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Far Infrared Spectra and the Calculation of Lattice Vibrations of Benzoic Acid[1]

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Polarized far infrared spectra from 400 to 30 cm^{-1} of benzoic acid single crystals have been measured. Three bands polarized parallel to the C_2^s screw axis b were observed at 104, 86, and 62 cm^{-1}, and three bands polarized parallel to the a-axis at 106, 76, and 65 cm^{-1}. The lattice vibrations of benzoic acid have been calculated assuming the rigidity of the molecule during the lattice vibrations and applying a simple force field. The bands at 104, 86, and 62 cm^{-1} were assigned to the rotational vibrations of A_u symmetry species: the O–H···O stretching, the ring torsional and the O–H···O out-of-plane bending modes, respectively, and the bands at 106, 76, and 65 cm^{-1} to those of B_u symmetry species. The force constant K(O···H) related to the hydrogen bonds in the cyclic dimer was calculated to be 0.35 mdyn/Å.

The far infrared spectra of carboxylic acid dimers in the vapor phase and in solutions have been studied by several investigators.[2–9] It has been well established in both formic and acetic acids[3,5,8] that the three infrared active vibrations associated with the hydrogen bonds in the cyclic dimer are, from the higher frequencies, the O···H stretching+O–H···O in-plane bending, the O–H···O out-of-plane bending and the ring torsional modes; they are approximately rotational vibrations of the monomers.

Only a few works have been carried out on the low frequency Raman spectra of dimeric carboxylic acids.[10,11] The three Raman active hydrogen-bond vibrations would be the O···H stretching, the O–H···O in-plane bending and the O–H···O out-of-plane bending modes; they can be regarded as translational vibrations of the monomers.

In crystalline solids, provided that the Bravais unit cell contains more than two dimers, translational vibrations of the dimers are also expected to appear in the far infrared spectra and rotational vibrations of the dimers in the low frequency Raman spectra. In such a crystalline state, the low frequency vibrational modes would become complicated due to the interactions between the rotational and translational motions.

Thus it is interesting to study the low frequency vibrational spectra of carboxylic acid dimers in crystalline solids. Simple carboxylic acids such as formic and acetic acids do not exist as hydrogen-bonded dimers in the crystal; they are chain polymers. Benzoic acid is a suitable sample for this purpose because its Bravais unit cell contains two dimers.

The low frequency vibrational spectra of benzoic acid single crystals have been studied by Stanevich,[6] Statz and Lippert,[9] and Maier and Schifferdecker.[12] Recently Wyncke *et al.*[13] measured polarized far infrared spectra of single crystals and proposed an assignment for the infrared active lattice vibrations. Their assignment is based on the assumption that the frequencies of the rotational vibrations of the monomers are in the inverse order of the corresponding moment of inertia. The assumption, however, is not appropriate in the case of benzoic acid because of the strong hydrogen bonds in the dimer.

More recently, Colombo and Furic[14] observed polarized Raman spectra and gave an assignment of the Raman active lattice vibrations. They separated translational vibrations of the monomers from rotational vibrations of the dimers by the difference in the temperature dependence of these two groups of vibrations. The separation, however, does not seem convincing.[15]

The purpose of this paper is to give an assignment for the lattice vibrations of benzoic acid based on the normal coordinate calculations as well as the polarized far infrared spectra of the single crystals.

Experimental

Single crystals of benzoic acid were grown from a saturated ethanol solution by slow evaporation at 30°C. The evaporation rate was adjusted so that crystals of centimeter dimensions were formed over a period of several weeks. The crystals were obtained as fine needles with b as needle axis, sometimes as small rectangular plates developed on (001).

X-Ray measurements were carried out with CuK_α radiation by using oscillation and Weissenberg photographic methods. Oscillation photographs indicated that the C_2^s

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[15] Still more recently Colombo *et al.* have given a newer assignment based on their normal coordinate analysis (private communication).

screw axis (*b*-axis) was always along the longer edge of the rectangular crystal plates. The cell dimensions obtained are: $a\cdot sin\beta=5.44$, $b=5.14$, and $c\cdot sin\beta=21.8$ Å, which are in good agreement with the values reported by Sim *et al.*[16]

The infrared spectra were recorded with a Hitachi FIS-3 far infrared spectrometer. For the infrared polarization measurements a polarizer made up of a stack of polyethylene sheets was used and the sample, about 20 mm long, 10 mm wide and 0.2 mm thick, prepared by cleaving a suitable crystal plate, was attached to the slit 45° tilted with respect to the vertical in order to minimize the polarization effects in the spectrometer. The spectrum of the powder was recorded in a Nujol mull between silicon plates.

Calculation of Lattice Vibrations

The crystal structure of benzoic acid is monoclinic $P2_1/c-C_{2h}^5$, with two cyclic dimers in a Bravais unit cell (Fig. 1). The cell dimensions are: $a=5.52\pm0.02$, $b=5.14\pm0.02$, $c=21.90\pm0.05$ Å and $\beta=97°$.[16] The O···O distance of the two hydrogen bonds in the dimer is 2.65 Å. The bond length O–H and C–H were assumed to be 1.03 and 1.08 Å, respectively, in this frequency calculation.

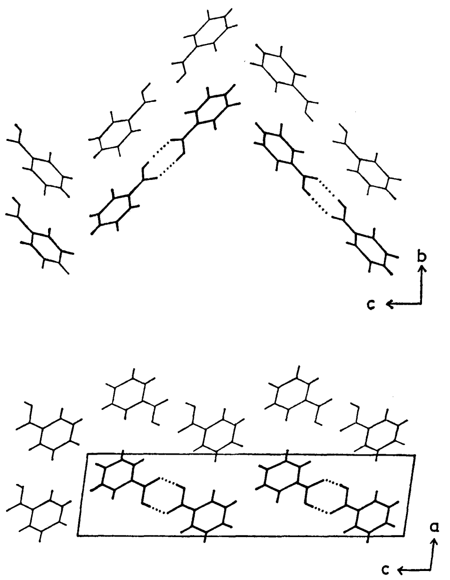

Fig. 1. Crystal structure of benzoic acid.

The calculation of the lattice vibrations has been carried out using the method developed by Shimanouchi *et al.*[17] and assuming that the molecule is not distorted during the vibrations. The intermolecular potential can be expressed as the sum of the potential associated with the hydrogen bonds in the dimer V_h, and the potential representing the interactions between the atoms of different dimers V_i. The interactions between atoms more than 3 Å apart were neglected,

$$V = V_h + V_i$$

$$\begin{aligned} V_h = {} & (1/2)\sum_i K(\mathrm{O\cdots H})\Delta q_i^2 \\ & + (1/2)\sum_i H_{//}(\mathrm{O{-}H\cdots O})r_{\mathrm{OH}}q_{\mathrm{OH}}\Delta\alpha_i^2 \\ & + (1/2)\sum_i H_\perp(\mathrm{O{-}H\cdots O})r_{\mathrm{OH}}q_{\mathrm{OH}}\Delta\beta_i^2 \\ & + (1/2)\sum_i H(\mathrm{C{=}O\cdots H})r_{\mathrm{CO}}q_{\mathrm{OH}}\Delta\gamma_i^2 \\ & + (1/2)\sum_i Y(\mathrm{C{=}O})\Delta\tau_i^2 + \sum_{i\neq j} p(\mathrm{O\cdots H, O\cdots H})\Delta q_i\Delta q_j \end{aligned}$$

$$\begin{aligned} V_i = {} & (1/2)\sum_i F_i(\mathrm{O\cdots H})\Delta q_{1i}^2 + (1/2)\sum_i F_i(\mathrm{C\cdots H})\Delta q_{2i}^2 \\ & + (1/2)\sum_i F_i(\mathrm{H\cdots H})\Delta q_{3i}^2 \end{aligned}$$

where $Y(\mathrm{C{=}O})$ is the force constant of the torsion around the C=O bond and $p(\mathrm{O\cdots H, O\cdots H})$ is the force constant representing the resonance interaction between the two O···H bonds in the dimer.

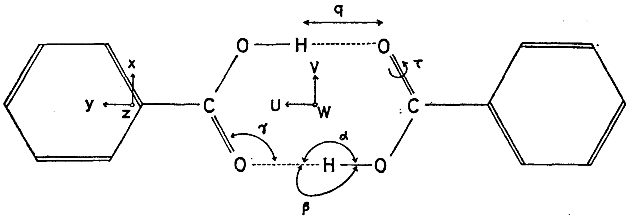

Fig. 2. Coordinates related to the hydrogen bonds in the cyclic dimer.

Results and Discussion

1. Infrared Active Lattice Vibrations. The far infrared spectrum from 400 to 30 cm^{-1} of benzoic acid powder suspended in Nujol is given in Fig. 3. The bands at 106, 78, and 63 cm^{-1} are reduced to weak and broad bands in the spectrum of cyclohexane solution, as shown in Fig. 4. These bands are therefore considered to be due to lattice vibrations. Although

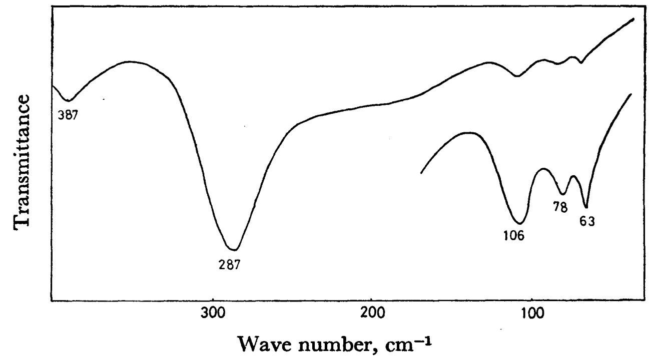

Fig. 3. Far-infrared spectrum of benzoic acid powder in Nujol mull.

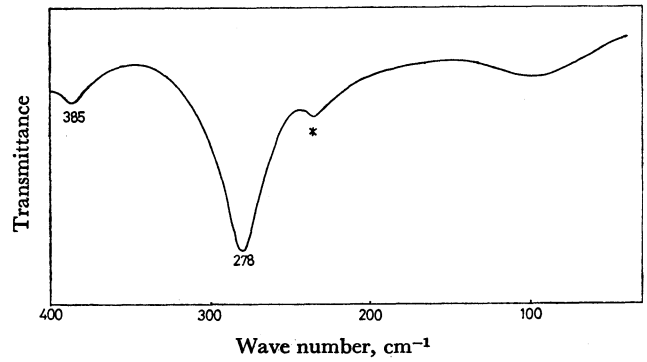

Fig. 4. Far-infrared spectrum of benzoic acid in cyclohexane solution. *band due to cyclohexane.

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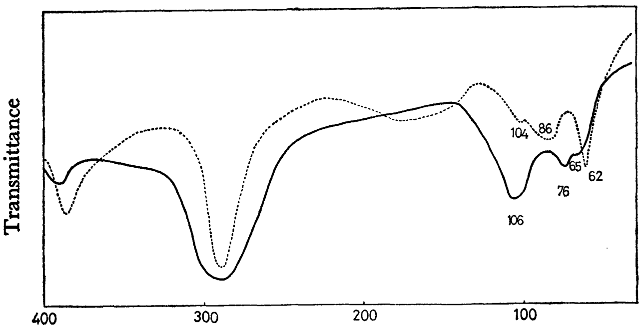

Fig. 5. Polarized far-infrared spectra of benzoic acid single crystals.
······Electric vector parallel to the *b*-axis
——Electric vector perpendicular to the *b*-axis (parallel to the *a*-axis)

Wyncke *et al.*[13]) reported two weak bands at 36 and 29 cm^{-1}, we could find no bands between 60 to 30 cm^{-1}.

In the polarized spectrum of the single crystal shown in Fig. 5, the lattice vibrations occur at 104, 86, and 62 cm^{-1}, when the electric vector of the incident light is parallel to the *b*-axis (C_2^1 screw axis) and at 106, 76, and 65 cm^{-1}, when the electric vector is parallel to the *a*-axis. Thus the bands at 104, 86, and 62 cm^{-1} are assigned to the lattice modes of symmetry species A_u, while the bands at 106, 76, and 65 cm^{-1} to those of B_u species. The polarization measurement, however, does not agree with the observation of Wyncke *et al*;[13]) their *a* and *b* axes correspond to our *b* and *a* axes, respectively.

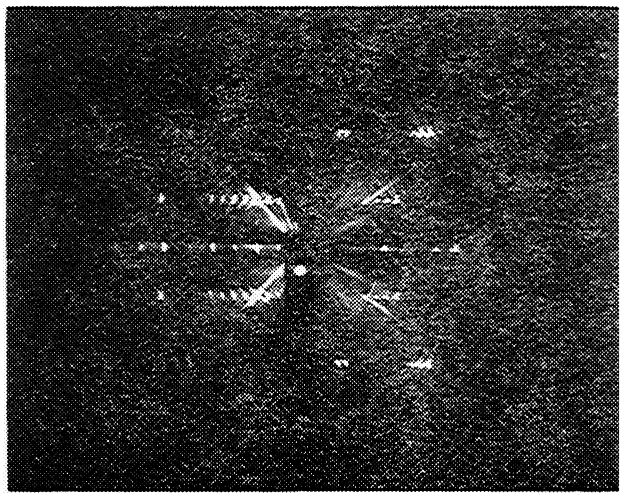

Fig. 6. X-ray oscillation photograph around the *b*-axis.

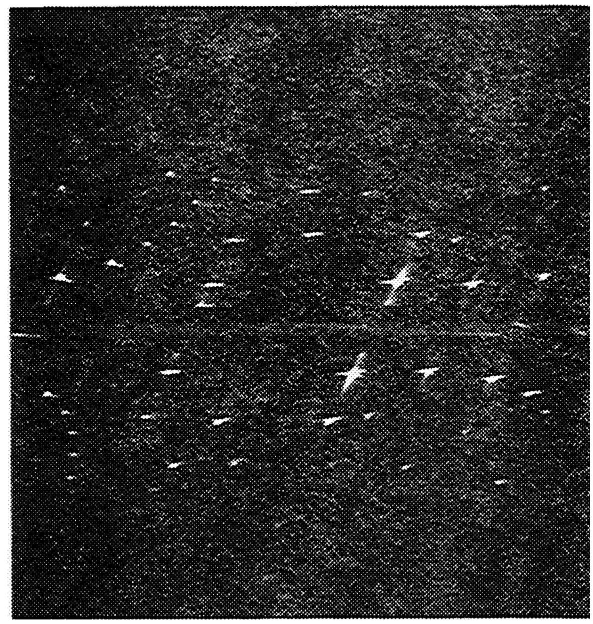

Fig. 7. Weissenberg photograph around the *b*-axis.

The X-ray oscillation photograph around our *b*-axis which is parallel to the longer edge of the rectangular crystal is given in Fig. 6. The photograph clearly shows that the screw axis C_2^1 lies along our *b*-axis. Moreover, the cell dimensions, $a \cdot sin\beta = 5.44$, $b = 5.14$, and $c \cdot sin\beta = 21.8$ Å, calculated from this photograph and the Weissenberg photograph (Fig. 7) are in substantial agreement with the results $a = 5.52$, $b = 5.14$, $c = 21.90$ Å, and $\beta = 97°$ obtained by Sim *et al.*[16]) This suggests that Wyncke's *a* and *b* axes should be interchanged.

Infrared active lattice vibrations of benzoic acid are approximately described as rotational vibrations of the monomers R_x, R_y, and R_z and translational vibrations of the dimers T_U, T_V, and T_W (Fig. 2). The former can be regarded as the O–H···O out-of-plane bending, the O–H···O torsional and the O···H stretching+O–H···O in-plane bending vibrations, respectively. The frequencies of the former depend mainly on the force constants related to the hydrogen bonds in the cyclic dimer, while the frequencies of the latter are determined mainly by interaction force constants between atoms of different dimers. Accordingly, the

TABLE 1. OBSERVED AND CALCULATED FREQUENCIES AND APPROXIMATE LATTICE MODES OF BENZOIC ACID SINGLE CRYSTSLS

Symmetry Species	Obsd. (cm^{-1})	Calcd. (cm^{-1})	Assignment
A_g	122	126	O···H stretch (T_y)
	114	113	O–H···O *i*-bend(T_x)
	93	100	O–H···O *o*-bend(T_z)
	74	59	R_U
	49	51	R_W
	45	34	R_V
B_g	126	122	O···H stretch(T_y)
	114	113	O–H··· O *i*-bend(T_x)
	96	100	O–H···O *o*-bend(T_z)
	72	60	R_U
	31	41	R_W
	27	20	R_V
A_u	104	108	O···H stretch+O–H···O *i*-bend (R_z)
	86	84	ring torsion(R_y)
	62	63	O–H···O *o*-bend(R_x)
	—	39	T_V
	—	9	T_W
B_u	106	110	O···H stretch+O–H···O *i*-bend(R_z)
	76	74	ring torsion(R_y)
	65	58	O–H···O *o*-bend(R_x)
	—	17	T_U

TABLE 2. HYDROGEN-BOND FREQUENCIES OF CARBOXYLIC ACID DIMERS (cm^{-1})

	Approximate Modes	$(HCOOH)_2$ vapor[7]		$(CH_3COOH)_2$ vapor[7]		$(C_6H_5COOH)_2$ solid	
						A_u	B_u
IR Active	O···H stretch+ O–H···O *i*-bend(R_z)	248		188		104	106
	O–H···O *o*-bend(R_x)	164		80[a]	79[c]	62	65
	ring torsion (R_y)	68		50		86	76
						A_g	B_g
Raman Active	O–H···O *o*-bend(T_z)	243[a]	260[c]	128[a]	130[c]	93	96
	O–H···O stretch(T_y)	221[a]	224[b]	193[a]	210[b]	122	126
	O–H···O *i*-bend(T_x)	103[a]	91[b]	95[a]	81[b]	114	114

a) Calculated values by Miyazawa and Pitzer[3]
b) Calculated values by Kishida and Nakamoto[5]
c) Calculated values by Jacobsen, Mikawa and Brash[8]

frequencies of rotational vibrations of the monomers are anticipated to be higher than those of translational vibrations of the dimers, because hydrogen bonding forces are usually stronger than non-bonding interaction forces.

The principal moment of inertia of the monomer are in the order $I_z>I_x>I_y$. If we assume that the force field around each monomer has spherical symmetry, *viz*., the effective force constants for R_x, R_y, and R_z are approximately the same, the frequencies of the rotational vibrations of the monomer would be in the order $\nu(R_y)>\nu(R_x)>\nu(R_z)$. Actually the assumption is not acceptable because two monomers are combined together by strong hydrogen bonds to form a cyclic dimer in the crystal, and the largest hydrogen-bond force constant K(O···H) is almost solely effective for R_z. This suggests that the frequency of R_z is the highest in spite of the biggest moment of inertia I_z. It is not easy to tell, *a priori*, which frequency is higher, $\nu(R_x)$ or $\nu(R_y)$. The effective force constant for R_x might be slightly larger than that for R_y, whereas the moment of inertia for R_y is smaller than that for R_x.

2. *Raman Active Lattice Vibrations.* Raman active lattice vibrations of benzoic acid can be classified approximately into two groups: translational vibrations of the monomers T_x, T_y, and T_z, and rotational vibrations of the dimers R_U, R_V, and R_W. The former are in other expressions, the O–H···O in-plane bending, O···H stretching and the O–H···O out-of-plane bending vibrations, respectively. For the same reason as that for infrared active lattice vibrations, the frequencies of translational vibrations of the monomers are supposed to be higher than those of rotational vibrations of the dimers, and the highest frequency of these vibrations would be the O···H stretch $\nu(T_y)$.

The moment of inertia of the dimer is in the order

TABLE 3. INTER-MOLECULAR FORCE CONSTANTS OF BENZOIC ACID

Force Constants	mdyn/Å	Inter-atomic Distances (Å)
in Dimers		
K(O···H)	0.350	1.61
$H_{\parallel}$ (O–H···O)	0.030	
$H_{\perp}$(O–H···O)	0.048	
H(C=O···H)	0.038	
Y(C=O)	0.010[a]	
p(O···H, O···H)	−0.060	
between Dimers		
F(O···H)	0.025	2.55
F(O···H)	0.020	2.62
F(C···H)	0.030	2.88
F(C···H)	0.025	2.94
F(C···H)	0.010	3.04
F(H···H)	0.038	2.43
F(H···H)	0.015	2.70
F(H···H)	0.008	2.75
F(H···H)	0.006	2.84
F(H···H)	0.004	3.03

a) in mdyn. Å

TABLE 4. HYDROGEN-BOND FORCE CONSTANTS OF CARBOXYLIC ACIDS (mdyn/Å)

Force Constants	HCOOH Ref. 3	HCOOH Ref. 5	CH_3COOH Ref. 3	CH_3COOH Ref. 5	succinic[18] and adipic[19] acid	C_6H_5COOH this work
K(O···H)	0.330	0.360	0.330	0.460	0.360	0.350
$H_{\parallel}$ (O–H···O)	0.025	0.015	0.025	0.020	0.010	0.030
H(C=O···H)	0.012	0.010	0.012	0.005	0.010	0.038
$H_{\perp}$(O–H···O)	0.025	···	0.025	···	0.055	0.048
Y(C=O)[a]	0.012	···	···	···	0.024	0.010
p(O···H, O···H)	···	···	···	···	···	−0.060

a) in mdyn. Å

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[18] M. Suzuki and T. Shimanouchi, *J. Mol. Spectrosc.*, **28**, 394 (1968).

[19] M. Suzuki and T. Shimanouchi, *ibid.*, **29**, 415 (1969).

$I_W > I_V > I_U$. The effective force constants for R R_V, and R_W would not differ much from each other, because it is highly improbable that some strong interaction forces are operative along particular directions between the dimers. Thus, the rotational vibrations of the dimers would be in the order $\nu(R_U) > \nu(R_V) > \nu(R_W)$.

3. Assignment of Lattice Modes. The observed and calculated frequencies along with their approximate lattice modes are listed in Table 1. The Raman frequencies (A_g and B_g species) are those measured by Colombo *et al.*[14] The calculated frequencies are in fairly good agreement with the observed. In the frequency calculation, it was assumed that the molecule of benzoic acid was not distorted during lattice vibrations; in other words, the coupling between intra-molecular vibrations and lattice vibrations was ignored. This might be a good approximation when the frequencies of all the intra-molecular vibrations are high and are far apart from the frequencies of lattice vibrations. In the case of benzoic acid, the frequencies of the C–C torsion and the C–O torsion, which are intra-molecular vibrations, are very low, presumably around 200 cm^{-1}, and the interactions between these two intra-molecular vibrations and the lattice vibrations can not be neglected. This could be one reason why we see minor discrepancies between calculated and observed frequencies.

The lattice modes assigned to the observed and calculated frequencies are more or less approximate ones. The actual lattice mode should be expressed as a linear combination of these approximate modes. However, only the mode of largest weight or contribution is given in the table. Hydrogen-bond vibrations of several carboxylic acids are summerized in Table 2. We see that in formic and acetic acids $\nu(R_x)$ is higher than $\nu(R_y)$, while in benzoic acid $\nu(R_x)$ is lower than $\nu(R_y)$. This is probably attributed to the fact that in formic and acetic acids the difference between I_x and I_y is smaller than that in benzoic acid, and the effect of the difference in the force constants becomes important. Besides this, the frequencies of formic and acetic acids given in the table are those of isolated dimers in the vapor phase and are free from interaction forces between the dimers, while in benzoic acid crystals the effects of these interaction forces can no longer be neglected.

4. Force Constants. The intermolecular force constants obtained from the calculation of the lattice vibrations are shown in Table 3. The non-bonding interaction force constants $F(\mathrm{H}\cdots\mathrm{H})$ and $F(\mathrm{C}\cdots\mathrm{H})$ were fixed to the values reported for benzene and naphthalene.[20] Other force constants were determined by a least square method to get the best fit between observed and calculated frequencies.

A resonance interaction force constant $p(\mathrm{O}\cdots\mathrm{H}, \mathrm{O}\cdots\mathrm{H})$ between the two O···H bonds in the cyclic dimer was introduced in this calculation. The same type of force constant has been used in the calculation of 1-methylthymine ($p = -0.09$ mdyn/Å).[21] Without this force constant the Raman active O···H stretching (T_y) frequencies 122 and 126 cm^{-1}, and the infrared active O···H stretching+O–H···O in-plane bending (R_x) frequencies 104 and 106 cm^{-1} cannot be explained simultaneously. This resonance force constant is not used in the normal-coordinate calculation of formic and acetic acid dimers (Table 4). This is probably because the Raman active frequencies of these acids are not exactly known (Table 2), and the hydrogen-bond force constants were determined using infrared frequencies alone. The negative value of this force constant is consistent with the physical meaning of "resonance interaction", *i.e.* the potential energy of the configuration in which the two O···H distances in the cyclic dimer are lengthened or shortened simultaneously is lower than that of the configuration in which one O···H is lengthened while at the same time the other is shortened.

We thank Dr. Midori Goto of the Government Chemical Industrial Research Institute Tokyo for the measurement of X-ray photographs.

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21) I. Harada and R. C. Lord, *Spectrochim. Acta*, **26A**, 2305 (1970).