Vibrational Spectra of Crystalline Hexacarbonyl-chromium,-molybdenum, and -tungsten in the 4 000 cm^{-1} Region

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The Raman spectra of polycrystalline transition metal hexacarbonyls $M(CO)_6$, M = Cr, Mo, W, in the 4 000 cm^{-1} region are reported. The spectra are interpreted using a two-phonon model. In marked contrast to the spectra in the 2 000 cm^{-1} region, factor-group effects appear to be negligible, so that the spectra are much simpler than might be expected from the wealth of peaks in the fundamental region.

THE study of vibrational anharmonicity has been largely confined to i.r. studies of species in the gas phase or in solution. Although the resonance Raman effect may sometimes be used to obtain overtones of a high order, Raman studies have largely been confined to fundamental modes. Exceptions exist however, a well known exception being the azide anion where a quite strong band at *ca.* 1 270 cm^{-1} is a Fermi resonance-enhanced overtone of a mode giving rise to an i.r. band at *ca.* 640 cm^{-1} (the latter mode being Raman inactive).[1]

In the present paper we describe both Raman and i.r. studies of polycrystalline metal hexacarbonyls in the

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[1] P. Gray and T. C. Waddington, *Trans. Faraday Soc.*, 1957, **53**, 901.

4 000 cm^{-1} region. There are several aspects of the vibrational spectra of these compounds which make such a study of interest. First, detailed i.r. solution data are available and indicate appreciable solvent dependence. This suggests that spectra in the overtone region may be rather different for solid and solution samples. Secondly, such a study complements those made of the solid-state vibrational spectra of metal carbonyls in the 2 000 cm^{-1} region.[2] Finally, the hexacarbonyls have been the subject of a recent single-crystal Raman investigation.[3]

It is clear that there are several differences to be expected between vibrational spectra of metal carbonyls obtained for solid state and solution samples. First, gross shifts of spectral bands may occur, the ' static-field effect '. Secondly, the bands may be split due to differences in molecular and site symmetries, ' site-group splitting '. Thirdly, vibrational coupling between individual molecules may lead to additional fine structure, ' factor-group splitting '. Fourthly, additional peaks may occur due to combinations of internal and lattice modes. Finally, anharmonic effects may cause additional splittings of degenerate overtone levels.

Despite the considerable study which has been made of the vibrational spectra of metal carbonyls there appears to be no data on their Raman spectra in the ν(CO) overtone region and very little i.r. data on solid-state species in the same region. Here we present and discuss such data for the species $M(CO)_6$ (M = Cr, Mo, or W). In addition we report improved i.r. data in the 2 000 cm^{-1} region.

RESULTS AND DISCUSSION

In interpreting i.r. and Raman spectral data obtained from solids, it is necessary to recognise the repetitive nature of the crystal lattice and consider the whole Brillouin zone. The observed transitions in crystal spectra are such that both energy and wave-vector conservation occurs and thus the observed spectra will depend on the dispersion characteristics of the lattice. This means that little can be said, in general, about overtone and combination bands since the conservation conditions will be satisfied for two-phonon processes if the two phonons have equal and opposite wave vectors, the wave vector associated with the electromagnetic field in this region being essentially zero. Fortunately two alleviating circumstances occur. First, critical points exist within the Brillouin zone, usually characterised by distinct subgroups of the space group. The high density of states at these critical points means that relatively sharp peaks occur in the two quantum spectra due to transitions involving these states, as opposed to broad continua from other parts of the zone. Secondly, for molecular crystals with weak interactions between individual groups, the k dependence of the internal-mode frequencies will be small. In such a situation the overtone and combination spectra are expected to be related to those obtained in solution studies. The simple metal carbonyls almost certainly fall into this latter class and so it seemed of value to attempt to record and interpret the Raman spectra in the 4 000 cm^{-1} region of the hexacarbonyls of chromium, molybdenum, and tungsten relevant to the present studies.

In the 4 000 cm^{-1} region an isolated $M(CO)_6$ molecule is expected to give rise to the following two-phonon bands:

Overtone or combination	I.r. active	Raman active
$(A_{1g} \times A_{1g})$		A_{1g}
$(E_g \times E_g)$		$A_{1g} + E_g$
$(T_{1u} \times T_{1u})$		$A_{1g} + E_g + T_{2g}$
$A_{1g} + E_g$		E_g
$A_{1g} + T_{1u}$	T_{1u}	
$E_g + T_{1u}$	T_{1u}	

In solution studies [4] the i.r. spectra were enriched by an additional combination band involving a low-frequency T_{2g} mode. Solution Raman data have not been reported and we were unable to obtain such spectra. (Even the Raman spectra of polycrystalline samples in this region are rather weak.)

There appears to be a close correspondence between the i.r. spectral features in the solution and solid state (Table 1). A band at 3 987 cm^{-1} in a CCl_4 solution of $Mo(CO)_6$ correlates with two bands at 3 945 and 3 960 cm^{-1} in the solid. (In the chromium compound this band has three components.) Similarly, a band at 4 095 cm^{-1} in solution correlates with three bands between 4 040 and 4 075 cm^{-1}, and the 4 194 cm^{-1} band in solution correlates with three bands in the 4 100—4 150 cm^{-1} region. Two points seem clear. First, there is a correlation between solution and solid-state spectra, the solid-state spectral features being at a lower frequency than their solution counterparts. (This is in contrast with the 2 000 cm^{-1} region where the average of the solid-state frequencies is quite close to the solution values.) Secondly, the number of components observed seems to be equal to the degeneracy of the vibration in the isolated molecule. The most evident explanation is that site-group (C_s) effects dominate.

The Raman spectra are more difficult to discuss. First, there are no solution spectra with which to make a comparison. Secondly, more overtone and combination bands are predicted for the isolated molecule, even without consideration of the possibility of triple combination bands such as observed in the i.r. However, progress is possible provided that a number of reasonable assumptions are made.

We note the correspondence between solution (CCl_4) and solid-state frequencies in the 2 000 cm^{-1} region (Table 2), the average of the solid-state frequencies being within a few wavenumbers of the observed solution values. The Raman and i.r. spectra are similar in this respect in the fundamental region and we assume that a comparable similarity holds in the 4 000 cm^{-1} region. First, we note that the frequency shifts of the centres of gravity of the bands in the solid-state overtone i.r. spectra lie between

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[2] H. J. Buttery, S. F. A. Kettle, G. Keeling, I. Paul, and P. J. Stamper, *J.C.S. Dalton*, 1972, 2487.

[3] D. M. Adams, W. S. Fernando, and M. A. Hooper, *J.C.S. Dalton*, 1973, 2264.

[4] J. M. Smith and L. M. Jones, *J. Mol. Spectroscopy*, 1966, **20**, 248.

40 and 90 cm^{-1} to low frequency of the values calculated using 2 000 cm^{-1} solution spectral data (Table 1) and assume that the corresponding shifts in the solid-state Raman spectra will be of the same order of magnitude. Secondly, we assume that the dominant features in the 4 000 cm^{-1} region are associated with two-phonon processes involving internal modes.

TABLE 1

I.r. bands (cm^{-1}) for M(CO)$_6$ (M = Cr, Mo, or W)

	Assignment		Cr(CO)$_6$			Mo(CO)$_6$			W(CO)$_6$		
Solution[a] (CCl$_4$)	ν_6 T_{1u}		1 985s			1 985s			1 980s		
	^{13}C		1 954w			1 956w			1 950w		
Solid (KBr disc)	ν_6 T_{1u}	$2A'$	2 010vw			2 005vw			2 000 (sh)		
			1 980m			1 970m			1 965m		
		A''	1 955w[b]			1 955w[b]			1 943w[b]		
Solution[a] (CCl$_4$)	$(\nu_3 + \nu_6)$ T_{1u}		3 984vw			3 987vw			3 974vw		
	$(\nu_1 + \nu_6)$ T_{1u}		4 089w			4 095vw			4 091w		
	$(\nu_1 + \nu_6 + \nu_{11}{}^c)$ T_{1u}		4 186vvw			4 194vvw			4 189vvw		
					Calc.[d]			Calc.[d]			Calc.[d]
Solid (KBr disc)	$(\nu_3 + \nu_6)T_{1u}$	$2A'$	3 945m	(3 963)	4 004	3 945m	(3 952)	4 004	3 929m	(3 935)	3 993
			3 960 (sh)			3 960m			3 940 (sh)		
		A''	3 985w								
	$(\nu_1 + \nu_6)T_{1u}$	$2A'$	4 040m	(4 057)	4 098	4 040m	(4 060)	4 102	4 028m	(4 049)	4 101
			4 060s			4 065s			4 055s		
		A''	4 070 (sh)			4 075 (sh)			4 065 (sh)		
	$(\nu_1 + \nu_6 + \nu_{11}{}^c)T_{1u}$	$2A'$	4 100w	(4 117)	4 198	4 100w	(4 120)	4 202	4 095w	(4 113)	4 201
			4 110w			4 115 (sh)			4 105 (sh)		
		A''	4 142m			4 147m			4 140m		

[a] Data from ref. 4. Solution data obtained by us for W(CO)$_6$ were in agreement. [b] Possibly ^{13}C. [c] $\nu_{11}(T_{2g})$ at *ca.* 100 cm^{-1}. [d] From solution data. Anharmonic effects may be gauged by comparison with the experimental data above. Values in parentheses are the mean of the data listed on the left.

TABLE 2

Raman bands ($\Delta\bar{\nu}$/cm^{-1}) for M(CO)$_6$ (M = Cr, Mo, or W)

	Assignment[a]		Cr(CO)$_6$		Mo(CO)$_6$		W(CO)$_6$	
Solution[b] (CCl$_4$)	ν_1	A_{1g}	2 113p, w		2 117p, w		2 121p, w	
	ν_3	E_g	2 019s		2 019s		2 013s	
Solid[c]	ν_1	A_{1g}—$A_g(+B_{2g})$	2 114 (9)		2 114 (13)		2 117 (14)	
	^{13}C		2 108 (1)		2 109 (2)		2 113 (2)	
Solid[c] (low temp.)	ν_3 $E_g{}^d$	A_g	2 038 (2)		2 033 (2)		2 030 (2)	
		+						
		B_{1g}	2 026 (19)		2 023 (18)		2 018 (20)	
		+	2 020 (7)		2 016 (7)		2 013 (6)	
		B_{2g}	2 008 (100)		2 004 (100)		1 997 (100)	
		+						
		B_{3g}	2 003 (32)		2 000 (40)		1 992 (37)	
	^{13}C*		1 965 (4)		1 963 (4)		1 955 (5)	
			1 963 (sh)		1 961 (sh)		1 954 (sh)	
					Calc.[e]			
Solid (room temp.)	$(\nu_6 \times \nu_6)$	T_{2g}	3 892	3 970	3 891	3 970	3 872	3 960
		E_g	3 912		3 908		3 892	
		A_{1g}	3 950		3 935		3 932	
	$(\nu_3 \times \nu_3)$	E_g A_{1g}	3 985	4 038	3 980	4 038	3 970	4 026
	$(\nu_1 + \nu_3)$	$A' + A''$	4 120	4 132	4 120	4 136	4 112	4 134
					4 143		4 140	
	$(\nu_1 \times \nu_1)$	A_{1g}	4 207	4 226	4 210	4 234	4 208	4 242

[a] For solid-state 2 000 cm^{-1} region, taken from ref. 3. [b] Data from ref. 4. Solution data obtained by us for W(CO)$_6$ were in agreement. [c] Figures in parentheses are relative peak heights. [d] It is to be noted that Tables 4(*a*) and 5 of ref. 3 appear to be inconsistent. [e] Using solution data with no allowance for anharmonicity or solid-state effects.

* Isotope-enrichment studies have shown this assignment to be incorrect. The features originate in the weak Raman activity of factor-group modes derived from the molecular T_{1u} vibration (S. F. A. Kettle, unpublished work).

The solid-state Raman spectra in the 4 000 cm^{-1} region showed four main features. At low energy a group of three peaks were, on average, 50—60 cm^{-1} to low energy of the position expected for the $T_{1u}{}^2$ vibration if this were simply $2\nu(T_{1u})$ (solution). The second feature is a single band between 50 and 60 cm^{-1} below $2\nu(E_g)$ (solution). Either a single band (Cr) or a pair of bands (Mo, W) were a little below the $[\nu(A_{1g})$ (solution) + $\nu(E_g)$(solution)$]$ value, whilst the final feature, a single band, was 20—35 cm^{-1} below $2\nu(A_{1g})$ (solution). In all spectra the overtone peaks covered a range of *ca.* 320 cm^{-1}, sufficient to make the above assignments the only reasonable ones. However, they left unresolved the individual assignment of the bands associated with $\nu(T_{1u}{}^2)$. Bands of A_{1g}, E_g and T_{2g} symmetries are expected, but whether the observed splitting is due to these components (*i.e.* is anharmonic in origin) or to site-group effects (such as may be important in the i.r.) is not clear. The latter explanation seems the more probable in view of the observation of two peaks corresponding to $[\nu(A_{1g}) + \nu(E_g)]$, a case where splitting due to anharmonicity cannot occur. Also, we note the absence of splitting in the $\nu(E_g{}^2)$ peaks.

In order to investigate the splitting of the $\nu(T_{1u}{}^2)$ region further we carried out perturbation calculations for both this and the $\nu(E_g{}^2)$ region. These calculations, which assume that the splitting originates in anharmonicity, show (Appendix) that, to first order, the components would be split: $A_{1g} \sim E_g > T_{2g}$ for $\nu(T_{1u}{}^2)$ and $E_g > A_{1g}$ for $\nu(E_g{}^2)$ whilst to second order $\nu(T_{1u}{}^2)$ splits as $A_{1g} > E_g > T_{2g}$. Comparison with the observed spectra shows that the splitting between A_{1g} and E_g components is greater than that between E_g and T_{2g} so that anharmonicity only explains the spectra if second-order perturbation effects exceed first-order effects. Whilst not an impossible situation, this suggests that effects other than anharmonicity are important.

A most interesting feature of both i.r. and Raman spectra in the 4 000 cm^{-1} region is the apparent lack of factor-group splitting. The magnitude of the factor-group splitting of vibrational bands depends, to first order (neglecting quadrupole and higher multipole interactions), on the value of a sum of integrals of the form (1),[5] where

$$\int(\phi_p{}'\phi_r)^*V_{pr}(\phi_p\phi_r{}')\mathrm{d}\tau \qquad (1)$$

ϕ_p and ϕ_r are wavefunctions for the molecule at the pth or rth site in the solid, the prime indicates an excited state, and V_{pr} is the potential between a pair of sites. This integral is, experimentally, related to an i.r. absorption coefficient. Now, the strongest vibrational overtone and combination bands in our spectra are much weaker than the corresponding fundamentals. It is therefore not surprising that we observed no factor-group splittings in these spectra notwithstanding the occurrence of such splittings in the fundamental region.

It is to be noted that this absence of factor-group splitting is entirely consistent with the assumption that it is valid to assume that little dispersion occurs for the ν(CO) overtone vibrations since both depend on the magnitude of the intermolecular couplings. Additionally, absence of significant dispersion implies that there is no ' repulsion ' involving modes with a different vibrational origin and with which mixing might occur at regions of the Brillouin zone remote from $k = 0$. Again, that this should be so seems reasonable; dispersion would have to be exceptionally large for the frequency of any other mode to rise to *ca.* 4 000 cm^{-1}.

Conclusions.—Although considerable ambiguity surrounds the interpretation of some aspects of our results, one most important point is clear; factor-group splitting is not important in the ν(CO) overtone region notwithstanding its importance for the corresponding fundamental modes. We conclude that, in marked contrast to the isolated-molecule situation, the harmonic pattern of bands in an overtone region for a crystalline material cannot, in general, be predicted by summing frequencies of fundamental modes when the latter show factor-group splitting. This conclusion follows both from our i.r. and Raman studies. In future work Raman studies will probably be the more important because bands in the i.r. which are split by factor-group effects are almost invariably rather broad, so that, even if the band shape clearly indicates the existence of splitting, the precise band frequencies are difficult to determine, thus preventing a precise numerical comparison of observed and predicted values. In the present work we have been fortunate in the i.r. facilities available to us but, even so, we have been able to resolve peaks in the fundamental region which, at most, correspond to a site-group model, notwithstanding the fact that factor-group splitting undoubtedly occurs.

Our data do not enable us to determine uniquely the relative importance of the various perturbations which determine the 4 000 cm^{-1} region spectra of the metal hexacarbonyls. The static-field effect seems generally important as do site-group effects in the i.r. spectra. It is possible that anharmonic effects are seen in the Raman spectra but they do not provide a completely convincing explanation of all the observations (although we have not considered the possible consequences of coupling between vibrational states of the same symmetry species).

EXPERIMENTAL

The metal hexacarbonyls were obtained from commercial sources and sublimed before use.

Raman spectra were recorded using a Spex 1401 spectrometer with 488 nm (blue) excitation. Spectra of polycrystalline samples, contained in capillary tubes, were obtained at liquid-nitrogen temperatures for the carbonyl fundamental region, with a spectral resolution of *ca.* 1 cm^{-1}. The carbonyl-overtone region was recorded at room temperature as there was no significant change in the spectra on reduction of temperature whilst there was a decrease in signal consequent on using the low-temperature cell. Spectral resolution was *ca.* 2 cm^{-1} for $W(CO)_6$ and *ca.* 4 cm^{-1} for $Cr(CO)_6$ and $Mo(CO)_6$. I.r. spectra were recorded as KBr discs, of concentration dependent on the spectral region under investigation, using a Perkin–Elmer 325 grating spectrometer. In the carbonyl-fundamental region a broad band was obtained with small ripples on the main absorption. This region was restudied using a Digilab FTS 14 interferometer which has facilities to accumulate a large number of scans and to electronically smooth the resulting data. Two hundred scans of resolution 2 cm^{-1} were accumulated for both background and sample and the ratioed spectrum smoothed, expanded, and recorded.* This procedure enabled the small ripples to be accurately characterised and thus provide the data given in Table 1. Figures 1 and 2 show spectra obtained from $W(CO)_6$. Those from the other compounds were of similar form.

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[5] D. A. Dows, ' Physical Chemistry of the Organic Solid State, ' vol. 2, p. 657.

* We are indebted to Mr. D. H. Chenery for recording these spectra.

APPENDIX

The relative energies of the overtone levels $(T_{1u} \times T_{1u})$ and $(E_g \times E_g)$ were obtained by perturbation theory. Appropriate Hermite polynomials corresponding to the harmonic oscillator wavefunctions were taken as a basis. The corresponding overtone functions follow immediately from the appropriate coupling coefficients.[6] The third- and fourth-order terms appearing in the potential-energy expansion are as in (A1) [7] where the Q terms are normal co-

$$V' = \sum_{i,j,k} \alpha_{ijk}Q_iQ_jQ_k + \sum_{i,j,k,l} \beta_{ijkl}Q_iQ_jQ_kQ_l \qquad \text{(A1)}$$

ordinates and α_{ijk} and β_{ijkl} are constants; V' was used as the pertubation Hamiltonian.

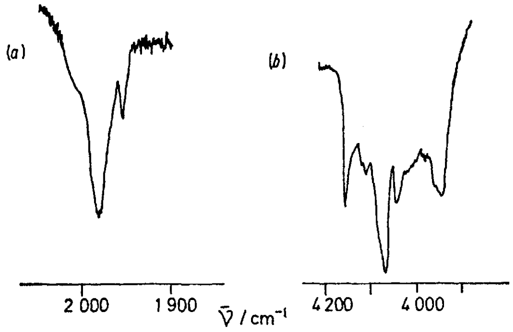

FIGURE 1 I.r. spectra of W(CO)$_6$: (a) the 2 000 cm^{-1} region, recorded on a Digilab FTS 14 spectrometer; (*b*) the 4 000 cm^{-1} region, recorded on a Perkin-Elmer 325 instrument

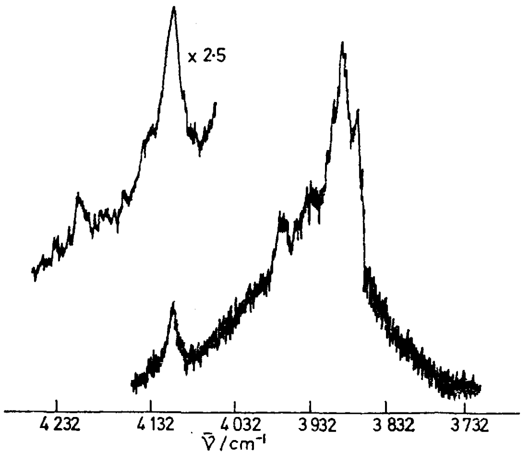

FIGURE 2 Raman spectrum of W(CO)$_6$ in the 4 000 cm^{-1} region

The first term in V' makes no contribution whilst from the second arise terms of the form (A2).[8] We neglected

$$\langle|Q_i^2Q_j^2|\rangle \text{ and } \langle|Q_i^4|\rangle \qquad \text{(A2)}$$

coupling between the (T_{1u}) and (E_g) sets as a first approximation, because of the experimental observation that the splitting between members of the individual sets is smaller than that between the sets themselves. It follows, therefore, that there are only four non-zero integrals, (A3) and (A4), where $\gamma_x = 4\pi^2\nu_x/\boldsymbol{h}$ and the suffix x refers either to the T_{1u} or E_g species.

$$\langle|Q_x^4| = \frac{\frac{3}{4}(2\nu_x^2 + 2\nu_x + 1)}{\gamma_x^2} \qquad \text{(A3)}$$

$$\langle|Q_{x_1}^2Q_{x_2}^2|\rangle = \frac{\frac{1}{4}(4\nu_x^2 + 4\nu_x + 1)}{\gamma_x^2} \qquad \text{(A4)}$$

Thus for the (T_{1u}^2) set we find energies $A_{1g} = \beta_{nn}(45/4\gamma_t^2)$, $E_g = \beta_{nn}(45/4\gamma_t^2)$, and $T_{2g} = \beta_{nn}(33/4\gamma_t^2)$ where $\gamma_t = \gamma_{t_{2g}}$ and $\beta_{nn} = \beta_{t_nt_nt_nt_n}(n = 1\text{—}3)$. That is, to first order, A_{1g} and E_g remain degenerate while T_{2g} is lowered in energy relative to these two levels. Extension to second-order perturbation theory is straight forward, leading to terms in $\beta_{nm} = \beta_{t_nt_nt_mt_m}$ $(n \neq m)$. A fuller discussion of this approach is given in ref. 8. The inclusion of coupling between states of the same symmetry species, for instance $E_g(E_g^2)$ and $E_g(T_{1u}^2)$, is desirable but difficult because of the uncertainty of zero-order energies. Since such an extension would also introduce new parameters such as β_{ttee} we have not attempted it.

[4/1498 *Received*, 19*th July*, 1974]

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[6] J. S. Griffiths, 'The Theory of Transition-metal Ions,' Cambridge University Press, 1971, p. 36.

[7] G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules,' Van Nostrand, 1959, p. 204.

[8] E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, 1955, p. 290.