General Theoretical Concepts for Solid State Reactions: Quantitative Formulation of the Reaction Cavity, Steric Compression, and Reaction-Induced Stress Using an Elastic Multipole Representation of Chemical Pressure

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Abstract: A general theory for solid state reactions, particularly of organics, that is based on the previously developed concept of chemical pressure is presented. Elastic multipoles are used to formulate the theory, subsequently yielding quantities that can be calculated using experimental data such as atomic displacement parameters, optical and acoustic phonon dispersion, or elastic constants. From this treatment, quantitative descriptions of the reaction cavity, steric compression, and reaction-induced stress are obtained. Analogies to atomic and frontier orbitals are noted. Further insight is gained into phonon assistance, the definition of homogeneity of a reaction, and the role of the product molecules, as perturbations, on the activation energy. The correlation of the chemical pressure to structural changes associated with the reaction is also examined. The generality and unifying aspects of the theory are demonstrated by application to detonation, thermal, and photochemical reactions in solids.

1. Introduction

Parallels can be drawn between the status of organic solid state chemistry nearing the conclusion of the twentieth century and the status of organic chemistry during the final years of the nineteenth century. In both, remarkable strides had been made during the last halves of their centuries and detailed and effective phenomenological frameworks had been developed with many useful concepts. For organic chemistry, fruitful ideas ranged from the role of optical activity by van't Hoff and Le Bel to the concept of aromaticity initiated by the fabled dream of Kekule. For organic solid state chemistry, the topochemical principle[1,2] has provided a useful conceptual basis for the growth of the field. From this foundation, much illuminating experimental work and many concrete ideas about solid state reactions have developed. Among these are the formulation of the reaction cavity concept,[3] the postulate of steric compression,[4] the examination of the role of defects, particularly by Thomas and co-workers,[5] the careful study of the role of local stress,[6] the development of the phenomenology of the hydrogen bond,[7] the further elaboration of the ideas of crystal engineering,[8] the development of the use of conformational polymorphism,[9] the notation of the halogen effect,[10] the control of crystal growth and reactivity,[11] and the proposal of phonon assistance of reactions.[12] In addition to these, much fascinating chemistry has been observed for many other systems by other investigators who have advanced important contributions to organic solid state chemistry.[13] Particular focus has been on photochemical reactions of solids,[14] and these studies have proven particularly useful for elucidating the mechanisms of solid state reactions.

A distinguishing characteristic of solids is their structure. Thus, it is not surprising that the major thrust of studies on organic solid state reactions has focused on X-ray structural analysis of reactant and product crystals. In spite of the use of a technique so intimately involved with the characteristics of solids themselves, the emphasis has been largely on the local structure associated with the reacting species in the solid. This has led to some lack of attention to another unusual property of solids, their display of collective properties.

One manifestation of collective properties is a phase transition. Indeed, consideration of a solid state reaction leads to the conclusion that, by its very nature, a reaction in a crystal must be accompanied by some change in the phase. This has

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been emphasized recently by Dunitz.[15] Recent study of the 2,5-distyrylpyrazine single-crystal to single-crystal photoreaction[14] by Eckhardt and co-workers[16] has further stressed the importance of collective excitations on the fate of a solid state reaction.

What is missing from this richness of results is a quantitative, unifying framework. As at the turn of this century, formalisms must be developed that can join these many creative ideas and useful results into a serviceable structure. For organic chemistry, it may be argued that the major breakthrough came with the Lewis dot structures which were followed soon by quantum theories of valence. While organic solid state chemistry does not require such fundamental developments as quantum mechanics, it does require a theoretical structure that can bring together the salient aspects of chemistry and the solid state that are necessary for any complete understanding of solid state reactions.

Initial, but circumscribed, quantitative approaches have been made most notably by Baughman.[17] A more complete formulation was advanced by Nagaosa and co-workers,[18] who developed a unified approach to photoinduced structural changes, and by Luty and Fouret,[19] who developed the microscopic idea of the chemical pressure in a reaction cavity. From the latter, a theory of solid state reactivity was developed. Although it provides a useful conceptual framework and expressions for calculation, the theory does not lend itself easily to computation. Extension to simpler ideas based on local molecular behavior and straightforward macroscopic solid state properties could permit the forging of a new framework for greater ease of understanding solid state reactions and, perhaps more importantly, yield a theoretical construct that works with calculational ease through direct connection to measurable or easily computed properties. Any theory pretending to model a reaction in the molecular solid state must take into account both a molecular transformation which is in the realm of chemistry and structural changes related to it which are normally considered to be the province of physics. Such structural changes are not, in general, a sum of local variances, because the collective nature of the solid state has to be considered.

A molecular transformation necessarily involves electronic degrees of freedom, and such a process can be seen as a reorganization of an electron distribution. Given that thermal energies are usually barely noticeable on the scale of electronic transitions, it is safe to predict that the electronic structure of a molecule and its changes would never become a problem of statistical mechanics, even in a condensed phase. Yet, there are numerous examples in which electronic structure is strongly affected by such a phase. Solid state reactions are particularly important processes in which the condensed phase couples to a molecular geometry which in turn can radically alter electronic structure. Solids can also afford a direct coupling between electronic structure and an environment, thereby leading to a specific "solvent effect". This is well understood for electron-transfer processes in a solution[20] where the solvent effect arises from a coupling of the electron-transfer dipole with a polarizable medium characterized by the dielectric susceptibility and having some mechanical susceptibility which may be associated with a slowly varying field.[20]

For a reaction in the solid state, the situation is more complicated, since the lattice at an initial stage of reaction plays the role of a solvent but also becomes a reactant itself in the course of the reaction. Due to the many-body nature of the solid state, the perturbation due to a chemical transformation at a site is transmitted to other sites via collective excitations. Thus, a solid state transformation should be considered as a self-consistent and highly correlated process of creation of perturbations which, in the case of a solid state reaction, are the product molecules.

A molecular solid can be conveniently modeled by considering the molecular electronic degrees of freedom to be embedded in an electrically, but predominantly mechanically, susceptible medium. Therefore, any chemical transformation at a lattice site will be recognized by the lattice as both an electrical and a mechanical (e.g. stress) perturbation which interacts with surrounding sites through electrical and mechanical fields. The relative importance of the fields depends on the particular nature of the on-site transformation. The importance of structure to chemistry leads one to conclude that it is the mechanical field of a crystal that will be essential for the description of most solid state reactions. Indeed, early discussions of organic solid state reactions have tended to stress the importance of the static structure of a reactant molecule and its environment which is usually defined as a molecular cavity. This "geometrical approach" is known as the topochemical principle[1,2] and is widely used in solid state organic chemistry. However, it has not been confronted with a realistic description of a crystal which would be expected to provide a relation to elastic properties. A need for such a connection seems quite obvious and has been postulated.[4]

The importance of lattice stress in solid state reactions has been previously suggested beginning with Baughman's work[17] on the role of strain in the kinetics of solid state polymerization and later by the research of Hollingsworth and McBride[4,6,21,22] on the structural role of strain. It became evident that "...because of stress generated by reaction, the intermediates often follow indirect trajectories rather than least-motion paths, and the mechanical properties of the surrounding medium can become as influential on reaction as its shape is".[4] In the only current, albeit approximate, approach,[22] the reacting crystal has been treated as an isotropic continuous elastic medium with a molecular cavity represented as a sphere. It has been estimated that a 10% radial expansion of the cavity would require an internal pressure of about 10 kbar, which is consistent with pressures that have been suggested for some reactions.[21,22] These findings indicate that the effect of local stresses must be important for solid state reactions.

However, an approximation which treats a molecular crystal as an isotropic elastic medium is not adequate, especially in the context of the highly "stereospecific" reactivity observed in the solid state. Such an approximation neglects the high degree of anisotropy of a crystal and fails to provide a specific molecular mechanism by which a local stress is transmitted through the lattice by interaction between local stresses. This is reflected by Hollingsworth and McBride who observed that since "...it is difficult to predict how a single molecule should

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respond to local stress", then "...properly understanding reactions in rigid media and fully realizing their synthetic potential will require better insight into the mechanical properties of solids at the molecular level".[6] This contribution suggests a way to approach this problem.

In a highly anisotropic molecular crystal, the molecular mechanism by which a local mechanical perturbation is transmitted through the lattice is very important and therefore, a theory related to crystal elasticity is required. The chemical pressure concept[19] was a first attempt in this direction. The behavior reported by McBride and co-workers[4,6,21,22] is consistent with that theoretical description.[19] The theory emphasizes that the deformation energy due to the formation of product molecules is a many-body phenomenon and thus is nonadditive. This implies that regardless of how localized the initial perturbation may be in a chemical reaction, the cooperative nature of the crystal environment cannot be discounted and must of necessity have an influence on the reaction itself. Recent work of Peachey and Eckhardt[16] strongly supports this.

The theory outlined by Luty and Fouret[19] can be further elaborated to generate a close relation to elasticity theory. The local stress effect can be described in terms of elastic multipoles[23] with the lattice deformation energy arising from their interaction. The multipoles, being a measure of the chemical pressure, allow for characterization of both the geometry and the energetics of a reaction cavity within the same conceptual framework. The chemical pressure, chemically induced stress, addresses both the local characteristics of a reaction represented by elastic multipoles of a reaction cavity and the resultant collective consequences of the local perturbations which are the structural changes due to interaction of the elastic multipoles. Such a description not only provides a conceptual link between the topochemical principle[1,2] and phonon assistance,[12] which have been suggested in the past as descriptive mechanisms for solid state reactions, but also serves as an approach that allows for categorization of a solid state reaction with such phenomena as crystal or glass phase transitions. That such a unified approach is needed is evident when one considers additional solid state transformations such as the molecular-to-atomic transition in solid iodine,[24] the neutral-to-ionic transition (molecular bistability) in some charge-transfer organic compounds,[25] or other electron-induced transitions[26] in molecular solids.

The theoretical formulation begins with a description of a molecular crystal with a model that emphasizes a susceptibility approach to the mechanical properties of a crystal and shows a level of approximation where the mechanics of a crystal are described only by the elastic constant tensor. Additionally, it is demonstrated how the atomic displacement parameters (ADP's) extracted from a crystal structure determination can be useful in the analysis of the mechanical properties of a crystal. In section 3, local perturbations are introduced into the perfect lattice. From a coupling to the mechanics of the lattice, the chemical pressure is derived and it is shown how it induces structural changes. The chemical pressure is then described as a distribution of forces acting on atoms which form a cavity for a perturbed lattice site. This allows introduction of the concept of elastic multipoles and their use in deriving a description of the molecular reaction cavity. These elastic multipoles are mechanical analogs of electrical multipoles. The similarity is developed to show that an expansion of the elastic multipoles can be used to describe the distribution of forces in a reaction cavity in the same way a radial charge distribution about an atom is represented by an expansion of atomic orbitals. In section 4, interactions are calculated between elastic multipoles, e.g. the lattice deformation energy is derived. The elastic properties of the reactant crystal are altered due to a distribution of the elastic multipoles, and this effect is calculated also. An average over the elastic multipole distribution allows for calculation of the free energy for a reacting crystal akin to that of a two-level (Ising pseudospin) system with a field and with interactions renormalized by contributions from lattice deformation energies. Finally, in section 5 are presented some of the possible applications of the concept of chemical pressure induced by a reaction and expressed in terms of elastic multipoles. Thermal polymerization, photoinduced reactions, and shock-induced reactions are shown to fall within the framework of the theory with the focus on the macroscopic nature of the reactions through collective interactions between perturbed molecules.

2. A Model of a Reacting Molecular Crystal

A model of a molecular crystal must be simple but contain all features important and relevant to the problem. We shall concentrate on mechanical properties of the crystal at a molecular level that involve a mechanical response of molecules to perturbations due to local transformations. The essential concept of a molecular crystal is that it contains well-defined molecules which weakly interact with each other. This is expressed in the Hamiltonian

$$H = \sum_n H_n^0[\mathbf{Q}(n)] - {}^1/_2\sum_n\sum_{n'}{}'\mathbf{Q}(n)\mathbf{W}(n,n')\mathbf{Q}(n') + \sum_n H_n[\sigma(n);\mathbf{Q}(n)] \qquad (2.1)$$

The first term represents single-molecule contributions with $H_n^0[\mathbf{Q}(n)]$ as the Hamiltonian of a molecule at the nth lattice site (in a field of others) being a function, not necessarily harmonic, of dynamical variables $\mathbf{Q}(n)$. We shall limit ourselves to molecular displacements—translational, $\mathbf{u}$, and rotational, θ—so $\mathbf{Q}(n)\{u_x,u_y,u_z;\theta_x,\theta_y,\theta_z\}$. This restriction is mainly for maintaining clarity of the presentation rather than any conceptual constraint. Solid state theories are marked by an obscuring abundance of notation, and we hope to make the presentation as manageable as possible. Indeed, the dynamical variable $\mathbf{Q}(n)$ can embody intramolecular degrees of freedom or a set of them which may be appropriate for description of motion of rigid sections of the molecules. Regardless of how large the set of degrees of freedom included in $\mathbf{Q}(n)$ may be, the formalism remains the same. Obviously, the meaning of the corresponding couplings will be appropriately inclusive. The second term in the Hamiltonian describes coupling between the variables of two different (the prime sign in the summation) molecules by a force constant matrix $\mathbf{W}$. Here, and throughout the paper, the standard matrix notation for tensor—tensor or tensor—vector products is assumed. The last term describes perturbations, characterized by an operator $\sigma(n)$, which couples to the dynamical variables. This part of the Hamiltonian need not be specified here but will be developed in the next section.

The basic question is what the response of an individual molecule in the crystal is to an effective field, $\mathbf{h}^{\mathbf{Q}}(n)$, at site n,

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which couples to the variable $\mathbf{Q}(n)$. A stress field is an example. Since we are interested in structural changes, the response will be defined as a statistical average of the dynamical variable, $\langle\mathbf{Q}(n)\rangle$, taken with the Hamiltonian 2.1. Within the linear approximation, it is

$$\langle\mathbf{Q}(n)\rangle = \mathbf{X}^0\,\mathbf{h}^{\mathrm{Q}}(n) \tag{2.2}$$

where $\mathbf{X}^0$ is the single-molecule susceptibility

$$\mathbf{X}^0 = \beta[\langle\mathbf{QQ}\rangle_0 - \langle\mathbf{Q}\rangle_0\langle\mathbf{Q}\rangle_0] \tag{2.3}$$

with $\beta = (1/kT)$. The thermal averages $\langle ...\rangle_0$ are calculated within the classical approximation with the single-molecule Hamiltonian. The single-molecule susceptibility is a 6 × 6 tensor and depends on temperature through the anharmonicity of the Hamiltonian, $H_n^0[\mathbf{Q}(n)]$. In the limit $T \rightarrow 0$, only the harmonic part of the Hamiltonian will contribute to the thermal averages in eq 2.3 and consequently, $\lim_{T\to 0}(\mathbf{X}^0)^{-1} = \mathbf{W}(nn)$. In the language of lattice dynamics, the inverse of the single-molecule susceptibility is the so-called self-term in the dynamical matrix. The local effective field which couples to the variable $\mathbf{Q}$ is conveniently approximated by a mean field

$$\mathbf{h}^{\mathrm{Q}}(n) = \sum_{n'}\mathbf{W}(nn')\langle\mathbf{Q}(n')\rangle + \mathbf{V}^{\mathrm{Q}}(n) \tag{2.4}$$

where

$$\mathbf{V}^{\mathrm{Q}}(n) = -\left(\frac{\partial H_n[\sigma(n);\mathbf{Q}(n)]}{\partial\mathbf{Q}(n)}\right)_{\sigma(n)} \tag{2.5}$$

stands for the perturbing field. This field depends on the particular nature of the local transformation specified by an exact form of the Hamiltonian, $H_n[\sigma(n);\mathbf{Q}(n)]$. With relations 2.2 and 2.4, we get

$$\langle\mathbf{Q}(n)\rangle = \sum_{n'}\mathbf{X}(nn')\mathbf{V}^{\mathrm{Q}}(n') \tag{2.6}$$

where $\mathbf{X}(nn')$ is the (nn') submatrix of the matrix

$$\mathbf{X} = [(\mathbf{X}^0)^{-1} - \mathbf{W}]^{-1} \tag{2.7}$$

which is the nonlocal response function. This is the key function for our problem since it tells us how a perturbation at site n' is transmitted to and causes a response of a molecule at site n. The response function for a particular pair of molecules (nn') has to be calculated as a corresponding block matrix of the inverse matrix constructed from the block diagonal matrix $(\mathbf{X}^0)^{-1}$ and force constant matrix $\mathbf{W}$. This mathematical procedure reflects the physical fact that a perturbation at a given site is transmitted to another site via *all* other molecules coupled together by a network of "springs" characterized by the force constants, i.e. how it is transmitted by collective excitations of the molecules in the lattice. It follows from formula 2.6 that a quantitative estimation of a structural change due to local perturbation(s) and associated energetics requires a knowledge of the response function as well as a specification of the perturbation field $\mathbf{V}^{\mathrm{Q}}(n)$. Insofar as the response function is concerned, this would be equivalent to solving the lattice dynamical problem and then recognizing which of the lattice vibrations (phonons) are most likely to be responsible for mediation of interactions between particular perturbations. Intuitively, one can expect that local stresses introduced by local transformations of molecules would be transmitted mostly by the strain field, and therefore, the response function should be expressed in terms of the elastic properties of the crystal. To see how the response function is related to some measurable properties, such as elastic constants, phonon frequencies, and Debye–Waller factors, we shall represent the function in reciprocal ($\mathbf{q}$) space for ease of inclusion of lattice periodicity and relation to diffraction results.

We introduce the Fourier transform of the force constant matrix

$$\mathbf{W}(\mathbf{q}) = N^{-1}\sum_{n'}\mathbf{W}(nn')\exp\{i\mathbf{q}[\mathbf{R}(n') - \mathbf{R}(n)]\} \tag{2.8}$$

where $\mathbf{R}(n)$ is a position vector of a molecule at site n and N is the number of lattice sites. The response function can now be written as a $\mathbf{q}$-dependent, generalized susceptibility:

$$\mathbf{X}(\mathbf{q}) = \mathbf{X}^0[1 - \mathbf{X}^0\mathbf{W}(\mathbf{q})]^{-1} \tag{2.9}$$

The inverse of this matrix is an effective, temperature-dependent, dynamical matrix. The eigenvalues $\omega^2(\mathbf{q}j)$ and eigenvectors $\mathbf{e}(\mathbf{q}j)$ characterize phonons in the jth dispersion branch for a given $\mathbf{q}$ vector. Thus,

$$\mathbf{X}^{-1}(\mathbf{q}) = \sum_j\omega^2(\mathbf{q}j)\mathbf{e}(\mathbf{q}j)\mathbf{M}\mathbf{e}(-\mathbf{q}j) \tag{2.10}$$

where $\mathbf{M}$ is the mass moment-of-inertia tensor and the orthogonality relation $\mathbf{e}(\mathbf{q}j)\mathbf{e}(-\mathbf{q}j) = \delta_{jj'}$ is obeyed.

The response function $\mathbf{X}(nn')$ is calculated from the transformation

$$\mathbf{X}(nn') = N^{-1}\sum_{\mathbf{q}}\mathbf{X}(\mathbf{q})\exp\{i\mathbf{q}[\mathbf{R}(n') - \mathbf{R}(n)]\} \tag{2.11}$$

and for $n = n'$ can be related to phonon frequencies as

$$\mathbf{X}(nn) = N^{-1}\sum_{\mathbf{q}}\sum_j\omega^{-2}(\mathbf{q}j)\mathbf{e}(\mathbf{q}j)\mathbf{M}^{-1}\mathbf{e}(-\mathbf{q}j) \tag{2.12}$$

From its definition, the susceptibility is directly related to molecular Debye–Waller factors represented by the tensor $\mathbf{B}$.

$$\mathbf{X}(nn) = \beta\langle\mathbf{Q}(n)\mathbf{Q}(n)\rangle = \beta\mathbf{B} \tag{2.13}$$

The thermal average is taken with the total Hamiltonian of the unperturbed crystal. The tensor $\mathbf{B}$ is represented as blocks of tensors[27] known as the translational (**T**), librational (**L**), and cross (**S**) molecular tensors of thermal vibrations. The tensor

$$\mathbf{B} = \begin{pmatrix}\mathbf{T} & \mathbf{S}\\ \mathbf{S}^T & \mathbf{L}\end{pmatrix} \tag{2.14}$$

can be constructed from anisotropic ADP's, assuming rigid molecules. It can be generalized to include the lowest intramolecular vibrations as well.[28] This will be obtained when intramolecular degrees of freedom are included in the set described by the variable $\mathbf{Q}(n)$ (see eq 2.1). The important conclusion is that the mechanical response function $\mathbf{X}(nn)$ can be found from crystal structure analysis and the usually neglected set of ADP's, which can also be very useful in calculations of the lattice deformation energy. The simple relation between the **T**, **L**, and **S** tensors of the thermal amplitudes and the mechanical response function $\mathbf{X}(nn)$ allows insight into how a single molecule in a crystal will respond to

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a field which couples to its translational and/or rotational displacements. The magnitude and principal directions of the **B** tensor of a molecule *reflect the geometrical arrangement of the neighboring molecules.* In terms of solid state chemistry, one can view the response function $\mathbf{X}(nn)$ as an effective, mechanical susceptibility which measures the response of a molecular cavity to a mechanical field. It is important to note that the response accounts for pair correlations between displacements of molecules.

A better interpretation and possible approximations for the response function $\mathbf{X}(nn')$ $(n \neq n')$ are required however. The function is calculated formally from eq 2.11, where $\mathbf{X}(\mathbf{q})$ is the inverse of the dynamical matrix, and complete calculations would require an integration over the Brillouin zone of the matrix for *every* pair of molecules. An obvious approximation is the long-wavelength approximation ("mesoscopic limit"), which assumes that the distance $\mathbf{R}(n') - \mathbf{R}(n)$ is on a mesoscopic scale. For large distances, only contributions with $\mathbf{q} \cong 0$ are important. Therefore, the dynamical matrix can be expanded and expressed in terms of optical phonon frequencies, $\omega(0j)$, and the elastic constant tensor **C**

$$\lim_{\mathbf{q}\to 0} \mathbf{X}^{-1}(\mathbf{q}) = \sum_j \omega^2(0j)\mathbf{e}(0j)\mathbf{M}\mathbf{e}(0j) + {}^1/_2\nu\mathbf{q}\mathbf{C}\mathbf{q} \tag{2.15}$$

where ν stands for the volume of a unit cell.

The approximation 2.15 when introduced into eq 2.11 allows for decomposition of the response function into contributions from optical and acoustic phonons. Since the function depends on the inverse of optical phonon frequencies, it is clear that their contribution will be much more important. This is why in the mesoscopic limit, the response function $\mathbf{X}(nn')$ can be approximated as

$$\mathbf{X}(nn') \cong 2(N\text{v})^{-1}\sum_{\mathbf{q}}[\mathbf{q}\mathbf{C}\mathbf{q}]^{-1} \exp\{i\mathbf{q}[\mathbf{R}(n')-\mathbf{R}(n)]\} \tag{2.16}$$

Calculations of this function are not easy, particularly for low-symmetry molecular crystals. However, it is important to notice that the response function can be calculated from the known elastic constant tensor, which may itself be calculated from knowledge of the acoustic phonons' dispersion. The long-wavelength approximation, which allows for simplification of the response function, means that on a mesoscopic length scale, the crystal is treated as an anisotropic elastic medium.

This model describes the mechanical response functions for a molecular crystal in the simplest, viable approximation and shows how they can be calculated from experimentally determined properties: molecular Debye–Waller factors, optical phonon frequencies, and elastic constants. It is now necessary to specify the perturbations and describe them quantitatively.

3. Local Perturbations: Chemical Pressure and the Elastic Multipoles of a Reaction Cavity

Suppose that a molecular crystal with mechanical properties as specified in the previous section is locally perturbed and that the perturbations are of a chemical nature: substitutional, ionized or excited host molecules, reaction-generated product molecules, etc. To each lattice site is assigned a variable, $\sigma(n)$, with the value $+1$ if the site is occupied by a perturbation, otherwise $\sigma(n) = 0$. The concentration of perturbations is defined as $x = [N^{-1}\sum_n\langle\sigma(n)\rangle]_{\text{av}}$ where the square brackets indicate a configurational average. With this definition, the perturbed crystal can be seen as a virtual "solid solution", $\mathrm{H}_{1-x}\,\mathrm{P}_x$, where every site is occupied by a host molecule (H) with probability $1 - x$ or a perturbation (P) with probability x. This "average picture" of the crystal will be useful when thermodynamic aspects are treated. The formation of the perturbations in the host lattice is an obvious case of mixing, and the degree of heterogeneity or homogeneity of the process is of importance and will be discussed at the end of section 4. Before this, however, it is necessary to view every site as being occupied by either an H or a P molecule.

An introduction of a perturbation of a given type at site n of a perfect lattice costs energy.

$$H_n = [\Delta E^0 + \sum_{n'}\Delta E(nn')]\sigma(n) + \sum_{n'} f[\sigma(n),\sigma(n')] \tag{3.1}$$

The first term, ΔE^0, represents the difference in energies of perturbed and unperturbed molecules. The second term accounts for the fact that the perturbation with energy ΔE^0 above the ground state of the crystal is created *in* the crystal. The last term describes a possible direct interaction between perturbations at different sites. Let us concentrate on the second term which represents couplings to molecular degrees of freedom.

$$\Delta E(nn') = \mathbf{v}(nn')\mathbf{Q}(n) = -\mathbf{v}(nn')\mathbf{Q}(n') \tag{3.2}$$

This equation defines forces, $\mathbf{v}(nn')$, which couple the perturbation with degrees of freedom of surrounding molecules.

Now, the energy cost of introducing the perturbation is

$$H_n = [\Delta E^0 + \mathbf{Q}(n)\mathbf{v}(n)]\sigma(n) \tag{3.3}$$

where $\mathbf{v}(n)$ is the total extra force generated at the site n which is occupied by a perturbation. The force is acting on all surrounding molecules, since it is defined as a sum $\mathbf{v}(n) = \sum_{n'}\mathbf{v}(nn')$. This is an excess force associated with the local transformation $1 - \sigma(n) \rightarrow \sigma(n)$ which is of a chemical nature and for this reason called the "chemical pressure". To grasp the role of the excess force, an analogy can be drawn to the molecular orbital theory of reactivity.[29] In that theory, the frontier orbitals, the HOMO and LUMO, play an essential role. The excess force $\mathbf{v}(n)$ is a measure of the change in energy of the frontier orbitals of the nth molecule in the crystal with respect to the reaction path described by the set of coordinates $\mathbf{Q}(n)$. A relation to the *local* stress tensor arises from the definition of a stress.

It can be shown that when the chemical pressure is represented by central forces, only the diagonal elements of the stress tensor are generated and the force distribution in the cavity of the nth molecule, $\mathbf{v}(n)$, is directly related to a *local* pressure. The chemical pressure is easily recognized as arising from different kinds of couplings. For example, if perturbations are introduced by exciting the host molecules into an electronically excited state, $\mathbf{v}(n)$ corresponds to the so-called Stokes shift and is simply related to the D term in the theory of molecular excitons.[30] $\mathbf{v}(n)$ can also be related to the Grüneisen parameters if one considers, as a perturbation, a molecule in a vibrationally excited state and accounts for coupling to a lattice strain. Thus, the chemical pressure represents all extra forces which are generated *locally* in a crystal due to a transformation. The forces generated by the perturbations at a given site can be treated as the "applied" field in this formalism (see eq 2.4), so

$$\mathbf{V}^{\mathbf{Q}}(n) = \mathbf{v}(n)\langle\sigma(n)\rangle \tag{3.4}$$

and the structural change induced by the chemical pressure is

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(30) Davydov, A. S. *Theory of Molecular Excitons*, Plenum Press: New York, 1971.

$$\langle \mathbf{Q}(n)\rangle = \sum_{n'} \mathbf{X}(nn')\mathbf{v}(n')\langle \sigma(n')\rangle \tag{3.5}$$

In this description, it is assumed that a perturbation at site *n* acts on surrounding molecules, which means that the forces depend on distances between the centers of mass of the molecules. This is, however, too crude a description for a molecular crystal, and a perturbation at a site would be better represented by a set of forces acting on atoms of surrounding molecules. In particular, consideration is focused on those atoms which form a cavity for the molecule being transformed (the perturbation). Therefore, a more detailed description of the chemical pressure, $\mathbf{v}(n)$, is needed. This requires the involvement of concepts of elasticity.

The chemical pressure at a given site *n*, defined as an arrangement of extra forces acting on surrounding molecules, forms a distribution within the cavity surrounding the molecule. Although the distribution, $\mathbf{v}(n) = \sum_{n'}\mathbf{v}(nn')$, depends on the geometry of the environment of the *n*th molecule through interaction of the perturbation with its surroundings, this information is hidden in a molecule−molecule interaction representation. To uncover it, atoms of surrounding molecules which form a cavity for the molecule *n* must be considered explicitly. Let the set of vectors $\{\mathbf{r}(n\xi)\}$ joining the center-of-mass of the perturbing molecule *n* to the atoms forming the molecular cavity be defined. The chemical pressure in the cavity, which may be regarded as the reaction cavity, is now described as a distribution of forces acting on the atoms, $\mathbf{v}(n) = \sum_\xi \mathbf{v}(n\xi)$. These forces, actually their negatives, may be identified with steric compression. Equation 3.3 is rewritten as

$$H_n = \sigma(n)[\Delta E^0 + \sum_\xi \mathbf{Q}[\mathbf{r}(n\xi)]\mathbf{v}(n\xi)] \tag{3.6}$$

The set of displacement vectors, $\mathbf{Q}[\mathbf{r}(n\xi)]$, which measure the deformation due to the force distribution, can be expanded, and the second term of eq 3.6 is then written as

$$\sum_i\sum_\xi Q_i[\mathbf{r}(n\xi)]\mathrm{v}_i(n\xi) = \sum_i Q_i(n)\sum_\xi \mathrm{v}_i(n\xi) + \sum_i\sum_j \epsilon_{ij}(n)\sum_\xi r_j(n\xi)\mathrm{v}_i(n\xi) + \ldots \tag{3.7}$$

where

$$\epsilon_{ij}(n) = \left(\frac{\partial Q_i[\mathbf{r}(n\xi)]}{\partial r_j(n\xi)}\right) \tag{3.8}$$

is a local strain which is assumed to be homogeneous within the cavity of the *n*th molecule. The tensor is, in general, nonsymmetric and can be further decomposed into a symmetric part, the macroscopic strain which is homogeneous in the crystal, and an inhomogeneous part.[31] The latter is related to internal strains and thus to displacements of molecules within the unit cell $\mathbf{Q}(n)$. The expansion in 3.7 allows for definition of the elastic multipoles of the cavity at the *n*th site

$$\mathbf{V}(n) = \sum_\xi \mathbf{v}(n\xi) \qquad \text{(the net force)}$$

$$P_{ij}(n) = \sum_\xi r_i(n\xi)\mathrm{v}_j(n\xi) \qquad \text{(an elastic dipole)}$$

and so on, as is consistent with elasticity theory.[23] The elastic multipole concept helps to represent the geometry and energetics of a molecular cavity in greater detail. In particular, the elastic dipole and higher multipoles explicitly contain in their definitions the shape of the cavity and the chemical pressure distribution inside of it. Using again the perspective of molecular orbital theory, we may view the distribution of forces in the reaction cavity as being "shaped" by the frontier orbitals participating in a chemical process and the elastic multipole expansion as being determined by the angular distribution of those orbitals. The elastic multipoles are a quantitative measure of how much a cavity of a perturbed molecule differs from a sphere at equilibrium pressure. (For a spherical cavity of radius *r* and isotropic pressure *p*, the elastic dipole moment is $4\pi pr^3$.) The elastic dipole is easily related to the *local* stress tensor $\mathbf{p}(n) = \mathrm{v}^{-1}\mathbf{P}(n)$. The chemical pressure, as an excess stress, can be parametrized, with the help of spherical unit tensors,[23] in a form which explicitly divides it into isotropic pressure (p_s) and anisotropic stresses (p_m), e.g.

$$p_{ij} = p_s\delta_{ij} + \sum_m p_m a_m \tag{3.9}$$

where

$$p_s = {}^1/_3(p_{xx} + p_{yy} + p_{zz})$$

$$p_0 = {}^1/_{\sqrt{6}}(2p_{zz} - p_{xx} - p_{yy})$$

$$p_{1c} = \sqrt{2}p_{xz}$$

$$p_{1s} = \sqrt{2}p_{yz}$$

$$p_{2c} = {}^1/_{\sqrt{2}}(p_{xx} - p_{yy})$$

$$p_{2s} = \sqrt{2}p_{xy}$$

and the real spherical unit tensors are

$$\mathbf{a}_0 = {}^1/_{\sqrt{6}}\begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2\end{pmatrix},\ \mathbf{a}_{1c} = {}^1/_{\sqrt{2}}\begin{pmatrix}0 & 0 & 1\\ 0 & 0 & 0\\ 1 & 0 & 0\end{pmatrix},$$

$$\mathbf{a}_{1s} = {}^1/_{\sqrt{2}}\begin{pmatrix}0 & 0 & 0\\ 0 & 0 & 1\\ 0 & 1 & 0\end{pmatrix},\ \mathbf{a}_{2c} = {}^1/_{\sqrt{2}}\begin{pmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 0\end{pmatrix},$$

$$\mathbf{a}_{2a} = {}^1/_{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$$

The parametrization of the local stress reveals that every perturbation will act, first of all, as a center of dilitation and then, depending on the symmetry of the perturbed cavity, as a center of shear stresses. The above decomposition of the elastic dipole is analogous to the s (isotropic part) and d (shear stress, which is anisotropic) atomic orbitals. A net force would be partitioned like p orbitals. This partitioning of the chemical pressure also suggests the simplest approximation one might use to represent local stress, namely, as an isotropic excess pressure at the *n*th cavity. The model used by Hollingsworth and McBride[22] is essentially this approximation.

In this model, the elastic multipoles can assist in quantitatively understanding solid state reactivity, thereby augmenting the intuitive constructs that have been offered, for example, by

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(31) Born, M.; Huang, K. *Dynamical Theory or Crystal Lattices*; Oxford University Press: Oxford, 1954. Sharp, N. D.; Walmsley, H. *Chem. Phys. Lett.* **1994**, *222*, 546.

Thomas et al.[32] The scope for chemically modifying the molecule has been investigated by determining the tightness of the lattice packing at each site. This has been done by specifying a parameter known as the *local packing density* n_i, defined as $\sum_{j=1}^{s} r_{ij}^{-2}$, where s is an integer specifying the maximum number of atoms regarded as local to the atom i, i.e. to those atoms that form the cavity. It has been found that the higher the value of the packing density at a particular site, the less likely it is that substitution at this site will preserve the reactive structure.[32] This is essentially a "rule" based on geometry and indicates how strong the need is to have a better measure of the energetics and geometry of a reaction cavity. The use of elastic multipoles offers such a measure.

The energy change due to perturbation at the nth cavity is now expressed as

$$H_n = \sigma(n)[\Delta E^0 + \mathbf{Q}(n)\mathbf{V} + \epsilon(n)\mathbf{P} + ...] \tag{3.10}$$

where it is assumed that perturbations are the same at every perturbed site. Therefore, the elastic multipoles are site-independent. The *local* strain tensor, $\epsilon(n)$, and internal strain, $\mathbf{Q}(n)$, are corresponding variables which couple to the elastic multipoles. The "locality" of these quantities depends on how spacially extensive the effect of a perturbation originated at a site n is. The effect of lattice dilatation is contained in eq 3.10 as the isotropic pressure term $\sum_n\sum_i\epsilon_{ii}(n)$, which results in the readjustment of the lattice constants.

With the introduction of elastic multipoles, structural changes are measured by an average displacement

$$\langle \mathbf{Q}(n)\rangle = \sum_{n'}[\mathbf{X}(nn')\mathbf{V} + \mathbf{X}'(nn')\mathbf{P} + ...]\langle\sigma(n')\rangle \tag{3.11}$$

where $\mathbf{X}'(nn')$ is the first derivative of the response function $\mathbf{X}(nn')$ with respect to the position vector of the n' molecule, $\mathbf{R}(n')$. This equation may be considered as an introduction of elastic multipoles equivalent to that performed with eq 3.7.

4. Interaction of Elastic Multipoles: The Free Energy

The interaction of elastic multipoles decreases the crystal energy by the amount of the lattice deformation energy. The lattice deformation energy is the elastic analogue of the lattice polarization energy. It is work done against the chemical pressure, itself a distribution of forces, which appears at different sites of the crystal. It may also be viewed as an electron–phonon coupling. The deformation energy is

$$\Phi_{\mathrm{def}} = -{}^1/_2\sum_n\langle\mathbf{Q}(n)\rangle\mathbf{V}^{\mathbf{Q}}(n) \tag{4.1}$$

which from eq 2.6 is equivalent to

$$\Phi_{\mathrm{def}} = -{}^1/_2\sum_n\sum_{n'}\mathbf{V}^{\mathbf{Q}}(n)\mathbf{X}(nn')\mathbf{V}^{\mathbf{Q}}(n') \tag{4.2}$$

and

$$\Phi_{\mathrm{def}} = -{}^1/_2\sum_n\sum_{n'}\langle\mathbf{Q}(n)\rangle\mathbf{X}^{-1}(nn')\langle\mathbf{Q}(n')\rangle \tag{4.3}$$

When the local stresses are described in terms of elastic multipoles, the equation becomes

$$\Phi_{\mathrm{def}} = -{}^1/_2\sum_n\sum_{n'}\sum_k\sum_l\frac{1}{k!l!}P_{i(k)}(n)P_{j(l)}(n')\nabla_{(k)(l)}X_{ij}(nn')\langle\sigma(n)\sigma(n')\rangle \tag{4.4}$$

where $P_{i(k)}(n)$ stands for a component of an elastic multipole characterized by the k indices and where the corresponding derivatives of the response function $\mathbf{X}(nn')$ are indicated.

The deformation energy can be decomposed into the self-energy of the perturbed cavities and their interactions with perturbation centers. The self-energy is just the energy needed to put the separate perturbations into the elastic medium and is calculated for $n = n'$. When the perturbation is characterized by a distribution of forces within a cavity acting on the atoms ξ forming the cavity, this energy is

$$\Phi_{\mathrm{self}} = -\beta N^{-1}\sum_n\sum_\xi\sum_i\sum_j \mathrm{v}_i(n\xi)U_{ij}(n\xi)v_j(n\xi)\langle\sigma(n)\rangle \tag{4.5}$$

where $\mathbf{U}(n\xi)$ stands for the tensor of the anisotropic ADP's of atoms ξ which form the cavity at site n. In the derivation of this equation, the same arguments are employed as in the formulation of eq 2.13. The ADP's may be obtained from X-ray structure analysis, but the chemical pressure of the cavity as a set of forces acting on the atoms ξ must be calculated. The important property of the self-deformation energy is that it is proportional to the concentration of perturbations.

The lattice deformation energy which arises from interactions of perturbations at different sites ($n \neq n'$), is calculated from eq 4.4 using a response function, $\mathbf{X}(nn')$, that is as general as possible. The simplest approximation is given by eq 2.16 where the function is expressed in terms of elastic properties only. Even within this approximation, it is very difficult to calculate the function for crystals of low symmetry. In fact, the function is known in an analytical form only for an isotropic elastic medium and a hexagonal simple lattice.[33] For other cases, one has to calculate it numerically, but some simplifications can be made when one is interested in interaction between perturbations along a particular, preferably high-symmetry, direction in a crystal. The important property of the function is that it can be negative or positive for some directions, thereby representing highly anisotropic elastic interactions between perturbations.

Overall, the lattice deformation energy is negative and stabilizing, but the directional dependence of the contributions for $n \neq n'$ can be of essential importance for developing a "clustering pattern" in the crystal. This can be analyzed by taking into account the fact that the deformation energy depends on $\langle\sigma(n)\sigma(n')\rangle$, the function describing correlation of perturbations at different sites. It then becomes clear from eq 4.4 that a particular configuration of perturbations measured by the probability $\langle\sigma(n)\sigma(n')\rangle$ can be either favored, if the interaction energy is negative, or disfavored, if it is positive. As long as the interaction is calculated with the response function approximated by eq 2.16, predictions concerning the correlation of perturbations would improve with increasing distance between the correlated sites. This is akin to a polarizable medium where interaction of two charges moderated by a static dielectric constant as a screening parameter becomes more accurate with increasing distance between the charges.

The final goal is to determine the free energy changes in the crystal that are related to a local transformation, $1 - \sigma(n) \rightarrow$

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[32] Wright, J. D. *Molecular Crystals*; Cambridge University Press: Cambridge, U.K., 1987. Thomas, N. W.; Ramdas, S.; Thomas, J. M. *Proc. R. Soc. London* **1985**, *A400*, 219.

[33] DeWit, R. *Solid State Phys.* **1960**, *10*, 247.

$\sigma(n)$. This will be completely described by

$$\Delta F = -\beta^{-1}[\ln Z]_{\text{av}} \tag{4.6}$$

where the partition function Z is calculated from an effective Hamiltonian, $H_{\text{eff}}(\sigma)$, which describes the local transformation in the lattice.

$$Z = \underset{\{\sigma\}}{Tr} \exp[-\beta H_{\text{eff}}(\sigma)] \tag{4.7}$$

In order to find the effective Hamiltonian, the perturbed crystal is represented by variables which are related to elastic multipoles. Taking into account eqs 2.1, 2.11, and 3.9, one obtains

$$H_{\text{eff}}(\mathbf{Q},\epsilon,\sigma) = {}^1\!/_2\sum_n\sum_{n'}\mathbf{Q}(n)\mathbf{X}^{-1}(nn')\mathbf{Q}(n') + {}^1\!/_2 v\sum_n \epsilon(n)\mathbf{C}\epsilon(n) + \sum_n \sigma(n)[\Delta E^0 + \mathbf{Q}(n)\mathbf{V} + \epsilon(n)\mathbf{P}] \tag{4.8}$$

where direct interaction between perturbations and higher elastic multipoles has been neglected. The Hamiltonian can be further simplified by assuming that the inhomogeneous part of the local strain is included in the $\mathbf{Q}(n)$ variable. Therefore, the strain, ϵ, can be treated as homogeneous and site independent. With these approximations, the effective Hamiltonian is similar to that derived for orientational glasses.[34] The coarse-graining procedure used in that derivation corresponds to our formulation of the elastic multipoles of cavities and the approximation used to express the response function, $\mathbf{X}(nn')$, through the elastic properties.

The crystal free energy is obtained from $F = -\beta[\ln Z']_{\text{av}}$, where Z' is the partition function calculated by integration over ϵ and $\mathbf{Q}(n)$ and summation over σ states. The free energy has to be a minimum with respect to the macroscopic strain, ϵ, and the internal strain, $\mathbf{Q}(n)$. The conditions for the mechanical equilibrium yield the important relations

$$[\langle\epsilon\rangle]_{\text{av}} = -v^{-1}\mathbf{SP}[N^{-1}\sum_n\langle\sigma(n)\rangle]_{\text{av}} \tag{4.9}$$

and

$$\langle\mathbf{Q}(n)\rangle = \sum_{n'}\mathbf{X}(nn')\mathbf{V}\langle\sigma(n')\rangle \tag{4.10}$$

The above equations now describe structural changes and replace eq 3.11 which defines displacement as a series expanded in terms of elastic multipoles that measures such changes. The structural change is measured by the macroscopic strain, eq 4.9, and the internal strain, eq 4.10. The macroscopic strain is present because there is a non-zero concentration (x) of perturbations to which it is proportional. The strain caused by the elastic dipole depends on the crystal compressibility measured by the elastic compliance tensor $\mathbf{S}$. Relation 4.10 corresponds to the first term in eq 3.11 where the mechanical response due to higher elastic multipoles in the earlier expression has been replaced by the macroscopic strain.

As an immediate result of the above relations, renormalization of the mechanical properties of the crystal due to the perturbations is achieved. First, the elastic compliance, $\mathbf{S} = \mathbf{C}^{-1}$, has to be calculated as a matrix of second derivatives of the total free energy with respect to homogeneous stress. This means that $S_{ijkl} = \beta N[\langle\epsilon_{ij}\epsilon_{kl}\rangle]_{\text{av}}$ can be calculated with the Hamiltonian 4.8. The result is

$$\mathbf{S} = \mathbf{S}^0(1 + \mathbf{pSp}X_\sigma) \tag{4.11}$$

where $\mathbf{S}^0$ is the elastic compliance tensor of the unperturbed crystal and X_σ stands for the correlation function of the perturbations:

$$X_\sigma = \beta[N^{-1}\sum_n\sum_{n'}\langle\sigma(n)\sigma(n')\rangle]_{\text{av}} \tag{4.12}$$

The thermal average of the product $\sigma(n)\sigma(n')$ has to be taken with the effective Hamiltonian of the crystal, $H_{\text{eff}}(\sigma)$.

The relation 4.10 also shows that the response function, $\mathbf{X}(nn')$, will be renormalized due to the presence of perturbations. Calculating the renormalized function, $\mathbf{X}(nn') = \beta\langle\mathbf{Q}(n)\mathbf{Q}(n')\rangle$, with the total Hamiltonian yields

$$\bar{\mathbf{X}}(nn') = \mathbf{X}(nn')[1 + \beta N^{-1}\mathbf{V}\sum_{n''}\mathbf{X}(n'n'')\mathbf{V}\langle\sigma(n')\sigma(n'')\rangle] \tag{4.13}$$

where $\mathbf{X}(nn')$ is the unperturbed response function. With the help of this equation, one can estimate changes in molecular Debye–Waller factors. These would be proportional to the correlation function $\langle\sigma(n)\sigma(n')\rangle$.

The effective Hamiltonian, $H_{\text{eff}}(\sigma)$, is calculated from eq 4.8 by integrating out the mechanical degrees of freedom with the result

$$H_{\text{eff}}(\sigma) = \Delta\sum_n\sigma(n) - {}^1\!/_2\sum_n\sum_{n'}{}' J(nn')\sigma(n)\sigma(n') \tag{4.14}$$

which is the Ising Hamiltonian with the "field" $\Delta = \Delta E^0 - \Phi_{\text{self}}$. The self-deformation energy is expressed as

$$\Phi_{\text{self}} = \mathbf{pS}^0\mathbf{p} + \beta\mathbf{VBV} \tag{4.15}$$

where the contributions from elastic dipoles and net forces (torques) are separated. Equation 4.5 can be equivalently used to calculate the energy . The self-deformation energy plays exactly the same role in a solid state reaction as the solvation energy does in a liquid state reaction. However, the important difference is that in the solid state, it is the total deformation energy (eqs 4.1–4.4) that plays the role of "solvation" energy and determines the activation energy for a transformation.

The activation energy can be calculated with the help of Figure 1 which schematically illustrates the meaning of the deformation energy. If a process involves both $\langle\mathbf{Q}\rangle$ and $\langle\epsilon\rangle$, and since the structural changes and the variables are not directly coupled, the question arises, which path will the system follow? Some insight can be gained by remembering that a "fast" field can follow a "slow" one but not vice versa. This means that for every state of the system that is characterized by a macroscopic strain, there will be a thermal equilibrium for the internal strain, $\mathbf{Q}$. Therefore, the internal strain ($\mathbf{Q}$ − field) can be integrated out for every state of strain, and the process will follow the macroscopic strain ϵ-path with $\Delta E^0 \rightarrow \Delta E^0 - \Phi^Q_{\text{def}}$, and the activation energy calculated as

$$\Delta E_{\text{act}} = \frac{[\Delta E^0 - \Phi^Q_{\text{def}}]^2}{4\Phi^\epsilon_{\text{def}}} \tag{4.16}$$

If, however, the only structural change involved is the internal

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[34] (34) Vollmayer, H.; Kree, R.; Zippelius, A. *Phys. Rev.* **1991**, *B44*, 12238. Walasek, K.; Lukierska-Walasek, K. *Phys. Rev.* **1993**, *B48*, 12550.

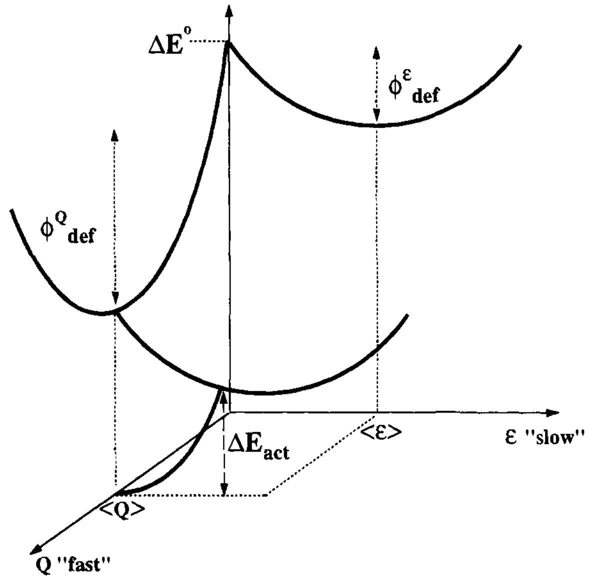

Figure 1. Schematic illustration of deformation energies due to homogeneous strain, ϵ, and internal strain, **Q**. The strains are involved in the solid state transformation but are not themselves directly coupled. The activation energy is indicated along the ϵ-path.

strain, $\langle \mathbf{Q} \rangle$, then the activation energy is calculated as

$$\Delta E_{\mathrm{act}} = \frac{[\Delta E^0]^2}{4\Phi^Q_{\mathrm{def}}} \tag{4.17}$$

The corresponding deformation energies must be equal

$$\Phi^{\epsilon}_{\mathrm{def}} = {}^1/_2\mathbf{pS}^0\mathbf{p}[N^{-1}\sum_n \sum_{n'} \langle \sigma(n)\sigma(n') \rangle]_{\mathrm{av}} \tag{4.18}$$

and

$$\Phi^Q_{\mathrm{def}} = {}^1/_2[N^{-1}\sum_n \sum_{n'} \mathbf{VX}(nn')\mathbf{V}\langle \sigma(n)\sigma(n') \rangle]_{\mathrm{av}} \tag{4.19}$$

The important aspect of the deformation energies is that they depend on the correlation function between perturbations. Therefore, these correlations influence the activation energies. As will be demonstrated in the following discussion, the function can be expressed in terms of the average concentration of perturbations, and consequently, the activation energy will be concentration-dependent. This can have an important effect on the kinetics of solid state reactions.

The coupling term in eq 4.14 contains, in general, contributions from direct and indirect interactions.

$$J(nn') = f[\sigma(n),\sigma(n')] + \mathbf{VX}(nn')\mathbf{V} + \mathbf{pS}^0\mathbf{p} \tag{4.20}$$

With the Hamiltonian 4.14, the free energy difference due to the local transformations can be calculated from eq 4.6, and thermodynamical quantities can be calculated from the partition function, eq 4.7. The configurational average contains the information on the concentration of perturbations, their spacial distribution, and their mutual correlation. In terms of solid state chemistry, it corresponds to the amount of product molecules and their clustering by, say, oligomerization. For every particular solid state transformation, the configurational average has to be calculated or assumed in order to calculate the susceptibility, X_σ (eq 4.12). With the effective Hamiltonian, it can be calculated from the relation

$$X_\sigma^{-1} = [N^{-1}\sum_{n'}\{\chi^{-1} - J(nn')\}]_{\mathrm{av}} \tag{4.21}$$

where χ is the *local*, two-state susceptibility, $\chi = \beta\langle\sigma\rangle_0(1 - \langle\sigma\rangle_0)$, and the expectation values, $\langle\sigma(n)\rangle_0$, are calculated with the local part of the effective Hamiltonian.

$$\langle\sigma\rangle_0 = (1 + e^{\beta\Delta})^{-1} \rightarrow e^{-\beta\Delta} = \langle\sigma\rangle_0(1 - \langle\sigma\rangle_0)^{-1} \tag{4.22}$$

Clearly, the mean value, $\langle\sigma\rangle_0$, is associated with the degree of chemical transformation which takes place at a site with energy difference Δ.

Including the coupling between perturbed sites, the susceptibility X_σ can be calculated within the mean field approximation

$$X_\sigma = \beta[N^{-1}\sum_n \langle\sigma(n)\rangle(1 - \langle\sigma(n)\rangle)]_{\mathrm{av}} \tag{4.23}$$

where

$$\langle\sigma(n)\rangle = {}^1/_2(\tanh {}^1/_2\beta(-\Delta + J\langle\sigma(n)\rangle) + 1) \tag{4.24}$$

with $J = \sum_{n'}J(nn')$. Now, the mean value, $\langle\sigma(n)\rangle$, not only is associated with the degree of a chemical transformation at site n but also includes the effect of interactions between sites. In this guise, it corresponds to a "nonideal solution" as traditionally formulated by equilibrium chemical thermodynamics. If the transformation $1 - \sigma(n) \rightarrow \sigma(n)$, which is a source of lattice perturbations, involves quantum overlap or a tunneling effect between the two states, then the effective Hamiltonian, eq 4.14, has to be modified to $-t\sigma_x + H_{\mathrm{eff}}(\sigma)$, where t is the overlap integral, σ_x stands for the Pauli matrix, and the σ operator is understood now as the σ_z matrix. The quantum overlap between the states leads to energy differences at every site, $\Delta_t = (\Gamma^2(\sigma) + 4t^2)^{1/2}$, where the mean field is given by $\Gamma(\langle\sigma\rangle) = \Delta - J\langle\sigma\rangle$. The degree of chemical transformation at a site is therefore

$$\langle\sigma\rangle_t = {}^1/_2(\Gamma\Delta_t^{-1} \tanh {}^1/_2\beta\Delta_t + 1) \tag{4.25}$$

where the term $\Gamma\Delta_t^{-1}$ measures the degree of quantum mixing of the two states.

A comment is warranted concerning the configurational average which has to be obtained when calculating the susceptibilities. When doing so, one has to account for possible cluster formation in the "product" state ($\sigma(n) = 1$). Therefore, taking the average, $[N^{-1}\sum_n\sigma(n)\rangle]_{\mathrm{av}}$, requires inclusion of the concentrations of clusters such as oligomers containing, say, m molecules. Then for linear oligomers, the susceptibility, X_σ, can be approximated by the expression $\beta(1 - x)\sum_m x^m$.

Finally, the simplest expression for the free energy change is obtained by assuming a uniform distribution of the "reacting" sites. The free energy change per molecule is

$$\Delta f = \Delta F/N = \Delta x - {}^1/_2 Jx^2 + \beta^{-1}[x \ln x + (1 - x)\ln(1 - x)] \tag{4.26}$$

for nondegenerate states of the perturbation. The concentration is defined as $x = [N^{-1}\sum_n\langle\sigma(n)\rangle]_{\mathrm{av}}$ and represents the degree of transformation for a whole system with a uniform distribution of the transformed sites. The thermal average, $\langle\sigma(n)\rangle$, itself determines the degree of the transformation at a particular site due to quantum mixing (in general) and thermal agitation. The above equation holds an important message. Solid state chemical reactions can be modeled by an interacting boson gas

($J \neq 0$), where the interaction between reacting centers is due to local chemical pressures and is mediated by an elastic strain field.

For a chemical transformation to proceed in a crystal, it is necessary that the field will not be zero, e.g. $\Delta \neq 0$. The interaction term, J, will then determine if the transformation will proceed as if occurring in an ideal ($J = 0$) or a nonideal ($J \neq 0$) solid solution. It is most likely that the strength of the interaction between perturbed sites dictates whether the reaction proceeds as a homogeneous (strong coupling) or inhomogeneous process.

The categorization of homogeneous and heterogeneous solid state reactions is widely used but not clearly defined. It obviously depends on the meaning of "phase" and the level of "graininess". Microscopically, every compound has its separate phase space; therefore, every reaction is heterogeneous on that scale. On macroscopic or mesoscopic length scales, however, the process can be viewed as being homogeneous if the reactant and product molecules form a solid solution and there is no macroscopic phase separation. Otherwise, the reaction is called heterogeneous. Apart from an important role played by structural defects, the long-range nature of the elastic interaction between perturbed sites might determine the homogeneity or heterogeneity of the process in the macroscopic sense. Due to the long-range nature of the elastic dipole−elastic dipole interaction, there is a shape-dependence effect[23] analogous to the electric dipole interaction.

Lastly, there will be a phase transition given by the interaction term. A necessary but not sufficient condition for a phase transition to occur is $J \neq 0$. This condition, supplemented by $\Delta = {}^1/_2 J$, gives the thermodynamic equilibrium between phases with different concentrations of perturbations and, in effect, predicts a discontinuous phase transition. The condition $\Delta = {}^1/_2 J$ is equivalent to $\Delta E^0 = \Phi_{\mathrm{def}}$ and is a limit of stability of the system against a single-molecule perturbation. For $\Delta E^0 \leq \Phi_{\mathrm{def}}$, a spontaneous process for formation of perturbations will proceed even with the presence of an activation barrier. In terms of the Ising model, the situation when a reaction proceeds ($\Delta \neq {}^1/_2 J$) corresponds to a suppresion of the phase transition due to a random field. Equilibrium for the chemical reaction corresponds to thermodynamic equilibrium between domains of an Ising "ferromagnet". A continuous transition takes place at a critical temperature calculated from the condition $X_\sigma = 0$, which is fulfilled for $x = {}^1/_2$ and gives $kT_c = {}^1/_4 J$.

5. Discussion

It is illuminating to briefly survey some well-known solid state transformations that can be interpreted and analyzed within the framework of the present theory. In particular, the focus will be on what effects are responsible for chemical pressure and how elastic multipoles can be defined and identified.

A. Temperature-Induced Polymerization. It is well-known that this transformation causes substantial strain in the monomer lattice, so mechanical properties play an important role. Baughman[17] has used a simplified description of the properties to explain the important autocatalytic effect for thermal polymerization. From the perspective of this theory, Baughman's model is based on the following assumptions: (i) The monomer crystal is treated as an elastic continuum characterized by the elastic constant tensor $\mathbf{C}^{\mathrm{m}}$. (ii) Perturbations to the monomer crystal are polymer chains of a mesoscopic size and thus are treated as an elastic medium as well. The energy needed to create a unit volume of a polymer is, therefore, $\Delta E^0 = {}^1/_2 \epsilon_{\mathrm{p}} \mathbf{C}^{\mathrm{p}} \epsilon_{\mathrm{p}}$ where $\mathbf{C}^{\mathrm{p}}$ is the elastic constant tensor of the polymer and ϵ_{p} is the strain characteristic of the unit volume of the polymer. (iii) The effect of polymerization in the monomer lattice is considered by introducing local stresses at the expense of energy ΔE^0, e.g., the system may be modeled by elastic dipoles embedded in the monomer elastic medium. The elastic dipole is defined, therefore, as a purely mechanical local stress, $\mathbf{p} = \mathbf{C}^{\mathrm{p}} \epsilon_{\mathrm{p}}$. Observe that in the model, the initiation effect is neglected and therefore, the nature of the elastic dipole is purely mechanical.

The autocatalytic effect for the thermal polymerization is due to a concentration dependence of the activation energy. This is readily found from eq 4.16 with appropriate assignments of the parameters.

$$\Delta E_{\mathrm{act}} = {}^1/_8 \epsilon_{\mathrm{p}} \mathbf{C}^m \epsilon_{\mathrm{p}} [N^{-1} \sum_n \sum_{n'} \langle \sigma(n) \sigma(n') \rangle]_{\mathrm{av}}^{-1} \qquad (5.1)$$

The perturbation−perturbation correlation function can be approximated by x^2 for uncorrelated perturbations, by $x(1 - x)$ for correlated but uniformly distributed sites of a polymerized monomer, and by $(1 - x)\sum_m x^m$ for correlated, linear oligomers. The concentration dependence of the activation energy explains the autocatalytic effect for thermal polymerization. Baughman's equation[17] for the activation energy corresponds to the $x(1 - x)$ approximation for the correlation function.

Another important effect of the polymerization on the monomer lattice is modification of the elastic properties of the monomer due to the introduced perturbations. The effective elastic compliance tensor can be calculated from eq 4.11 by keeping in mind that the elastic dipole has been identified as $\mathbf{C}^{\mathrm{p}} \epsilon^{\mathrm{p}}$. Finally, the resulting strain due to the polymerization is calculated from eq 4.9 and can be approximated by a linear dependence on the concentration for a uniform distribution of polymerized sites. For the thermal polymerization, the degree of conversion can be calculated from the corresponding equations with $\Delta(\Delta_t)$ and J calculated by assuming the elastic dipoles as the only perturbations.

B. Photoinduced Reactions. Photoinduced reactions are often considered as being most typical for solid state reactions. There have been a few theoretical studies[18,35,36] where emphasis has been focused on structural change. Nagaosa's treatment[18] is the most similar to ours since his development also led to the Ising spin Hamiltonian as a model for the process. However, our treatment of the mechanical response function and the lattice deformation energy is more extensive. Also, it gives a direct relation to elasticity theory and insight into local, mechanical perturbations. On the other hand, Nagaosa has concentrated on the kinetic aspect of the Ising model, and for this reason, both theories can be considered as being complementary. The model for a photoinduced reaction is based on the following assumptions cast in the mold of the theory developed here: (i) Due to illumination of the crystal, molecules are in electronically excited states with energy ΔE^0. The collective excitation (an exciton) is then localized due to self-trapping.[37] The self-trapped state represents the feedback effect of the chemical pressure introduced into the lattice by an excited molecule. (ii) The self-trapped, localized state has energy $\Delta = \Delta E^0 - \Phi_{\mathrm{def}}$. The deformation energy has to be larger than the exciton band width so that the localized state will be well-separated from the band. The deformation energy is the energy of interaction of the elastic multipoles which can be represented by the chemical pressure. The strength of the multipoles depends on how strongly the D term (the change in van der Waals energy on excitation) in the exciton energy depends on molecular displacements.

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The total energy balance for a crystal expresses the assumption that energy gained by the lattice due to deformation is used to create self-trapped, excited molecules. Therefore, as long as $\Phi_{\mathrm{def}} \geq (m - 1)\Delta$, a cluster of m excited molecules will be created. A spontaneous creation, where $m \rightarrow \infty$, requires $\Phi_{\mathrm{def}} \geq \Delta E^0$. In case of photoinduced polymerization, oligomerization depends on the mutual relation between excitation energy and lattice deformation energy. The closer these values are, the larger the oligomers are that can be formed.

Recent extensive studies of crystal-to-crystal polymerization in 2,5-distyrylpyrazine (DSP)[16] provide an excellent illustration of this. The reaction proceeds in a two-stage fashion. Irradiation with light of wavelength between 480 and 400 nm yields an oligomer which is on average a trimer. Further or initial irradiation with light of wavelength less than 400 nm causes formation of a high polymer. The spectroscopic studies have shown that this wavelength dependence of the reaction is due to two separate electronic states. Therefore, in terms of the present theory, the dependence corresponds to different ΔE^0 energies and their relationships to corresponding deformation energies. The effect of the polymerization in the crystal on optical phonon frequencies has also been studied, but this dynamical aspect has not been considered and is left for further development. It has been found[16] that mode softening, postulated as the phonon assistance mechanism,[12] is a *result* of the photoreaction rather than necessarily being a cause of the reaction itself. This argument may be posed in general for phonon assistance[12] within the framework of the present theory. In other words, the internal strain, $\langle \mathbf{Q} \rangle$, induced by a reaction can (and should) reflect patterns of lattice normal modes. This corresponds to elastic multipoles and strains being expressed in terms of the normal mode coordinates.

The theory formulated above can also explain recent experiments on photoinduced phase transitions[38,39] in terms of a photoinduced reaction. An interesting aspect which follows from this analogy is the possibility for formation of reactant/product domain walls[39] and their motion, perhaps by quantum tunneling, in the course of the reaction.

C. Shock-Induced Reaction (Detonation). Shock-induced reactions are of great relevance to organic energetic materials. In particular, development of a mechanism for detonation of molecular materials is of current interest. Recently, a theoretical model has been proposed[40] to describe the initiation step in chemical reactivity (dissociation) of shocked energetic materials. The essence of the model is that the mechanical energy of the shock creates vibrationally "hot" molecules in an indirect process which involves heat. The mechanical energy in the compressed solid is stored in the phonon heat bath and is subsequently transferred by intramolecular "doorway" modes into the energetic molecules, thus making them vibrationally hot. Details of this transfer have been elaborated,[40,41] and it is considered to be the initiation of the detonation process. The next stage involves creation of hot molecules over macroscopic distances, and it is at this stage where the present theory offers a model for the macroscopic nature of the shock-induced reaction which includes the interaction between randomly distributed hot molecules. Within the context of the theory formulated here, these concepts may framed as the following assumptions: (i) A crystal is treated as an elastic medium, with a strain-dependent compressibility, **S**, thereby creating a nonlinear response. The shock is represented as an uniaxial stress $p_{ii}{}^0$, and the response to the stress is measured by lattice strain. (ii) The perturbations are vibrationally "hot" molecules, *i.e.* molecules that are in localized, vibrationally excited states. The molecules have to be hot enough to be able to dissociate. The energy of the hot molecule will be $\Delta E^0 = \sum_j n_j \hbar\omega_j$ (with the usual notation n_j for the occupation number and ω_j for frequency of a mode), which can be approximated by a vibrational quasi-temperature, $k\theta_{vib}$. In the summation over the vibrational modes, the most important are the so-called doorway modes[40,41] of large-amplitude significant anharmonicity and low frequency (relative to other intramolecular modes). (iii) The vibrationally hot molecules introduce local, mechanical perturbations into the lattice, and it is assumed, for simplicity, that the perturbation is a local stress that is represented by an appropriate elastic dipole. The dipole is defined as $P_{ij} \propto \sum \omega_j \gamma_{ij}{}^j$ where $\gamma_{ij}{}^j$ stands for the strain Grüneisen parameter of the mode j and the ijth component of the strain tensor.

This formulation of the elastic dipole seems to be the most obvious, but it can be argued that Grüneisen parameters for vibrational modes are small and, therefore, the local stress would be small. This, however, will not be true for doorway modes. On the other hand, as the energy ΔE^0 has to be equal to that stored in the phonon modes, it is possible that the local stress is determined by the Grüneisen parameters of the lattice modes.

The energy of the compressed crystal can be written as

$$\Delta E = m(\Delta E^0 + \mathbf{P}\epsilon) + {}^1\!/_2 N \mathrm{v}_0 (\epsilon \mathbf{C} \epsilon + \sum_i p_{ii}{}^0 \epsilon_{ii}) \quad (5.2)$$

where **P** is the elastic dipole and v_0 stands for the initial volume of the unit cell. The final volume under the uniaxial stress p_{ii} is calculated as

$$\mathrm{v_f} = -\mathrm{v}_0 \sum_{ij} \sum_{kl} S_{ijkl} [p_{kk}{}^0 \delta_{kl} + p_{kl} x] \quad (5.3)$$

where $\boldsymbol{p} = \mathrm{v}_0{}^{-1}\mathbf{P}$ is the local stress related to the elastic dipole created by a hot molecule and $x = m/N$ is the fraction of the hot molecules. The energy is finally found as $\Delta E = \Delta E^0 x - \Phi_{\mathrm{def}}(x)$, where the deformation energy is

$$\Phi_{\mathrm{def}}(x) = {}^1\!/_2 \mathrm{v}_0 \sum_{ij} \sum_{kl} S_{ijkl} [p_{ii}{}^0 \delta_{ij} + p_{ij} x][p_{kk}{}^0 \delta_{kl} + p_{kl} x] \quad (5.4)$$

and under the condition $\Phi_{\mathrm{def}}\ (x = 1) \geq \Delta E^0\ (= k\theta_{\mathrm{vib}})$, corresponding to $\Delta E \leq 0$, the vibrationally hot molecules are created spontaneously. Equation 5.2 with the condition $\Delta E = 0$ gives an energy balance analogous to the one considered by Tokmakoff, Fayer, and Dlott[41] where the first two terms of our equation have been replaced by heat related to entropy transport that is stored in a phonon bath. The phonon heat capacity would correspond to our ΔE^0, and the volume-dependent entropy would correspond to interaction of the elastic dipole with lattice strain as expressed by Grüneisen parameters.

The process can then be explained by the following scenario. Assume that a vibrational excitation level in the crystal is reached by the up-pumping mechanism suggested by Dlott and Fayer.[40] The excitation can then be localized by the mechanism of self-trapping. The self-trapped state with large lattice distortion is separated from the moving vibrational exciton state. In the case of low-frequency, large-amplitude doorway modes, the lattice distortion energy is sizeable and localizes the state by the amount of energy Φ_{def} below that of the free-moving vibrational exciton. This energy is released when the shock-created free-vibrational exciton relaxes to the self-trapped state

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and can be used to create other self-trapped vibrationally hot molecules. At the condition $\Phi_{\mathrm{def}} \geq \Delta E^0$, an infinite number of such molecules is simultaneously created. This can be seen as a direct pumping of the vibrationally hot molecules by the mechanical energy of the shock once the initiation at one molecule occurs. Defects and impurities help to localize the collective states which are well-known effects.

6. Conclusions

The idea of chemical pressure in solid state reactions can be extended by a model based on elastic multipoles. Generalization of the theory of chemical pressure and solid state reactions can then be achieved. This development allows the quantitative definition of several basic concepts of solid state reactivity that have heretofore resisted such description.

The concepts of reaction cavity and steric compression have been suggested previously and have proven useful for a qualitative understanding of solid state reactions. Although these ideas have proven useful in thinking about solid state reactions, they have also remained somewhat nebulous, thereby limiting their applicability. The present formulation of how chemical reactions in solids possess both local and global characteristics has illuminated these concepts. The cavity surrounding a product molecule is discussed as well as the forces that are associated with its production. These forces can be generalized as the chemical pressure and, as such, may be directly related to the concept of steric compression, being *local* and *molecular* counterparts of stress and related to compression in a macroscopic sense. The cavity that is defined can be identified with the reaction cavity. The elastic multipoles, being a representation of a force distribution, are found to be ideal to describe both the geometry and energetics of the reaction cavity. The symmetry of the reaction cavity is reflected by the elastic multipoles, and their changes in a course of reaction are described by the appropriate components of their tensors. Thus, one can define an "order parameter" for a solid state reaction and relate it to a "continuous symmetry measure" that has been recently advocated.[42]

The lattice deformation energy and strain can be related to the energetics of the solid state reaction. Both are related to ideas developed regarding the role of stress in solid state reactivity. The demonstration of how local stresses, represented by elastic multipoles, couple and interact through the elasticity of the lattice that can subsequently lead to a phase transition is another relevant outcome of the theory. The role of clustering of products and the heterogeneity of the reaction can also be elucidated. The mechanical response of the lattice to the reaction, the reaction cavity, and the steric compression as formulated by the theory can be calculated by use of measurable quantities: atomic displacement parameters and optical and acoustic (for the elasticity) phonon spectra. Thus, while the theory joins important experimental parameters, it provides a uniform framework that can be applied to thermal-, light-, and shock- (detonation) induced reactions. A direct correspondence to the molecular orbital theory of reactivity and concepts mirroring that of hard and soft acids and bases[43] can be envisioned. The elastic multipole formulation can also be extended to understanding properties of ordered molecular films.

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