Raman Frequencies of Metal Clusters: $Ir_4(CO)_{12}$

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RECENTLY Gager, Lewis, and Ware[1] have suggested that Raman spectroscopy may be an effective probe in the study of metal–metal bonds. In view of the current interest in metal clusters, we report here our initial results in an investigation of the Raman scattering of polynuclear metal carbonyls.

Maroni and Spiro[2] have considered the vibrations of metal clusters of cubic symmetry. For tetrahedral metal clusters, M_4, three normal modes are expected, of symmetries A_1, F_2, and E, all of them Raman active. Similarly, for octahedral clusters, Mg, three Raman active modes are expected: A_{1g}, F_{2g}, and E_g. In either case the G matrix elements corresponding to these symmetry species are, in the order listed, 4 μ, 2 μ, and 1 μ, where μ is the reciprocal of the mass of M. If the motions of the cluster are well separated from those of any associated ligands, and if further, they are adequately characterized by a single metal–metal force constant (interaction constants negligible), then the fundamental Raman active cluster frequencies are predicted to lie in the ratios 2 : 2 : 1 in the order given. This approximate model has been found adequate to interpret the low-frequency[2] Raman spectra of the hydroxy-bridged clusters $Bi_6(OH)_{12}{}^{6+}$, $Pb_4(OH)_4{}^{4+}$, $Tl_4(OEt)_4$. These results suggested that the observation of three intense low-frequency Raman bands whose frequencies are close to the ratios 2 : 2 : 1 might be diagnostic for tetrahedral or octahedral metal clusters.

This model is nicely tested by the molecule $Ir_4(CO)_{12}$ which has been shown by Wei and Dahl[3] to have T_d point symmetry in the crystal lattice, and significantly, to be without bridging carbonyls. In this molecule, then, the cluster is held together by metal–metal bonds alone. We have obtained the low-frequency Raman spectrum for a polycrystalline sample of $Ir_4(CO)_{12}$, as supplied by

Alfa Inorganics, Inc. The spectrometer[4] used was provided with a He–Ne laser source. Three strong emissions were observed, at frequencies 208, 164, and 105 cm.$^{-1}$ which are assigned respectively to the A_1, F_2, and E modes of the Ir_4 cluster. Unfortunately a suitable solvent for the compound has not been found; therefore, we have been unable to test the polarization of the bands. We note that the frequency ratios are 2 : 1·57 : 1·01, close to that anticipated on the basis of the simple model. A single metal–metal force constant of 1·3 m dynes/Å predicts the frequencies within 10 cm.$^{-1}$. The bands are almost equal in intensity and are comparable to another strong band, at 458 cm.$^{-1}$, which we assign to metal–carbon stretching.

The analogous compounds $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ are similar in structure to $Ir_4(CO)_{12}$, but the overall symmetry is lowered to C_{3v} by bridging carbonyls.[3] We expect similar Raman spectra for these analogues. However, if the lower symmetry is significantly reflected in the bonding within the clusters, a splitting of the F_2 mode is predicted.

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[1] H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Comm.*, 1966, 616.

[2] V. A. Maroni and T. G. Spiro, to be published.

[3] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 1821.

[4] R. E. Miller, D. L. Rousseau, and G. E. Leroi, Technical Report No. 22, ONR Contrast 1858 (27), N.R. 014–203 May 1967 [Available from Defence Documentation Center, Cameron Station, Alexandria, Virginia 22314].