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Microscopic and Bulk Elastic Properties in Supramolecular Systems: Guest–Host Interactions in Dianin's Inclusion Compounds

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Abstract—The relationship of bulk properties of materials to the microscopic interactions of the moieties that comprise them is demonstrated by connecting the guest–host interactions of a series of crystals of Dianin's inclusion compounds to their bulk moduli of elasticity and linear compressibilities. These quantities' values are presented for the guest-free Dianin's lattice, the clathrand, as well as Dianin's inclusion compounds with ethanol and heptanol guests. The role of collective vibrational states of the crystals is emphasized in determining the bulk elastic properties of these supramolecular materials. Microscopic guest–host interactions are examined to rationalize the trends in the observed macroscopic elastic properties. The use of elastic multipoles and mechanical susceptibilities is suggested as a way of modeling the interactions of molecules in solids so that the collective and local interactions can be included in designing the desired bulk properties of materials. The use of elastic multipoles in a fashion similar to atomic orbitals in understanding intermolecular interactions in a solid is discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Materials chemistry continues to increase in importance as indicated by the number of papers published each year and by the number of researchers entering the field. Although materials science has existed as a separate discipline for decades, chemists have not been major players. With the advent of new molecular systems that display novel properties and the recognized approach of devices on the molecular scale, the role of chemistry is of increasing importance in the creation and assembly of new materials. Since most devices must be ponderable and robust, it is natural that solids be a major focus. Thus, the assembly of molecules into useful solid materials and the susceptibility of such systems to chemical reaction becomes of great importance.

There are many considerations in creating a new material. From the chemist's viewpoint, the main problem is how to get molecules possessing particular properties to assemble into solids which exhibit specific bulk characteristics that lie within a defined range. Assembly may be achieved through solid state reactions or by crystallization through careful control of the interparticle interactions of the moieties comprising the solid. In either case, the great difficulty that arises is being able to extrapolate the bulk behavior from the properties of individual molecular entities.

For solids whose attributes are those of an oriented gas, the bulk responses of the material can be easily understood by taking a given molecular property and allowing for its modification through geometrical corrections due to packing. In this case, the properties are merely tensorially additive and anisotropic only because of molecular orientations. However, most condensed matter exhibits properties that are significantly altered from those observed for the single molecule. Chemists are unsurprised that six carbon and six hydrogen atoms form a substance whose properties are not those of a simple mixture of those atoms. Bonding significantly alters the properties of the aggregate of these atoms, the molecule. In solids, it is the intermolecular forces that lead to similar, albeit not as profound, modification of fundamental particle properties. A homely analogy is that of the often reported loss of an individual's typical behavior when part of a large crowd. The 'mob psychology' of the molecular entities comprising the solid is paramount in understanding its bulk properties.[1]

A common manifestation of collective properties is found in the optical properties of dye crystals[2–5] where it is sometimes reported as chromoisomerism.[6] A striking example is found in a study of the squarylium dye, 2,4-bis(4-dimethylamino-2-hydroxyphenyl) cyclobutadienediylium-1,3-diolate (HEAPS), which presents both monoclinic and triclinic crystals.[7] The HEAPS molecule's geometry is *identical* in

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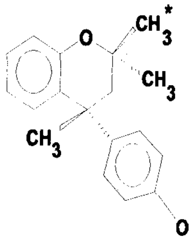
the two lattices although their relative orientations are significantly different. The monoclinic crystal resembles a piece of highly polished copper while the triclinic one looks like shiny, blueish gun-metal. The electronic spectra vary widely for different faces of a given crystal and cannot be explained by an oriented-gas model. The unusual optical response of HEAPS crystals is accounted for by the coupling of the electronic excitations of the molecules with each other and with the incident photic field—the so-called exciton–polariton coupling. These pseudoparticles, excitons and polaritons, represent collective interactions of electromagnetic *excitations of the crystal* which must be invoked if the bulk optical properties are to be understood. The treatment of collective interactions through pseudoparticles is a common approach in trying to understand bulk phenomena of condensed phases.

While it is possible to deduce certain simple structural contributions to bulk behavior, e.g. covalently bound or hydrogen-bonded moieties to achieve increased hardness, most properties arise from collective interactions which involve many molecular properties. Systematic study of how bulk properties can be affected by chemical modification of the constituent molecules would provide insight into this problem. The related question of how chemical reactions are influenced by collective interactions is also pertinent.[8]

A bulk property of fundamental importance is the modulus of elasticity. Clearly, this bulk quantity must represent the anisotropic interactions of the crystal and must conform to the crystal's symmetry. A necessary property of any solid, indeed any condensed phase, is that it exhibit elasticity. The very formation of such a phase requires the presence of forces between the particles that comprise the material; any assembly of molecules must exhibit elastic behavior. Crystallization itself is a process in which elastic interactions are created. Further, a solid state reaction necessarily changes the crystal's elastic interactions and has been shown to be greatly influenced by the elastic forces of the lattice in which it occurs.[9] From this perspective, elastic forces can be envisaged as the 'bonding' responsible for the architecture of supramolecular systems.

Elasticity suggests a way of thinking about the assemblage of molecules in to crystals or reactions of molecules in crystals. It embodies collective interactions, since the intermolecular force constants can be combined to yield the elastic constants of a crystal which, in turn, can be used to determine the bulk modulus. We show later that there is a way of formulating these elastic interactions into a formalism that is recognizable to chemists and which can be related to ways of thinking that pervade chemistry. The study of elasticity of organic solids is, therefore, an important aspect of understanding their properties and reactivity.

Experimentally, it is desirable to find systems where some of the particles comprising the crystal can be easily changed without massive reorganization of the underlying structure itself or without destroying crystallinity. Inclusion compounds meet this criterion with their usually facile substitution of many different guests in a host lattice. Dianin's inclusion compounds are ideal for such a study since their crystals are relatively easy to grow and, most importantly, a guest-free crystal, a so-called clathrand, has been reported that has the same framework as the inclusion compounds. This provides an ideal reference for perturbations by guests.



Dianin's Molecule: 4-p-hydroxylphenyl-2,2,4-triphenylchroman
(* waist methyl group)

These systems are also useful for understanding reactions in molecular crystals. In such reactions, the products are, until there is a large conversion, essentially inclusions or guests within the host lattice of the reactant molecules. Thus, the reaction trajectory of a solid state reaction is controlled for most of the course of the reaction by the environment, essentially the elasticity, of the reactant–host lattice.[10] Depending upon the nature of the guest–host interaction, the solid state reaction may proceed as a crystal-to-crystal reaction (an intact reaction), or the reacting solid may shatter (a broken reaction). In either case, the guest–host interaction affects the elasticity of the medium. Inclusion compound crystals clearly can serve as models for guest–host interactions of intact reactions.

In their own right, inclusion crystals, a subclass of supramolecular systems, exhibit interesting and novel physical properties. Other inclusion crystals, such as the cyclodextrins, exhibit chemical behaviors that are not found in unaggregated states. This widens the paradigm of chemistry beyond that focused on materials with strong bonds between atoms comprising the substance. Our view must be changed to encompass not only organization, composition, geometry, and topology but also the energetics of molecular assemblies. The fashion in which these features interplay to define molecular architecture can be identified as molecular recognition and assembly. This concept is of greater universality than crystal packing.

It is thus necessary to obtain linkage between the mechanical and molecular description of supramolecular systems, or equivalently, between a structural and a dynamic description in terms of bonding, intermolecular interactions, and stereochemistry. This requires understanding of host–host, host–guest, and guest–guest interactions. In the crudest approximation, these may be modeled by two non-interacting subsystems: an elastic host framework with guest molecules contained by steric barriers. However, a host–guest relationship limited only to steric considerations misses major characteristics of these systems. The interplay between the host lattice and guest molecules may manifest itself through a modified conformation of the guests or hosts or a difference in guest or host motional freedom from that found in other phases. The temperature and pressure dependence of these behaviors are notable since they reveal the importance of collective interactions. For example, the

Table 1. Crystallographic and physical constants for Dianin's inclusion compounds

Crystal data	Clathrand[13]	Ethanol[14]	Heptanol[15]
Number of guests	0	2	1
Crystal system	Trigonal	Trigonal	Trigonal
Space group	$\mathbf{R\bar{3}}$	$\mathbf{R\bar{3}}$	$\mathbf{R\bar{3}}$
a (Å)	26.94±0.01	26.969±0.002	27.12±0.03
c (Å)	10.94±0.01	10.990±0.002	11.02±0.02
a (°)	90.00	90.00	90.00
b (°)	90.00	90.00	90.00
g (°)	120.00	120.00	120.00
Z (Hexagonal)	18	24	21
r_{calc} (kg/m^3)	1162	1223	1210
Melting point (°C)	160.2	169.2	163.5

temperature dependence of the thermal conductivity of clathrate hydrates as well as Dianin's inclusion compounds is uncharacteristic of crystalline materials.[11] And certain urea inclusion compounds demonstrate stress-induced domain reorientations that show long-range interactions and cooperative phenomena.[12]

The inclusion crystals fail to conform to the conventional description of a crystalline phase in an interesting way: they are neither mixed crystals nor molecular solutions. They are characterized by a well-defined host framework and, very often, statically or dynamically disordered, and possibly quite flexible, guests. This very complex structure is mirrored by large energetic variances among the various interactions. Thus, application of the traditional harmonic model to inclusion compound lattice dynamics is problematic. For example, the host lattice of Dianin's compound clathrates is built from stacks of highly ordered supramolecular units composed of six molecules that form cages where guests, undergoing significant motions relative to the host, reside.

In this paper, we report the bulk moduli of elasticity and linear compressibilities for Dianin's clathrand and the ethanol and heptanol Dianin's clathrates. We discuss how these vary and suggest basic microscopic interactions that account for these differences. In the next section we present the basic structural information for these compounds. We next describe the nature of the inelastic light scattering measurements that permit the materials' elastic constants to be obtained with subsequent determination of their bulk moduli of elasticity and linear compressibilities. Arguments based on microscopic interactions are presented for the observed trends in these quantities. The concept of elastic multipoles is then advanced and discussion ensues on how this model can be used to understand solid state reactions and bulk mechanical properties of assemblages of molecules.

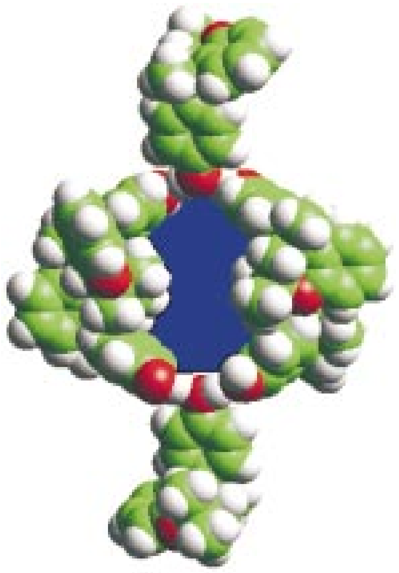


Figure 1. View of Dianin's compound cage with two opposite chroman molecules removed.

Elastic Properties of Dianin's Inclusion Compounds

Crystal growth and structure

The ethanol and heptanol inclusion compound crystals were grown from chroman solutions with the respective guests as solvent. The clathrand was grown from decanol solutions. The solutions were initially formed at a temperature of 45°C (ethanol and heptanol clathrates) or 65°C (clathrand) and crystals grown through slow cooling at rates of approximately 1°C per day. Details are available elsewhere.[16]

The three Dianin's clathrate systems investigated in this study crystallize in the same trigonal space group with six individual Dianin's molecules per unit cell (hexagonal setting). Table 1 lists the pertinent crystallographic and physical data for these three systems. The only structural differences arise from variation in the unit cell dimensions that are dependent upon the type and number of guests.

Dianin's clathrate geometries are based on a hexameric supramolecular unit made up of six host Dianin's molecules linked together by hydrogen bonds through the phenolic hydroxyl groups. A distorted hexagon of oxygen atoms is associated with alternate chromans of opposite handedness (R and S) lying above and below the plane. Two such groups are stacked along the c-axis (referenced to a hexagonal unit cell) so that the bulky, pendant side groups interlock to form the walls of the cage. Fig. 1 displays a single-cage representation of Dianin's supramolecule. The equatorial waist is produced by inward-pointing methyl groups of the individual Dianin's molecules (marked by an asterisk in the drawing of the molecule). The three-fold crystallographic c-axis lies in the direction of the long-axis of the cage. The cage extends ~11 Å along this axis and is ~6.2 Å wide at its points of maximum extension at z~0.3 Å and z~0.7 Å. The top and bottom of the cages created by the hydrogen-bonded hexamer possess a diameter of ~2.8 Å and the inward-pointing methyl groups reduce the waist diameter of the cage to ~4.0 Å.

The two ethanol molecules per cavity in Dianin's compound host lattice are triply disordered as required by the three-fold rotation axis of the space group. However, only one heptanol molecule, also three-fold disordered about the cage axis and by inversion, is present in each cage and it assumes an extended gauche conformation along the cage axis in order to be included.

Inelastic light scattering

In condensed phases, thermal fluctuations give rise to sound waves that propagate through the medium. As with any sound wave, rarefaction and compression occurs and thus, for a condensed phase, the wave's properties must be a function of the elasticity. The propagating sound wave may be regarded as a grating from which Bragg diffraction may be observed. Clearly, the molecules in the unit cells of the lattice must be vibrating, and those vibrations involve collective translations of molecular centers of mass. These excitations, acoustic phonons, move through the lattice at the speed of sound. Their velocity depends on how easily the molecules in the unit cell can be displaced and is directly related to the equilibrium forces holding the masses in place.

An experimental technique that permits direct determination of a crystal's elasticity is Brillouin scattering.[17] The experimental utility of Brillouin scattering stems from its ability to probe the dynamics of elastic waves (acoustic phonons) of small amplitude in the crystal at equilibrium. Thus, it provides data for the determination of the stiffness matrix which is indispensable for description of a crystal's interactions, strength, and anisotropy.

Scattering in an anisotropic medium typified by the low symmetries of molecular crystals admits fewer assumptions than possible for high symmetry lattices. If we let $\mathbf{k}_\mathrm{s}$, $\mathbf{k}_\mathrm{i}$, and $\mathbf{q}$ represent the quasimomenta (wavevectors) of the scattered, incident, and acoustic waves, respectively, then conservation of momentum requires:

$$\mathbf{k}_\mathrm{s} = \mathbf{k}_\mathrm{i} \pm \mathbf{q} \tag{1}$$

and because of conservation of energy:

$$\hbar\omega_\mathrm{s} = \hbar\omega_\mathrm{i} \pm \hbar\omega_\mathrm{a} \tag{2}$$

where $\hbar\omega_\mathrm{s}$, $\hbar\omega_\mathrm{i}$ and $\hbar\omega_\mathrm{a}$ are the energies of the scattered and incident photons and acoustic phonon, respectively. Applying the law of cosines to these two equations results in the Brillouin shift equation:[16]

$$\delta\omega = \omega_0(v/c)(n_\mathrm{i}^2 + n_\mathrm{s}^2 - 2n_\mathrm{i}n_\mathrm{s}\cos\theta)^{1/2}. \tag{3}$$

Here, $\delta\omega$ is the frequency shift of the inelastically scattered light, ω_0 the frequency of the incident light, v the velocity of the phonon in the crystal, and c is the speed of light in vacuo. The indices of refraction of the medium in the direction of the incident and scattered light are n_i and n_s, respectively, and θ is the scattering angle. Measurement of the frequency shifts of the Brillouin components as a function of scattering angle and phonon propagation directions, $\mathbf{q}$, permits determination of a crystal's elastic constants using the Christoffel determinant:[18]

$$|\Gamma_{ij}(\mathbf{q}) - \rho v^2\mathbf{1}| = 0 \tag{4}$$

where ρ is the crystal density and $\Gamma_{ij}(\mathbf{q}) = c_{ijkl}q_kq_l$. The q_k and q_l are the direction cosines for the acoustic wave's wavevector, $\mathbf{q}$, to orthogonal reference axes k and l and c_{ijkl} are the elastic constants. The elastic wave velocities are the experimentally determined quantities and the elastic constants are derived from them.[19]

The Brillouin scattering apparatus used for measurement of elastic constants is similar to that employed in polarized, solid-state, Raman scattering experiments. However, the frequency shifts of an organic solid's acoustic phonons typically occur between 0.2 and 0.5 cm^{-1} and, as shown by Eq. (3), are angle dependent. Therefore, a multipass Fabry–Perot interferometer is employed in place of a multiple grating monochromator to resolve the Brillouin components. The angle between the incident and scattered light must be appropriately varied, and the laser line must be operated in single mode. A complete description can be found elsewhere.[20]

Experimental results: the bulk moduli and linear compressibilities

Detailed results of the Brillouin scattering measurements have been reported[16] and are not appropriate for discussion here. However, they have been used to obtain the bulk elastic properties of these Dianin's systems. The bulk modulus has more direct physical manifestations than the elastic tensor itself. The adiabatic bulk modulus, B_s, i.e. the ratio of applied hydrostatic pressure to resultant fractional change in volume is

$$B_\mathrm{s} = \left(\sum_{i,j=1}^{3} s_{iijj}\right)^{-1} \tag{5}$$

where the s_{iijj}'s refer to the appropriate elements of the compliance tensor. The bulk moduli for the three Dianin's derivatives are 5.58×10^9, 5.53×10^9, and 3.86×10^9 $\mathrm{N/m^2}$ for the clathrand and the ethanol and heptanol clathrates, respectively.

The unit cell dimensions of the clathrand and ethanol clathrates are very similar and the same trend is observed for their respective bulk moduli. However, the heptanol clathrate differs conspicuously from these two. The roles of these guests thus requires examination. The ethanol guest molecules must have a different function than the heptanol guests. The clathrand is the stiffest indicating that the cage assumed by this system is the most rigid and that the role of the guests is destabilizing. The ethanol guests are small enough to sit in the cavity in an unconstrained manner with little effect on the architecture or energetics of the system. Conversely, the heptanol guest significantly changes the unit cell dimensions. Within the regime of the stability of the crystal, the heptanol guest effects changes that cause the framework lattice to soften indicating a significant coupling between the guest and host molecules.

This behavior is not obvious within the context of the elasticity describing a continuous medium and homogeneous deformations. For molecular and especially bicomponent supramolecular crystals like Dianin's clathrand and its clathrates, it is imperative to take into account the repositioning of the molecules which minimizes the crystal energy when the lattice is under stress. This makes it possible to distinguish between the external and internal regimes of the crystal's elastic response as well as the interplay between external and internal strains and stresses leading to a renormalization of the effective elasticity via the coupling. The elastic regimes naturally reflect the behavior

Table 2. Linear compressibilities of Dianin's clathrand and two clathrates

β (10^{-11})	Clathrand	Ethanol	Heptanol
β_{xx}	0.844	0.634	0.904
β_{yy}	0.844	0.634	0.904
β_{zz}	0.106	0.539	0.778

of the phonon bath. The internal strains correspond to 'frozen' displacement patterns of Raman-active, optical phonons, whereas the external strains refer to zone-centered, acoustic phonons. This permits focus on the roles of the particular guests and neglect of the effect of the coupling intrinsic to the supramolecular character of Dianin's compound hexamers.

Obviously, the guest–host coupling is small for the ethanol clathrate. The ethanol molecules behave as if they have enough space to remain free in the cavity and thus the host framework dictates the crystal's behavior. This is consistent with the findings of Haeberlen et al. whose solid state NMR studies show that the two ethanols are exchanging positions within the cage.[21] Significant ethanol mobility is also indicated by dielectric measurements.[22] The situation changes for the heptanol clathrate. The heptanol, tightly positioned in the cavity, interacts with the host lattice and significantly affects the crystal's elasticity. This is attributed to the hydroxyl groups of the heptanol which are positioned to effectively compete for hydrogen bonds with the oxygens that comprise the hydrogen-bonded hexamer found at the top and bottom of the host cage. In addition, the heptanol is forced to thread through the waist of the cage and, because of the van der Waals diameter of the methylene chain, expansion of the waist occurs which also decreases the bulk modulus from that of the clathrand and ethanol inclusion compounds.

Complementary evidence is provided by another bulk quantity that conveys a more direct physical picture of the elastic forces for these three systems: the linear compressibility, β_{kk}. This is defined as the relative decrease in length of a line in the k-direction, e.g. a principal axis of the elastic constant tensor, under unit hydrostatic pressure, and is also related to components of the compliance tensor, s_{ijkl} (the numerical inverses of the elastic constant tensor) by the expression

$$\beta_{kk} = \sum_{i,j=1}^{3} s_{ijkk} l_i l_j \tag{6}$$

where the l_i and l_j are the direction cosines of the unit vectors. The values for the linear compressibilities along the major axes for the three clathrates are displayed in Table 2.

Comparison of the linear compressibilities along the $z(c)$-axis shows that the smallest compressibility for the three systems is parallel to the long-axis of the cage. The clathrand is shown to be the least compressible of the three in this direction followed by the ethanol and heptanol clathrates, respectively. The ethanol value argues that these guests could well be engaged in some minor competitive hydrogen-bonding with the cage's hydrogen-bonded hexameric unit. Even though the heptanol molecule is parallel to the cage axis it actually weakens the cage both in the axial direction due to the competitive hydrogen bonding and forced expansion of the cage. These results agree with the bulk moduli trends which show that the introduction of guest molecules dramatically weakens the host lattice in the $z(c)$-axis direction.

When the compressibility in the $xy(ab)$-plane is examined, the ethanol is shown to be the least compressible with the heptanol the most. This shows even more clearly than do the bulk moduli that the guests significantly influence the 'in-plane' structure. The ethanols are space-filling and essentially provide bulk to buttress the cage while the heptanol, because of its competitive hydrogen-bonding and dilatation of the cage waist, significantly softens the cage in directions perpendicular to the cage axis.

These results and the conclusions that flow from them are possible because of the close relationship of the systems studied and the fact that the perturbation, the guest, can be readily modified with concomitant monitoring of the bulk property. Thus, inclusion compounds are ideal for their ease in relating microscopic and macroscopic behaviors.

The trends in the bulk elastic properties of these Dianin's inclusion compounds can thus be related to the microscopic guest–host interactions. Although more detailed pictures of the interactions can be deduced from the trends in the elastic constants, the bulk moduli demonstrate convincingly, and on the microscopic level, that the observed trends can not only be rationalized by microscopic interactions but that in knowing these it is possible to control bulk trends. For example, significant reduction of the bulk elastic properties can be anticipated by including a guest such as hexanediol. This guest should increase the competitive hydrogen bonding and thereby reduce the bulk modulus.

The elastic multipole model for inclusion compounds and solid state reactions

Experimental studies of inclusion compounds often show nonphonon degrees of freedom. A resonant scattering model of the temperature evolution of the thermal conductivity indicates strong phonon scattering from guest vibrations.[23] That is, the matrix of localized guest vibrations behaves as if immersed in a continuum of elastic waves. The heat capacity analysis and NMR data also show that guests experience more intricate motions that just regular translational and librational modes. If disorder of the guests is modeled through averaging their positions over all cages, the ensuing array of guests might not reflect the periodicity of the host framework, e.g. a single guest may fill either the lower or upper part of the hour-glass cage of Dianin's inclusion compound. By taking Dianin's clathrand as the reference material, the clathrates will manifest their interactions as internal stresses or, equivalently, internal strains.

A model that combines the behavior and the dynamics of constituent molecular species into a complete picture is required. The differences in the unit cell dimensions between clathrates of the same compound usually allows for interpreting their crystallographic data as a specific distortion of the host framework. The deformation of the host lattice may be gauged by the strain energy as if it was under stress brought about by the forces ascribed to guests. This situation is best studied with a reference compound such as a clathrand. The relevant strains can then be computed from its assumed homogenous deformation. This permits determination of corresponding stresses that may be viewed as the distribution of forces between the guest and host units. Such an approach emphasizes the strain and stress fields that merge the dynamical behavior of the guests and host framework. It directly links the micro- and macroscopic properties that are characteristic of specific crystal architecture and dynamics. These strain/stress fields of particular symmetry describe the intermolecular interactions in analogy to how bonding describes interatomic interactions.

Clearly, the presence of stress and strain fields indicates the importance of elastic properties. The field properties suggest the use of quantities that will allow modeling of the energetics akin to how an electric dipole interacts with a polarization field. Or in further analogy, how the dielectric constant or electrical susceptibility are related to the electronic structure of a solid. Such a parallelism exists for the elastic (mechanical) behavior of a solid. The applicable concept is the elastic dipole (multipole) that has been introduced in the treatment of defects in crystals.[24,25] The aptness of this is clear when it is realized that either a guest in an inclusion compound or a product molecule in a reacting crystal can be viewed as 'defects' in their host crystals.

The elastic multipole has parallels to the electric multipole, yet there is not one-to-one correspondence. Nevertheless, the formalisms and conceptual frameworks are sufficiently similar to be useful for thinking about organic solids. For example, the interaction energy density of an electric dipole per unit concentration for those dipoles aligned in the nth orientation is:

$$\mathbf{u}_n = -\sum_{i=1}^{3} \mu_i^{(n)} E_i \tag{7}$$

where the $\mu_i^{(n)}$ are the Cartesian components of the nth electric dipole per unit volume per unit concentration and $\mathbf{E}$ is the electric field. The corresponding energy density of the interaction of the 'defects' with the stress field is:

$$\mathbf{u}_n = -\sum_{i,j=1}^{3} p_{ij}^{(n)} s_{ij} \tag{8}$$

where s_{ij} is the stress tensor and p_{ij} is the elastic dipole which reflects the homogeneous strain (without a rotation) in the crystal with components aligned along nth direction is introduced. However, the mechanical properties can also be defined using stresses, P_{ij}, i.e. as the negative stresses required to maintain the strain per unit concentration of 'defect.' These definitions are complementary and can be obtained from each other with the help of the elastic stiffness tensor $\mathbf{P}=f(\mathbf{C},\mathbf{p})$.

Another way to introduce the 'defect' and its mechanical effect on the lattice is through an elastic multipole expansion in the vein of the expansion of the potential of an electric charge distribution. This amounts to consideration of the distribution of forces that are different from those in the perfect or reference lattice. The displacements due to these forces can, after suitable mathematical manipulation, be expanded in a Taylor series that yields elastic multipoles.[23,24] The first nonvanishing multipole is the elastic dipole

$$p_{ij} = \sum_{k}^{N} r_{ik} f_{kj} \tag{9}$$

where the sum is taken over all forces $\mathbf{f}$ at position $\mathbf{r}$. In analogy with the two charges comprising the electric dipole, the elastic dipole represents two opposing forces whose magnitude goes to infinity as the distance between them approaches zero. In contrast to the electric dipole which is a vector, the elastic dipole is a tensor since strain is a symmetrical second rank tensor. The interaction energy between two elastic dipoles $\mathbf{p}_n$ and $\mathbf{p}_m$ is:

$$E = -\mathbf{p}_n \cdot \mathbf{e}_m \tag{10}$$

where $\mathbf{e}_m$ refers to the strain field due to the elastic dipole $\mathbf{p}_n$. Both the strain field and elastic dipole are related to the elastic behavior of the solid which, in turn, is a manifestation of the collective interactions of the molecules comprising the crystal.

It is also possible to define a mechanical susceptibility in analogy with its electrical counterpart.[8,9] This embodies the response of the medium to a mechanical field such as that created by a guest or product molecule in a lattice. This quantity can be directly related to molecular Debye–Waller factors and atomic displacement parameters (ADPs).[8,9] The mechanical susceptibility can then be used to calculate the deformation energy created by the 'defects' introduced in a given lattice.

The elastic multipoles embody the shape of the cavity in which the guest or product molecule is located together with the excess forces created by either of those entities. Since the multipoles are necessarily centered at some site, they can be represented by spherical harmonics, the same functions that are used to describe the angular dependence of hydrogen-like atomic orbitals.[8,9] For example, the elastic dipole could have 's-character' which would represent the hydrostatic stress and 'd-character' which would characterize the anisotropic (shear) stresses associated with an elastic dipole. In analogy with linear combinations of atomic orbitals, elastic multipoles as represented by spherical harmonics can be used to describe the excess forces created by the presence of a guest or product in the host lattice. This approach suggests that elastic multipoles can be used to understand the interaction of molecules in aggregate and parametrized to provide predictive capability.

Direct application to Dianin's clathrates can be made. The ethanol guest in its clathrate interacts little with the cage but does provide 'filler'. The elastic interaction is essentially spherical and would be represented by an s-type elastic dipole. The heptanol clathrate, however, is softened by competitive hydrogen-bonding of the guest with the hydrogen-bonded hexamers that define the top and bottom of the cage and by the expansion of the waist forced by

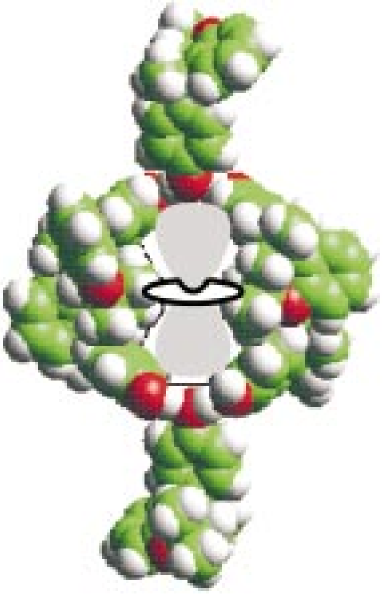


Figure 2. Representation of the heptanol guest modeled by an elastic multipole as a d_z^2 spherical harmonic in Dianin's inclusion compound cage. The shaded area represents forces directed toward the center of the cage. The clear area represents forces directed radially toward the cage.

accommodation of the heptanol. This suggests that a d_z^2 elastic dipole (Fig. 2) would provide a first-order representation of the heptanol guest. Necessary parametrization for calculation must await further measurements of elastic properties, e.g. for ethanol and heptanol crystals.

This approach clearly applies to cases where a medium is perturbed by introduction of particular molecular moieties. Guests in inclusion compounds and products in solid-state reactions are obvious situations where the model may be used, since the guests or products affect and are affected by the distribution of forces in the lattice. This model may also treat concerted motions of guest and/or host molecules, either local or extended, that occur in terms of specific rearrangements of molecules involved in molecular assembly, phase transitions, or reactions. This model leads to the conclusion that a solid-state reaction is a continual process of transformation between mechanical and chemical energies.[9]

Unfortunately, there is a paucity of information available on the elastic properties of organic solids and, therefore, it is not possible to perform the calculations indicated by the theory or, for that matter, to compare such results to experimental data. Once sufficient information is obtained on representative systems, it may be anticipated that 'transferable' elastic information can be created so that predictive power regarding solid-state reactions and guest–host interactions can be obtained. In analogy with concepts in acid–base chemistry, it is conceivable that parametrization of mechanical 'hardness' or 'softness' of molecules in solids can be developed and used for predicting assembly, bulk properties, and reactivity of solids.[26] To achieve this, a concerted and systematic program of measurement of the elastic properties of model organic solids must be undertaken.

Conclusions

Inclusion compounds are particularly useful systems for modeling solid state reactions since the latter invariably create guest-product molecules in a host–reactant lattice. In either the inclusion compound or a reacting solid, the presence of guest or product molecules must be accommodated by the host lattice. To do this, the lattice must deform. The capacity to deform is measured by the elasticity of the lattice. Thus, the elastic properties of organic solids is important to understanding their formation and reactivity.

The acoustic phonons, collective vibrational excitations of the entire lattice, are intimately related to the elasticity. Inelastic light scattering measurements from these phonons can be exploited to obtain the bulk elastic properties: the linear compressibilities and bulk moduli. In the case of Dianin's inclusion compounds of ethanol and heptanol as well as the clathrand, the significantly softer lattice of the heptanol clathrate can be rationalized in terms of specific guest–host interactions, mainly competitive hydrogen bonding and dilatation of the constricted waist of the supramolecular cage.

A more quantitative and formally familiar conceptual structure can be erected using elastic multipoles. These may be related to the guest or product molecules in a lattice and how deformational forces created by these molecules can be represented by the elastic multipoles. Expansion of the elastic multipoles as spherical harmonics allows them to be treated in a way analogous to that of atomic orbitals. Conceptually, this permits representation of the forces involved in guest–host interactions or creation of product molecules in a reactant lattice as a 'mechanical bonding' problem. The parallelism with electric dipoles and susceptibility suggests that elastic dipoles and mechanical susceptibility can be used for understanding of interactions of molecules in crystals or other systems such as Langmuir films. Development must await the time when sufficient data on the elastic properties of model organic solids is available.

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