

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><sup>1</sup>. 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.

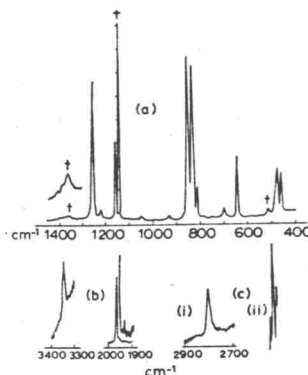


Fig. 1. Raman spectra of guest molecules in  $\beta$ -quinol clathrates. (a) SO<sub>2</sub>, Kr 5682 Å excitation, 23 mW at sample, SO<sub>2</sub> bands marked \*; (b) C<sub>2</sub>H<sub>2</sub>; (c) HCl, (i) sample at room temperature, (ii) sample at 77° K. Spectra (b) and (c) used Kr 5208 Å excitation, 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>.