Resonance Raman Spectrum of $K_4Mo_2Cl_8$

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Summary A resonance-Raman spectrum of the complex $K_4Mo_2Cl_8$ has been recorded with 488·0 and 514·5 nm excitation; five harmonics of v_1 (the "Mo–Mo stretching" fundamental) have been located accurately, and from these data it is deduced that $\omega_1 = 347\cdot1 \pm 0\cdot5$ cm^{-1} and $X_{11} = 0\cdot50 \pm 0\cdot08$ cm^{-1}.

RAMAN SPECTRA of molecules are typically obtained under conditions in which v_0, the exciting frequency, is well removed from v_e, the frequency of the first allowed electronic transition of the molecule. When v_0 is brought into coincidence with v_e, a so-called resonance-Raman spectrum of the molecule is obtained, this being characterised by high-intensity overtone progressions in a totally symmetric fundamental.[1,2] From the results so far (primarily on tetrahedral molecules), such fundamentals have been found to be very close to harmonic oscillators.[3] A recent report[4] of the Raman spectrum of the complex $(enH)_2Mo_2Cl_8\cdot2H_2O$ obtained with 488·0 nm excitation claimed the observation of progressions in the Mo–Mo stretching fundamental out to the third overtone. However, neither the second overtone (which surprisingly alone appeared as a doublet) nor the third overtone were at the correct frequencies for such an assignment. Accordingly we have reinvestigated the Raman spectrum of this ion in the solid state as the complex $K_4Mo_2Cl_8$ by use of both 488·0 (1·6W) and 514·5 (1·9W) nm excitation *i.e.* with exciting frequencies which are close to the lowest electronic transition of the ion ($\lambda_{max} = 517$ nm by diffuse reflectance). The rotating-sample technique[5] was employed.

The resonance-Raman spectrum of the complex $K_4Mo_2Cl_8$ obtained under the conditions above displays an enormous enhancement to the intensity of v_1, the "Mo–Mo stretching" fundamental relative to the intensity of other
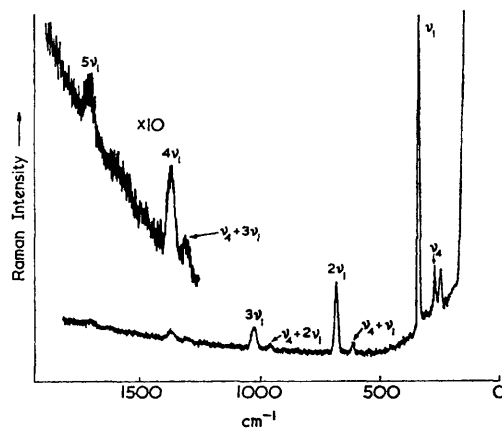

FIGURE. Resonance-Raman spectrum of the complex $K_4Mo_2Cl_8$ obtained with Ar$^+$ 488·0 nm excitation, slit widths 150/250/150 μm.

fundamentals, and an overtone progression in v_1 out to $5v_1$ (Figure). The accurately evaluated frequencies of each member of the progression are given in the Table. The harmonic frequency (ω_1) and the anharmonicity constant (X_{11}) may be deduced from the following relationship[6]

between the overtone frequency, $\nu(n)$, and the vibrational quantum number, n,

$$\nu(n) = G(n) - G(0) = n\omega_1 - X_{11}(n^2 + n) + \ldots\ldots$$

Thus a plot of $\nu(n)/n$ versus n should be a straight line with gradient $- X_{11}$ and intercept $\omega_1 - X_{11}$. The results for the solid material are: $\omega_1 = 347\cdot1 \pm 0\cdot5$ cm^{-1} and $X_{11} = 0\cdot50 \pm 0\cdot08$ cm^{-1} (least-squares analysis). Hence, in common with fundamentals which have previously been shown to display the resonance-Raman effect, this fundamental also is very close to being harmonic. The overtones also characteristically show[1,3] (a) a progressive decrease in intensities with increase in n and (b) a progressive increase in half-band widths with increase in n (Table).

A second, much weaker progression $(\nu_4 + n\nu_1)$ is also evident in the Figure out to $n = 3$; ν_4, the 277 cm^{-1} band, arises from a metal–chlorine stretching fundamental belonging to the symmetry species a_{1g}, b_{1g} or e_g. A plot

widths of the first three bands (27, 35, and 60 cm^{-1} respectively) are considerably bigger than for the corresponding bands of solid $K_4Mo_2Cl_8$. Thus owing to the structural change in solution, no depolarisation ratios for the fundamentals of the Mo_2-Cl_8^{4-} ion could be obtained, and the species to which ν_4 belongs could not be ascertained.

It is interesting that only one of the three totally symmetric fundamentals of the $Mo_2Cl_8^{4-}$ ion (i.e. that which is primarily Mo–Mo stretching in nature)[8] should display the resonance-Raman effect; not even the first overtone of either ν_2, the a_{1g} species Mo–Cl stretch (Table), or ν_3, the a_{1g} species ClMoCl bend, could be observed. This suggests that the lowest allowed electronic transition, ν_e, with which ν_0 is in coincidence, is one which involves transfer of an electron from the highest filled bonding molecular orbital associated with the Mo–Mo quadruple bond viz the δ ($^1b_{2g}$) orbital, i.e. the transition is either $^1B_{1u}\leftarrow^1A_{1g}$ [$^1a_{2u}\sigma_n(1)\leftarrow$ $^1b_{2g}\delta]^9$ (although this is electric dipole forbidden) or $^1A_{2u}\leftarrow$

TABLE. Raman-spectral data on the progressions $n\nu_1$ and $\nu_4 + n\nu_1$ observed for the complex $K_4Mo_2Cl_8$ in the solid state (cm^{-1}, 488·0 nm excitation).[a]

	$n\nu_1$ Progression				$\nu_4 + n\nu_1$ Progression		
n	$\nu_1(n)$	$\nu_1(n)/n$	$\Delta\nu_{\frac{1}{2}}$	n	$\nu_4 + \nu_1(n)$	$\nu_1(n)/n$	$\Delta\nu_{\frac{1}{2}}$
1	345·9	345·9	11	0	276·7	—	—
2[b]	691·8	345·9	17	1	621·9	345·2	14
3	1035·4	345·1	23	2	966·1	344·7	19
4	1378·1	344·5	30	3	1308·7	344·0	24
5	1720·5	344·1	38				

[a] Other bands occur in the Raman spectrum of the complex at 315·5(vw), 276·7(m) and 252·7(m) cm^{-1}, and in its i.r. spectrum at 307(m) and 275(m) cm^{-1}. These are assigned to MoCl stretching fundamentals ($a_{1g} + b_{1g} + e_g + a_{2u} + b_{2u} + e_u$ in D_{4h}). Additionally, a Raman-active band is seen at 190·8 cm^{-1}. All bands are $\pm 0\cdot5$ cm^{-1}. The 253 cm^{-1} band displays a pre-resonance Raman effect.   [b] The intensity ratio $I(2\nu_1)/I(\nu_1) = 0\cdot35$ for 514·5 nm excitation, $0\cdot22$ for 488·0 nm excitation, and ca. 0 for 568·2 and 647·1 nm excitation, consistent with most exact resonance at the first wavelength.[3a,c]   However, the overall spectrum with 514·5 nm as opposed to 488·0 nm excitation is marred by the presence of significant fluorescence background.

of $\nu(n)/n$ versus n for this progression leads to the values $\omega_1 = 346\cdot5 \pm 1$ cm^{-1} and $X_{11} = 0\cdot6 \pm 0\cdot12$ cm^{-1}. The values of ω_1 and X_{11} for this progression are less accurate than those obtained from the $n\nu_1$ progression owing to the lower intensities of the bands, the fewer members observed, and the larger half-band widths of each for given n; the values of ω_1 and X_{11} obtained from the $\nu_4 + n\nu_1$ progression nevertheless are in agreement with those obtained from the $n\nu_1$ progression.

The complex $K_4Mo_2Cl_8$, when dissolved in 1M hydrochloric acid and sealed in vacuo, forms a purple solution in which the lowest electronic transition is at 513 nm ($\epsilon_{max} \approx 550$). The $Mo_2Cl_8^{4-}$ ion is known to be hydrolysed in solution,[7] but the Mo_2^{4+} entity is undoubtedly preserved therein owing to the observation of a Raman progression ($n\nu_1$) characteristic of this entity on excitation of the solution with 488·0 or 514·5 nm radiation, viz 355·7, 708·5, 1056·8, 1404·7 cm^{-1}, $\omega_1 = 358\cdot7 \pm 0\cdot7$, $X_{11} = 1\cdot5 \pm 0\cdot2$ cm^{-1}. The half-band

$^1A_{1g}$ ($b_{1u}\delta^* \leftarrow b_{2g}\delta$).[10]   It is undoubtedly significant that the pronounced progression observed[10] in this band in its electronic spectrum at 5K ($n \times 351$ cm^{-1}) occurs for the same fundamental as that displaying the resonance-Raman effect. The rather surprising fact that the ground and excited state frequencies of the ν_1 (a_{1g}) fundamental are approximately equal may be attributed to a difference between the extent of mixing of the MoMo and MoCl stretching fundamentals in the two electronic states.

In conclusion, resonance-Raman spectroscopy would appear to have considerable potential as a technique for the diagnosis of metal–metal bonding in complex species.

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