

The spectroscopy of the group VIb transition metal hexacarbonyls using the electron impact method^{a)}

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The electron energy-loss spectra of Cr(CO)₆, Mo(CO)₆, and W(CO)₆ were measured at impact energies of 25, 50, and 100 eV and at scattering angles from 0° to 90°. The differential cross sections (DCS's) were obtained for several features in the 3–7 eV energy-loss region. The symmetry-forbidden nature of the $^1A_{1g} \rightarrow ^1A_{1g}, 2t_{2g}(\pi) \rightarrow 3t_{2g}(\pi^*)$ transition in these compounds was confirmed. Several low energy excitations were assigned to ligand field transitions on the basis of the energy and angular behavior of their associated DCS's. No transitions which could clearly be assigned to singlet \rightarrow triplet excitations involving metal orbitals were located in these molecules. In addition, a number of states lying above the first ionization potential were observed for the first time. Several of these excitations seem to correspond quite well to some of the transitions observed in free CO.

I. INTRODUCTION

The group VIb transition metal hexacarbonyls are currently the focus of a large amount of research which has been stimulated by the catalytic properties exhibited by these compounds.^{1–7} These compounds have also been studied as models for the binding of CO to transition metal surfaces.^{8–10} Understanding the electronic structures and bonding of these systems is very important for understanding their reactivity and thus gaining insight into their catalytic activity.¹¹

The bonding of CO to a transition metal atom or surface is thought to occur through a combination of σ - and π -type bonding.¹² The lone pair electron density of the carbon atoms is thought to delocalize into empty metal d orbitals thus forming a σ type of interaction. Backdonation of metal "lone pair" d orbitals into the π^* orbital of CO form the π interaction. It is this synergetic interaction which results in very little net charge transfer occurring between the metal and the CO thus allowing the metal to be coordinated in relatively low oxidation states. Theoretical studies have been performed on this system¹³ and a wide variety of techniques and methods of experimentation have also been used to ascertain the exact nature of this bonding.

In this study we have applied the technique of low-energy, variable-angle, electron-impact spectroscopy^{14,15} to the group VIb transition metal carbonyls. This technique has been applied with great success to a large number of small organic molecules¹⁶ and more recently to inorganic systems.¹⁷ It not only provides information on excited states optically accessible from the ground state but also on those states which are optically inaccessible from the ground

state.^{14,15} The behavior of the measured differential cross section (DCS) as a function of scattering angle Θ and incident electron energy E_0 permits identification of the nature of various transitions in the electron energy loss spectra of these compounds. Electron impact also allows easy access to the high energy, > 10 eV, region of the spectrum. This is important in that many of the intraligand absorptions occur in this region of the spectrum. Such transitions are important in determining the nature of the metal-CO bond and can also be compared with electron energy-loss measurements of CO adsorbed on metal surfaces.²⁰

We have obtained electron energy-loss spectra with incident electron energies of 25 and 50 eV and at scattering angles of 10° intervals from 10° to 90°. High resolution energy-loss spectra were also measured at 100 eV incident energy and low scattering angles ($< 10^\circ$) in order to produce spectra comparable to optical spectra.²¹

II. PREVIOUS WORK

A. Experimental

For a series of compounds whose photochemistry has been studied as much as the group VIb metal hexacarbonyls, little attention has been given to the electronic spectroscopy of these compounds. Most of the previous studies have been performed in solution or solid matrices and were almost always done in the energy region below the quartz cutoff frequency^{22–28} (approximately 7 eV). Some work has been done in the gas phase,^{29–31} with one VUV study reported by Iverson and Russell.³²

Photoionization studies of the transition metal hexacarbonyls have been performed by Vilesov and Kurbatov³³ and Lloyd and Schlag.³⁴ A number of UV photoelectron spectroscopic studies of this series have also been reported.^{35–38} Plummer and co-workers^{39,40} have studied the UV and x-ray photoelectron spectroscopy of the metal carbonyls in detail and have also made some interesting comparisons with CO adsorbed on transition metal surfaces. Giordan *et al.*⁴¹ and Tossel *et al.*⁴² have used electron transmission spectroscopy

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to study the negative ion states of the transition metal hexacarbonyls.

B. Theoretical

A large number of theoretical studies, most of which use semiempirical methods, have been performed on these compounds with the emphasis being on the metal-CO bonding in the ground state.⁴³⁻⁴⁶ There have also been a number of semiempirical calculations performed to determine the energy levels of the excited states of these complexes.^{31,47-53} Hillier and Saunders⁵⁴ and Moncrieff *et al.*⁵⁵ report the only *ab initio* study of a member of this series, done on the Cr compound.

III. EXPERIMENTAL

The apparatus used in these studies has been described previously^{56,57} and is an updated version of the Simpson-Kuyatt^{58,59} type electron impact spectrometer. Briefly, it consists of an electron gun-2.25 in. mean radius hemispherical electron energy analyzer-detector system. The monochromator can be rotated from -15° to $+100^\circ$ with respect to the analyzer system. The sample may be contained in a static gas cell or be in an effusive molecular beam. The entire experiment is under the control of a microcomputer which sweeps the electron energy-loss and accumulates the energy-loss spectrum. The sample pressure is maintained at a few millitorr, in the pressure regime free of multiple scattering events.

The entire inlet system may be heated to approximately 150°C for working with substances which have low vapor pressures. Careful monitoring of the electron-impact spectra was done in order to avoid decomposition of the hexacarbonyls. This was accomplished by looking for the strong, sharp CO bands in the 6-9 eV energy-loss region. Sample inlet conditions were adjusted to avoid CO contamination. The samples of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ all came from the Aldrich Chemical Co. and had stated purities of 99%. The solid samples were degassed and admitted into the instrument without further purification.

IV. RESULTS

The spectra of all of the group VIb transition metal hexacarbonyls are very similar in appearance. One can divide these spectra into two regions. The first one extends from 3.5 to 7.0 eV and consists primarily of metal-to-ligand charge transfer (MLCT) bands and metal *d*-to-*d* ligand field (LF) bands. The region above 7.0 eV most likely consists of ligand-to-ligand, ligand-to-metal, and Rydberg-type excitations. We will discuss the results on a molecule-by-molecule basis. The tentative assignments given in Table I are based on those of Beach and Gray.³¹

A. Chromium hexacarbonyl

The high energy (100 eV incident electron energy) and low angle (0°) spectrum of $\text{Cr}(\text{CO})_6$ is shown in Fig. 1(a). The appearance of the energy-loss spectrum agrees quite well with the vapor-phase optical spectra of Gray and

TABLE I. Metal hexacarbonyl transition energies (eV).

Assignment ^a	Chromium hexacarbonyl		Molybdenum hexacarbonyl		Tungsten hexacarbonyl	
	Present results	Previous work	Present results	Previous work	Present results	Previous work
$^1A_{1g} \rightarrow ^1T_{1g}$	3.78 sh ^b	3.60 ^c	3.65 sh 3.82 sh	3.64 ^c 3.84, ^{c,d} 3.89, ^{b,h} 3.96, ^e 3.95, ⁱ 3.78, ^f 3.83, ^f	3.61 sh 3.75 4.00 sh	3.66, ^d 3.52, ^e 3.54, ^e 3.51, ^f 3.53, ^f 3.56, ^f 3.71, ^f 3.77, ^f 4.04, ^g 3.96, ^g 3.93, ^f
$^1A_{1g} \rightarrow ^1T_{1u}^{(1)}$	4.46	4.44, ^{c,d} 4.37, ^d 4.43, ^{e,i} 4.44 ^f 4.36, ^f 4.35, ^j 4.47, ^b 2.95, ^j 3.9, ⁿ 3.99 ⁿ	4.32	4.29, ^{d,f} 4.33, ^e 4.32, ^g 4.34, ^{h,i} 4.27, ^e 4.53, ⁱ 4.30, ^f 4.35 ⁱ	4.32	4.28, ^d 4.33, ^g 4.27, ^e 4.30, ^{e,f} 4.34 ⁱ 3.75, ^m 3.80, ^m 4.39 ^f
$^1A_{1g} \rightarrow ^1T_{2g}$	4.73 sh	4.82 ^c	4.65 sh	4.66, ^e 4.67, ^g 4.62, ^e 4.60, ^f 4.69 ^f	4.54 sh 4.86 sh	4.61, ^g 4.51, ^e 4.54, ^g 4.55, ^f 4.84, ^e 4.15, ^p 4.41, ^m 4.71, ^f 4.79, ^f
$^1A_{1g} \rightarrow ^1T_{1u}^{(2)}$	5.51	5.48, ^c 5.39, ^d 5.28, ⁱ 5.51, ^g 5.41, ^e 5.54, ^p 5.33, ^f 5.58, ^f 5.99, ^g 5.27, ^k 5.6, ^j 5.52, ^j 5.2, ⁿ 4.8, ⁿ 4.6 ⁿ	5.44	5.39, ^{d,h,i} 5.45, ^e 5.44, ^{g,p} 5.32, ^e 5.28 ^{l,i}	5.55	5.41, ^d 5.53, ^g 5.44, ^e 5.56, ^p 5.39, ^g 5.43, ^f 5.55 ^f
$^1A_{1g} \rightarrow ^1A_{1g}$	6.35 sh	6.31, ^e 6.36, ^g 6.33, ^p 6.38, ^j 6.35, ^j 5.9 ⁿ	6.33	6.38, ^e 6.42 ^{g,p}	6.24 sh	6.26, ^g 6.24, ^e 6.36 ^p
$[t_{2g}(\pi) \rightarrow t_{2g}(\pi^*)]$	7.46 7.71	7.42 ^p 7.70 ^p	7.08 sh 7.36 7.65, 7.85 8.30	7.47 ^p 8.32 ^p 8.40 ^f	6.54 sh 7.66 8.38	6.52, ^g 6.55, ^e 6.36 ^p 7.65 ^p 8.43 ^p
IP 1		8.40 ^q		12.39 ⁱ		8.56 ^q
SES	8.80 10.18, 11.6, 12.4	8.79 ^p	9.65 sh 10.23, 11.43, 11.52, 12.50 12.19, 12.83	9.75 ^g 13.32 ^r	8.80, 9.96, 10.38 11.63, 12.26	
IP 2		13.38 ^q				13.27 ^q
SES	13.4, 14.2					

^a Assignments based on Ref. 31.

^b sh indicates shoulder.

^c Reference 31.

^d Reference 22.

^e Reference 30.

^f Reference 28.

^g Reference 29.

^h Reference 24.

ⁱ Reference 21.

^j Reference 50.

^k Reference 48.

^l Reference 23.

^m Reference 53.

ⁿ Reference 51.

^o Reference 52.

^p Reference 32.

^q Reference 44.

^r Reference 36.

^s Vertical IP's.

Beach⁹ and Iverson and Russell.³² Attempts to measure the DCS's for the various transitions were complicated due to severe overlapping of the various bands. After attempts at using various deconvolution procedures had failed, the approach of simply dividing the spectrum into regions and measuring the DCS of a particular energy-loss range was adopted.⁶⁰ It was hoped that this procedure might indicate the presence of any possible spin-forbidden transitions which may be present. The exception to this was the excitation present at 6.35 eV which was deconvoluted using a procedure similar to that described previously.^{61,62} The results of the DCS measurements are displayed in Figs. 2 and 3. The angular dependence of most of these DCS's are similar and no evidence for the presence of spin-forbidden transitions is apparent in all of the bands studied with one exception.

It has been found helpful in the past¹⁵ to plot the ratios of the DCS's for a given transition to that of a known, totally allowed transition as a function of scattering angle. It has been previously determined that, for systems with no significant spin-orbit coupling, the DCS ratio of spin-forbidden to spin-allowed transitions increases by one to two orders of magnitude as the scattering angle is increased from 10° to 90°. DCS ratios are plotted in Figs. 4 and 5 and with one exception, no case can be made for the presence of spin-forbidden transitions. Spectra taken at $E_c = 25$ eV and $\theta = 10^\circ$ and 90° are shown in Fig. 6. Careful observation of these spectra and of others at intermediate angles shows the presence of two reproducible shoulders at 3.78 and 4.73 eV.

The intensities of these features seem to be very slightly enhanced in going from 10° to 90° when compared with that of the 4.46 eV transition which has been assigned to a fully allowed MLCT type of excitation. This may indicate the presence of some forbidden character in these bands.

The shoulder at 3.78 eV has been previously assigned to a LF transition³¹ while the bands observed at 4.46 and 5.51 eV correspond to the MLCT transitions. The 5.51 eV band has a much larger intensity than the 4.46 eV band. This has been explained³¹ as being due to a larger change in the M-CO bond dipole moment associated with the $^1A_{1g} \rightarrow ^1T_{1u}^{(1)}, 2t_{2g} \rightarrow 2t_{2u}$ transition as compared to that associated with the $^1A_{1g} \rightarrow ^1T_{1u}^{(2)}, 2t_{2g} \rightarrow 4t_{1u}$ transition. The 4.73 eV shoulder has been assigned to a second LF band and also shows a similar enhancement with angle as does the shoulder at 3.78 eV. A shoulder is observed on the high energy side of the 5.51 eV band with a maximum at 6.35 eV. This band has been previously assigned³¹ as a LF $^1A_{1g} \rightarrow ^1A_{1g}, t_{2g}(\pi) \rightarrow t_{2g}(\pi^*)$ symmetry-forbidden transition. This is confirmed by the behavior of the intensity of this transition, as shown in Fig. 7, which increases significantly as one goes from 0° to 6° scattering angle using 100 eV incident electrons. This type of behavior is characteristic of such symmetry-forbidden excitations.³¹ The interesting observation is made that the DCS's and their ratios to the intense MLCT band at 5.51 eV for this particular transition (Figs. 2, 3, 4, and 5) display characteristics expected for spin-forbidden excitations at 25 eV incident energy. At 50 eV incident energy, this

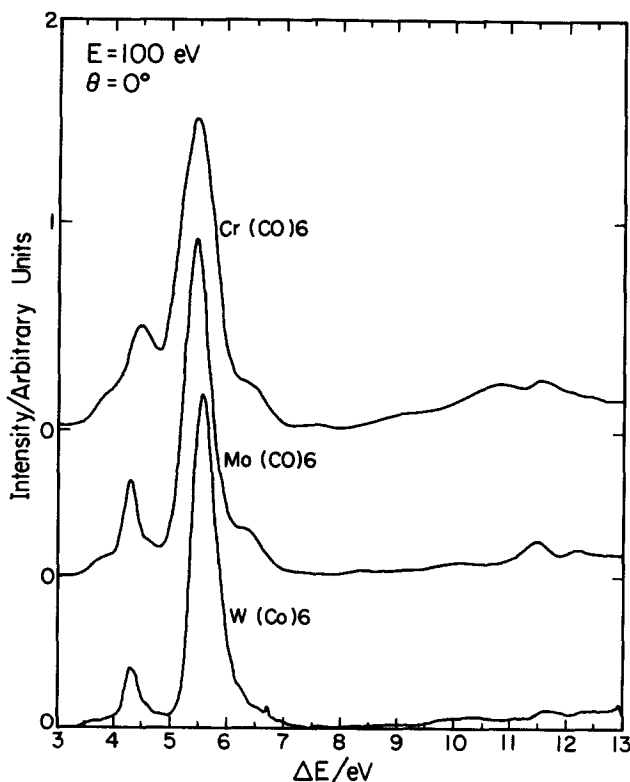


FIG. 1. High resolution electron energy-loss spectrum of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $E_0 = 100$ eV, $\theta = 0^\circ$. Resolution = 45 meV FWHM for $\text{Cr}(\text{CO})_6$, resolution = 40 meV FWHM for $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$.

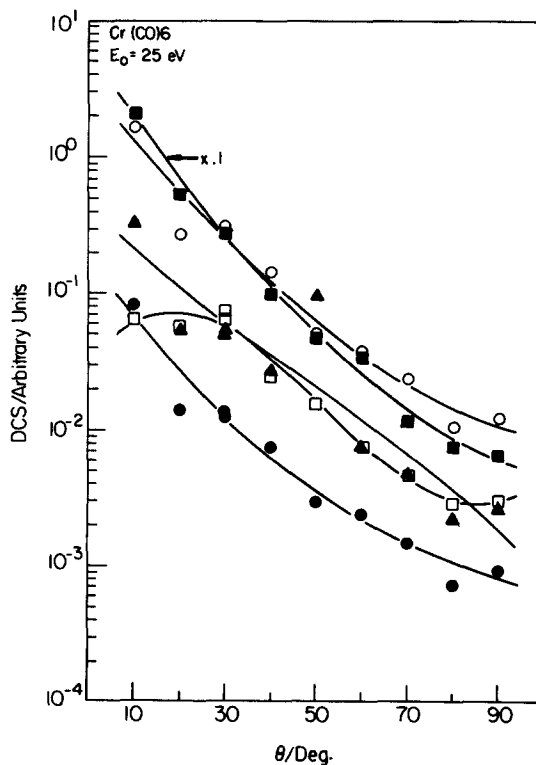


FIG. 2. DCS plot of $\text{Cr}(\text{CO})_6$, $E_0 = 25$ eV. Elastic scattering = ■; $P_1(2.5-4.1$ eV) = ●; $P_2(4.1-4.8$ eV) = ▲; $P_3(4.8-7.2$ eV) = ○; $P_4(6.35$ eV symmetry forbidden transition) = □. The same arbitrary units are used for all curves.

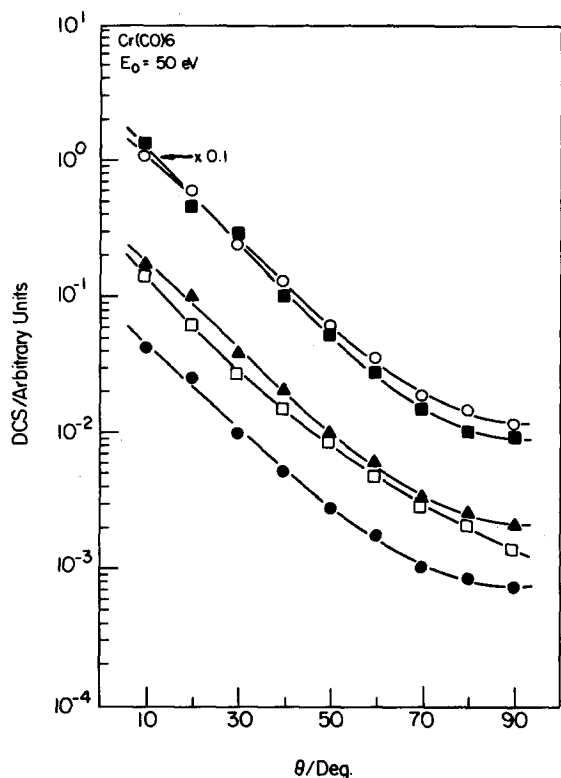


FIG. 3. DCS plot of $\text{Cr}(\text{CO})_6$, $E_0 = 50$ eV. Elastic scattering = \blacksquare ; $P_1(2.5 \rightarrow 4.1$ eV) = \bullet ; $P_2(4.1 \rightarrow 4.8$ eV) = \blacktriangle ; $P_3(4.8 \rightarrow 7.2$ eV) = \circ ; $P_4(6.35$ symmetry forbidden transition) = \square . The same arbitrary units are used for all curves.

spin-forbidden behavior vanishes. This energy dependence of the DCS indicates the possible presence of an underlying spin-forbidden transition, possibly due to a CO intraligand absorption. The transitions at 7.46 and 7.71 eV have not been

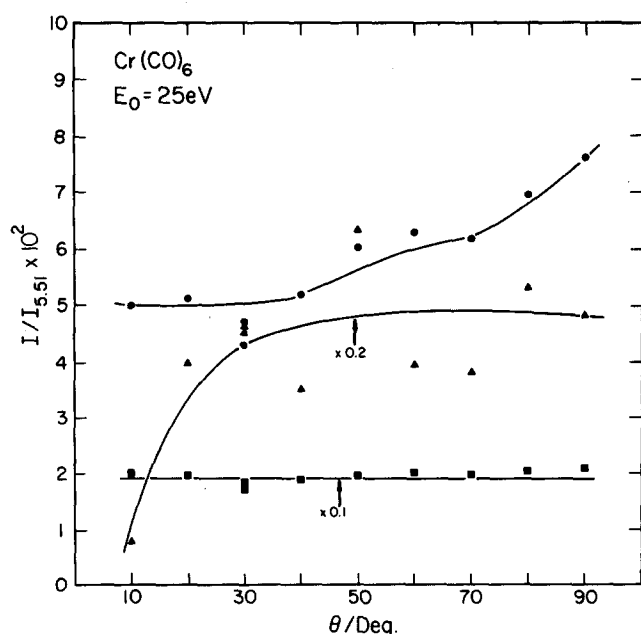


FIG. 4. Plot of the ratios of the DCS's of the various transitions of $\text{Cr}(\text{CO})_6$ to that of the transition $P_3(4.8 \rightarrow 7.2$ eV) at $E_0 = 25$ eV; $P_1/P_3 = \bullet$; $P_2/P_3 = \blacksquare$; $P_4/P_3 = \blacktriangle$. See the caption for Fig. 2.

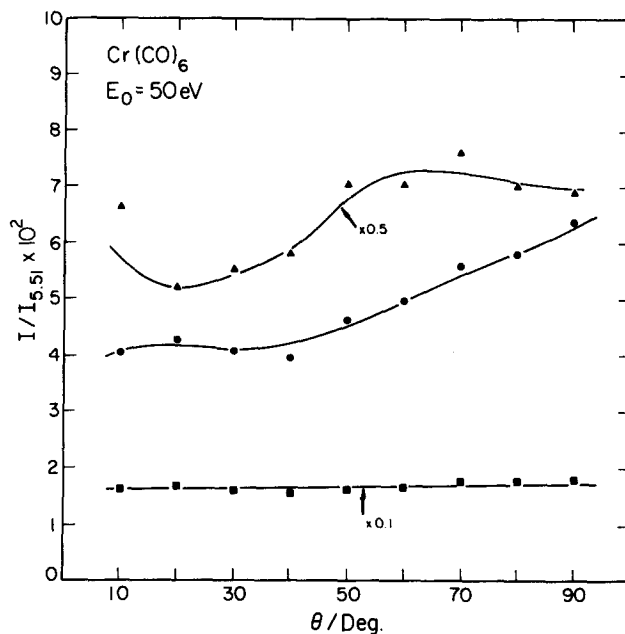


FIG. 5. Plot of the ratios of the DCS's of the various transitions of $\text{Cr}(\text{CO})_6$ to that of the transition $P_3(4.8 \rightarrow 7.2$ eV) at $E_0 = 50$ eV, $P_1/P_3 = \bullet$, $P_2/P_3 = \blacksquare$, $P_4/P_3 = \blacktriangle$. See the caption for Fig. 2.

assigned but may be due to components of the $d \rightarrow p$ metal-metal bands terminating in the $5t_{1u}$ orbital. A number of bands are observed above 7 eV energy loss. One can turn to the work on CO bound to metal surfaces to possibly explain some of these transitions. Avouris *et al.*²⁰ have recently studied the electronic excitations of CO bound to various metal substrates. In all the cases they studied, they found adsorbate bands in the 5–6 and 8–9 eV energy-loss regions. These were assigned to triplet and singlet $5\sigma \rightarrow 2\pi^*$ CO-type transi-

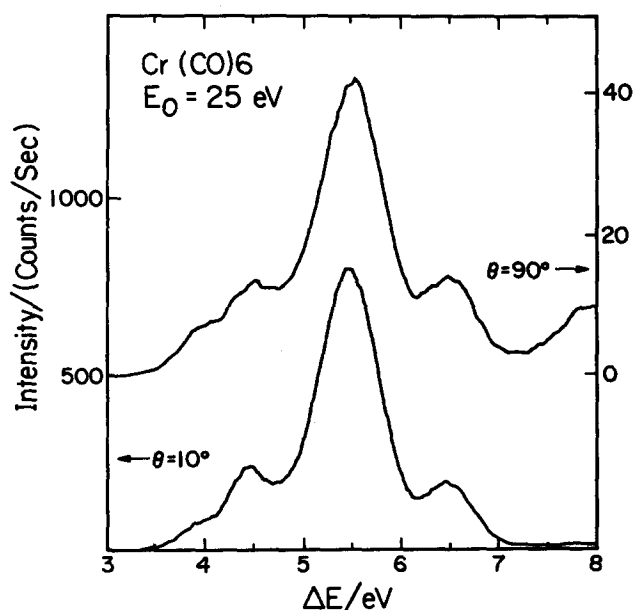


FIG. 6. Low angle (10°) and high angle (90°) spectra between 3.0 and 8.0 eV energy loss of $\text{Cr}(\text{CO})_6$ with $E_0 = 25$ eV.

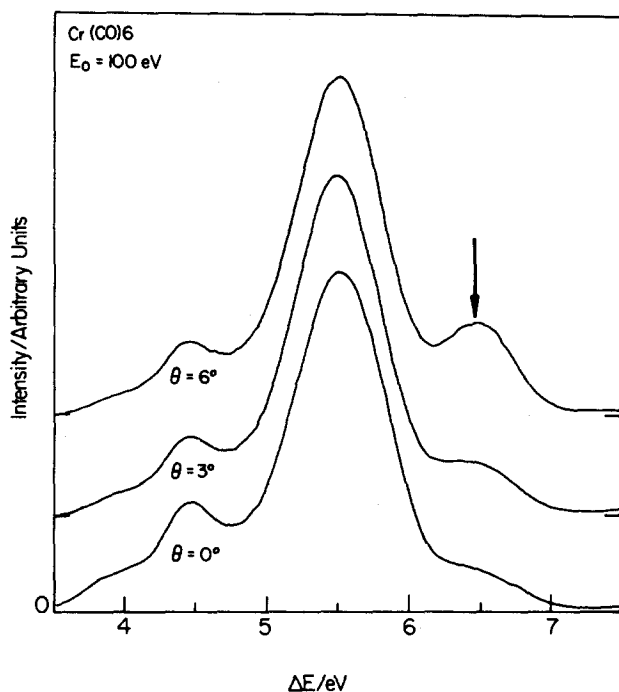


FIG. 7. Plot of the electron energy-loss spectra of $\text{Cr}(\text{CO})_6$ in the 3.5 to 7.5 eV energy-loss region at incident energy $E_0 = 100$ eV with $\theta = 0^\circ, 3^\circ$, and 6° to show the emergence of symmetry-forbidden transitions. Tick marks on the ordinate axis indicate the base lines of the successive spectra. The arbitrary units for each spectrum are different and are chosen so that the displayed height of the intensity of the 5.51 eV transition is the same for all displayed spectra.

tions, respectively. Their findings indicated that the transition energies of bound CO were not significantly perturbed from those of free CO. In $\text{Cr}(\text{CO})_6$ the 5–6 eV band would be buried beneath the intense MLCT and LF bands but there is a band observed at 8.80 eV which may correspond to the $5\sigma \rightarrow 2\pi^*$ singlet excitation. The triplet component of this excitation may be responsible for the anomalous behavior of the DCS for the 6.35 eV transition at $E_0 = 25$ eV. The remainder of the spectrum consists of transitions to superexcited states (SES) at 10.8, 11.6, 12.4, 13.4, and 14.2 eV. These have not been assigned but may be due to Rydberg-type excitations or to other intraligand excitations.

B. Molybdenum hexacarbonyl

Figure 1(b) shows the 100 eV, 0° electron energy-loss spectrum of $\text{Mo}(\text{CO})_6$ in the energy-loss region from 3 to 13 eV. With the exception of the symmetry-forbidden transition DCS at 25 eV, the DCS's and their ratios do not indicate the presence of any spin-forbidden transitions. In Fig. 8, the 25 eV and 10° and the 25 eV and 90° spectra are compared. One finds that the transitions at 3.65, 3.82, and 4.65 eV are all enhanced by a factor of about 2 in going from a 10° to a 90° scattering angle. This is much less than the usual one to two orders of magnitude of enhancement observed for triplet states.¹⁵

The shoulder observed at 3.65 eV in the 25 eV 90° spectrum has been observed by Beach and Gray³¹ in solid state spectra at 77 K and has been assigned to the $^1A_{1g} \rightarrow ^3T_{1g}$

transition. The enhancement observed seems to indicate some amount of forbidden character associated with this shoulder but it does not definitively confirm this assignment. The shoulders appearing at 3.82 and 4.65 eV also show an enhancement similar to that observed for the shoulder at 3.65 eV. As with $\text{Cr}(\text{CO})_6$, the two most intense features in the spectrum are the MLCT bands at 4.32 and 5.44 eV. In addition, LF bands are observed as shoulders at 3.82 and 4.65 eV. The shoulder at 6.33 eV has been assigned as the symmetry-forbidden $^1A_{1g} \rightarrow ^1A_{1g}, 2t_{2g}(\pi) \rightarrow 3t_{2g}(\pi^*)$ transition on the basis of the angular behavior of its intensity.

Additional bands have been observed at 7.08, 7.36, 7.65, 7.85, and 8.30 eV, some of them may belong to metal $d-p$ type excitations. Transitions to states above the first IP occur at 9.65, 10.23, 11.43, 11.52, 12.19, 12.50, 12.83, and 13.26 eV. These, as in $\text{Cr}(\text{CO})_6$, are most likely due to Rydberg excitations or intraligand absorptions.

C. Tungsten hexacarbonyl

Figure 1(c) shows the 100 eV, 0° energy-loss spectrum of $\text{W}(\text{CO})_6$ between 3 and 13 eV. As is the case with the other two members of this series, the DCS's and their ratios show no forbidden behavior, the exception once again being the symmetry-forbidden transition at 25 eV incident energy. Comparing the 25 eV and 10° spectrum to the 25 eV and 90° spectrum (Fig. 9), one finds that the transitions at 3.61, 3.75, and 4.54 eV are, as was the case for $\text{Mo}(\text{CO})_6$, enhanced by about a factor of 2 with respect to the fully allowed transitions. As with $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$, the two most intense transitions are assigned to MLCT type, $^1A_{1g} \rightarrow ^1T_{1u}$ excitations. They occur at 4.32 and 5.55 eV, which are very close to the values of 4.46 and 5.51 eV observed for $\text{Cr}(\text{CO})_6$ and 4.32 and 5.44 eV observed for

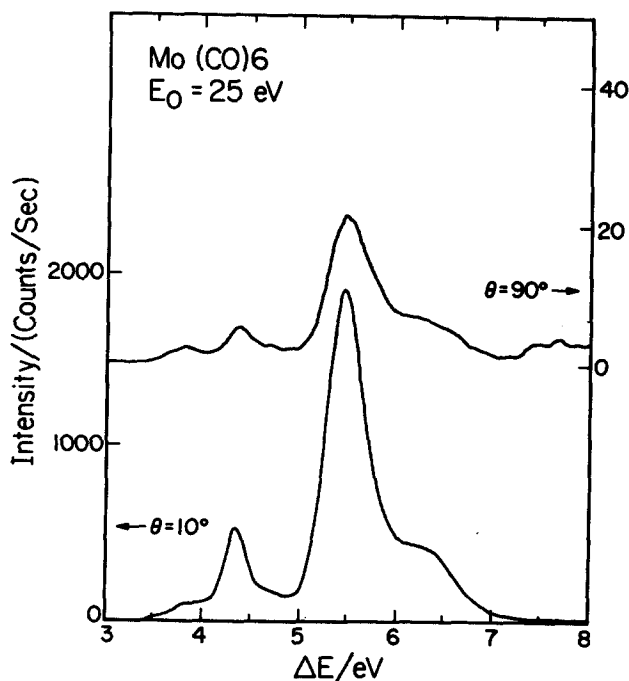


FIG. 8. Low angle (10°) and high angle (90°) spectra (between 3.0 and 8.0 eV energy loss) of $\text{Mo}(\text{CO})_6$, $E_0 = 25$ eV.

$\text{Mo}(\text{CO})_6$. The LF bands occur at 3.84 and 4.65 eV, which are also very close in energy to those seen in $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$. The shoulder at 3.61 eV has been assigned by Beach and Gray³¹ to the ${}^1A_{1g} \rightarrow {}^3T_{1g}$ transition and the MCD measurements of Chastain *et al.*²⁸ seem to confirm this assignment. On the basis of our DCS measurements we can make no definitive statement confirming this assignment. Again at 6.24 eV occurs a symmetry-forbidden transition, as identified by the angular behavior of the intensity of this band relative to the 5.55 eV band. As with the other hexacarbonyls this is most likely the ${}^1A_{1g} \rightarrow {}^1A_{1g}, 2t_{2g}(\pi) \rightarrow 3t_{2g}(\pi^*)$ transition. Other bands are observed below the first IP at 6.54, 7.66, and 8.38 eV. A number of transitions to SES states are observed at 8.80, 9.96, 10.38, 11.63, and 12.26 eV. These again are probably due to Rydberg or intraligand transitions.

V. PHOTOCHEMISTRY

The transition metal carbonyls probably have the most extensively studied photochemistry of any organometallic species.^{7,63,64} Recent work includes photodissociation in low temperature matrices and glasses,⁶⁵⁻⁶⁷ laser photodissociation,⁶⁸ multiphoton dissociation and ionization,⁶⁹⁻⁷³ and picosecond laser studies.⁷⁴ Excitation of any of the LF or MLCT bands is known to cause photodissociation of the type



A number of studies have indicated that the energetically low-lying triplet states of these molecules are important in many of these processes.^{65,68,75} The work of Nasielski and

Colas⁷⁵ indicates that the measured quantum yield for photodissociation of somewhat less than unity⁷⁶ may be accounted for by the radiationless decay of a relatively long-lived triplet state. Rest and Sodeau⁶⁵ have observed phosphorescence at 400 nm in mixed matrices of $\text{Cr}(\text{CO})_6$ and have assigned it to the $\text{Cr}(\text{CO})_6, {}^3T_{1g} \rightarrow {}^1A_{1g}$ transition. This places the triplet state for $\text{Cr}(\text{CO})_6$ at about 3.1 eV. In this study we have found no band which is consistent with this assignment.

VI. DISCUSSION

We undertook this investigation with the hope of locating and definitively assigning the low-lying triplet states of these transition metal hexacarbonyl compounds on the basis of the angular and energy dependence of the corresponding electron-impact DCS's. The major problem with using the DCS's to assign the transitions of these compounds involves the high atomic number of the metal atom. The rules correlating the behavior of the DCS with the transition type are based on a large body of data obtained from experiments with polyatomic molecules consisting primarily of first and second row elements. In these compounds the spin of the electron is considered to be a constant of the motion, i.e., a "good" quantum number. However, in the presence of the high electric fields experienced by the electron as it travels near an increased nuclear charge, as is the case with the heavier elements, the spin-orbit interaction becomes nonnegligible.⁷⁷ This results in the spin angular momentum no longer being a good quantum number. The behavior of the DCS for transitions in systems involving various degrees of spin-orbit coupling is not known since only a few electron-impact studies involving compounds containing heavy nuclei have been performed.^{17-19,78-80}

From the DCS plots and ratio plots, the only transition which displays any forbidden character is the one assigned to the ${}^1A_{1g} \rightarrow {}^1A_{1g}, 2t_{2g}(\pi) \rightarrow 3t_{2g}(\pi^*)$ excitation. This excitation displays behavior characteristic of a symmetry-forbidden transition at incident energies of 100 eV. The DCS for this transition at 25 eV incident energy behaves similarly to those for spin-forbidden transitions in light atom systems. Particularly interesting is the fact that this behavior essentially disappears as the incident energy is increased to 50 eV. This is also indicative of spin-forbidden-type transitions and points out the possibility of there being an underlying spin-forbidden transition present which only contributes significantly to the DCS at 25 eV. The plausibility of this argument is supported by the work of Avouris *et al.*²⁰ who, as mentioned earlier, studied the electronic excitations of CO bound to metal surfaces and found that some of the CO triplet and singlet transitions were not significantly perturbed from their gas phase values. If this holds true for the metal hexacarbonyls, the first CO triplet would fall within the region of the ${}^1A_{1g} \rightarrow {}^1A_{1g}, 2t_{2g}(\pi) \rightarrow 3t_{2g}(\pi^*)$ transition for metal hexacarbonyls. One would expect that since this would be primarily an intraligand excitation, its DCS would behave similarly to that of free CO. This would also explain the presence of the transitions in the 8-9 eV range observed in all of these molecules. More work is clearly needed to confirm if this is indeed the case. In addition, a number of

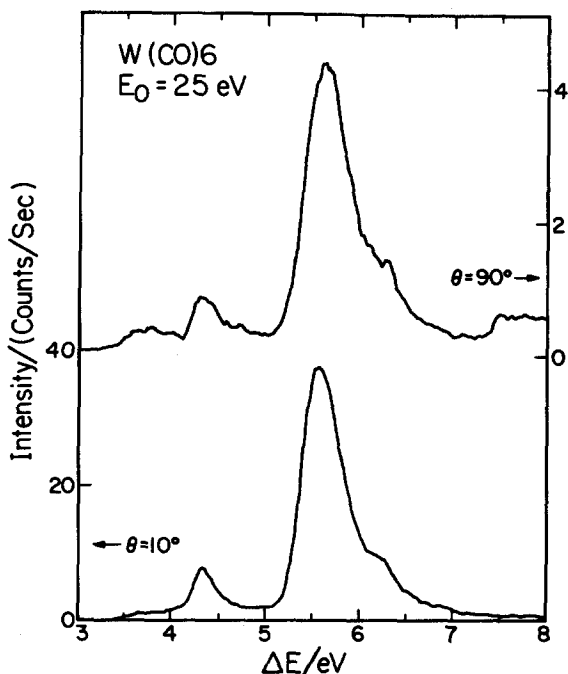


FIG. 9. Low angle (10°) and high angle (90°) spectra (between 3.0 and 8.0 eV energy loss) of $\text{W}(\text{CO})_6$, $E_0 = 25$ eV.

SES bands have been observed in all three compounds, which seem to correspond to the 10.78, 11.40, and 12.37 bands seen in free CO.⁸¹ These transitions differ from the free CO values by a few tenths of an eV. The presence of relatively unperturbed CO transitions is supported by the bands in the photoelectron spectra³⁵ which have been observed to be reasonably close in energy to those of free CO.

We have also noticed that the shoulders on the low-energy side of the first MLCT bands, which have been previously assigned as triplets in Mo(CO)₆ and W(CO)₆,³¹ all show the same relative degree of enhancement as a function of angle as do the bands assigned to the LF excitations. This suggests that all of these bands belong to a common type of transition. The question must be answered as to whether they belong to a spin-allowed LF transition or some type of LF or MLCT spin-forbidden transition. The angular behavior of the DCS's for these bands indicates that they have the character of transitions in systems for which spin-orbit coupling is small and thus, based on this information, no definite statement may be made either way. To further clarify this situation, we can look at the incident energy dependence of the ratio of the DCS of the bands in question to the DCS of the first MLCT band as a function of incident energy (Table II). For spin-forbidden transitions this ratio should rise dramatically as one approaches the threshold excitation energy.¹⁵ For spin-allowed transitions this ratio climbs slowly from threshold to peak at 5 to 10 eV above it and then slowly decreases as the incident energy is raised. The energy behavior of this ratio which we observe does not appear to indicate the presence of a spin-forbidden transition but rather a weak spin-allowed one.

From the evidence we have on the angular and energy behavior of these low-lying bands we tentatively assign them to LF bands. The LF bands are formally *g*→*g* symmetry-forbidden but they do not display the high energy, low angle intensity behavior characteristic of such transitions. This can be explained if the LF excited state is significantly distorted which would tend to remove some of the symmetry constraints on the transition. The symmetry forbiddenness of these bands might also explain the slight enhancement observed on increasing the scattering angle.

The lack of spin-forbidden behavior on the part of the DCS's may also be caused in part by the way in which they were obtained from the energy-loss spectra. The transitions for these compounds are heavily overlapped. If the singlet-triplet splitting were small enough, and the triplet state intensity small compared to the overlapping singlet, then the singlet would dominate the behavior of the DCS of the combination of the two bands.

TABLE II. Ratios of the area of the lowest MLCT band to that of the lowest energy shoulder as measured at 20° scattering angle.

	<i>E</i> ₀ (eV)		
	100	50	25
Cr(CO) ₆	4.05	3.93	3.77
Mo(CO) ₆	4.83	4.82	4.23
W(CO) ₆	4.25	4.06	3.52

VII. SUMMARY AND CONCLUSIONS

In summary we have measured the electron energy-loss spectra of Cr(CO)₆, Mo(CO)₆, and W(CO)₆ at incident energies of 25, 50, and 100 eV and at scattering angles from 10° to 90°. We have confirmed, on the basis of the low angle dependence of the differential cross section, the symmetry-forbidden nature of the $2t_{2g}(\pi) \rightarrow 3t_{2g}(\pi^*)$, $^1A_{1g} \rightarrow ^1A_{1g}$ transitions located at 6.35, 6.33, and 6.24 eV for Cr(CO)₆, Mo(CO)₆, and W(CO)₆, respectively. We have also tentatively assigned a number of low-lying ligand field bands on the basis of the energy and angular behavior of the DCS's. In addition a number of transitions to superexcited states were observed above 9 eV energy loss, some of which corresponded quite well with transitions in free CO. No excitations were located which could confidently be assigned to singlet-triplet excitations involving metal orbitals.

The results of the present research point out the need for additional theoretical studies, especially on the electronic structures of these compounds and on the dynamics of electron scattering from strongly spin-orbit coupled species.

The first area of additional study should involve the electronically excited states of the molecules. Almost all the theoretical calculations of the electronic spectra of the compounds have focused on Cr(CO)₆,⁴⁷⁻⁵¹ with one study devoted to W(CO)₆,⁵³ and one examining the spectra of all three molecules.³¹ Regarding the calculations of the Cr(CO)₆ spectrum, transition energies were inaccurate by as much as 30% in some cases. All yielded assignments which generally agreed, two major exceptions being the assignment of the lowest state at 3.78 eV and the assignment of the state located at 6.35 eV (our work has supported the assignment of Beach and Gray³¹ for the 6.35 eV transition). What is now needed are additional theoretical studies of the molybdenum and tungsten hexacarbonyls. A detailed study of the effect of metal binding on the CO-to-CO transitions would also be useful, especially in extending the results of this work to those from studies of CO bound to metal surfaces.

The second area of theoretical study should involve the behavior of the DCS of low-energy electron scattering from targets with varying degrees of spin-orbit coupling. The calculations performed need not be exact since only qualitative trends are desired. They should be done for both direct and exchange scattering processes. It is hoped that the present work will stimulate efforts in the previously mentioned areas since such studies would be useful for the interpretation of electron energy-loss spectra of organometallic compounds.

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¹J. A. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity* (Harper and Row, New York, 1978), pp. 524-536.

²M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Organomet. Chem.* **70**, 283 (1974).

³E. Koerner van Gustorf and F. W. Guerals, *Fortsch. Chem. Forsch.* **13**, 366 (1969).

⁴G. S. Lewandos and R. Pettit, *J. Am. Chem. Soc.* **93**, 7087 (1971).

⁵G. L. Leigh and E. O. Fischer, *J. Organomet. Chem.* **4**, 461 (1965).

- ⁶E. O. Fischer and H. P. Fritz, *Angew. Chem.* **73**, 353 (1961).
⁷M. Wrighton, *Chem. Rev.* **74**, 401 (1974), and references therein.
⁸E. Muettterties, *Science* **194**, 1150 (1976).
⁹E. Muettterties, *Science* **196**, 839 (1977).
¹⁰E. W. Plummer, W. R. Salaneck, and J. S. Miller, *Phys. Rev. B* **18**, 1673 (1978).
¹¹J. N. Halpern, *Annu. Rev. Phys. Chem.* **16**, 103 (1965).
¹²Reference 1, p. 526.
¹³D. E. Sherwood and M. B. Hall, *Inorg. Chem.* **22**, 93 (1983), and references therein.
¹⁴A. Kuppermann, J. K. Rice, and S. Trajmar, *J. Phys. Chem.* **72**, 3894 (1968).
¹⁵S. Trajmar, J. K. Rice, and A. Kuppermann, *Adv. Chem. Phys.* **18**, 15 (1970).
¹⁶A. Kuppermann, W. M. Flicker, and O. A. Mosher, *Chem. Rev.* **79**, 77 (1979).
¹⁷R. Rianda, R. P. Frueholz, and A. Kuppermann, *J. Chem. Phys.* **70**, 1056 (1979).
¹⁸A. Chutjian, S. K. Srivastava, S. Trajmar, W. Williams, and D. C. Cartwright, *J. Chem. Phys.* **64**, 4791 (1976).
¹⁹S. K. Srivastava, D. C. Cartwright, S. Trajmar, A. Chutjian, and W. Williams, *J. Chem. Phys.* **65**, 208 (1976).
²⁰Ph. Avouris, N. J. DiNardo, and J. E. Demuth, *J. Chem. Phys.* **80**, 491 (1984), and references therein.
²¹E. N. Lassetre, A. Skerebele, and M. A. Dillon, *J. Chem. Phys.* **50**, 1829 (1969).
²²W. Strohmeier and K. Gerlach, *Z. Phys. Chem.* **27**, 439 (1961).
²³R. T. Lundquist and M. Cais, *J. Organomet. Chem.* **27**, 1167 (1962).
²⁴H. Saito, J. Fuhita, and K. Saito, *Bull. Chem. Soc. Jpn.* **41**, 359 (1968).
²⁵W. C. Trogler, S. R. Desjardins, and E. I. Solomon, *Inorg. Chem.* **18**, 2131 (1979).
²⁶L. Baraldi, G. Gottarelli, and B. Samori, *J. Phys. (Paris)* **40**, 204 (1979).
²⁷A. M. F. Hezemans, P. J. F. M. Van de Coulwijk, D. J. Stufkens, and G. Boxhoorn, *Chem. Phys. Lett.* **73**, 550 (1980).
²⁸S. K. Chastain and R. W. Mason, *Inorg. Chem.* **20**, 1395 (1981).
²⁹H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.* **85**, 2922 (1963).
³⁰D. S. Alderdice, *J. Mol. Spectrosc.* **15**, 509 (1965).
³¹N. A. Beach and H. B. Gray, *J. Am. Chem. Soc.* **90**, 5713 (1968).
³²A. Iverson and B. R. Russell, *Chem. Phys. Lett.* **6**, 307 (1970).
³³F. E. Vilesov and B. L. Kurbatov, *Dokl. Acad. Nauk. SSSR* **140**, 1364 (1961).
³⁴D. R. Lloyd and E. W. Schlag, *Inorg. Chem.* **8**, 2544 (1969).
³⁵D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, New York, 1970), pp. 361-371.
³⁶B. R. Higgenson, D. R. Lloyd, P. Burroughs, D. M. Gibson, and A. F. Orchard, *J. Chem. Soc. Faraday Trans. 2* **69**, 1659 (1973).
³⁷D. S. Rajoria, L. Kovnat, E. W. Plummer, and W. R. Salaneck, *Chem. Phys. Lett.* **49**, 64 (1977).
³⁸J. L. Hubbard and D. L. Lichtenberger, *J. Am. Chem. Soc.* **104**, 2132 (1982).
³⁹E. W. Plummer, W. R. Salaneck, and J. S. Miller, *Phys. Rev. B* **18**, 1673 (1978).
⁴⁰G. Loubriel and E. W. Plummer, *Chem. Phys. Lett.* **64**, 234 (1979).
⁴¹J. C. Giordan, J. H. Moore, and J. A. Tossell, *J. Am. Chem. Soc.* **103**, 6632 (1981).
⁴²J. A. Tossell, J. H. Moore, and J. K. Olthoff, *J. Am. Chem. Soc.* **106**, 823 (1984).
⁴³E. J. Baerends and P. Ros, *Mol. Phys.* **30**, 1735 (1975).
⁴⁴K. Tatsumi and J. Fueno, *Bull. Chem. Soc. Jpn.* **49**, 939 (1976).
⁴⁵W. Heijser, E. J. Baerends, and P. Ros, *J. Mol. Struct.* **63**, 109 (1980).
⁴⁶D. Saddei, J. Fruend, and G. Hohlneicher, *Chem. Phys.* **55**, 339 (1981).
⁴⁷M. I. Ba'n, Sz. Fenyi, and M. Hegyhati, *Theory Struct. Complex Compounds Papers Symposium, Wroclaw, Poland, 1964*, pp. 195-202.
⁴⁸D. G. Carroll and S. P. McGlynn, *Inorg. Chem.* **7**, 1285 (1968).
⁴⁹K. G. Caulton and R. F. Fenske, *Inorg. Chem.* **7**, 1273 (1968).
⁵⁰A. G. Schreinder and T. L. Brown, *J. Am. Chem. Soc.* **90**, 3366 (1968).
⁵¹J. B. Johnson and W. G. Klemperer, *J. Am. Chem. Soc.* **99**, 7132 (1977).
⁵²B. E. Bursten, D. G. Freier, and R. F. Fenske, *Inorg. Chem.* **19**, 1810 (1980).
⁵³C. Y. Yang, R. Arratia-Perez, and J. P. Lopez, *Chem. Phys. Lett.* **107**, 112 (1984).
⁵⁴J. H. Hillier and V. R. Saunders, *Mol. Phys.* **22**, 1025 (1971).
⁵⁵D. Moncrieff, P. C. Ford, I. H. Hillier, and V. R. Saunders, *J. Chem. Soc. Chem. Commun.* **1983**, 1108.
⁵⁶C. F. Koerting, K. N. Walzl, and A. Kuppermann, *J. Chem. Phys.* (submitted).
⁵⁷C. F. Koerting, Ph.D. thesis, California Institute of Technology, 1985.
⁵⁸J. A. Simpson, *Rev. Sci. Instrum.* **35**, 1698 (1964).
⁵⁹C. E. Kuyatt and J. A. Simpson, *Rev. Sci. Instrum.* **38**, 103 (1967).
⁶⁰L. Vuskovic and S. Trajmar, *J. Chem. Phys.* **78**, 4947 (1982).
⁶¹R. P. Frueholz, R. Rianda, and A. Kuppermann, *J. Chem. Phys.* **68**, 775 (1978).
⁶²R. P. Frueholz, R. Rianda, and A. Kuppermann, *Chem. Phys.* **30**, 315 (1978).
⁶³A. Vogler, in *Concepts of Inorganic Photochemistry*, edited by A. W. Adamson and P. D. Fleishaur (Wiley, New York, 1975), pp. 269-295.
⁶⁴G. L. Geoffroy and M. S. Wrighton, *Organometallic Photochemistry* (Academic, New York, 1979), p. 68.
⁶⁵A. J. Rest and J. R. Sodeau, *J. Chem. Soc. Faraday Trans. 2* **73**, 1691 (1977).
⁶⁶M. J. Boyland, J. D. Black, and P. S. Braterman, *J. Chem. Soc. Dalton Trans.* **9**, 1646 (1980).
⁶⁷M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A* **1971**, 2939.
⁶⁸T. R. Fletcher and R. N. Rosenfeld, *J. Am. Chem. Soc.* **105**, 6359 (1983).
⁶⁹M. A. Duncan, T. G. Dietz, and R. E. Smalley, *Chem. Phys.* **44**, 415 (1979).
⁷⁰D. P. Gerrity, L. J. Rothberg, and V. Vaida, *Chem. Phys. Lett.* **74**, 1 (1980).
⁷¹G. J. Fisanick, A. Gedanken, T. S. Eichelberger IV, N. A. Kuebler, and M. B. Robin, *J. Chem. Phys.* **75**, 5215 (1981).
⁷²D. P. Gerrity, L. J. Rothberg, and V. Vaida, *J. Chem. Phys.* **77**, 2222 (1983).
⁷³D. G. Leopold and V. Vaida, *J. Am. Chem. Soc.* **105**, 6809 (1983).
⁷⁴J. D. Simon and K. S. Peters, *Chem. Phys. Lett.* **98**, 53 (1983).
⁷⁵J. Nasielski and A. Colas, *Inorg. Chem.* **17**, 237 (1977).
⁷⁶J. Nasielski and A. Colas, *J. Organomet. Chem.* **101**, 215 (1975).
⁷⁷Gordon Baym, *Lectures in Quantum Mechanics* (Benjamin, Reading, MA., 1969), p. 460.
⁷⁸W. Williams, S. Trajmar, and A. Kuppermann, *J. Chem. Phys.* **62**, 3031 (1975).
⁷⁹W. Williams and S. Trajmar, *Phys. Rev. Lett.* **33**, 187 (1974).
⁸⁰S. Trajmar, W. Williams, and S. Srivastava, *J. Phys. B* **10**, 3323 (1977).
⁸¹G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950), pp. 521-522.