Diffuse X-ray scattering and the internal modes of molecular crystals

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Diffuse X-ray scattering and the internal modes of molecular crystals

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We investigate the effect of the internal modes of vibration of a molecular crystal on the diffuse X-ray diffraction pattern. Use is made of optical transform techniques to model the six in-plane modes of benzene. While the contribution of each mode to the scattering pattern is quite distinctive and characteristic of the particular mode, the combined effect of all the modes is of a form not easily separated from the scattering due to the external modes.

1. Introduction

In view of David Craig's early interest in the vibrational modes of benzene, his later interest in the organic solid state, and our own interest in diffuse X-ray scattering from molecular crystals, we have chosen as our contribution to this issue an account of some recent work on the effect of the internal modes of vibration of a molecular crystal on its diffuse X-ray scattering pattern. We describe some experiments using optical transform techniques (see Lipson 1973) on a simple two-dimensional model system of benzene molecules arranged on a regular rectangular lattice, and we investigate the effect of the six in-plane modes on the scattering pattern.

Although the theory of thermal diffuse scattering in terms of lattice modes has been well established for many years (see e.g. Born 1943, Lonsdale 1943), molecular crystals present some rather special difficulties which discourage a completely rigorous analysis. On the one hand the large number of atoms and often low symmetry means that a normal coordinate analysis is not usually a viable proposition, while on the other, treatment in terms of the rigid-body motions of the molecule neglects completely the 'internal' modes. Thomas and Ghosh (1975) (see also Willis and Pryor 1975, p. 192) have shown that the internal modes of a molecular crystal do contribute significantly to the mean square amplitude of vibration at room temperature and at low temperatures their contribution is dominant. For benzene itself Johnson (1970) has deduced from spectroscopic data that r.m.s. displacements at room temperature due to internal modes are ~ 0.03–0.04 Å for carbon, which corresponds to about 15–20 per cent of the total.

2. Background

The thermal diffuse X-ray scattering pattern of a molecular crystal (particularly of aromatic molecules) has a very striking appearance and two seemingly distinct types of diffuse scattering are evident. The first type of TDS occurs as diffuse peaks localized around the stronger lattice (Bragg) peaks, while the second consists of broader regions of diffuse scattering which, although having a distinctive pattern in reciprocal space, are not associated with the lattice peaks and occur at quite general positions in reciprocal space. Cases of each type of scattering can be found for example in Wooster (1962). The first type of scattering may be attributed to the low-frequency acoustic modes of the

crystal and similar TDS scattering is found for all types of crystal. It is this type of scattering which may be measured to yield elastic constants for the crystal (see e.g. Prasad and Wooster 1956). The second type of scattering is found only in molecular crystals and is often attributed to the 'independent rigid-body' motions of the molecules (see e.g. Amoros and Amoros 1968).

Since strictly speaking all TDS is attributable to modes of vibration of the whole crystal, this dissemination into two distinct types of scattering appears somewhat artificial. However, Amores *et al.* (1960) showed that the assumption of independent rigid-body motion leads to a description of the second type of TDS in terms of the Difference Fourier Transform (DFT) and this gives good agreement with the observed scattering for many examples. In simplest terms the DFT function may be written as

$$DFT = |F_m|^2 \{1 - \exp(-2M)\}$$

where $\exp(-M)$ is the normal Deby–Waller factor and F_m is the molecular scattering factor. An optical simulation of this form of DFT is shown in figure 2 (*a*). It is the molecular scattering factor, F_m, the Fourier transform of the molecular electron density, which gives the function the characteristic and easily recognizable distribution in reciprocal space.

It is instructive to consider the different contributions to the atomic displacements and to the X-ray scattering pattern in terms of the different regions of the phonon dispersion-curve diagram. We show in figure 1 a schematic diagram of the dispersion curves for a molecular crystal. The scattering of an X-ray photon as a result of interaction with a phonon of wavevector **q** results in scattered intensity at points in
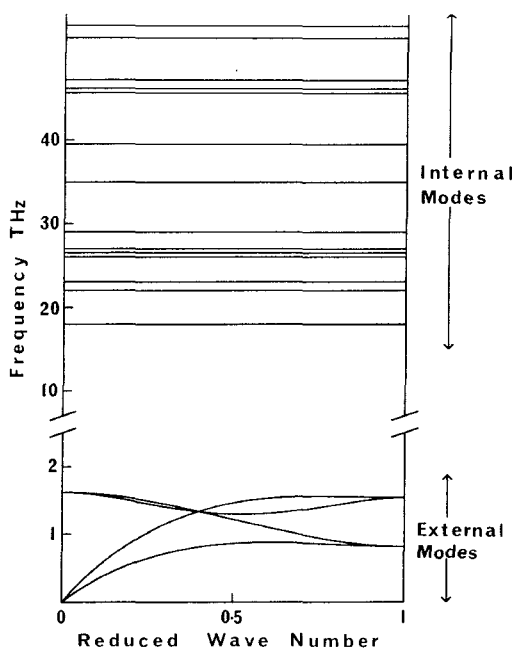

Figure 1.   Phonon dispersion curves for a typical molecular crystal, showing dispersionless internal modes and dispersive external modes. At room temperature kT is about 6 THz.

reciprocal space displaced from the Bragg peaks by the vector **q**. This means that at each point in diffraction space there is a contribution to the scattering from modes of vibration in each of the phonon branches. (Note that in neutron scattering the contribution from individual branches may be recorded separately using energy resolution.) The intensity occurring will depend not only on geometrical structure factors applicable to each mode but also on the phonon population.

All of the external phonon branches lie well below the value of kT at room temperature and so all modes on these branches will be well populated with phonons. By far the highest population will occur for the modes with the lowest energies near the zero wave-number end of the acoustic branches, and it is this region which results in the first type of TDS scattering. The remaining regions of the external branches are seen to be relatively dispersionless, i.e. the energy changes only slowly with wavevector and the population of these regions of the phonon branches will be relatively constant. This leads to the approximation that apart from the regions near the Bragg peaks the diffuse scattering can be well described by assuming independent rigid-body motions. The internal modes occur generally well above kT and will be predominantly in their ground state. (Consequently their contribution changes little when the temperature is reduced.)

Although at room temperatures the external modes are undoubtedly responsible for the major part of the diffuse scattering, as we mentioned earlier the effect of the internal modes on the mean-square amplitudes is not negligible and it is therefore somewhat surprising that their contribution to the diffuse scattering seems to have been ignored. Because these internal modes are practically dispersionless they may to a very good approximation be considered to arise from independent motions of the molecules, and since the average shape of the molecule in each of the modes will have a scattering factor similar to F_m, it seemed a possibility that their contribution to the diffuse scattering could be of a form very similar to the Amoros DFT, and as a consequence this scattering would perhaps not have been recognized. In order to investigate this possibility we undertook the present study on a model system of benzene molecules.

3. Optical experiments

For X-ray diffraction the hydrogen scattering factors are small in comparison with those for carbon and, moreover, decay more rapidly with diffraction angle, so for the purpose of this work we neglect the effects of the hydrogen atoms. We deal only with the six in-plane modes of benzene which involve the carbon atoms. These modes are depicted in figure 2 and further details are given in the table.

Each of these modes was simulated in an optical diffraction experiment by plotting on a photographic film individual molecular representations, one at each site of a square lattice. For details of this technique see Harburn *et al.* (1974). Each realization was of the molecule distorted from its equilibrium hexagonal geometry by a random amount of the appropriate normal coordinate. The random variables used were normally distributed with zero mean and a variance chosen to give a suitable mean-square atomic displacement. The scale of this photographic plot, which was chosen for convenience, was such that the basic $12.5\,\mu m$ plotting grid represented $0.1\,\text{Å}$, and transparent $50\,\mu m$ diameter apertures were used to represent the atoms. The molecules were placed on a lattice of a spacing representing a unit cell dimension of $4.8\,\text{Å}$ which was again chosen for convenience. In all, each diffraction mask contained 28 900 molecular representations and covered an area of $10 \times 10\,\text{cm}$. A small portion of a typical diffraction mask is shown in figure 3 (*i*). Optical diffraction patterns were
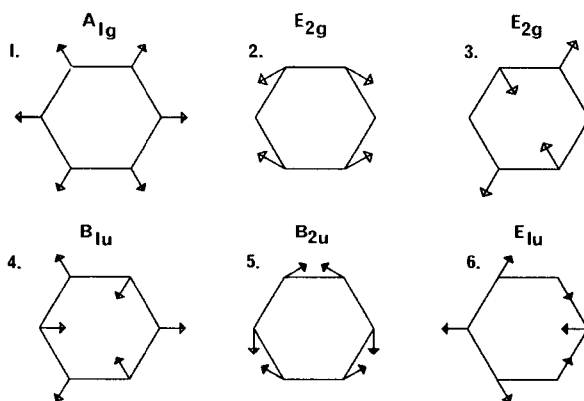
Figure 2.   The six in-plane modes of benzene. See also the table.

The six in-plane modes of benzene in which the effects of hydrogen are neglected. The modes are listed in the order in which they appear in figure 2. The frequency number and symmetry are as given by Herzberg (1966) and the frequencies as given by Painter & Koenig (1977).

Mode	Number	Symmetry	Frequency (cm^{-1})	Degeneracy
1	v_2	A_{1g}	992	1
2	v_{16}	E_{2g}	1596	2
3	v_{18}	E_{2g}	606	2
4	v_6	B_{1u}	1008	1
5	v_9	B_{2u}	1309	1
6	v_{13}	E_{1u}	1479	2

obtained from these masks using an optical diffractometer similar to that described by Harburn et al. (1975). Because of the finite resolution of the plotting grid the magnitude of the atomic displacements was chosen somewhat larger ($\sim 3 \times$) than the 0·03–0·04 Å expected in real crystals. This is not expected to affect the distribution of the intensity substantially but only to increase its magnitude. For the degenerate modes 2, 3 and 6 the effects of the symmetry-equivalent motions were included simultaneously by subjecting the atoms to independent random displacements along the two normal coordinates. In these cases the total r.m.s. displacement for each atom was set to be the same as for the single modes 1, 4 and 5. The optical transforms for each of the modes are shown in figures 3 (b)–(g). Diffraction masks including combinations of the modes were also generated. In each case the total r.m.s. displacement was maintained at the chosen level by suitably reducing the amount of each contributing mode. We here show, because of space limitations, only the pattern obtained from a mask containing an equal mix of all six modes (figure 3 (h)).
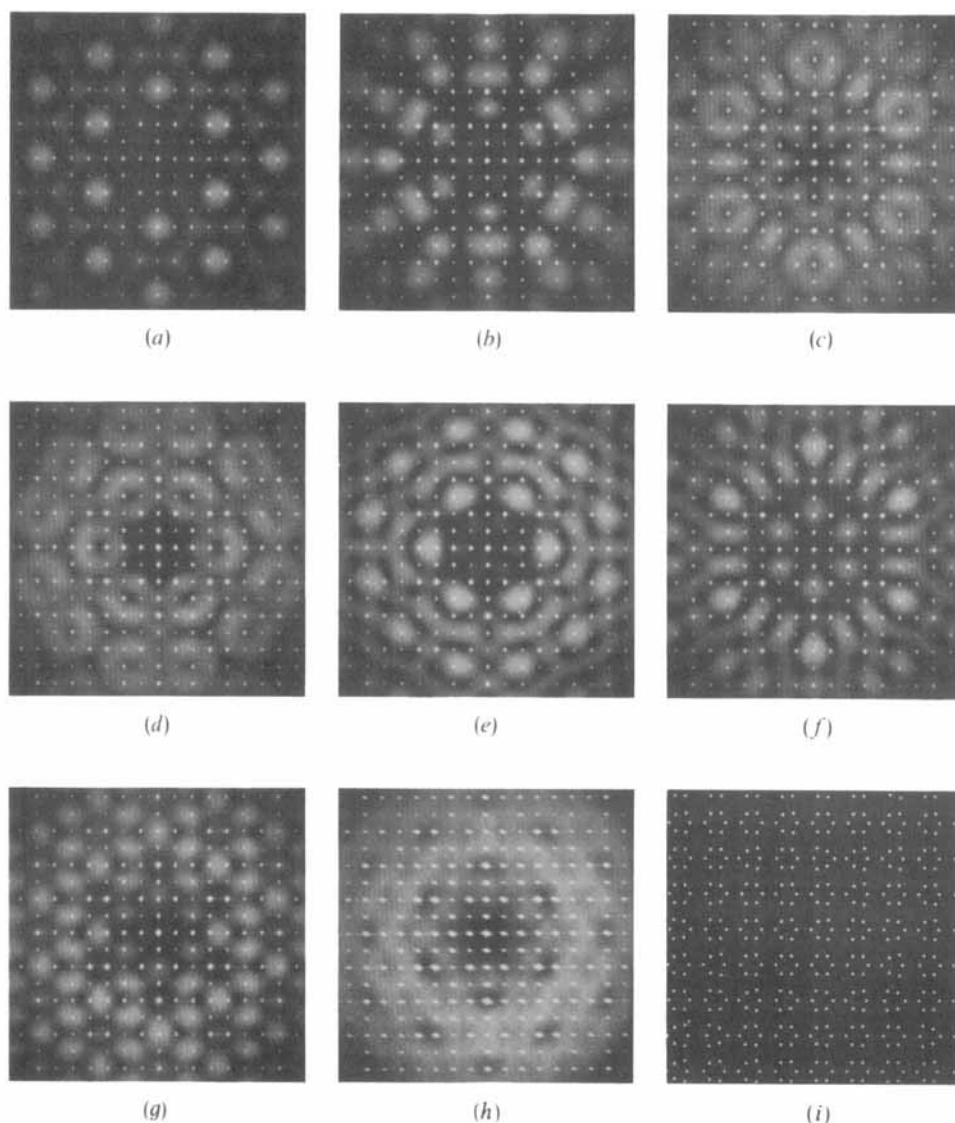
Figure 3. Optical diffraction patterns of simulated vibration modes of benzene. (*a*) DFT Function. (*b*) Mode 1. (*c*) Mode 2. (*d*) Mode 3. (*e*) Mode 4. (*f*) Mode 5. (*g*) Mode 6. (*h*) Modes 1–6. (*i*) Portion of mask used for (*e*).

4. Discussion

The optical diffraction pattern of each of the six benzene vibration modes (figure 3) shows a pattern of broad diffuse peaks arranged in a striking spatial pattern whose features are obviously unrelated to the Bragg peaks but rather derive from the size and orientation of the benzene molecules. In no case is the pattern similar to the DFT pattern of figure 3 (*a*), so that individually there is little reason to suppose that they could not be distinguished from it. However, we see from 3 (*h*), obtained from the mask which included all six modes in combination, that a quite different pattern emerges. Here no very distinct peaks are to be seen and in fact the pattern displays rather a

uniform distribution but containing a series of minima which form a distinctive pattern. Close inspection shows that these minima coincide with the positions of the maxima in the DFT of figure 3 (*a*). The effect of adding this contribution of the internal modes to the DFT scattering would thus merely reduce the relative height of the peaks somewhat and add a certain amount of structureless background scattering. There seems little doubt that this scattering would be difficult to separate from that due to the external modes.

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