

methods are developing so rapidly that fast publication in this field is essential, even at the cost of sacrificing elegant presentation, if the aim of reaching a maximum number of the crystallographic community at the right time is to be achieved.

The contents of the book do not give a balanced account of the different schools of thought, as the title might suggest. The Buffalo–Bari–Amsterdam–Glasgow school is well represented, the York school is present but the absence of the Washington school is regretted.

On the positive side, it must be said that much of the material it contains is of high quality and of enduring value. That, coupled with a modest price, makes it a worthwhile purchase for individuals interested in direct methods and an essential acquisition for the crystallographic library shelf.

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Molecular spectroscopy. Vol. 5. Senior reporters R. F. BARROW, D. A. LONG and J. SHERIDAN. Pp. ix + 277. London: The Chemical Society, 1978. Price £26.00, \$52.00.

Two articles in this volume are of considerable crystallographic interest. This review mainly concentrates on these two chapters.

In the spectral region between 2 and 20 μm , tunable laser spectroscopy is now used. In Chapter 5 (by S. D. Smith) spin-flip laser technology is discussed. In practice, a spin-flip laser is based on a laser cavity consisting of a crystal of InSb and a pump laser of either CO_2 , for the range 9.3–10.8 μm , or CO, for the range 5.3–6 μm .

Chapter 6 (by R. Schrader) is devoted to Raman and infrared spectroscopy of molecular crystals. Vibrational spectroscopy of molecular crystals is of fundamental interest for the study of intramolecular vibrations, for the study of crystal structures and the dynamics of crystals, and also for the study of intermolecular forces and interactions. Up to six different Raman spectra can be observed by using single crystals. The discussion covers (i) vibrational states of a free molecule in the gaseous state, (ii) the oriented-gas model, (iii) the site-group model, (iv) the factor-group model and (v) the coupling of motions of the unit cells within a crystal.

Factor-group analysis is realized in the following steps: (a) vibrational states of the free molecule, (b) vibrational states of the molecule under the constraints of its site symmetry, (c)

vibrational states of the unit cell and (d) correlation of the degrees of freedom of motion of the free molecule, of the molecule on its lattice site, and of the unit cell.

In the case of unknown molecular or crystal symmetry the analysis of crystal spectra can lead to conclusions about the probable crystal symmetry: for example, the low-temperature phase (<116 K) of hexamethylbenzene.

The calculation of vibrational frequencies in molecular crystals is discussed. Intermolecular elastic forces, vibrations of linear lattices and vibrations of polyatomic unit cells and three-dimensional lattices are observed. Interatomic-force constants for different non-bonded pairs of atoms ($\text{H}\cdots\text{H}$, $\text{S}\cdots\text{H}$, $\text{O}\cdots\text{H}$ and $\text{N}\cdots\text{N}$) are given.

Shimanouchi and co-workers treat a unit cell as a 'giant molecule', which is attached to its neighbours by elastic forces (flexible-molecule model and simplified method, treating molecules as rigid units). Calculations with the 'rigid-molecule' model and with the 'flexible-molecule' model have been performed for many molecular crystals.

Intermolecular charge-transfer plays an important role. Several authors have succeeded in reproducing the vibrational spectra of organic polymers by similar calculation methods.

Raman and IR intensities are theoretically important and, in practice, are useful additional parameters of the vibrational bands, especially for the study of molecular crystals. Most previous work was based upon relative intensities and is discussed in the oriented-gas-model approximation and the so-called Kastler–Rousset model (for example, the thiourea crystal). Translational vibrations and librational modes observed in Raman or IR spectra can be explained by intermolecular perturbations of the valence-electron system of the crystal, as shown by quantum-mechanical calculations (molecular orbitals).

The vibrational spectra of molecular crystals are sensitive detectors of changes in structural features. A number of studies of molecular crystals have concentrated on the investigation of the lattice vibrations which are the most specific feature of the crystalline state. A number of measurements have been reported of the internal molecular modes in molecular single crystals.

In studies of the crystalline state, methods of vibrational spectroscopy are used in combination with other methods – X-ray scattering by molecular crystals, reorientational processes, and neutron spectroscopy.

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