Metal–Metal Stretching Frequencies in Raman Spectra

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SINCE Woodward's study of the mercurous ion[1] very few Raman spectra have been reported[2–4] for species containing metal–metal (M–M) bonds. In view of the current interest in such compounds it seems appropriate to re-emphasise the suitability of Raman spectroscopy as a means of investigating M–M bonds and to report here some results of this kind. Despite the mixing of internal co-ordinates (bond lengths and interbond angles) which may occur in a normal mode of vibration, several features of simple M–M compounds—relative atomic masses, bond force constants, and molecular symmetry—usually permit one of the normal modes to be described as chiefly a vibration of the M–M bond.

From our observations, metal–metal stretching frequencies, ν(M–M), fall in the region 120—200 cm.$^{-1}$ for a wide range of metals. They appear as very intense Raman-active fundamentals which are often the strongest features in the spectrum. Indeed, high Raman intensity appears to be a characteristic of ν(M–M), owing to the large change in polarizability when a covalent bond between two atoms of high atomic number is deformed. In contrast, ν(M–M) may prove difficult to detect by far-infrared spectroscopy. *This is particularly marked in binuclear M–M systems*: when the molecule is centrosymmetric ν(M–M) is, of course, totally forbidden in the infrared. However, if a centre of symmetry is lacking, ν(M–M) becomes formally permitted in the infrared. A far-infrared investigation of many binuclear M–M compounds[5] has shown that, even when the molecule is *heteronuclear*, ν(M′–M) is frequently so weak as to escape observation unless coupling with other frequencies such as metal–halogen vibrations is extensive. In polynuclear species the antisymmetric M–M vibrations, however, become strongly permitted in the infrared;[6] the Raman and infrared data are then complementary. The high Raman intensity also tends to offset some of the inherent difficulties in applying this technique to slightly insoluble or highly coloured materials, and Raman spectroscopy is the best means of detecting ν(M–M) in binuclear compounds.

Table 1 summarises the M–M frequencies which have been observed in the present work together with earlier published data. The assignment of the bands cited therein as ν(M–M) is based on consideration of their polarisation, low frequency, intensity, and a comparison with analogous molecules not containing M–M bonds.

Structure determinations of the mercurous complexes[9] show that they may be considered as linear molecules of type X–Hg–Hg–X, point group $D_{\infty h}$, for which three bond-stretching fundamentals are expected: ν_1 [Σ_g^+, ν(Hg–Hg), Raman], ν_2 [Σ_g^+, ν(Hg–X), Raman], ν_3 [Σ_u^+, ν(Hg–X), infrared]. We have observed all three fundamentals for solid mercurous nitrate dihydrate

TABLE 1

Metal–metal stretching frequencies

Compound	State	(M–M)	cm.$^{-1}$	Reference
Sn_2Me_6	liquid	Sn–Sn	190	2
Sn_2Ph_6	solid	Sn–Sn	208	a
$Sn(SnPh_3)_4$	solid	Sn–Sn	207	a, c
$Hg_2(NO_3)_2$	aqueous	Hg–Hg	169	1
$Hg_2(NO_3)_2,2H_2O$	solid	Hg–Hg	170	a
Hg_2Cl_2	solid	Hg–Hg	166	a, 7
Hg_2Br_2	solid	Hg–Hg	133	a
$Ph_3SnMn(CO)_5$	solution	Sn–Mn	174	a
$Mn_2(CO)_{10}$	solution	Mn–Mn	157	a
$MnRe(CO)_{10}$	solution	Mn–Re	182	a, b
$Re_2(CO)_{10}$	solution	Re–Re	128	8
Cd_2^{2+}	melt	Cd–Cd	183	4
$[Co(CO)_4]_2Cd$	solution	Co–Cd	152	3, c
$[Co(CO)_4]_2Hg$	solution	Co–Hg	161	3, c

[a] This work.

[b] $MnRe(CO)_{10}$ also shows a Raman line at 157 cm.$^{-1}$ which we tentatively attribute to $Mn_2(CO)_{10}$ impurity, formed by disproportionation.

[c] The totally symmetric frequency is quoted.

TABLE 2

Fundamental frequencies and force constants of mercurous compounds

Compound	ν_1	ν_2	ν_3 (cm.$^{-1}$)	k_1	k_2	k_{12} (md./Å)
$Hg_2(OH_2)_2(NO_3)_2$	170	389	382	1·93	1·42	−0·05
Hg_2Cl_2	166	275	261	2·13	1·21	0·03
Hg_2Br_2	133	204	180	1·93	1·09	0·17

[effectively $Hg_2(OH_2)_2^{2+}$], mercurous bromide, and mercurous chloride (for which our results concur with the recent assignment by Goldstein[10]). From these three frequencies it is possible to calculate[11] the bond-stretching force constants k_1(Hg–Hg), k_2(Hg–X), and the interaction constant, k_{12}, between adjacent bonds, with the results set out in Table 2. The relative values of k_1 are seen to be consistent with the known trend in Hg–Hg bond lengths in these compounds.[12]

The ν(M–M) values for the dimetal decacarbonyls are also worthy of comment. Lack of data precludes the calculation of accurate force constants, because ν(M–M) will be coupled with the other a_1 vibrations, in particular the totally symmetric CMC deformation. However, by treating the carbonyls approximately as "diatomic" molecules, having a reduced mass, μ, given by $1/\mu = 1/(M + 5m_{CO}) + 1/(M' + 5m_{CO})$, rough M–M force constants may be obtained. The values, k(Mn–Mn) = 1·4, k(Mn–Re) = 2·3, and k(Re–Re) = 1·6 md./Å, while not reliable in an absolute sense, probably retain relative significance and point to an unusual order of bond strengths in this series; namely, Mn–Re > Re–Re > Mn–Mn.

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