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J. E. D. DAVIES

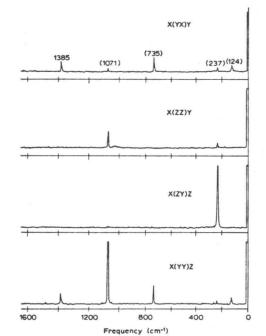


Fig. 3. Raman spectra of LiNO₃ in the four unique polarization orientations. (Reproduced from R. E. Miller, R. R. Getty, K. L. Treuil and G. E. Leroi, J. Chem. Phys., 51 (1969) 1385.)

of an S_4 site symmetry. The $v_1(a_1)$ band of carbon tetrachloride can be resolved into three components in the Raman spectrum of the polycrystalline solid. Ito assigned these bands as being due to isotopic splitting rather than to factor group splitting^{1.72}. This assignment has been confirmed recently since the Raman spectrum of solid C³⁵Cl₄ displays only one component for the $v_1(a_1)$ band^{1.73}.

X-Ray diffraction studies have shown that crystalline methyl chloride has a C_3 site symmetry and C_{2v}^2 space group. The vibrational spectra are in accord with such a structure, and the spectra of the crystalline bromide and iodide suggest that these two compounds have a similar structure to that of the chloride (refs. 174, 175) (Fig. 4).

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EFFECT OF PHASE AND PRESSURE ON VIBRATIONAL SPECTRA

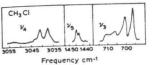


Fig. 4. Raman bands of polycrystalline CH₃Cl at high resolution (< 1.0 cm⁻¹ spectral slitwidth). (Reproduced from C. W. Brown and E. R. Lippincott, J. Chem. Phys., 52 (1970) 786).

The infrared¹⁷⁶⁻¹⁸² and Raman^{11,179,181} spectra of the polycrystalline methylene halides have been investigated by several workers. The spectroscopic data indicate that the site symmetries are C_2 , C_3 and C_{23} for the chloride, bromide and iodide, respectively.

Several infrared studies on polycrystalline chloroform have been reported (refs. 183–186). Ito originally reported two components for the doubly degenerate modes in the Raman spectrum¹⁷⁴ of solid CHCl₃, but recent work has shown that three components are present¹⁸⁷. Comparison of the infrared and Raman spectra suggests a C_s site symmetry in a D_{2h}^{2h} space group.

The infrared spectra of several matrix-isolated chlorinated tetrahedral molecules have been studied and isotopic splitting of several bands were observed (ref. 188).

Crystalline osmium tetroxide is known to have C_2 site symmetry and space group C_{2h}^6 . The Raman spectrum¹⁸⁹⁻¹⁹¹ of the solid is consistent with this structure. RuO₄ gives a similar Raman spectrum which suggests a similar crystal structure.

The infrared and Raman spectra of liquid, crystalline and matrix isolated carbon suboxide¹⁹², and the gas phase Raman spectrum¹⁹³ support a quasilinear structure for the molecule.

The infrared and Raman spectra of a number of sulphate salts have been reported, and attempts have been made to correlate the observed spectra with the known crystal structures. The vibrational spectra of numerous anhydrous sulphate (refs. 194–203) salts have been reported together with low temperature infrared spectra²⁰⁴ of single crystals of K_2SO_4 , BaSO₄, SrSO₄ and PbSO₄.

Several hydrated sulphate salts have also been investigated²⁰⁵⁻²¹⁰. An interesting observation is that the $v_1(a_1)$ mode of SO₄²⁻ appears as a triplet in the

solid state spectra of some rare earth sulphate pentahydrates²⁰⁷. The spectra of several alums²¹¹, double sulphates²¹³, langbeinites²¹³ and Tutton salts^{213,214} have been reported together with a single crystal Raman study²¹² of several alums.

Phosphate salts have also been examined, and the spectra are in accord with a D_{24} site symmetry²¹⁵ for the phosphate ion in YPO₄ and YbPO₄: a C_1 site symmetry²¹⁶ in Ca₈H₂(PO₄)₆ · 5H₂O; C_{3v} site symmetry in strontium and barium

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