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On the Determination of Interaction Energy Functions
II. Crystalline Formic Acid

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A procedure for deriving molecular interaction energy functions from known equilibrium properties of crystals is described. Formic acid is successfully used as a model test system. The known equilibrium properties of formic acid which were employed are: the average molar internal energy, the minimum nature of the internal energy, and the lack of rotatory motion of each of the molecules in the crystal. The molecular interaction energy functions are represented as pairwise sums of atom-atom terms, which in turn are expressed as 1-4-6-12 inverse power expansions of atom-atom distances.

INTRODUCTION

Empirically derived molecular interaction energy functions, which can reasonably account for mechanical and thermal properties of molecular systems, have obvious usefulness in both the physical and biological sciences. In this paper we will present a procedure for deriving molecular interaction energy functions from known equilibrium properties of crystals. Formic acid is used as a model molecular system. The known equilibrium properties of formic acid crystals which were employed are: the average molar internal energy, the minimum nature of the internal energy when the crystal is in its equilibrium geometry, and the lack of rotatory motion of each of the molecules in the crystal.

FORMULATION OF THE AVERAGE INTERNAL ENERGY OF A CRYSTAL

We view a molecular crystal as occupying all of space (no boundaries). In this view, the average internal energy of a crystal can be calculated as the average internal energy of a unit cell (to be referred to as the zero-th unit cell), which is completely surrounded by an infinite number of unit cells. The average molar internal energy of a unit cell ($\bar{\phi}$) is represented by

$$\bar{\phi} = \frac{\sum_{h=1}^{n} \phi_h}{n}$$

where n represents the number of molecules per unit cell. ϕ_h is the molecular interaction energy per h-th molecule in the zero-th unit cell, resulting from interactions between the h-th molecule in the zero-th unit cell with all other molecules surrounding it.

$$\phi_h = \frac{1}{2} \sum_{k=\text{all molecules in the crystal except the } h\text{-th}} \phi_{hk}$$

We chose to describe the molecular interaction energy function, ϕ_{hk}, as the pairwise sum of the molecular atom-atom interaction energies existing between the atoms of molecule h and those of molecule k. If we represent the molecular atom-atom interaction energy function describing the interaction energy between atom i of molecule h and atom j of molecule k as ϕ_{ij}, then

$$\phi_{hk} = \sum_{i=1}^{l} \sum_{j=1}^{m} \phi_{ij}$$

where l is the total number of atoms in molecule h and m, that in k. ϕ_{ij} in turn is expressed as an expansion in intermolecular atom-atom distances, R_{ij},

$$\phi_{ij} = A_{ij}R_{ij}^{-1} + B_{ij}R_{ij}^{-4} + C_{ij}R_{ij}^{-6} + D_{ij}R_{ij}^{-12}.$$

The coefficients of the four term expansion are evaluated as follows (coefficients are expressed as kcal. Å^{2n} where n is either $\frac{1}{2}$, 2, 3, or 6):

$$A_{ij} = 331.9833 q_i q_j,$$

where q_i and q_j are referred to as fractional charges located at the atom centers.

$$B_{ij} = -\tfrac{1}{2}\, 331.9833(\alpha_i q_j^2 + \alpha_j q_i^2),$$

where α_i is referred to as the polarizability of atom i and α_j, that of atom j.

For C_{ij} we used the Slater–Kirkwood formula:

$$C_{ij} = -\frac{3}{2} \frac{e\hbar \alpha_i \alpha_j}{m^{1/2}\left[\left(\frac{\alpha_i}{N_i}\right)^{1/2} + \left(\frac{\alpha_j}{N_j}\right)^{1/2}\right]},$$

where e is the charge of one electron; m is the electron mass; $\hbar$ has its usual meaning. N_i is the effective number of valence electrons for atom i and N_j, that for atom j.

For D_{ij} we used the relationship

$$D_{ij} = D_i D_j$$

where D_i and D_j are positive scalars associated with their respective atoms.

In this paper we treat the q's, α's, and D's as adjustable parameters, their values being determined by the known properties of the crystal. For a detailed discussion of the above model for molecular interaction energy functions and for the values employed for the "effective number of valence electrons" see [1].

THERMAL DATA

Ideally, the interaction energy of a crystal, which is to be used to derive molecular interaction energy functions, should represent the difference in energy at 0°K between motionless molecules in their equilibrium crystal geometry and identical motionless molecules sufficiently separated so as to have negligible interaction energy. At the present time, the residual molar vibrational energy of crystalline formic acid at 0°K is not available. We therefore did not take the difference between the zero point molar vibrational energies of the crystal and the gas into account. The energy we used was obtained by constructing a Born–Haber cycle.

$$\begin{tikzcd}
\mathrm{HCOOH_{solid}}\ (0^\circ\mathrm{K}) \arrow[r, "\Delta H_1"] \arrow[d, "\Delta H_3"'] & \mathrm{HCOOH_{gas}}\ (0^\circ\mathrm{K}) \arrow[d, "\Delta H_2"] \\
\mathrm{HCOOH_{solid}}\ (281.4^\circ\mathrm{K}) \arrow[r, "\Delta H_4"] & \mathrm{HCOOH_{gas}}\ (281.4^\circ\mathrm{K})
\end{tikzcd}$$

At 0°K ΔH_1, the molar enthalpy, is equal to $\Delta E_0{}^0$, the molar internal energy, the negative of which we are interested in. $\Delta E_0{}^0$ can be set equal to

$$\Delta E_0{}^0 = \Delta H_3 + \Delta H_4 - \Delta H_2 .$$

ΔH_2 was evaluated by using the usual quantum statistical equations in which we employed the vibrational frequencies presented by Mueller and Spangenberg [2] and considered formic acid as a perfect gas. We obtained a value of 2420 cal/mole.

To obtain ΔH_3 we integrated the molar heat capacity from 15 to 281.4°K and applied Debye's extrapolation from 0 to 15°K.

$$\Delta H_3 = \int_0^{15} 3 \cdot R \cdot \frac{4 \cdot \pi^5}{5} \frac{T^3}{\theta_D{}^3}\, dT + \int_{15}^{281.4} C_P\, dT$$

where R is the universal gas constant, T is the absolute temperature, and θ_D, the Debye theta. The heat capacity measurements of crystalline formic acid between 15°K and 281.4°K, as determined by Stout and Fisher [3], were employed to evaluate the second integral numerically. The Debye θ was determined from the heat capacity measurement at 15°K. The value we obtained for ΔH_3 is 2 cal + 2557 cal = 2559 cal/mole.

The vapor pressure of formic acid at 281.4°K is 17.94 mm of Hg [4]. The vapor consists primarily of dimers, the degree of dissociation being 0.09035 [5]. To obtain ΔH_4 we employed the formula

$$\Delta H_4 = \Delta H_a + \Delta H_b + \Delta H_c$$

where, at 281.4°K, ΔH_a represents the enthalpy change which occurs when 0.09035 moles of crystalline formic acid sublimate to monomer; ΔH_b represents the enthalpy change which occurs when 0.90935 moles of crystalline formic acid sublimate to 0.454825 moles of dimer; ΔH_c represents the enthalpy change which occurs when 0.454825 moles of gaseous dimeric formic acid completely dissociate. The sublimation enthalpy at 281.4°K, ΔH_{sub}, is equal to $\Delta H_a + \Delta H_b$. The value employed in this paper for ΔH_{sub}, 7876 cal./mole, was determined from vapor pressure measurements by Coolidge [6]. The dissociation enthalpy, as determined by Halford [7], is 14,551 cal/mole of dimer. Thus ΔH_4 is 14,494 cal/mole.

Finally, $\Delta E_0{}^0$ is evaluated to be 14,633 cal/mole. The quantity we used for the average internal energy of the crystal was rounded off to −14.6 kcal/mole.

MECHANICAL DATA

For the equilibrium geometry of the formic acid crystal we used the x-ray crystallographic structure determined at −50°C by Holtzberg et al. [8]. The crystallographic C—H and O—H bond lengths and the angles referring them to the O = C—O structure have not been determined; for these, we used those of the dimer determined by electron diffraction [9], i.e., considering the molecule planar, C—H is 1.10 Å, O—H is 0.97 Å, H—C = O is 123°, and C—O—H is 114°. A C—O—H angle of 114° results in linear "hydrogen bonds" in the crystal.

The unit cell is orthorhombic and contains four molecules. The space group is PNA.

PROCEDURE

Essentially, the procedure consists of adjusting molecular interaction energy functions, expressed in terms of inverse powers of interatomic distances, so as to make them account as much as possible for the known equilibrium properties of molecular crystals. A damped oscillation least squares method [10] is used with the coefficients of the molecular interaction energy functions as adjustable parameters.

In particular, treating the formic acid molecule as a rigid structure, the following known equilibrium properties were employed:

(1) The average internal energy of the crystal, $\bar{\phi}$.
(2) The minimum nature of $\bar{\phi}$ when the crystal is in its observed geometry.
(3) The lack of rotatory motion of each of the molecules in the crystal.

Considering each of the three properties:

(I) To accurately evaluate in a feasible manner the average internal energy of the crystal, $\bar{\phi}$, we found it necessary to transform slowly converging lattice sums into quickly converging ones. The method we employed to do this is that developed by Nijboer and De Wette [11]. Briefly, $\bar{\phi}$ can be arranged into summable components of the type:

$$\phi_{h,i} = \sum_{\substack{k \\ k \neq h}} \sum_{j} \frac{E_{h,i,k,j}}{R^{2n}_{h,i,k,j}} \tag{1}$$

where $E_{h,i,k,j}$ is the coefficient of the R^{2n} term describing the interaction of the i-th atom of h-th molecule in the zero-th unit cell with the j-th atom of the k-th molecule in the crystal. The summation is to be taken over all the atoms in the crystal, omitting those of the h-th molecule of the zero-th unit cell.

Let us place the crystal in a cartesian coordinate system with the origin located at a lattice site such that the basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ characterize the zero-th unit cell. Let the vector $\mathbf{R}_\lambda$ be represented as

$$\mathbf{R}_\lambda = \lambda_1 \mathbf{a}_1 + \lambda_2 \mathbf{a}_2 + \lambda_3 \mathbf{a}_3$$

where λ_1, λ_2, and λ_3 are positive or negative integers. Let $\mathbf{R}_j$ represent the vector from the j-th atom in the h-th molecule of the zero-th unit cell to the i-th atom in the zero-th unit cell. Then

$$\phi_{h,i} = \sum_{\lambda}{}' \sum_{j} \frac{E_j}{|\,\mathbf{R}_{\lambda,j}\,|^{2n}} + \sum_{j}{}' \frac{E_j}{|\,\mathbf{R}_j\,|^{2n}} \tag{2}$$

with

$$\sum_{\lambda}{}' = \sum_{\lambda_1=-\infty}^{+\infty} \sum_{\lambda_2=-\infty}^{+\infty} \sum_{\lambda_3=-\infty}^{\infty\,\prime}$$

where the prime indicates that the term (0, 0, 0), the zero-th unit cell, is to be omitted. The sum over j in the first term of the sum goes over all the atoms in each of the unit cells considered.

$$\mathbf{R}_{\lambda,j} = \mathbf{R}_\lambda - \mathbf{R}_j$$

In the second term of the sum, j is taken over all atoms in the zero-th unit cell except those in the h-th molecule. E_j is equivalent to $E_{h,i,k,j}$.

The second term in equation (2) is evaluated directly. According to the method developed by Nijboer and De Wette,

$$\begin{aligned}\sum_\lambda{}' \sum_j \frac{E_j}{|\mathbf{R}_{\lambda,j}|^{2n}} = \frac{1}{\Gamma(n)} \Big[& \sum_\lambda{}' \sum_j \frac{E_j \cdot \Gamma(n, \pi\, |\mathbf{R}_{\lambda,j}|^2)}{|\mathbf{R}_{\lambda,j}|^{2n}} \\ & - \sum_j{}' \frac{E_j \cdot \gamma(n, \pi\, |\mathbf{R}_j|^2)}{|\mathbf{R}_j|^{2n}} - \frac{\pi^n \delta_{ij} E_j}{n} \\ & + \frac{\pi^{2n-3/2}}{V_a} \sum_\lambda \sum_j E_j\, e^{(2\pi i \mathbf{h}_\lambda \cdot \mathbf{R}_j)}\, |\mathbf{h}_\lambda|^{2n-3} \Gamma(-n + \tfrac{3}{2}, \pi\, |\mathbf{h}_\lambda|^2) \\ & + \frac{\pi^n \sum_j E_j}{V_a(n - \frac{3}{2})} \Big] \end{aligned} \tag{3}$$

where $\Gamma(n)$ is the gamma function, $\Gamma(n, x)$ is the incomplete gamma function, $\gamma(n, x) = \Gamma(n) - \Gamma(n, x)$. $\sum_j'$ is the sum over all the atoms in the zero-th cell except the i-th atom of the h-th molecule. The symbol δ_{ij} is the usual Kronecker delta referable to the i-th atom of the h-th molecule. V_a is the unit cell volume. $\sum_\lambda \sum_j$ means that the summation is to be taken over all the atoms in all the molecules in all unit cells. $\mathbf{h}_\lambda$ is the usual reciprocal lattice vector.

For $n > \frac{3}{2}$, equation (3) is absolutely convergent. For $n < \frac{3}{2}$ but positive, equation (3) is conditionally convergent. For $n = \frac{1}{2}$, $\lambda = 0$ $(\lambda_1 = \lambda_2 = \lambda_3 = 0)$, the fourth term of equation (3) is indeterminate since $|\mathbf{h}_0| = 0$ and $\sum_j E_j = 0$. The evaluation of this term clearly depends on the way in which the limit $\mathbf{h}_\lambda \to 0$ is taken. For the crystal lattice under consideration in this paper, a correct way of taking this limit leads to the solution

$$-\frac{2\pi}{V_a} \sum_j E_j(\omega_1 R_{j1}^2 + \omega_2 R_{j2}^2 + \omega_3 R_{j3}^2), \tag{4}$$

where $\omega_1 = 0.09916$, $\omega_2 = 0.56802$, and $\omega_3 = 0.33282$. R_{j1}, R_{j2}, and R_{j3} are the x, y, and z components of $\mathbf{R}_j$, respectively.

Of practical significance in evaluating equation (3) is the use of a scaling factor so as to make term 1 and term 4 converge at about the same rate. We have found it convenient to use the inverse of the cubic root of the unit cell volume as a scaling factor. When the crystal is scaled so that

$$\mathbf{a}_i' = \text{scale factor} \cdot \mathbf{a}_i \qquad i = 1, 3$$

where $\mathbf{a}_i'$ represents the i-th basis vector of the slaced crystal, we found in every case that equation (3) converged with λ_1, λ_2, λ_3 going from $+3$ to -3. The value obtained for the scaled crystal must, of course, be multiplied by the scale factor raised to the $2n$-th power in order to obtain the correct value for the unscaled crystal.

(II) The requirement that $\bar{\phi}$ is a minimum, when the crystal is in its observed geometry, is met when all of the following three conditions are satisfied:

(1) The total force on each molecule in the unit cell must be zero, i.e.,

$$F_{h,j} = \sum_{i=1}^{m} F_{h,i,j} = \sum_{i=1}^{m} (-\partial\bar{\phi}/\partial C_{h,i,j})_{\text{equilibrium}} = 0$$

for each molecule h in the unit cell and for each j, $j = x, y, z$. $F_{h,j}$ represents the total force experienced by molecule h in the j direction. $F_{h,i,j}$ represents the force exerted on the i-th atom of molecule h in the j direction. $C_{h,i,j}$ refers to the j-th coordinate of the i-th atom in the h-th molecule of the unit cell. The sum is taken from 1 to m, where m is the number of atoms in the h-th molecule.

It may be noted that, for a given size and shape of a unit cell, the set of force equations determines the relative positions of the molecules in a unit cell.

(2) The components of stress for the entire unit cell must be zero.

$$S_{j,k} = \sum_{h} \sum_{i=1}^{m} (F_{h,i,j} \cdot C_{h,i,k})_{\text{equilibrium}} = 0$$

for each $j, k = x, y$, or z. $\sum_h$ is to be taken over all molecules in the unit cell.

There are only six independent stress equations instead of nine since $S_{x,y} = S_{y,x}$, $S_{x,z} = S_{z,x}$, and $S_{y,z} = S_{z,y}$.

It may be noted that the stress equations determine the size and shape of the unit cell.

(3) Satisfaction of conditions (1) and (2) insures that $\bar{\phi}$ is an extremum but not that it is a minimum. To insure this, it is necessary that each of the characteristic roots of the matrix

$$\frac{\partial^2\bar{\phi}}{\partial d_i\, \partial d_j} \tag{5}$$

be greater than zero; d_i and d_j represent independent geometric parameters determining the value of $\bar{\phi}$.

The d's were chosen from the following parameters:

(a) Four sets, each composed of six parameters. Each of the sets relates one of the four molecules in a unit cell to the origin. The six parameters are the three polar coordinates and the three Eulerian angles (see [12] for a detailed description).

(b) One set, composed of six parameters, which describes the size and shape of the unit cell. The six parameters are the norms of the basis vectors and the three independent angles between them.

For convenience, equation (5) was evaluated numerically for each of the pairs of independent parameters.

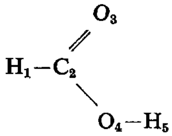
(III) To satisfy the requirement that no molecule in the crystal is undergoing rotatory motion, it is necessary and sufficient that each molecule in the zero-th unit cell have zero torque around each of three orthogonal axes referable to the molecule, i.e., the following torque equations must be satisfied:

$$T_{h,j} = \sum_{i=1}^{m} (F_{h,i,l} \cdot C_{h,i,k} - F_{h,i,k} \cdot C_{h,i,l})_{\text{equilibrium}} = 0$$

where j, k, l represent each of the three cyclic permutations of x, y, z, i.e. (x, y, z), (y, z, x), and (z, x, y). The sum is over all m atoms in the h-th molecule and the equations apply to each of the molecules in the zero-th unit cell.

TABLE I

Parameter Values Derived from the Equilibrium Properties of Crystalline Formic Acid



	q_i	$\alpha_i \times 10^{24}$ cm^3	D_i
H_1	−0.1734	0.0000	25.000
C_2	0.3953	2.0490	1789.000
O_3	−0.1996	0.4211	135.000
O_4	−0.0594	0.0499	271.000
H_5	0.0371	0.2901	3.466

RESULTS

By treating the q's, α's, and D's as variable parameters, the molecular interaction energy model described in this paper accounted perfectly for the known equilibrium properties of crystalline formic acid. The values found for the parameters are listed in Table I.

DISCUSSION

In the first paper of this series [13], a procedure was presented for shaping molecular interaction energy surfaces to desired contours and depths. If so desired, this procedure could be incorporated into the one presented in this paper so as to insure that the crystal interaction energy surface has as its lowest point the known equilibrium internal energy and geometry of the crystal.

A procedure for empirically deriving interaction energy functions is of little practical value unless one can obtain a set of functions which are transferable to different molecules. Williams (14) has demonstrated the feasibility of deriving one set of interaction energy functions applicable to a wide variety of crystalline hydrocarbons.

The conditionally convergent terms in infinite lattice sums of the R^{-1} type (equation (4)) account for the nonspherical shape dependence of these sums. It has been customary to set these terms to zero. We have found that they make a significant contribution to the total lattice sum for molecules and, an even greater contribution to individual atom-atom terms. We will consider these conditionally convergent terms in detail and present a general solution for their evaluation in a future publication.

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