New Raman Spectroscopic Evidence and Reassignment of the Spectra of Dimanganese and Dirhenium Decacarbonyls

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Summary New Raman spectroscopic evidence for solutions and oriented single crystals is presented from which a reassignment is made for the ν(CO) frequencies of the title compounds.

MANY differing assignments for the ν(CO) vibrations of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ have been suggested, although the frequencies of all the predicted modes have not yet been determined *experimentally*. Previous assignments for $Mn_2(CO)_{10}$ have been summarised by Bor.[1]

Table 1 shows the distribution of modes for the molecular point symmetry and the factor group symmetry; Table 2 shows the results and assignments for both compounds in solution; Table 3 shows the Raman spectroscopic results for an oriented single crystal of $Re_2(CO)_{10}$.

TABLE 1

Correlation table for $M_2(CO)_{10}$

D_{4d}		C_2 (site)	C_{2h} (2 molecules)
$2a_1$	Raman-active	$2a$	$2A_g + 2A_u$
e_2		$a + b$	$A_g + B_g + A_u + B_u$
e_3		$a + b$	$A_g + B_g + A_u + B_u$
$2b_2$	I.r.-active	$2b$	$2B_g + 2B_u$
e_1		$a + b$	$A_g + B_g + A_u + B_u$

We have established the positions of the four expected Raman-active fundamentals for $Mn_2(CO)_{10}$ in solution. The band at 2116 cm^{-1} is clearly polarised (a_1), the other three having depolarisation ratios 0·7—0·75. Measurements on oriented single crystals of $Mn_2(CO)_{10}$ enabled us to classify all of the Raman lines as A_g or B_g under factor group symmetry C_{2h}. These results can be correlated to molecular (D_{4d}) symmetry, allowing unequivocal assignments. The intensity of the 1990 cm^{-1} line shows different dependence upon orientation from the other A_g lines but it always moves in conjunction with the 160 cm^{-1} A_g line (due to Mn–Mn stretching): we therefore assign it to the axial carbonyl stretch, present in solution at 1997 cm^{-1}.

TABLE 2

Raman lines (cm^{-1}) *observed for petrol solutions of* $M_2(CO)_{10}$

M=Mn	M=Re	Assignment
2116	2128	ν_1, a_1
2024	2029	ν_{25}, e_2
1997	1993	ν_2, a_1
1981	(1980)[a]	ν_{31}, e_3

[a] Estimated; see text.

For $Re_2(CO)_{10}$ the single-crystal results can be explained on the assumption that the a_1 (axial) and e_3 modes are almost coincident in solution. The A_g (axial) mode interacts with the A_g component of the e_3 mode, leading to the observed splitting pattern which differs from that of $Mn_2(CO)_{10}$.

TABLE 3

Correlation of the ν(CO) *frequencies of* $Re_2(CO)_{10}$

D_{4d}		C_{2h}
I.r. (solution)	Raman (solution)	Raman (crystal)
	2128, a_1	2126, A_g
2074, b_2		2074, B_g
	2029, e_2	2025, A_g 2017, B_g
2013, e_1		
	1993, a_1	1977[a] A_g
	(1980), e_3	1990[a] A_g 1972 B_g
1974, b_2		

[a] Almost certainly in resonance.

In the lower frequency region (10—700 cm^{-1}) we have observed all five predicted modes of a_1 species for $Re_2(CO)_{10}$, and all but one for $Mn_2(CO)_{10}$. The band at 394 cm^{-1} of $Re_2(CO)_{10}$, previously reported as polarised in solution,[2,3] is definitely depolarised and gives rise to two components 390 (B_g) and 394 (A_g) in the solid state; both observations require the 394 cm^{-1} band to be of *e*-symmetry. We find many more bands below 150 cm^{-1}, for both compounds, than reported by Quicksall and Spiro.[4] The full assignment will be published elsewhere.[5]

The presence of only one clearly polarised band in the ν(CO) region appears to be a general property of the $M(CO)_5$ unit. For $Mn(CO)_5Br$ we find only one polarised band in solution (at 2139 cm^{-1}). The lowest-frequency ν(CO) band, at 2007 cm^{-1}, has a high depolarisation ratio and cannot be identified as definitely polarised. This is contrary to the report of Hyams and Lippincott[6] for $Mn(CO)_5Br$, but consistent with that of Cotton *et al.*[7] for $Mn(CO)_5CF_3$.

We thank the S.R.C. for generous support.

(*Received, June 2nd,* 1970; *Com.* 852.)

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