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with a D_{xh} site symmetry for the azide ion, but the spectra of barium azide¹⁰⁰ suggest the presence of an asymmetric azide ion in the unit cell.

The vibrational spectra of a number of dicyanide complexes have been reported. The vibrational spectra of potassium copper(1) dicyanide¹⁰¹ indicate a non-linear structure for the Cu(CN)₂⁻ ion. The vibrational spectra of thallium gold(1) dicyanide¹⁰² indicate a significant non-ionic interaction between thallium and the Au(CN)₂ group. This is in contrast to KAu(CN)₂ where the anion is linear both in solution and in the solid state. The vibrational spectra of KAg(CN)₂ have been interpreted in terms of a $D_{\infty h}$ site symmetry¹⁰³, a C_i site symmetry¹⁰⁴

The single crystal Raman spectrum¹⁰⁶ and variable temperature Raman spectra^{107,108} of sodium nitrite have been reported. The infrared spectra of the metaborate ion, BO₂⁻, isolated in alkali halide lattices^{109,110} have been reported, together with the infrared spectra of matrix isolated alkali metal metaborates¹¹¹. The infrared spectra of the alkali metal metathioborates, which are isostructural with the corresponding metaborates, have also been reported¹¹².

D. Tetra-atomic and 3-coordinate species

The infrared^{113,114} and Raman¹¹⁵ spectra of crystalline acetylene and deuterated species indicate the presence of two crystalline modifications. The low temperature modification belongs to the D_{28}^{18} space group, with C_{28} site symmetry, while the high-temperature modification belongs to the T_h^{0} space group. The polarized infrared spectrum of single crystals of diacetylene has been reported¹¹⁰. The infrared spectra of solid hydrogen disulphide¹¹⁸ have been reported. The infrared spectra of crystalline exanogen and cyanogen-¹⁵N₂ exhibit a factor group splitting of the v_3 band^{119–121}.

The infrared spectra of crystalline phosphine^{122,123} and arsine¹²⁴ at 82 °K are consistent with a C_3 , or C_3 site symmetry, while SbH₃ has a C_3 or C_1 site symmetry.

The far infrared spectrum¹²⁵ of crystalline NH₃ is consistent with a T^4 space group, whilst the infrared spectrum of matrix isolated¹²⁶ NH₃ exhibits a sharp single v₂ band. The temperature dependent changes observed in the band contours of the infrared spectra of a number of solid samples with coordinated NH₃ groups indicates a rotation of the NH₃ groups relative to the rest of the molecule¹²⁷.

The gas phase Raman spectra of the trihalides of aluminium, gallium and indium at high temperatures are consistent with the presence of the monomeric MX_3 species¹²⁸. In the liquid and solid states the spectra are consistent with the presence of M_2X_6 dimer species. GaBr₂Cl and GaCl₂Br can be identified in the gaseous phase Raman spectra of mixtures of GaCl₃ and GaBr₃ at high temperatures⁷⁵. The equilibrium $M_4 \rightleftharpoons 2M_2$ for phosphorus and arsenic have also been studied using gas phase Raman spectroscopy¹²⁹.

The trihalides of the Group V elements have C_{3v} point group in solution.

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EFFECT OF PHASE AND PRESSURE ON VIBRATIONAL SPECTRA

The Raman spectra of polycrystalline arsenic trichloride and tribromide are consistent with a C_1 site symmetry¹³⁰, while that of arsenic triiodide is consistent with an S_6 factor group^{131,132}. The Raman spectra of polycrystalline antimony^{132,133} and bismuth triiodide¹³² are also consistent with an S_6 factor group, while the Raman spectrum of solid SbCl₃ has been interpreted in terms of a dimeric structure¹³⁴. The vibrational spectra of the solid mercurous halides¹³⁵ and of matrix isolated¹³⁶ ClF₃, BrF₃ and BrF₅ have also been reported.

The free nitrate ion is of D_{3h} symmetry, but the vibrational spectra of nitrates in solution¹³⁷⁻¹³⁹ and as melts¹⁴⁰ display considerable broadening, and in some cases a splitting, of the degenerate stretching mode, consistent with ion-ion interactions.

The solid state spectra of nitrate salts show considerable splitting of the vibrational bands and numerous studies have been reported. Single crystal vibrational studies have been reported for the lithium^{141,142} (Fig. 3), sodium¹⁴³, caesium¹⁴⁴ and strontium¹⁴⁵ salts. The vibrational spectra of powders of the rare earth nitrates¹⁴⁶, the alkali metal nitrates^{147,148} and the alkaline earth nitrates¹⁴⁹ have been reported. The effect of phase transitions on vibrational spectra have been investigated for sodium nitrate^{150–152}, potassium nitrate^{153–156}, ammonium nitrate¹⁵⁷ and nitrosonium nitrate¹⁵⁸.

The solid state infrared spectra of the main group and transition metal carbonates^{159,160}, of rare earth carbonates¹⁶¹ and of cobalt(III) carbonate complexes¹⁶² show numerous deviations from the spectra expected for a carbonate anion of D_{3h} point group. The advantages of using plane polarized laser radiation over mercury are sources was demonstrated when depolarization measurements on calcite using laser excitation were found to be fully consistent with the known structure¹⁶³. Previous measurements using mercury are excitation had given anomalous results.

The vibrational spectra of a series of SnCl₃⁻ salts show a marked cation dependence. With large cations¹⁶⁴ such as AsPh₄⁺, the solid state spectra are very similar to the spectrum of an othereal solution¹⁶⁵ of SnCl₃⁻, but with small cations (ref. 80) such as K⁺, the observed solid state spectrum bears little resemblance to that of ethereal SnCl₃⁻, indicating considerable coupling between the lattice modes and the intramolecular fundamentals.

E. Penta-atomic and 4-coordinate species

The infrared¹⁶⁶ and Raman¹⁶⁷ spectra of methane indicate that the molecule can undergo hindered rotation in both the liquid and solid states. The infrared spectra of CH_4 and CD_4 isolated in noble gas matrices indicate a rotational motion^{168,169}, while the Raman spectrum¹⁷⁰ of methane in a krypton matrix also supports the concept of free rotation in this matrix.

The infrared and Raman spectra¹⁷¹ of Phase I of polycrystalline CF_4 are very similar to the liquid state spectra, whereas the spectra of Phase II are indicative

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