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# Density Functional Study of the Primary Photoprocesses of Manganese Pentacarbonyl Chloride (MnCl(CO)<sub>5</sub>)

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Density functional calculations have been performed on the ground and excited states of MnCl(CO)<sub>5</sub> in order to explain the photochemistry of MX(CO)<sub>5</sub> complexes (M = Mn, Re; X = Cl, Br, I). As found earlier for Mn<sub>2</sub>(CO)<sub>10</sub> (Inorg. Chem. 1996, 35, 2886), the e<sub>g</sub>-type unoccupied 3d orbitals in the pseudooctahedral environment are located rather high in the virtual orbital spectrum, and the corresponding ligand-field (LF) excitations are more than 1 eV above the lowest excitations. Potential energy curves (PECs) nevertheless show that the lowest excited states, which involve transitions to the Mn–Cl σ\* orbital at equilibrium geometry, are dissociative for axial and equatorial CO loss. The mechanism is again, as in Mn<sub>2</sub>(CO)<sub>10</sub>, a strongly avoided crossing of the lowest excited state (a<sup>1,3</sup>E) with the higher dissociative LF states (different ones for CO<sub>ax</sub> and CO<sub>eq</sub> dissociation) which rapidly descend upon Mn–CO bond lengthening. In spite of the lowest excitation being to the Mn–Cl σ\*-orbital, Mn–Cl homolysis cannot occur out of the lowest excited state. The photochemical behavior of Mn<sub>2</sub>(CO)<sub>10</sub>, MnH(CO)<sub>5</sub>, and MnCl(CO)<sub>5</sub> is compared. The mechanisms of CO loss are found to be very similar, but there is a large difference with respect to the breaking of the σ bond (Mn–Mn, Mn–H, or Mn–Cl). Only in the case of Mn<sub>2</sub>(CO)<sub>10</sub>, the lowest broad absorption band contains the σ → σ\* excitation and leads to σ bond breaking.

## 1. Introduction

Detailed insight into photochemical pathways of organometallic compounds is rapidly accumulating due to the use of sophisticated equipment for the detection of excited states and reactive intermediates.<sup>1</sup> At the same time, the advances in quantum mechanical methods and computer technology have made feasible extensive calculations on both ground and excited states of simple organometallic complexes. Especially the calculation of potential energy curves (PECs) has proven to be very valuable in describing the photochemistry of transition metal complexes<sup>2</sup> (see also refs 3–5).

In this paper we will focus on the photochemistry of MnCl(CO)<sub>5</sub>. Many studies on the photochemistry of metal pentacarbonyl halides show that CO loss is the primary photoprocess.<sup>6,7</sup> From these studies it is known that in MnCl(CO)<sub>5</sub> only the Mn–CO bond is photolytically cleaved and that no Mn–Cl bond homolysis occurs. In the absence of coordinating species, the photochemistry yields the halide-linked dimer Mn<sub>2</sub>(CO)<sub>8</sub>Cl<sub>2</sub>, while in the presence of coordinating species the *cis* substituted product is formed. It is somewhat surprising that the photosubstitution reaction is highly stereospecific, yielding only the *cis* isomer. Within the usual ligand-field picture (cf. Wrighton *et al.*<sup>7</sup>), one would expect the LUMO to be the metal d<sub>z<sup>2</sup></sub> orbital, which is assumed to have more antibonding interaction with the axial CO than with the chlorine. Irradiation into the lowest ligand-field (LF) band increases the population of this d<sub>z<sup>2</sup></sub> orbital and would be expected to result in loss of CO *trans* to chlorine. The LF view thus predicts a different primary photoproduct than experiment suggests. This inconsistency can be resolved if one assumes that indeed an intermediate resulting from axial CO loss occurs (a square pyramid with Cl in the apical position), but that this intermediate is susceptible to an excited state rearrangement to a square pyramid with Cl in basal position. Subsequent addition of a coordinating ligand then results in a *cis* substituted product. The possible rearrangement pathways of the MnCl(CO)<sub>4</sub> intermediate have received considerable attention recently (cf. Pierloot *et al.*<sup>4</sup> and Matsubara *et al.*<sup>8c</sup>). One expects in the LF picture to have the other e<sub>g</sub>-type orbital (d<sub>x<sup>2</sup>-y<sup>2</sup></sub>) at higher energy than the d<sub>z<sup>2</sup></sub> orbital, because Cl is a weaker σ donor than CO. Occupation

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of this orbital would lead to equatorial CO loss. In view of the dramatic increase of the quantum yield when going to higher excitation energies and the temperature dependence of both the quantum yield and the lifetime, Wrighton *et al.*<sup>7</sup> concluded that indeed such a higher lying photoactive excited state with  $d_{x^2-y^2}$  character is present. These results were supported by the calculations by Pierloot *et al.*<sup>4,5</sup>

This picture of the photochemistry of  $\text{MnCl}(\text{CO})_5$  is based on the accepted paradigm of photolabilization of metal-carbonyl bonds by ligand field excitation. We have, however, recently found<sup>3b</sup> in the case of  $\text{Mn}_2(\text{CO})_{10}$  that this picture may require considerable adjustment and refinement. The calculation of PECs for CO dissociation and Mn–Mn bond breaking, and an analysis of the electronic structure of the ground and excited states,<sup>3a</sup> revealed that among the lowest excited states the  ${}^{1,3}E_1$  ( $d_{\pi} \rightarrow \sigma^*$ ) state is Mn–CO<sub>ax</sub> dissociative, although it is not Mn–CO antibonding and cannot unequivocally be assigned as a LF excited state. There are, however, strongly Mn–CO antibonding  $3d-e_g$ -type orbitals located at fairly high energy in the virtual orbital spectrum. Excitations to such orbitals lead to LF excited states with strongly dissociative PECs. These PECs rapidly become lower in energy with increasing Mn–CO distance and cross the low-lying excited  ${}^{1,3}E_1$  states. In this way these low-lying excited states become Mn–CO dissociative, although the avoided crossing may lead to a barrier. This picture is at variance with the LF picture indicated above for the photochemistry of  $\text{MnCl}(\text{CO})_5$ , which assumes a population of dissociative LF states directly upon low-energy irradiation.

The  $\text{MnCl}(\text{CO})_5$  system is well-suited for further investigation of this issue, since it offers the additional possibility of photochemical cleavage of a metal–ligand  $\sigma$  bond and may thus be compared to other well-studied  $\text{Mn}(\text{CO})_5\text{L}$  systems such as  $\text{MnH}(\text{CO})_5$  and  $\text{Mn}_2(\text{CO})_{10}$ . In  $\text{Mn}_2(\text{CO})_{10}$  the Mn–Mn bond is broken with approximately equal probability as the Mn–CO bond upon irradiation into the lowest absorption band. This may be attributed<sup>3b</sup> to transition to the low-lying  ${}^3B_2$ , of Mn–Mn  $\sigma \rightarrow \sigma^*$  character, which is nearly degenerate with the Mn–CO dissociative  ${}^{1,3}E_1$  states. However, the Mn–H bond of  $\text{MnH}(\text{CO})_5$  is broken only upon high-energy irradiation, with relatively low quantum yield, although Mn–CO dissociation occurs as in  $\text{Mn}_2(\text{CO})_{10}$  from the low-lying excited states. Veillard *et al.* explained the wavelength dependent photochemistry of  $\text{MnH}(\text{CO})_5$  by calculating CASSCF/CCI correlation diagrams for both axial CO and H loss.<sup>8</sup> It was found that the lowest excited state is dissociative with respect to axial CO, whereas higher excited states are dissociative with respect to both axial CO and hydrogen. This conclusion was confirmed by full calculation of the PECs by Daniel,<sup>2g</sup> although these PECs demonstrated that the picture is complicated by several avoided crossings, resulting in small barriers.

In order to elucidate the photochemistry of  $\text{MnCl}(\text{CO})_5$  and study the similarities and differences with other  $\text{Mn}(\text{CO})_5$  derivatives, we have calculated PECs for both axial and equatorial CO loss and for Cl homolysis. The results are discussed in section 4 and indicate that both axial and equatorial CO loss can occur, but only due to a (strongly) avoided crossing with the lowest excited state by a dissociative LF excited state, which is high-lying at the equilibrium geometry but descends rapidly upon Mn–CO bond lengthening. Mn–Cl bond breaking does not occur. The CO loss mechanisms of  $\text{MnH}(\text{CO})_5$ ,  $\text{MnCl}$ –

$(\text{CO})_5$ , and  $\text{Mn}_2(\text{CO})_{10}$  are compared as well as the breaking of the  $\sigma$  bond (Mn–Mn, Mn–H, Mn–Cl). The first are very similar, the latter are very different in these compounds.

Before dealing with the photochemistry of the title compound, we first elucidate in section 3 the electronic structure of  $\text{MnCl}(\text{CO})_5$ , which is a prerequisite for understanding the photochemistry. The electronic structure of manganese pentacarbonyl halides has been the subject of many theoretical,<sup>9,10</sup> ultraviolet photoelectron spectroscopic (UPS),<sup>11–16</sup> and UV–vis spectroscopic studies.<sup>7,17–19</sup> For the present purpose in particular the molecular orbital structure and the excitation spectrum are relevant and will be discussed in section 3. Section 4 discusses the photochemistry and section 5 contains the Conclusions, in particular with respect to the role of LF excited states in the photodissociation process.

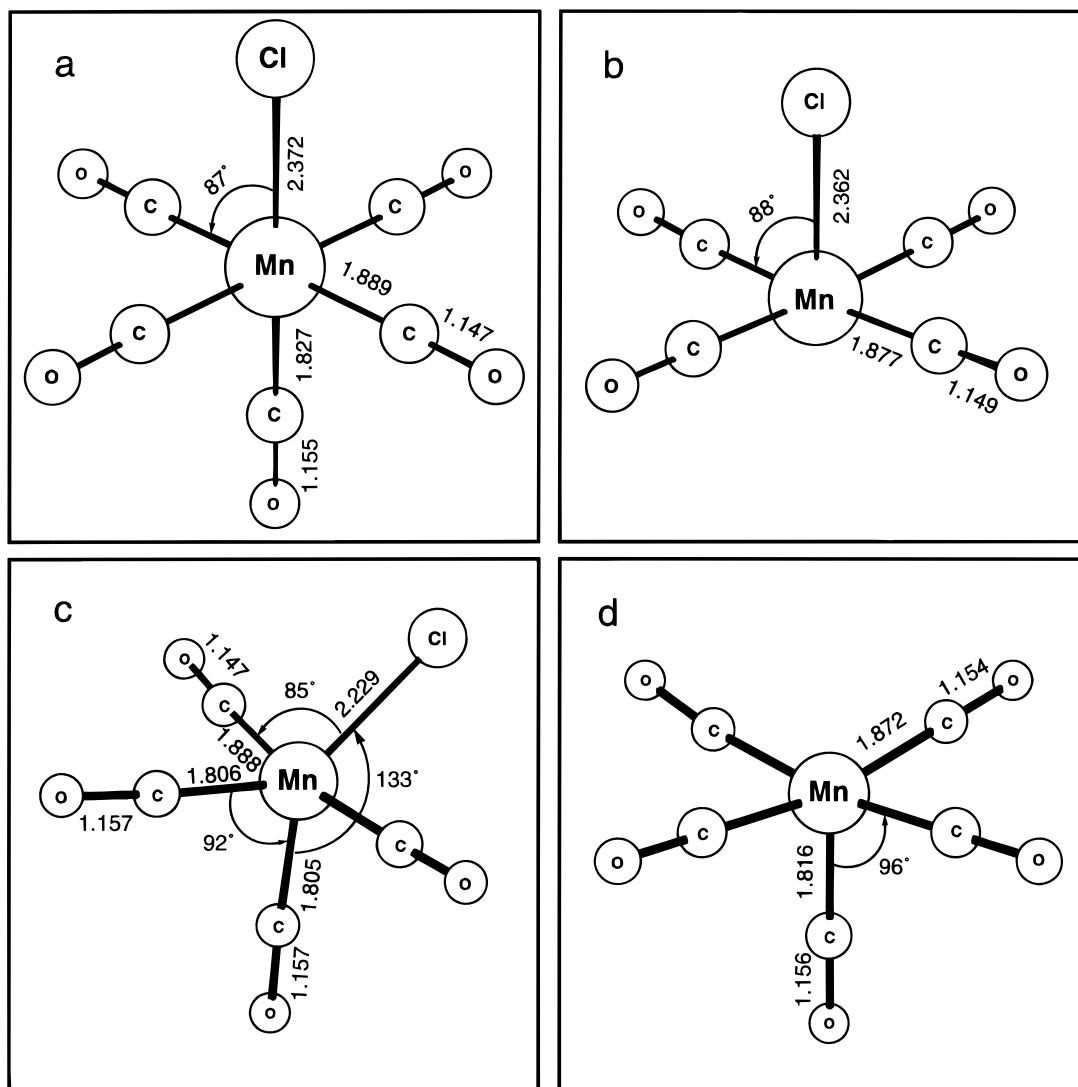
## 2. Computational Details

All calculations have been performed using the Amsterdam density functional program package ADF.<sup>23</sup> The computational scheme is characterized by the use of a density-fitting procedure to obtain accurate Coulomb and exchange potentials in each self-consistent field (SCF) cycle, by the accurate and efficient numerical integration<sup>24</sup> of the Hamiltonian matrix elements and the possibility to freeze core orbitals. We used an uncontracted double- $\zeta$  STO basis set with one polarization function for all atoms, except for the manganese orbitals for which a triple- $\zeta$   $3d,4s$  basis with one  $4p$  function was used. The  $1s$  oxygen and carbon cores were kept frozen as well as the  $1s$ – $2p$  cores for manganese and chlorine.

The ground and excited state energies included Becke's<sup>25</sup> nonlocal corrections to the local expression<sup>26</sup> of the exchange energy and Perdew's<sup>27</sup> nonlocal corrections to the local expression (Vosko–Wilk–Nusair<sup>28</sup> parametrization of electron gas data) for the correlation energy.

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**Figure 1.** Geometry of (a)  $\text{MnCl}(\text{CO})_5$ , (b) apical  $\text{MnCl}(\text{CO})_4$ , (c) basal  $\text{MnCl}(\text{CO})_4$ , and (d)  $\text{Mn}(\text{CO})_5$  (bond distances in angstroms).

The original proof of the Hohenberg–Kohn theorem<sup>29</sup> is only valid for the ground state of a system, and while it has been extended to the lowest state of any given symmetry,<sup>30</sup> this still does not suffice for a full description of the photochemical properties of molecules. However, the approximate method introduced by Ziegler *et al.*<sup>31</sup> for the calculation of excited states has been used with good results for both atomic<sup>32</sup> and molecular systems.<sup>33</sup> It has recently been applied successfully for the calculation of a two-dimensional potential energy surface for the photodissociation of  $\text{H}_2\text{O}$  in its first excited state<sup>34</sup> and compared to *ab initio* calculations and experiment. The photochemistry of  $\text{Mn}_2(\text{CO})_{10}$  has also been investigated with this method.<sup>3b</sup> In its simplest form, the method of ref 31

incorporates the relaxation effects in the excited state by an SCF calculation on a single-determinantal state, representing one of the multiplet states. Although this method yields results which are in keeping with experiment, it is only formally justified for the lowest state of each symmetry. Therefore, we will avoid drawing conclusions from the quantitative results of calculations on higher states. We feel, however, justified to use these results qualitatively.

The geometry of  $\text{MnCl}(\text{CO})_5$  as specified in Figure 1a was taken from an earlier density functional theory (DFT) study on this molecule.<sup>35</sup> In order to be able to compare the dissociation with experiment, geometry optimizations have been performed for the  $\text{Mn}(\text{CO})_5$  and  $\text{MnCl}(\text{CO})_4$  photoproducts using gradient techniques.<sup>36</sup> The results are shown in Figure 1b–d. The photoproducts resulting from axial CO or Cl loss have geometries which have only relaxed a little.  $\text{MnCl}(\text{CO})_4$  with an equatorial vacancy, however, shows considerable relaxation. In order to keep calculations tractable, geometry optimizations were not carried out at all points on the PEC. However, in order to assess at which point during the dissociation relaxation can come into play, we have optimized the geometry of the  $\text{MnCl}(\text{CO})_5$  fragment at a fixed distance  $\text{Mn}-\text{CO}_{\text{eq}}$  of 2.3 Å, at which point the PECs approach their asymptotic shape (see below). The optimized geometry at this point differed only slightly from the

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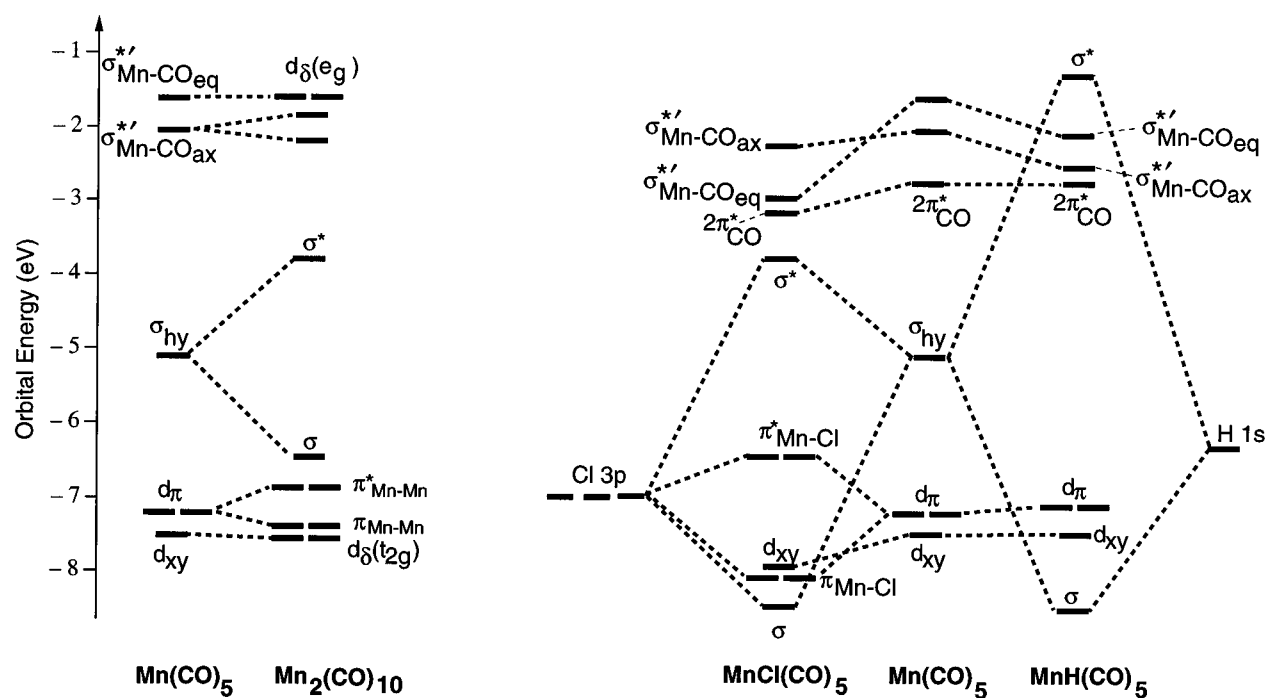
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**Table 1.** Orbital Energies and Percent Composition<sup>a</sup> (Based on Mulliken Population Analysis per MO) of the Lowest Unoccupied and Highest Occupied MnCl(CO)<sub>5</sub> Orbitals in Terms of Mn, Cl, CO<sub>ax</sub>, and CO<sub>eq</sub> Fragments

orbital	orbital character	ε (eV)	percent composn				OP <sup>b</sup>		
			Mn	Cl	CO <sub>ax</sub>	CO <sub>eq</sub>	Mn-Cl	Mn-CO <sub>ax</sub>	Mn-CO <sub>eq</sub>
Unoccupied Orbitals									
16e	CO π*	-1.944	2 (d <sub>xz/yz</sub> )	1 (p <sub>z</sub> )	37 (2π*)	59 (2π*)		0.02	-0.04
15e	"t <sub>2g</sub> "	-2.785	22 (d <sub>xz/yz</sub> )		42 (2π*)	35 (2π*)		-0.04	-0.05
23a <sub>1</sub>	"e <sub>g</sub> "; d <sub>z<sup>2</sup></sub> σ*	-2.796	39 (d <sub>z<sup>2</sup></sub> )	2 (p <sub>z</sub> )	16 (5σ)	41 (34 2π*, 7 5σ)	-0.01	-0.16	0.03
8b <sub>1</sub>	CO π*	-2.796	11 (d <sub>x<sup>2</sup>-y<sup>2</sup></sub> )			88 (80 2π*, 8 2π*)			-0.03
3b <sub>2</sub>	"t <sub>2g</sub> "	-2.983	31 (d <sub>xy</sub> )			69 (2π*)			-0.11
7b <sub>1</sub>	"e <sub>g</sub> "; d <sub>x<sup>2</sup>-y<sup>2</sup></sub> σ*	-2.994	49 (d <sub>x<sup>2</sup>-y<sup>2</sup></sub> )			50 (31 5σ, 19 2π*)			-0.14
14e	CO π*	-3.197	5 (d <sub>xz/yz</sub> )		6 (2π*)	89 (2π*)		0.01	-0.02
22a <sub>1</sub>	(Mn-Cl) σ*	-3.786	26 (20 d <sub>z<sup>2</sup></sub> , 6 p <sub>z</sub> )	20 (p <sub>z</sub> )		55 (2π*)	-0.08	-0.02	0.06
Occupied Orbitals									
13e	Cl p <sub>π</sub> - d <sub>π</sub>	-6.447	18 (d <sub>xz/yz</sub> )	74 (p <sub>x/y</sub> )	3 (2π*)	3 (5σ)	-0.02	0.01	-0.01
2b <sub>2</sub>	"t <sub>2g</sub> "	-8.010	68 (d <sub>xy</sub> )			32 (2π*)			0.05
12e	"t <sub>2g</sub> " d <sub>π</sub> + Cl p <sub>π</sub>	-8.030	54 (d <sub>xz/yz</sub> )	22 (p <sub>x/y</sub> )	8 (2π*)	15 (2π*)	0.03	0.01	0.02
21a <sub>1</sub>	Cl p <sub>σ</sub>	-8.386	18 (10 d <sub>z<sup>2</sup></sub> , 8 p <sub>z</sub> )	72 (p <sub>z</sub> )	3 (5σ)	7 (2π*)	0.06		
11e	CO 5σ	-11.409	6 (p <sub>x/y</sub> )	1 (p <sub>x/y</sub> )	13 (2π*)	78 (65 5σ, 13 2π*)		0.04	-0.01
20a <sub>1</sub>	CO 5σ	-11.982	22 (d <sub>z<sup>2</sup></sub> )	1 (p <sub>z</sub> )	47 (5σ)	28 (2π*)		0.07	-0.01

<sup>a</sup> The major contribution is reported between parentheses; if there are several contributions of more than 5%, these are made explicit. <sup>b</sup> The Mulliken overlap populations are per orbital, based on a norm 1 of the orbital, i.e., an orbital occupation of 1 electron for occupied and virtual orbitals alike.

**Figure 2.** Orbital interaction diagrams for the formation of Mn(CO)<sub>5</sub>L, where L = Mn(CO)<sub>5</sub>, Cl, or H. The Cl 3p is not at the atomic level but is positioned so as to correctly suggest the composition of the orbitals.

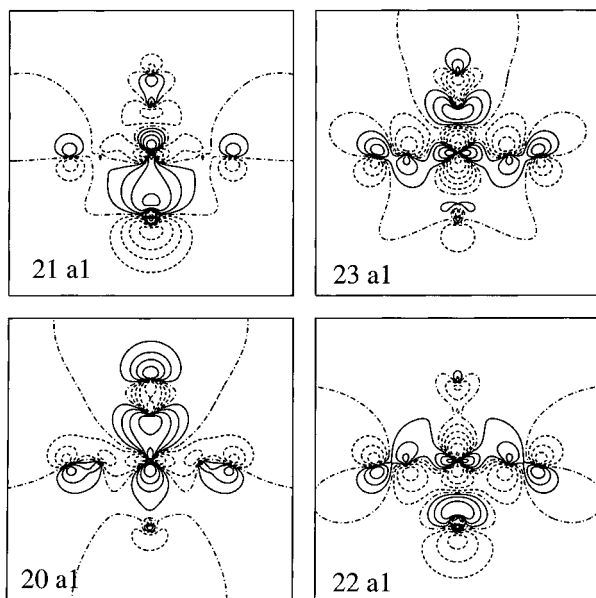
"frozen" geometry. Furthermore femtosecond resolved experiments showed that the Mn-CO dissociation in Mn<sub>2</sub>(CO)<sub>10</sub> occurs at a time scale of 20 fs.<sup>1b</sup> Since we find similar dissociative PECs as in Mn<sub>2</sub>(CO)<sub>10</sub>, the photodissociation process may be similar and thus much faster than the vibrations, which occur on the picosecond time scale. Therefore, it is not obvious that full geometry optimization along a Mn-CO dissociation coordinate would be justified, and we choose to calculate the PECs using a frozen geometry of the photodissociation fragments.

### 3. Electronic Structure

**Ground State Electronic Structure.** In order to better understand the photochemical behavior of MnCl(CO)<sub>5</sub>, it is first of all necessary to know the characters of the highest occupied and lowest unoccupied molecular orbitals. These characters as

well as the orbital energies are presented in Table 1. An orbital interaction diagram for the formation of MnCl(CO)<sub>5</sub> out of Mn(CO)<sub>5</sub> and Cl is shown in Figure 2.

The relevant occupied orbitals of Mn(CO)<sub>5</sub> are the fully occupied d<sub>xy</sub> and the E pair of d<sub>xz/yz</sub> or d<sub>π</sub> orbitals, which together correspond to the t<sub>2g</sub> orbitals in O<sub>h</sub> symmetry, and the singly occupied σ<sub>hy</sub> orbital, which is a 3d<sub>z<sup>2</sup></sub>-4p<sub>z</sub>-2π\*<sub>⊥</sub> hybrid, with its lobe directed toward the vacancy (the 2π\*<sub>⊥</sub> denotes an a<sub>1</sub> combination of 2π\* orbitals of the equatorial CO's that are perpendicular to the equatorial plane). We refer to ref 3a for a detailed explanation of the orbital structure of Mn(CO)<sub>5</sub>. In particular, it has been stressed that in Mn(CO)<sub>5</sub> one does not have a simple e<sub>g</sub>-type (mostly 3d<sub>z<sup>2</sup></sub>) LUMO, but due to mixing with the 4p<sub>z</sub> of Mn and the 2π\*<sub>⊥</sub> of the equatorial CO's, there are two a<sub>1</sub> orbitals with considerable d<sub>z<sup>2</sup></sub> character. The lowest one, the present σ<sub>hy</sub> orbital (10a<sub>1</sub> in ref 3a) has little axial CO

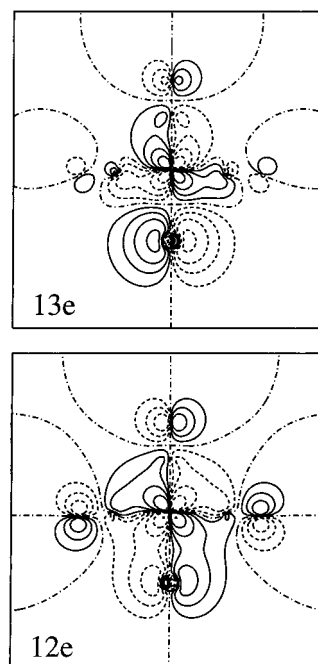


**Figure 3.** Contour plot of the  $20a_1$ ,  $21a_1$ ,  $22a_1$ , and  $23a_1$  orbitals in the  $xz$ -plane. Contours values are  $\pm 0.5$ ,  $\pm 0.2$ ,  $\pm 0.1$ ,  $\pm 0.05$ ,  $\pm 0.02$ , and 0 ( $e/\text{bohr}^3$ )<sup>1/2</sup>.

$5\sigma$  character, and this orbital completely lacks the expected antibonding with the CO  $5\sigma$ . On the other hand, the higher one ( $11a_1$  in ref 3a), which is at considerably higher energy, lying within the CO  $\pi^*$  manifold, has considerable antibonding with the axial CO (it is denoted  $\sigma^*(\text{Mn}-\text{CO}_{\text{ax}})$  in Figure 2). Excitation to this latter orbital leads to strongly  $\text{Mn}-\text{CO}_{\text{ax}}$  dissociative states. Due to the large amplitude of the  $\text{Mn}(\text{CO})_5$   $\sigma_{\text{hy}}$  toward the vacant coordination site, interaction with a coordinating ligand is mostly through this orbital. In  $\text{Mn}_2(\text{CO})_{10}$  this leads to symmetrical  $\sigma$  and  $\sigma^*$  orbitals (the  $\text{Mn}-\text{Mn}$  bonding and antibonding combinations of the higher lying  $\sigma^*(\text{Mn}-\text{CO}_{\text{ax}})$  do not split much due to their much lower amplitude at the vacant site). In the case of  $\text{MnCl}(\text{CO})_5$  a bonding  $\sigma$  orbital is formed with Cl  $p_\sigma$  (the  $21a_1$ ; see Table 1) with predominantly Cl character, and an  $\text{Mn}-\text{Cl}$   $\sigma$  antibonding orbital with mostly  $\text{Mn}(\text{CO})_5$  character, the  $22a_1$  LUMO of  $\text{MnCl}(\text{CO})_5$ . We will denote this orbital as  $\sigma^*(\text{Mn}-\text{Cl})$ , or just  $\sigma^*$ . The high-lying  $\sigma^*(\text{Mn}-\text{CO}_{\text{ax}})$  of  $\text{Mn}(\text{CO})_5$  is practically unperturbed by the bonding with Cl, and it is found as the  $23a_1$  orbital of  $\text{MnCl}(\text{CO})_5$ . It is still about 1 eV above the  $\sigma^*(\text{Mn}-\text{Cl})$ . Note that we differentiate between  $\sigma$  antibonding between Mn and L, denoted by  $\sigma^*$ , and  $\sigma$  antibonding between Mn and  $\text{CO}_{\text{ax}}$ , denoted by an additional prime,  $\sigma^{*'}$ . The situation is somewhat analogous to having two axial hybrids on Mn, one leading to (anti)bonding with axial CO, the other one with the other axial ligand L. The orbital plots in Figure 3 demonstrate the  $\text{Mn}-\text{Cl}$  bonding and antibonding characters of  $21a_1$  and  $22a_1$ , respectively, and the  $\text{Mn}-\text{CO}$  bonding and antibonding character of the  $20a_1$  and  $23a_1$  (not  $22a_1$ !), respectively.

The description of the remaining occupied and unoccupied orbitals is straightforward. In the unoccupied spectrum we have fairly close to the strongly  $\text{Mn}-\text{CO}_{\text{ax}}$  antibonding  $\sigma^{*'}$  orbital ( $23a_1$ ) the strongly  $\text{Mn}-\text{CO}_{\text{eq}}$   $\sigma$  antibonding  $7b_1$  orbital derived from the  $d_{x^2-y^2}$  component of the  $e_g$ -orbitals. We will also denote the  $\text{Mn}-\text{CO}_{\text{eq}}$   $\sigma$  antibonding character by  $\sigma^{*'}$ . The  $14e$ ,  $3b_2$ ,  $8b_1$ ,  $15e$ , and  $16e$  orbitals are mainly composed of CO  $2\pi^*$  orbitals. Some have a considerable admixture of metal 3d character, such as the  $3b_2$ , and  $15e$  which may be classified as the antibonding counterparts (" $t_{2g}^*$ ") of the occupied bonding  $t_{2g}$ -like orbitals.

In the occupied spectrum we have above the Cl- $p_\sigma$  ( $21a_1$ ) the metal-carbonyl  $\pi$  bonding  $t_{2g}$ -like 3d orbitals and the Cl



**Figure 4.** Contour plot of the  $12e$  and  $13e$  orbitals in the  $xz$ -plane. Contours: see caption to Figure 3.

$p_\pi$  orbitals. The  $12e$  is the  $\pi$  bonding and the  $13e$  the  $\pi$  antibonding combination of  $3d_\pi$  and Cl  $p_\pi$  orbitals (see Figure 4), while the  $2b_2$  ( $d_{xy}$ ) remains a purely  $3d_\pi-2\pi^*$  bonding orbital. Note that the  $2b_2$  and  $12e$  remain almost degenerate, the loss of one  $2\pi^*$  bonding interaction in  $12e$  apparently being compensated by the Cl  $3p_\pi$  bonding, but the antibonding with Cl  $3p_\pi$  pushes the  $13e$  up so that it becomes more than 1.5 eV higher than its  $t_{2g}$  partners. This gap between the HOMO and lower orbitals will be important for the excitation spectrum.

The  $13e$  has more Cl character than the  $12e$  orbital (74 and 22%, respectively), although the Cl  $3p$  orbital energy of the atom is lower than the  $\text{Mn}(\text{CO})_5$  " $t_{2g}$ "- $d_\pi$  orbital energy. This can be explained by taking the charges on the atoms into account. Since the chlorine atom bears a charge of approximately  $-0.4e$ , its orbital energies are all shifted upward, whereas the  $\text{Mn}(\text{CO})_5$  orbital energies are shifted downward because of the positive charge on this fragment. This has been taken into account in the qualitative orbital interaction diagram of Figure 2, by positioning the  $\text{Mn}(\text{CO})_5$   $d_\pi$  orbital below the Cl  $3p$  orbital so that the  $\text{MnCl}(\text{CO})_5$   $12e$  orbital will have more metal character, whereas the  $13e$  orbital has more chlorine character. We wish to caution, however, that the relative Mn  $3d_\pi$  and Cl  $3p_\pi$  character of the  $12e$  and  $13e$  orbitals is susceptible to considerable change upon removing an electron out of these orbitals by ionization or excitation. We find orbital relaxation in such ionized or excited states to strongly increase the metal character of the  $13e$ . These effects are not peculiar to DFT calculations. Recent CASSCF/CASPT2 calculations by Wilms and Daniel<sup>37</sup> show more pronounced Mn 3d character of  $13e$  already in the ground state and predominant 3d character of the  $13e$  in the first excited state.

**Excited States.** The  $13e$  HOMO lies 1.5 eV above the other occupied orbitals, and excitations from this orbital to the lowest virtual orbitals are, therefore, of particular interest. Also the lowest excitations from the  $2b_2$  and the  $12e$  have been calculated. Higher excitations than the  $2b_2 \rightarrow 23a_1$  and  $12e \rightarrow 23a_1$  have not been calculated, since those would be too high in energy to play an important role in the photochemistry of  $\text{MnCl}(\text{CO})_5$ .

(37) Wilms, M. P.; Daniel, C. Private communication.

**Table 2.** Energies (cm<sup>-1</sup>) and Intensities for Electronic Transitions in MnCl(CO)<sub>5</sub>

state	transition	character	type	energy (cm <sup>-1</sup> )	intensity	exptl bands <sup>a</sup>
a <sup>3</sup> E	13e → 22a <sub>1</sub>	MnCl π* → MnCl σ*	Mn/Cl LF	21 207		
a <sup>1</sup> E	13e → 22a <sub>1</sub>	MnCl π* → MnCl σ*	Mn/Cl LF	23 604 <sup>b</sup>	0.083 1	26 520
b <sup>3</sup> E	13e → 7b <sub>1</sub>	MnCl π* → d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	Mn/CO LF	29 118		
a <sup>3</sup> A <sub>1</sub>	13e → 14e	MnCl π* → 2π*	Mn,Cl → CO CT	30 020		
a <sup>1</sup> A <sub>1</sub>	13e → 14e	MnCl π* → 2π*	Mn,Cl → CO CT	30 539 <sup>b</sup>	0.139	
c <sup>3</sup> E	13e → 3b <sub>2</sub>	MnCl π* → 2π*	Mn,Cl → CO CT	30 861		
d <sup>3</sup> E	13e → 8b <sub>1</sub>	MnCl π* → 2π*	Mn,Cl → CO CT	30 936		
b <sup>1</sup> E	13e → 7b <sub>1</sub>	MnCl π* → d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	Mn/CO LF	32 138 <sup>b</sup>	0.000 201	
c <sup>1</sup> E	13e → 3b <sub>2</sub>	MnCl π* → 2π*	Mn,Cl → CO CT	33 022 <sup>b</sup>	0.000 371	
a <sup>3</sup> B <sub>2</sub>	2b <sub>2</sub> → 22a <sub>1</sub>	d <sub>xy</sub> → MnCl σ*	Mn/Cl LF	33 077		
d <sup>1</sup> E	13e → 8b <sub>1</sub>	MnCl π* → 2π*	Mn,Cl → CO CT	34 226 <sup>b</sup>	0.107	
e <sup>3</sup> E	12e → 22a <sub>1</sub>	MnCl π → MnCl σ*	Mn/Cl LF	34 584		
a <sup>3</sup> A <sub>2</sub>	2b <sub>2</sub> → 7b <sub>1</sub>	d <sub>xy</sub> → d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	Mn/CO LF	34 749		
a <sup>1</sup> B <sub>2</sub>	2b <sub>2</sub> → 22a <sub>1</sub>	d <sub>xy</sub> → MnCl σ*	Mn,Cl LF	34 834		
e <sup>1</sup> E	13e → 23a <sub>1</sub>	MnCl π* → MnCO <sub>ax</sub> σ*	Mn/CO LF	35 011 <sup>b</sup>	0.005 25	
f <sup>3</sup> E	13e → 23a <sub>1</sub>	MnCl π* → MnCO <sub>ax</sub> σ*	Mn/CO LF	35 034		
f <sup>1</sup> E	12e → 22a <sub>1</sub>	MnCl π → MnCl σ*	Mn/Cl LF	35 995 <sup>b</sup>	0.892	37 000
g <sup>3</sup> E	2b <sub>2</sub> → 14e	d <sub>xy</sub> → 2π*	Mn → CO CT	37 820		
a <sup>1</sup> A <sub>2</sub>	2b <sub>2</sub> → 7b <sub>1</sub>	d <sub>xy</sub> → d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	Mn/CO LF	38 376		
g <sup>1</sup> E	2b <sub>2</sub> → 14e	d <sub>xy</sub> → 2π*	Mn → CO CT	39 148 <sup>b</sup>	2.49	
b <sup>3</sup> A <sub>1</sub>	21a <sub>1</sub> → 22a <sub>1</sub>	MnCl σ → MnCl σ*	Mn/Cl LF	39 549		
b <sup>1</sup> A <sub>1</sub>	21a <sub>1</sub> → 22a <sub>1</sub>	MnCl σ → MnCl σ*	Mn/Cl LF	43 745 <sup>b</sup>	2.74	43 000

<sup>a</sup> Reference 18. <sup>b</sup> Symmetry allowed.

Transition intensities were estimated with the program Dipole.<sup>38</sup> The total transition dipole moment was approximated by the transition dipole moment between the initial and final MO.

The results are shown in Table 2.

As expected the two lowest excited states are the triplet and singlet states corresponding to the 13e → 22a<sub>1</sub> (Mn–Cl π\* → Mn–Cl σ\*) transition. These states are calculated at 21 207 and 23 604 cm<sup>-1</sup>, respectively. As mentioned earlier, the character of both the 12e and 13e orbitals changes upon excitation from the 13e orbital. In the excited state, the 12e acquires more Cl 3p character, while the Mn d<sub>xz/yz</sub> character of the 13e orbital increases. The calculated transition energies are in reasonable agreement with the first broad band in the experimental spectrum. The character of the first transition is beyond doubt, although the different ways it has been denoted may reflect genuine differences of opinion rather than being just a matter of semantics. In the past it has always been designated as a d → d (d<sub>π</sub> → d<sub>z<sup>2</sup></sub>) or LF transition. This, however, should not carry the implication—as it sometimes did—of antibonding Mn–CO<sub>ax</sub> character and therefore expected photoactivity with respect to axial CO dissociation. Our present results and the orbital composition of Pierloot *et al.*<sup>4,5</sup> indicate that the Mn–Cl π\* → Mn–Cl σ\* transition, or the Mn/Cl LF transition, is a more appropriate description. This has also been suggested by McLean.<sup>19</sup> It is not a Mn/CO LF transition. This difference in character, from what has been generally assumed, sheds some doubt on the assumption of Mn–CO<sub>ax</sub> dissociative character. This point will be addressed in the next section.

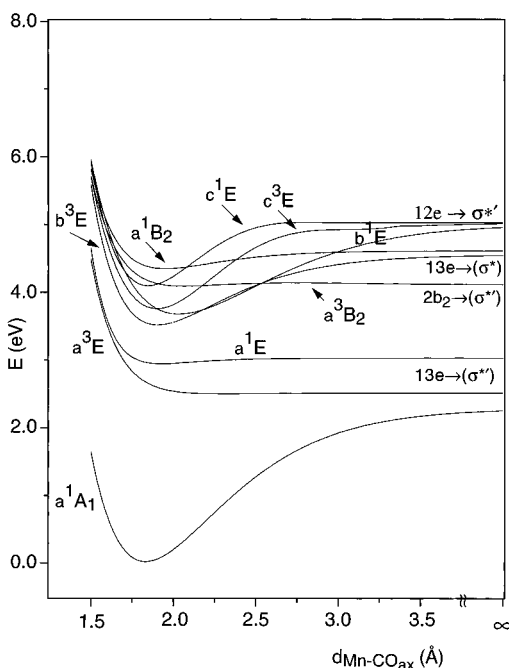
The 22a<sub>1</sub> lies about 1 eV below the other virtual orbitals, and excitations to those higher virtuals come at energies that are some 8000 cm<sup>-1</sup> higher than the 13e → 22a<sub>1</sub> transition. Because of the near degeneracy of the 14e, 7b<sub>1</sub>, 3b<sub>2</sub>, 8b<sub>1</sub>, 23a<sub>1</sub>, and 15e orbitals, many excitations out of the 13e to this set of virtuals are present between 29 000 and 35 000 cm<sup>-1</sup>, of which all transitions to singlet states are allowed. The first transition with Mn/CO LF character, the 13e to 7b<sub>1</sub> (d<sub>x<sup>2</sup>-y<sup>2</sup></sub>), occurs at 29 118 cm<sup>-1</sup> and 32 138 cm<sup>-1</sup> for triplet and singlet, respectively. This LF transition has the expected low intensity, but this excited state is interesting in view of its probably strongly Mn–CO<sub>eq</sub> dissociative character. At similar energy, at 30 020

and 30 539 cm<sup>-1</sup>, the first charge transfer (CT) excitations occur, corresponding to the singlet and triplet 13e → 14e transitions. They have Mn,Cl → CO 2π\* CT character and much higher intensity. Although an e → e transition gives rise to A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, and B<sub>2</sub> states, only the mean energy of these states has been calculated, since no major differences between these four states are expected. As seen from the intensities in Table 2, the 13e → 14e transition may contribute to the high-energy side of the first band, which may partly account for its broadness. The lowest Mn/CO<sub>ax</sub> LF transitions, the 13e → 23a<sub>1</sub>, Mn–Cl π\* → Mn–CO<sub>ax</sub> σ\* triplet and singlet states, have been calculated at 35 034 and 35 011 cm<sup>-1</sup>, respectively. They have low intensity, as was the case for the Mn/CO<sub>eq</sub> LF transitions, but are photochemically very interesting since, according to the results for Mn<sub>2</sub>(CO)<sub>10</sub>,<sup>3b</sup> these states are expected to be strongly Mn–CO<sub>ax</sub> dissociative.

Until ca. 35 000 cm<sup>-1</sup> we encounter most of the excitations out of 13e into the 22a<sub>1</sub>–15e set of virtuals (which have all been calculated except the ones into 15e), but above this energy transitions out of the 2b<sub>2</sub>, 12e, and 21a<sub>1</sub> start to play a role. At 33 077 cm<sup>-1</sup> the first transition arising out of the HOMO-1 orbital, to the <sup>3</sup>B<sub>2</sub>(2b<sub>2</sub>(d<sub>xy</sub>) → 22a<sub>1</sub>(σ\*)) triplet excited state, is found, its singlet component being located at 34 834 cm<sup>-1</sup> (the A<sub>1</sub> → B<sub>2</sub> transition is forbidden). The 12e → 22a<sub>1</sub> (σ\*) excitations are very close. The intensity is surprisingly large, and these transitions will contribute to the band around 37 000 cm<sup>-1</sup>, although the 2b<sub>2</sub> → 14e transition at 39 148 cm<sup>-1</sup> has high intensity and will contribute most. This is a genuine CT transition, which can account for the strong solvatochromic behavior<sup>17</sup> of the corresponding band.

The 2b<sub>2</sub> (d<sub>xy</sub>) → 7b<sub>1</sub> (d<sub>x<sup>2</sup>-y<sup>2</sup></sub>) Mn/CO LF transition, which may be expected to be Mn–CO<sub>eq</sub> dissociative, is calculated in this region, at 38 376 cm<sup>-1</sup> (singlet; the triplet is at 34 749 cm<sup>-1</sup>). This transition is forbidden.

The only interesting transition from the point of view of Mn–Cl bond breaking is the Mn–Cl σ → σ\*, 21a<sub>1</sub> → 22a<sub>1</sub> excitation. The triplet and singlet states corresponding to this transition are located at 39 549 and 43 745 cm<sup>-1</sup>, respectively. They will contribute to the high-energy band at 43 000 cm<sup>-1</sup>, but other transitions which were not calculated here, will also contribute to this band.



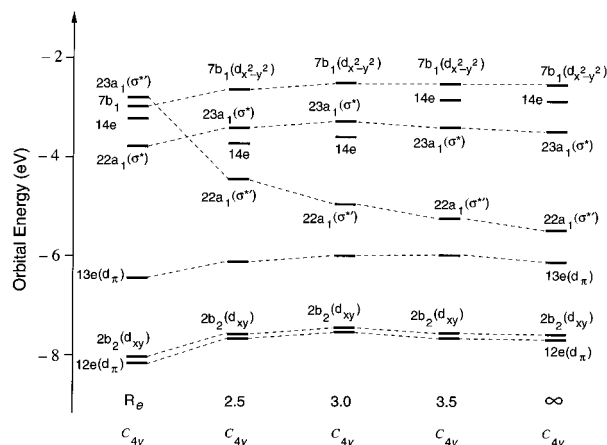
**Figure 5.** Potential Energy Curves for the dissociation of axial CO in  $\text{MnCl}(\text{CO})_5$ .

#### 4. Photochemistry

**Potential Energy Curves for Axial CO Loss.** For the ground and lowest excited states we have calculated PECs for loss of the axial CO ligand. The  $a-c^{1,3}E$  curves are shown in Figure 5. Of all the curves above the  $c^3E$  we have, apart from the “companion”  $c^1E$ , only drawn  $a^{1,3}B_2$ , since these are the only dissociative ones. The  $a^{1,3}B_2$  curves around  $R_e$  in fact cross many PECs of other symmetries (not shown in the figure, but see the excitation energies at  $R_e$  in Table 2), which, however, all have bonding shapes similar to  $c^{1,3}E$ . That these higher excited states (except for the  $a^{1,3}B_2$ ) do not readily lead to CO dissociation may be judged already from the behavior of the relevant orbital energies as a function of Mn–CO distance (see discussion below). Their energies are too high anyway to be populated by the UV–vis excitation used in the photochemical experiments.

The calculated PEC for the ground state has a shallow minimum, which agrees well with the rather low IR frequency for Mn–C vibrations. The asymptotic dissociation limit lies at 2.31 eV above the equilibrium energy, corresponding to a dissociation energy of 222 kJ/mol. This is near the DFT value of 200 kJ/mol for  $\text{Mn}_2(\text{CO})_{10}$ .<sup>3b</sup> Restricted Hartree–Fock calculations by Davy and Hall lead, as usual in the case of a metal–carbonyl bond, to a much lower dissociation energy of 86.9 kJ/mol.<sup>10</sup> When relaxation effects are included, our calculated dissociation energy drops to 176 kJ/mol and the CO’s bend toward the Cl, because of the bonding overlap between these fragments. No experimental dissociation energies are known since thermal loss of an equatorial CO is more favorable (*vide infra*).

Before discussing the excited state PECs, it is instructive to consider the orbital characters and energies in the ground state at various Mn–CO<sub>ax</sub> distances (Figure 6). The most remarkable feature in Figure 6 is the steep descent of the Mn–CO<sub>ax</sub>  $\sigma$  antibonding  $23a_1$  orbital (it is accompanied by a rise of the  $\sigma$  bonding  $20a_1$  orbital, not shown in the figure), whereas the other orbitals are relatively little affected. As a result the  $23a_1$  ( $\sigma^*$ ) orbital very soon crosses the Mn–Cl  $\sigma$  antibonding orbital  $22a_1$  ( $\sigma^*$ ), already near a Mn–CO<sub>ax</sub> distance of 2 Å.

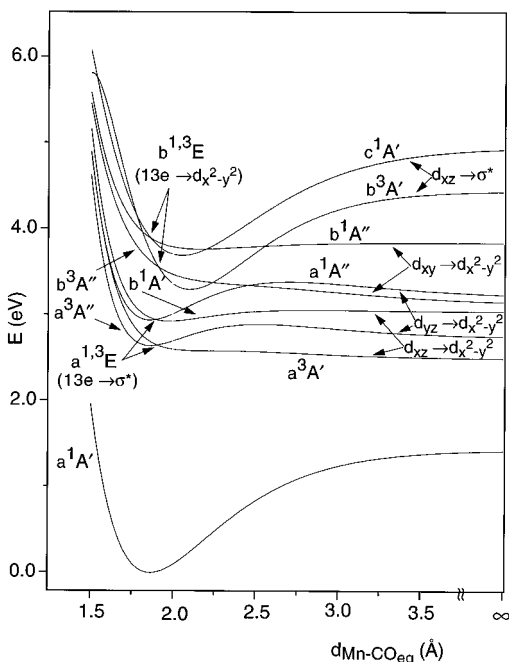


**Figure 6.** Orbital energies and dominant characters of the highest occupied and lowest unoccupied MO’s at several Mn–CO<sub>ax</sub> bond lengths.

The lowest excited states of E symmetry,  $a^1E$  and  $a^3E$ , will have  $13e \pi^* \rightarrow 22a_1 \sigma^*$  character before the crossing point, but change to  $13e \pi^* \rightarrow 23a_1 \sigma^{*'}$  in the crossing region. Since the  $13e \pi^* \rightarrow 22a_1 \sigma^*$  excitation does not affect the Mn–CO<sub>ax</sub> bond, we would expect the  $a^1E$  and  $a^3E$  PECs to be bonding, i.e., exhibit a minimum close to the equilibrium distance and curve upward at longer distances. A barrier would then indicate the avoided crossing to the descending PEC of the excited state with  $13e \pi^* \rightarrow 23a_1 \sigma^{*'}$  character, which is asymptotically calculated to lie at much lower energy than the  $13e \pi^* \rightarrow 22a_1 \sigma^*$  (Mn–Cl) state (cf. Figures 5 and 6). We note, however, that the singlet  $a^1E$  PEC in Figure 5 has only a very weak minimum, and the triplet  $a^3E$  none at all. The lack of a barrier can be understood from the very rapid lowering of the  $23a_1$  ( $\sigma^*$ ) orbital with Mn–CO<sub>ax</sub> distance, which leads to very rapid descent of the initially high-lying  $13e \rightarrow 23a_1$  ( $\sigma^*$ ) state. This leaves the  $a^{1,3}E$  PECs hardly any room to curve upward, and apparently a sufficiently large interaction between the states exists to make the crossing strongly avoided and virtually suppresses any barrier. Exactly the same situation has been observed for axial CO dissociation in  $\text{Mn}_2(\text{CO})_{10}$ .<sup>3b</sup> Of course, the  $13e \rightarrow 23a_1$  ( $\sigma^*$ ) states, which are the  $e^1E$ ,  $f^3E$  states at equilibrium geometry, cross with the lower  $1,3E$  states before becoming the lowest one. This means that  $13e \rightarrow \sigma^{*'}$  character shows up in successively lower E states before ending up in the lowest one, the  $a^{1,3}E$ .

The next higher E PECs are bonding, since no Mn–CO<sub>ax</sub> antibonding orbital is occupied in these states. The first correspond at  $R_e$  to excitations to  $d_{x^2-y^2}$  ( $b^{1,3}E$ ) or  $2\pi^*$  ( $c$  and  $d^{1,3}E$ ). It is clear from Figure 6 that asymptotically, at large Mn–CO<sub>ax</sub> distance, the first excited states above the low-lying  $13e \rightarrow \sigma^{*'}$  will be  $13e \rightarrow \sigma^*$  and  $12e \rightarrow \sigma^{*'}$ . So  $b^{1,3}E$  and  $c^{1,3}E$  will asymptotically hold this character. This implies that the electronic character of these states changes during CO<sub>ax</sub> dissociation, first to  $13e \rightarrow \sigma^{*'}$  character when this excitation “on its way down” crosses these excited states, and next to their asymptotic nature. As a consequence these PECs do not exhibit such a deep well as the ground state PEC but are more shallow. The  $b^{1,3}E$  states, which have  $13e \rightarrow 7b_1$  ( $d_{x^2-y^2}$ ) character at  $R_e$  (see Table 2), asymptotically hold the  $13e \rightarrow \sigma^*$  character that the  $a^{1,3}E$  had at  $R_e$ . The  $c^{1,3}E$  states become asymptotically  $12e \rightarrow \sigma^{*'}$  excited states. The excitation out of the  $12e$  orbital leads to considerable orbital relaxation, asymptotically even more so than at  $R_e$ . As a result  $12e$  virtually loses all 3d character, which explains the small singlet–triplet splitting of the asymptotic  $c^1E$  and  $c^3E$  curves. The avoided crossing to the  $12e \rightarrow \sigma^{*'}$  excited state does not make the  $c^{1,3}E$  PECs dissociative, the asymptotic





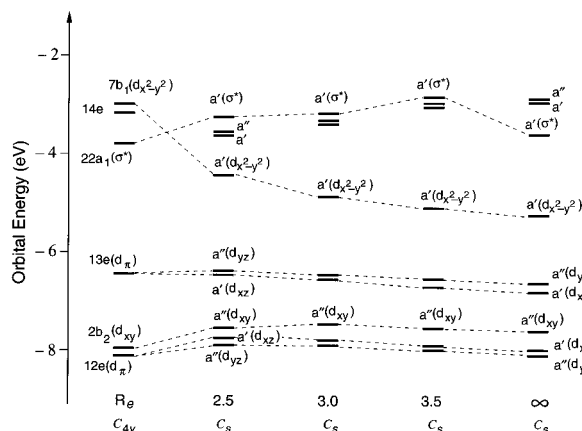
**Figure 7.** Potential energy curves for the dissociation of equatorial CO in  $\text{MnCl}(\text{CO})_5$ .

energy is still 0.9–1.25 eV above the energy at equilibrium distance. The avoided crossing, however, clearly shows up in the flat behavior of the  $c^{1,3}E$  PECs at larger distances.

We have drawn in Figure 5 one set of PECs for another symmetry, namely, the pair of dissociative states  $a^3B_2$  and  $a^1B_2$  states that correspond at equilibrium geometry to excitation from the second highest occupied molecular orbital to the Mn–Cl  $\sigma^*$  orbital, i.e., the  $2b_2 \rightarrow 22a_1$ ,  $d_{xy} \rightarrow \text{Mn–Cl } \sigma^*$  transition. As in the case of the  $a^{1,3}E$   $13e \rightarrow 22a_1$  excited state, the dissociative behavior is brought about by a change of character, again due to the rapid descent of the  $\sigma^*$  orbital. The  $a^{1,3}B_2$  states correspond asymptotically to the  $d_{xy} \rightarrow \text{Mn–CO}_{ax} \sigma^*$  transition. The  $a^3B_2$  and  $a^1B_2$  states mirror, at a higher energy, the behavior of the  $a^3E$  and  $a^1E$  states since they correspond to excitations out of  $2b_2$  rather than  $13e$  but are otherwise analogous. They are very slightly bonding for the singlet state and dissociative for the triplet state. We have chosen to present this behavior in the figure, although strictly speaking the avoided crossing of these  $B_2$  curves with the  $B_2$  states arising from the lower lying (at  $R_e$ )  $13e \rightarrow 14e$  should be taken into account. The “diabatic”  $a^{1,3}B_2$  PECs in the figure are, however, interesting for the photochemistry upon higher energy excitation; see below.

**Potential Energy Curves for Equatorial CO Loss.** For equatorial CO loss excitations from the  $13e$  HOMO to the three lowest virtual orbitals at equilibrium geometry and the  $2b_2 \rightarrow 22a_1$  transition are investigated. The PECs for the states that correspond at equilibrium geometry to  $a^{1,3}E$  ( $13e \rightarrow \text{Mn–Cl } \sigma^*$ ) and  $b^{1,3}E$  ( $13e \rightarrow d_{x^2-y^2}$ ) are displayed in Figure 7. The set of  $13e \rightarrow \text{CO } 2\pi^* \text{ Mn,Cl} \rightarrow \text{CO CT}$  transitions ( $a^{1,3}A_1$ ,  $c^{1,3}E$ ,  $d^{1,3}E$ , see Table 2) have been omitted from the figure.

Again the minimum in the ground state PEC is rather shallow in accord with the low frequencies of the Mn–C vibrations. The asymptotic dissociation limit lies at 1.43 eV, which corresponds to a dissociation energy of 138 kJ/mol. When relaxation effects are included, the dissociation energy drops to 99 kJ/mol, in reasonable agreement with the experimental value of 115 kJ/mol.<sup>39</sup> Davy and Hall report a restricted Hartree–Fock (RHF) dissociation energy of 77 kJ/mol.<sup>10</sup>



**Figure 8.** Orbital energies and dominant characters of the highest occupied and lowest unoccupied MO's at several Mn–CO<sub>eq</sub> bond lengths.

Before discussing the nature of the excited state PECs, we focus on the behavior of the orbitals during the release of CO. The orbital energies at several Mn–CO<sub>eq</sub> distances are shown in Figure 8 together with their predominant character. As in the case of axial CO loss, the energy of the Mn–CO  $\sigma$  antibonding orbital, in this case the  $7b_1 d_{x^2-y^2}$  orbital, decreases very rapidly upon elongating the Mn–CO distance. It crosses the  $22a_1$  Mn–Cl  $\sigma^*$  orbital at approximately 2.2 Å, which crossing will be avoided since both the  $B_1$  and  $A_1$  symmetries in  $C_{4v}$  change to  $A'$  in the  $C_s$  point group symmetry that holds upon Mn–CO<sub>eq</sub> bond elongation. As a result the  $a'$  LUMO changes character from Mn–Cl  $\sigma^*$  to “ $d_{x^2-y^2}$ ” (Mn–CO<sub>eq</sub>  $\sigma$  antibonding) after the crossing. The lowest excited states in the CO-loss product will clearly be the excitations from the three highest occupied orbitals to the  $d_{x^2-y^2}$  LUMO, as indeed indicated in Figure 7. Note that the  $13e$  orbitals, which are degenerate in  $C_{4v}$  symmetry, split into an  $a'$  (“ $d_{xz}$ ”) and an  $a''$  (“ $d_{yz}$ ”) orbital, assuming the leaving CO to be the one along the  $x$ -axis (and Cl along the  $z$ -axis). For notational convenience we denote these orbitals as  $d_{xz}$  and  $d_{yz}$ , also in Figures 7 and 8, but of course we should keep in mind that these Mn–Cl  $d_{\pi-p\pi}$  antibonding orbitals have in the ground state actually more Cl  $p_{\pi}$  character, while the  $12e$  derived pair has more  $d_{\pi}$  character (however, considerable changes in the relative Cl and Mn contributions occur upon excitation; see above).

The PECs of the lowest  $A'$  and  $A''$  states, arising from the  $a^{1,3}E$  states, show a similar dissociative behavior (at least the  $A'$  components) as the lowest  $E$  states for the dissociation of an axial CO. The situation is indeed very similar: the dissociative states arising from  $13e \rightarrow 7b_1 (d_{x^2-y^2})$  excitations, which are at  $R_e$  some 8000–9000  $\text{cm}^{-1}$  higher than the lowest excited states of  $E$  symmetry, rapidly cross upon Mn–CO<sub>eq</sub> bond lengthening with the states located below them, and the  $A'$  and  $A''$  states resulting from the lowest  $E$  states ( $a^{1,3}E$ ) rapidly change character from  $13e \rightarrow 22a_1$  Mn–Cl  $\sigma^*$  at equilibrium geometry to  $13e \rightarrow d_{x^2-y^2}$  Mn–CO<sub>eq</sub>  $\sigma^*$  character at larger Mn–CO<sub>eq</sub> distances.<sup>41</sup> The crossing is so soon that these  $A'$  and  $A''$  states are either weakly bonding or dissociative. The difference in behavior of the  $A'$  and  $A''$  states is striking. The  $A'$  states are purely ( $a^3A'$ ) or nearly ( $b^1A'$ ) dissociative, whereas the  $a^1A''$  and  $a^3A''$  states still exhibit a clear bonding minimum. This difference can be explained if one takes into account the

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 (41) For reasons of clarity orbitals in  $C_s$  symmetry are designated by their symmetry label in the  $C_{4v}$  ground state equilibrium geometry.

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the radicals. The absence of Mn–Cl homolysis is therefore attributed to the high thermodynamic stability of the Mn–Cl bond.

The  $^3A_1$  state correlating with the  $^2A_1 + ^2P$  ground state of the radicals corresponds from ca. 2.7 Å onward to the Mn–Cl  $\sigma \rightarrow \text{Mn–Cl } \sigma^* 21a_1 \rightarrow 22a_1$  transition. The orbital energies (not shown here) show the expected behavior of, on the one hand, rapid lowering of the Mn–Cl  $\sigma^* 22a_1$  LUMO, which without crossings becomes asymptotically the singly occupied  $\sigma_{\text{hy}}$  hybrid of the  $\text{Mn}(\text{CO})_5^*$  radical, and, on the other hand, an increase in energy of the Mn–Cl  $\sigma 21a_1$ , which asymptotically becomes the  $\text{Cl } 3p_\sigma$  atomic orbital. The diminishing gap between these orbitals corresponds to the dissociative character of the  $a^3A_1$  PEC in the asymptotic tail.

At the equilibrium geometry the lowest  $^3A_1$  state, arising from the  $13e \rightarrow 14e$  transition, has a lower energy than the  $\sigma \rightarrow \sigma^*$  state and an avoided crossing between these two states will thus occur. Therefore, the PEC of the  $13e \rightarrow 14e$  triplet state has also been calculated near equilibrium geometry. The barrier resulting from the avoided crossing is clearly visible on the  $a^3A_1$  PEC in Figure 9. The  $\sigma \rightarrow \sigma^*$  excitation energy has been calculated at shorter distances than 2.7 Å, and a sketch of the steeply descending  $\sigma \rightarrow \sigma^*$  state is given in Figure 9, without however trying to map out in detail the avoided crossings through which the  $\sigma \rightarrow \sigma^*$  character descends (except for the last one). Excitation to the  $b^1A_1, a^3A_1$  ( $13e \rightarrow 14e$ ) at  $R_e$  or to nearby higher excited states can only yield the radical products after crossing the barrier in the  $a^3A_1$  PEC. In this region, many states are present (not drawn in Figure 9) and internal conversion toward lower states will probably be rather fast. As a consequence Mn–Cl bond homolysis is unlikely. It is in fact not even observed with high-energy radiation.<sup>7</sup>

**Photochemistry of  $\text{MnCl}(\text{CO})_5$ .** Irradiation of  $\text{MnCl}(\text{CO})_5$  with low-energy light results in occupation of the  $a^1E$  state. The excited molecules can then either lose axial (*trans*-) or equatorial (*cis*-) CO after overcoming only a small barrier in both directions or undergo intersystem crossing to the  $a^3E$  state. From this latter state axial and equatorial CO loss can occur without any barrier. Indeed, photochemical *cis*- and *trans*-CO exchange has been observed in  $^{13}\text{C}$ O exchange experiments.<sup>43</sup> It should, however, be cautioned that this does not strictly prove the occurrence of both primary photoprocesses, since fast rearrangements may also occur during these exchange processes. Our results do point to the occurrence of both reactions. In this respect they do not substantiate the assumption that photochemical *trans*-CO dissociation is most likely for this type of complex. This assumption has been generally made, and the absence of *trans*-substituted photoproducts upon irradiation of metal pentacarbonyl halides in the presence of a Lewis base has been attributed<sup>7</sup> to rapid rearrangement of the apical  $\text{MnCl}(\text{CO})_4$  primary photoproduct resulting from *trans*-CO loss to  $\text{MnCl}(\text{CO})_4$  with Cl in the basal plane. This point has recently been studied in detail by Pierloot *et al.*<sup>4</sup> and Matsubara *et al.*<sup>8c</sup> The results of these studies are relevant for the present work in that we certainly cannot exclude *trans*-CO loss.

The  $A''$  components of the  $b^3E$  and  $b^1E$  states, which are located at higher energy, are also dissociative for equatorial CO loss, due to crossing by the  $2b_2(d_{xy}) \rightarrow 7b_1(d_{x^2-y^2})$  state (see Figure 7), but not for axial CO (see Figure 5). The presence of these states can account for the increase in quantum yield when going to shorter wavelength excitation. Irradiation at 366 nm ( $27\,322\text{ cm}^{-1}$ , 3.39 eV) results in CO loss with a quantum yield of 0.06, whereas irradiation at 313 nm ( $31\,948\text{ cm}^{-1}$ , 3.96 eV) gives a quantum yield of 0.44. Irradiation at 313 nm results in

population of the  $b^1E$  and  $b^3E$  states, most likely by population of the  $a^1A_1$  which has high intensity, followed by intersystem crossing. The  $A''$  components of  $b^1,^3E$  are dissociative for the equatorial CO. The 313 nm radiation may just not be able to populate the higher lying  $aB_2$  states, which are dissociative for the axial CO. Even if the  $aB_2$  states could be reached, release of CO from these states may have lower probability since nonradiative decay to close-lying excited states is expected to be rather fast because of the large density of states in this region. It is therefore expected that the ratio of equatorial to axial CO loss changes in favor of equatorial CO loss when the wavelength of excitation is shortened.

**Comparison of the Photochemistry of  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{MnH}(\text{CO})_5$ , and  $\text{MnCl}(\text{CO})_5$ .** In this section we will compare the results from calculations of the PECs of  $\text{Mn}_2(\text{CO})_{10}$  by Rosa *et al.*,<sup>3</sup> those of  $\text{MnH}(\text{CO})_5$  by Daniel *et al.*,<sup>28</sup> and the present results on  $\text{MnCl}(\text{CO})_5$ . These can be taken as prototype for respectively  $\text{Mn}(\text{CO})_5(M')$  ( $M' = \text{Mn}(\text{CO})_5$ ,  $\text{Re}(\text{CO})_5$ , etc.),  $\text{MnR}(\text{CO})_5$  ( $R = \text{H}, \text{CH}_3$ ), and  $\text{MnX}(\text{CO})_5$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ). All of these molecules can be built up by combining  $\text{Mn}(\text{CO})_5$  and another fragment with a singly occupied orbital. The differences between the molecules must thus stem from differences in these fragments and their interaction with  $\text{Mn}(\text{CO})_5$ .

As shown above, the photochemistry of organometallic compounds is primarily determined by the relative energies of the occupied and virtual orbitals in the ground state and their dependence on the geometry. The orbital interaction diagrams for the three compounds are given in Figure 2. [The orbital energies for  $\text{MnH}(\text{CO})_5$  and  $\text{Mn}_2(\text{CO})_{10}$  were calculated using the same basis set and functional as those for  $\text{MnCl}(\text{CO})_5$ , in previously optimized geometries.<sup>3,35</sup>] The compounds  $\text{MnH}(\text{CO})_5$  and  $\text{MnCl}(\text{CO})_5$  both have the Mn–H/Cl  $\sigma$  bonding orbital, with much H 1s and Cl  $3p_\sigma$  character, respectively, located below the occupied Mn 3d orbitals. In the case of  $\text{MnH}(\text{CO})_5$  the e ( $d_\pi$ ) orbitals are the  $d_{xz/yz}$  orbitals, in  $\text{MnCl}(\text{CO})_5$  the e orbitals split into two sets of Mn–Cl  $\pi$  and  $\pi^*$  orbitals. In the case of  $\text{Mn}_2(\text{CO})_{10}$  the ordering is reversed; here the Mn–Mn  $\sigma$  orbital is the HOMO and the e ( $d_{xz/yz}$ ) orbitals (the  $e_1 \pi$  bonding and  $e_3 \pi$  antibonding sets) are at lower energy.<sup>3a</sup> The relatively high energy of the  $\sigma$  orbital in the case of  $\text{Mn}_2(\text{CO})_{10}$ , when compared to  $\text{MnCl}(\text{CO})_5$  and  $\text{MnH}(\text{CO})_5$ , is caused by the rather high energy of the  $\text{Mn}(\text{CO})_5 \sigma_{\text{hy}}$  hybrid, when compared with the H 1s and Cl  $3p$  orbitals, and by the relatively weak interaction between the  $\sigma_{\text{hy}}$  orbitals.

In the case of  $\text{MnCl}(\text{CO})_5$  and  $\text{Mn}_2(\text{CO})_{10}$  the Mn–L ( $L = \text{Cl}$  or  $\text{Mn}(\text{CO})_5$ )  $\sigma^*$  orbital is the LUMO, whereas the Mn– $\text{CO}_{\text{ax}}$  and Mn– $\text{CO}_{\text{eq}}$   $\sigma^{*'}$  antibonding orbitals are located at higher energy (we denote the Mn– $\text{CO}_{\text{ax}}$  and Mn– $\text{CO}_{\text{eq}}$   $\sigma$  antibonding orbitals, “ $d_z$ ” and “ $d_{x^2-y^2}$ ”, respectively, both as  $\sigma^{*'}$ ).  $\text{MnH}(\text{CO})_5$  is special in that the Mn–H  $\sigma^*$  orbital is located at very high energy, considerably above the  $\sigma^{*'}$  orbitals. The LUMO is in this case a CO  $2\pi^*$  orbital. The diagram highlights the remarkably stronger interaction of the  $\text{Mn}(\text{CO})_5 \sigma_{\text{hy}}$  hybrid with H 1s than with another  $\text{Mn}(\text{CO})_5 \sigma_{\text{hy}}$ .

The three complexes show a strikingly similar behavior with respect to CO loss, which in all three cases occurs upon irradiation into the lowest energy band. In all cases the  $d_{xz/yz} \rightarrow \text{LUMO}$  excited state is dissociative for axial and equatorial<sup>44</sup> CO loss, but only after an (avoided) crossing of the LUMO with the Mn– $\text{CO}_{\text{ax}}$  or Mn– $\text{CO}_{\text{eq}}$   $\sigma^{*'}$  orbital, respectively. Whether there is a small barrier or not is not important here. Such a barrier may have a large influence on the quantum yield,

(44) Daniel *et al.* did not calculate PECs for the loss of equatorial CO. There is, however, no reason to assume a different behavior than  $\text{MnCl}(\text{CO})_5$ .

but it can be overcome by several mechanisms.<sup>45</sup> In the case of Mn<sub>2</sub>(CO)<sub>10</sub> there is also the transition  $\sigma \rightarrow \sigma^*$  at approximately the same energy (calculated at slightly lower energy but experimentally assigned to slightly higher energy than the  $d_{xz/yz} \rightarrow \sigma^*$ ). The  $\sigma \rightarrow \sigma^*$  excited state of Mn<sub>2</sub>(CO)<sub>10</sub> is, however, not Mn–CO dissociative. Thus, we may conclude that Mn–CO dissociation is very similar in these cases. It has little to do with the nature of the LUMO but is caused by the strongly Mn–CO antibonding nature of the  $\sigma^*$  orbitals. The rapid descent upon Mn–CO bond lengthening of these orbitals leads to the CO dissociation in the lowest excited state. This feature of the electronic structure is peculiar to the Mn(CO)<sub>5</sub> fragment, although the substituent influences the precise position of the dissociative state with respect to the other states.

The Mn–H/Cl/Mn homolysis shows large differences between these molecules, which is caused by the large influence of the substituent on the energy of the important orbitals. In the case of Mn<sub>2</sub>(CO)<sub>10</sub>, the  $\sigma \rightarrow \sigma^*$  triplet state is part of the lowest energy band and bond homolysis thus occurs very easily, being the primary photoprocess, together with Mn–CO dissociation, upon irradiation into the lowest band. In the case of MnH(CO)<sub>5</sub> and MnCl(CO)<sub>5</sub> the  $\sigma \rightarrow \sigma^*$  transitions are at too high energy to be excited directly in the usual photochemical experiment. At long distances the  $^3(\sigma \rightarrow \sigma^*)$  excited state will become much lower in energy, and asymptotically it will go to the ground states of the radical fragments. An avoided crossing will thus eventually occur with the lowest  $^3A_1$  state, making the lowest  $^3A_1$  PEC dissociative at long distances. However, the lowest  $^3A_1$  state at equilibrium geometry, corresponding to the 13e  $\rightarrow$  14e excitation, is already considerably higher than the  $d_{xz/yz} \rightarrow$  LUMO type excited state, which is responsible for the lowest band in the experimental spectrum. Even if irradiation takes place at sufficiently high energy to populate the lowest  $^3A_1$ , the barrier in the lowest  $^3A_1$  PEC, related to the avoided crossing (see Figure 9), will drastically reduce the quantum yield for Mn–H/Cl dissociation.

These results fit in nicely with the experimental observations that a primary photoprocess of all of these complexes is Mn–CO dissociation, with higher quantum yield for higher energy radiation due to increased Mn–CO<sub>eq</sub> dissociation. In Mn<sub>2</sub>(CO)<sub>10</sub> the Mn–Mn bond homolysis<sup>46</sup> is fully competitive with Mn–CO bond dissociation upon irradiation in the lowest band (1:1), the propensity to Mn–CO bond breaking increasing at higher energy. In MnH(CO)<sub>5</sub> and MnCl(CO)<sub>5</sub> Mn–H/Cl bond homolysis occurs much less readily. Mn–H bond dissociation only occurs upon irradiation with high energy<sup>47</sup> but in much lower yield than Mn–CO bond dissociation, whereas for MnCl(CO)<sub>5</sub> no Mn–Cl bond homolysis has (yet) been found.<sup>7</sup> The difference between these systems with respect to the Mn–Mn/H/Cl homolysis can be understood immediately from the positions of the  $\sigma$  and  $\sigma^*$  molecular orbitals (Figure 2).

## 5. Conclusions

We have considered both the photochemical Mn–CO dissociation and Mn–L  $\sigma$  bond homolysis in the complexes Mn(CO)<sub>5</sub>L with L = Cl, H, and Mn(CO)<sub>5</sub>.

As for the Mn–L photolysis, which readily occurs for the Mn–Mn bond in Mn<sub>2</sub>(CO)<sub>10</sub>, but not for the Mn–Cl and Mn–H bonds in MnCl(CO)<sub>5</sub> and MnH(CO)<sub>5</sub> respectively, we have been able to explain this behavior on the basis of the relative positions of the  $\sigma$  and  $\sigma^*$  orbitals in the occupied and virtual orbital level spectra.

As for the metal–carbonyl dissociation our calculations point to a mechanism of photochemical CO loss that differs substantially from the generally accepted one, which invokes dissociation occurring upon ligand-field excitation. In the case of MnCl(CO)<sub>5</sub> Wrighton *et al.*<sup>7</sup> suggested on the basis of ligand field theory that transitions to the lowest excited state would imply occupation of a  $d_z^2$ , which would, due to antibonding with axial CO, lead directly to axial CO loss. Higher energy excitation would lead to occupation of the higher  $d_{x^2-y^2}$  orbital and result in loss of an equatorial CO. This explanation directly accounts for the increase in quantum yield upon higher energy excitation. A similar explanation of the photochemistry was presented by Pierloot *et al.*<sup>4</sup>

Our calculations, however, demonstrate that the LUMO is not antibonding for either axial or equatorial CO. *The lowest excited state only becomes dissociative for both axial and equatorial CO after avoided crossing with a state which is Mn–CO dissociative but which is at too high energy at  $R_e$  to be populated directly.* The high-lying states are the 13e  $\rightarrow$  23a<sub>1</sub> ( $d_z^2 \sigma^*$ ) and 13e  $\rightarrow$  7b<sub>1</sub> ( $d_{x^2-y^2} \sigma^*$ ) LF excited states for axial and equatorial CO loss, respectively. The calculations show that the nature of the LUMO at the equilibrium geometry does not primarily determine the photochemistry of this complex. The geometry dependence of all antibonding orbitals has to be taken into account. This result—which substantiates previous findings for Mn<sub>2</sub>(CO)<sub>10</sub><sup>3b</sup>—implies an important *caveat* for the general practice of trying to interpret photochemical events in transition metal complexes on the basis of molecular orbital diagrams *at the equilibrium geometry*. A very clear example is Cr(CO)<sub>6</sub>, where we have recently found<sup>48</sup> precisely the same situation to apply: the ligand-field excited states are at  $R_e$  at high energy, but they descend so rapidly upon Cr–CO bond lengthening that they very soon cross the lowest excited state, which has CT character at  $R_e$ , so that the lowest excited state PEC becomes dissociative. Recent sophisticated CASSCF/CASPT2 calculations of the optical spectrum of Cr(CO)<sub>6</sub> by Pierloot *et al.*<sup>49</sup> provide support for this reassessment of the role of LF states in the photochemical metal–carbonyl dissociation process in that they show that the LF excited states of Cr(CO)<sub>6</sub> are—contrary to the original assignment by Beach and Gray<sup>50</sup>—located rather high in the spectrum, the photodissociative lowest excited states having clear CT character at  $R_e$ .

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