Electron energy loss spectroscopic study of $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ in the vapour phase[†]

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Abstract. Electron energy loss spectra (EELS) of Cr, Mo and W hexacarbonyls in the vapour phase are reported. Most of the bands observed are similar to those in optical spectra, but the two high energy transitions in the 9·8–11·2 eV region are reported here for the first time. ,Based on the orbital energies from the ultraviolet photoelectron spectra and the electronic transition energies from EELS and earlier optical studies, the molecular energy level schemes of these molecules are constructed.

Keywords. Electron energy loss spectra; transition metal hexacarbonyls; molecular energy level schemes.

1. Introduction

Transition metal carbonyls have been a subject of active investigation because of their importance both in theoretical chemistry and in photochemical processes. Theoretical and electronic spectroscopic studies have hitherto been concerned with the estimation of the amount of π bonding. Studies have clearly established the important role of the $\pi^*(CO)$ orbital in the stability of the carbonyls. The electronic absorption spectra of the carbonyls reported in the literature cover transitions only upto ≈ 8 eV (Robin 1975). Theory however, predicts the presence of transitions at still higher energies (Trogler *et al* 1979; Johnson and Klemperer 1977). The present investigation is aimed at obtaining information on higher energy excitations in three metal hexacarbonyls by employing electron energy loss spectroscopy (EELS). This technique is specially suited to probe transitions in the vacuum ultraviolet region. Besides showing the close similarity of the electronic spectra of the hexacarbonyls, we have been able to construct molecular energy level diagrams by making use of ultraviolet photoelectron spectroscopic data (Turner *et al* 1970; Higginson *et al* 1973).

2. Experimental

The spectrometer employed in the present study has been fully described earlier (Hedge *et al* 1985). An electron beam of 50 eV with a full width at half maximum

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(FWHM) of 300 meV was used in the present study. Commercial samples of the hexacarbonyls were used without further purification. Samples were kept at room temperature and the vapours were admitted into the collision chamber by a needle valve. Room temperature vapour pressure was sufficient to give an energy loss count rate of 10^4 c/s. All these spectra were recorded at least five times to establish the peak positions. We did not observe any CO impurity which could be present as a dissociation product.

3. Results and discussion

In figure 1 we show the electron energy loss spectra of the hexacarbonyls. The spectra are similar and exhibit clear band maxima. In order to assign the EEL features we
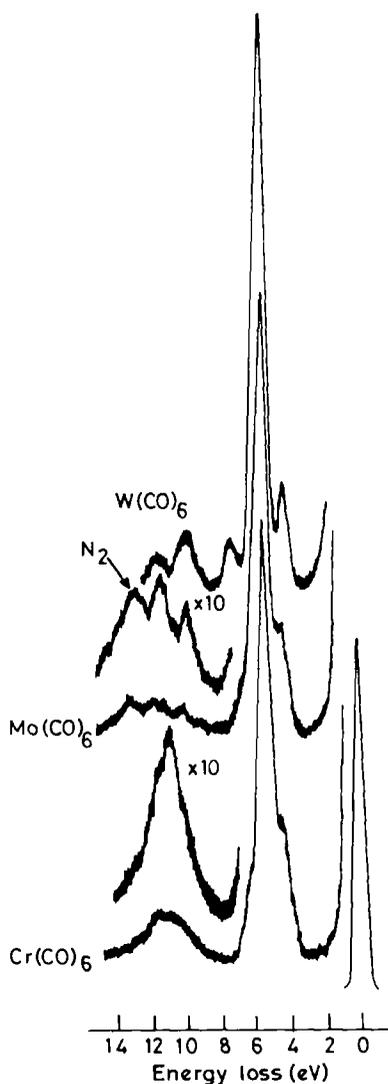

Figure 1.   Electron energy loss spectra of $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$.

need to have information on the occupied orbitals as well as the unoccupied ones. Ionization energies of the hexacarbonyls have been determined by photoelectron spectroscopy (Turner *et al* 1970; Higginson *et al* 1973). The predominantly metal d (t_{2g}) orbital ionization is at $\approx 8.5\,\text{eV}$ in all these carbonyls. The 13·3–16·2 eV region has ionizations due to orbitals derived from the 5σ and 1π orbitals of CO. In the 18 eV region, ionization occurs from the ligand 4σ derived levels. With regard to the unoccupied levels of the carbonyls, we follow the ordering obtained by Johnson and Klemperer (1977) from their SCF-X$_\alpha$-MSW calculations on Cr(CO)$_6$ and assume the same ordering to hold for the other two carbonyls. The first few unoccupied orbitals of interest are $9a_{1g}$, $9t_{1u}$, $3t_{2g}$, $2t_{2u}$, $6e_g$, $10t_{1u}$ and $2t_{1g}$ in order of increasing energy. Out of these, $9t_{1u}$, $3t_{2g}$, $2t_{2u}$ and $2t_{1g}$ are CO 2π-derived orbitals while $9a_{1g}$, $10t_{1u}$ and $6e_g$ are predominantly metal- (s, p and d) derived orbitals.

In table 1 we have summarized the electronic transitions of the three hexacarbonyls. Since the metal t_{2g} MO is at 8·5 eV and the other occupied ligand MOs are below 13·3 eV, all the lower energy transitions arise from t_{2g} MO. The lowest energy transition $(2t_{2g} \rightarrow 9a_{1g})$, is observed around 3·8 eV (Beach and Gray 1968); this transition is not observed in EELS. The next transition is due to a charge-transfer excitation $(2t_{2g} \rightarrow 9t_{1u})$ and is observed around 4·4 eV in optical spectroscopy (Beach and Gray 1968). The first EEL feature is due to this transition. The band in the 4·5–4·8 eV region (Beach and Gray 1968) found in the optical spectra is very weak and is not observed in EELS. The optical transition around 5·5 eV (Beach and Gray 1968) has the highest intensity and is due to the second charge-transfer transition $(2t_{2g} \rightarrow 2t_{2u})$. This is observed in EELS in the 5·2–5·4 eV region. Asymmetry found in the optical spectra in the blue side of this band is considered to be due to the presence of a transition-centred around 5·9 eV (Beach and Gray 1968). EEL spectra do not show any apparent asymmetry probably due to the low resolution. The asymmetry in the vacuum ultraviolet spectra (Iverson and Russell 1970) is also not significant. The transition in the 6·2–7·0 eV region has been observed in the optical spectra (Beach and Gray 1968) and has been assigned to the $2t_{2g} \rightarrow 2t_{1g}$ transition. The splitting of this band in W(CO)$_6$, observed in the optical spectra (Iverson and Russell 1970) is not seen in EELS.

Table 1. Electronic transitions of Cr(CO)$_6$, Mo(CO)$_6$ and W(CO)$_6$ and the assignments.

			Transition energy			
Cr(CO)$_6$		Mo(CO)$_6$		W(CO)$_6$		
EELS	Optical	EELS	Optical	EELS	Optical	Assignment
–	3.60[T,a] 3.91[S,a]	–	3.63[T,a] 4.05[S,a]	–	3.53[T,a] 3.96[S,a]	$2t_{2g} \rightarrow 9a_{1g}$
4·31	4.44[a]	4·31	4.32[a]	4·30	4.29[a]	$2t_{2g} \rightarrow 9t_{1u}$
–	4.83[a]	–	4.66[a]	–	4.54[a]	$2t_{2g} \rightarrow 3t_{2g}$
5·19	5.48[a]	5·28	5.44[a]	5·40	5.52[a]	$2t_{2g} \rightarrow 2t_{2u}$
6·16	6.32[b]	6·34	6.42[b]	7·00	6.35[b] 6.56[b]	$2t_{2g} \rightarrow 2t_{1g}$
10·39	–	9·86	–	9·80	–	$8t_{1u} \rightarrow 2t_{2u}$
11·10	–	11·19	–	11·00	–	$8t_{1u} \rightarrow 2t_{1g}$

T–triplet; S–singlet; [a]–from Beach and Gray (1968); [b]–From Iverson and Russell (1970).

An earlier optical study of Iverson and Russell (1970) reported two transitions in the 7·4–8·9 eV region, but the EEL spectra do not show evidence for them clearly. There are, however, two transitions in the EEL spectra above the first ionization energy in the 9·8–11·2 eV region; these two transitions, reported for the first time, probably arise from the second occupied level, $8t_{1u}$ as shown in table 1. An SCF-X_α-DV calculation (Trogler *et al* 1979) predicts the $8t_{1u} \rightarrow 9a_{1g}$ transition at 12·39 eV. From the molecular energy level scheme (figure 2) constructed on the basis of previous studies (Beach and Gray 1968; Iverson and Russell 1970; Higginson *et al* 1973), this transition works out to have an energy of 8·5 eV, but we do not see any EELS feature
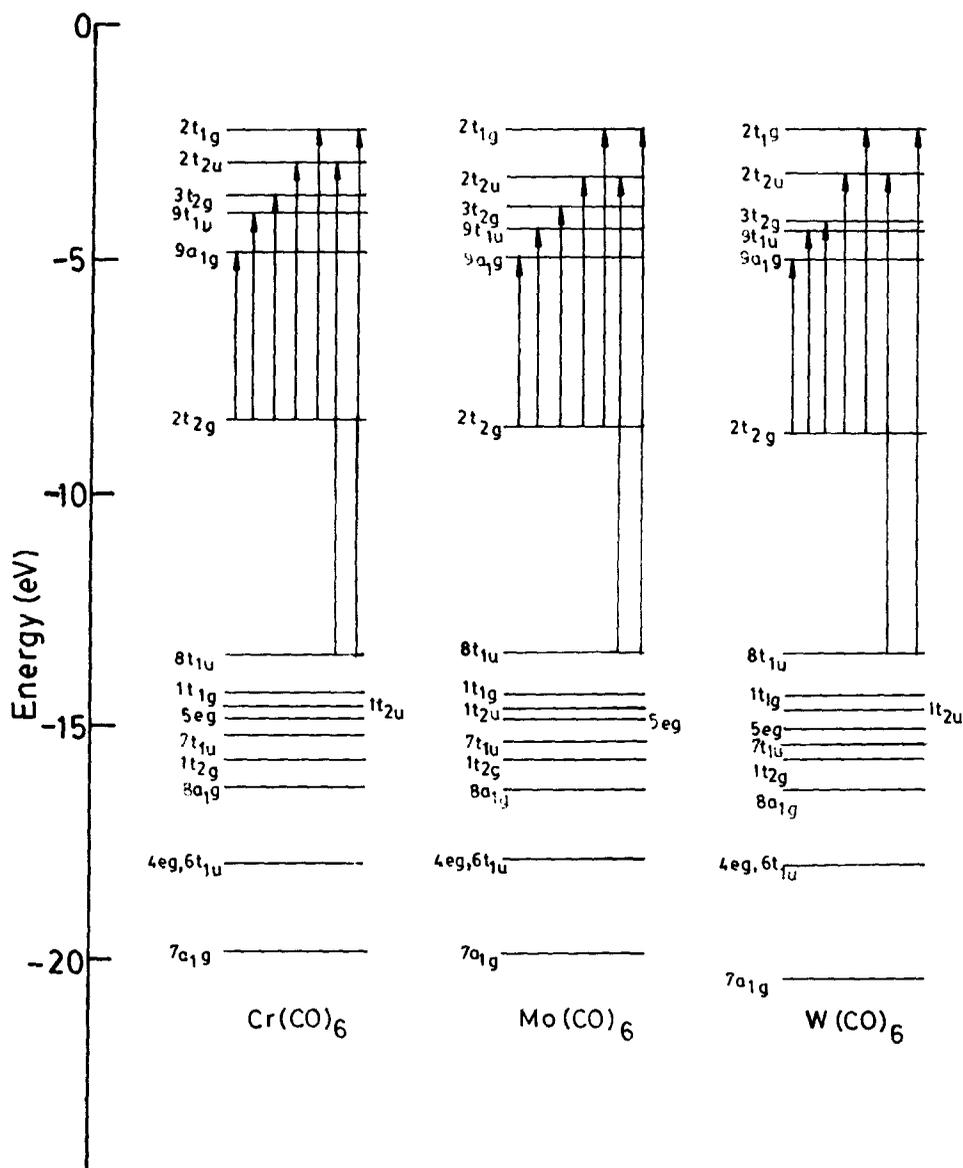

Figure 2. Molecular orbital energy level schemes of the hexacarbonyls.

in this energy region. The transition at 10·39 eV in the case of $Cr(CO)_6$ has been assigned to the $8t_{1u} \rightarrow 2t_{2u}$ excitation on the basis of term-value arguments. Similarly, the second transition is assigned to $8t_{1u} \rightarrow 2t_{2g}$ excitation. This can also be assigned to the $8t_{1u} \rightarrow 10t_{1u}$ transition with a quantum defect of 0·6. We have made similar assignments for the bands in the other two carbonyls as well as those shown in the energy level scheme (figure 2).

It is interesting to compare the carbonyl spectra with that of CO adsorbed on the respective metal surfaces. Unfortunately data are available only for the W(100) surface (Chesters *et al* 1976). There is only one transition in the above discussed energy region. This transition at 5·3 eV has been assigned to the CO valence excitation ($5\sigma \rightarrow 2\pi$). However, it could be regarded as a charge-transfer transition from the metal to the 2π level of CO also (Shin-ichi Ishi and Ohno 1984). In the absence of more experimental data, nothing further could be stated.

Acknowledgements

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