

phosphate²¹⁷; C_s site symmetry in fluorapatite^{218,219}, $Ca_{10}(PO_4)_6F_2$ and in chlorapatite²²⁰, $Ca_{10}(PO_4)_6Cl_2$.

Other oxoanions which have been examined are perchlorates²²¹⁻²²⁵, molybdates and tungstates²²⁶⁻²³⁴, perrhenates²³⁵⁻²³⁸, permanganates²³⁹⁻²⁴¹, pertechnates²⁴²⁻²⁴³, chromates(V)²⁴⁴⁻²⁴⁶, chromates(VI)²⁴⁷⁻²⁴⁸, selenates (refs. 249, 250) and garnets²⁵¹⁻²⁵⁴.

The vibrational spectra of several ammonium²⁵⁵⁻²⁵⁹ and phosphonium (refs. 260-263) salts have been examined, and deuteration studies have been used to classify the lattice modes into translatory and rotatory modes.

Tetrahedral²⁶⁴⁻²⁷¹ and square planar²⁷² tetrahalo salts have been examined together with borohydride salts²⁷³ and silicates²⁷⁴.

The following tetracoordinate species have been examined: the tetracyanonickelate(II) ion²⁷⁵, tetracyanoethylene²⁷⁶⁻²⁷⁸, *trans*-bis(dimethylsulphide)dibromoplatinum(II)²⁷⁹; tetrakis(thioacetamide)copper(I) chloride²⁸⁰ and tetrakis(thiourea)nickel(II) dichloride²⁸⁰.

F. Hexa-atomic and 5-coordinate species

The gas phase Raman spectra of the pentachlorides and pentabromides of Sb, Nb, Ta and Mo are consistent with the presence of trigonal bipyramidal species²⁸¹. In the solid state TaX_5 , NbX_5 and $MoCl_5$ exist as M_2X_{10} dimers²⁸². Solid NbF_5 and SbF_5 consist of *cis*-F-bridged polymers²⁸³, whilst matrix-isolated SbF_5 is reported as being of C_4 point group²⁸⁴. Solid $SbCl_5$ exists in two modifications, the spectrum of the high-temperature phase resembling that of the liquid (refs. 285, 286). The vibrational spectra of crystalline hydrazine²⁸⁷⁻²⁸⁹ are consistent with a C_2^2 space group, while the spectra of liquid tetrafluorohydrazine

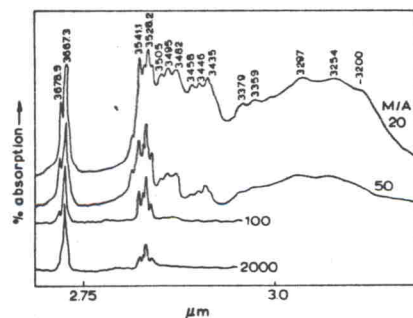


Fig. 5. OH stretching mode of CH_3OH in argon at various concentrations. (Reproduced from A. J. Barnes and H. E. Hallam, *Trans. Faraday Soc.*, 66 (1970) 1920.)

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indicate the presence of both the *trans* and the *gauche* isomers²⁹⁰⁻²⁹².

The infrared and Raman spectra of B_2Cl_4 and B_2F_4 suggest a staggered D_{2d} configuration in the gaseous²⁹³ and liquid²⁹⁴ states, whilst B_2Cl_4 possesses the planar D_{2h} configuration in the solid state²⁹³. Oxalyl chloride²⁹⁵ is reported to have C_{2h} site symmetry whilst glyoxal²⁹⁶ has a C_i site symmetry. The low temperature modification of acetonitrile has either the D_{2h}^1 or D_{2h}^2 space groups²⁹⁷, whilst trifluoroacetonitrile has a C_3 site symmetry and a C_2 factor group²⁹⁸.

The infrared spectrum of matrix-isolated methanol monomer has been obtained. Concentration studies resulted in the identification of the open chain dimer, trimer and tetramer species²⁹⁹ (Fig. 5). The infrared spectrum of the high temperature phase of crystalline methanethiol indicates an orthorhombic unit cell containing eight molecules³⁰⁰. The site symmetry in crystalline carbonyl cyanide is reported to be either C_s or C_2 in a C_2 lattice³⁰¹. The infrared and Raman spectra of crystalline $HReO_4$ are consistent with the C_3 structure $HOREO_3$. Aqueous solutions ($\leq 80\%$) contain only the ReO_4^- anion³⁰².

Deuteration studies have been used to classify the lattice modes of solid ethylene³⁰³⁻³⁰⁵. The single crystal Raman spectrum of the five coordinate species bis(trimethylamine)trichloroindium(III) has been reported³⁰⁶.

G. Species with seven or more atoms

The Raman spectra of XeF_6 have been studied in the gaseous, liquid and solid states³⁰⁷. The results indicate that either the ground state vapour phase molecules possess a symmetry lower than O_h or they have some very unusual electronic properties that markedly influence the vibrational spectrum.

The vibrational spectra of polycrystalline UF_6 indicate a D_{4h} site symmetry (ref. 308). The infrared spectra of crystalline³⁰⁹ CrF_6 , MoF_6 , and OsF_6 also indicate a distortion of the regular octahedral structure found in the vapour phase.

The Raman spectrum of solid SF_6 shows a splitting of all three fundamentals into a number of components³¹⁰. Comparison with previous infrared data indicates that a centre of symmetry is maintained at the site. There are substantial differences between the solution³¹¹ and solid state³¹² Raman frequencies of WCl_6 .

The vibrational spectra of a variety of hexahalometallates have been reported (refs. 313-320). Splittings of several of the fundamental bands have been observed in the solid state spectra.

The infrared³²¹⁻³²³ and Raman³²⁴⁻³²⁶ spectra of single crystals of sodium nitroprusside have been reported and assigned. Other hexacoordinate salts which have been studied have been hexanitro salts³²⁷ and ruthenium nitrosopentahalides (ref. 328).

The Raman spectrum of sulphur vapour¹²⁹ at 180 °C indicates the presence of the S_6 , S_7 and S_8 species. The Raman spectra of polycrystalline^{329,330} and single crystal³³¹ samples of rhombic sulphur show site and factor group splitting of the fundamental bands. The Raman spectrum of solid Si_2Cl_6 displays five of the

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