

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 crystals¹ and of compounds in the gaseous phase² 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 Menzies³ (1953) and by Loudon⁴ (1964), while the infrared spectra of crystals have been reviewed by Vedder and Hornig⁵ (1961), by Dows⁶ (1963 and 1965) and by Mitra and Gielisse⁷ (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 halides⁸ 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 cm^{-1} ;
- (iii) their frequency and intensity are temperature¹¹ and pressure¹² 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 phases¹³.

(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), ethylene²⁰⁵, the ammonium ion²⁵⁸ and the phosphonium ion²⁶¹. Single crystal Raman spectroscopy can also be used to classify lattice modes²³¹.