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He-I AND He-II EXCITED PHOTOELECTRON SPECTRA OF CYCLOHEPTATRIENETRICARBONYL COMPLEXES OF GROUP VIA METALS

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Summary

Photoelectron spectra of Group VIA metal complexes $M(CO)_3(\eta^6\text{-}C_7H_8)$ have been assigned using experimental criteria along with quantum-mechanical calculations. A general agreement between computed and measured ionization energies has been found for molecular orbitals mainly ligand in character. Similar correlations do not hold for the highest orbitals, mainly metal *d* based. The energies associated with ionization processes are, in this case, largely dominated by the relaxation terms. The variations of intensities of these bands on changing the energy of ionizing radiation were of crucial significance in the assignment.

Introduction

The electronic structure of cycloheptatrienetricarbonyl complexes of Group VIA metals has been investigated using He-I photoelectron (PE) spectroscopy. Sweigart et al. [1] assigned only the low energy bands in He-I PE spectra of such complexes by simple analogy to spectra of corresponding arenetricarbonyl compounds [2]. However, that study did not provide an explanation for differences in spectral pattern observed on going from arene- to cycloheptatrienetricarbonyl complexes [1,2].

Recently the use of the more energetic He-II (40.8 eV) photoionizing radiation has improved the ability of the PE technique to provide a more accurate picture of bonding in molecules. Thus a combined He-I/He-II analysis may reveal variations of relative photoionization cross-sections which, in turn, provides indications of the composition of the molecular orbitals (MOs) responsible for the various PE bands. Quantum-mechanical calculations can be also of value in analysis of PE data.

We report here results of an investigation on the bonding in the title complexes based on comparisons of He-I and He-II PE spectra, as well as on MO calculations.

Experimental and calculation

The complexes $M(CO)_3(\eta^6\text{-}C_7H_8)$ were prepared according to published procedures (M = Cr [3a], Mo [3b], W [3c]) and purified by fractional sublimation in vacuo. PE spectra were measured on a PS/18 Perkin—Elmer spectrometer modified by inclusion of a high current power supply and a hollow cathode source to give a high output of He-II photons (Helectros Development).

The spectra were calibrated by reference to peaks of admixed inert gases and to He ($1\,s^{-1}$) self-ionization. Band areas were usually evaluated from raw spectra using a Dupont 310 curve resolver. Only in the case of expanded scale spectra were the spectral profiles fitted to a series of Gaussian components using a Fortran IV computer programme (by courtesy of Dr. Riggi). Band intensities were always corrected for variation of the analyser transmittance with electron kinetic energy.

Valence electron self-consistent field molecular orbital calculations (SCF-MO) were performed using a modified CNDO method which proved suitable for transition metal complexes [4]. The calculations were carried out only for the representative complex $Mo(CO)_3(\eta^6\text{-}C_7H_8)$. The geometrical parameters of this molecule are known from a X-ray diffraction study [5] while the close similarity of PE spectra as well as of IR and NMR spectra [6] of presently studied complexes allows confident extension of findings for the molybdenum complex to the others of the series. The C_s symmetry has been adopted. Table 1 lists computed eigenvalues, the composition and dominant character of each eigenvector and, finally, the experimental ionization energies (*IE*s) of PE bands to which each group of MOs refers. It is evident that the computed eigenvalues fit the *IE* data quite well within Koopmans' approximation.

Results and discussion

The PE spectra of the complexes $M(CO)_3(\eta^6\text{-}C_7H_8)$ (M = Cr, Mo, W) are shown in Fig. 1—3. Pertinent experimental *IE*s and intensity data are given in Table 2. Each spectrum shows four bands (labelled a, b, c and d in Fig. 1—3) in the region up to 11 eV. Bands a and b overlap each other in each spectrum, and in case of the tungsten complex (Fig. 3), band a shows an evident splitting in form of the shoulder a′.

The next spectral region (up to 15 eV) generally consists of a very broad slightly resolved structure; it is possible, however, to distinguish, at least, four *IE*s related to peaks (g, l) or shoulders (e, f). On switching to He-II excitation

(Continued on p. 516)

TABLE 1

PERTINENT CNDO RESULTS ON Mo(CO)$_3$(η^6-C$_7$H$_8$)

Symmetry	Energy (eV) [a]	Molybdenum			Carbonyl				Cycloheptatriene			IE (eV) (exper.)	Dominant character
					carbon		Oxygen		carbon		hydrogen		
		4d	5p	5s	2s	2p	2s	2p	2s	2p	1s		
22a′	7.44	43	—	—	—	6	—	28	—	2	—	7.44	metal (d_{z^2})
21a′	7.93	40	—	—	—	5	—	32	—	6	—	7.82	metal (d_{xz}, $d_{x^2-y^2}$, d_{z^2})
14a″	8.23	30	1	—	—	3	—	27	—	28	—		metal (d_{yz}, d_{xy})
20a′	9.49	1	—	—	—	—	—	3	—	80	4	9.28	ring π
13a″	10.54	—	—	—	—	—	—	—	—	74	14	10.67	ring π/σ
19a′	11.26	—	—	—	2	5	—	8	—	42	12		ring σ
18a′	11.50	—	—	2	8	28	—	37	—	18	—		carbonyl 5σ
12a″	11.62	3	—	—	5	23	—	41	—	15	—	11.79	carbonyl 5σ
11a″	11.66	—	—	—	—	4	—	12	—	67	8		ring σ(C—C)
17a′	11.78	6	—	—	7	3	—	40	—	14	4		carbonyl 5σ
16a′	12.20	—	—	—	—	2	—	4	—	65	17		ring σ(C—H)
10a″	12.75	—	—	—	—	10	—	43	—	36	—	12.37	ring carbonyl σ
15a′	12.90	—	—	—	—	15	—	57	—	15	—		carbonyl 1π
9a″	12.91	—	—	—	—	19	—	73	—	—	—		carbonyl 1π
14a′	13.26	—	—	—	—	15	—	52	—	25	—		carbonyl 1π
8a″	13.37	1	—	—	—	11	—	32	—	45	—	13.16	ring π
13a′	13.85	5	—	—	—	17	—	37	—	19	5		carbonyl 1π
7a″	14.10	9	—	—	—	27	—	51	—	—	—	13.77	carbonyl 1π
12a′	14.46	—	—	—	—	19	—	34	—	16	4		carbonyl 1π
11a′	15.32	8	—	—	—	7	—	12	—	43	14		ring σ
10a′	15.71	—	—	—	8	—	2	8	—	47	25	15.09	ring σ
6a″	15.75	2	—	—	7	—	2	7	—	48	19		ring σ
9a′	16.79	7	—	—	32	7	15	20	—	4	2		carbonyl 4σ
5a″	17.01	9	—	—	27	7	16	17	—	11	6	16.79	carbonyl 4σ
8a′	17.06	1	—	—	7	31	12	15	—	22	4		carbonyl 4σ

[a] Empirically reduced by a 8% factor.

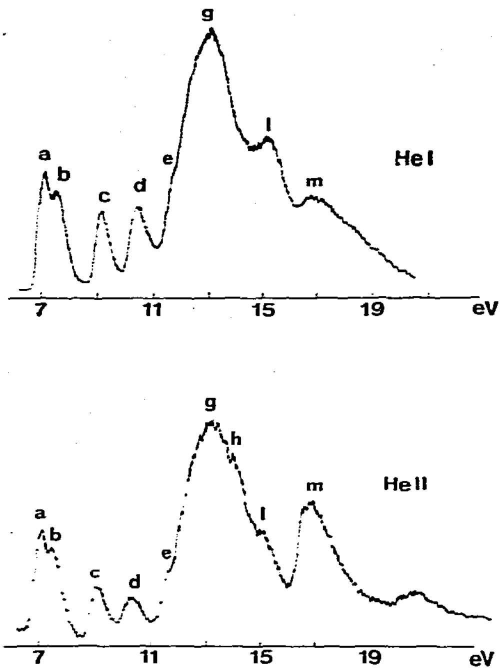

Fig. 1. The PE spectra of $Cr(CO)_3(\eta^6\text{-}C_7H_8)$.

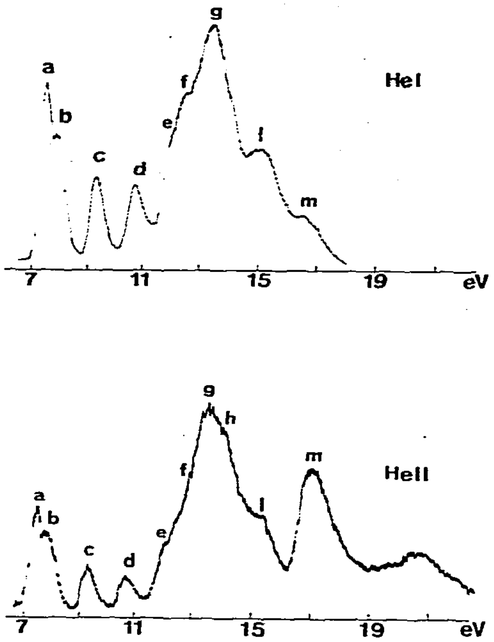

Fig. 2. The PE spectra of $Mo(CO)_3(\eta^6\text{-}C_7H_8)$.

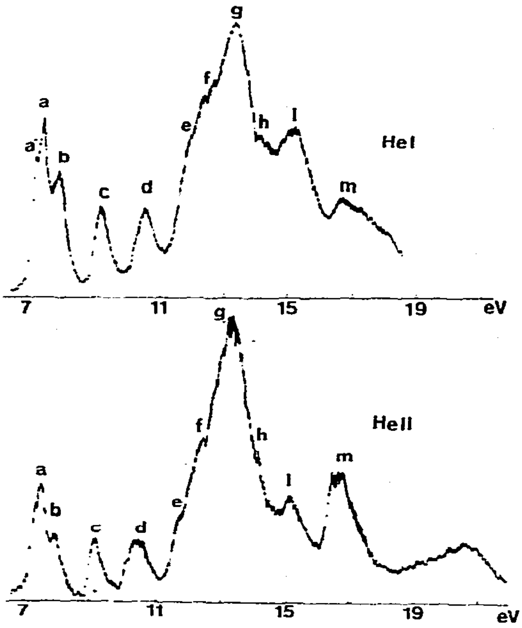

Fig. 3. The PE spectra of $W(CO)_3(\eta^6\text{-}C_7H_8)$.

TABLE 2

PERTINENT PE DATA ON THE STUDIED COMPLEXES

$Cr(CO)_3(\eta^6\text{-}C_7H_8)$			$Mo(CO)_3(\eta^6\text{-}C_7H_8)$			$W(CO)_3(\eta^6\text{-}C_7H_8)$		
IE (eV)	Intensities		IE (eV)	Intensities		IE (eV)	Intensities	
	He-I	He-II		He-I	He-II		He-I	He-II
						(7.32)	0,61 ^{a} } 2,8 ^{b}	0,95 ^{a} } 2,9 ^{b}
7.18	0,75 ^{a} } 2,2 ^{b}	1.72 ^{a} } 2,9 ^{b}	7,44	1,70 ^{a} } 2.6 ^{b}	1.85 ^{a} } 3,0 ^{b}	7.48	0,90 ^{a}	0,83 ^{a}
7.58	1.45 ^{a}	1.20 ^{a}	7,82	0,90 ^{a}	1.15 ^{a}	7.97	1.29 ^{a}	1,12 ^{a}
9,2	1,0 ^{b}	1,0 ^{b}	9,28	1,0 ^{b}	1,0 ^{b}	9.29	1,0 ^{b}	1,0 ^{b}
10.43	1,5 ^{b}	0,9 ^{b}	10,67	1,2 ^{b}	0,8 ^{b}	10.43	1,3 ^{b}	0,9 ^{b}
11.73			11,79			11.89		
—			12,37			12.40		
13.34			13,20			13.24		
14.11			13,77			13.98		
15.12			15,09			15.12		
16.94			16,79			16.80		

^{a} Gaussian analysis. ^{b} Du Pont curve resolver.

the relative intensity of the feature f increases with respect to e, although the ill-resolved structure precludes any quantitative evaluation. In the higher IE region (to 18 eV) a further band is present (band m). It increases markedly in relative intensity under He-II radiation.

MO calculations (Tab. 1) indicates that the three highest filled levels possess dominant metal character. Among them the MOs 22a′ and 21a′ provide the largest contribution to the metal—carbonyl bond while the MO 14a″ is the main source of metal—ring bonding. These MOs find counterparts in the more symmetric (C_{3v}) arene-tricarbonyl complexes, as shown in Table 3. The CNDO calculations indicates that the MOs 21a′ and 14a″ remain nearly degenerate.

In each spectrum the PE bands a and b (Fig. 1—3) must be assigned, irrespective of the order, to ionization from these MOs. Various factors support this assignment: (i) in $Cr(CO)_3(\eta^6\text{-}C_7H_8)$ the He-I and He-II the overall intensity of bands a + b relative to ring π system (Table 2) compares well with that reported for *d* ionization in $Cr(CO)_3(\eta^6\text{-}C_6H_6)$ [2] and (ii) the trend of intensities of bands a + b in presently studied complexes (Tab. 2) follows that expected from the so called "heavy metal effect", as observed in the PE spectra of other Group VIA metal complexes [7]. However, detailed assignment of these bands deserves further comments for each spectrum.

In the case of molybdenum and tungsten complexes the intensity ratio of band a to that of band b (a + a′ to b in the case of tungsten) suggests the occurrence of two ionization events in the band a. This fact is particularly evident in the spectrum of the tungsten complex where the first band is clearly split in two components of approximately equal intensity (Fig. 4; Tab. 2).

Their separation (0.27 eV) is close to the value of spin orbit multiplet splitting measured. in PE spectra of several tungsten complexes [1,7]. Evidently, despite the low molecular symmetry, the spin-orbit coupling effects are not completely quenched by operation of the off-diagonal elements of spin-orbit matrix. In our opinion the degeneracy of the corresponding MOs is not accidental, but follows as result of a higher (than C_s) symmetry of the field actually experienced by the central metal atom. It is known that the non planar arrangement of the olefinic carbon atoms in the free C_7H_8 ligand is changed to almost planar upon coordination to the $M(CO)_3$ groups [5]. Thus the electron density by-passes the out-of-plane methylene group and forms a quasi-aromatic system which provides to the metal a field of higher symmetry than C_s.

Because of symmetry arguments (Tab. 3), it turns out that the band a (a + a′ in the case of tungsten) must be related to 21a′ and 14a″ MOs while the band b represents the ionization from the MO 22a′. Within the Koopmans' approximation, this implies an energy ordering of metal *d* based MOs (21a′ = 14a″ > 22a′)

TABLE 3

CORRELATIONS OF *nd* BASED ON METAL MOLECULAR ORBITALS IN C_{3v} AND C_s COMPLEXES

$M(CO)_3(\eta^6\text{-}C_6C_6)$ (ref. 2) (C_{3v})		$Mo(CO)_3(\eta^6\text{-}C_7H_8)$ (C_s)
$17a_1$	- - - - - - - - - - - - - - →	$22a'$
$17e$	- - - - - - - - - - - - - - -	$21a'$ $14a''$

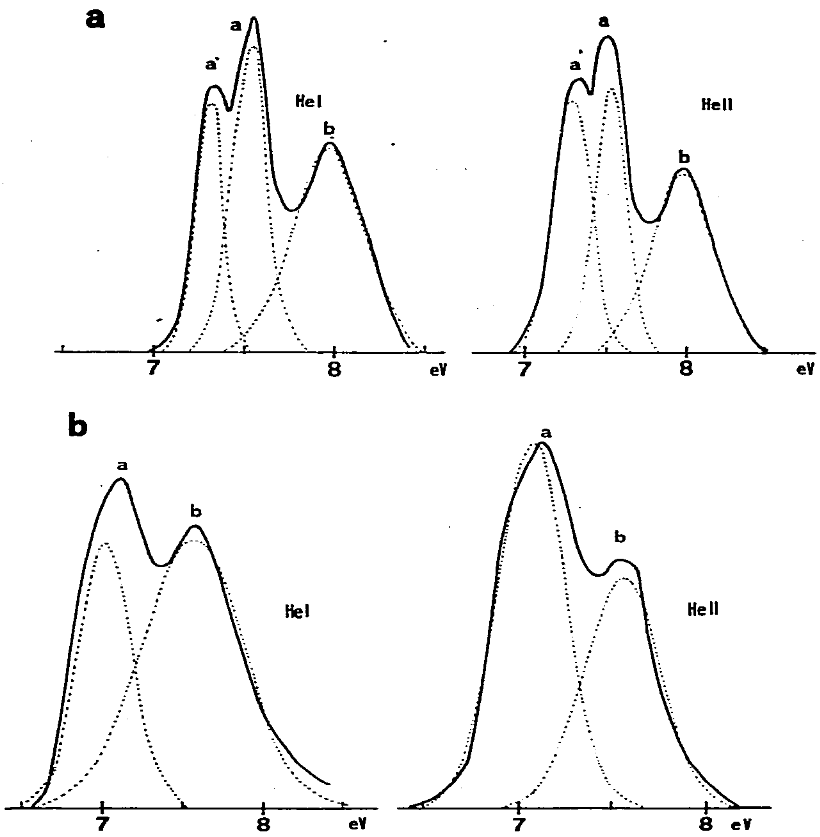

Fig. 4. Gaussian analysis of first bands in PE spectra of (a) the tungsten complex and (b) the chromium complex.

which is at variance to that indicated by CNDO calculations (Tab. 1).

When considering the chromium complex, the profile of band envelope a — b in the He-I spectrum appears modified with respect to the previous cases: the band b increases in intensity and its higher *IE* tail is broadened. A careful Gaussian analysis of the band develope indicates that the ratio of the intensity of band a to that of band b is reversed (Tab. 2; Fig. 4). This fact implies an energy ordering of metal *d* based MOs: 22a' > 21a' = 14a'' in agreement with CNDO calculation.

However such agreement, in our opinion is purely furtuitous. It is well known that, photoelectron *IE*s strictly relate to the energies of ion states produced upon ejection of electrons from various ground state MOs. It has been shown that *IE*s of *d* subshells in transition metal complexes are largely determined by relaxation energies [2,8]. As a general rule, the more important the *d* contribution in a particular MO the higher are the relaxation energies associated with the corresponding ion states; further, along a particular group of the Periodic Table, higher relaxation energies are associated with lighter elements [9]. In fact, our CNDO calculations unambigously indicate that the 22a' MO possesses the highest metal *d* contribution. Thus, it must be expected that the relaxation energy associated with the $^2A'$ (22a′) ion state will be larger than those for the ion states correlating with the remaining 21a′ and 14a″ MOs. So we are confident that the ground state energy ordering of filled metal *d* subshells in the complexes studied is 21a′ = 14a″ > 22a′. In the chromium complex, upon ionization differential relaxation energies among *d* subshells result in an inverted ordering of corresponding ion states. In the case of molybdenum and tungsten complexes, smaller differential relaxation energies lead only to a reduced separation between energies of ion states corresponding to above MOs.

Noteworthy, within our assignments are the nearly constant *IE*s of the *d* subshells having larger ligand contributions (21a′ and 14a″) and so less influenced by relaxation energies, which closely agree with the trend of corresponding *IE*s found in the Group VIA metal complexes $M(CO)_6$ [7] and $M(PF_3)_6$ [9] *. Further support for this assignment is provided by the trend of relative intensity of bands a and b on passing from He-I to He-II spectrum of chromium complex; in the He-II spectrum of the band a undergoes a pronounced increase of intensity (Tab. 2; Fig. 4). This behaviour is certainly related to the larger contribution to the 22a′ MO from the chromium 3*d* orbitals which possess considerably higher cross-sections at He-II wavelength [2]. A similar effect is not observed in the He-II spectrum of the tungsten complex; it is well known, however, that W 5*d* orbitals have comparable cross-section both at He-I and He-II wavelengths [7]. The PE bands in the higher *IE* region of the three spectra can be confidently assigned assuming the validity of Koopmans' approximation; no differential relaxation energies are expected for ionizations of MOs which are mainly *C*(2*p*, 2*s*) and O(2*p*, 2*s*) based.

Bands c and d certainly relate to ionization from ring MOs, having dominant C 2*p* character (respectively 20a′ and 13a″). Their lower (than *d* subshells) cross section (Tab. 2) at He-II wavelength is in agreement with the smaller C 2*p* cross-section under He-II radiation. Notably, the intensity of band d is considerably reduced with respect to that of band c, upon switching to the He-II radiation.

However, analysis of CNDO eigenvectors (Tab. 1) clearly indicates that the MO (13a″) correlating with band *d* consists of a σ/π mixture of C 2*p* atomic orbitals and has a significant contribution from orbitals localized on the methylene group. This explains the trend toward reduced He-II intensity, since it is well known that H 1*s* AOs have fairly small cross-section at the He-II wavelength [10]. The very complicated band systems that follows up to 14 eV can be associated with ionization both from cycloheptantriene σ MOs and carbonyl 1π and 5σ MOs. It is known that under He-II radiation hydrocarbon σ MOs as well as carbonyl 5σ MOs have cross-sections significantly smaller than those of carbonyl 1π MOs [2]. Thus, in accordance with CNDO calculation, we assign the shoulder e which is weak in the He-II spectrum, to ionization from the group MOs 17′a′-19a′, having predominant ring σ and carbonyl 5σ character. The feature f, which seems higher in the He-II spectra corresponds to the group of MOs 9a″ to 16a′ carbonyl 1π in nature. The peak g and the shoulder h (which clearly increases in the He-II spectra) can be confidently assigned to the 8a″—

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* In the case of carbonyl or fluorophosphine complexes differential relaxation effects among *d* subshells cannot occur because the *d* subshells are degenerate by symmetry.

14a′ and 12a′—13a′ groups of MOs, respectively. The increased intensity of the shoulder h in the He-II spectra agrees well with the carbonyl 1π character of corresponding MOs. Turning attention to band l and m, the CNDO calculations suggests correlations respectively with the 6a″—11a′ and 8a′—9a′ groups of MOs. The pronounced increase of intensity of band m is in agreement with the dominant C 2*s* and O 2*s* character in the corresponding MOs [11,12].

Finally, some remarks may be made about the description of the bonding in Group VIA metal cycloheptatrienetricarbonyl complexes which emerges from present study. Mulliken orbital population analysis of deorthogonalized eigenvectors indicates that C_7H_8 ring ligand behaves as acceptor of electron density from the metal into orbitals mainly π^* in character (atomic charge on each ring carbon atom −0.2 e). The shift to higher *IE* of upper filled MO mainly localized on the ring (20a′, 13a″) when compared to the *IE* of corresponding MO in the uncomplexed ring ligand [13] is a clear indication of such back-bonding donation. Moreover the "carbonyl" ionizations appear shifted to lower *IE* with respect to corresponding *IE*s in parent hexacarbonyl complexes [7]. This shift, analogous to that detected in corresponding arenetricarbonyl complexes [1,2], may be an indication that the CO ligands accept more electron density than in simple hexacarbonyls.

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