

## Notes and News

*Acta Cryst.* (1979). A35, 701

### Request for Donations of Publications and Geological Specimens

On 18 March 1978 a fire destroyed a large part of the University of Lisbon, namely the building where the Faculty of Science and the Natural History Museum were located. The Mineralogical and Geological Museums were almost completely destroyed, together with all records and specimens, as was the Library belonging to the Geological Society of

Portugal, entrusted to the Department, and all its books, maps, etc. were lost in the fire.

Under these circumstances, teaching and research activities are almost impossible, and the Department is making an appeal for international assistance, requesting donations of books, magazines and geological specimens (including minerals, rocks and fossils).

Offers of assistance should be sent to Professor C. A. de Matos Alves, Head of the Department of Mineralogy and Geology, Faculty of Science, University of Lisbon, Lisbon, Portugal.

## Book Reviews

*Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.*

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**Molecular vibrations in crystals.** By J. C. DECIUS and R. M. HEXTER. Pp. xii + 391. Maidenhead, England: McGraw-Hill, 1977. Price, US \$29.50, £15.60.

Group theoretical methods, applied to the vibrational analysis of isolated molecules, culminated in the FG matrix formalism and are well known to every chemist interested in infrared or Raman spectroscopy.

The present book extends these methods to the more complex situation in which the molecules, neutral or ionized, are embodied in a crystal without loss of individuality. This leads to the use of internal coordinates as dynamic variables. In this approach the force constants matrix **F** has a clear physical significance. The difficulty is transferred to the calculation of the **G** matrix, both matrices being necessary in order to write down the equations of motion with the aid of these coordinates.

To develop this programme, the authors explain in detail the fundamental notions of space group and wave vector group and how to construct translationally adapted internal coordinates. The reader is progressively accustomed to the various difficulties by working out simple examples; linear crystals, linear polymers, tridimensional mono- or diatomic crystals, including calculation of phonon dispersion curves. Infrared and Raman selection rules for one or two phonon processes and analysis of Van Hove's critical points are carefully studied.

An important part of the book is devoted to the calculation of the splitting into multiplets of the molecular vibrational levels by two methods: (a) the FG matrices (on the basis of 'normal molecular coordinates'); (b) the vibrational exciton. Intermolecular force models currently used, dipole-dipole or atom-atom interactions, are compared. An interesting discussion concerns the effect of the crystallite shape on the multiplet splitting resulting from long range forces, and the effect of these forces on the splitting of LO and TO modes is carefully discussed. The last chapter

deals with the problems of impurities, of isotopic substitutions in crystals and of molecules in rare gas matrices.

Finally, numerous clear tables complement this book: characters, selection rules, correlation tables, list of the 230 space groups, and tabulation of all distinct sites in every space group. This well documented book is thus very useful to the research worker in solid-state vibrational spectroscopy.

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**Direct methods in crystallography.** Edited by H. A. HAUPTMAN. Pp. 301. Obtainable from Polycrystal Book Service, PO Box 11567, Pittsburgh, Pennsylvania 15238, USA. 1978. Price \$13.50.

This book contains the proceedings of the Symposium on Direct Methods in Crystallography held in Buffalo in early August 1976. The reviewer received his copy in mid-January 1979. Such a phase shift places him in a delicate situation. Should he necessarily assert that all is best in the best of all possible worlds and so be agreeable to the editor?

About 95% of the material presented here has already been published elsewhere, in many articles in *Acta Crystallographica*, in a book and in lecture notes on schools and meetings held in York (1974), Prague (1975), Erice (1978) and Twente (1978). The idea of capturing within the covers of a single volume the essential contributions of the participants, as stated in the preface, is indeed a very good one but the final product, hampered by such a delay, can today only interest a minority of specialists or historians. Direct

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  $\mu\text{m}$ , 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  $\text{CO}_2$ , for the range 9.3–10.8  $\mu\text{m}$ , or CO, for the range 5.3–6  $\mu\text{m}$ .

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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