Vapour-phase Raman Spectra of Chromium, Molybdenum, and Tungsten Hexacarbonyls

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Vapour-phase Raman spectra of the hexacarbonyls $[M(CO)_6]$ (M = Cr, Mo, or W) have been recorded for the first time, and four of the six Raman-active fundamentals in the case of $[Mo(CO)_6]$ and $[W(CO)_6]$, and five of the six in the case of $[Cr(CO)_6]$; have been located. The values obtained compare well with those obtained from analyses of the wavenumbers of combination bands in the infrared. The half-band widths of the $v_1(a_{1g})$, $v_2(a_{1g})$, $v_3(e_g)$, and $v_{11}(t_{2g})$ fundamentals are 5—6, 9—13, 18—20, and 16—18 cm^{-1} respectively at the sample temperatures of 369 (Cr), 378 (Mo), and 377 K(W). Rotational contours (OP, RS) to the non-totally symmetric bands are obscured by the presence of underlying hot bands. Vapour–solution wavenumber shifts are positive for the $v_1(a_{1g})$ and $v_3(e_g)$ bands (both of which are CO-stretching modes), but negative for the $v_2(a_{1g})$ and $v_{11}(t_{2g})$ bands (MC-stretching and CMC-bending modes respectively). The relative values of the CO bond-polarisability derivatives, $\alpha_\perp'/\alpha_\parallel'$, from vapour-phase measurements, lie in the -0.26_5 to -0.24 region.

ALTHOUGH the infrared spectra of the metal hexacarbonyls $[M(CO)_6]$ (M = Cr, Mo, or W) have been extensively studied in all states of matter,[1-6] the corresponding Raman spectral studies have so far been confined to the molecules in solution [6-8] or in the crystalline state.[6,8] It is desirable, in view of known solvent shifts of various fundamental frequencies,[4] to have available precise vapour-phase frequencies for the Raman-active fundamentals. The latter are known only as a result of analyses of combination-band spectra in the i.r., account being taken of various anharmonicity corrections.[6] The objects of the present study, therefore

were to obtain accurately calibrated vapour-phase Raman spectra of the three hexacarbonyls, to compare the wavenumbers of the fundamentals so obtained with those deduced from i.r.-active combination bands, and to study the half-band widths, contours, and vapour–solution wavenumber shifts of the observed Raman bands. The relative values of the CO bond-polarisability derivatives $\alpha_\perp'/\alpha_\parallel'$ have also been deduced.

EXPERIMENTAL

The metal hexacarbonyls are white crystalline solids whose vapours decompose above *ca.* 120 °C to deposit the

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[2] L. H. Jones, *J. Chem. Phys.*, 1962, **36**, 2375.
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TABLE 1

Raman-active fundamental frequencies of the metal hexacarbonyls in the vapour phase

Molecule	Symmetry	Designation	I.r. analysis (wavenumber/cm⁻¹)		Raman study (wavenumber/cm⁻¹)		$\Delta\bar{\nu}_{\downarrow}$
			A [a]	B [b]	$\bar{\nu}$ [c]	ρ	
[Cr(CO)₆]	a_{1g}	ν_1	2 118.7	2 115.5	2 115.8w	0.0	5
		ν_2	379.2	379.2	377.3m	0.0	13
	e_g	ν_3	2 026.7	2 025.4	2 024.3m	3/4	20
		ν_4	390.6	391.0	389.4vw	dp	
	t_{2g}	ν_{10}	532.1	535.8			
		ν_{11}	89.3	88.1	89.2s	3/4	18
[Mo(CO)₆]	a_{1g}	ν_1	2 120.7	2 121.6	2 119.7w	0.0	5
		ν_2	391.2	391.2	389.8m	0.0	9
	e_g	ν_3	2 024.8	2 026.6	2 025.2m	3/4	20
		ν_4	381	379.1			
	t_{2g}	ν_{10}	477.4	480.1			
		ν_{11}	79.2	77.3	78.3s	3/4	16
[W(CO)₆]	a_{1g}	ν_1	2 126.2	2 122.0	2 121.1w	0.0	6
		ν_2	426	426.4	421.7m	0.0	10
	e_g	ν_3	2 021.1	2 021.6	2 019.4m	3/4	18
		ν_4	410	410.4			
	t_{2g}	ν_{10}	482.0	483.0			
		ν_{11}	81.4	81.2	83.9s	3/4	17

[a] Value deduced (generally) from the single i.r.-active combination band preferred by Jones et al.[6] [b] Average value deduced from all the observed i.r.-active combination bands which involve the relevant fundamentals and which are in close agreement with one another. [c] w = Weak, m = medium, and s = strong.

metal as a mirror. The vapour pressures of chromium, molybdenum, and tungsten hexacarbonyls are given by the expressions [9] log $(p/\text{mmHg}) = -(A/T) + B$, where A and B are 3 622.9 and 11.475 respectively for Cr, 3 788.3 and 11.727 4 respectively for Mo, and 3 640.4 and 10.947 respectively for W. Thus, at the operating temperatures of 369, 378, and 365 K for the chromium, molybdenum, and tungsten hexacarbonyls respectively, the vapour pressures would be 45.4, 50.7, and 9.4 mmHg respectively.*

Clearly, in order to get sufficient Raman signal, the temperature of the sample must be held as near to 120 °C as is feasible bearing in mind the need to avoid thermal decomposition of the sample. In order to succeed with this technically difficult operation, the samples were sealed in vacuo into Pyrex ampoules ca. 5 cm long and 1 cm in diameter. The ampoules were placed inside a modified version of the small lagged furnace described previously.[10]

The spectra were recorded using a Spex 1401 spectrometer in conjunction with the 514.5-nm line of a Coherent Radiation model CR12 Ar⁺ laser, the power available with this exciting line being 1.2—5.5 W. Signal detection was accomplished by photon counting (cooled RCA C31034 grade I phototube) with a linear response. The spectra were calibrated by reference to emission lines of neon, and all the values quoted are averages of four or five measurements in each case. The accuracy of each measurement should be ±0.5 to ±1.0 cm⁻¹. Band intensities were measured by the cut-and-weigh procedure and corrected for the spectral response of the instrument.

RESULTS AND DISCUSSION

Fundamental Frequencies.—The 33 normal modes of vibration of the [M(CO)₆] molecules belong to the irreducible representations $2a_{1g} + 2e_g + t_{1g} + 4t_{1u} + 2t_{2g} + 2t_{2u}$; of these modes, only the $4t_{1u}$ are i.r. active and only the $2a_{1g} + 2e_g + 2t_{2g}$ modes are Raman active. The fundamentals are conventionally labelled: ν_1, ν_2 (a_{1g}); ν_3,

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.
[9] T. N. Rezukhina and V. V. Shvyrev, *Vestnik Moskov. Univ.*, 7, No. 6, *Ser. Fiz.-Mat. i Estestven. Nauk*, 1952, No. 4, 41 (*Chem. Abs.*, 1953, 47, 4676h).

ν_4 (e_g); ν_5 (t_{1g}); ν_6—ν_9 (t_{1u}); ν_{10}, ν_{11} (t_{2g}); and ν_{12}, ν_{13} (t_{2u}); the subscript conventionally increases with decreasing frequency of the fundamental within each representation.

The observed vapour-phase Raman spectra of the three hexacarbonyls are shown in Figure 1. Four, and in the case of [Cr(CO)₆] five, of the six Raman-active fundamentals could be observed. The wavenumbers of the fundamentals are given in Table 1. The two a_{1g} fundamentals (ν_1 and ν_2) are clearly identified by the zero values for their depolarisation ratios. The Raman-active fundamentals not, in general, observed were $\nu_4(e_g)$ and $\nu_{10}(t_{2g})$ which, according to the analysis of the i.r.-active combination-band spectra by Jones et al.,[6] should occur in the 380—410 cm⁻¹ region for the former and in the 477—532 cm⁻¹ region for the latter. These two fundamentals evidently give rise to only very small polarisability changes. Only in the case of [Cr(CO)₆] could the $\nu_4(e_g)$ band be observed, and then only in an $I_\perp$ spectrum (Figure 2); in an I_{total} spectrum it is hidden beneath the contour of the much more intense $\nu_2(a_{1g})$ band. The observed bands for each molecule lie in the intensity order $\nu_4(e_g) < \nu_1(a_{1g}) < \nu_2(a_{1g}) < \nu_3(e_g) < \nu_{11}$-$(t_{2g})$ before correction for frequency factors.

The big intensity difference between the (unobserved) ν_{10} and the ν_{11} bands arises because for ν_{10} the polarisability ellipsoid associated with the MC_4 framework can be regarded as changing in the opposite sense to that associated with the MO_4 framework (hence leading to a cancellation of polarisability changes during the vibration), whereas for ν_{11} the polarisability ellipsoids move in the same sense (hence leading to large polarisability changes during the vibration).

As well as the Raman spectral results, Table 1 includes the results of the combination-tone analyses (involving the four i.r.-active fundamentals ν_6 to ν_9) of Jones et al.[6]

[10] R. J. H. Clark, B. K. Hunter, and D. M. Rippon, *Inorg. Chem.*, 1972, 11, 56.

In column A is given the wavenumber preferred by Jones *et al.*[6] for each fundamental and deduced either from the wavenumber of a particular combination band or in some other way. In column B we give the average value deduced from an analysis of all the
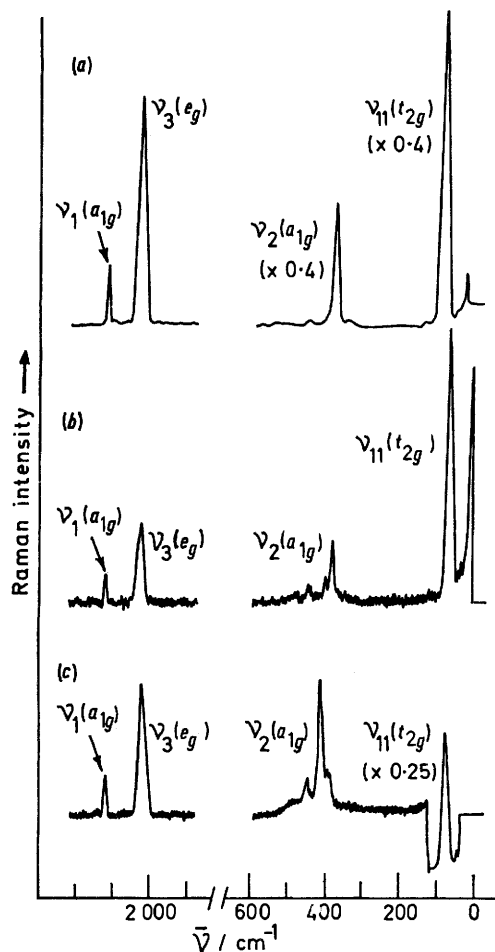

FIGURE 1 Raman spectra in the vapour phase with 514.5-nm excitation: (a) [Cr(CO)₆], scanning speed (s.s.) 100 cm⁻¹ min⁻¹, slit widths (s.w.) 400, 500, and 400 μm (8 cm⁻¹), slit height (s.h.) 10 mm, time constant (t.c.) 0.4 s, gain 20 000 count s⁻¹, laser power ≈ 5.5 W, and temperature 380 K. (b) [Mo(CO)₆], s.s. 50 cm⁻¹ min⁻¹, s.w. 300, 300, and 300 μm (6 cm⁻¹), s.h. 50 mm, t.c. 1 s, gain 2 000 count s⁻¹, laser power ≈ 1 W, and 377 K; (c) [W(CO)₆], s.s. 50 cm⁻¹ min⁻¹, s.w. 400, 500, and 400 μm (8 cm⁻¹), s.h. 50 mm, t.c. 1 s, gain 5 000 count s⁻¹, laser power ≈ 3 W, and 366 K

observed i.r.-active combination bands which involve the fundamental in question and which are in close agreement with one another. The observed values of the Raman-active fundamentals agree slightly better with the corresponding values listed in column B, the maximum discrepancy being 1.9 cm⁻¹ for [Cr(CO)₆], 1.9 cm⁻¹ for [Mo(CO)₆], and 4.7 cm⁻¹ for [W(CO)₆] (2.7 cm⁻¹ if v_2 is ignored). The very good agreement between the results of the i.r. analyses and the Raman results provides convincing proof of the correctness of the i.r. based combination-band analyses on the funda-

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

mentals in question. (Nevertheless some doubts remain about the correctness of the assignments of some of the other combination bands.[11])

Some additional higher-order bands of low but constant intensity were also observed in the spectra of each hexacarbonyl. In the case of [Cr(CO)₆] (Figure 2), these weak features occurred at 571.7, 533.2, 446.2, 344.5, and 130.7 cm⁻¹, the first four of which had depolarisation ratios of zero, the last being depolarised. Those bands having zero values for their depolarisation ratios evidently arise from dominant A_{1g} components of binary sum or difference bands or overtones ($T_{1u} \times T_{1u} = T_{2u} \times T_{2u} = T_{1g} \times T_{1g} = T_{2g} \times T_{2g} = A_{1g} + E_g + T_{1g} + T_{2g}$; $T_{1u}^2 = T_{2u}^2 = T_{1g}^2 = T_{2g}^2 = A_{1g} + E_g + T_{2g}$). Thus the band at 571.7 cm⁻¹ probably arises from $v_7 - v_9$ (expected at 570.9 cm⁻¹ on the basis of the analysis of Jones *et al.*[6]), that at 533.2 cm⁻¹ may arise from $v_8 + v_9$ (expected[6] at 537.7 cm⁻¹), that at 446.2 cm⁻¹ may arise from either $v_{10} - v_{11}$ (expected[6] at 442.4 cm⁻¹) or $v_{12} - v_{13}$ (expected[6] at 443.0 cm⁻¹), that at 344.5 cm⁻¹ probably arises from $v_8 - v_9$ (expected[6] at 343.3 cm⁻¹), and that at 130.7 cm⁻¹ may arise from $2v_{13}$ (expected[6]
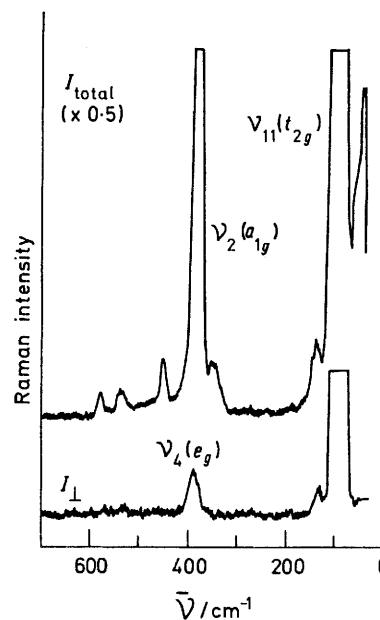

FIGURE 2 Combination-band region of [Cr(CO)₆]. The temperature and instrumental conditions were as given in Figure 1 for [Cr(CO)₆], except that the gain was 5 000 count s⁻¹

at 135.8 cm⁻¹). For [Mo(CO)₆], an additional weak broad band with a depolarisation ratio of zero was observed at 450.9 cm⁻¹ which may arise from either $v_8 + v_9$ (expected[6] at 448.8 cm⁻¹) or $v_{12} - v_{13}$ (expected[6] at 447.2 cm⁻¹). Similarly for [W(CO)₆], additional weak bands with zero values for their depolarisation ratios occurred at 460.2 and 403.7 cm⁻¹. The former arises either from $v_{12} - v_{13}$ (expected[6] at 459.9 cm⁻¹) or $v_8 + v_9$ (expected[6] at 456.4 cm⁻¹), whereas the latter may arise from $v_{10} - v_{11}$ (expected[6] at 400.6 cm⁻¹).

Band Contours.—The Raman band contours of degenerate fundamentals of a number of spherical-top

molecules have recently been analysed.[10,12-16] The most closely related study is that on metal hexafluorides of O_h symmetry.[16] In accordance with the appropriate selection rules, the $\nu_1(a_{1g})$ band should consist solely of a Q branch in each case, whereas $\nu_2(e_g)$ and $\nu_5(t_{2g})$ bands may display pronounced rotational branches. The separations between the branches of the e_g modes of these simple MF_6 molecules depend on the moment of inertia of the molecule according to [16] $\Delta\nu_{OP,RS} \approx 4.41$-$(BkT/hc)^{\frac{1}{2}}$. Thus the $\Delta\nu_{OP,RS}$ value for an e_g fundamental of $[Mo(CO)_6]$ is calculated to be 8.2 cm^{-1}. For triply degenerate fundamentals, the $\Delta\nu_{OP,RS}$ values also depend on ζ_i, the Coriolis coupling constant of the ith fundamental. The ζ value for a given triply degenerate fundamental is only uniquely defined if there is a single fundamental of the molecule belonging to the symmetry species in question. If not, then only the sum of the ζ_i for all the fundamentals of the given symmetry species is fixed. In the case of the (two) t_{2g} fundamentals for the molecules $[M(CO)_6]$, the ζ values (ζ_{10} and ζ_{11}) sum to -1.[17] Unfortunately, contours analogous to those previously observed for metal hexafluorides could not be discerned for the metal hexacarbonyls, undoubtedly because of the influence of large numbers of underlying hot bands at the temperatures of measurement. Thus the metal hexacarbonyls differ from the hexafluorides in (a) having lower volatilities and thus the need for higher sample temperatures for effective Raman studies, and (b) having many degenerate low-lying and therefore highly populated fundamentals [in particular, $\nu_9(t_{1u})$, $\nu_{11}(t_{2g})$, and $\nu_{13}(t_{2u})$, all of which lie below 100 cm^{-1}]. Despite this unsatisfactory situation, the half-band widths of the fundamentals of each metal hexacarbonyl (Table 1) are in broad agreement with expectation. Thus the $\Delta\nu_{\frac{1}{2}}$ values of the a_{1g} bands (5—6 cm^{-1} for ν_1, 9—13 cm^{-1} for ν_2) are much less than for the e_g (18—20 cm^{-1}) or t_{2g} (16—18 cm^{-1}) bands, consistent with the fact that O, P, R, and S branches for the a_{1g} bands of spherical-top molecules are forbidden.

Vapour-solvent Shifts.—Like the vapour-solvent shifts previously reported [4] for the $\nu_6(t_{1u})$ CO-stretching fundamental of the hexacarbonyls, those observed for the $\nu_1(a_{1g})$ and $\nu_3(e_g)$ CO-stretching fundamentals are small and positive. Thus, with reference to the literature values for the fundamental wavenumbers in solution (CCl$_4$ for $[Cr(CO)_6]$ and $[Mo(CO)_6]$, and CS$_2$ for $[W(CO)_6]$),[6] $\nu_{vap.} - \nu_{soln.}$ is in the range 3.0—4.5 cm^{-1} for the $\nu_1(a_{1g})$ fundamental and 6.4—9.6 cm^{-1} for the $\nu_3(e_g)$ fundamental. However, for the MC stretching and CMC bending fundamentals, the solvent shifts are of the opposite sign, viz. for the $\nu_2(a_{1g})$ and $\nu_{11}(t_{2g})$ fundamentals the $\nu_{vap.} - \nu_{soln.}$ values are in the ranges -5.4 to -12.4 cm^{-1} and -8.1 to -12.7 cm^{-1} respectively.

Raman Band Intensities and $\alpha_\perp'/\alpha_{\parallel}'$ Values.—The intensities of the four observed Raman bands of each molecule, corrected for the spectral response of the instrument, are given in Table 2 relative to that of the

TABLE 2

Relative intensities and frequency-corrected relative intensities of the Raman-active fundamentals of $[Cr(CO)_6]$, $[Mo(CO)_6]$, and $[W(CO)_6]$

Molecule	$I(\nu_j)/I(\nu_1)$			
	$\nu_1(a_{1g})$	$\nu_2(a_{1g})$	$\nu_3(e_g)$	$\nu_{11}(t_{2g})$
$[Cr(CO)_6]$	1.000	9.27	10.8	34.3
$[Mo(CO)_6]$	1.000	4.07	8.47	34.0
$[W(CO)_6]$	1.000	3.26	8.48	23.2
	$f(\nu_1)I(\nu_j)/f(\nu_j)I(\nu_1)$			
$[Cr(CO)_6]$	1.000	0.86$_8$	10.1	0.27$_4$
$[Mo(CO)_6]$	1.000	0.39$_6$	7.9$_2$	0.20$_9$
$[W(CO)_6]$	1.000	0.36$_6$	7.8$_7$	0.16$_7$

* All the intensity data are corrected for the spectral response of the instrument. Both relative intensities as well as frequency-corrected relative intensities are listed because the former approach those evident from actual spectra, whereas the latter (which may differ by two orders of magnitude from the former) are the quantities of fundamental interest.

$\nu_1(a_{1g})$ band in each case. From the intensities of the $\nu_1(a_{1g})$ and $\nu_3(e_g)$ fundamentals [$I(\nu_1)$ and $I(\nu_3)$ respectively] it is possible to deduce values for the ratio of the perpendicular ($\alpha_\perp'$) to parallel ($\alpha_{\parallel}'$) components to the CO bond-polarisability derivatives. The deduction is based on the assumption that it is possible to separate approximately the CO-derived polarisabilities from the MC ones.[18] The relation,[19] which is accordingly based on Wolkenstein's assumptions,[20] is as in (1) where

$$\frac{I(\nu_1)}{I(\nu_3)} = \frac{f(\nu_1)}{f(\nu_3)} \left\{ \frac{5[1 + 2(\alpha_\perp'/\alpha_{\parallel}')]^2}{7[1 - (\alpha_\perp'/\alpha_{\parallel}')]^2} \right\} \quad (1)$$

the frequency factor for any band j of frequency ν_j is given by expression (2). The frequency-corrected

$$f(\nu_j) = \frac{1}{\nu_j} \left[\frac{(\nu_0 - \nu_j)^4}{1 - \exp(-hc\nu_j/kT)} \right] \quad (2)$$

relative intensities (relative scattering activities), $f(\nu_1)$-$I(\nu_j)/f(\nu_j)I(\nu_1)$, of each observed band are also included in Table 2; it will be noted that the frequency-corrected relative intensities of the $\nu_{11}(t_{2g})$ band differ substantially from the uncorrected values, owing to the very low value of ν_j in each case {e.g. $f(\nu_{11})/f(\nu_1)$ for $[Cr(CO)_6]$ is 179.0 at 388 K and for 514.5-nm excitation}.

The $f(\nu_1)I(\nu_3)/f(\nu_3)I(\nu_1)$ values obtained are uniformly higher than those reported [21] for these molecules in dichloromethane solutions (Table 3), although the differences are barely significant, bearing in mind the likely errors in each set of intensity measurements. The

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[15] R. J. H. Clark and D. M. Rippon, *J. Mol. Spectroscopy*, 1972, **44**, 479.

[16] Y. M. Bosworth, R. J. H. Clark, and D. M. Rippon, *J. Mol. Spectroscopy*, 1973, **46**, 240.
[17] R. S. McDowell, *J. Chem. Phys.*, 1964, **41**, 2557.
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[19] Y. M. Bosworth and R. J. H. Clark, *J.C.S. Dalton*, 1974, 1749.
[20] M. Eliashevich and M. Wolkenstein, *J. Phys. U.S.S.R.*, 1945, **9**, 101, 326.
[21] S. F. A. Kettle, I. Paul, and P. J. Stamper, *J.C.S. Dalton*, 1972, 2413.

values lead to a quadratic equation in $\alpha_{\perp}'/\alpha_{\parallel}'$ both solutions to which are included in Table 3. For reasons

TABLE 3

The ratio $\alpha_{\perp}'/\alpha_{\parallel}'$ derived from the $\nu_1(a_{1g})$ and $\nu_3(e_g)$ carbonyl-stretching fundamentals of the metal hexacarbonyls

Molecule	$\dfrac{f(\nu_1)}{f(\nu_3)} \times \dfrac{I(\nu_3)}{I(\nu_1)}$		$\dfrac{a_{\perp}'}{\alpha_{\parallel}'}$ (vapour phase)		$\dfrac{\alpha_{\perp}'}{\alpha_{\parallel}'}$
	vapour phase	CH$_2$Cl$_2$ soln.[a]	root 1	root 2	(CH$_2$Cl$_2$ soln.[a])
[Cr(CO)$_6$]	10.1	7.1	-0.26_5[b]	-0.85	-0.23
[Mo(CO)$_6$]	7.9	7.0	-0.24[c]	-0.90	-0.23
[W(CO)$_6$]	7.9	6.3	-0.24[d]	-0.90	-0.22

[a] Ref. 21.   [b] ±0.025.   [c] ±0.03.   [d] ±0.05.

which have been argued previously,[19] the chemically significant root is the one for which this ratio lies between -0.5 and 2.86 (root 1 in Table 3) in agreement with the choice made by Kettle et al. The resulting $\alpha_{\perp}'/\alpha_{\parallel}'$ values are small and negative for each molecule, and not significantly different from the solution-phase values obtained previously. Accordingly the longitudinal and transverse components of the bond-polarisability changes are definitely of opposite signs, a situation which, for simple octahedral $[\mathrm{MX_6}]^{n-}$ ions, is only approached by the $[\mathrm{PtX_6}]^{2-}$ ions [19] for which the electronic configuration of the metal atom is likewise t_{2g}^6. The significance of this observation is, however, not clear.