

Intermolecular Potential, Vibrational Spectra, and Structures of Amino Acid Crystals. I. Distortion of Molecules and Equilibrium Crystal Structure

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A general method of the crystal packing optimization is developed for the molecular crystals consisting of non-rigid molecules. The intramolecular potential is described as a general harmonic force field in terms of a suitable set of internal symmetry coordinates, and the intermolecular potential as a sum of the pairwise atom-atom interaction terms. The adjustable structure parameters are those among the six cell constants, a , b , c , α , β , and γ , and the translations and the rotations of the molecules which maintain the crystal symmetry. The intermolecular force is separated into two parts, one of which determines the location of the center of mass and the orientation of the principal axes of each molecule and the other leads to a certain molecular distortion. The calculated distortion may be used, in addition to the difference between the calculated and the observed crystal structures, as a check point of the reliability of the model potential. The importance of this separation in the rigid molecule approximation is pointed out.

In order to search for the equilibrium structure of a given molecular crystal by taking account of all the degrees of freedom of atomic motions in the asymmetric unit, we should pay attention to both the intramolecular (internal) and the intermolecular (external) parts of the potential function. Any molecular crystals maintain their structures on the balance of the forces expressed as the gradients of these two parts. Confining the discussion to those crystals in which all the molecules are symmetrically equivalent, we shall denote the intramolecular and the intermolecular potentials per molecule as V_{in} and V_{ex} , respectively. The contribution of V_{in} to the forces acting on the atoms may be estimated if the atomic displacements on the change from the gaseous state to the crystal are known experimentally and also the change of V_{in} on the change of state is assumed to be negligible. Warshel and Lifson carried out extensive calculations of this type for a number of hydrocarbons using the Cartesian coordinates of atoms as the working coordinates.¹⁾ This method cannot be applied to amino acids for which the structures in the isolated zwitterionic form are unknown. Neither is the rigid molecule approximation applicable in this case, since the low-frequency intramolecular vibrations of amino acids couple appreciably with the lattice modes. The internal rotations around single bonds have been taken into account by several authors in the conformation analyses of molecular crystals.^{2,3)} In a series of studies on vibrational spectra of simple amino acids, however, we observed that some of the skeletal deformation frequencies were lower than the torsional frequencies of the NH_3^+ and the CH_3 groups.^{4–7)}

In this report, we propose a convenient procedure of the potential energy minimization for the crystals of amino acids and similar non-rigid molecules. General expressions for the increments of the structure parameters in the Newton-Raphson iteration are given by taking account of the effect of V_{in} without any knowledge on the structure of the isolated molecules. Application of the method to α -glycine, L-alanine and DL-alanine crystals will be given in the subsequent paper.

Theory

Molecular Distortion. The $3N$ degrees of freedom of motions of a non-linear N atomic molecule may be described by a set of $3N-6$ internal symmetry coordinates, denoted in a vector form as \mathbf{S}_{in} , and 6 external coordinates, \mathbf{S}_{ex} , representing the translation and the rotation of the whole molecule. These coordinates can be constructed from the Cartesian displacement coordinates \mathbf{x} of the atoms through the transformations

$$\mathbf{S}_{\text{in}} = \mathbf{B}_{\text{in}}\mathbf{x} \quad \text{and} \quad \mathbf{S}_{\text{ex}} = \mathbf{B}_{\text{ex}}\mathbf{x}. \quad (1)$$

The matrix \mathbf{B}_{in} is related to the well known \mathbf{G} matrix by

$$\mathbf{G} = \mathbf{B}_{\text{in}}\mathbf{m}^{-1}\tilde{\mathbf{B}}_{\text{in}}, \quad (2)$$

where \mathbf{m} is a $3N \times 3N$ diagonal matrix consisting of the atomic masses.⁸⁾ Since \mathbf{S}_{ex} is so chosen as to fulfill the Eckart condition and is normalized,⁹⁾ it follows that

$$\mathbf{B}_{\text{in}}\mathbf{m}^{-1}\tilde{\mathbf{B}}_{\text{ex}} = \mathbf{0} \quad (3)$$

and

$$\mathbf{B}_{\text{ex}}\mathbf{m}^{-1}\tilde{\mathbf{B}}_{\text{ex}} = \mathbf{E}, \quad (4)$$

where \mathbf{E} is a 6×6 identity matrix. Next we denote the vector of the external forces along the Cartesian coordinates by

$$\mathbf{f}_{\text{x}}^{\text{ex}} = [-\partial V_{\text{ex}}/\partial x_1 - \partial V_{\text{ex}}/\partial y_1 \cdots - \partial V_{\text{ex}}/\partial z_N]^T,$$

and introduce the vectors of generalized forces $\mathbf{f}_{\text{in}}^{\text{ex}}$ and $\mathbf{f}_{\text{ex}}^{\text{ex}}$ corresponding to the coordinates \mathbf{S}_{in} and \mathbf{S}_{ex} , respectively. In accordance with Eq. 1, the transformation from the generalized forces to $\mathbf{f}_{\text{x}}^{\text{ex}}$ is expressed as

$$\mathbf{f}_{\text{x}}^{\text{ex}} = \tilde{\mathbf{B}}_{\text{in}}\mathbf{f}_{\text{in}}^{\text{ex}} + \tilde{\mathbf{B}}_{\text{ex}}\mathbf{f}_{\text{ex}}^{\text{ex}}. \quad (5)$$

Premultiplying Eq. 5 by $\mathbf{G}^{-1}\mathbf{B}_{\text{in}}\mathbf{m}^{-1}$ and using Eqs. 2 and 3, we obtain

$$\mathbf{f}_{\text{in}}^{\text{ex}} = \mathbf{G}^{-1}\mathbf{B}_{\text{in}}\mathbf{m}^{-1}\mathbf{f}_{\text{x}}^{\text{ex}}. \quad (6)$$

Similarly, the use of Eqs. 3 and 4 after premultiplying by $\mathbf{B}_{\text{ex}}\mathbf{m}^{-1}$ leads to

$$\mathbf{f}_{\text{ex}}^{\text{ex}} = \mathbf{B}_{\text{ex}}\mathbf{m}^{-1}\mathbf{f}_{\text{x}}^{\text{ex}}. \quad (7)$$

Equations 6 and 7 enable us to partition the external

force into two parts, one tending to distort the molecule and the other tending to displace and rotate it. At the equilibrium position, $\mathbf{f}_{\text{ex}}^{\text{ex}}$ should vanish while $\mathbf{f}_{\text{in}}^{\text{ex}}$ is not necessarily a zero vector since it can be offset by the internal force, $\mathbf{f}_{\text{in}}^{\text{in}}$, which arises from a certain distortion of the molecule associated with the change of the environment from the isolated state into the crystal, *i.e.*,

$$\mathbf{f}_{\text{in}}^{\text{ex}} = -\mathbf{f}_{\text{in}}^{\text{in}}. \quad (8)$$

Kurittu and Pawley gave a general expression of this distortion in terms of the normal coordinates of the free molecule.¹⁰⁾ An alternative way, being applicable to the cases where the molecular structure in the free state is unknown, is to express the distortion in terms of the internal symmetry coordinates \mathbf{S}_{in} of the molecules in the crystal. Denoting such a distortion by $\mathbf{S}_{\text{in}}^{\text{ex}}$ and using Eqs. 6 and 8, we have

$$\mathbf{S}_{\text{in}}^{\text{ex}} = -\mathbf{F}^{-1} \mathbf{f}_{\text{in}}^{\text{in}} = \mathbf{F}^{-1} \mathbf{G}^{-1} \mathbf{B}_{\text{in}} \mathbf{m}^{-1} \mathbf{f}_x^{\text{ex}}, \quad (9)$$

where \mathbf{F} is the usual potential energy matrix for the internal vibrations defined by

$$2V_{\text{in}} = \tilde{\mathbf{S}}_{\text{in}} \mathbf{F} \mathbf{S}_{\text{in}}.$$

The Cartesian components of the internal force are given by

$$\mathbf{f}_x^{\text{in}} = \tilde{\mathbf{B}}_{\text{in}} \mathbf{f}_{\text{in}}^{\text{in}}, \quad (10)$$

since $\mathbf{f}_{\text{ex}}^{\text{in}}$ vanishes from the definition in contrast to the case of $\mathbf{f}_{\text{ex}}^{\text{ex}}$ in Eq. 5. When the \mathbf{F} matrix does not change on going from the gaseous state to the crystal, $\mathbf{S}_{\text{in}}^{\text{ex}}$ represents the structure change of the molecule on the change of state. In the procedure of Kurittu and Pawley,¹⁰⁾ one starts from the geometry of the undistorted molecule, and calculates the external force iteratively at the varying atomic positions until the final balance between V_{in} of the distorted molecule and V_{ex} is attained. On the other hand, the calculation in the present formulation is performed once for the distorted molecule, and the structure of the isolated molecule is inferred by subtracting $\mathbf{S}_{\text{in}}^{\text{ex}}$ from the structure in the crystalline state. Obviously, our method is valid only for infinitesimal distortions while that of Kurittu and Pawley is applicable to larger ones. An advantage of our method is that we can incorporate all the degrees of freedom of atomic motions implicitly in the conformation analysis of molecular crystals, using the same number of adjustable parameters as the rigid molecule approximation, *viz.*, the lattice constants and the translations and the rotations of the whole molecule.

Changes of Lattice Constants and External Coordinates. The potential energy per unit cell of a uniformly deformed molecular crystal under a small strain may be expressed as

$$V = V_0 - \tilde{\mathbf{f}}_0 \boldsymbol{\sigma} - \tilde{\mathbf{f}}_x \mathbf{x}_\rho + (1/2)(\tilde{\partial} \mathbf{F}_{\sigma\sigma} \boldsymbol{\sigma} + \tilde{\mathbf{x}}_\rho \mathbf{F}_{xx} \mathbf{x}_\rho) + \tilde{\partial} \mathbf{F}_{\sigma x} \mathbf{x}_\rho, \quad (11)$$

where $\boldsymbol{\sigma}$ is the strain vector,

$$\boldsymbol{\sigma} = [\sigma_{xx} \sigma_{yy} \sigma_{zz} \sigma_{yz} \sigma_{zx} \sigma_{xy}]^T,$$

which leads to the macroscopic deformation of the crystal, and \mathbf{x}_ρ is the vector of the microscopic Cartesian displacements of the atoms in the unit cell.¹¹⁾ We

retain the linear terms in Eq. 11 considering the cases when no minima of the adopted model potential correspond to the experimentally determined structure. The vector \mathbf{f}_x is the sum of the external and the internal forces, and is given by

$$\mathbf{f}_x = \mathbf{f}_x^{\text{ex}} + \mathbf{f}_x^{\text{in}} = (\mathbf{E} - \tilde{\mathbf{B}}_{\text{in}} \mathbf{G}^{-1} \mathbf{B}_{\text{in}} \mathbf{m}^{-1}) \mathbf{f}_x^{\text{ex}} \quad (12)$$

from Eqs. 6, 8, and 10. The matrix \mathbf{F}_{xx} is equivalent to the \mathbf{F} matrix for the optical active crystal vibrations in terms of the Cartesian displacements, and can be diagonalized by the transformation into the normal coordinates,

$$\mathbf{x}_\rho = \mathbf{L}_x \mathbf{q}_\rho. \quad (13)$$

In order to determine \mathbf{f}_σ , $\mathbf{F}_{\sigma\sigma}$, and $\mathbf{F}_{\sigma x}$ in Eq. 11 and then to calculate the derivatives of V with respect to the lattice constants and the external coordinates, it is useful to follow the treatment of elastic constants of molecular crystals due to Shiro and Miyazawa in a slightly modified manner including the linear terms.¹²⁾

Specifying each unit cell with an index vector \mathbf{L} , we can express the Cartesian displacements of the i th atom in the cell \mathbf{L} (denoted as the atom \mathbf{Li} hereafter) of the uniformly deformed lattice as

$$\mathbf{x}_i(\mathbf{L}) = \mathbf{D}^i(\mathbf{L}) \boldsymbol{\sigma} + \mathbf{E}^i \mathbf{x}_\rho, \quad (14)$$

where $\mathbf{D}^i(\mathbf{L})$ consists of the Cartesian coordinates of the atom \mathbf{Li} evaluated with reference to the origin of the cell $\mathbf{0}$ when $\boldsymbol{\sigma} = \mathbf{0}$, $X_i^0(\mathbf{L})$, $Y_i^0(\mathbf{L})$, and $Z_i^0(\mathbf{L})$, *viz.*,

$$\mathbf{D}^i(\mathbf{L}) = \begin{bmatrix} X_i^0(\mathbf{L}) & 0 & 0 & 0 & Z_i^0(\mathbf{L})/2 & Y_i^0(\mathbf{L})/2 \\ 0 & Y_i^0(\mathbf{L}) & 0 & Z_i^0(\mathbf{L})/2 & 0 & X_i^0(\mathbf{L})/2 \\ 0 & 0 & Z_i^0(\mathbf{L}) & Y_i^0(\mathbf{L})/2 & X_i^0(\mathbf{L})/2 & 0 \end{bmatrix},$$

and the elements of \mathbf{E}^i are given in terms of Kronecker's delta as

$$(\mathbf{E}^i)_{jk} = \delta_{k-j, 3(i-1)}.$$

The atomic displacement vector for the cell \mathbf{L} is obtained by collecting $\mathbf{x}_i(\mathbf{L})$ columnwise, and is written in the form

$$\mathbf{x}(\mathbf{L}) = \mathbf{D}_x(\mathbf{L}) \boldsymbol{\sigma} + \mathbf{x}_\rho, \quad (15)$$

where

$$\mathbf{D}_x(\mathbf{L}) = \sum_i \tilde{\mathbf{E}}^i \mathbf{D}^i(\mathbf{L}).$$

The pairwise interaction potential between the atoms $\mathbf{0i}$ and \mathbf{Lj} may be expanded as the power series of the relevant Cartesian displacements in the form

$$V^{ij}\{r_{ij}(\mathbf{L})\} = V^{ij}\{r_{ij}^0(\mathbf{L})\} - \tilde{\mathbf{f}}_{ij}(\mathbf{L})\{\mathbf{x}_i(\mathbf{0}) - \mathbf{x}_j(\mathbf{L})\} + \frac{1}{2}\{\tilde{\mathbf{x}}_i(\mathbf{0}) - \tilde{\mathbf{x}}_j(\mathbf{L})\} \mathbf{F}_{ij}(\mathbf{L}) \{\mathbf{x}_i(\mathbf{0}) - \mathbf{x}_j(\mathbf{L})\}, \quad (16)$$

where $r_{ij}(\mathbf{L})$ is the distance between $\mathbf{0i}$ and \mathbf{Lj} , and the superscript 0 denotes the value when $\boldsymbol{\sigma} = \mathbf{0}$. The linear and the quadratic coefficients in Eq. 16 are given by

$$\mathbf{f}_{ij}(\mathbf{L}) = -\{\partial V^{ij} / \partial r_{ij}(\mathbf{L})\} \mathbf{e}_{ij}^0(\mathbf{L})$$

and

$$\mathbf{F}_{ij}(\mathbf{L}) = \{\partial V^{ij}/\partial r_{ij}(\mathbf{L})\}\{\mathbf{E} - \mathbf{e}_{ij}^0(\mathbf{L})\tilde{\mathbf{e}}_{ij}^0(\mathbf{L})\}/r_{ij}^0(\mathbf{L}) \\ + \{\partial^2 V^{ij}/\partial r_{ij}(\mathbf{L})^2\}\mathbf{e}_{ij}^0(\mathbf{L})\tilde{\mathbf{e}}_{ij}^0(\mathbf{L}),$$

respectively, where $\mathbf{e}_{ij}^0(\mathbf{L})$ denotes the unit vector along the direction from Lj to $0i$. Substituting Eq. 14 into Eq. 16, dividing by $1 + \delta_{ij}$ and summing over all the intermolecular atom pairs $0i$ and Lj such that $i \leq j$, we obtain the portion of the potential energy in Eq. 11 arising from V_{ex} . Since we are dealing with a homogeneous deformation, the contribution of V_{in} to Eq. 11 can be evaluated by writing down V_{in} for the cell 0 in terms of the Cartesian displacements as

$$V_{in} = -\tilde{\mathbf{f}}_x^T \mathbf{x}(0) + (1/2)\tilde{\mathbf{x}}(0)\mathbf{F}_{xx} \mathbf{x}(0),$$

and substituting Eq. 15. Carrying out these calculations, we have

$$\mathbf{f}_\sigma = \sum_{i \leq j, L} (1 + \delta_{ij})^{-1} \tilde{\mathbf{D}}^{ij}(\mathbf{L}) \mathbf{f}_{ij}(\mathbf{L}) + \tilde{\mathbf{D}}_x(0) \mathbf{f}_x^{in}, \quad (17)$$

$$\mathbf{F}_{\sigma\sigma} = \sum_{i \leq j, L} (1 + \delta_{ij})^{-1} \tilde{\mathbf{D}}^{ij}(\mathbf{L}) \mathbf{F}_{ij}(\mathbf{L}) \mathbf{D}^{ij}(\mathbf{L}) + \tilde{\mathbf{D}}_x(0) \mathbf{F}_{xx} \mathbf{D}_x(0) \quad (18)$$

and

$$\mathbf{F}_{\sigma x} = \sum_{i \leq j, L} (1 + \delta_{ij})^{-1} \tilde{\mathbf{D}}^{ij}(\mathbf{L}) \mathbf{F}_{ij}(\mathbf{L}) (\mathbf{E}^i - \mathbf{E}^j) \\ + \tilde{\mathbf{D}}_x(0) \mathbf{F}_{xx} \mathbf{e}_x^{in}, \quad (19)$$

where

$$\mathbf{D}^{ij}(\mathbf{L}) = \mathbf{D}^i(0) - \mathbf{D}^j(\mathbf{L}).$$

Substituting Eq. 13 into Eq. 11, and using the condition that the potential energy is stationary with respect to the microscopic deformation, we have

$$\mathbf{q}_\rho = \mathbf{A}^{-1} \tilde{\mathbf{L}}_x \mathbf{f}_x - \mathbf{A}^{-1} \tilde{\mathbf{L}}_x \tilde{\mathbf{F}}_{\sigma x} \boldsymbol{\sigma}, \quad (20)$$

where \mathbf{A} is the diagonal matrix of the eigenvalues of $\mathbf{m}^{-1/2} \mathbf{F}_{xx} \mathbf{m}^{-1/2}$ corresponding to the genuine normal modes, and the eigenvectors for the translations of the whole crystal are excluded from \mathbf{L}_x . By eliminating \mathbf{q}_ρ from Eqs. 13 and 20 and substituting the result into Eq. 11, the potential energy is rewritten as

$$V = V_0 - (\tilde{\mathbf{f}}_\sigma - \mathbf{L}_x \mathbf{A}^{-1} \tilde{\mathbf{L}}_x \tilde{\mathbf{F}}_{\sigma x}) \boldsymbol{\sigma} \\ + (1/2) \tilde{\boldsymbol{\sigma}} (\mathbf{F}_{\sigma\sigma} - \mathbf{F}_{\sigma x} \mathbf{L}_x \mathbf{A}^{-1} \tilde{\mathbf{L}}_x \tilde{\mathbf{F}}_{\sigma x}) \boldsymbol{\sigma}. \quad (21)$$

The quadratic part of Eq. 21 divided by the volume of the unit cell gives the matrix of the elastic constants as derived by Shiro and Miyazawa.¹²⁾

Let a set of infinitesimal changes of the cell dimensions be denoted in a vector form

$$\Delta \mathbf{a} = [\Delta a \ \Delta b \ \Delta c \ \Delta \alpha \ \Delta \beta \ \Delta \gamma]^T,$$

and those required to eliminate the linear terms in Eq. 21 be $\Delta \mathbf{a}^*$. By differentiating Eq. 21 with respect to $\boldsymbol{\sigma}$ and using the transformation

$$\boldsymbol{\sigma} = \mathbf{A} \Delta \mathbf{a}, \quad (22)$$

the vector $\Delta \mathbf{a}^*$ is derived to be

$$\Delta \mathbf{a}^* = (\tilde{\mathbf{f}}_\sigma - \tilde{\mathbf{f}}_x \mathbf{L}_x \mathbf{A}^{-1} \tilde{\mathbf{L}}_x \tilde{\mathbf{F}}_{\sigma x}) (\mathbf{F}_{\sigma\sigma} \\ - \mathbf{F}_{\sigma x} \mathbf{L}_x \mathbf{A}^{-1} \tilde{\mathbf{L}}_x \tilde{\mathbf{F}}_{\sigma x})^{-1} \mathbf{A}^{-1} \quad (23)$$

Derivation of the transformation matrix \mathbf{A} and its

inverse is given in Appendix.

The first term of Eq. 20 represents those microscopic displacements of the atoms which are required to minimize the energy of a stress-free crystal in the first-order approximation. These displacements may also be expressed in terms of the internal symmetry and the external coordinates in the form

$$\mathbf{S}_{in}^* = -\mathbf{B}_{in} \mathbf{L}_x \mathbf{A}^{-1} \tilde{\mathbf{L}}_x \mathbf{f}_x \quad (24)$$

and

$$\mathbf{S}_{ex}^* = -\mathbf{B}_{ex} \mathbf{L}_x \mathbf{A}^{-1} \tilde{\mathbf{L}}_x \mathbf{f}_x. \quad (25)$$

Iterative minimization of the potential energy can now be carried out by the Newton-Raphson method in which $\Delta \mathbf{a}^*$ and \mathbf{S}_{ex}^* are used as the correction vectors.¹³⁾ The normalized external coordinates are not so convenient to visualize the actual position and orientation of each molecule in the unit cell. Instead, we may use the translations along the principal axes of inertia, T_1^* , T_2^* , and T_3^* , and the rotations around those axes, R_1^* , R_2^* , and R_3^* . Denoting the vector of these quantities as \mathbf{T}_{ex}^* and introducing a 6×6 diagonal matrix

$$\mathbf{M}^{-1/2} = \text{diag}[M^{-1/2} \ M^{-1/2} \ M^{-1/2} \ I_1^{-1/2} \ I_2^{-1/2} \ I_3^{-1/2}],$$

where M is the molecular mass and I_1 , I_2 , and I_3 are the principal moments of inertia of the molecule, we have

$$\tilde{\mathbf{T}}_{ex}^* = [T_1^* \ T_2^* \ T_3^* \ R_1^* \ R_2^* \ R_3^*] = \tilde{\mathbf{S}}_{ex}^* \mathbf{M}^{-1/2}. \quad (26)$$

When the unit cell has any symmetry elements, calculation of Eq. 25 for the non-totally symmetric species of the factor group can be avoided by using a set of properly chosen symmetry coordinates. If all the rotations R_i^* are small, the combined rotation is defined uniquely as their vector sum, the magnitude of which is

$$\theta = |R_1^{*2} + R_2^{*2} + R_3^{*2}|^{1/2},$$

and the direction cosine between the axis of the rotation and the i th principal axis is

$$l_i = R_i^*/\theta.$$

In the frame of the principal axes, the rotation is performed by using the transformation matrix familiar in crystallography¹⁴⁾ which consists of the diagonal elements

$$\theta_{ii} = \cos \theta + l_i^2 (1 - \cos \theta)$$

and the off-diagonal elements

$$\theta_{ij} = l_i l_j (1 - \cos \theta) + (j - i) (-1)^{i+j} l_{6-i-j} \sin \theta / |i - j|.$$

The Cartesian coordinates of the k th atom in the molecule after the correction of the structure according to $\Delta \mathbf{a}^*$ and \mathbf{T}_{ex}^* are calculated from those before the correction, x_k^0 , y_k^0 , and z_k^0 , by

$$x_k^* = \sum C_{xi} [\sum \theta_{ij} \{C_{xj}(x_k^0 - x_g^0) + C_{yj}(y_k^0 - y_g^0) \\ + C_{zj}(z_k^0 - z_g^0)\} + T_i^*] + (1 + \sigma_{xx}) x_g^0 \\ + \sigma_{xy} y_g^0 + \sigma_{xz} z_g^0, \quad (27)$$

where C_{xi} is the direction cosine between the x axis and the i th principal axis, and x_g^0 , y_g^0 , and z_g^0 are the coordinates of the center of mass of the molecule before the correction, and similar expressions for the y and the z components.

Discussion

In the procedure described above, the internal correction vector S_{in}^* is excluded from the iteration and the internal structure of the molecules is accordingly kept unchanged throughout the energy minimization. If the matrix $L_x A^{-1} \tilde{L}_x$ is positive definite, the force f_{ex}^{ox} tends to vanish when the external correction vector S_{ex}^* diminishes according to Eq. 25, since

$$f_x = \tilde{B}_{ex} f_{ex}^{ox}$$

and the matrix $B_{ex} L_x A^{-1} \tilde{L}_x \tilde{B}_{ex}$ has an inverse, and S_{in}^* in Eq. 24 is made automatically a zero vector at a potential minimum. This condition is fulfilled by any model potential for which all the calculated lattice frequencies are real. In this respect, the present scheme of the crystal packing analysis resembles that based on the rigid molecule approximation in which the molecular structure can be chosen in the same way as that determined experimentally. The present method affords, however, a useful information not available from the rigid molecule approximation, i.e., the molecular distortion vector S_{in}^* , which may be compared with the structure data in the gaseous state or the results of theoretical calculations on the electronic states of the isolated molecule.

The use of Eqs. 12 and 17 including f_x^{in} is essential in the calculation of Δa^* even when the rigid molecule approximation is adopted. In this case, the terms arising from V_{in} should be excluded from Eqs. 18 and 19, and the elements of A and L_x in Eq. 23 related to the internal modes should be absent. Since the rigid molecule approximation is the limiting case that the diagonal elements of F become infinite, the distortion S_{in}^* turns out to be infinitesimal but the product

$$f_{in}^{in} = -FS_{in}^*$$

remains undiminished because it is determined purely by the external force. This point has so far been overlooked and f_x^{ex} instead of f_x has been used as the net force acting on the atoms by many investigators who have adopted the rigid molecule approximation.

In contrast to the case of Δa^* , the effect of f_{in}^{in} on T_{ex}^* is expected to be important only for non-rigid molecules. If we use f_x^{ex} in place of f_x in Eq.

25, it follows from Eq. 5 that

$$S_{ex}^* = -B_{ex} L_x A^{-1} \tilde{L}_x (\tilde{B}_{in} f_{in}^{ex} + \tilde{B}_{ex} f_{ex}^{ex}). \quad (28)$$

If the internal and the external modes do not couple with each other, the matrix of the coefficients of f_{in}^{ex} in Eq. 28 vanishes and f_x^{ex} leads to the same T_{ex}^* as f_x does. This condition is approximately fulfilled when the crystal consists of nearly rigid molecules, whereas there are no simple conditions for the cancellation of the contributions of f_{in}^{in} to f_x and f_e in Eq. 23.

In order to check the effect of the internal force on the packing analysis of α -glycine, L-alanine, and DL-alanine crystals, the correction vectors Δa^* and T_{ex}^* were calculated from Eqs. 23 and 25, respectively, and also from the same equations in which f_x^{in} was set equal to zero. In this calculation, the atomic coordinates, the potential parameters and the ranges of the lattice sums were taken in the same way as those in our previous studies on the crystal vibrations of these amino acids.^{5,7)} As shown in Table 1, the correction vectors of each amino acid calculated for the cases $f_x^{in} \neq 0$ and $f_x^{in} = 0$ are roughly parallel to each other. As to the individual components of Δa^* and T_{ex}^* , however, there is no systematic trend in signs and relative magnitudes of the differences between the values obtained from the two calculations. Some of the components of T_{ex}^* change quite sensitively when f_x is replaced by f_x^{ex} , owing probably to the coupling between the internal and the external modes. These results suggest that we should take account of the internal force of non-rigid molecules correctly in searching for the crystal structure corresponding to the energy minimum for a given model potential. Similar consideration may be required when we try to adjust the potential parameters in such a way as to minimize the correction vectors.

We wish to express our sincere thanks to Prof. Kenji Osaki and Prof. Takeo Matsubara of Kyoto University for their valuable advices. The numerical calculations were carried out on FACOM 230-75 and M200 computers at the Data Processing Center of Kyoto University.

TABLE 1. COMPONENTS OF CORRECTION VECTORS Δa^* AND T_{ex}^*

f_x^{in}	α -Glycine		L-Alanine		DL-Alanine	
	$\neq 0$	$= 0$	$\neq 0$	$= 0$	$\neq 0$	$= 0$
Δa^*	0.414	0.401	-0.353	-0.145	1.003	0.650
Δb^*	1.013	1.158	1.063	0.754	-0.388	-0.278
Δc^*	-0.270	-0.353	0.082	0.107	-0.409	-0.308
$\Delta \beta^*$	0.032	0.031				
T_1^*	0.048	0.049	0.026	0.020	-0.020	-0.019
T_2^*	0.486	0.473	0.099	0.066	0.048	0.051
T_3^*	-0.491	-0.444	-0.091	-0.021	-0.007	-0.007
R_1^*	-0.063	-0.038	0.020	0.042	-0.070	-0.060
R_2^*	0.070	0.072	0.010	0.037	-0.017	-0.013
R_3^*	-0.036	-0.013	0.082	0.095	0.133	0.131

Δa^* , Δb^* , Δc^* , and T_i^* are in Å, and $\Delta \beta^*$ and R_i^* are in radian.

Appendix

Let the Cartesian coordinates of the atoms in a unit cell be defined in the framework where the x axis coincides with the a axis and the y axis lies on the ab plane. Then the matrix of the transformation from the fractional coordinates along the cell axes to the Cartesian coordinates is given by

$$\mathbf{C} = \begin{bmatrix} a & b \cos \gamma & c \cos \beta \\ 0 & b \sin \gamma & -c \sin \beta \cos \alpha^* \\ 0 & 0 & c \sin \beta \sin \alpha^* \end{bmatrix}, \quad (\text{A1})$$

where the asterisk denotes the lattice constants of the reciprocal lattice.¹⁴⁾ By labelling the quantities at the equilibrium under vanishing stress with the subscript 0, the inverse of \mathbf{C} at the equilibrium is expressed as

$$\mathbf{C}_0^{-1} = \begin{pmatrix} 1 & \cos \gamma_0 & \cos \beta_0^* \\ a_0 & a_0 \sin \gamma_0 & a_0 \sin \gamma_0 \sin \beta_0^* \\ 0 & 1 & \cos \alpha_0^* \\ 0 & b_0 \sin \gamma_0 & b_0 \sin \gamma_0 \sin \alpha_0^* \\ 0 & 0 & 1 \\ & & c_0 \sin \beta_0 \sin \alpha_0^* \end{pmatrix}. \quad (\text{A2})$$

The elements of the matrix \mathbf{CC}_0^{-1} are related to the strain components by

$$(\mathbf{CC}_0^{-1})_{ij} = \delta_{ij} + \sigma_{ij}, \quad (\text{A3})$$

where δ_{ij} is Kronecker's delta and the subscripts 1, 2, and 3 for σ_{ij} represent x, y, and z, respectively.¹⁵⁾ Substituting Eqs. (A1) and (A2) into Eq. (A3), expanding each of the six independent elements of \mathbf{CC}_0^{-1} as a power series of the variations of the lattice constants and neglecting the higher-order terms, we obtain Eq. (22) in the text. The transformation matrix can be factored into two matrices

$$\mathbf{A}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & c \\ 0 & 0 & 1 & -r & -p & -pr \\ 0 & r & -r & -1 & c & cr-p \\ p & cr & b/s & 0 & -1 & -r \\ -c & c & 0 & 0 & 0 & -1 \end{pmatrix},$$

where

$$p = \cot \beta_0^* / \sin \gamma_0, \quad r = \cot \alpha_0^*, \quad s = \sin \alpha_0^*,$$

$$b = \cot \beta_0 \quad \text{and} \quad c = \cot \gamma_0$$

and

$$\mathbf{A}_2 = \text{diag}[a_0^{-1} b_0^{-1} c_0^{-1} (\sin \gamma_0 \sin \beta_0^*)^{-1} (\sin \alpha_0^*)^{-1} 1],$$

and is written as $\mathbf{A} = \mathbf{A}_1 \mathbf{A}_2$. By a straightforward manipulation, an expression for the inverse of \mathbf{A}_1 was obtained as

$$\mathbf{A}_1^{-1} = \sin^2 \gamma_0 \begin{pmatrix} 1+c^2 & 0 & 0 & 0 & 0 & 0 \\ c^2 & 1 & 0 & 0 & 0 & c \\ 0 & 0 & 0 & 0 & 0 & 0 \\ pc & -pc & 0 & 0 & 0 & p \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -c & c & 0 & 0 & 0 & -1 \end{pmatrix}$$

$$+ \sin^2 \beta_0 \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ b^2 & a^2 & s^2 & -as & bs & -ab \\ bq & a(s-bp) & ws & (bp-s)s & qs & -aq \\ -b/s & arb & bs & -ab & -1 & r \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

where

$$q = (pr-c)s = \cot \gamma_0^* / \sin \beta_0, \quad a = rs = \cos \alpha_0^*$$

and

$$w = bc - rs = \cos \alpha_0 / \sin \beta_0 \sin \gamma_0.$$

Since \mathbf{A}_2 is diagonal, it follows immediately that

$$\mathbf{A}_2^{-1} = \text{diag}[a_0 \ b_0 \ c_0 \ \sin \gamma_0 \ \sin \beta_0^* \ \sin \alpha_0^* \ 1],$$

and we can express the inverse of \mathbf{A} analytically as $\mathbf{A}^{-1} = \mathbf{A}_2^{-1} \mathbf{A}_1^{-1}$.

References

- 1) A. Warshel and S. Lifson, *J. Chem. Phys.*, **53**, 582 (1970).
- 2) D. E. Williams, *Acta Crystallogr., Sect. A*, **28**, 629 (1972).
- 3) F. A. Momany, L. M. Carruthers, and H. A. Scheraga, *J. Phys. Chem.*, **78**, 1621 (1974).
- 4) K. Machida, A. Kagayama, Y. Saito, Y. Kuroda, and T. Uno, *Spectrochim. Acta, Part A*, **33**, 569 (1977).
- 5) K. Machida, A. Kagayama, Y. Saito, and T. Uno, *Spectrochim. Acta, Part A*, **34**, 909 (1978).
- 6) K. Machida, A. Kagayama, and Y. Saito, *J. Raman Spectrosc.*, **7**, 188 (1978).
- 7) K. Machida, A. Kagayama, and Y. Saito, *J. Raman Spectrosc.*, **8**, 133 (1979).
- 8) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).
- 9) C. Eckart, *Phys. Rev.*, **47**, 552 (1935).
- 10) J. Kritt and G. S. Pawley, *Acta Crystallogr., Sect. A*, **29**, 615 (1973).
- 11) M. Born and K. Huang, "Dynamical Theory of Crystal Lattices," Oxford University Press, London (1954), Chap. 3.
- 12) Y. Shiro and T. Miyazawa, *Bull. Chem. Soc. Jpn.*, **44**, 2371 (1971).
- 13) See for example, Ref. 1.
- 14) G. S. Pawley, "Advances in Structure Research by Diffraction Methods," Pergamon Press, Oxford (1972), Vol. 4, pp. 1-64.
- 15) J. L. Schlenker, G. V. Gibbs, and M. B. Boisen, Jr., *Acta Crystallogr., Sect. A*, **34**, 52 (1978).