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## Nucleic Acid-Protein Interactions and Nucleic Acid Synthesis in Viral Infection

Miami Winter Symposia, Volume 2

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Symposia on biochemical topics have been arranged by the Department of Biochemistry and the Program in Cellular and Molecular Biology of the University of Miami for a number of years. In January 1969 the Department of Biochemistry joined with the University-affiliated Papanicolaou Cancer Research Institute to continue this tradition by presenting pairs of Symposia on closely related biochemical topics which attracted national interest. The full report of the 1970 meeting was published as the first volume of a continuing series under the title: *Miami Winter Symposia*. The present volume, the second in this series, contains the report of the January 1971 Symposia and includes all discussions as well as the full text of the reports.

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### REVIEW

#### THE EFFECT OF PHASE AND PRESSURE CHANGES ON VIBRATIONAL SPECTRA

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### 1. INTRODUCTION

This review is concerned with the effect of phase and pressure changes on infrared and Raman vibrational spectra. The review will be concerned with work published between 1963 and 1970 inclusive and it is worth while first of all to mention some of the significant spectroscopic advances which have occurred during the period under review.

The most significant development has undoubtedly been the introduction of the laser as a Raman source and the consequent availability of commercial Raman spectrometers. As a result of this development many publications now

report both the infrared and Raman spectra of compounds and in some cases the spectra of compounds in the gaseous, liquid and solid states are also reported. The introduction of the laser source has also meant that the Raman spectra of single crystals<sup>1</sup> and of compounds in the gaseous phase<sup>2</sup> can be readily obtained.

Other developments during this period which the author regards as being significant have been the availability of commercial far-infrared spectrometers and the use of the matrix isolation technique to study not only the spectra of unstable species such as free radicals, but also the spectra of isolated molecules.

Although it is hoped that the review is a comprehensive one, certain restrictions have been imposed on the subject matter, and these will be explained at the beginning of each section.

## 2. PHASE CHANGES

### A. Introduction

The phase changes considered in this review are the gaseous to solid or the liquid/solution to solid phase changes. The review is restricted to papers dealing with molecular crystals or complex ions in crystals. Thus topics such as the vibrational spectra of semi-conductors and the alkali halides will not be discussed.

Previous reviews on the Raman effect in crystals have been written by Menzies<sup>3</sup> (1953) and by Loudon<sup>4</sup> (1964), while the infrared spectra of crystals have been reviewed by Vedder and Hornig<sup>5</sup> (1961), by Dows<sup>6</sup> (1963 and 1965) and by Mitra and Gielisse<sup>7</sup> (1964). This review will be concerned with work published since 1963, and it will thus partially overlap with the reviews of Loudon and of Mitra and Gielisse.

Considerable differences can be observed between the vibrational spectra of the gaseous, liquid and solid states and these can be classified as:

#### (a) Frequency shifts

It is well known that vibrational frequencies are usually displaced to lower wave number on changing phase, the usual order being  $\nu(\text{gas}) > \nu(\text{liquid}) > \nu(\text{solid})$ .

#### (b) Loss of rotational fine structure

One of the main differences between the spectra of compounds in the gaseous and other states is the absence of the rotational fine structures of vibrational bands present in gaseous phase spectra. Some compounds such as the methyl halides<sup>8</sup> do, however, exhibit wings on either side of vibrational bands in the liquid phase, and this has been attributed to rotational motion in the liquid state.

#### (c) Site group splitting

The vibrational bands corresponding to the *degenerate* vibrations in the

gaseous state can appear as doublets or triplets in the solid state spectrum if the site symmetry in the solid is of lower symmetry than the point group of the isolated molecule.

#### (d) Factor group splitting

In the solid state spectra of some compounds the bands corresponding to the *non-degenerate* vibrations of the isolated molecule can be split into a number of components. To account for this effect one must consider not only the site symmetry but also the number of molecules in the unit cell and its space group.

In solid state spectra the activities of vibrational modes are governed by the site symmetry and the factor group. Since these can differ from the point group of the isolated molecule, it is not surprising that solid state spectra can contain frequencies due to vibrations which are normally inactive for the isolated molecule.

#### (e) The appearance of lattice vibrations

Solid state spectra contain lattice vibrations which arise from the translational and rotational motions of the isolated molecule. Bands due to lattice vibrations can be distinguished from those due to intramolecular vibrations since they are characterized by the following properties:

- (i) they are absent from the vibrational spectra of the gaseous and liquid\* states;
- (ii) they have low frequency values\*\*, usually less than  $200 \text{ cm}^{-1}$ ;
- (iii) their frequency and intensity are temperature<sup>11</sup> and pressure<sup>12</sup> dependent.

#### (f) Polymorphism

The solid may exist in different crystalline phases, and since each phase will have a characteristic vibrational spectrum, the spectrum will change at the transition temperature between the two phases<sup>13</sup>.

#### (g) Rotational isomers

In some instances the vibrational spectrum may be simplified on solidification. This usually signifies that the liquid consists of a mixture of rotational

\* Low frequency bands which are not vibrational fundamentals can be observed in the infrared and Raman spectra of some liquids. For a comprehensive discussion of the origin of these bands see refs. 9 and 10 and references therein.

\*\* The lattice modes of hydrogen-containing compounds can be classified as being of translational or rotational origin from a study of the effect of deuteration on the band frequencies. The frequencies of translational lattice modes are inversely proportional to the *mass* of the molecule, while the frequencies of rotational lattice modes are inversely proportional to the *moments of inertia* of the molecule. This method has been used to classify the lattice modes of species such as acetylene (ref. 114), ethylene<sup>205</sup>, the ammonium ion<sup>258</sup> and the phosphonium ion<sup>261</sup>. Single crystal Raman spectroscopy can also be used to classify lattice modes<sup>231</sup>.

isomers, while only one of these isomers is favoured in the solid state<sup>14</sup>.

A consideration of the above effects shows that, in general, the solid state gives rise to a more complicated vibrational spectrum than the liquid or gaseous states. Spectroscopic studies, both infrared and Raman, in which some or all of the above effects have been observed will now be discussed. The compounds are classified according to the number of atoms they contain or to the coordination number of the species.

#### B. Diatomic molecules

An analysis of the Raman spectrum of liquid hydrogen<sup>15</sup> suggested that the molecules can undergo rotational motion in the liquid state. The rotational Raman spectrum of solid hydrogen consists of two lines while the fundamental vibrational band consists of four lines<sup>16</sup>. The frequencies and shapes of the vibrational Raman lines have been studied for a series of *ortho/para* ratios<sup>17</sup>. The infrared spectra of solid H<sub>2</sub>, HD and D<sub>2</sub> have also been observed<sup>18,19</sup>.

The infrared spectra of solid  $\alpha$  and  $\beta$  oxygen<sup>20</sup>, and the far infrared spectrum (ref. 21) of solid  $\alpha$  oxygen have been reported. The infrared spectrum of the  $\alpha$  phase is consistent with a site symmetry of C<sub>2v</sub> in a space group of C<sub>2h</sub>. The Raman spectra of each of the four condensed phases have been observed<sup>22</sup>.

The low frequency Raman<sup>23</sup> and far infrared<sup>24</sup> spectra of solid  $\alpha$ -nitrogen have been reported.

The Raman spectra of crystalline chlorine<sup>25,26</sup> and bromine<sup>27</sup> have been observed. The stretching frequencies show fine structure due to both isotopic splitting and to intermolecular coupling, and the lattice and intramolecular frequencies indicate stronger intermolecular forces in solid bromine than in solid chlorine. The intensities of the infrared active lattice modes of crystalline Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub> have been reported<sup>28</sup>, and a weak absorption has been observed in the infrared in the region of the stretching frequency of solid bromine and iodine<sup>29</sup>.

The hydrogen halides have been the subjects of several spectroscopic studies, both on the crystalline compounds and on the matrix isolated species.

The infrared<sup>30</sup> and Raman<sup>31</sup> spectra of crystalline HF and DF both consist of four bands in the intramolecular stretching region. Direct observation of a lattice band near 200 cm<sup>-1</sup> enabled two of the bands to be assigned as combination bands. The infrared<sup>32-34</sup>, Raman<sup>35,36</sup> and far infrared<sup>37</sup> spectra of crystalline HCl, DCl, HBr and DBr have been reported by several workers. These studies indicate that the low temperature orthorhombic phase contains non planar, hydrogen-bonded, zig-zag chains. The high temperature cubic phase shows no strong lattice bands and gives very broad Raman bands in the stretching region.

The infrared<sup>38</sup> spectra of HF in noble gas matrices in the region of the fundamental vibrational frequency suggests that rotation occurs in these matrices. Direct observation of the  $J = 1 \leftarrow J = 0$  frequency in the far infrared<sup>39</sup> spectrum provides additional evidence that both HF and DF rotate in noble gas matrices.

There is ample evidence to support the view that HCl, DCl, HBr, DBr and HI rotate in noble gas matrices from infrared spectra in the intramolecular stretching region<sup>40-44</sup> and from direct observation of the  $J = 1 \leftarrow J = 0$  frequency in the far infrared spectra<sup>45</sup>. There is conflicting evidence for nitrogen matrices. Harvey and Shurvell<sup>46</sup> claim that HCl and HBr do rotate in a nitrogen matrix, but recent work by Hallam and his co-workers<sup>45,47</sup> finds no evidence for rotation in a nitrogen matrix. There is also evidence<sup>47,48</sup> to suggest that HCl, HBr and HI rotate in CH<sub>4</sub>, CF<sub>4</sub> and SF<sub>6</sub> matrices, but that rotation is prevented in CO, CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> matrices.

Recent far infrared<sup>54,55</sup> and Raman<sup>56</sup> studies on  $\beta$ -quinol clathrate compounds (Fig. 1) indicate that both HCl and HBr can rotate in the  $\beta$ -quinol host lattice.

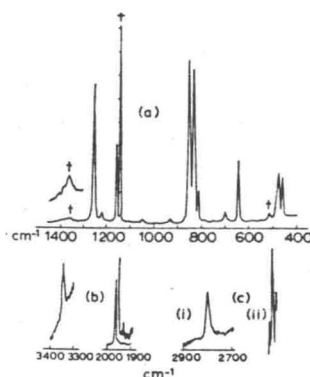


Fig. 1. Raman spectra of guest molecules in  $\beta$ -quinol clathrates. (a) SO<sub>2</sub>, Kr 5682 Å excitation, 23 mW at sample. SO<sub>2</sub> bands marked \*; (b) C<sub>2</sub>H<sub>2</sub>; (c) HCl, (i) sample at room temperature, (ii) sample at 77 K. Spectra (b) and (c) used Kr 5208 Å excitation, 30 mW at sample. All spectra were recorded using 3 cm<sup>-1</sup> slit width. (Reproduced from J. E. D. Davies, *Chem. Commun.*, (1971) 270.)

Bands due to isolated molecules in matrices are only observed at high matrix/absorber ratios. Increasing the concentration of the absorber results in the appearance of new bands in the infrared spectra and these can be assigned to dimers, trimers and other multimetric species<sup>44,49-51</sup>.

Carbon monoxide does not rotate in argon<sup>52</sup>, krypton<sup>53</sup> or sulphur hexafluoride<sup>48</sup> matrices, but there is evidence to suggest that it does rotate in a xenon matrix<sup>53</sup>.

### C. Triatomic and 2-coordinate species

The far infrared spectra of  $H_2O$  in noble gas matrices<sup>57</sup> and the infrared spectrum of  $D_2O$  in a nitrogen matrix<sup>58</sup> 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 value<sup>59</sup>.

Solid  $H_2S$  and  $D_2S$  exist in three modifications. The Raman spectra<sup>60</sup> of the two higher temperature phases are consistent with their known disordered crystal structures. The Raman<sup>60</sup> and far infrared<sup>61</sup> spectra of the lowest temperature phase suggest a  $C_1$  site symmetry. The infrared spectra of  $H_2S$  and  $D_2S$  in argon<sup>62</sup>, krypton<sup>62</sup>, and nitrogen<sup>63</sup> matrices have been reported, whilst the Raman frequency of the  $\nu_1(a_1)$  mode of  $H_2S$  in the  $\beta$ -quinol clathrate is closer to the gas phase value than to the liquid or solid state values<sup>66</sup>.

The Raman bands<sup>64</sup> of crystalline  $SO_2$  show a fine structure due to factor group splitting and to isotopic splitting. The infrared spectra of the various isotopic species of  $SO_2$  trapped in krypton matrices have been observed<sup>65</sup>, and the Raman spectrum of the  $SO_2/\beta$ -quinol clathrate has also been reported<sup>66</sup>.

The Raman spectrum of polycrystalline  $CO_2$  has been reported<sup>66,67</sup>. Comparison of the infrared and Raman spectra of polycrystalline  $CS_2$  shows no coincidences between the frequencies indicating that the centre of symmetry is preserved even in the crystalline state<sup>68</sup>. The infrared spectrum of polycrystalline carbonyl sulphide contains a broad, asymmetric  $\nu_3$  band. A study of the matrix-isolated molecule indicates that the asymmetry can be attributed to the different isotopic species of the molecule<sup>69</sup>. The Raman spectrum of polycrystalline nitrous oxide has been reported<sup>67</sup> and bands due to the various isotopic species have been observed in the infrared spectrum of the polycrystalline solid<sup>70</sup>.

The Raman<sup>71</sup> and far infrared<sup>72</sup> spectra of polycrystalline HCN and DCN show that the solid exists in two phases. The infrared spectra of HCN adsorbed on alkali halide films<sup>73</sup> and of the matrix isolated molecule<sup>74</sup> 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 molecules<sup>75</sup>. The Raman spectrum<sup>75</sup> of gaseous " $GaCl_2$ " consists of bands due to  $GaCl$  and  $GaCl_3$ , whilst in the liquid<sup>76</sup> and solid<sup>77</sup> states the Raman spectra of " $GaCl_2$ " are consistent with an ionic structure  $Ga^+GaCl_4^-$ .

The red to yellow phase transition of solid mercuric iodide above 126° has been followed by means of Raman spectroscopy<sup>78</sup>. There are marked differences between the spectra of non-molecular red  $HgI_2$  and the molecular yellow phase (Fig. 2).

The gaseous phase Raman spectra<sup>79</sup> of  $GcCl_2$ ,  $TeCl_2$ ,  $SnCl_2$ ,  $PbCl_2$  and  $PbBr_2$  show that the monomeric species are non-linear in the gaseous phase. The solid state Raman spectrum of stannous chloride<sup>80</sup> differs considerably from the

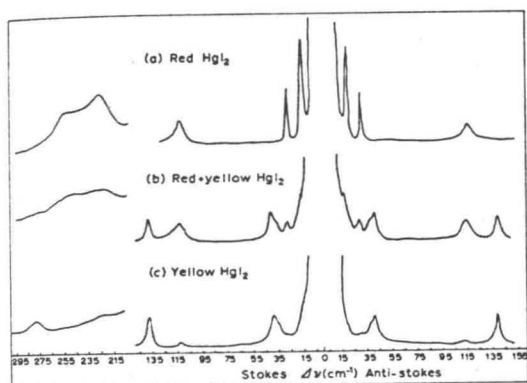


Fig. 2. (a) Raman spectrum of room-temperature red  $HgI_2$ . (b) Raman spectrum of the red and yellow  $HgI_2$  mixture at the point of incomplete phase conversion. (c) Raman spectrum of yellow  $HgI_2$  just above the transition point. Residual trace of red  $HgI_2$  is indicated. (Reproduced from 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  $SnCl_2$  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 nickel<sup>81</sup>; the difluorides of cobalt, nickel and zinc<sup>82</sup>; the dihalides of cadmium and mercury<sup>83</sup>; the difluorides<sup>84,85</sup>, dichlorides<sup>86,87</sup>, dibromides<sup>86,87</sup> and di-iodides<sup>86</sup> of the alkaline earth elements.

Other triatomic species which have been studied spectroscopically are hydrated magnesium chloride and bromide<sup>88</sup>, the dihydrate of copper(II) dichloride<sup>89</sup>, solid ozone<sup>90</sup> at 10°K, matrix isolated<sup>91</sup> HOCl and HOBr, matrix isolated<sup>92</sup> CsOH and CsOD and matrix isolated<sup>93</sup> RbOH and NaOH.

The infrared spectrum of ammonium thiocyanate displays splittings of all the degenerate modes of the  $NH_4^+$  and  $NCS^-$  ions<sup>94</sup>. The infrared and Raman spectra of solid methyl mercury(II) thiocyanate contain no coincidences, suggesting that the unit cell is centrosymmetric<sup>95</sup>. The Raman spectrum of KSCN at room temperature displays the expected factor group splitting of the CN vibrational mode<sup>96</sup>. 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 potassium<sup>98</sup> and caesium<sup>99</sup> azide are consistent

with a  $D_{2h}$  site symmetry for the azide ion, but the spectra of barium azide<sup>100</sup> 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(I) dicyanide<sup>101</sup> indicate a non-linear structure for the  $\text{Cu}(\text{CN})_2^-$  ion. The vibrational spectra of thallium gold(I) dicyanide<sup>102</sup> indicate a significant non-ionic interaction between thallium and the  $\text{Au}(\text{CN})_2$  group. This is in contrast to  $\text{KAu}(\text{CN})_2$  where the anion is linear both in solution and in the solid state. The vibrational spectra of  $\text{KAg}(\text{CN})_2$  have been interpreted in terms of a  $D_{2h}$  site symmetry<sup>103</sup>, a  $C_1$  site symmetry<sup>104</sup> and a  $C_2$  site symmetry<sup>105</sup>.

The single crystal Raman spectrum<sup>106</sup> and variable temperature Raman spectra<sup>107,108</sup> of sodium nitrite have been reported. The infrared spectra of the metaborate ion,  $\text{BO}_2^-$ , isolated in alkali halide lattices<sup>109,110</sup> have been reported, together with the infrared spectra of matrix isolated alkali metal metaborates<sup>111</sup>. The infrared spectra of the alkali metal metathiorates, which are isostructural with the corresponding metaborates, have also been reported<sup>112</sup>.

#### D. Tetra-atomic and 3-coordinate species

The infrared<sup>113,114</sup> and Raman<sup>115</sup> spectra of crystalline acetylene and deuterated species indicate the presence of two crystalline modifications. The low temperature modification belongs to the  $D_{2h}^8$  space group, with  $C_{2h}$  site symmetry, while the high-temperature modification belongs to the  $T_h^6$  space group. The polarized infrared spectrum of single crystals of diacetylene has been reported<sup>116</sup>. The infrared spectra of solid hydrogen peroxide<sup>117</sup> and hydrogen disulphide<sup>118</sup> have been reported. The infrared spectra of crystalline cyanogen and cyanogen-<sup>15</sup>N<sub>2</sub> exhibit a factor group splitting of the  $\nu_3$  band<sup>119-121</sup>.

The infrared spectra of crystalline phosphine<sup>122,123</sup> and arsine<sup>124</sup> at 82 °K are consistent with a  $C_{3v}$  or  $C_3$  site symmetry, while  $\text{SbH}_3$  has a  $C_3$  or  $C_1$  site symmetry.

The far infrared spectrum<sup>125</sup> of crystalline  $\text{NH}_3$  is consistent with a  $T_d$  space group, whilst the infrared spectrum of matrix isolated<sup>126</sup>  $\text{NH}_3$  exhibits a sharp single  $\nu_2$  band. The temperature dependent changes observed in the band contours of the infrared spectra of a number of solid samples with coordinated  $\text{NH}_3$  groups indicates a rotation of the  $\text{NH}_3$  groups relative to the rest of the molecule<sup>127</sup>.

The gas phase Raman spectra of the trihalides of aluminium, gallium and indium at high temperatures are consistent with the presence of the monomeric  $\text{MX}_3$  species<sup>128</sup>. In the liquid and solid states the spectra are consistent with the presence of  $\text{M}_2\text{X}_6$  dimer species.  $\text{GaBr}_2\text{Cl}$  and  $\text{GaCl}_2\text{Br}$  can be identified in the gaseous phase Raman spectra of mixtures of  $\text{GaCl}_3$  and  $\text{GaBr}_3$  at high temperatures<sup>75</sup>. The equilibrium  $\text{M}_4 \rightleftharpoons 2\text{M}_2$  for phosphorus and arsenic have also been studied using gas phase Raman spectroscopy<sup>129</sup>.

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

The Raman spectra of polycrystalline arsenic trichloride and tribromide are consistent with a  $C_1$  site symmetry<sup>130</sup>, while that of arsenic triiodide is consistent with an  $S_6$  factor group<sup>131,132</sup>. The Raman spectra of polycrystalline antimony<sup>132,133</sup> and bismuth triiodide<sup>132</sup> are also consistent with an  $S_6$  factor group, while the Raman spectrum of solid  $\text{SbCl}_3$  has been interpreted in terms of a dimeric structure<sup>134</sup>. The vibrational spectra of the solid mercurous halides<sup>135</sup> and of matrix isolated<sup>136</sup>  $\text{ClF}_3$ ,  $\text{BrF}_3$  and  $\text{BrF}_5$  have also been reported.

The free nitrate ion is of  $D_{3h}$  symmetry, but the vibrational spectra of nitrates in solution<sup>137-139</sup> and as melts<sup>140</sup> 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<sup>141,142</sup> (Fig. 3), sodium<sup>143</sup>, caesium<sup>144</sup> and strontium<sup>145</sup> salts. The vibrational spectra of powders of the rare earth nitrates<sup>146</sup>, the alkali metal nitrates<sup>147,148</sup> and the alkaline earth nitrates<sup>149</sup> have been reported. The effect of phase transitions on vibrational spectra have been investigated for sodium nitrate<sup>150-152</sup>, potassium nitrate<sup>153-156</sup>, ammonium nitrate<sup>157</sup> and nitrosonium nitrate<sup>158</sup>.

The solid state infrared spectra of the main group and transition metal carbonates<sup>159,160</sup>, of rare earth carbonates<sup>161</sup> and of cobalt(III) carbonate complexes<sup>162</sup> 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 arc sources was demonstrated when depolarization measurements on calcite using laser excitation were found to be fully consistent with the known structure<sup>163</sup>. Previous measurements using mercury arc excitation had given anomalous results.

The vibrational spectra of a series of  $\text{SnCl}_3^-$  salts show a marked cation dependence. With large cations<sup>164</sup> such as  $\text{AsPh}_4^+$ , the solid state spectra are very similar to the spectrum of an ethereal solution<sup>165</sup> of  $\text{SnCl}_3^-$ , but with small cations (ref. 80) such as  $\text{K}^+$ , the observed solid state spectrum bears little resemblance to that of ethereal  $\text{SnCl}_3^-$ , indicating considerable coupling between the lattice modes and the intramolecular fundamentals.

#### E. Penta-atomic and 4-coordinate species

The infrared<sup>166</sup> and Raman<sup>167</sup> spectra of methane indicate that the molecule can undergo hindered rotation in both the liquid and solid states. The infrared spectra of  $\text{CH}_4$  and  $\text{CD}_4$  isolated in noble gas matrices indicate a rotational motion<sup>168,169</sup>, while the Raman spectrum<sup>170</sup> of methane in a krypton matrix also supports the concept of free rotation in this matrix.

The infrared and Raman spectra<sup>171</sup> of Phase I of polycrystalline  $\text{CF}_4$  are very similar to the liquid state spectra, whereas the spectra of Phase II are indicative

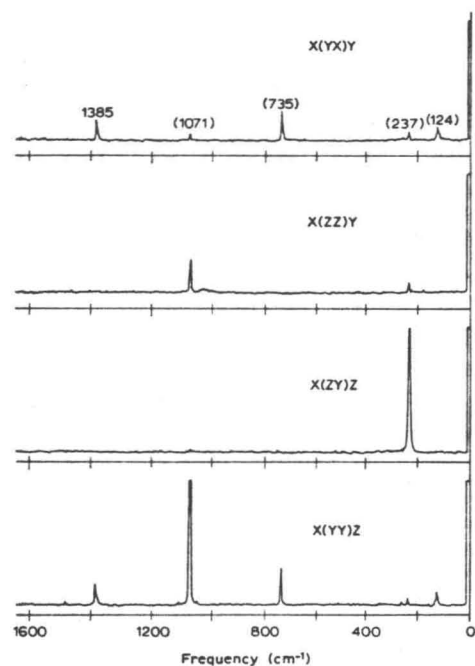


Fig. 3. Raman spectra of  $\text{LiNO}_3$  in the four unique polarization orientations. (Reproduced from R. E. Miller, R. R. Getty, K. L. Treuil and G. E. Leroi, *J. Chem. Phys.*, 51 (1969) 1385.)

of an  $S_4$  site symmetry. The  $\nu_1(a_1)$  band of carbon tetrachloride can be resolved into three components in the Raman spectrum of the polycrystalline solid. It is assigned these bands as being due to isotopic splitting rather than to factor group splitting<sup>172</sup>. This assignment has been confirmed recently since the Raman spectrum of solid  $\text{C}^{35}\text{Cl}_4$  displays only one component for the  $\nu_1(a_1)$  band<sup>173</sup>.

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).

*J. Mol. Structure*, 10 (1971) 1-30

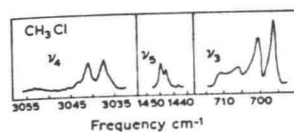


Fig. 4. Raman bands of polycrystalline  $\text{CH}_3\text{Cl}$  at high resolution ( $< 1.0 \text{ cm}^{-1}$  spectral slitwidth). (Reproduced from C. W. Brown and E. R. Lippincott, *J. Chem. Phys.*, 52 (1970) 786.)

The infrared<sup>176-182</sup> and Raman<sup>11,179,181</sup> spectra of the polycrystalline methylene halides have been investigated by several workers. The spectroscopic data indicate that the site symmetries are  $C_2$ ,  $C$ , and  $C_2$ , for the chloride, bromide and iodide, respectively.

Several infrared studies on polycrystalline chloroform have been reported (refs. 183-186). It originally reported two components for the doubly degenerate modes in the Raman spectrum<sup>174</sup> of solid  $\text{CHCl}_3$ , but recent work has shown that three components are present<sup>187</sup>. Comparison of the infrared and Raman spectra suggests a  $C$  site symmetry in a  $D_{2d}^2$  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 spectrum<sup>189-191</sup> of the solid is consistent with this structure.  $\text{RuO}_4$  gives a similar Raman spectrum which suggests a similar crystal structure.

The infrared and Raman spectra of liquid, crystalline and matrix isolated carbon suboxide<sup>192</sup>, and the gas phase Raman spectrum<sup>193</sup> 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 spectra<sup>204</sup> of single crystals of  $\text{K}_2\text{SO}_4$ ,  $\text{BaSO}_4$ ,  $\text{SrSO}_4$  and  $\text{PbSO}_4$ .

Several hydrated sulphate salts have also been investigated<sup>205-210</sup>. An interesting observation is that the  $\nu_1(a_1)$  mode of  $\text{SO}_4^{2-}$  appears as a triplet in the solid state spectra of some rare earth sulphate pentahydrates<sup>207</sup>.

The spectra of several alums<sup>211</sup>, double sulphates<sup>213</sup>, langbeinites<sup>213</sup> and Tutton salts<sup>213,214</sup> have been reported together with a single crystal Raman study<sup>212</sup> of several alums.

Phosphate salts have also been examined, and the spectra are in accord with a  $D_{2d}$  site symmetry<sup>215</sup> for the phosphate ion in  $\text{YPO}_4$  and  $\text{YbPO}_4$ ; a  $C_1$  site symmetry<sup>216</sup> in  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ ;  $C_{3v}$  site symmetry in strontium and barium

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phosphate<sup>217</sup>;  $C_3$  site symmetry in fluorapatite<sup>218,219</sup>,  $Ca_{10}(PO_4)_6F_2$  and in chlorapatite<sup>220</sup>,  $Ca_{10}(PO_4)_6Cl_2$ .

Other oxoanions which have been examined are perchlorates<sup>221-225</sup>, molybdates and tungstates<sup>226-234</sup>, perrhenates<sup>235-238</sup>, permanganates<sup>239-241</sup>, pertechnates<sup>242-243</sup>, chromates(V)<sup>244-246</sup>, chromates(VI)<sup>247-248</sup>, selenates (refs. 249, 250) and garnets<sup>251-254</sup>.

The vibrational spectra of several ammonium<sup>255-259</sup> 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.

Tetrahedral<sup>264-271</sup> and square planar<sup>272</sup> tetrahalo salts have been examined together with borohydride salts<sup>273</sup> and silicates<sup>274</sup>.

The following tetracoordinate species have been examined: the tetracyanonickelate(II) ion<sup>275</sup>, tetracyanoethylene<sup>276-278</sup>, *trans*-bis(dimethylsulphide)dibromoplatinum(II)<sup>279</sup>, tetrakis(thioacetamide)copper(I) chloride<sup>280</sup> and tetrakis(thiourea)nickel(II) dichloride<sup>280</sup>.

#### 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 species<sup>281</sup>. In the solid state  $TaX_5$ ,  $NbX_5$  and  $MoCl_5$  exist as  $M_2X_{10}$  dimers<sup>282</sup>. Solid  $NbF_5$  and  $SbF_5$  consist of *cis*-F-bridged polymers<sup>283</sup>, whilst matrix-isolated  $SbF_5$  is reported as being of  $C_4$  point group<sup>284</sup>. 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 hydrazine<sup>287-289</sup> are consistent with a  $C_2$  space group, while the spectra of liquid tetrafluorohydrazine

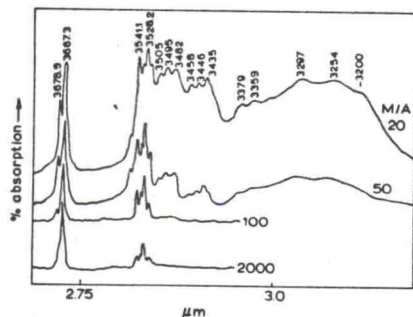


Fig. 5. OH stretching mode of  $CH_3OH$  in argon at various concentrations. (Reproduced from A. J. Barnes and H. E. Hallam, *Trans. Faraday Soc.*, 66 (1970) 1920.)

indicate the presence of both the *trans* and the *gauche* isomers<sup>290-292</sup>.

The infrared and Raman spectra of  $B_2Cl_4$  and  $B_2F_4$  suggest a staggered  $D_{2d}$  configuration in the gaseous<sup>293</sup> and liquid<sup>294</sup> states, whilst  $B_2Cl_4$  possesses the planar  $D_{2h}$  configuration in the solid state<sup>293</sup>. Oxalyl chloride<sup>295</sup> is reported to have  $C_{2h}$  site symmetry whilst glyoxal<sup>296</sup> has a  $C_2$  site symmetry. The low temperature modification of acetonitrile has either the  $D_{2h}$  or  $D_{2d}$  space groups<sup>297</sup>, whilst trifluoroacetonitrile has a  $C_3$  site symmetry and a  $C_2$  factor group<sup>298</sup>.

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 species<sup>299</sup> (Fig. 5). The infrared spectrum of the high temperature phase of crystalline methanethiol indicates an orthorhombic unit cell containing eight molecules<sup>300</sup>. The site symmetry in crystalline carbonyl cyanide is reported to be either  $C_4$  or  $C_2$  in a  $C_2$  lattice<sup>301</sup>. The infrared and Raman spectra of crystalline  $HReO_4$  are consistent with the  $C_3$  structure  $HOReO_3$ . Aqueous solutions ( $\leq 80^\circ$ ) contain only the  $ReO_4^-$  anion<sup>302</sup>.

Deuteration studies have been used to classify the lattice modes of solid ethylene<sup>303-305</sup>. The single crystal Raman spectrum of the five coordinate species bis(trimethylamine)trichloroindium(III) has been reported<sup>306</sup>.

#### G. Species with seven or more atoms

The Raman spectra of  $XeF_6$  have been studied in the gaseous, liquid and solid states<sup>307</sup>. 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 crystalline<sup>309</sup>  $CrF_6$ ,  $MoF_6$ , 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 components<sup>310</sup>. Comparison with previous infrared data indicates that a centre of symmetry is maintained at the site. There are substantial differences between the solution<sup>311</sup> and solid state<sup>312</sup> 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 infrared<sup>321-323</sup> and Raman<sup>324-326</sup> spectra of single crystals of sodium nitroprusside have been reported and assigned. Other hexacoordinate salts which have been studied have been hexanitro salts<sup>327</sup> and ruthenium nitrosopentahalides (ref. 328).

The Raman spectrum of sulphur vapour<sup>129</sup> at  $180^\circ C$  indicates the presence of the  $S_6$ ,  $S_7$  and  $S_8$  species. The Raman spectra of polycrystalline<sup>329,330</sup> and single crystal<sup>331</sup> 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

seven expected isotopic components for the symmetric Si-Cl stretching mode<sup>332</sup>. The Raman spectrum of  $\text{Re}_2\text{O}_7$  is consistent with the presence of a monomeric species in the gaseous and liquid states, whilst the completely different solid state spectrum is indicative of the polymeric nature of the solid<sup>333</sup> (Fig. 6). The solid state spectra of several dichromate salts<sup>248</sup> show evidence of site and factor group splitting.

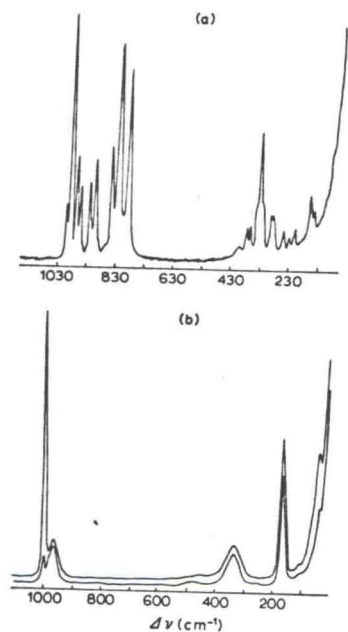


Fig. 6. (a) The Raman spectrum of solid  $\text{Re}_2\text{O}_7$ . (b) The Raman spectrum of liquid  $\text{Re}_2\text{O}_7$  at 350 °C. (Reproduced from I. R. Beattie and G. A. Ozin, *J. Chem. Soc., A*, (1969) 2615.)

The vibrational spectra<sup>334,335</sup> of several eight coordinate ions such as  $\text{Mo}(\text{CN})_8^{4-}$  and  $\text{W}(\text{CN})_8^{4-}$  are consistent with a square antiprismatic structure ( $D_{4d}$ ) in solution, and with a dodecahedral structure ( $D_{2d}$ ) in the solid state.

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#### H. Compounds of phosphorus(V), selenium(IV) and tellurium(IV)

Halide compounds of P(V), Se(IV) and Te(IV) are discussed separately since they show similar properties to those of phosphorus pentachloride, viz. whilst it has the covalent structure in non-polar solvents it exists in the ionic form,  $\text{PCl}_4^+ \text{PCl}_6^-$ , in the solid state.

The gas phase Raman spectrum of  $\text{PCl}_5$  is consistent with the presence of the trigonal bipyramidal  $D_{3h}$  species. With increasing temperature new bands appear in the spectrum due to the  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$  dissociation<sup>281</sup>.

The vibrational spectra of benzene and methylene chloride solutions of  $\text{PCl}_5$  are consistent with the presence of the covalent form<sup>336</sup>. The covalent form can also be trapped in the solid by deposition of the vapour onto a cold window at -185 °C. As the temperature is allowed to increase the spectrum changes as disproportionation from the covalent  $\text{PCl}_5$  to the ionic form occurs<sup>337</sup>. The single crystal Raman spectrum of  $\text{PCl}_5$  exhibits splittings of the degenerate bands due to the low site symmetry of the  $\text{PCl}_4^+$  and  $\text{PCl}_6^-$  ions<sup>338</sup>.

The vibrational spectra of  $\text{CH}_3\text{PCl}_4$  suggest the ionic formulation  $\text{CH}_3\text{PCl}_3^+ \text{Cl}^-$  in the solid state, whilst in non-ionizing solvents the compound is monomeric<sup>339</sup>. Vibrational spectra also suggest ionic formulations for the following compounds:  $\text{PBr}_4(\text{PBr}_4^- \text{Br}^-)$ <sup>340</sup>;  $\text{PBr}_7(\text{PBr}_4^- \text{Br}_3^-)$ <sup>340</sup>;  $\text{P}_2\text{Br}_4\text{F}_6(\text{PBr}_4^- \text{PF}_6^-)$ <sup>340</sup> and for the addition compounds formed between  $\text{PCl}_5$  and  $\text{MCl}_3$ ,  $\text{MCl}_4$  and  $\text{MCl}_5$  species<sup>341</sup>.

The solid state vibrational spectra of the tetrahalides of Se(IV) and Te(IV) have been interpreted in terms of an ionic  $\text{MX}_3^+ \text{X}^-$  formulation<sup>342-344</sup>, although one paper favours the covalent structure for the solid state<sup>345</sup>. The solution vibrational spectra differ from the solid state spectra and they suggest that the tetrahalides exist as the monomeric  $\text{C}_2v$  species at low concentrations<sup>346-348</sup>. The vapour phase Raman spectrum of  $\text{TeCl}_4$  is consistent with the presence of the monomeric  $\text{C}_2v$  species<sup>349</sup>, but the gas phase Raman spectrum of  $\text{SeCl}_4$  indicates complete dissociation<sup>350</sup> to  $\text{SeCl}_2$  and  $\text{Cl}_2$  (Fig. 7).

#### I. Miscellaneous studies

##### (i) Benzene, substituted benzenes and condensed aromatics

The Raman spectra of crystalline benzene and benzene- $d_6$  have been reported (refs. 351, 352). Splittings are observed for all the Raman active degenerate vibrations but for none of the non-degenerate vibrations<sup>354</sup>. The low frequency Raman bands have been assigned to rotational lattice modes<sup>353</sup>, whereas the low frequency infrared bands are due to translational lattice modes<sup>355</sup>. The infrared spectra of  $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$  mixed crystals<sup>356-358</sup>, and polarised infrared spectra<sup>359</sup> of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$  have also been reported.

Solid state vibrational spectra have been reported for a variety of phenols (refs. 360-363), for a series of monosubstituted benzenes<sup>364,365</sup>, and for benzoyl

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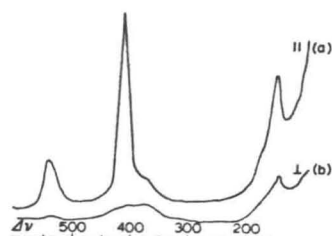


Fig. 7. The gas-phase Raman spectrum of selenium tetrachloride vapour at 350 °C and a pressure of approximately 1 atm in the cell. (a) Parallel polarization and (b) crossed polarization measurements, showing the complete dissociation to selenium dichloride and chlorine. (Reproduced from G. A. Ozin and A. V. Voet, *Chem. Commun.*, (1970) 896.)

chloride<sup>366</sup>. Spectra have also been reported for such disubstituted compounds as *p*-dichlorobenzene<sup>367</sup>, guaiacol<sup>368</sup>, *p*-toluidine<sup>369</sup>, *o*- and *m*-toluic acid<sup>370</sup>, *o*- and *p*-tolunitrile<sup>371</sup>, and a series of *o*-haloaryl compounds<sup>372</sup>. The solid state spectra of iododurene<sup>373</sup>, tetrachloro- and pentachlorotoluene<sup>374</sup>, have also been reported.

The vibrational spectra of polycrystalline<sup>375-377</sup> and of single crystals<sup>378</sup> of naphthalene, naphthalene-*d*<sub>8</sub><sup>379</sup>, and of 1,5-dimethylnaphthalene<sup>380</sup> have been reported. The infrared<sup>381,382</sup> and Raman<sup>383,384</sup> spectra of single crystals of anthracene and the infrared spectrum<sup>381</sup> of anthracene-*d*<sub>10</sub> have been reported. Other condensed aromatic molecules whose solid state spectra have been reported are pyrene<sup>385</sup>, perylene<sup>386</sup>, biphenyl<sup>387,388</sup>, terphenyl<sup>389</sup>, quaterphenyl<sup>390</sup>, benzil<sup>391</sup>, 9,10-anthraquinone<sup>392</sup>, benzophenone<sup>393</sup>, fluorene<sup>394</sup>, acenaphthene (refs. 395-397), paracyclophane<sup>398</sup>, biphenylene<sup>399</sup>, triphenylene<sup>400</sup>, and carbazole<sup>401</sup>.

#### (ii) Heterocyclic compounds

The infrared<sup>402,404</sup> and Raman<sup>403,404</sup> spectra of crystalline pyridine indicate the existence of two coexisting crystalline forms of symmetry  $D_{2h}^1$  and  $D_{2h}^2$ . The vibrational spectra of crystalline hydrogen-bonded pyridinium halides have been reported<sup>405</sup>. Crystalline pyrimidine<sup>406</sup>, pyrazine<sup>407,408</sup>, phenazine<sup>409</sup>, quinoline (ref. 410), and imidazole<sup>411,412</sup> have also been examined. Both cyanuric triazide<sup>413</sup> and cyanuric chloride<sup>414</sup> belong to the  $C_{3h}^2$  space group.

The vibrational spectra of *p*-dioxane indicate the existence of two crystalline phases<sup>415</sup>. The solid state vibrational spectra of ethylene oxide, ethylene sulphide, and trimethylene oxide have been examined<sup>416</sup>. Crystalline state infrared spectra (refs. 417-419) of thiophene, furan and pyrrole exhibit bands due to the  $a_2$  vibrational modes. These modes are IR inactive for the  $C_{2v}$  point group of the isolated

molecules, and the spectra are compatible with a  $C_{2v}^1$  space group. Crystalline thietane exists in two crystalline phases<sup>420</sup>, and the infrared spectrum of crystalline *p*-dithiane has been reported<sup>421</sup>.

#### (iii) Cycloalkanes

Polycrystalline cyclopropane has  $C_3$  site symmetry and the space group is one of eight primitive  $D_{2h}$  groups<sup>422,423</sup>. Cyclopentane exists in three crystalline modifications<sup>424-427</sup> with the transition temperatures at 122 °K and 138 °K. Cyclohexane<sup>13,428,429</sup> exists in two crystalline forms with a transition at 186 °K. The high temperature form has four molecules in the unit cell, whilst there are eight molecules in the unit cell of the low temperature form.

#### (iv) The Raman spectra of adsorbed species

The use of infrared spectroscopy for the study of adsorbed species has been well documented<sup>430</sup> and will not be discussed in this review. During the period under review several publications appeared describing the use of Raman spectroscopy for the study of adsorbed species, and these will be discussed briefly.

Pershina and Raskin<sup>431</sup> studied the Raman spectra of several adsorbed species and found that the spectra could be classified into three groups:

(i) No changes were observed in the spectra of compounds such as benzene, naphthalene, and biphenyl on adsorption.

(ii) The spectra of compounds with a polar group ( $CH_3CN$ ,  $C_6H_5COCH_3$ ,  $CH_3NO_2$ ) showed shifts of 10-15  $cm^{-1}$  in the frequencies of the C-O, C=N and  $NO_2$  groups on adsorption.

(iii) The spectra of  $SbCl_3$ ,  $SbBr_3$  and dichloroethane showed high shifts of all Raman bands on adsorption.

Pershina and Raskin concluded that the differences in the Raman spectra of the adsorbed species corresponded to the changes in the Raman spectra of the compounds during the liquid/crystal phase transition.

Using laser excitation, Hendra and Loader<sup>432a</sup> have found that the spectra of adsorbed  $CCl_4$  is similar to that of the liquid, while adsorbed  $Br_2$  and  $CS_2$  give frequencies similar to the gas phase values. The Raman spectrum of adsorbed *trans*-dichloroethylene does not contain any bands due to the Raman inactive modes, indicating that the adsorbed molecule retains its centre of symmetry.

The Raman spectrum of acetaldehyde adsorbed onto silica gel<sup>432b</sup> shows none of the bands of liquid acetaldehyde, the carbonyl band being noticeably absent. The adsorbed spectrum closely resembles that of paraldehyde, and the data suggest that condensation of acetaldehyde has been catalysed at the surface, leaving a physically adsorbed cyclic product.

The Raman spectra<sup>433</sup> of pyridine adsorbed onto alumina, titanium dioxide, magnesium oxide and silica gel have been used to distinguish between physical

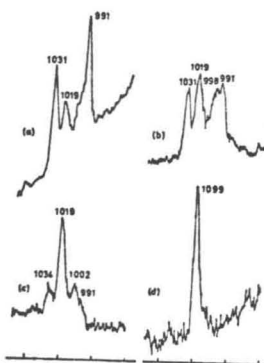


Fig. 8. The Raman spectrum of pyridine adsorbed on to  $\gamma$ -alumina. (a) 0.217 g, (b) 0.147 g, (c) 0.111 g pyridine on 1.19 g alumina, (d) after evacuation at 90 °C. (Reproduced from P. J. Hendra, J. R. Horder and E. J. Loader, *Chem. Commun.*, (1970) 563.)

and chemical adsorption, and to indicate the nature of the bonding of pyridine to these surfaces (Fig. 8).

The Raman spectrum of acetone adsorbed onto  $\gamma$  alumina<sup>434</sup> exhibits bands at 1575, 1625 and 1685–1703  $\text{cm}^{-1}$  which are not present in the spectrum of liquid acetone. The first two bands are due to an electron donor–electron acceptor complex. The band at 1685–1703  $\text{cm}^{-1}$  is attributed to a hydrogen-bridge bond between the C–O group and a surface hydroxyl group.

#### (v) The Raman spectra of black compounds

A restrictive requirement of Raman spectroscopy is that the sample should not absorb the exciting wavelength. This restriction resulted in all studies using the mercury arc 4358 Å exciting line being confined to colourless samples. The advent of tuneable laser sources has almost totally overcome the "colour problem", nevertheless black compounds still present an exciting challenge to the Raman spectroscopist.

The usual technique for obtaining the Raman spectra of black compounds is the back scattering method, in which the same surface is used for excitation and for collection of the Raman scattered radiation. Due to the absorption characteristics of the material the observed spectra are induced in a thin surface layer, and it is thus surprisingly possible to excite the spectra of black samples with any exciting wavelength provided it is of sufficient power.

The first report of the Raman spectrum of an opaque material appeared in 1965 when Russell reported the Raman spectrum of silicon using He/Ne excitation

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(ref. 435). Beattie and Gilson have recently reported the Raman spectra of the nearly opaque materials  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  using both He/Ne and  $\text{Ar}^+$  (green 5145 Å) excitation<sup>436</sup>.

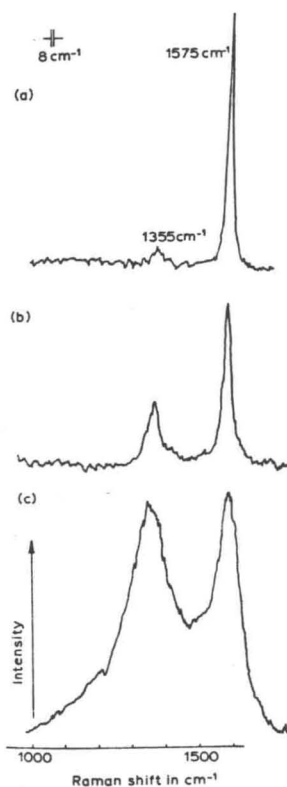


Fig. 9. Comparison of the Raman spectra of (a) stress-annealed pyrolytic graphite, (b) a commercial graphite and (c) activated charcoal. (Reproduced from F. Tuinstra and J. L. Koenig, *J. Chem. Phys.*, 53 (1970) 1126.)

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The complex formed between niobium tetrafluoride and pyridine is a black compound, whose Raman spectrum has been obtained using He/Ne excitation<sup>437</sup>. Comparison of the low frequency infrared and Raman spectra suggests that the complex has the *trans*-NbF<sub>4</sub> · 2py structure.

The Raman spectra of single crystals of graphite and other graphite materials have been obtained using blue Ar<sup>+</sup> 4880 Å excitation<sup>438</sup> (Fig. 9). Single crystals of graphite show a single band at 1575 cm<sup>-1</sup>. Other materials like stress-annealed pyrolytic graphite, commercial graphites, activated charcoal, lampblack and vitreous carbon, give an additional band at 1355 cm<sup>-1</sup>. The intensity of the additional band is inversely proportional to the crystallite size and can be used to estimate the crystallite size in the surface layer of any carbon sample.

The compounds Re<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub> · 2H<sub>2</sub>O and Re<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>Br<sub>4</sub> · 2H<sub>2</sub>O are extremely dark blue and dark green, respectively, so much so that in bulk they appear to be black compounds. The Raman spectra have been obtained using Kr 6471 Å excitation<sup>439</sup>. The spectra contain a strong band at 280 cm<sup>-1</sup>, which is possibly due to the vibrational mode of the Re-Re bond, which is thought to have a bond order of the order of four.

### 3. PRESSURE CHANGES

Lippincott et al.<sup>440</sup> first described a high-pressure diamond anvil cell for use in infrared spectroscopy in 1959. During the period under review, this type of cell has been adapted for use in Raman and far-infrared spectroscopy and a number of interesting pressure-induced changes have been reported.

Several publications have appeared concerned with the effect of pressure on far-infrared spectra. It has been shown that the internal modes of vibration of a polyatomic species show only small minor shifts under high pressure, while lattice modes show much larger shifts<sup>12</sup>. Thus the  $\nu_4(f_2)$  band of Na<sub>2</sub>SO<sub>4</sub> at 622 cm<sup>-1</sup> is displaced to 625 cm<sup>-1</sup> on increasing the pressure to 35,000 atm, while the lattice mode at 183 cm<sup>-1</sup> shifts to 235 cm<sup>-1</sup>. It has also been observed that changes in band shapes and intensities occur; in general, bands become broader with increasing pressure<sup>441,442</sup>.

Pressure effects (up to 50,000 atm) upon the symmetric and antisymmetric metal halogen stretching modes of coordination compounds have been measured (ref. 443) (Fig. 10). The frequencies are relatively insensitive to pressure, but the intensities of the symmetric bands decrease to a much greater extent than the intensities of the antisymmetric bands. This technique has thus been proposed as a method of distinguishing symmetric and antisymmetric metal-halogen stretching modes.

The red → yellow phase transition in mercuric iodide can be induced at a pressure of 13 kilobars. This transition has been followed using Raman spectroscopy.

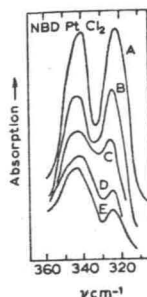


Fig. 10. Pt-Cl stretching bands as a function of pressure in (NBD)PtCl<sub>2</sub>, a square-planar structure. (NBD = norbornadiene) Curves are displaced vertically: (A) atmospheric pressure (341, 322 cm<sup>-1</sup>); (B) 6000 atm (345, 325 cm<sup>-1</sup>); (C) 12,000 atm (343, 326 cm<sup>-1</sup>); (D) 18,000 atm (343, 326 cm<sup>-1</sup>); (E) 24,000 atm (345, 325 cm<sup>-1</sup>). (Reproduced from C. Postmus, K. Nakamoto and J. R. Ferraro, *Inorg. Chem.*, 6 (1967) 2194.)

copy<sup>444,445</sup> and the spectral changes are similar to those observed during the temperature-induced<sup>78</sup> red → yellow phase transition at 126 °C. The effect of pressure on the Raman spectrum of α-quartz has been reported<sup>446</sup>, together with the pressure-induced phase transition in thallos iodide<sup>447</sup>.

The effect of pressure on the infrared spectra of coordination<sup>448,449</sup> complexes containing (CH<sub>3</sub>)<sub>2</sub>S, pyrazine and 2,2'-bipyridyl have been observed. It is found that certain molecular vibrations of the ligands are much more pressure sensitive than others. The frequencies of the lattice modes of square planar and octahedral platinum and palladium compounds have been found to be much more pressure dependent than the frequencies of the internal modes<sup>450</sup>. A high-pressure spectroscopic study of hydrogen-bonded compounds has shown that increasing pressure shortens the hydrogen bond<sup>451,452</sup>.

Pressure studies on calcium carbonate indicate that a new polymorph is produced at pressures greater than 50 kilobars having a vaterite-type structure<sup>453</sup>. Trioxane is thought to undergo a change in molecular conformation from C<sub>3v</sub> to D<sub>3h</sub> at high pressure<sup>454</sup>.

The liquid and solid phase Raman spectra of Br<sub>2</sub> and CS<sub>2</sub> have been obtained at high pressure<sup>455</sup>. Single crystals of three polymorphs of CH<sub>3</sub>CN and CD<sub>3</sub>CN have been studied at high pressure and the data have been used to predict likely crystal structures for the three crystalline phases<sup>456</sup>. The effect of pressure on the Fermi resonance doublet in the infrared spectrum of NH<sub>4</sub><sup>+</sup> isolated in CsBr has been reported<sup>457</sup>.

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### MOLECULAR STRUCTURE OF NITROGEN TRICHLORIDE AS DETERMINED BY ELECTRON DIFFRACTION

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#### ABSTRACT

Nitrogen trichloride was found to have a bond length of  $r_e = 1.759 \pm 0.002$  Å and a Cl-N-Cl angle of  $107.1 \pm 0.5^\circ$ . The bond angle is larger than that found in  $\text{NF}_3$ , consistent with the (recently revised) trends displayed by the trihalides of phosphorus and arsenic, but much lower than the  $120^\circ$  angle reported for the isoelectronic molecule  $\text{N}(\text{SiH}_3)_3$ . Moreover, a comparison between selected compounds reveals that the N-Cl bond length is appreciably greater, relatively, than the N-Si bond length. Accordingly, the bond angles and bond lengths suggest a greater reluctance of the nitrogen lone pairs to delocalize onto Cl than onto  $\text{SiH}_3$  groups. Mean amplitudes of vibration of  $\text{NCl}_3$  were derived both from the diffraction data and from recently published infrared and Raman frequencies. The values agree within the estimated uncertainties.

#### INTRODUCTION

Nitrogen trichloride, a simple molecule, has long invited speculation about its unknown structure. On the one hand it is isoelectronic with  $\text{N}(\text{SiH}_3)_3^1$ , a planar molecule. On the other hand, it is expected to be pyramidal according to the Valence-Shell-Electron-Pair-Repulsion (VSEPR) model of Sidgwick and Powell, and Gillespie and Nyholm<sup>2</sup>. Indeed, the VSEPR postulates call for bond angles smaller than tetrahedral and smaller, even, than those in  $\text{NH}_3$  because of the high electronegativity of chlorine. Until recently, the propensity of the compound to explode discouraged direct structural studies. Improved techniques for handling the material led to infrared and Raman work in the liquid and vapor phases<sup>3-5</sup>, in which the compound was diluted by inert substances. These investigations revealed that  $\text{NCl}_3$  is pyramidal rather than planar. They have also suggested that the bond angle is in the vicinity of  $108^\circ$ . It looked possible to extend the dilu-