A Complete Assignment of the Ultraviolet Photoelectron Spectrum of $MnRe(CO)_{10}$

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In the course of our UV-Photoelectron spectroscopy (UPS) study of mononuclear transition metal carbonyls and of binuclear carbonyls possessing a metal–metal bond [1–8] we investigated the complexes $MM'(CO)_8(L\text{-}L)$ (M,M' = Mn, Re; L-L = i-Pr-DAB = i-Pr-N = CH-CH = N-i-Pr). The results of these spectra, which will be published in a forthcoming article, have been used to correlate the bonding properties and photochemistry of these complexes [9–11] to those of the unsubstituted carbonyls $MM'(CO)_{10}$ (M,M' = Mn, Re). Of these latter complexes, only the UP spectra of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ have been published [12, 13]. The nature of the σ- and π metal–metal interaction between the $Mn(CO)_5$· and ·$Re(CO)_5$ fragments in $MnRe(CO)_{10}$ is still unknown. In this communication we present the He(I) and He(II) photoelectron (pe) spectra of $MnRe(CO)_{10}$ and discuss the metal–metal interaction deduced from these spectra.

After synthesizing the title compound according to literature methods [14] and after identifying its purity with FT-IR [12, 14], the complex was measured on a Perkin-Elmer PS18 spectrometer modified with a Helectros He(I)/He(II) source. The spectra were calibrated with respect to Xe and Ar lines as internal calibrant.

The He(I) and He(II) pe spectra of $MnRe(CO)_{10}$ are shown in Fig. 1.

Table I shows that there is hardly any difference in ionization energy (I.E.) between the $a_1(d_{z^2} + d_{z^2})$ orbital of $Mn_2(CO)_{10}$ (8.02 eV) and $Re_2(CO)_{10}$ (8.06 eV). Therefore, about the same I.E. is expected for the a_1 orbital of $MnRe(CO)_{10}$, and this is in fact

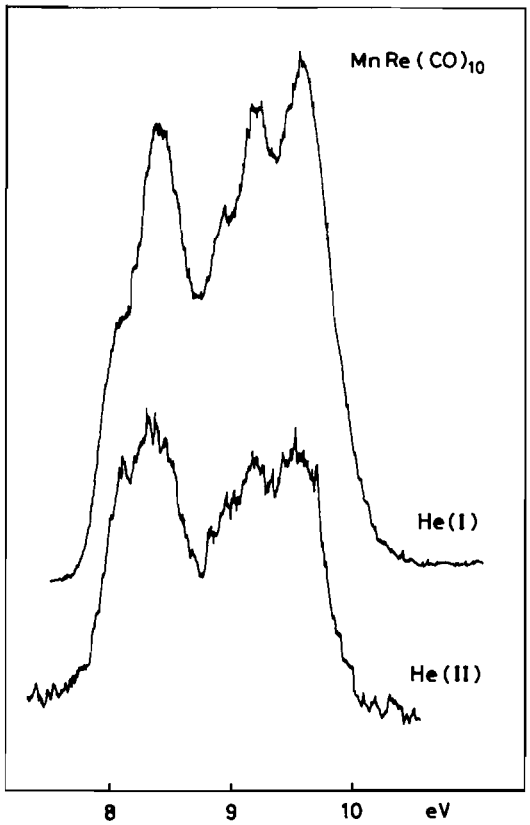

Fig. 1. Expanded He(I) and He(II) photoelectron spectra of $MnRe(CO)_{10}$.

observed (8.08 eV). The I.E. s of the metal $e(d_{xz}, d_{yz})$ and $b_2(d_{xy})$ orbitals of the fragments $Mn(CO)_5$ and $Re(CO)_5$ can also be derived from the data of the corresponding decacarbonyl complexes. The e levels of $Mn(CO)_5$ are found by taking the mean value of the known e_3 and e_1 levels of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ resp. [12, 13]. In the case of e^{Re} spin–orbit coupling has to be taken into account. The values of the corresponding b_2 levels of the $Mn(CO)_5$ moieties will be equal to the known e_2 levels of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ ($e_2^{M-M} = b_2^{M} + b_2^{M}$), since there is hardly any σ-interaction between these two b_2 orbitals. The values of the e^{Mn} and b_2^{Mn} of the $Mn(CO)_5$ fragment are 8.69 eV and 9.03 eV resp.

TABLE I. Observed Vertical Ionization Energies (eV).

Compound orbital	a_1	e_3	e_1	e_2	ref.
$Mn_2(CO)_{10}$	8.02	8.35	9.03	9.03	[12]
$Re_2(CO)_{10}$	8.06	8.56/8.86	9.28/9.60	9.60	[13]
$MnRe(CO)_{10}$	8.08	8.34	9.12	9.56	[This work]
Assignment	a_1	e^{Mn}	$b_2^{Mn} + e^{Re,,}$	$e^{Re,} + b_2^{Re}$	

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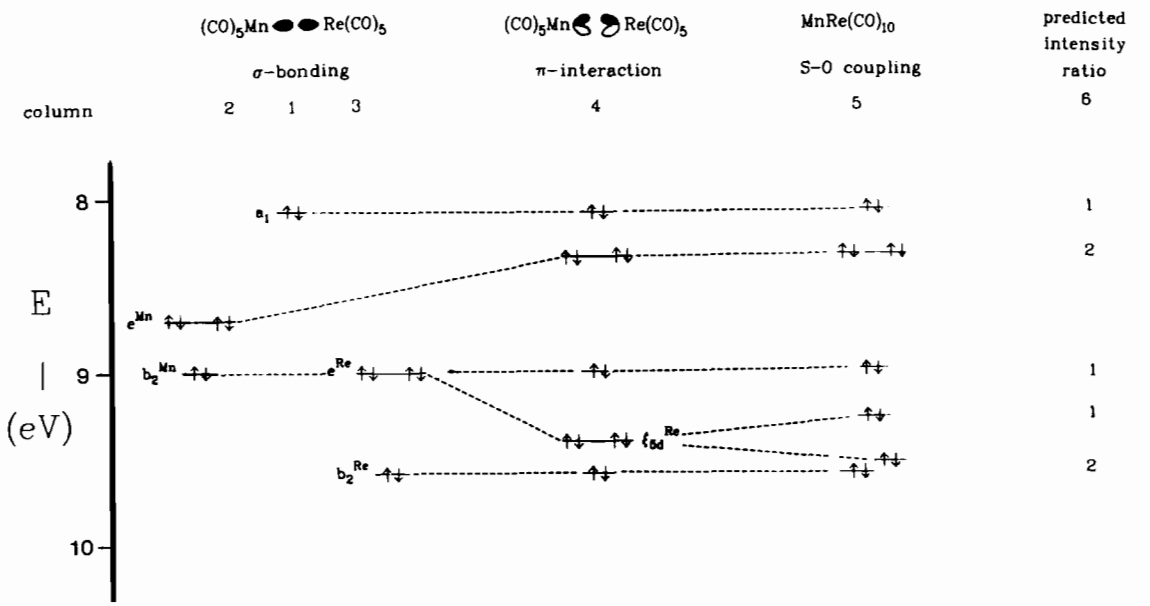

Fig. 2. Constructed level diagram for $MnRe(CO)_{10}$ and predicted He(I) band intensity ratios.

For the $Re(CO)_5$ fragment the corresponding I.E.s are 9.08 and 9.60 eV. The values of the a_1, e^{Mn}, $b_2{}^{Mn}$, e^{Re} and $b_2{}^{Re}$ orbitals are depicted in columns 1–3 of Fig. 2, in order to derive an interaction diagram for $MnRe(CO)_{10}$ by the following procedure.

Firstly, a simple σ-bonding is assumed between the Mn and Re d_{z^2} orbitals (column 2). Secondly, the known metal–metal π interaction between the e levels of 0.68 eV has to be considered (4) and thirdly, a spin–orbit coupling of the Re 5d atom of 0.30 eV has to be taken into account (column 5). With the aid of these three interactions a qualitative m.o. diagram can be constructed, as is illustrated in Fig. 2.

After mixing the two fragments $(CO)_5Mn^{\bullet}$ and $^{\bullet}Re(CO)_5$ completely, it is obvious that the bands in the He(I) pe will exhibit an intensity ratio of 1:2:2:2, which is in fact observed.

It can be concluded that in the mixed binuclear decacarbonyl complex $MnRe(CO)_{10}$ the interaction between the two e (d_{xz} and d_{yz}) levels is the same as was found for the $M_2(CO)_{10}$ (M = Mn, Re) complexes.

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