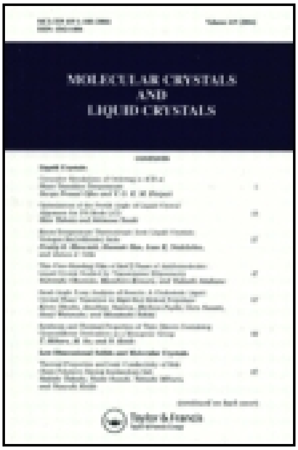

Molecular Crystals

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Diffraction Studies of Molecular Motion

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Diffraction Studies of Molecular Motion‡

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Abstract—The accuracy of present-day X-ray and neutron diffraction studies is such that root-mean-square vibrational amplitudes of atoms in complex structures can be determined to an accuracy of 0.01 Å or better. These amplitudes are usually in agreement with spectroscopically derived frequencies where these are available. With the aid of suitable models, amplitudes of rigid body rotations, translations, screw motions, and of internal rotations may be obtained. Such information is invaluable in the interpretation of spectra from complex crystals and in the understanding of intermolecular forces. Several examples from recent work at Brookhaven will be given.

Introduction

Diffraction studies of crystal structures continue to play an important role in the investigation of many problems in the solid state. In particular, the chemistry of the solid state depends intimately on structure; without an understanding of the geometrical structural relationships of molecules, any discussion of reaction mechanisms hangs on an extremely tenuous thread. There are few chemists today who do not make use of the results of crystal structure determinations in their work. Furthermore, advances in automated data collection and structure solution and refinement have made it possible to include in the attack on a chemical problem the solution of several related crystal structures.

Although geometrical relationships are important for the understanding of reactions and phase transformations in solids, energy

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relationships are equally important. It is the forces between molecules that determine what they will do in any circumstance. There are many ways of studying intermolecular forces, and it is perhaps not so widely realized that diffraction is again one of the best methods.

(In making this statement and the arguments that follow, I am not suggesting that diffraction should be used alone in any such study; nor should it be entirely neglected. Any problem of dynamics in the solid state can only be adequately understood if several techniques have been brought to bear on it. These might include vibrational and electronic spectroscopy, nuclear magnetic resonance phenomena, and diffraction.)

In a conventional diffraction study of a crystal structure, the pertinent quantities available from the experiment are the amplitudes of motion of the individual atoms in the crystal. Since these motions depend on the potential field in which each atom moves, we are thus in a position to learn something about these potential fields and hence about force constants governing the intermolecular interactions. As in most techniques used for the study of complex systems, the amount of information available is considerably less than the complexity of the situation demands for a complete description. Hence, some model must be introduced in order to bridge the gap between what is measured and what is needed. It is in the choice of a suitable model that consideration of the results of other types of experiments becomes important. We may imagine the situation is as indicated in Fig. 1.

In this paper, I will attempt to give some idea of the accuracy with which vibrational amplitudes can be determined and to make a few remarks about models. I will not pursue the discussion to the point of obtaining actual potential functions for molecular crystals. This topic will have been discussed by others at this conference.

Before getting to the present examples, I would like to offer some prognoses regarding a related field—namely, neutron spectroscopy—which is, after all, a form of diffraction. Neutron inelastic scattering from single crystals can be used to measure the complete phonon dispersion curves (vibrational spectra) for molecular crystals. A wealth of information regarding intermolecular forces is available in such experiments. A combination of these results with conventional structural and spectroscopic studies can lead to a detailed description

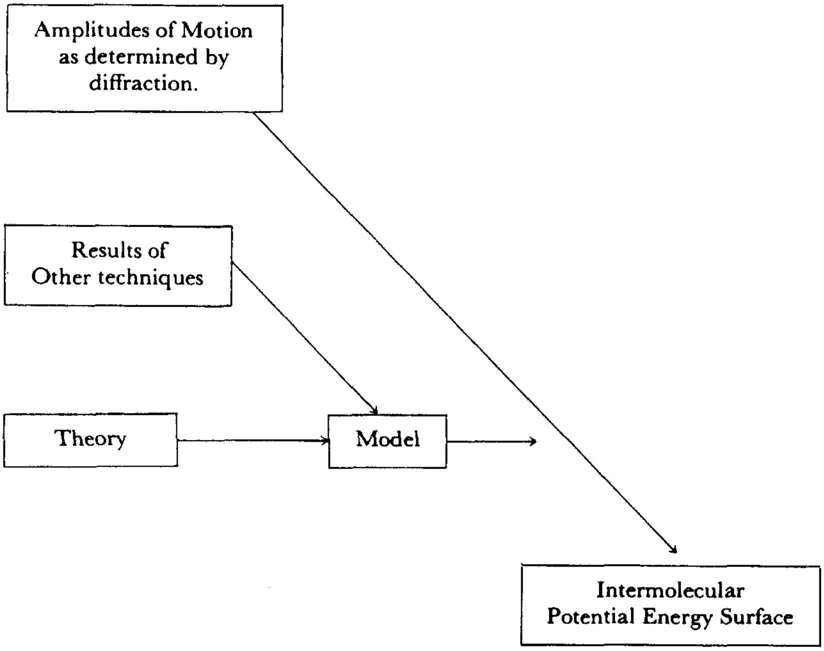

Figure 1. Derivation of potential energy surfaces from diffraction data.

of intermolecular force fields that was thought impossible some years ago. A number of laboratories are doing work along these lines, and at Brookhaven we contemplate a broad attack on the study of intermolecular forces in molecular crystals by these techniques.

Vibration Amplitudes Determined by Diffraction Theory

The structure factor F for a Bragg reflection characterized by a reciprocal lattice vector $\mathbf{h}$ may be written in terms of the position vectors of the atoms $\mathbf{r}_i$, the atomic scattering factors f_i and the *temperature factor* T_i as

$$F(\mathbf{h}) = \sum_i f_i(\mathbf{h}) T_i(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}_i) \tag{1}$$

The temperature factor $T_i(\mathbf{h})$ depends not only on the reciprocal lattice vector $\mathbf{h}$ but on parameters describing the motion of the individual atoms. The form of T_i as a function of these parameters constitutes a model of the (thermal) motion. T_i is in fact the Fourier transform of the time-average distribution of the atomic position:

$$T_i(\mathbf{h}) = \int \rho_i(\mathbf{r}) \exp(-2\pi i \mathbf{h}\cdot\mathbf{r})\, d\mathbf{r} \qquad (2)$$

One of the techniques used in the analysis of crystal structure data is Fourier inversion of the structure factors to obtain a scattering density distribution:

$$\rho(\mathbf{r}) = \sum_j F(\mathbf{h}) \exp(2\pi i \mathbf{h}_j\cdot\mathbf{r}) \qquad (3)$$

Ideally, one could look at the peaks in this scattering density distribution to determine precisely the form of the motions of the individual atoms. In actual practice, $\rho(\mathbf{r})$ is a convolution of the motion of the atoms, the distribution of scattering density for an atom at rest,‡ and a function describing the data cut-off (series termination).

The most fruitful approach in the determination of vibrational amplitudes from diffraction studies has been to assume a model for $\rho(\mathbf{r}_i)$ and hence for $T_i(\mathbf{h})$ and to refine the parameters of this model by least squares procedures—just as the other parameters of a crystal structure are usually determined.

The model which is most often used is the model of harmonic motion. The position distribution of a point undergoing three-dimensional harmonic motion may be described as a Gaussian function

$$\rho(\mathbf{r}_i) = \rho^0(\mathbf{r}_i) \exp(-\tfrac{1}{2}\mathbf{r}'\mathbf{U}^{-1}\mathbf{r}_i) \qquad (4)$$

where **U** is a second order tensor whose elements give the second moments of the position distribution of the atom. Since the Fourier transform of a Gaussian is also a Gaussian, we find that

$$T_i(\mathbf{h}) = \exp(-2\pi^2 \mathbf{h}'\mathbf{U}\mathbf{h}) \qquad (5)$$

The components of **U** can be determined by a least squares refinement to fit the observed structure factors. Now the exponent of Eq. (4) describes an ellipsoid:

$$\mathbf{r}_i'\mathbf{U}^{-1}\mathbf{r}_i = 1 \qquad (6)$$

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‡ Dr. Philip Coppens in another paper at this symposium discusses the determination of bonding effects in electron density distributions as determined by X-ray diffraction studies.

with principal axes whose lengths are given by the square roots of the eigenvalues of **U**. The lengths of these axes are the root-mean-square (rms) amplitudes in the principal directions of vibration.

A useful pictorial representation of the motion is obtained by drawing the ellipsoid corresponding to Eq. (6). Figure 2, for example, illustrates the motion of the atoms in a methyl group in an organic compound (potassium hydrogen diaspirinate) as determined by neutron diffraction.[1] One can clearly see the hindred rotation of the methyl group in the large amplitudes of vibration of the hydrogen atoms perpendicular to the C—H bonds. A model of harmonic motion has already been imposed to reach this stage of presentation. It is probably approximately correct. Further specifications of model must be given if we are to say anything more.

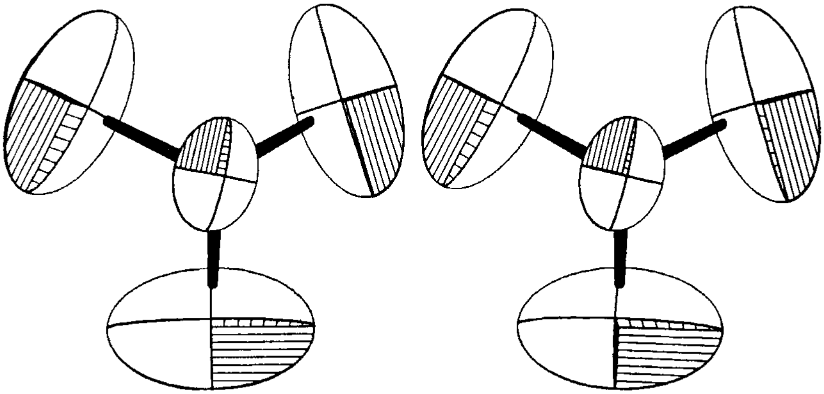

Figure 2. Amplitudes of thermal motion in the methyl group of potassium dihydrogen aspirinate. This, as well as several of the other figures, are stereo drawings and may be viewed by a small hand-held stereoscope.

One such extension would be to assume that methyl group is rigid —that the CH_3 group moves as an entity with a fixed geometrical configuration. If we assume this model and assume that the description of the methyl group as given in Fig. 2 is valid, we may conclude that the ellipsoid for the central carbon atom properly describes the translational motion of the group as a whole and that the difference between the ellipsoids describing the hydrogen atom motions and that describing the carbon atom motion gives a true picture of the hindered rotation. The rms components perpendicular to the bonds of the difference ellipsoids have magnitudes 0.52, 0.50 and 0.57Å (each to ± 0.02) respectively. The mean value is 0.53Å. For a harmonic oscillator in its ground state, this amplitude would correspond to a frequency of 65 cm^{-1}. At room temperature, where the experiment was done, there would in fact be a large population in the excited states; taking this into consideration would lead to a fundamental frequency of 100 cm^{-1}. A more realistic model for the motion would be governed by a potential of the form $V = V_0(1 - \cos 3\theta)$. The barrier height V_0 would be only a few hundred cm^{-1}. By examining the rms amplitudes as a function of temperature and by considering refinements of the model for the motion, one could obtain reasonably accurate parameters for the potential function assumed.

With regard to accuracy, we may note that in careful diffraction studies the mean square amplitudes of vibration can be determined to about 10 per cent. A root mean square amplitude of 0.20 Å might thus have an associated error of 0.01 Å. It follows that vibrational frequencies can also be determined to this accuracy *providing a suitable model exists*; unfortunately, the models for internal rotation modes of complex crystals are probably not adequate. We must also note that crystallographic experiments may be plagued by systematic errors which can increase the errors in the determination of the rms amplitudes by an order of magnitude. The present experimental situation is that a careful worker can achieve the accuracy quoted; the average crystal structure reported in the literature has probably not achieved this accuracy.

Some Further Examples

Potassium hydrogen bisacetylsalicylate—whose methyl group we have just discussed—has been the subject of both accurate X-ray[2] and neutron diffraction studies. The agreement between these studies was good and suggests that amplitudes of motion accurate to 10 per cent may be obtained by either method. There may be, however, systematic differences between the two methods, and these differences have been exploited with great success by Dr. Coppens, whose paper has also been presented in this symposium.

It seems worthwhile to draw attention to some of the other points in the potassium hydrogen diaspirinate structure which are characteristic of high accuracy structural investigations. The dimeric anion in this crystal has the structure shown in Fig. 3. The two

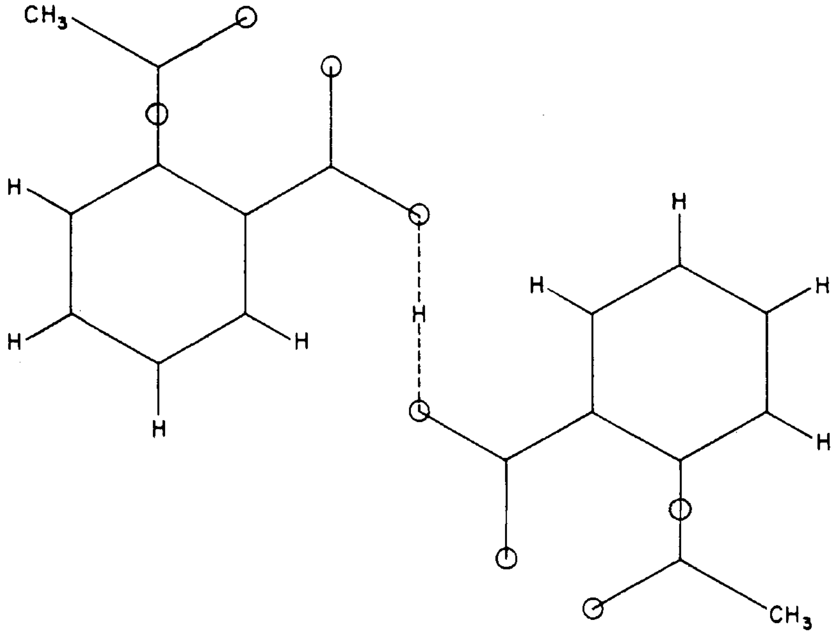

Figure 3. The hydrogen diaspirinate anion, a typical hydrogen bonded dimer found in a number of carboxylic acid salts.

aspirin anions are bound together by a symmetric hydrogen bond. The ellipsoids of thermal motion are illustrated in Fig. 4. The

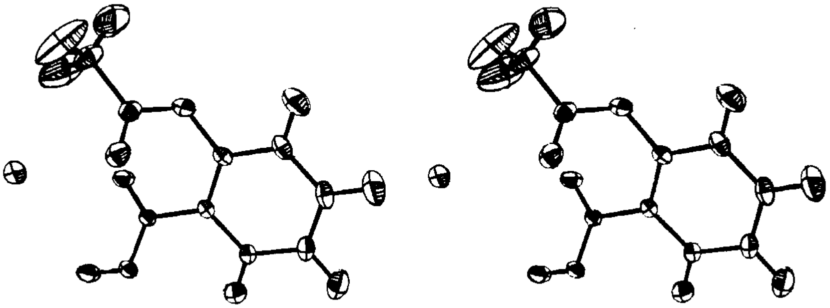

Figure 4. Half of the diaspirinate anion, showing thermal ellipsoids.

hindered rotation of the methyl group is again obvious. Furthermore, in the motion of the hydrogen atoms on the benzene ring, one may clearly see the superposition of the oscillatory motion of the molecule as a whole and the bending vibrations of the hydrogen atoms with respect to the C_6 ring. Our interest in potassium hydrogen diaspirinate was in the nature of the short, strong hydrogen bond.

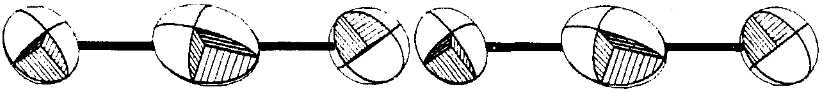

Figure 5. Thermal ellipsoids in the the short O–H–O hydrogen bond in the diaspirinate anion.

The amplitudes of atomic motions for the three atoms involved are shown in Fig. 5. An attempt to subtract out the rigid body motions of the molecule results in an ellipsoid for the hydrogen atom (Fig. 6) which can be interpreted in terms of a potential surface for the hydrogen bond similar to that shown in Fig. 7. The details will be found elsewhere.[1,3]

Figure 6. Identical to Fig. 5, but the hydrogen atom motion has been corrected for the molecular rigid body motions. The remaining amplitudes are typical of the motion of a hydrogen atom in the field of the two oxygen atoms in a short, symmetric hydrogen bond.

The motions of many molecular crystals can be described in terms of the motions of rigid bodies; the amplitudes of internal vibrations are typically an order of magnitude smaller than those characteristic of the motions of the molecules as a whole in the crystal lattice. This is fortunate in that we can assume to a first approximation that the motions of all the atoms in the molecule are due to the motions of the molecule as a rigid body. (The main exceptions are the cases where there may be internal rotations such as that of the methyl group just described, and internal vibrations involving hydrogen atoms—which may have relatively large amplitudes because of the small mass of the hydrogen atom.) In the general case, there are 20 independent

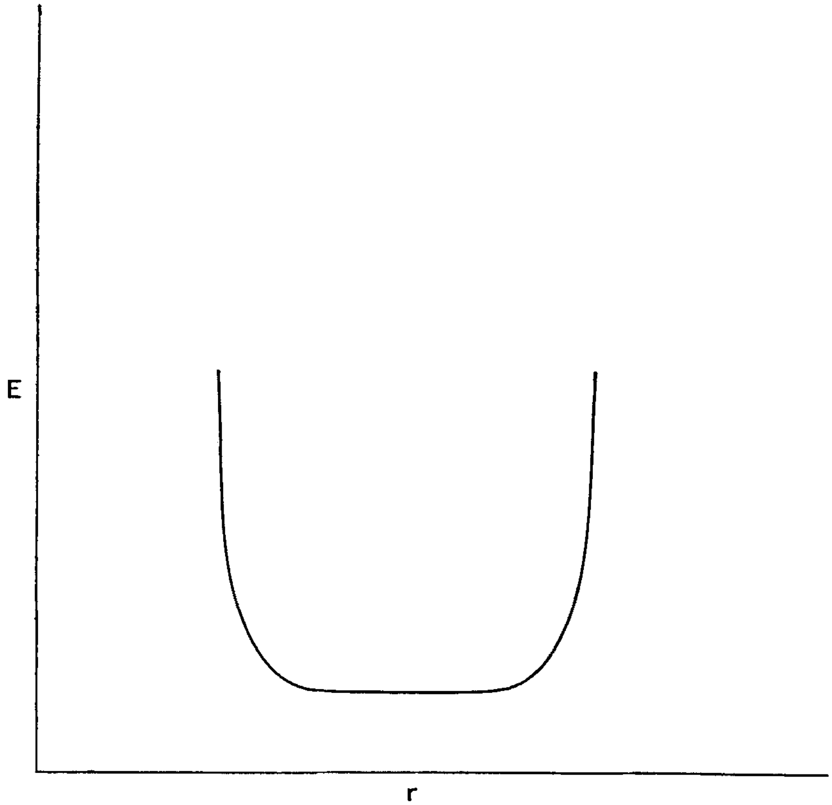

Figure 7. The potential energy surface for motion of the hydrogen atom in a short, symmetrical hydrogen bond.

parameters describing the motion of a rigid body in a crystal. These motions may be described in terms of the following parameters.[4]

1. A symmetric tensor (6 parameters) describing the amplitudes and directions of the principal translations of the rigid body.
2. A symmetric tensor (six parameters) describing the amplitudes and directions of the rotations of the rigid body.
3. An asymmetric tensor (nine parameters) describing the correlations between the rotations and the translations to give effective screw motions.

A conservation condition reduces the effective number of parameters to 20. There is no unique way of breaking the parameters down in this way; the details of the *description* depend on the choice of origin. Schomaker and Trueblood have suggested that the most convenient way to describe these motions is as follows:

The amplitudes and directions of three pure translations
(again six parameters)
The directions of three rotation-translation (screw) axes
(three parameters)
The positions of these axes relative to some origin—perhaps the center of mass of the molecule
(six parameters)
The amplitudes of rotation with respect to the screw axes
(three parameters)
The translation accompanying each of the rotations—the screw pitch
(three parameters)

Again one of these is redundant, and there is a certain degree of arbitrariness; Schomaker and Trueblood propose a convention which will probably become a standard—namely, that the trace of the rotation-translation tensor be set to zero.

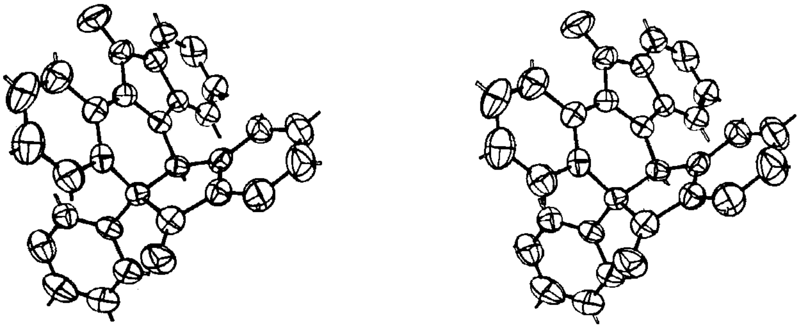

Figure 8. The molecular structure of 14c-Hydro-5a-phenylbenz(a)-indeno (2-1-c) fluorene-5, 10, dione. ($C_{30}H_{18}O_2$ phenylcinnamalone).

To clarify the nature of these motions, let us refer to Figs. 8 and 9. The structure analyzed was that of a relatively rigid organic molecule—phenylcinnamalone.[5] The pure translations were approximately isotropic with rms amplitudes of 0.21, 0.20, 0.19 Å. Figure 9 indicates that two screw axes intersect at some distance from the molecular mass center and that the other screw axis does not intersect the first two. There is no translation motion associated with one of the rotation axes. For the axis with an rms amplitude of 2.3°, this rotation is accompanied by a translation of 0.05Å. The rotation with a rms amplitude of 3.3° is accompanied by a translation of 0.03Å. The interpretation of these rigid body motions in terms of intermolecular potentials will be interesting indeed.

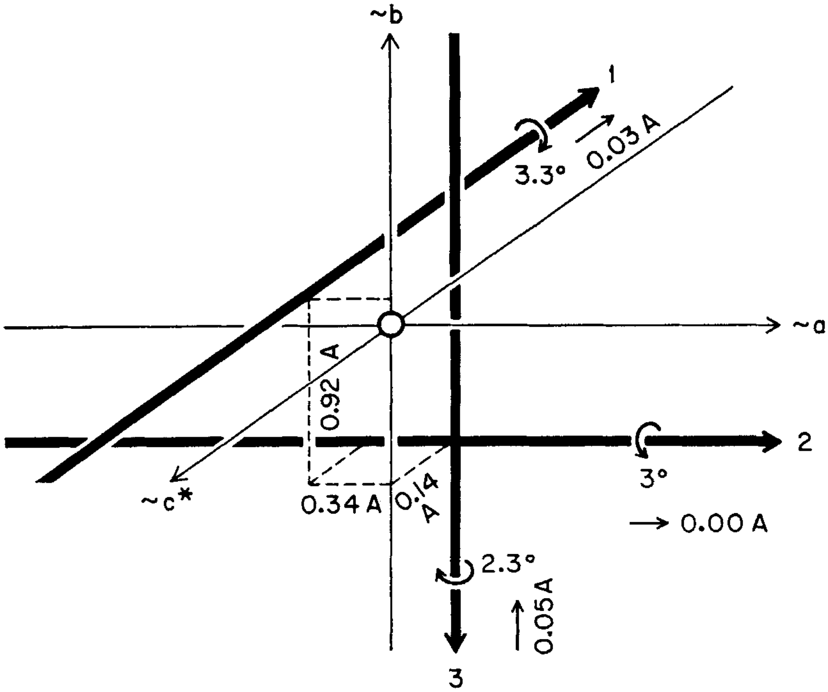

Figure 9. Components of screw-rotation motions in phenylcinnamalone.

Although most treatments of rigid body motion to date have fit the individual atomic U tensors to a set of rigid body parameters, this approach does neglect the fact that the internal modes make a small but significant contribution to the atomic motions. If a complete normal coordinate model were available, one could of course attempt to refine parameters involving both the internal and external modes.

In the absence of such information, it seems reasonable to calculate the amplitudes of the internal modes from spectroscopic data on the same or related molecules, to subtract these amplitudes from the observed amplitudes, and finally to analyze the residuals in terms of rigid body motions (including internal rotations if necessary.) Such an approach has been suggested and applied by C. K. Johnson.[6]

The possible applicability of these approaches to molecules in general may be illustrated by three molecules chosen at random from our recent experience at Brookhaven.

Decaborane. We have recently carried out a neutron diffraction refinement of the structure of an isotopically substituted decaborane $^{11}B_{10}{}^{2}H_{14}$.[7] The molecular structure with the ellipsoids of thermal vibration are shown in Fig. 10. Decaborane has a cage-like structure and, except for some extra bending motion associated with the singly-bonded hydrogens, should approximate rigid-body motion very well. The nearly isotropic rotation of the molecule about its center-of-mass is obvious from an examination of the figure.

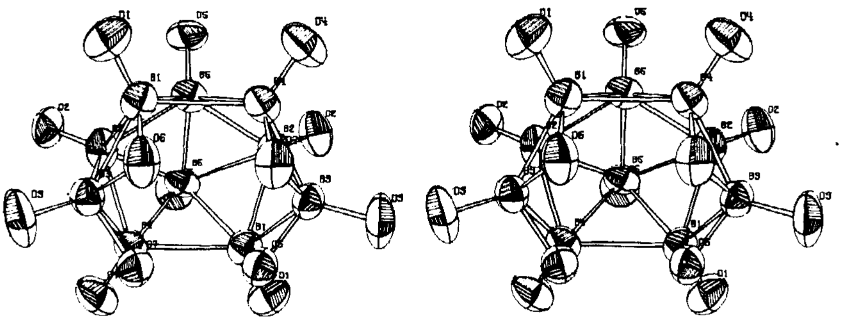

Figure 10. Thermal ellipsoid plot of decaborane as determined by neutron diffraction.

In the oncolytic drug methylglyozal*bis*guanylhydrazine dihydrochloride monohydrate (Fig. 10, Hamilton and LaPlaca[8]) several effects are obvious. (i) The rigid carbon-nitrogen backbone of the molecule is not undergoing particularly large amplitudes of rotation perpendicular to the axis of the molecule; (ii) There is some suggestion of a larger amplitude of rotation around the long molecular axis; (iii) The methyl groups as well as the amino groups are undergoing larger amplitudes of internal rotation; (iv) the translational motions

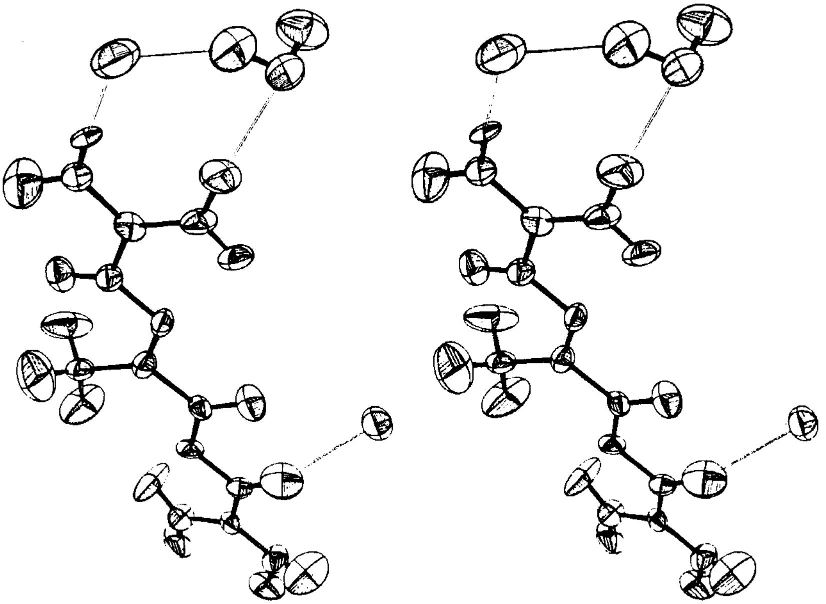

Figure 11. Thermal ellipsoid plot of methylglyoxalbisguanylhydrazone dihydrochloride monohydrate.

of the chloride ion and the water molecule are considerably greater than those of the methylGAG positive ion; (v) some wagging of the water molecule is apparent; (vi) the lack of agreement among the NH_2 groups and the peculiar shapes of some of the ellipsoids suggests that the accuracy of this study was not as high as we might have hoped.

In a phenanthrenequinone triisopropylphosphite adduct,[9] Fig. 12,

Figure 12. Thermal ellipsoid plot of 2,2,2-triisopropoxy-4,5-(2′,2″-biphenyleno)-1,3,2-dioxaphospholene.

a general picture of rotation around the center of mass is again seen—the amplitudes of the far-out atoms on the phenanthrene ring being considerably larger than those close to the central phosphorus atom. Superimposed on the overall molecular rotation is the internal rotation in the isopropoxy groups leading to very large amplitudes for the rotations of the terminal $(CH_3)_2C$— group around the C—O bond. (The hydrogen atoms are not shown).

Conclusions and Prognosis

Present-day experimental diffraction techniques allow the determination of amplitudes of atomic motion in molecular crystals to accuracies of a few per cent. These motions in many cases may be adequately described in terms of the motions of rigid-body molecules. Although these rigid-body motions have been determined for many molecules, their interpretation in terms of intermolecular force fields has been conspicuous by its absence. The coupling of information concerning rigid body amplitudes from diffraction studies and frequencies obtained from conventional and neutron spectroscopic techniques should lead over the next few years to an enormous increase in our understanding of intermolecular force fields.

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