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Photochemistry of the Group 6 Hexacarbonyls in Low-Temperature Matrices. IV.[1-3] Tetracarbonylmolybdenum and Tricarbonylmolybdenum

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Abstract: Uv photolysis of $Mo(CO)_6$ in a CH_4 matrix produces $Mo(CO)_5$ and two secondary photolysis products, which grow sequentially. Their spectra and growth patterns are consistent with an assignment to $Mo(CO)_4$ and $Mo(CO)_3$. This assignment is proved by detailed ^{13}CO substitution studies which show that the $Mo(CO)_4$ adopts a C_{2v} structure (angles 174°, 107°) and the $Mo(CO)_3$ a C_{3v} structure (angle 105°). The spectra of $Mo(CO)_4$ and $Mo(CO)_3$ in CH_4 are sufficiently similar to the spectra in Ar and to the spectra of the Cr and W systems for a preliminary assignment of the bands of these systems to be made. The origin of these asymmetric structures is discussed in relation to recent theories of bonding in carbonyl fragments.

The first three papers[1-3] in this series discussed the structure and properties of $M(CO)_5$ (M = Cr, Mo, W), the primary photolysis products of the metal hexacarbonyls in a matrix. The C_{4v} structure of $M(CO)_5$ in CH_4 and Ar matrices was demonstrated using isotopic substitution.[2] While long-wavelength irradiation of $M(CO)_5$ caused the regeneration of $M(CO)_6$, on prolonged uv photolysis further bands appeared.[1,4] In this paper, it is shown that these secondary photolysis products are low-symmetry carbonyls containing fewer than five CO groups.

Experimental Section

All experiments were performed at 20°K on an Air Products Displex CS202 refrigerator equipped with an automatic temperature controller. The detailed equipment has been described elsewhere.[1,5] Matrices were deposited by the pulsed technique with concentrations of 1:3000. Ir spectra were taken on a modified Grubb Parsons Spectromajor using the second order of the lower grating giving 0.6 cm^{-1} resolution. Spectra were calibrated with DCl and DBr and are accurate to ± 0.3 cm^{-1}. Uv-visible spectra were taken on a Perkin-Elmer 356 (see ref 5). The photolysis lamp, a Phillips HPK 125W medium pressure Hg arc, was used in conjunction with a water filter to remove heat. Visible radiation was removed with a $CoSO_4$-$NiSO_4$ filter[6] and uv radiation with a Pyrex filter (λ >285 nm) or a Calflex C filter (λ >375 nm). All ir spectra were taken with a Ge filter to remove the visible radiation of the Nernst glower. Isotopic samples were prepared by the gas-phase photolysis method.[2,7] The matrix gases were obtained from BOC (Grade X). The calculations were performed using the methods of refinement described for the $M(CO)_6$ and $M(CO)_5$ species.[2]

Results

Even after many hours of irradiation with the unfiltered Hg lamp, the bands of the secondary photolysis products of $Mo(CO)_6$ in an argon matrix were weak in comparison to those of $Mo(CO)_5$. However, photolysis of $Mo(CO)_6$ in a methane matrix yielded $Mo(CO)_5$ very much more rapidly than in argon; on further uv photolysis new bands grew in similar positions to those observed for Ar, but in much higher yield. Within a few minutes these bands became the strongest in the spectrum and further weaker bands were detected (Figure 1).

Irradiation with long-wavelength light (λ >375 nm) caused reconversion of the secondary photolysis products to $Mo(CO)_5$ and $Mo(CO)_6$. By following the growth and decay of optical density of each band, those bands belonging to the same system were identified. Optical density plots for all the observed bands show that the ir and uv-visible bands form three groups (A-C) in addition to $Mo(CO)_6$, $Mo(CO)_5$, and CO (Figure 2, Table I). The plots also show that on progressive uv photolysis, groups A and B reach a maximum in succession. The band at 1911 cm^{-1} (C) was never observed in high yield. Like the weak high-frequency band of $Mo(CO)_5$, the high-frequency bands of A and B must be A_1 modes and can reasonably be compared. The decrease in frequency in the order $Mo(CO)_5$ > A > B ($Mo(CO)_5$, 2093; A, 2057; B, 1981 cm^{-1}) is precisely that expected for decreasing numbers of CO groups. With the removal of each CO group, the π back-bonding to the remainder increases, causing a decrease in the frequency (cf. the nickel carbonyls[8] except that ν(CO), 4 > 3 > 1 > 2, the amonotonic order apparently being related to the absence of an f_{CO-CO} term in the monocarbonyl).

Species A has four quite separate bands in the C-O stretching region (Figure 1), indicating that it contains a minimum of four CO groups. B has a high-frequency band and a closely spaced doublet at low frequency which may be split by a "matrix effect" (see below). The manner in which

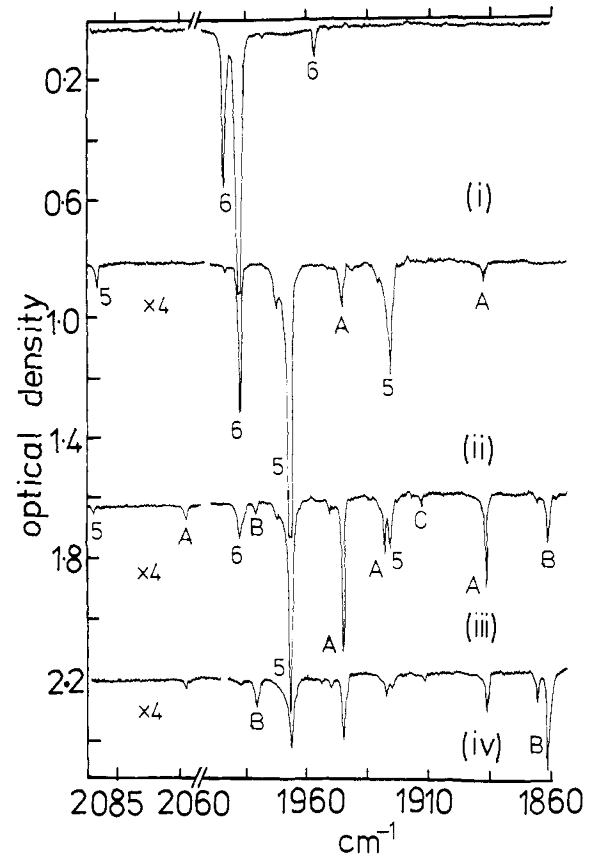

Figure 1. $Mo(CO)_6$ in CH_4 at 20°K: (i) after deposition, (ii) after 1 min uv photolysis, (iii) after 18 min, (iv) after 45 min further photolysis. High-frequency section (>2020 cm^{-1}) is taken from a different experiment with about four times as much material. Band marking: 6 = $Mo(CO)_6$; 5 = $Mo(CO)_5$; A, B, and C refer to groups of bands in Table I.

$Mo(CO)_5$, A, and B grow in turn, the frequency, and the number of the bands associated with A and B strongly suggest that A is $Mo(CO)_4$ and B is $Mo(CO)_3$. Braterman and Black have independently photolyzed $Mo(CO)_6$ in hydrocarbon glasses and reached similar conclusions.[9] An isotopic study of $Mo(CO)_6$ in CH_4 matrices was undertaken to prove the assignment and to determine the structures of the fragments.

^{13}CO Enriched Spectra. A sample of $Mo(CO)_6$ was enriched to about 50% ^{13}CO so that it contained a scrambled mixture of all possible isotopic species. The bands of the enriched spectra were assigned in the same way as the ^{12}CO spectra using optical density plots. The bands of $Mo(CO)_6$ and $Mo(CO)_5$ are discussed elsewhere.[1]

System A. The assignment of bands to system A is straightforward using the optical density plots. It is interesting to note that there is only one band between 1885 and 1845 cm^{-1} (see Figure 3i). Since the ^{12}CO spectrum has four widely spaced bands, the structure of A may be tentatively assigned as a C_{2v} tetracarbonyl (cf. SF_4, *cis*-$Fe(CO)_4I_2$). Under C_{2v} symmetry the two most intense bands may be assigned to the B_1 and B_2 stretches and the weaker two bands to A_1 modes (cf. $Fe(CO)_4$[10]). CO-factored force constants can then be obtained and the complete isotopic frequency pattern calculated. Only one assumption about the interaction force constants is required in order to calculate an initial isotopic spectrum. Assuming[10] $k_{11} = k_{22}$ the *pattern* of the observed spectrum was reproduced immediately and all the observed bands could be assigned. Refinement of all the force constants independently allowed all 20 bands to be fitted with a root-mean-square error of only 0.38 cm^{-1} (Table II).

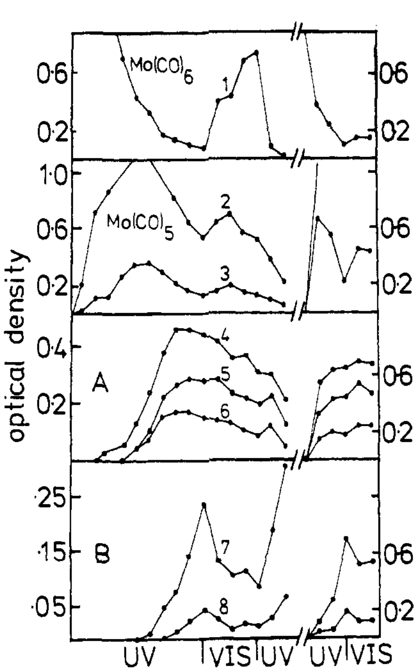

Figure 2. Optical density plots of $Mo(CO)_6$ photolysis products. Abscissa represents photolysis steps in two different experiments (separated by break in axis). Ordinate axis on left refers to first experiment, on right to second experiment: (1) 1987 cm^{-1}, (2) 1967 cm^{-1}, (3) 1926 cm^{-1}, (4) 1945 cm^{-1}, (5) 1887 cm^{-1}, (6) 1927 cm^{-1}, (7) 1862 cm^{-1}, (8) 1981 cm^{-1}.

Table I. Bands Observed on Pholoysis of $Mo(CO)_6$ in CH_4 without ^{13}CO Enrichment[a]

System	Ir bands, cm^{-1}	Ir assignment	Uv–visible bands, nm
$Mo(CO)_6$ (O_h)	1993 (0.26)	T_{1u}	223
	1987 (1.0)		285.5
	2010 (0.008)	A_1 $Mo(CO)_5(^{13}CO)$	291
	1956 (0.04)	A_1 $Mo(CO)_5(^{13}CO)$	307
			324
$Mo(CO)_5$(C_{4v})	2093 (0.01)	A_1	247
	1972 (0.08)	E	411
	1967 (1.0)		
	1929 (0.04)	A_1	
	1926 (0.25)		
	1940 (0.02)	A′ rad $Mo(CO)_4(^{13}CO)$	
	1923 (0.02)	A′ rad $Mo(CO)_4(^{13}CO)$	
	1885 (0.01)	A_1 ax $Mo(CO)_4(^{13}CO)$	
A, $Mo(CO)_4$ (C_{2v})	2057 (0.06)	A_1	530
	1949 (0.17)	B_2	
	1945 (1.0)		
	1927 (0.30)	A_1	
	1887 (0.67)	B_1	
B, $Mo(CO)_3$ (C_{3v})	1981 (0.23)	A_1	317
	1866 (0.18)	E	
	1862 (1.0)		
C, $Mo(CO)_2$(?) ($D_{\infty h}$(?))	1915 (0.23)	Σ_u	
	1911 (1.0)		
Polymer bands	2045	Never normally exceeded OD = 0.03	
	2000		

[a] Intensities in brackets. Bands paired together indicate matrix splittings. For further details of ^{13}CO substituted compounds see ref 2.

The intensity ratios of the C–O stretching modes are related to the molecular bond angles via the eigenvectors of the Wilson **FG** matrix.[11] For the ^{12}CO bands the square roots of the three intensity ratios are related to the bond angles between the two pairs of equivalent CO groups and the ratio of their bond moment derivatives. The two solutions

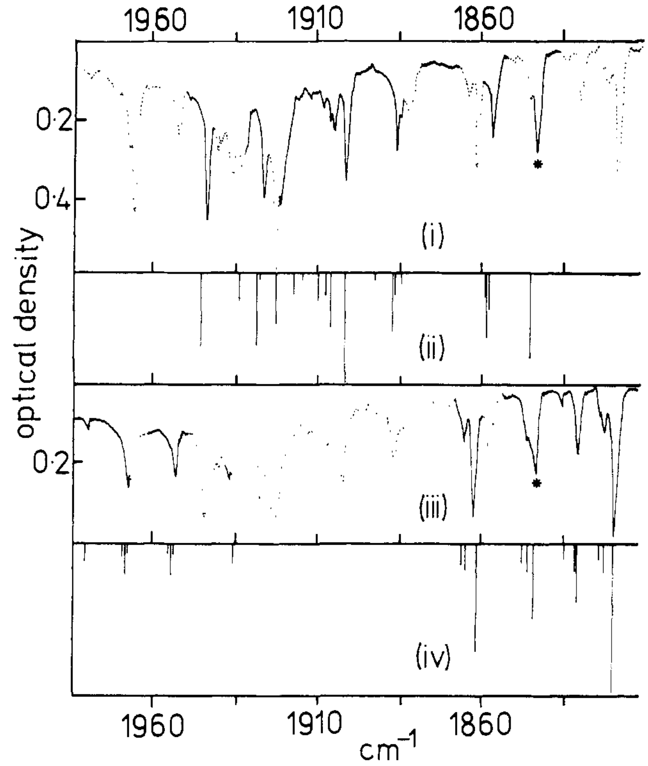

Figure 3. Mo(CO)$_6$ in CH$_4$ at 20°K enriched with 55% ^{13}CO: (i) 90 min uv photolysis (full line A, dotted line B + Mo(CO)$_5$); (ii) theoretical spectrum of Mo(CO)$_4$; (iii) 30 min further uv photolysis (full line B, dotted line A + Mo(CO)$_5$); (iv) theoretical spectrum of Mo(CO)$_3$. Asterisk implies strongly overlapping bands.

correspond to different signs of the square roots of the intensity ratios and different phases of the two A$_1$ modes relative to each other.[10] For each of them a complete isotopic intensity pattern was calculated.

The isotopic pattern in the low-frequency region (<1950 cm^{-1}; Figure 3ii) was similar for the "in-phase" and "out-of-phase" solutions and fitted the observed spectrum well. However, the solutions differed considerably in the high-frequency region. This distinction allows the two possible sets of bond angles to be distinguished in the same way as was used for[2] Mo(CO)$_5$. Inspection of the observed and calculated spectra (Figure 4) reveals that the out-of-phase solution (bond angles 174 and 107°) is the correct one, in contrast to Mo(CO)$_5$ for which the in-phase solution was found to be correct.[2] It should be noted that there is no a priori reason why one solution should hold rather than another, but it is likely that the same one of the solutions will be right for all molecules of a given symmetry. Thus, Poliakoff and Turner rightly chose the out-of-phase solution for C_{2v} Fe(CO)$_4$ on chemical grounds,[10] but the choice of the in-phase solution for *cis*-W(CO)$_4$L$_2$ compounds[12] may have been wrong.

System B. The ^{13}CO bands of system B were particularly easy to identify because the 1862 cm^{-1} band is the most intense band on prolonged photolysis and has the lowest frequency. Consequently, there is little interference from other species in the isotopic spectrum. To low frequency (1815-1865 cm^{-1}) the principal feature of B's spectrum was a quartet of evenly spaced bands (Figure 3iii) which can immediately be recognized as the spectrum of a tricarbonyl.[13] A number of other weaker bands can also be assigned to B.

Table II. Mo(CO)$_4$ Isotopic Spectrum[a]

Isotopic molecule	Assignment	Obsd, cm^{-1}	Calcd, cm^{-1}
Mo(^{12}CO)$_4$	A$_1$	2057.2	2056.5
	B$_1$	1944.7	1945.6
	A$_1$	1927.2	1927.6
	B$_2$	1887.2	1886.9
Mo(^{12}CO)$_3$(^{13}CO)(ax)	A'	2042.7	2042.6
	A'	1933.0	1933.2
	A'	1909.9	1909.7
	A''	1887.2	1886.9
Mo(^{12}CO)$_3$(^{13}CO)(eq)	A'	2052.2	2052.3
	A''	1944.7	1944.7
	A'	1917.7	1917.6
	A'		1858.3
Mo(^{12}CO)$_2$(^{13}CO)$_2$ (ax-ax)	A$_1$	2024.7	2024.6
	A$_1$		1914.4
	B$_1$	1903.0	1902.2
	B$_2$	1887.2	1886.9
Mo(^{12}CO)$_2$(^{13}CO)$_2$ (eq-eq)	A$_1$		2048.2
	B$_1$	1944.7	1945.6
	A$_1$		1892.3
	B$_2$	1844.7	1844.8
Mo(^{12}CO)$_2$(^{13}CO)$_2$ (ax-eq)		2037.5	2037.6
		1927.9	1927.8
		1906.6	1906.2
		1857.6	1857.9
Mo(^{13}CO)$_3$(^{12}CO)(ax-eq-eq)	A'	2032.4	2032.7
	A'	1922.5	1922.5
	A'		1886.6
	A''	1844.7	1844.8
Mo(^{13}CO)$_3$(^{12}CO)(ax-ax-eq)	A'	2017.3	2017.7
	A'	1907.8	1907.7
	A''	1903.0	1902.2
	A'		1857.6
Mo(^{13}CO)$_4$	A$_1$		2010.7
	B$_1$	1903.0	1902.2
	A$_1$		1884.6
	B$_2$	1844.7	1844.8

[a] Force constants (mdyn/Å): $k_1 = 15.941$; $k_2 = 14.929$; $k_{11} = 0.657$; $k_{12} = 0.437$; $k_{22} = 0.553$. Bond angles and bond moments (out of phase, in phase): axial-axial, 174.4, 132.4, ±5°; eq-eq, 107.4, 131.6, ±5°; μ_1'/μ_2', 0.936, 0.757, ±0.1°.

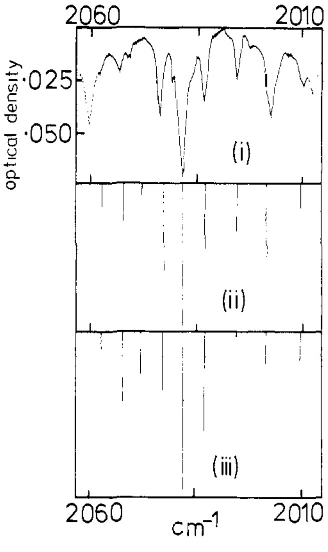

Figure 4. Mo(CO)$_6$ in CH$_4$ at 20°K enriched with 50% ^{13}CO, with four times the quantity of material in Figure 3. High-frequency region of A: (i) after 100 min uv photolysis (only bands of A marked solid, dotted bands due to Mo(CO)$_5$ and Mo(CO)$_6$); (ii) theoretical spectrum of Mo(CO)$_4$ (out-of-phase solution, represents about 20 times expansion of Figure 3ii); (iii) theoretical spectrum of Mo(CO)$_4$ (in-phase solution).

The presence of both a high- and low-frequency band for B in the ^{12}CO spectrum shows that its maximum symmetry must be C_{3v}. (A D_{3h} tricarbonyl has only one ir active band.) However, the splitting of the low-frequency band into two unequal components 4 cm^{-1} apart could either indicate that there were three ir active fundamentals or that the band was split by a "matrix effect". Three structures are possible: (i) a C_{3v} pyramidal structure with two ir active

Table III. $Mo(CO)_3$ Isotopic Spectrum[a]

Isotopic molecule		Obsd, cm^{-1}	Calcd, cm^{-1}
$Mo(^{12}CO)_3$	A_1	1981.1	1980.4
	E	1862.2	1861.6
$Mo(^{12}CO)_2(^{13}CO)$	A_1	1968.5	1968.7
	B_1	1862.2	1861.6
	A_1	1831.1	1830.9
$Mo(^{12}CO)(^{13}CO)_2$	A_1	1953.8	1954.8
	A_1	1843.7	1844.0
	B_1	1819.7	1820.1
$Mo(^{13}CO)_3$	A_1	1936.6	1936.2
	E	1819.7	1820.1

[a] Force constants: $k_1 = 14.608$; $k_{11} = 0.614$. Bond angle: 105 ± 1.5°.

bands (A_1 + E) with the E mode split by a matrix effect; (ii) a C_{2v} T or Y-shaped planar structure with three bands ($2A_1 + B_2$); or (iii) a C_s distorted pyramid with three bands ($2A' + A''$). The latter two structures have identical **F** and **G** matrices, but are expected to give different intensity ratios. Initially we attempted to fit the spectrum to the C_{2v} structure.

All the observed isotopic bands could readily be assigned under C_{2v} symmetry; force constants were calculated and refined to give a satisfactory fit to the observed frequencies. From the intensities of the three ^{12}CO bands two intensity ratios were obtained and from them a bond angle and bond moment ratio were calculated (unique angle = 194°, $\mu_1'/\mu_2' = 0.88$). In turn, the isotopic intensity pattern was calculated from the force constants, bond angle, and bond moment ratio. However, the isotopic intensity pattern fitted the experimental data very poorly in the low-frequency region. In particular the weak bands were calculated to be much more intense relative to the 1862 and 1820 cm^{-1} bands than actually observed. It also seemed strange that the force constants should be so similar ($k_1 = 14.683$; $k_2 = 14.601$; $k_{12} = 0.600$; $k_{22} = 0.610$) despite such an asymmetric structure. Use of a C_s structure brought no improvement and both structures had to be rejected.

Under C_{3v} symmetry the third band of $Mo(CO)_3$ at 1865 cm^{-1} must be assigned to a "matrix splitting" of the 1862 cm^{-1} band. The isotopic spectrum shows weak bands separated from the more intense bands by different intervals. This is consistent with a distortion of some molecules or a low-symmetry site, but not with multiple trapping of a C_{3v} molecule which should produce simple doubling of all the lines. If it is assumed that the molecular symmetry is C_{3v}, but some molecules suffer a C_s distortion which splits the ^{12}CO E mode into two equally intense components, the spectrum may be assigned.

From the intensity ratios of the bands it was deduced that about 40% of the molecules would be distorted. The entire spectrum was then assigned and force constants, bond angles, and intensity ratios were calculated. The observed frequencies of the more intense bands fitted well under C_{3v} symmetry (Table III). A complete intensity pattern obtained by adding together the intensity pattern for the C_{3v} and C_s distorted molecules (Figure 3iv), fitted the observed pattern much better than the C_{2v} molecule alone. The closeness of force constants of the C_s molecule is now explained. The bond angle of the C_{3v} molecule was calculated to be 105° from the ^{12}CO intensity ratios using the above assumptions. The distortion of the C_s molecule was found to be less than 10 min of arc (i.e., the bond angle when projected in the plane deviates less than 10′ from 120°).

System C. The structure of system C could not be proved by isotopic substitution because it was only obtained in low yield, and its isotopic bands overlapped with those of $Mo(CO)_5$ and $Mo(CO)_4$. Photolysis with $285 < \lambda < 350$ nm caused a slight decrease in the $Mo(CO)_3$ intensity and an increase in the band of C at 1912 cm^{-1}; photolysis with $230 < \lambda < 280$ nm restored the $Mo(CO)_3$ intensity entirely. We tentatively assign C as $Mo(CO)_2$, although it is surprising that its band should be at such high frequency.[14]

Table IV. Comparison of $M(CO)_x$ Frequencies (cm^{-1})

	Cr			Mo			W	
	CH_4	Ar	Atoms Ar–CO	CH_4	Ar	Atoms Ar–CO	CH_4	Ar
$M(CO)_6$	1985	1990	1987	1987	1993	1988	1982	1987
$M(CO)_5$	2088	2093		2093	2098		2092	2097
	1961	1966	1963	1967	1973	1969	1957	1963
	1932	1936	1932	1926	1933	1929	1926	1932
$M(CO)_4$	2051			2057			2052	
	1935	1940	1938	1945	1951	1948	1932	1939
	1929	1934		1927			1924	
	1888	1896	1890	1887	1895	1890	1886	1894
$M(CO)_3$	1979			1981			1975	
	1859	1867	1866	1862	1869	1866	1857	1865
$M(CO)_2$ (?)	1903			1911		1910		

Comparison with Other Spectra of Lower Carbonyls. We are now in a position to compare the band of the lower carbonyls in CH_4 to the bands in Ar which appear on prolonged photolysis in low yield. Three new bands are observed at 1951, 1895, and 1869 cm^{-1} and a shoulder appears at 1933 cm^{-1}. All the bands of $Mo(CO)_6$ and $Mo(CO)_5$ are shifted 6-7 cm^{-1} relative to methane. The assignment of the bands to C_{2v} $Mo(CO)_4$ and C_{3v} $Mo(CO)_3$ by comparison with the CH_4 bands is unequivocal, despite the lack of isotopic data and high-frequency bands. There is thus no reason to suppose that the structures differ substantially in Ar matrices (Table IV).

The frequencies may also be compared with those of Graham, obtained[6] by cocondensation of Mo atoms with CO–Ar mixtures. With 1:400 CO–Ar the observed bands were at 1948, 1910, 1890, and 1866 cm^{-1} in addition to those of $Mo(CO)_6$ and $Mo(CO)_5$. These bands again correspond closely to those observed by photolysis in Ar and CH_4. The frequency shift of the atom bands relative to photolysis in Ar is due to the presence of CO. The 1910 cm^{-1} band fits approximately with band C obtained by photolysis of $Mo(CO)_6$ in CH_4 (Table IV).

It is also instructive to compare the spectra of $Mo(CO)_4$ and $Mo(CO)_3$ to those obtained by prolonged photolysis of $Cr(CO)_6$ and $W(CO)_6$ in CH_4 matrices. For neither of these complexes are large yields of lower carbonyls obtained unless the reversal of $M(CO)_5$ to $M(CO)_6$ is suppressed by using a $CoSO_4$-$NiSO_4$ filter to remove the visible radiation of the Hg arc (i.e., leaving $230 < \lambda < 350$ nm). Even then the yields are substantially smaller than for molybdenum; the reason for the difference in photosensitivity is not understood.

Under these conditions $Cr(CO)_5$ and $W(CO)_5$ are photolyzed to yield secondary products with bands which closely correspond to those of $Mo(CO)_4$ and $Mo(CO)_3$ (Table IV). However, the problems of matrix splittings and band overlaps are much more acute than for the Mo system. For these reasons and because of the lower yields, no isotopic substitution has been attempted. Nevertheless, a provisional assignment of ^{12}CO bands is straightforward when the spectra are compared to those of $Mo(CO)_4$ and $Mo(CO)_3$ (Table IV). Frequencies for $Cr(CO)_3$ and $Cr(CO)_2$ are quoted after annealing which removed some of the matrix splittings.

Bands due to lower carbonyls are also observed on extended photolysis of $Cr(CO)_6$ and $W(CO)_6$ in Ar matrices. The stronger bands can be identified and fit in with this

Table V. $Cr(CO)_4$ Visible Band (nm)

Ar	404	Xe	395
CF_4	400	CH_4	393

scheme (Table IV and Ref. 15). All the bands observed on cocondensation of CO-Ar mixtures with Cr atoms[15] can also be assigned except those obtained with high metal evaporation rates.

$Cr(CO)_4$ shows a characteristic band in the visible which appears in all matrices after long photolysis. Unlike $Cr(CO)_5$ its position is not strongly dependent[16] on the matrix (Table V), and hence probably its interaction with the matrix is small.

These comparisons show that there is no evidence that the group 6 tetracarbonyls have a substantially different structure in different matrices.

Discussion

The structures found for $Mo(CO)_4$ and $Mo(CO)_3$ are surprisingly asymmetric. Indeed, Kettle's theory,[17] which predicted highly symmetric carbonyls, does not fit the observations at all. Although a d^6 tetrahedral tetracarbonyl should be subject to a first-order Jahn–Teller distortion, a square-planar structure should be stable. A D_{3h} d^6 tricarbonyl should also be Jahn–Teller stable, yet neither of these structures are adopted. However, these structures do fit the predictions of Burdett for low spin d^6 systems almost exactly. Using simple molecular orbital calculations,[18] he predicted a C_{2v} structure with bond angles of 170 and 90° for the tetracarbonyls, and a C_{3v} structure with a 97° bond angle for the tricarbonyl.

The d^6 molybdenum system makes interesting comparison with the d^8 iron system. $Fe(CO)_4$ has a C_{2v} structure (angles 120 and 140°) and $Fe(CO)_3$ has a C_{3v} structure (angle 108°). Again, these structures and angles fit with the MO calculations. These conclusions lend weight to Burdett's contention that the structures are not primarily determined by Jahn–Teller distortions away from highly symmetric structures. He has rationalized the structures on the basis of maximum overlap between ligand orbitals and the "holes" in the metal atom d electron system.[19]

The structures found for the lower carbonyls are very little distorted from those obtained by selective removal of ligands from an octahedron. Molybdenum tetracarbonyl has a "cis divacant" structure and $Mo(CO)_3$ a "cis trivacant" structure. It could therefore be argued that the molecules adopt these structures because the matrix is acting as a clamp. However, there is considerable evidence against this argument. (a) The structures appear to be little dependent on the matrix or on whether they are prepared by photolysis or by cocondensation of atoms and CO. (b) Braterman and Black have shown[9] that $Mo(CO)_4Pcx_3$ in a glass can be isomerized photochemically from the cis-vacant to the trans-vacant structure. This observation strongly suggests that the matrix is softened enough for the minimum energy structure to be obtained. Recently Poliakoff has obtained evidence for similar isomerization of $W(CO)_4CS$ in Ar and CH_4 matrices.[20] (c) We have succeeded in generating oriented $Cr(CO)_5$ in a CH_4 matrix using polarized photolysis.[21] The $Cr(CO)_5$ can then be reoriented in the opposite direction without conversion to $Cr(CO)_6$. This observation again shows the local softening of the matrix during photolysis. (d) The structures of $Mo(CO)_4$ and $Mo(CO)_3$ agree with those predicted theoretically.

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(22) Note Added in Proof: Elian and Hoffman (M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975)) have also considered the geometries of carbonyl fragments, with results broadly in agreement with Burdett.[18] In particular $Mo(CO)_4$ is predicted C_{2v} (165°, 95°) and $Mo(CO)_3$, C_{3v} (94°); again this is remarkably close to the experimental observations.