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The vacuum ultraviolet spectrum of $[Mn_2(CO)_{10}]$

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Abstract

The vacuum ultraviolet electronic spectrum of $[Mn_2(CO)_{10}]$ in the gas phase at 40°C has been recorded in the 210–110 nm region. The spectrum shows a set of three broad bands, poorly resolved. The first band appears at ~ 50000 cm^{-1} and lies in the classical UV region, thus being responsible for the strong absorption observed in the limit of the UV spectrum. A second extremly intense band system centred at about 70000 cm^{-1} dominates the region of high energy.

Introduction

The electronic structure and spectral properties of transition metal carbonyls constitute a topic of growing interest because of their rich photochemistry. Optical absorption spectra in the classical ultraviolet energy region for a wide number of such compounds have been reported, both in solution and in the gas phase. For technical reasons, research in the vacuum UV region (below 200 nm) is rarer. At present, and as far as we can ascertain, the vacuum UV spectra of some mononuclear carbonyl derivatives only (those of Group 6, Cr, Mo and W [1] and that of Fe [2]) have been recorded. As far as dinuclear carbonyl compounds are concerned, no descriptions of their vacuum UV spectrum have been published.

In this work, the gas phase electronic absorption spectrum of $[Mn_2(CO)_{10}]$ in the region going from 210 to 110 nm (47000–90900 cm^{-1}) has been recorded. The electronic features of $[Mn_2(CO)_{10}]$ have been completed with the spectrum reported by Levenson *et al.* [3] in the classical UV region, recorded in solution and in a nematic phase, which allowed an analysis of the polarization properties of the absorptions. After describing the experimental conditions, attempts to assign qualitatively the low lying bands, based on *ab initio* HF calculations, will be reported.

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Experimental section

The spectrum of $[Mn_2(CO)_{10}]$ was recorded by use of a laboratory made vacuum ultraviolet spectrometer described elsewhere [4], with slight modifications. In brief, the radiation produced in a windowless spark source [5] was dispersed by a monochromator with a holographic grating on a toric support. A beam splitter separated the reference and the sample. The cell was equipped with lithium fluoride windows limiting transmission to about 105 nm. The vacuum ultraviolet (VUV) light source was converted to UV-visible using a sodium salicylate coated window at the exit of the cell and monitored by a photomultiplier. The whole machine was run entirely by a personal computer.

$[Mn_2(CO)_{10}]$ was commercially available (Merck) and purified by sublimation before use. Due to the low vapour pressure of $[Mn_2(CO)_{10}]$, a thermostatic system was made and added to the cell, thus allowing heating and then maintenance of moderate temperatures. $[Mn_2(CO)_{10}]$ was introduced into the cell as a solid. After pumping, it was slowly warmed up to 40°C, then pumped out. The process was repeated several times and finally, the spectrum was recorded at 40°C. Unfortunately, in order to avoid deposition of products on the cell pressure control system (cooler than the cell itself), we had to disconnect it, i.e. the intensities reported are relative.

Theoretical

Two different SCFMO-HF calculations were carried out. In the first, SCF-I, the effective core potential (ECP) approximation was used both for Mn and for C and O. For Mn atoms the basis set (3/2/5)/[2/1/3] and ECP parameters of Hay *et al.* [6] were employed, while for C and O atoms the pseudopotential values of Durand and Barthelat [7] together with a double-ζ basis set for the valence were chosen. These calculations, with an overall total of 206 basis functions, were performed using the HONDO-7 package [8]. In order to obtain a better description of the Mn–Mn bond, a second set of calculations, SCF-II, was carried out. Using this approach, the inner electrons of Mn atoms were described by a model potential as proposed by Huzinaga *et al.* [9]. For valence electrons a (6/6/5)[2/2/3] basis set was used. For C and O atoms, the standard 4-31G basis set was chosen. These calculations (232 basis functions) were undertaken using the CADCPAC-4 program [10].

The experimental geometry reported by Dahl and Rundle [11] was used in the calculations (Fig. 1) and D_{4d} symmetry was assumed. Numerical optimization of the Mn–Mn inter-atomic distance using SCF-II led to a slightly larger Mn–Mn bond length (d(Mn–Mn) = 3.04 Å).

Results

The vacuum UV spectrum

In Fig. 2, the gas phase vacuum UV spectrum of $[Mn_2(CO)_{10}]$ in the 210–110 nm (47000–90900 cm^{-1}) region is reported. The spectrum has a set of three broad bands, poorly resolved. The band at lower energy is also the least intense. It appears at about 200 nm (50000 cm^{-1}) and shows a prominent shoulder at 197 nm

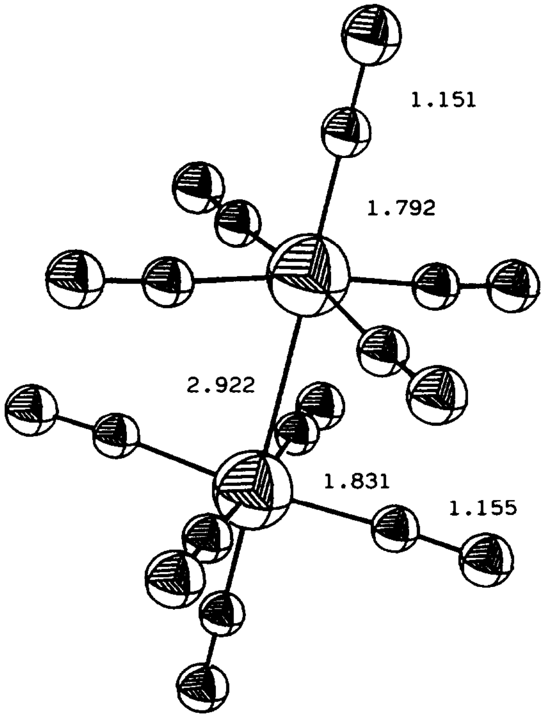

Fig. 1. Molecular structure of $[Mn_2(CO)_{10}]$ [11].

(50800 cm^{-1}). This band spreads into the classical UV region and is responsible for the strong absorption observed at its limit.

The second absorption is extremely intense and lies between 160 and 130 nm, with a maximum centred at 140 nm (71400 cm^{-1}). This band is preceded by two well-differentiated shoulders, one at 145 nm (69000 cm^{-1}) and the other, less prominent, at 153 nm (65400 cm^{-1}). Finally, at wavelengths lower than 130 nm, a third absorption of increasing intensity reaches the limit of our spectrometer.

In order to obtain the total view of the optical spectrum of $[Mn_2(CO)_{10}]$, the above description has to be completed by adding the classical region already recorded by Levenson *et al.* [3] (LGC), namely a relatively weak absorption at 29200 cm^{-1} (Band II) showing a small shoulder at 26700 cm^{-1} (Band I).

Discussion

The energies of the four highest occupied and lowest vacant orbitals obtained from SCF-I calculations are reported in Table 1. The HOMO and the LUMO are the σ_{Mn-Mn} ($1a_1$) and $\sigma^{\star}_{Mn-Mn}$ ($1b_2$) molecular orbitals formed from the Mn d_{z^2} atomic orbitals. Below the HOMO, a set of three degenerate d_π (e) orbitals close in energy are found. At an energy only slightly higher than that of the LUMO, there is a set of e type levels, mainly $\pi^{\star}_{CO}$ combinations somewhat mixed with Mn d orbitals.

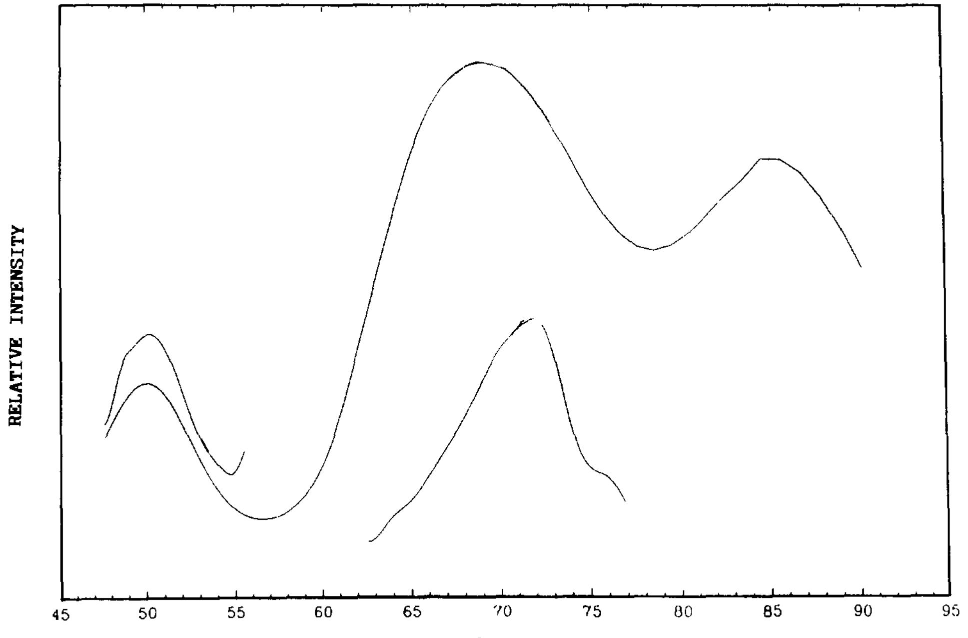

Fig. 2. The vacuum ultraviolet spectrum of $[\mathrm{Mn_2(CO)_{10}}]$

The ordering of occupied MOs found in our calculations agrees with the experimental intensity ratios (1 : 2 : 4) of the bands in the photoelectron spectrum as well as with the assignment proposed by Higginson *et al.* [12]. According to Koopmans' theorem, the first IP appearing at 8.02 eV arises from ionization of the $\sigma_{\mathrm{Mn-Mn}}$ level and is followed by a band at 8.35 eV, twice as intense, corresponding to a promotion of the e_3 electrons. The third band, 9.03 eV, is not resolved and was attributed to e_2 and e_1 orbitals. The IPs calculated using Koopmans' approximation were quite surprising. For the e type levels, the IPs were higher (12.17, 12.36 and 12.65 eV) than experiment, consistent with the well-known behaviour of this approximation. However, for the first band, an unusually low value was found (7.45 eV). The values obtained with the more complete theoretical frame, SCF-II,

Table 1

Calculated (SCF-I) orbital energies (a.u.) for frontier molecular orbitals of $\mathrm{Mn_2(CO)_{10}}$

Orbital	ϵ (au)
$2e_3(\pi^{*}_{\mathrm{CO}} + d_{\mathrm{Mn}})$	0.07326
$2e_2(\pi^{*}_{\mathrm{CO}} + d_{\mathrm{Mn}})$	0.07228
$2e_1(\pi^{*}_{\mathrm{CO}} + d_{\mathrm{Mn}})$	0.06789
$1b_2(\sigma^{*}_{\mathrm{Mn-Mn}})$	0.04755
$1a_1(\sigma_{\mathrm{Mn-Mn}})$	−0 27397
$1e_3(d_{\pi})$	−0 44725
$1e_2(d_{\pi})$	−0.45415
$1e_1(d_{\pi})$	−0.46493

were not significantly improved even after numerical optimization of the Mn–Mn bond distance (3.04 Å). It is worth noting that the IP of the free Mn atom is 7.43 eV [13]. These results suggest that probably the σ_{Mn-Mn} bond is destabilized at this level of calculation. Presumably introduction of electron correlation effects, as in other metal–metal systems [14], will increase the intermetallic electronic density, and a shortening of the inter-atomic bond distance together with a raising of the bond strength would be expected.

Our calculations seem to describe the $[Mn_2(CO)_{10}]$ structure as two weakly interacting $Mn(CO)_5$ fragments since the Mn–Mn bond order calculated from the SCF-I wave function is only 0.0704. However, it is worth noting that significant interactions between the two fragments are observed. Thus, the bond index of each Mn with the equatorial carbonyls of the other fragment is 0.0552. Indeed, the bond order associated with each pair of equatorial ligands belonging to different fragments is 0.0282. Taking into account all the interactions, the bond order between the $Mn(CO)_5$ moieties is 0.737. Significantly, more than half of this value corresponds to the interaction between equatorial carbonyls.

Focusing now on the electronic spectrum, and taking account of the orbital ordering of Table 1 as a qualitative guide, it seems reasonable to assign the lowest band (Band I) to the $A_1 \rightarrow B_2$ ($\sigma \rightarrow \sigma^*$) dipole-allowed transition. However, in the interpretation carried out by LGC, this transition was assumed to be responsible for Band II, while Band I was assigned to the $A_1 \rightarrow E_1$ ($d_\pi \rightarrow \sigma^*$) excitation, assuming that, due to electronic rearrangements, E_1 states would lie lower than B_2. In our opinion the validity of this assumption is open to criticism on the following grounds: (i) there is no reason to accept that the electronic rearrangement of the B_2 state should be less than that of E_1 states, and, in fact, in the photoelectron spectrum, the ground state of $[Mn_2(CO)_{10}]^+$ is $^2B_2$ and lies 0.3 eV lower than the first excited state, $^2E_3$. (ii) LGC were forced to this assignment to be consistent with the z polarization observed in Band II. However, as they noted, the polarization of Band I was not at all clear. Indeed, comparing the polarized and non-polarized spectra, it appears that Band II is a set of overlapping components. (iii) Comparing with the positions of the MLCT transitions observed for some mononuclear transition metal carbonyls ($[Cr(CO)_6]$ and $[Fe(CO)_5]$), they inferred that for Mn carbonyl derivatives they must be at about 38000 cm^{-1}, since the position of these transitions depends on the effective nuclear charge. However, $[Mn_2(CO)_{10}]$ is a dinuclear complex in which the number of π^*_{CO} levels is larger and some of them should appear at lower energies. Thus, MLCT transitions at about 30000 cm^{-1} cannot be *a priori* ruled out. For this reason and, taking into account the ratio of intensities of Bands I and II, in our opinion it would be preferable to assign the latter to the low components of MLCT transitions between Mn *d* orbitals and π^*_{CO} levels. Similarly the transitions observed in the limit of the classical UV spectrum culminating in the low energy region of the vacuum UV spectrum with the high intense absorption at 50000 cm^{-1} should also be of this nature. This band is assigned, by similarity with the spectrum of mononuclear metal carbonyls, to $\pi_{CO} \rightarrow \pi^*_{CO}$ internal ligand (IL) transitions.

Due to the lack of both experimental and theoretical work on the VUV electronic spectra of transition metal carbonyls, assignment of the extremely intense bands observed at energies higher than 60000 cm^{-1} is not at all obvious. However, because of their intensity, it seems reasonable to assign them to MLCT transitions arising from deeper metal *d* orbitals to higher π^*_{CO} levels. In the high energy region, and compared with the spectrum of free CO [15], excitations from σ_{Mn-CO} orbitals (mainly carbon lone pairs) towards π^*_{CO} levels are expected.

Finally, concerning the Rydberg bands, with an IP of 8.02 eV and a typical term value [16] of ~ 20000 cm^{-1}, the first transitions would start at about 45000 cm^{-1}, and due to their expected low intensity, they would be obscured by the lowest band observed in the VUV spectrum.

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