $\sigma^*$ (8e$_{ax}$ → 10b$_2$) and $\sigma$ → $\sigma^*$ (10a$_1$ → 10b$_2$) are responsible for the low-energy excitations (bands I

Photodissociation of Mn$_2$(CO)$_{10}$ and II) at 337–375 nm. [We stick to a notation where $\sigma$, $\pi$, and $\delta$ labels refer to the Mn–Mn axis and $\sigma$, $\sigma^*$, $\pi$, $\pi^*$, and $\delta^*$ indicate the Mn–Mn bonding respectively, antibonding character of the MO.] Possibly Mn–CO dissociative ligand field (LF) states are not close but occur at much higher energies. Excitation at low energy, in the experimental range 337–355 nm, will then bring the molecule either into the $\sigma \rightarrow \sigma^*$ $B_2$ or into the $d_{z^2} \rightarrow \sigma^*$ $E_1$ spin allowed excited state. This implies that the states arising from $d_{z^2}$ $\rightarrow \sigma$ and $\sigma \rightarrow \sigma^*$ dominate the photochemistry of Mn$_2$(CO)$_{10}$ upon excitation in the range 337–355 nm.

There can be little doubt that the respectively Mn–Mn bonding and antibonding nature of the $\sigma$ and $\sigma^*$ with respect to metal–metal cleavage makes the state $B_2$ corresponding to the $\sigma \rightarrow \sigma^*$ excitation photoactive with respect to Mn–Mn cleavage. However, we have found a remarkable lack of metal–CO antibonding character in the $\sigma^*$ orbital, and it seems unlikely that either the $\sigma \rightarrow \sigma^*$ $B_2$ state or the $d_{z^2} \rightarrow \sigma$ $E_1$ state would lead to CO loss. However, even if these states would not be photoactive by themselves for the dissociation of a carbonyl ligand, photodissociation of a carbonyl ligand at low energy might still occur upon excitation in these states if crossing occurs to the potential energy surfaces of excited states which are dissociative with respect to a metal–carbonyl bond. In our previous study we have identified LF type excitations to states that are probably Mn–CO dissociative (basically $d \rightarrow \sigma'$) and to states that are probably Mn–CO$_2$ dissociative ($d \rightarrow dp(\pi)$). We recall that we have denoted in our previous paper as $\sigma'$ and $\sigma''$ the 11$a_1$ and 11$b_2$ MOs, with considerable $d_z^2$ character, that are quite strongly antibonding with respect to the axial carbonyl ligands. The $dp(\pi)$ is the high-lying $9e_2$ ($d_z^2 - 2\gamma$) which is strongly antibonding with the $5\sigma$'s of the equatorial COs.

Since these presumably Mn–CO dissociative $d \rightarrow d$ excitations occur at much higher energy than the $\sigma \rightarrow \sigma^*$ and $d_{z^2} \rightarrow \sigma^*$ excitations, explicit calculations of potential energy surfaces (PESs) or the more readily visualized potential energy curves (PECs) are required to verify the crossing suggested above as possible explanation for the Mn–CO dissociation. The PEC curves provide the most important features of the energy profile of the primary photodissociative pathways, as proved for a number of organometallic systems.17–24 We have calculated, using a density functional approach, the ground- and excited-state potential energy curves corresponding to the homolysis of the Mn–Mn bond and to the dissociation of an axial as well as an equatorial carbonyl ligand.

### Method and Computational Details

The calculations reported in this paper are based on the Amsterdam density functional (DF) program package,25,26 characterized by the use of a density fitting procedure to obtain accurate Coulomb and exchange potentials in each self-consistent field (SCF) cycle, by accurate and efficient numerical integration of the effective one-electron Hamiltonian matrix elements and by the possibility to freeze core orbitals.

In order to improve the reliability of the computed potential energy curves, the integration accuracy and the fit set have been increased with respect to our previous calculations of the ground and excited states of Mn$_2$(CO)$_{10}$.

The molecular orbitals were expanded in an uncontracted double-$\zeta$ STO basis set for all atoms with the exception of the 3d Mn orbitals for which we used a triple-$\zeta$ STO basis set. As polarization functions one 4p STO was used for Mn atom. The cores (Mn, 1s–2p; C, O, 1s) have been kept frozen.

Three theoretical DF models have been adopted in the calculation of the energies of the reactants, of the products as well as of the dissociating system along the reaction paths, i.e., (i) the local spin density approximation, LSDA, characterized by the electron gas exchange (Xa) with $\alpha = 7/2$ together with the Vosko–Wilk–Nusair parameterization for correlation; (ii) the LSDA plus Becke’s29 nonlocal corrections to the exchange energy; (iii) the LSDA plus Becke’s nonlocal corrections to the exchange energy and Perdew’s30 nonlocal corrections to the correlation energy. However, we will report here only the potential energy curves calculated including both Becke’s and Perdew’s nonlocal corrections. This model represents to date one of the most efficient and accurate methods for the evaluation of bond energies within a DF framework, as shown by calculations on metal carbonyls,31 binuclear metal complexes32 including Mn$_2$(CO)$_{10}$ (see next sections), alkyl and hydride complexes,33 and complexes containing metal–ligand bonds for a number of different ligands.34 The calculations for Mn$_2$(CO)$_{10}$ were performed for the optimized geometry in $D_{4h}$ experimental symmetry (Figure 1). Potential energy curves were computed for the reaction paths corresponding to the Mn–Mn cleavage (Scheme 1), the loss of an axial (Scheme 2), and an equatorial (Scheme 3) carbonyl ligand, with the following assumptions:

(i) $D_{4h}$ symmetry is retained along the reaction path corresponding to the homolysis of the metal–metal bond. Support for this assumption comes from the fact that Mn(CO)$_3$ has $C_{3v}$ symmetry in its ground state.35,36 Bond lengths (except for the bond which dissociates) and

![Figure 1. Optimized structure of Mn$_2$(CO)$_{10}$ in $D_{4h}$ symmetry (bond distances in angstroms).](image-url)
the angle $C_{eq, MnMn}, \theta$, were optimized for each point along the reaction path. Geometry optimizations have always been performed at the LSDA level of theory using gradient techniques.\(^{37}\)

(ii) $C_{eq}$ and $C_{ax}$ symmetries respectively are retained along the reaction paths corresponding to the loss of an axial and an equatorial CO. By this hypothesis we assume that the primary product, $\text{Mn}_2\text{(CO)}_9$, is formed in a purely metal–metal bonded structure of $C_{eq}$, or $C_{ax}$ symmetry with an axial or an equatorial vacancy. Support for this assumption comes from the fact that, as has been recently demonstrated,\(^{12,28,39}\) the formation of a linear semibridged structure, $\text{Mn}_2\text{(CO)}_9(\mu-\eta^1:\eta^2\text{-CO})$ occurs only via secondary photolysis of a solvento species, $\text{Mn}_2\text{(CO)}_{10}$–(solv), which is the initial product following CO loss.

As for the dissociation of an axial CO, all geometrical parameters, except for the dissociating bond, were optimized for all the points on the potential energy curve.

As for the dissociation of an equatorial CO, in order to keep the calculations tractable, the bond parameters, except for the bond which dissociates, were kept constant along the reaction pathway. This assumption is justified by the following arguments: (i) the optimized structure of $\text{Mn}_2\text{(CO)}_9$ of $C_{eq}$ symmetry derived from $\text{Mn}_2\text{(CO)}_{10}$ with an equatorial vacancy does not show significant differences compared to the non-optimized one; (ii) during the reaction path corresponding to the axial CO loss the geometrical parameters also remain almost unchanged.

Excitation energies and singlet/triplet splittings have been computed according to the method by Ziegler et al.\(^{40}\) It is well-known that excited states of a metal within DFT than the ground state. Attempts to put the calculation of excited state energies on a similar basis as ground state energies\(^{41}\) have not yet led to practical schemes due to the theoretically defined functionals being unknown. Just using existing approximate functionals in this scheme\(^{42}\) leads to rather poor results. The method of ref 40 has been shown to yield quite accurate transition-state barriers on the ground state potential energy surface during a reaction.\(^{50}\) This would then be expected to hold true for an avoided crossing type barrier on the first excited state surface of a given symmetry as well. Our conclusions will all refer to the lowest excited state surfaces. We will also calculate higher excited states with the current method, as has been successfully done before at equilibrium geometries, but we will keep in mind the possibly larger errors for those excited state energies and will avoid overinterpreting them.

Metal–Metal Photodissociation

Before we comment on the essential features of the curves of the excited states connecting the reactant to the products along the reaction path shown in Scheme 1, it is useful to check whether the structures of the reactant and the products and their relative stabilities are correctly reproduced by our calculations, since this will ensure that the potential energy curves have the right slope.

As concerns the primary photoproduct following the homolytic cleavage of the $\text{Mn–Mn}$ bond, $\text{Mn(CO)}_3$ radical, experiments by Church et al.\(^{35}\) have demonstrated that this species has square-
Table 1. Comparison of the Calculated Metal–Metal Bond Energy, \( D(\text{Mn–Mn}) \), and First Ligand Dissociation Energies in \( \text{Mn}_2(\text{CO})_{10} \) with Experiments (Bond Energies, \( \text{kJ mol}^{-1} \))

<table>
<thead>
<tr>
<th>method</th>
<th>( E^{\text{LSDA}}_b )</th>
<th>( E^{\text{LSDA}}_a + E^{\text{LSDA}}_c )</th>
<th>( E^{\text{LSDA}}_f + E^{\text{LSDA}}_d )</th>
<th>( \text{expt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D(\text{Mn–Mn}) ) (^b)</td>
<td>258</td>
<td>28</td>
<td>135</td>
<td>104 ± 3; 79 ± 14 (^i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>88 ± 13; 94 (^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≥154; 171 (^i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>159 ± 21; ≥176 (^a)</td>
</tr>
</tbody>
</table>

\( \Delta H_{a} \) | 305 | 126 | 200 | |
\( \Delta H_{b} \) | 292 | 73 | 177 | 159 \(^a\) |
\( \Delta H_{d} \) | 261 | 76 | 165 | |

\(^a\) Bonding energy calculated by LSDA method. \(^b\) Bonding energy calculated combining nonlocal exchange correction by Becke with LSDA. \(^c\) Bonding energy calculated combining nonlocal corrections of both Becke and Perdew with LSDA. \(^d\) The calculated bonding energy \( D(\text{Mn–Mn}) = [2\Delta E_{\text{LSDA}} - \Delta E_{\text{CO}}] \) is with respect to the fragments in their ground state optimized geometries. \(^e\) Electron impact mass spectrometry from ref 56. \(^f\) Electron impact mass spectrometry from ref 57. \(^g\) Equilibrium studies using electron impact mass spectrometry from ref 57. \(^h\) Thermochemical estimate from ref 58. \(^i\) Kinetic studies in solution from refs 59 and 60. \(^j\) Electron impact mass spectrometry/photoelectron spectroscopy from ref 61. \(^k\) Photoacoustic calorimetry determination from ref 62. \(^l\) Laser photolysis from ref 63. \(^m\) The axial and equatorial CO dissociation energies, \( \Delta H_{a} \) and \( \Delta H_{b} \), corresponding to the process \( \text{Mn}_2(\text{CO})_{10} \rightarrow \text{Mn}_2(\text{CO})_{9} + \text{CO} - \Delta H \), is with respect to CO and a \( \text{Mn}_2(\text{CO})_8 \) fragment in a purely metal–metal bonded structure with an axial or equatorial vacancy, optimized within \( C_n \), \( C_4 \), or \( C_4^* \) symmetry constraint (see Figure 3a,b). \(^n\) The first ligand bonding energy, \( \Delta H_{ab} \), corresponding to the process \( \text{Mn}_2(\text{CO})_{10} \rightarrow \text{Mn}_2(\text{CO})_9 + \text{CO} - \Delta H \) is with respect to CO and a \( \text{Mn}_2(\text{CO})_9 \) fragment in a semibridged structure optimized within \( C_n \) symmetry constraint (see Figure 3d). \(^o\) References 63 and 65.

pyramidal, \( C_4 \) structure with an apical-basal Mn–CO bond angle of 96 ± 3\(^\circ\), and recent calculations\(^{65,61}\) also give the \( C_{4v} \) structure as the most stable one. The geometry of \( \text{Mn}_2(\text{CO})_{10} \) has been investigated by electron diffraction in the gas phase\(^{62}\) and by X-ray diffraction at room temperature\(^{53}\) and at 74 K.\(^{54}\) All of these experiments lead to nearly the same geometry, which is consistent with a \( D_{4h} \) symmetry. Functional density calculations by Folga and Ziegler\(^{51}\) give the eclipsed structure (\( D_{4h} \)) higher in energy by 142.4 \( \text{kJ mol}^{-1} \) than the staggered one. Since the \( \text{Mn}_2(\text{CO})_8 \) (\( C_{4v} \)) and \( \text{Mn}_2(\text{CO})_{10} \) (\( D_{4h} \)) optimized structures that we have recently calculated\(^{60}\) show reasonable agreement between theoretical and experimental geometries, we stick here to those geometries.

From the values of Table 1, where we report the metal–metal bond energy \( D(\text{Mn–Mn}) \) calculated using different theoretical DF models, the process \( \text{Mn}_2(\text{CO})_{10} \rightarrow 2\text{Mn}(\text{CO})_5 \) is calculated to be endothermic. One will notice that the LSDA overestimates considerably the metal bond energy; the addition of Becke’s nonlocal exchange correction yields a bond energy which is much too low. Adding however the nonlocal correlation correction yields a metal–metal bond energy which is in the range of the most recent experimental values obtained for \( D(\text{Mn–Mn}) \).\(^{55–63}\) Due to limitations in the present calculations, in particular with respect to the basis set, the theoretical value for \( D(\text{Mn–Mn}) \) is not the definitive density functional result, but it should be fairly close. We will present a comprehensive treatment of the effect of computational approximations to \( D(\text{Mn–Mn}) \) and other quantities elsewhere.

In order to locate possible photoactive states in the high-energy region of the spectrum, we have computed the potential energy curves for the \( \text{B}_2 \) and \( \text{E}_1 \) (these are the only symmetry allowed excitations in \( D_{4h} \) symmetry) excited states up to the \( \text{B}_2 \) state (\( \sigma \rightarrow \sigma^* \)), which is the highest state that may play a role in the \( \text{Mn–Mn} \) photodissociation, given the \( \text{Mn–Mn} \) bonding and antibonding characters respectively of the \( \sigma \) and \( \sigma^* \) orbitals. A selection of these curves is reported in Figure 2 (for clarity, six \( \text{E}_1 \) curves in this energy range have been omitted).

The \( \text{A}_1 \) ground state potential energy curve is rather flat near the minimum (see Figure 2), a feature also present in the potential curve computed by Veillard and Rhomer\(^{64}\) by configuration interaction (CI) calculations.

As expected, the \( \text{A}_1 \) potential energy curve corresponding to the \( \sigma \rightarrow \sigma^* \) excitation is strongly dissociative with respect to the \( \text{Mn–Mn} \) bond. The molecule will dissociate along this curve to the \( \text{Mn}(\text{CO})_5 \) radicals in their 2\( \text{A}_1 \) ground states. According to the experimental findings,\(^{14}\) recombination of the two \( \text{Mn}(\text{CO})_5 \) radicals to form \( \text{Mn}_2(\text{CO})_{10} \) will then easily occur along the ground state potential energy curve.

The corresponding \( \text{A}_1 \) potential energy curve shows a shallow minimum at a very large \( \text{Mn–Mn} \) distance (around 4 \( \AA \)), indicating that the \( \text{A}_1 \) state is a bound state, although the metal–metal bond is considerably weakened. Note that the \( \text{A}_1 \) curve between 4.5 \( \AA \) and infinity is just sketched, since no points at these large distances have been calculated. If the \( \text{A}_1 \) state would correspond to a \( \sigma \rightarrow \sigma^* \) excitation between the bonding and antibonding orbitals of a simple electron pair bond, a minimum in the \( \text{A}_1 \) curve would be expected and the dissociation would lead to \( \text{Mn}_2(\text{CO})_5^+ \) and \( \text{Mn}(\text{CO})_3^- \) moieties. However, although the triplet and singlet states arising from the \( \sigma \rightarrow \sigma^* \) excitation

\(^{(61)}\) Simões, M.; Beauchamp, J. L. Organometallics 1985, 4, 1238.
behave largely as expected for a prototype electron pair bond, the singlet excited state does not asymptotically go to ions since it will change through an avoided crossing (not drawn in the figure) to the obviously much lower 1B2 state arising from one Mn(CO)5 in its b2A1 excited state and the other one in its a2A1 ground state. The a1E1 potential energy curves corresponding to the dπ → σ* (8e1 → 10b2) excitation are weakly dissociative, although they show a very shallow minimum around 3.50 Å. This implies that both dπ → σ* and σ → σ* excitations may lead to Mn-Mn cleavage. An interesting feature shown by the potential energy curves reported in Figure 2 is the close proximity of the a1E1 and a1B2 PECs near the Mn-Mn equilibrium distance. We will see below that this feature has some relevance in the explanation of the concomitant Mn-Mn and Mn-CO bond photodissociation at low energy.

Coming now to the higher energy excited states, the 1/2E1 states from b upward are not photoactive with respect to Mn-Mn cleavage, although most of them correspond to excitations which depopulate the σ orbital. This is the case, for instance, for the b1/2E1 (σ → 2π*) states whose PECs are shown in Figure 2. Comparing the behavior of the b1/2E1 states, which correspond to depopulation of the Mn-Mn σ-bonding orbital, with that of the a1/2E1 states, which correspond to population of the Mn-Mn σ-antibonding orbital, suggests that depopulation of the σ-bonding orbital has a less detrimental effect on the Mn-Mn bond than population of the Mn-Mn antibonding σ* orbital, which in the case of the a1/2E1 states is by itself sufficient to break the bond.

As for the high-energy 3B2 and 1B2 states, these are not dissociative, although the b2B2 is barely bound indeed. The c1B2 and d1B2 correspond at the equilibrium distance to σ → σ* excitations. The triplet σ → σ* excited state moves through an avoided crossing from the c1B2 to the b2B2 state around 3.0 Å. Beyond this distance the b2B2 PEC corresponds to the σ → σ* excitation. Although it is not visible in the features of the PECs (more points would be required to resolve such detail), the singlet σ → σ* excited state traverses through avoided crossings from the d1B2 PEC to the c1B2 and b2B2 states between the equilibrium distance and 3.5 Å. At 3.5 Å the b2B2 state corresponds to the σ → σ* excitation.

Clearly high-symmetry allowed excitation into one of the c.d1B2 states does not bring the system into a photoactive state with respect to Mn-Mn bond dissociation. A possible mechanism for Mn-Mn bond dissociation, which will have to compete with Mn-CO bond breaking (see below), would consist of the molecule reaching through intersystem crossing the c1B2 and dissociating after crossing to a vibrationally excited b1B2 state. Such crossings may take place more efficiently in solution than in the gas phase. As a matter of fact, gas-phase photoexperiments indicate that excitation at λ ≤ 248 nm (the calculated excitation energy to d1B2 is 249 nm) only leads to CO loss,15 while solution photoexperiments indicate that excitation at λ ≤ 266 nm leads to both processes, CO loss and Mn-Mn cleavage;5-14 although the quantum yield of the latter is very low.

Phosphorization of a Carbonyl Ligand

As already mentioned, it is well-established that Mn2(CO)9 is the primary photoproduct following the loss of a carbonyl ligand, be it axial or equatorial. Since this is a transient species, informations regarding its structure have only been indirect, although matrix isolation experiments have been interpreted in terms of a linear semibridged structure.8,11 The only available calculations concerning the structure of Mn2(CO)9 were performed by Veillard and Rhomer,64 using ab initio methods. Four different structures have been investigated by these authors: two purely metal-metal bonded structures of C4, and C4 symmetry corresponding to the departure of one axial and respectively of one equatorial ligand from Mn2(CO)10, one dissymmetric structure of C3 symmetry with a semibridging carbonyl, and one symmetric with a classical CO bridge, of C2 symmetry. The authors however note some limitations of these calculations, in particular the use of fixed geometries. In order to get a more reliable evaluation of their relative stabilities, geometry optimization of these structures would be required. With this aim we have reinvestigated the structures proposed by Veillard and Rhomer as the most likely for Mn2(CO)9, including a purely metal-metal bonded structure, of C4 symmetry, with an equatorial vacancy and in the eclipsed configuration. This is also a possible structure for Mn2(CO)9 following the loss of an equatorial carbonyl from Mn2(CO)10. We have not attempted any calculation for the structure with a classical CO bridge since, according to the Veillard and Rhomer calculations,64 it is much higher in energy than the other ones. Similarly, structures with several bridging carbonyls have not been considered in this study. The optimized geometries for the investigated Mn2(CO)9 structures are reported in Figure 3.

All of these structures have a closed-shell ground state. From our calculations the structure with a semibridging carbonyl group Mn2(CO)9(μ-η1:η1-CO) is the lowest in energy, in agreement with the experimental findings,8,11 but in disagreement with CI calculations by Veillard and Rhomer64 that give the linear semibridged structure as much less stable than the two purely metal-metal bonded C4i (with an axial vacancy) and C3 (with an equatorial vacancy) structures. This discrepancy might be due to the fact that in the CI calculations the structures were not allowed to relax.

Concerning the relative stabilities of the different structures of Mn2(CO)9, we note that, compared to the linear semibridged structure, the staggered conformation of Mn2(CO)9 with an equatorial vacancy (Figure 3b) is only 12 kJ mol−1 less stable, while the eclipsed one (Figure 3c) is much higher in energy (41 kJ mol−1), indicating that the rotation barrier between these two conformations is not negligible. Furthermore, the energies of the purely metal-metal bonded structures of Mn2(CO)9 corresponding respectively to the departure of one axial and of one equatorial ligand from Mn2(CO)9 (Figure 3a,b) differ by 23 kJ mol−1, while Veillard and Rhomer64 find an energy difference of only 3 kJ mol−1.

Although our calculations indicate the semibridged structure as the most stable one for Mn2(CO)9, one should remember that it is not a primary photoproduct. As we already pointed out, this species is formed via secondary photolysis of a solvent compound, Mn2(CO)9(solv) (where solv represents a solvent molecule), which is clearly the prominent initial product following CO loss from Mn2(CO)10.28,36 The rate constant and the enthalpy of activation for semibridge formation from the solvent species have been recently estimated by Zhang et al.12 to be 1 × 106 s−1 and ~21 kJ mol−1, respectively. It seems quite reasonable then to consider as primary photoproducts following CO loss the purely metal-metal bonded structures of Mn2(CO)9, corresponding to the departure of one axial (see Figure 3a) or of one equatorial ligand (see Figure 3b), rather than the most stable semibridged structure. In fact the coordinatively unsaturated structures with an axial or an equatorial vacancy are the most likely precursors of the solvento species, being suitable for reaction with solvent molecules. Unfortunately, gas-phase experiments available to date do not give any indication about the structure of Mn2(CO)9 following CO loss.
We have computed, using different theoretical DF models, the energetics of the process \( \text{Mn}_2(\text{CO})_9 \rightarrow \text{Mn}_2(\text{CO})_9 + \text{CO} \) considering \( \text{Mn}_2(\text{CO})_9 \) in the purely metal–metal bonded structures mentioned above and, for comparison purposes, in the semibridged structure. The energy values, referred to as \( \Delta H_{\text{ax}} \), \( \Delta H_{\text{eq}} \), and \( \Delta H_{\text{sb}} \), respectively, are reported in Table 1 and compared to the only available first carbonyl ligand dissociation enthalpy of \( \text{Mn}_2(\text{CO})_9 \).\(^{63,65}\) As expected, on the basis of the relative stabilities of the \( \text{Mn}_2(\text{CO})_9 \) structures, the dissociation of an axial carbonyl requires more energy compared to the dissociation of an equatorial carbonyl.

Again it is found that adding the nonlocal exchange and correlation corrections to the LSDA energy expression improves considerably the agreement between theory and experiment. The \( \Delta H_{\text{ax}} \) and \( \Delta H_{\text{eq}} \) computed using the nonlocal exchange and correlation corrections are in reasonable agreement with the experimental datum, although the best value is obtained considering \( \text{Mn}_2(\text{CO})_9 \) in its most stable configuration. The relative stabilities of the reactant and the products corresponding both to axial and equatorial CO loss are correctly reproduced by our calculations, and this assures that the potential energy curves for the loss of a carbonyl ligand will have the right slope.

**Potential Energy Curves for the Loss of an Axial Carbonyl Ligand.** Before discussing the features of the PEC for the dissociation of a carbonyl ligand, it is useful to look at the level scheme of Figure 4 that we have constructed in order to follow the evolution of the \( \text{Mn}_2(\text{CO})_{10} \) MOs on elongating the Mn–COax bond to the dissociation limit. As far as the highest occupied levels are concerned, we note that, upon the lengthening of the Mn–COax bond, the 10a1-\( \sigma^* \) (19a1 in \( C_2V \) symmetry) level remains almost unchanged, while the 8e2-dz\(^*\) (16e1 in \( C_2V \) symmetry) is destabilized and becomes the highest occupied orbital when the Mn–COax distance is 2.5 Å. This is understandable in view of the negligible COax participation to the 10a1-\( \sigma^* \) and the Mn–COax \( \pi \) bonding character of the 8e2-dz\(^*\) (we refer to ref 16 for a detailed discussion of the characteristics of the various occupied and virtual orbitals).

The most interesting features of the scheme of Figure 4 are however concerned with the behavior of some virtual levels, namely, 10b2-\( \sigma^* \), the 11a1-\( \sigma^* \), and 11b2-\( \sigma^* \) (for clarity, the virtual levels 9e3, 7e2, 9e1, 10e1, 8e2, 10e3, and 11e1, which are located in the \(-3 \text{ to } -4 \text{ eV range and are insensitive to the Mn–COax bond distance, are not shown})\). The \( \sigma^* \) levels have much dz\(^2\) character and are strongly antibonding with the axial COs;\(^{16} \sigma(\sigma^*) \sim (d_z^2 \pm d_y^2) - (5\sigma^1 \pm 5\sigma^2) \), where the minus sign refers to \( \sigma^* \), the superscripts 1 and 2 refer to the left and right side of \( \text{Mn}_2(\text{CO})_{10} \), respectively. Note that the axial CO is leaving from the left side. As soon as the axial CO moves away, the symmetry of the system lowers and the 11a1-\( \sigma^* \) and 11b2-\( \sigma^* \) mix and form the \( \sigma^* + \sigma^* \) and \( \sigma^* - \sigma^* \) combinations corresponding to the 21a1 and the 22a1 \( C_4V \) orbitals. The first localizes on the side where CO is leaving (\( d_{z^2} - 5\sigma^2 \)), the second localizes on the other side (\( d_{x^2-y^2} - 5\sigma^2 \)). Owing to the strong Mn–COax \( \sigma \)-antibonding character of the \( \sigma^* \) orbitals, the 21a1 is downward shifted upon the lengthening of the Mn–COax bond; the 22a1 is not. Around 2.1 Å the 21a1-\( \sigma^* + \sigma^* \) starts to mix with the 20a1-\( \sigma^* \), and at 2.5 Å, the 20a1 has become mostly \( \sigma^* + \sigma^* \) and the 21a1 has acquired much \( \sigma^* \) character. In other words, in the range 2.1–2.5 Å these orbitals exhibit an (avoided) crossing. This will have important consequences for the lowest excited states. For instance, the lowest excited state of \( \text{Mn}_2(\text{CO})_9 \) with an axial vacancy will be the \( \Upsilon \) state resulting from \( 16e^* \rightarrow 20a_1(\sigma^* + \sigma^*) \) excitation. At equilibrium

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geometry (of Mn₂(CO)₁₀) the E state corresponding to dπ* excitation (8e⁻ 3f₁₁a₁) will be high lying, but it will rapidly become lower in energy and it will, after a number of avoided crossings with lower E states in the range 2.1–2.5 Å, eventually cross the dπ* excited state, which at equilibrium distance is the lowest one of E symmetry (8e⁻ 3f₁₀b₂ – σ*). A similar situation arises in A₁ symmetry (in C₄ᵥ). The lowest excited state at equilibrium geometry corresponds to σfσ* excitation, but this state will be crossed by the σf(σ’ + σ’*) excitation, which will asymptotically be the lowest excited state of A₁ symmetry.

The implication is that even if the lowest excited states of Mn₂(CO)₁₀ of σfσ* and dπ* character are not dissociative with respect to the Mn–CO ax bond, as a consequence of the lack of Mn–CO ax antibonding in the σ* orbital, photodissociation of an axial carbonyl ligand might still occur by curve crossing with the above mentioned Mn–CO ax dissociative states. Crucial questions are of course whether the asymptotic energy is not higher than the σfσ* and dπ* excited state energies at equilibrium geometry and if the avoided crossing does not lead to a high barrier.

The above suggestions have been checked out through the calculation of the potential energy curves for a number of 1,3 E excited states, viz., all those lying below the 1,3 E states that correspond at the equilibrium distance to the symmetry forbidden dπ → σ’ (8e⁻ 3 → 11a₁) ¹E₃ state (the symmetry allowed analogue dπ → σ’ (8e⁻ 1 → 11a₁) m¹E₂ state lies at much higher energy). The PECs for the lowest 1,3 A₁ excited states corresponding to σ → σ* excitation have also been computed. The potential energy curves corresponding to the loss of an axial CO are displayed in Figure 5.

From Figure 5, the bound nature (with respect to Mn–CO ax bonding) of the σ → σ* a³A₁ (a³B₁ in D₄d symmetry) is apparent. That this state, which is responsible for the Mn–Mn cleavage, is bonding with respect to an axial carbonyl, is in line with the negligible axial CO character of both σ and σ* orbitals. We note nevertheless that the well depth of the a³A₁ curve is much less than that of the a³A₁ ground state curve. This is due to the fact that this state does not connect to the σ → σ* excitation (19a₁ → 21a₁) in Mn₂(CO)₉ but becomes asymptotically the σ → (σ’ + σ*) excitation (19a₁ → 20a₁) in Mn₂(CO)₁₀, which has much lower excitation energy than the σ → σ* excitation. This crossing to the σ → (σ’ + σ*) excited state does not seem to involve a barrier.

In contrast to the behavior of the A₁ states, the a¹⁻¹E states corresponding to (8e⁻ → 10b₂) dπ → σ* excitation are dissociative with respect to axial CO loss. One would not expect...
The lack of an energy barrier in the a3 E PEC due to the avoided \( \pi \) energy barrier has been found. The rapid descent of \( d_\sigma \) by calculating the curve at a finer grid of distances, but no \( z \) completely in line with the strong \( d_\pi \) height as the “intended” minimum in the a3 E curve. A second difference in that it puts the asymptotic energy at about the same upward the a1,3 E PEC corresponds to a \( d_\pi \) crossing may be “explained” as being caused by the precipitous lowering of the \( d_\pi \) antibonding which makes the a3 E state, which is higher than a3 A1 at equilibrium geometry, lower in Mn2(CO)10, makes a crucial difference in that it puts the asymptotic energy at about the same height as the “intended” minimum in the a1 E curve. A second important factor, which apparently prevents the occurrence of any barrier, is the very rapid lowering in energy of the \( d_\pi \rightarrow d_\sigma^* \) excited state upon Mn–COax bond lengthening, which is completely in line with the strong \( d_\pi \cdot 5\sigma_{ax} \) antibonding in the \( d_\sigma^* \) that we stressed before.16 It is worth noting that from 2.2 Å upward the a13-E PEC corresponds to a \( d_\pi \rightarrow d_\sigma^* \) excitation, indicating that an “avoided crossing” with the LF dissociative state derived from \((8e_3 \rightarrow 11a_1) d_\sigma \rightarrow d_\sigma^* \) excitation has already occurred at this short distance. \( d_\sigma \) and \( d_\sigma^* \) in this paragraph actually stand for the appropriate localized orbitals, \textit{vide supra}. The lack of an energy barrier in the a1 E PEC due to the avoided crossing may be “explained” as being caused by the precipitous lowering of the \( d_\pi \rightarrow d_\sigma^* \) excitation, overtaking the \( d_\pi \rightarrow d_\sigma^* \) excitation before it has had time to curve upward. We have investigated the a1 E PEC more closely between 2.1 and 2.5 Å by calculating the curve at a finer grid of distances, but no energy barrier has been found. The rapid descent of \( d_\pi \rightarrow d_\sigma^* \) character can be traced through the multitude of excited states shown in the figure: at 1.6 Å the highest \( E \) state in the figure is \( d_\pi \rightarrow d_\sigma^* \); at 2.2 Å the lowest (a1 E) has this character. We conclude that we have been able to identify possible COax loss mechanisms in the low-lying excited states (the \( d_\pi \rightarrow d_\sigma^* \) excited states) of Mn2(CO)10. The dissociative nature of the corresponding PECs is basically due to the rapid lowering of the Mn(3d\( _\pi \))–COax (5\( \sigma \)) antibonding \( \sigma^* + \sigma^* \) orbital upon Mn–COax bond lengthening. This causes the first excitation energies in Mn2(CO)10 to be much lower than in Mn2(CO)10, which compensates for the Mn–CO bond breaking energy and puts the first excited states of the Mn2(CO)10 + dissociated CO system at about the same energy as the first excited states of Mn2(CO)10.

This picture of the axial CO dissociation is in excellent agreement with deductions from very recent time-resolved experiments.19 We note that axial CO dissociation may not only occur in the a1 E state but also by an intersystem crossing from the b1'A1 to the a1 E state. This is important since irradiation into the \( \sigma \rightarrow \sigma^* \) band will heavily populate b1'A1. Mn–Mn and Mn–COax bond breaking will result from different intersystem crossings from the b1'A1 to dissociative triplet states, one to the a3'A1 (≈a3'B2 in D4h symmetry), the other one to a1 E. These processes may therefore be competitive. We caution that our calculations probably have some inaccuracy in the relative energies of the b1'A1 and a1 E energies and therefore in the point of crossing of b1'A1 with a1 E. The intense first band in the UV spectrum most probably corresponds to the b1'A1 and the low-energy shoulder of this band to the a1 E. This means that a1 E and a3 E should be somewhat downshifted with respect to the \( \sigma \rightarrow \sigma^* \) states.

**Potential Energy Curves for the Loss of an Equatorial Carbonyl Ligand.** A first step in the understanding of the photodissociation mechanism of an equatorial carbonyl ligand is again provided by a level scheme (Figure 6) that illustrates the evolution of the highest occupied and lowest unoccupied Mn2(CO)10 MOs on elongating the Mn–COeq bond to the dissociation limit. Note that the leaving CO is along the \( z \)-axis, the Mn–Mn bond being the \( z \)-axis. \( \pi \)-Bonding will therefore be lost with a \( d_{\delta} \) orbital on Mn1 (\( 1d_\delta^1 \)) and a \( d_{\delta} \) orbital on Mn1 (\( 1d_\delta^1 \)).

As for the highest occupied levels, one will notice that, unlike in the case of Mn–COeq bond elongation, the 10a1-\( \sigma \) orbital (41a' in \( C_s \) symmetry) is destabilized by the lengthening of the
Mn–CO$_{eq}$ bond. This is in line with the Mn–CO$_{eq}$ π-bonding character of this orbital (through the involvement of 4p$_z$; see ref 16).

The 6e$_2$-d$_{x^2}$, 8e$_2$-d$_{xy}$, 9e$_2$-d$_{yz}$ orbitals are, upon $D_{4h} \rightarrow C_s$ symmetry lowering, split into two sets, 39a', 23a'' and 40a', 24a'', respectively. The a' levels are d$_{x^2}$ and d$_{xz}$; the first is destabilized for increasing Mn–CO$_{eq}$ bond length due to the loss of Mn–CO$_{eq}$ π-bonding character and becomes 40a'. In C$_1$ symmetry the two degenerate components of the 6e$_2$-d$_{xy}$($t_{2g}$) orbital, d$_{x^2}$ + d$_{y^2}$ and d$_{x^2}$ - d$_{y^2}$, mix to form localized 22a'' and 38a' orbitals. The former has d$_{x^2}$ character; the latter has d$_{y^2}$ character. As we are moving an equatorial carbonyl bonded to the manganese atom on the left (see Figure 1 and Scheme 3), the 22a''-d$_{x^2}$ is destabilized upon elongation of the Mn–CO$_{eq}$ bond; the 38a'-d$_{y^2}$ stays put.

Turning now to the virtual levels, the level scheme of Figure 6 displays a situation somewhat similar to that of Figure 4. Again a high-lying level is strongly downward shifted by Mn–CO$_{eq}$ bond lengthening. It is the a' component of the 9e$_2$-d$_{xy}$($e_g$) degenerate set consisting of (combinations of) d$_{x^2}$ and d$_{y^2}$, that are strongly antibonding with the 5e's of the equatorial carbonyls. Upon $D_{4h} \rightarrow C_s$ symmetry lowering the two d$_{x^2}$ + d$_{y^2}$ and d$_{x^2}$ - d$_{y^2}$ components of the 9e$_2$-d$_{xy}$($e_g$) mix to form the localized d$_{xy}$ and d$_{yz}$ orbitals. d$_{xy}$ is of course not affected by the departure of an equatorial CO from the left Mn. At a Mn–CO$_{eq}$ distance of about 2.1 Å d$_{yz}$ has descended from its position as 52a' to become 43a', and at 2.5 Å, a* and d$_{yz}$ have crossed and the a* character is mostly in 44a' and subsequently in 43a', while 42a' has become largely d$_{yz}$. In fact, in 42a' d$_{yz}$ hybridizes strongly with 4p$_z$ to reduce the antibonding with the CO at the negative x-axis, which of course helps to lower the orbital energy. In comparison to the behavior of the 6e$_2$-d$_{xy}$($t_{2g}$) derived set of orbitals, it is clear that the loss of a*-antibonding in 9e$_2$-d$_{xy}$($e_g$) has much more effect than the loss of π-bonding with the d$_{xy}$ orbital of the 6e$_2$-d$_{xy}$($t_{2g}$) set.

The consequence of the downward shift of the d$_{xy}$($e_g$)-d$_{yz}$ is that asymptotically the lowest excited states will correspond to excitations from the occupied d's to this orbital. The high-lying a' and a'′ excited states resulting from excitations to 9e$_2$-d$_{xy}$($e_g$)-d$_{yz}$ at equilibrium geometry will therefore after a number of avoided crossings with lower A′′ (A′′) states in the range 2.1–2.5 Å, become the lowest A′ (A′′) states. It follows that photodissociation of an equatorial carbonyl ligand at low energy might occur from the a′′-E$_3$ (d$_{xy}$ → d$_{yz}$) or a′′-E$_4$ (d$_{xy}$ → d$_{yz}$) states if their PECs are crossed by the above mentioned Mn–CO$_{eq}$ dissociative excited states, provided that the avoided crossings do not lead to high-energy barriers.

In order to verify the occurrence of the avoided crossings predicted so far, we have explicitly calculated the potential energy curves for the lowest three 1A′ and 1A′′ excited states. These PECs are displayed in Figures 7 and 9 for A′ and A′′ symmetries separately. Considering first the A′ excited states, it is noted that the a′A′ that corresponds at the equilibrium distance to the a → σ* excitation (1B$_2$) which is responsible for the Mn–Mn cleavage does not show Mn–CO$_{eq}$ dissociative character. The corresponding singlet b′A′ PEC has similar behavior. However, it is clear that the well depth of these excited state PECs is much smaller than that of the ground state a′A′. This is, of course, as in the case of Mn–CO$_{ax}$ dissociation, due to the much lower first excitation energy in Mn$_2$(CO)$_9$ than in Mn$_2$(CO)$_{10}$ at the equilibrium geometry, which in turn is mostly due to the lowering of the d$_{xy}$($e_g$)-d$_{yz}$ orbital. The next higher excited triplet state, b′A′, corresponding at the equilibrium distance to d$_{xz}$ → σ* excitation (1E$_1$), is weakly dissociative with respect to CO loss, after going over a barrier around 2.3 Å. The remaining PECs do not exhibit any dissociative character. We have mentioned the change in character of the lowest excited states along the Mn–CO$_{eq}$ coordinate, due to the LUMO changing from σ* to d$_{xy}$($e_g$)-d$_{yz}$. The difference in character between the low-lying excitations in Mn$_2$(CO)$_{10}$ at equilibrium geometry and in Mn$_2$-
Photodissociation of Mn$_2$(CO)$_{10}$


Figure 8. 3'A' potential energy curves for the dissociation of the Mn−CO$_9$ bond in Mn$_2$(CO)$_{10}$. The dominant character of the states along the photodissociation pathway is emphasized. On the left top are indicated the energies of the high-lying LF 3'A' photoactive states at the equilibrium distance. Their corresponding energies at the dissociation limit are indicated on the right side.

Figure 9. 1/3'A'' potential energy curves for the dissociation of the Mn−CO$_9$ bond in Mn$_2$(CO)$_{10}$.

(CO)$_9$ implies the presence of avoided crossings, or at least a switching of the orbital type of excitation, between the PECs in the region 2.1−3.0 Å. The nature of the A' excited states is illustrated in detail for the lowest a3'A', b3'A', and c3'A' excited states in Figure 8. The excitations to d$_9$ (we further denote the d$_9$(e$_2$)-d$_9$(e$_{2g}$) orbital as just d$_9$) are at high energy at the equilibrium geometry but rapidly become lower in energy and end up as the lowest excitations in Mn$_2$(CO)$_9$. a3'A', which corresponds to σ → σ* excitation up to 2.1 Å, acquires σ → d$_9$ and subsequently d$_9$* → d$_9$ character through crossing with the dissociative 10a$_1$ → 9e$_2$ (σ → d$_9$) and 8e$_3$ → 9e$_2$ (d$_9$* → d$_9$) derived states. In the absence of these crossings the a3'A' PEC would asymptotically correlate with the c3'A' excited state of σ → σ* character. Considering the nature of the a3'A' state more closely reveals that there is considerable localization of orbitals on one or the other side of the molecule, which is possible due to the symmetry lowering and which also occurs in the ground state of Mn$_2$(CO)$_9$. Therefore at longer Mn−CO$_9$ distances the symmetrical notation such as d$_9$* becomes less appropriate. In the a3'A' state the hole gains more d$_9$* than d$_9$ = d$_9$ + d$_9$ character. Excitations where the hole localizes on the same Mn as where the excited electron is located (i.e., Mn$_1$) tend to be lower in energy than excitations where the hole shows less localization (e.g., for excitation out of σ) or localizes on the other Mn. The σ orbital is built from two monomer orbitals with large overlap and does not localize readily. The d orbitals however have small overlap, and in many excited states there is a d hole that is completely localized on the left or on the right Mn. In the case of the a3'A' state we have noted that asymptotically there is still considerable σ → d$_9$ character, but the relatively favorable hole localization on Mn$_1$ causes the excitation to become more d$_9$* → d$_9$ like. This is denoted in the figure as d$_9$* → d$_9$.

The b3'A' state, which corresponds to R$_z$ to d$_9$* → σ* (3E$_1$) excitation, also changes character in the range 2.1−2.5 Å. We are able to identify at 2.3 Å the character as σ → d$_9$, but at 2.5 Å considerable d$_9$* (d$_9$) → d$_9$ has crept in. Asymptotically b3'A' still has a hole with much σ character, i.e., can best be classified as σ(d$_9$) → d$_9$. So the b3'A' PEC has “crossed” first the dissociative σ → d$_9$ excitation and next the dissociative d$_9$* → d$_9$ excitation. It is interesting to observe that the maximum at 2.3 Å in the b3'A' PEC is clearly due to an avoided crossing with the c3'A' PEC, as is apparent from the switching of σ → d$_9$ character from c3'A' to b3'A'. The d$_9$* → σ* character of b3'A' at equilibrium geometry moves to higher PECs and ends up (as mostly d$_9$* → σ*) in the F'A' excited state of Mn$_2$(CO)$_9$. The b3'A' PEC is dissociative in the sense that the asymptotic energy is lower than the energy at equilibrium geometry. The barrier due to avoided crossing is rather low (less than 10 kcal/mol).

The c3'A' PEC corresponding at the equilibrium distance to 10a$_1$ → 9e$_2$ (σ → 2π*) shows in the range 2.1−3.0 Å a behavior that results from interactions with other A' states. As expected, owing to the crossing with the dissociative 10a$_1$ → 9e$_2$ (σ → d$_9$) derived state, its dominant character at 2.1 Å is already σ → d$_9$, becoming at 2.3 Å d$_9$* → d$_9$, due to crossing with the dissociative 8e$_3$ → 9e$_2$ (d$_9$* → d$_9$) derived state. Asymptotically c3'A' becomes the σ → σ* of Mn$_2$(CO)$_9$. It is not dissociative.

With respect to higher excited states of 3'A' symmetry in Mn$_2$-
(CO)$_9$ we note that $d^1\alpha'$, which has $d^1_{x^2}-d_3$ character, is much higher than $a^1\alpha'$ because now the hole in $d_3$ is on the other Mn. Similarly $c^1\alpha'$ has the hole in a $d_3$ ($d^2_{x^2-y^2}$) on the right Mn atom (see below). The charge separation that occurs in these excited states makes them higher than $\sigma-\sigma^*$ even if this could not be expected on the basis of the orbital energy differences in Figure 6.

Turning now to the $\alpha'$ singlet states (see Figure 7), $b^1\alpha'$ and $c^1\alpha'$ behave as the corresponding $a^1\alpha'$ and $b^1\alpha'$ triplets. $b^1\alpha'$ crosses the 10$a_1$ $\rightarrow$ 9$e_2$ ($\sigma-\delta_3$) and 8$e_3$ $\rightarrow$ 9$e_2$ ($\delta_3-\alpha_3$) derived states and at the dissociation limit has $d^1_{x^2}$($\sigma$) $\rightarrow$ $\delta_3$ character. $c^1\alpha'$ crosses the same excited states and asymptotically has $\sigma$($d^1_{x^2}$) $\rightarrow$ $\alpha_3$ character. There is a relatively large $b^1\alpha'$/$c^1\alpha'$ triplet/singlet splitting due to the partial localization of the unpaired electrons on one manganese atom. The effect is that the $c^1\alpha'$ state, unlike $b^1\alpha'$, is not dissociative. The third singlet state, $d^1\alpha'$, behaves as the corresponding triplet $c^1\alpha'$ (i.e. has $\sigma$ $\rightarrow$ 2$\pi^*$ character) up to 3.0 Å, then crosses the 8$e_i$/8$e_3$ $\rightarrow$ 9$e_2$ ($\delta_3-\alpha_3$) derived state that has the hole localized on the right Mn atom, and asymptotically corresponds, as does the triplet $d^1\alpha'$, to a $d^1_{x^2}$ $\rightarrow$ $\delta_3$ excitation. The single triplet splitting is very small when the unpaired electrons are on different Mn atoms, hence, the close proximity of $d^1\alpha'$ and $d^1\alpha'$ in Mn$_2$(CO)$_9$.

We have now identified among the $\alpha'$ states one that is Mn--CO$_3$ dissociative, namely, the $3E_1(d^2_{x^2}-\sigma^*)$ derived $b^1\alpha'$ state. We recall that the $d^2_{x^2}-\sigma^*$ excitation is probably calculated too high with respect to the $\sigma-\sigma^*$ excitation, so $b^1\alpha'$ (and $c^1\alpha'$) should be somewhat downshifted in Figure 7. This means, in the same way as for axial CO dissociation, that after the allowed $\sigma-\sigma^*$ excitation to $b^1\alpha'$ an intersystem crossing from $b^1\alpha'$ to $b^1\alpha'$ may lead to equatorial CO dissociation. In contrast to the case of axial CO, the singlet corresponding to $d^2_{x^2}$ $\rightarrow$ $\sigma^*$ excitation is not dissociative for equatorial CO.

The PECs for the lowest $\alpha''$ states are shown in Figures 9 and 10. From the orbital character indicated at the PECs in the asymptotic limit the various avoided crossings that must have occurred may be deduced. We do not discuss these states in detail, their behavior can be understood in much the same way as that of the $\alpha'$ states. One difference is that now the $\sigma-\sigma^*$ states are absent. The lowest state, $a^3\alpha''$, corresponds at $R_e$ to the $a^3E_1$ ($d_3^2-\sigma^*$) state. Again the excitation will asymptotically be to $\delta_3$; i.e., the $a^3\alpha''$ changes character to asymptotically a $d^1_{x^2}$ $\rightarrow$ $\delta_3$ excitation, and the corresponding singlet $a^3\alpha''$ has the same character. We note that $d^1_{x^2}$ is a $d_3$ on the left Mn that is perpendicular to the leaving CO, so it does not lose $\pi$ bonding with it. It is therefore less destabilized than the $d^1_{x^2}$ and the $a^3\alpha''$($d^2_{x^2}$ $\rightarrow$ $\delta_3$) excited state is in Mn$_2$(CO)$_9$ at somewhat higher energy than the states in $\alpha'$ symmetry involving $d^1_{x^2}$ $\rightarrow$ $\delta_3$ excitation, such as $a^3\alpha'$ and notably $b^1\alpha'$. $a^3\alpha''$ evolves from the same $3E_1$ excited state at $R_e$ as $b^1\alpha'$. Whereas $b^1\alpha'$ has been observed to be just dissociative, in the sense that the energy at $R_e$ is about the same as the asymptotic energy, the asymptotic energy of $a^3\alpha''$ is somewhat higher (about 0.01 au, less than 10 kcal/mol), and the $a^3\alpha''$ PEC is not dissociative. There is one $\alpha''$ state that may be considered dissociative in the sense that its asymptotic energy is just below the energy at $R_e$ (although not below the minimum in the curve), namely, $b^3\alpha''$. $b^3\alpha''$ starts at $R_e$ as a component of $3E_3$ ($\sigma-2\pi^*$). Its energy is (close to $R_e$) practically equal to that of $b^1\alpha''$--$E_2$, also corresponding to $\sigma$ $\rightarrow$ 2$\pi^*$ and to that of $a^1\alpha''$, i.e., $1E_1$ ($d_3-\sigma^*$). Excitations to the $E_3$ states are symmetry forbidden, but the $b^1\alpha''$ state may become occupied by intersystem crossing from the allowed singlet excited state $a^1\alpha''$--$E_2$ ($d_3-\sigma^*$). It is not clear how efficient CO dissociation could be in this state since the $b^1\alpha''$ PEC exhibits a clear barrier due to avoided crossing at ca. 2.3 Å, where it switches to the $d^1_{x^2}$ $\rightarrow$ $\delta_3$ character that it will hold asymptotically. One wonders if population of the allowed $1E_1$--$a^1\alpha''$ ($d_3-\sigma^*$) might, by virtue of the shape of the $a^1\alpha''$ PEC, lead to CO dissociation by intersystem crossing to the $a^1\alpha''$ PEC since our calculations indicate very little difference between the $1E_1$--$a^1\alpha''$ energy at equilibrium geometry and the asymptotic $a^1\alpha''$ energy.

Summarizing, routes to equatorial CO dissociation along $\alpha''$ PECs are less obvious than in $\alpha'$ symmetry (along $b^1\alpha'$).
Summary

On the basis of the calculated potential energy curves the following understanding of the photochemistry of Mn\textsubscript{2}(CO)\textsubscript{10} is reached. Excitation at low energy, in the experimental range of 337–355 nm will bring the molecule into \( \sigma \rightarrow \sigma^* \) \( 1\text{B}_2 \) or into the nearly degenerate \( \delta_{3z} \rightarrow \sigma^* \text{E}_1 \) allowed excited states. From the \( \sigma \rightarrow \sigma^* \text{B}_2 \) state the molecule may reach, through intersystem crossing, the corresponding \( \sigma \rightarrow \sigma^* \text{B}_2 \) state which will lead to homolysis of the metal–metal bond along the \( 3\text{B}_2 \) curve (Figure 2), with formation of two Mn(CO)\textsubscript{5} radicals in their ground states. This is the standard explanation of the Mn–Mn bond homolysis, which is fully corroborated by our results.

For the more intriguing CO dissociation at these low excitation energies we can offer the following explanation. For the axial CO we have found the \( \sigma \rightarrow \sigma^* \) \( 1\text{B}_2 \) states (\( a^1\text{A}_1, b^1\text{A}_1 \), Figure 5) to be bound, but the spin allowed \( \delta_{3z} \rightarrow \sigma^* \text{E}_1 \) state to be purely dissociative, leading to the products CO and Mn\textsubscript{2}–(CO)\textsubscript{9}, the latter in the \( \text{E}_1 \) excited state. Also the \( \delta_{3z} \rightarrow \sigma^* \text{E}_1 \) state, that may be reached through intersystem crossing from the \( \delta_{3z} \rightarrow \sigma^* \text{E}_1 \) state or from the \( \sigma \rightarrow \sigma^* \) \( 1\text{B}_2 \) (\( b^1\text{A}_1 \)) state with which it is almost degenerate, is purely dissociative. The dissociative character of the \( \text{E}_1 \) curves is not due to intrinsic weakening of the Mn–CO\textsubscript{ax} bond upon the \( \delta_{3z} \rightarrow \sigma^* \) orbital excitation, but it is due to the strong lowering of the initially high-lying \( \sigma^* \) orbital that rapidly localizes to the Mn\textsuperscript{1−}CO\textsubscript{ax} antibonding \( \sigma^* + \sigma^* = \delta_{3z} \) (\( -5\sigma^* \)) orbital upon Mn–CO\textsubscript{ax} bond lengthening. This has the effect that the \( \text{E}_1 \) states change character to \( \delta_{3z} \rightarrow \delta_{3z}^* \) excitation. So the \( \text{E}_1 \) states evolve into LF type excited states in Mn\textsubscript{2}(CO)\textsubscript{9}. However, the LF \( \delta_{3z} \rightarrow \sigma^* \) excitation is initially, in Mn\textsubscript{2}(CO)\textsubscript{10}, much higher than the \( \delta_{3z} \rightarrow \sigma^* \) states already shortly after 2.0 Å. Ultimately, in Mn\textsubscript{2}(CO)\textsubscript{9}, the LF excitation is even much lower than the original \( \delta_{3z} \rightarrow \sigma^* \) excitation in Mn\textsubscript{2}(CO)\textsubscript{10}, releasing sufficient energy to break the Mn–CO bond. The dissociation of axial CO along the \( \text{E}_1 \) PECs proceeds barrierless due to the crossing to LF character taking place close to the equilibrium Mn–CO\textsubscript{ax} distance.

Dissociation of an equatorial CO may also occur but less readily. Due to the symmetry lowering the E states now split into \( \Lambda \) and \( \Lambda' \) states. Again, the \( \sigma \rightarrow \sigma^* \) excited states (\( a^1\Lambda, b^1\Lambda \)) are not dissociative with respect to the Mn–CO\textsubscript{eq} bond, but the \( b^1\Lambda' \) component of the \( \delta_{3z} \rightarrow \sigma^* \text{E}_1 \) state is dissociative; although its PEC is different from the corresponding \( \text{E}_1 \) for axial CO, it is very flat and has to pass a low barrier. In the same way as for axial CO, the \( \delta_{3z} \rightarrow \sigma^* \text{E}_1 \) states evolve into a LF type excited state, this time to a localized \( \delta_{3z}^* \) orbital. We note that the equatorial \( \delta_{3z}^* \) is in Mn\textsubscript{2}(CO)\textsubscript{10} considerably higher than the axial \( \delta_z \) (see ref 16); it comes down somewhat more slowly upon Mn–CO bond lengthening so that a barrier can develop in the \( \delta_{3z} \rightarrow \sigma^* \text{E}_1 \)–\( b^1\Lambda' \) PEC. Asymptotically the LF excited state to the equatorial \( \delta_{3z}^* \) is somewhat higher than that to the axial \( \delta_z \) and the \( \text{E}_1 \)–\( b^1\Lambda' \) PEC is less clearly dissociative than the \( \text{E}_1 \)–\( \text{E}_1 \) PECs for axial dissociation. This may be summarized in the picture that the pushing up effect of the CO lone pairs (\( 5\sigma \)) on the axial \( \delta_z \) is already diminished in Mn\textsubscript{2}(CO)\textsubscript{10}, by the replacement of one CO in the octahedral environment by the Mn(CO)\textsubscript{5} unit, \( \delta_z' \) therefore being lower than \( \delta_{3z} \), all along the Mn–CO\textsubscript{ax} and Mn–CO\textsubscript{eq} coordinate, respectively. Hence a downward shift of the \( \delta_{3z}^* \) LF excited state compared to the \( \delta_{3z}^* \) LF excited state, leading to the above noted consequence of more readily dissociating axial CO.

It is interesting to note that the phenomenon of CO dissociation upon excitation into the low-energy bands of Mn\textsubscript{2}(CO)\textsubscript{10} has led Meyer and Caspar\textsuperscript{66} to examine the possibility that these low-energy excitations include LF type excitation to \( \delta_{3z}^* \). We have ruled out this possibility on the basis of our calculated excitation energies (note the high \( \sigma \rightarrow \delta_3 \) and \( \sigma \rightarrow \delta_3 \) excitation energies in Figures 8 and 10), but the suggestion in a sense foreshadows the precipitous lowering of the LF excited states with Mn–CO bond lengthening that we find to play such a crucial role in the dissociation.

Our findings account for the occurrence of two primary photoproceses for Mn\textsubscript{2}(CO)\textsubscript{10} in the range 337–355 nm, with the molecule undergoing either the metal–metal bond homolysis or the loss of a carbonyl ligand, most probably the axial one. The intersection of the \( \sigma \rightarrow \sigma^* \) \( 1\text{B}_2 \) and \( 8\text{e} \rightarrow 10\text{e} \) \( \text{E}_1 \) surfaces enables both photoproceses to occur independently of the excitation wavelength in this range, which nicely agrees with the experimental findings.

Irradiation of Mn\textsubscript{2}(CO)\textsubscript{10} at \( \lambda \leq 266 \) nm may bring the molecule directly or indirectly into excited states that are strongly Mn–CO\textsubscript{ax} or Mn–CO\textsubscript{eq} antibonding, i.e., which lower their energy steeply upon Mn–CO bond stretching. This may start the Mn–CO dissociation process, during which the system may electronically relax to one of the dissociative low-energy excited states we have just discussed. No photoactive state for Mn–Mn bond homolysis is found in this high-energy region. Thus the only photochemical process that we predict upon excitation of Mn\textsubscript{2}(CO)\textsubscript{10} in the high-energy region is the loss of a carbonyl ligand, which is in agreement with gas-phase photoexperiments\textsuperscript{15} in that excitation of Mn\textsubscript{2}(CO)\textsubscript{10} at 248 and 193 nm leads to ligand loss with no evidence of metal–metal homolysis. The interpretation of condensed-phase experiments that establish the occurrence, although with a very low quantum yield, of the metal–metal homolysis, when exciting Mn\textsubscript{2}(CO)\textsubscript{10} at 266 nm,\textsuperscript{14} would involve the assumption of low-probability crossing, due to the perturbative effect of the solvent, to the Mn–Mn dissociative states at low energy.

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