

C. Triatomic and 2-coordinate species

The far infrared spectra of H₂O in noble gas matrices⁵⁷ and the infrared spectrum of D₂O in a nitrogen matrix⁵⁸ indicate that both molecules rotate in these matrices. The intensity of the infrared bands due to the stretching modes of water in the polycrystalline solid was found to be about 30 times that of the vapour phase value and considerably higher than the liquid phase value⁵⁹.

Solid H₂S and D₂S exist in three modifications. The Raman spectra⁶⁰ of the two higher temperature phases are consistent with their known disordered crystal structures. The Raman⁶⁰ and far infrared⁶¹ spectra of the lowest temperature phase suggest a C₁ site symmetry. The infrared spectra of H₂S and D₂S in argon⁶², krypton⁶², and nitrogen⁶³ matrices have been reported, whilst the Raman frequency of the $\nu_1(a_1)$ mode of H₂S in the β -quinol clathrate is closer to the gas phase value than to the liquid or solid state values⁶⁶.

The Raman bands⁶⁴ of crystalline SO₂ show a fine structure due to factor group splitting and to isotopic splitting. The infrared spectra of the various isotopic species of SO₂ trapped in krypton matrices have been observed⁶⁵, and the Raman spectrum of the SO₂/ β -quinol clathrate has also been reported⁶⁶.

The Raman spectrum of polycrystalline CO₂ has been reported^{66,67}. Comparison of the infrared and Raman spectra of polycrystalline CS₂ shows no coincidences between the frequencies indicating that the centre of symmetry is preserved even in the crystalline state⁶⁸. The infrared spectrum of polycrystalline carbonyl sulphide contains a broad, asymmetric ν_3 band. A study of the matrix-isolated molecule indicates that the asymmetry can be attributed to the different isotopic species of the molecule⁶⁹. The Raman spectrum of polycrystalline nitrous oxide has been reported⁶⁷ and bands due to the various isotopic species have been observed in the infrared spectrum of the polycrystalline solid⁷⁰.

The Raman⁷¹ and far infrared⁷² spectra of polycrystalline HCN and DCN show that the solid exists in two phases. The infrared spectra of HCN adsorbed on alkali halide films⁷³ and of the matrix isolated molecule⁷⁴ have been reported.

The gaseous phase Raman spectra of the dihalides of mercury(II) and zinc(II) and of the mixed mercury dihalides are consistent with a linear structure for the monomeric molecules⁷⁵. The Raman spectrum⁷⁵ of gaseous "GaCl₂" consists of bands due to GaCl and GaCl₃, whilst in the liquid⁷⁶ and solid⁷⁷ states the Raman spectra of "GaCl₂" are consistent with an ionic structure Ga⁺GaCl₂⁻.

The red to yellow phase transition of solid mercuric iodide above 126° has been followed by means of Raman spectroscopy⁷⁸. There are marked differences between the spectra of non-molecular red HgI₂ and the molecular yellow phase (Fig. 2).

The gaseous phase Raman spectra⁷⁹ of GeCl₂, TeCl₂, SnCl₂, PbCl₂ and PbBr₂ show that the monomeric species are non-linear in the gaseous phase. The solid state Raman spectrum of stannous chloride⁸⁰ differs considerably from the

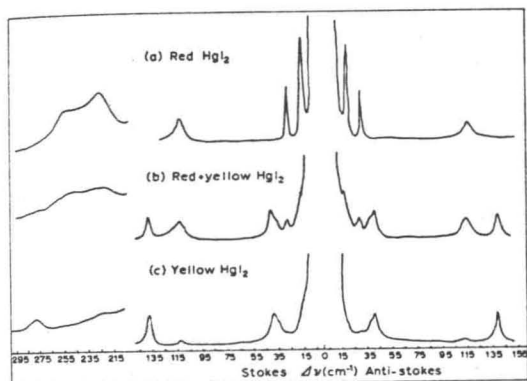


Fig. 2. (a) Raman spectrum of room-temperature red HgI₂. (b) Raman spectrum of the red and yellow HgI₂ mixture at the point of incomplete phase conversion. (c) Raman spectrum of yellow HgI₂ just above the transition point. Residual trace of red HgI₂ is indicated. (Reproduced from A. J. Melveger, R. K. Khanna, B. R. Guscott and E. R. Lippincott, *Inorg. Chem.*, 7 (1968) 1650.)

gaseous state spectrum since the solid state structure consists of halogen-bridged SnCl₂ units.

The infrared spectra of a number of metal dihalide monomeric species isolated in noble gas matrices have been reported: the dichlorides of manganese, iron, cobalt and nickel⁸¹; the difluorides of cobalt, nickel and zinc⁸²; the dihalides of cadmium and mercury⁸³; the difluorides^{84,85}, dichlorides^{86,87}, dibromides^{86,87} and di-iodides⁸⁶ of the alkaline earth elements.

Other triatomic species which have been studied spectroscopically are hydrated magnesium chloride and bromide⁸⁸, the dihydrate of copper(II) dichloride⁸⁹, solid ozone⁹⁰ at 10°K, matrix isolated⁹¹ HOCl and HOBr, matrix isolated⁹² CsOH and CsOD and matrix isolated⁹³ RbOH and NaOH.

The infrared spectrum of ammonium thiocyanate displays splittings of all the degenerate modes of the NH₄⁺ and NCS⁻ ions⁹⁴. The infrared and Raman spectra of solid methyl mercury(II) thiocyanate contain no coincidences, suggesting that the unit cell is centrosymmetric⁹⁵. The Raman spectrum of KSCN at room temperature displays the expected factor group splitting of the CN vibrational mode⁹⁶. The IR spectra of gaseous and solid HNCS and DNCS have been reported (ref. 97). The shift in frequency of $\nu(N-H)$ and $\nu(N-D)$ upon solidification suggests a very short, strong hydrogen-bond.

The vibrational spectra of potassium⁹⁸ and caesium⁹⁹ azide are consistent