Intermolecular Forces and Rotational Phase Transition in the C_2H_2 Crystal

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The potential energy of the acetylene crystal was calculated as a function of the rotational molecular orientations. The potential energy of this crystal has two kinds of minima, not a double minima; one arises from the quadrupole-quadrupole interaction, to which the high-temperature is due, while the other arises from the overlap repulsion interaction with which the low temperature structure is coincident. It was suggested that the mechanism of the phase transition in this crystal is a rotational transition between the two molecular orientations.

Acetylene is known to undergo a phase transition at 133°K. The crystal structure has been determined to be T_h^6-$Pa3$ at 156°K.[1] Below 133°K however, the information given by the X-ray analysis is ambiguous.

From the observed multiplet structure of the infrared-active fundamental vibrations[2,3] of the low-temperature phase, the acetylene molecules were determined to be located at the sites of the C_{2h} symmetry.

Recently, Ito *et al.*[4] have suggested, on the basis of the Laser Raman spectrum, that the low-temperature form has a layer-type orthorhombic structure belonging to the space group D_{2h}^{18}.

In the present article we calculated the intermolecular potential energy of crystalline acetylene in the expectation that the phase transition in this crystal would correspond to the rotational transition between two molecular orientations. The results indicate that there are two stable molecular orientations in this crystal; one of them corresponds to the high-temperature structure, while the other is coincident with the low-temperature structure.

Theoretical

The theoretical foundations for the calculation of the potential energy in the case where intermolecular separations are small enough for the overlap of the molecular wavefunction to be disregarded[5-9] are due mainly to Banerjee and Salem.[10] We will list the main points briefly and apply them to the case of acetylene.

(1) The molecular wavefunction, Ψ, of an acetylene molecule is expressible as an antisymmetrized sum of the products of the one-electron molecular orbitals:

$$\Psi = |\varphi_{C-H}\bar{\varphi}_{C-H}\varphi'_{C-H}\bar{\varphi}'_{C-H}\varphi^{\sigma}_{C-C}\bar{\varphi}^{\sigma}_{C-C}\psi^{\pi 1}_{C-C}\psi^{\pi 1}_{C-C}\psi^{\pi 2}_{C-C}\psi^{\pi 2}_{C-C}|$$

with:

$$\psi_{C-H} = (di_C + 1s_H)/(2+2S_{CH})^{1/2},$$

$$S_{CH} = \int di_C 1s_H d\tau,$$

$$\psi^{\sigma}_{C-C} = (di_C + di_C)/(2+2S)^{1/2},$$

$$S = \int di_C di_C d\tau$$

$$\psi^{\pi}_{C-C} = (\pi_C + \pi_C)/(2+2S_{\pi})^{1/2},$$

and

$$S_{\pi} = \int \pi_C \pi_C d\tau,$$

where di_C and $1s_H$ are the diagonal hybrid and the $1s$ orbital centered on the carbon and hydrogen atoms, respectively. π_C is the $2p\pi$ orbital centered on the carbon atom.

(2) The ionization potential, I and I', appear in terms of the conventional van der Waals energy:

$$W_{disp} = -(3/2)R^{-6}\alpha\alpha' II'/(I+I'), \quad (2)$$

are replaced by quantum mechanically-calculable averages. The results are:

$$W_{disp} = [(A-2B+C)\{\sin\theta\sin\theta'\cos(\phi-\phi') - 2\cos\theta\cos\theta'\}^2 + 3(B-C)\{\cos^2\theta+\cos^2\theta'\} + (2B+4C)]/R^6 \quad (3)$$

with:

$$A = e^2\alpha_{\parallel}\langle(\sum_i q_{\parallel},i)^2\rangle/4,$$

$$B = e^2\alpha_{\parallel}\alpha_{\perp}\langle(\sum_i q_{\parallel},i)^2\rangle\langle(\sum_i q_{\perp},i)^2\rangle/ 2\{\alpha_{\parallel}\langle(\sum_i q_{\perp},i)^2\rangle + \alpha_{\perp}\langle(\sum_i q_{\parallel},i)^2\rangle\},$$

and

$$C = e^2\alpha_{\perp}\langle(\sum_i q_{\perp},i)^2\rangle,$$

where $\langle(\sum_i q,i)^2\rangle$ are called the quantum mechanical averages and where

$$\langle(\sum_i q,i)^2\rangle = \langle\Psi|(\sum_i q,i)^2|\Psi\rangle.$$

$q_{\parallel},i$ and $q_{\perp},i$ are the coordinates of the ith electron along the directions respectively parallel to and perpendicular to the molecular symmetry axis (C–C bond). $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the corresponding components of the polarizability. θ and θ' are the angles which the two molecules, separated by the distance R, make with a line joining their center of gravity. φ and φ' are their azimuthal angles.

(3) The repulsive energy can be expressed as the sum of the interaction energies between individual atoms of the two molecules:

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$$W_{\text{repl}} = \sum_{i>j}\{V(H_i \cdots H_j) + V(H_i \cdots C_j)\} \quad (4)$$

with $V(\text{H}_i\cdots\text{H}_j)=21.3\times S^2/R$ and $V(\text{H}_i\cdots C_j)=49.0\times S^2/R$[11] where $V(\text{H}_i\cdots\text{H}_j)$ and $V(\text{H}_i\cdots\text{C}_j)$ are the intermolecular hydrogen-hydrogen and hydrogen-carbon repulsion energies respectively.[11] S is the overlap integral of $1s$ hydrogen atoms separated by the distance R. The C···C repulsion energy may be ignored, as usual.

(4) The pair potential energy between the molecules in the acetylene crystal is made up of Eqs. (3) and (4):

$$W = W_{\text{disp}} + W_{\text{repl}} \quad (5)$$

The potential energy of the crystal is, then, obtained by summing (5) over all the molecules in the crystal.

In this paper, besides the above interactions, we will also consider the following interaction energy and will examine the validity of the pair additivity assumption in the case of the acetylene crystal.

The acetylene molecule has a quadrupole moment of 3.00×10^{-26} c.g.s.e.s.u.;[16] therefore, at least the quadrupole-quadrupole interaction must be considered. This interaction can be expressed as:

$$\begin{aligned} Q_{ab} = {} & 3qq'[1-5\cos^2\theta-5\cos^2\theta'+17\cos^2\theta\cos^2\theta' \\ & + 2\sin^2\theta\sin^2\theta'\cos(\varphi-\varphi') \\ & + 16\sin\theta\sin\theta'\cos\theta\cos\theta'\cos(\varphi-\varphi')]/4R^5, \end{aligned} \quad (7)$$

where the q's are the observed quadrupole moments of the acetylene molecule and where the θ's and φ's are as defined in Eq. (3).

If the molecules of the polarizabilities, α_a, α_b, and α_c, make an abc triangle, the three-body non-additive force may be expressed as follows:[17,18]

$$E_3 = (9/16)\times I\times\alpha^3\times(3\cos\gamma_a\cos\gamma_b\cos\gamma_c+1)/(R_{ab}{}^3R_{bc}{}^3R_{ca}{}^3), \quad (8)$$

where the γ's are the inner angles of the triangle, the R's are the distances among the three molecules, α is the average polarizability, and I is the mean excitation energy, which can be considered as the ionization potential of the molecules. In the acetylene molecule, $I=11.40$ eV and $\alpha=33.3\times10^{-25}$ cm^3;[19] therefore, for the nearest molecules in the crystal, E_3 is of the order of 10^{-5} kcal/mol; this can be ignored in comparison with the other interaction energies.

Numerical Calculations

If the phase transition of the acetylene crystal corresponds to the transition between the two molecular orientations, the calculated potential energies for various orientations and displacements of the molecules in the crystal should have minima of more than two.

For the displacements of the molecules, no consideration will be made now because there is no drastic structural change which causes a large elongation or

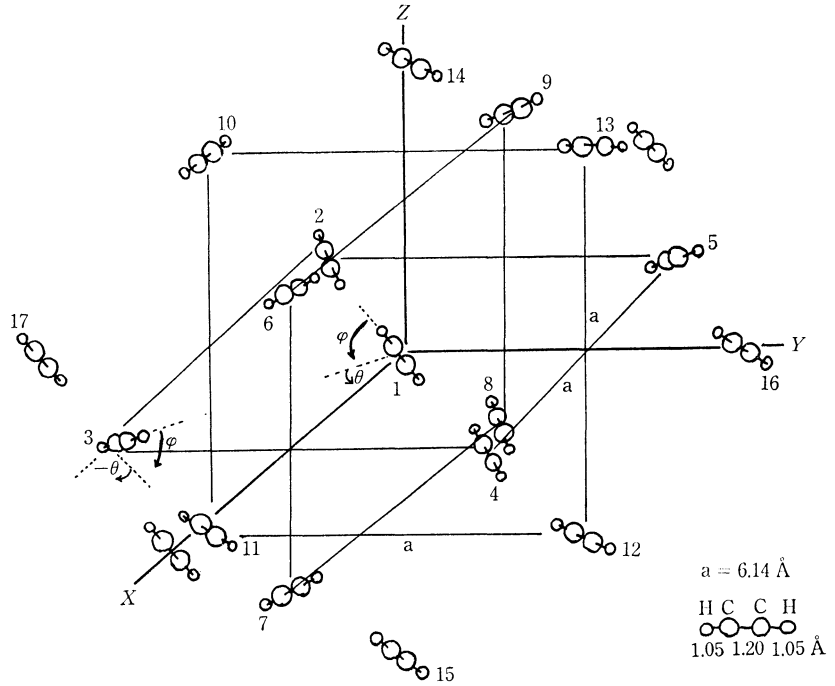

Fig. 1. Face centered position of cubic lattice of C_2H_2 crystal.

11) The coefficient of 21.3 was determined by Banerjee and Salem,[10] so $V(\text{H}\cdots\text{H})=k\times S^2/R$ reproduces the H···H potential obtained from the scattering experiments of Amdur *et al.*[12-14] The coefficient of 49.0 was obtained by using the empirical relation due to Adrian,[15] connecting $V(\text{H}\cdots\text{H})$ to $V(\text{H}\cdots\text{C})$: $V(\text{H}\cdots\text{H})=k'\times V(\text{H}\cdots\text{C})$.

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contraction of the lattice during the phase transition.[20] The displacements of the molecules will be discussed in detail in future works of this series.

In the present investigation we have made the calculations on the basis of Eqs. (3), (6), and (7) for various rotational orientations of the molecule.

We start from the structure in which the centers of gravity of the molecules are located on the face-centered position of the cubic lattice, with the unit-cell dimension of a=6.14 Å (see Fig. 1).

With respect to the central molecule, 1, at the origin of the coordinate, there are 18 first-neighbour molecules. We calculated the dispersion and quardrupole-quadrupole interaction energies for the molecules from the 1st to 5th nearest neighbours, but the repulsion energy for the 1st neighbours only. The 5th-nearest neighbours are separated from the point of origin by 30 Å.

Two kinds of molecular rotation are considered. One is the rotation measured by the deflection of the molecular axis from the (100) plane, and the other is the rotation measured by the deflection from the (011) plane. The angle of the former is indicated by φ, and the latter, by θ.

The integrals appearing in the quantum-mechanical averages and the overlap integrals are calculated using Simpson's formula.[21] All the computational work in this paper was done at the Computer Center of Tohoku University using the NEAC 2200-500-model Computer System.

Results and Discussion

Figures 2 and 5 indicate the variation in the dispersion energy with φ and θ. In Fig. 2 the values

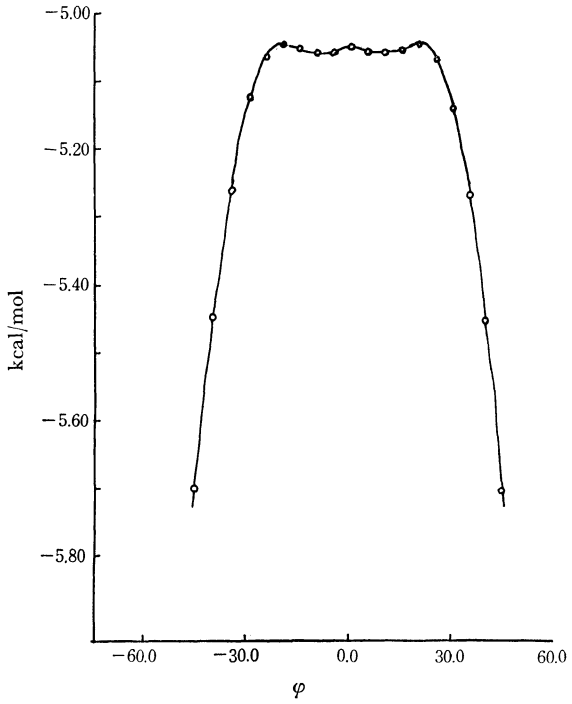

Fig. 2. Dispersion energy of C_2H_2 crystal.

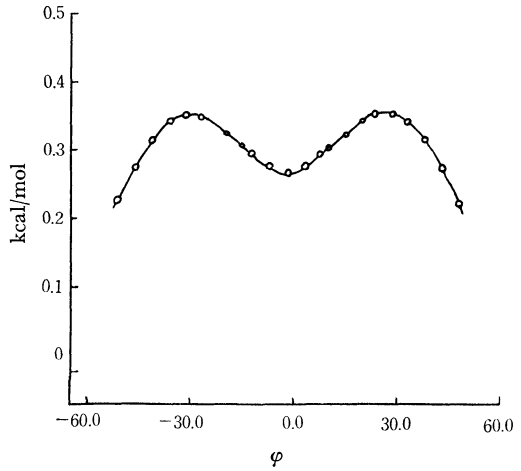

Fig. 3. Quadrupole Interaction energy of C_2H_2 Crystal.

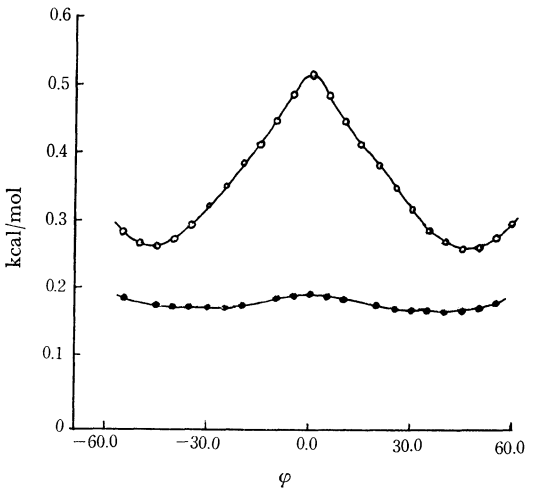

Fig. 4. Overlap repulsion energy of C_2H_2 crystal.
-○-○- H·····H, -●-●- C·····H

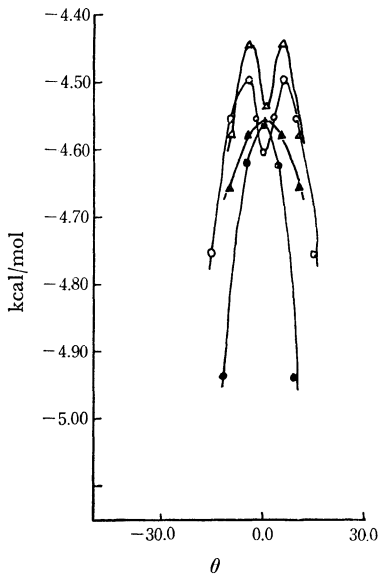

Fig. 5. Dispersion energy of C_2H_2 crystal
-○-○- φ=45.0 -△-△- φ=30.0
-▲-▲- φ=15.0 -●-●- φ=0

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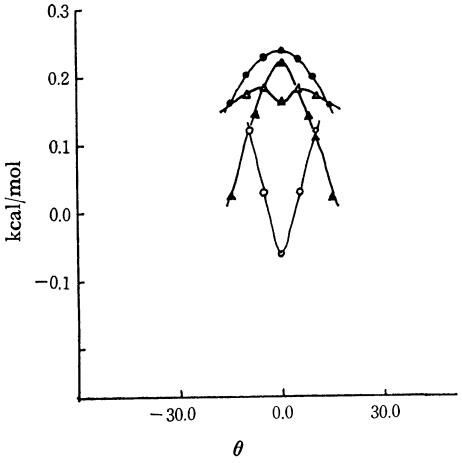

Fig. 6 Quadrupole-quadrupole interaction energy of C_2H_2
-●-●- φ= 0.0 -▲-▲- φ=15.0
-△-△- φ=30.0 -○-○- φ=45.0

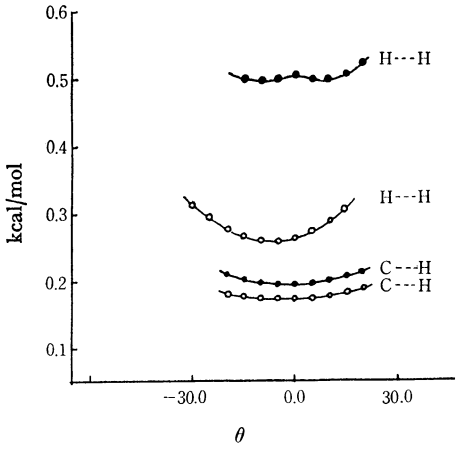

Fig. 7. Repulsion energy of C_2H_2
-●-●- φ=0.0 -○-○- φ=45.0

when θ is zero are indicated. The curves in which θ is different from zero are all more or less similar to the curve in Fig. 2 whenever θ is smaller than $\pm$10 degrees.

Figure 5 shows that the depth of the potential minimum decreases as φ becomes smaller.

The overlap repulsion energies are indicated in Fig. 4 and in Fig. 7. As we defined the dispersion attraction energy as negative, the repulsive energies are expressed in positive terms. When θ is zero, the curve indicating the variation with the φ has a minimum point at φ= 45°. When φ is constant, the variation with the θ has a minimum when θ is zero, as may be seen from Fig. 7.

The quadrupole interaction energy curves are indicated in Figs. 3 and 6. As in the case of the dispersion energy, the depth of the potential minimum seen in Fig. 6 decreases as the φ becomes smaller and disappears at φ=0.

No one of the above three interaction energies has double potential minimum, contrary to our expectations. However, the potential curves against φ may be worthy of note. In overlap repulsion energy curves the interaction energy has a minimum point at φ=45°, while in quadrupole-quadrupole interaction it has a minimum point at φ=0°. In short, the potential energy of crystalline acetylene has no double minima, but it has two kinds of minima. One arises from the overlap repulsion, and the other, from the quadrupole-quadrupole interaction.

Let us consider which of these two is the more stable. It may be seen from the curves in Figs. 5, 6, and 7 that when φ=0° the quadrupole-quadrupole and dispersion interaction energies reach a maximum at θ=0°, where the repulsion energy for H···H is at a minimum. On the contrary, when φ=45°, not only the repulsion but also the quadrupole-quadrupole and dispersion interaction energies have minima at θ=0°. Therefore, the orientation corresponding to φ=45° is more stable than the molecular orientation corresponding to φ=0°. We have assumed, therefore, that the former molecular orientation will be realized in low-temperature regions. The crystal structure proposed by Ito *et al.* for the low-temperature phase coincides with the structure of φ= 45°.

On the other hand, the molecular orientation corresponding to φ=0° coincides with the structure determined by X-ray analysis by Sugawara *et al.* for the high-temperature form.

The calculated lattice energy of the high-temperature form is 5.1 kcal/mol, while the experimental one[22] is 5.5 kcal/mol. Their coincidence is also quite good.

In conclusion, the potential energy of crystalline acetylene has two kinds of minima, not double minima; one arises from the quadrupole-quadrupole interaction, to which the high-temperature structure is due, and the other, from the overlap repulsion interaction, to which the low-temperature structure corresponds.

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