Solution and Single-crystal Raman Study of $M(CO)_6$, where M = Chromium, Molybdenum, and Tungsten

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For the three compounds $M(CO)_6$, where M = Cr, Mo, and W, $\nu_{10}(t_{2g})$ has been observed in solution for the first time; a solvent-effect study of ν_1, ν_2, and ν_3 is also reported. Single-crystal Raman experiments yielded symmetry species consistent with currently accepted assignments for these molecules except in the region below 120 cm^{-1} where many new lines were found for the molybdenum compound. In the $\nu(CO)$ region full factor-group splitting is shown by the $\nu_3(e_g)$ mode.

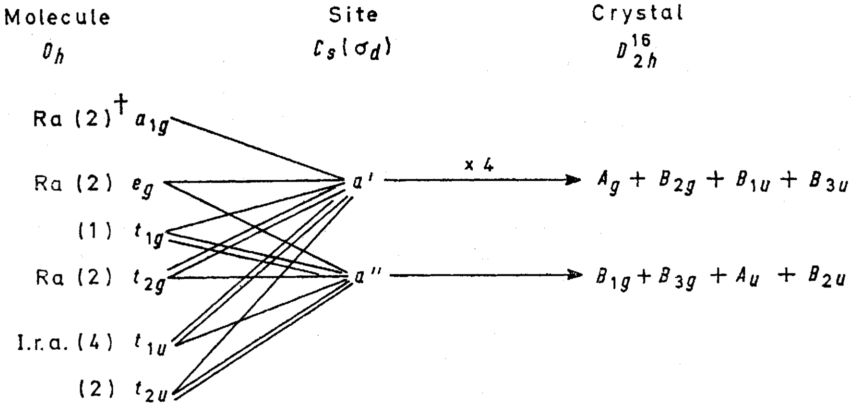
CONSIDERING the attention already lavished upon vibrational spectra of the Group VI metal hexacarbonyls, we must justify another study. No work has been reported upon single crystals of these compounds; we had hopes that observation of full unit-cell splitting would allow experimental distinction to be made between e_g and t_{2g} modes, and possibly reveal some of the inactive modes. Although these hopes were not entirely fulfilled some points of interest have arisen. All three hexacarbonyls were studied, with emphasis upon the molybdenum compound. With minor variations the results for chromium and tungsten hexacarbonyls mirrored those with molybdenum. The region below 150 cm^{-1} was not studied for $Cr(CO)_6$ or $W(CO)_6$ and will be reported later.

EXPERIMENTAL

Reagent grade materials were recrystallised several times before use. Large single crystals were obtained by slow evaporation of dichloromethane solutions. The optic axes were located by X-ray diffraction methods: crystal morphology is shown in Figure 1.

TABLE 1

Correlation table for $M(CO)_6$, and selection rules



† Numbers in parentheses are the numbers of normal modes of $M(CO)_6$, t_{1g} and t_{2u} modes are inactive. Ra = Raman-active. i.r.a. = i.r.-active.

Raman spectra were recorded with a Coderg PHO spectrometer with use of 632·8 nm excitation. For solution work spectroscopic grade solvents were dried and freshly distilled before use.

Selection Rules.—The Group VI metal hexacarbonyls crystallise in the orthorhombic space group *Pnma* (D_{2h}^{16}) with $z = 4$.[1] In the crystal the only symmetry element remaining to each molecule is a σ_d plane but, apart from the $\nu(CO)$ region, the effective symmetry is O_h, as in solution. Selection rules are in Tables 1 and 2. Crystallographic and experimentally used axes are directly related: $a = X, b = Y, c = Z$.

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[1] A. Whitaker and J. W. Jeffery, *Acta Cryst.*, 1967, **23**, 977.

RESULTS AND DISCUSSION

Solution Spectra.—Raman spectra of the Group VI hexacarbonyls in solution have been reported.[2] Five of the six predicted lines are well established but one of the three modes expected in the ν(M–CO), δ(MCO) region has never been observed directly for any of the three compounds. We have now found these (Table **3**) at 487(W), 476(Mo), and 535(Cr) cm^{-1} (see Figure 2). They are close to positions of lines attributed to $\nu_{10}(t_{2g})$ in solid-state Raman spectra.[3]

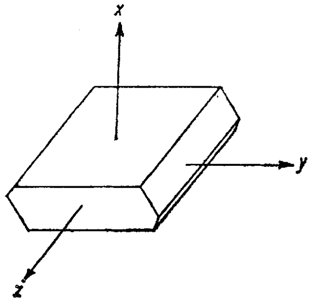

FIGURE 1 Morphology and crystal axes of $Cr(CO)_6$

TABLE 2

Unit-cell analysis for $M(CO)_6$

D_{2h}^{16}	N_T	T_A	T	R	N_i	Activity
A_g	22		2	1	19	xx,yy,zz
B_{1g}	17		1	2	14	xy
B_{2g}	22		2	1	19	xz
B_{3g}	17		1	2	14	yz
A_u	17		1	2	14	
B_{1u}	22	1	1	1	19	z
B_{2u}	17	1	0	2	14	y
B_{3u}	22	1	1	1	19	x

N_T = total number of unit cell modes, T_A = acoustic modes, T = translatory modes, R = rotatory modes, N_i = molecular internal modes.

The solvent sensitivity of ν_1, ν_2, and ν_3 has been investigated in order to complement a previous i.r. study.[4] The results given in Supplementary Publication, No. SUP 20818 (2 pp.) * are as undramatic as was feared. The frequency shifts induced are never more than 5 cm^{-1} with respect to the n-hexane value, the largest being in CH_2Cl_2, CH_3I, and $CHBr_3$, suggesting that solvent polarisability is involved in the shift mechanism

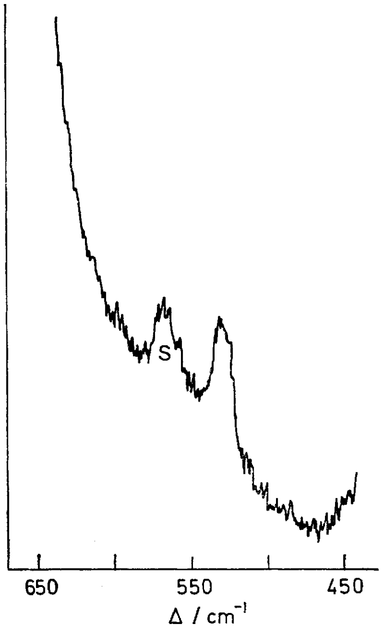

FIGURE 2 The ν_{10} line of $Cr(CO)_6$ in CH_2Cl_2 solution 632·8 nm excitation, 30 mW at sample; spectral slit-width 6 cm^{-1}

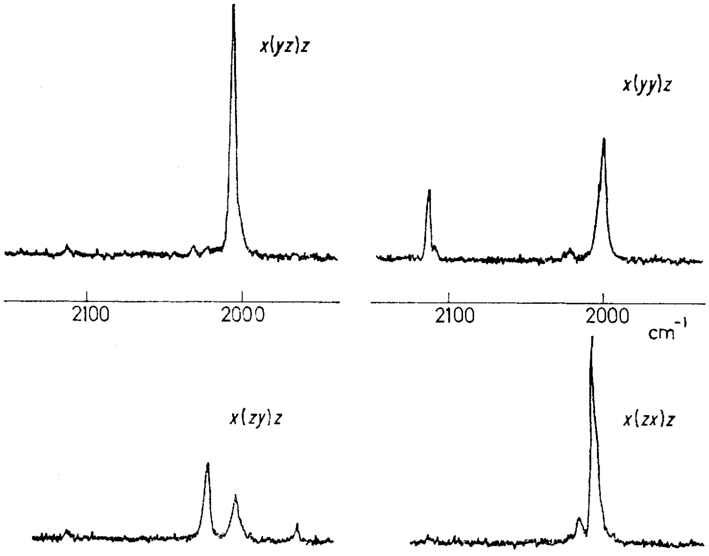

FIGURE 3 Single-crystal Raman spectra of $Mo(CO)_6$ in the ν(CO) region; 632·8 nm excitation, 30 mW at sample; spectral slit-width 1 cm^{-1}

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* For details of the Supplementary Publication scheme see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue. Items less than 10 pp. are sent as full size copies.

[2] R. L. Amster, R. B. Hannan, and M. C. Tobin, *Spectrochim. Acta*, 1963, **19**, 1489.

[3] L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, 1969, **8**, 2349.

[4] R. J. H. Clark and B. Crociani, *Inorg. Chim. Acta*, 1967, **1**, 12.

TABLE 3

Raman frequencies/cm^{-1} of $M(CO)_6$ in CH_2Cl_2 solution

		M = Cr	M = Mo	M = W
ν_1	a_{1g}	2114P	2116P	2119P
ν_3	e_g	2017	2019	2014
ν_{10}	t_{2g}	535	476	487
ν_2	a_{1g}	379P	401P	427P
ν_4	e_g	399	394	415
ν_{11}	t_{2g}	100	94	94

of these solvents. There is substantial band broadening with increase in solvent polarity, most noticeably associated with $\nu_3(e_g)$, but we have not followed it quantitatively.

TABLE 4A

Single-crystal Raman frequencies/cm^{-1} and intensities (arbitrary scale) for $Mo(CO)_6$

Assignment D_{2h}	Band	$x(yy)z$	$x(yx)z$	$x(zx)z$	$x(zy)z$	Assignment O_h
A_g	2114	41	4·5	4	4·5	ν_1, a_{1g}
A_g	2110	6	—	—	—	^{13}CO
B_{1g}	2032	—	5	—	—	ν_3, e_g [c]
B_{3g}	2024	6	5	4	45	
B_{2g}	2017	—	4	15	—	
B_{2g}	2007	—	—	123	—	
B_{1g}	2006	—	152	—	—	
$A_g + B_{3g}$	2005	*ca.* 10	—	—	27	
A_g	2002	73	—	—	*ca.* 7	
B_{3g}	1965	—	—	—	10	^{13}CO
B_{2g}	605	—	—	$\leqslant 1$	—	
$B_{1g} + B_{3g}$	596	—	$\leqslant 1$	—	<1	ν_7, t_{1u}
$A_g + B_{2g}$	594	$\leqslant 1$	—	$\leqslant 1$	—	
$A_g + B_{1g} + B_{2g} + B_{3g}$	478	2	<1	<1	<1	ν_{10}, t_{2g}
$A_g + B_{2g}$	409	72	12	16	11	ν_2, a_{1g}
$A_g + B_{2g} + B_{3g}$	395	8	—	3	2	ν_4, e_g
B_{1g}	393	—	4	—	—	
A_g	113	48	—	—	—	ν_9, t_{1u} + ν_{11}, t_{2g} + lattice modes
B_{2g}	109	—	—	43	—	
$B_{1g} + B_{3g}$	103	—	38	—	55	
A_g	96	90	—	—	—	
$A_g + B_{2g}$	93	90	—	14	—	
B_{3g}	91	—	—	—	14	
B_{1g}	88	—	20	—	—	
B_{1g}	75	—	<1	—	—	
A_g	49	4	—	—	—	Lattice modes
$B_{2g} + B_{3g}$	47	—	—	<1	5	
B_{1g}	46	—	1	—	—	
B_{3g}	39	—	—	—	11	
B_{2g}	34	—	—	2	—	
A_g	28	1	—	—	—	

TABLE 4B

Intensities in this Table are 200× those of Table 4A

Assignment D_{2h}	Band	$x(yy)z$	$x(yx)z$	$x(zx)z$	$x(zy)z$	Assignment O_h
A_g	1205	7 [a]	—	—	—	
A_g	1182	7 [a]	—	—	—	$2\nu_7$
$A_g + B_{1g}$	1024	10	6	—	—	$2\nu_{12}$
B_{2g}	1019	—	—	5	—	
$A_g + B_{1g} + B_{2g}$	961	13	6 [a]	7	—	$2\nu_{10}$ [b]
$A_g + B_{1g}$	823	3	6	—	—	$2\nu_2$ [b]
A_g	784	3	—	—	—	$2\nu_4$
$B_{1g} + B_{2g} + B_{3g}$	739	—	18	18	12	$\nu_4 + \nu_5$ [b]
A_g	735	40	—	—	—	
$A_g + B_{1g} + B_{2g} + B_{3g}$	694	40	8	8	7	$2\nu_5$
B_{2g}	605	—	—	12	—	See text [b]
$B_{1g} + B_{3g}$	596	—	5	—	33	ν_7, t_{1u}
$A_g + B_{2g}$	594	10	—	8	—	

[a] Broad. [b] Assignments differing from those of Jones *et al.* [c] See text for details.

Single-crystal Spectra.—Results are shown in Tables 4 and 5, and Figures 3 and 4. We consider each of the main regions separately, basing discussion upon $Mo(CO)_6$.

$\nu(CO)$ *region.* Because molybdenum hexacarbonyl forms a molecular crystal it is to be expected that the $\nu(CO)$ solid state spectrum will exhibit Raman lines close in frequency to those of its solutions but split about those positions in accord with the scheme of Table 1. The surprising feature of the observed spectra is the apparent complexity arising from the molecular e_g $\nu(CO)$ mode.

The high-frequency a_{1g} mode of the isolated molecule appears in the crystal at 2114 cm^{-1} with a dominant A_g component. In other orientations very weak lines are found which can only be attributed to residuals present owing to slight crystal and experimental imperfections. Although a B_{2g} component is formally allowed, re-orientation of the O_h a_{1g} tensor to crystal axes (the oriented gas model being used) predicts near-zero intensity, in accord with observation. (The A_g shoulder at 2110 cm^{-1} is attributed to a ^{13}CO mode.)

A considerable amount of fine structure is present in the 2000—2035 cm^{-1} region, Table 4A. We discount the possibility that any of this originates in the i.r.-active molecular t_{1u} mode, which becomes allowed in the solid by virtue of the site and correlation fields, as the t_{1u} mode is *ca.* 1990 cm^{-1} in the solid (the exact position is not easily determined from powder spectra owing to dispersion effects). The main features, *i.e.*, the bands/cm^{-1} at 2002 (A_g), 2006 (B_{1g}), 2007 (B_{2g}), and 2024 (B_{3g}), are readily accounted for as the expected site-plus-correlation-split components of the molecular e_g mode (Table 1) and cover a span of 22 cm^{-1} which is normal for carbonyl complexes.

TABLE 5

Single-crystal frequencies/cm^{-1} and assignments for $M(CO)_6$

M = Cr	M = W	Assignment D_{2h}^{16}	Assignment O_h
2109	2117	A_g	a_{1g}, ν_1
2104	2113	A_g	^{13}CO
2032	2029	B_{1g}	e_g, ν_3 [a]
2022	2017	$A_g + B_{2g}$	
2016	2013	B_{3g}	
2006	1999	$B_{1g} + B_{2g} + B_{3g}$	
2000	1995	A_g	
1962	1957		^{13}CO
534	485	$A_g + B_{1g} + B_{2g} + B_{3g}$	t_{2g}, ν_{10}
399	419	$A_g + B_{1g} + B_{2g} + B_{3g}$	e_g, ν_4
389	437	$A_g + B_{2g}$	a_{1g}, ν_2

[a] See text for details.

FIGURE 4 Part of the single-crystal Raman spectrum of $Mo(CO)_6$ in the lattice mode region. Spectral slit-width 2 cm^{-1}

The weaker additional bands at 2005, 2017, and 2032 cannot be due to LO/TO splitting as the crystal is centrosymmetric. We consider that the most probable origin is in the isotopic variants. Although ^{13}C is only 1·1% abundant, in $M(CO)_5$ (^{13}CO) it is 6·5% abundant, and the positions of the remaining weaker lines can be correlated with those calculated by Haas and Sheline for this species.[5] However, more detailed discussion is not warranted until experiments with isotopically pure materials have been done.

ν(Mo–C) *and* δ(MoCO) *regions.* In contrast with the ν(CO) region this part of the spectrum shows relatively few lines. Splitting is very slight and is insufficient to allow distinction to be drawn between e_g and t_{2g} modes. The solid-state spectrum therefore adds little to the conclusions from solution work. The symmetry species and band splittings are fully consistent with the molecular origins indicated in Table 4. We note that the 395/393 cm^{-1} pair are more intense than the line at 478 cm^{-1}, consistent with the approximate descriptions ν(Mo–CO), ν_4 and δ(MoCO), ν_{10}. Extremely weak lines at 596/594 cm^{-1} are consistent with $\nu_7(t_{1u})$, but there is no sign of $\nu_8(t_{1u})$ expected at *ca.* 370 cm^{-1} or of the two O_h-inactive modes $\nu_5(t_{1g})$ and $\nu_{12}(t_{2u})$ in the single-crystal spectra, although extremely weak features have been seen at *ca.* 370, 350, and 510 cm^{-1} in spectra of polycrystalline samples.[3]

The region below 120 *cm*$^{-1}$. An isolated $M(CO)_6$ molecule has three δ(CMC) modes in this region; $\nu_9(t_{1u})$, $\nu_{11}(t_{2g})$, and $\nu_{13}(t_{2u})$. For $Mo(CO)_6$ ν_9 is at 91 cm^{-1} in CCl_4 solution and we find ν_{11} at 94 cm^{-1} in CH_2Cl_2. Translatory and rotatory lattice modes (six of each, Table 2) are also expected in this region and may well mix in with the internal modes, as happens for octahedral complex cyanides.[6,7] The observed lines fall clearly into two regions, 28—49 and 75—113 cm^{-1}, with the implication that the lower group (showing a total of seven symmetry labels) is principally due to lattice modes. Some of these lines are weak; for example, that at 28 cm^{-1} compared with lines in the group above 70 cm^{-1}, but are quite definitely present as is clearly shown by Figure 4. There are insufficient lines to allow an explanation in terms of full splitting of ν_9, ν_{11}, and ν_{13} plus lattice modes. We consider the most likely event to be partial splitting into two or three lines of ν_9 and ν_{11}, absence of ν_{13} (none of the inactive modes have been found elsewhere in the spectrum), plus presence of most of the remaining allowed lattice modes, all these contributions interacting with mixing of internal co-ordinates.

Combinations and Overtones.—For molybdenum hexacarbonyl only, we have examined the weak features present on the Raman spectrum between 600 and 1205 cm^{-1} (Table 4B). In the light of our recent experience with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ [8] we are inclined to be sceptical of the value of detailed assignments of overtones and combinations. Assignments given on the right of Table 4B are those of Jones *et al.*[3] except where indicated: our assent in this connection means only that the symmetry species indicated experimentally do not

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[5] H. Haas and R. K. Sheline, *J. Chem. Phys.*, 1967, **47**, 2996.

[6] B. I. Swanson and L. H. Jones, *J. Chem. Phys.*, 1971, **55**, 4174.

[7] D. M. Adams and M. A. Hooper, *J.C.S. Dalton*, 1972, 160.

[8] D. M. Adams, M. A. Hooper, and A. Squire, *J. Chem. Soc.* (*A*), 1971, 71.

conflict with the given assignment. Presence of an A_g component of the 823 cm^{-1} line is as consistent with $2\nu_2$ as Jones's $\nu_5 + \nu_{10}$. We have difficulty in accepting $2\nu_8$ as the origin of the 739/735 cm^{-1} doublet when ν_8 itself is vanishingly weak; the combination $\nu_4 + \nu_5$ yields a line with O_h symmetry species $t_{1g} + t_{2g}$ which, in the crystal, will yield a vector of all possible D_{2h} Raman-active symmetry species. The 605 cm^{-1} line is most probably a combination of one of the ν(Mo–C), δ(MoCO) modes with a frequency below 120 cm^{-1}. As outlined above, we doubt whether the δ(CMoC) descriptions accorded ν_9, ν_{11}, and ν_{13} have much validity in the solid: we therefore regard the 605 cm^{-1} line as ν_{internal} plus ν_{lattice} with both components unspecified.

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