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Low Frequency Vibrations, Polarizability and Entropy of Carboxylic Acid Dimers[1]

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A normal coördinate treatment of the low frequency vibrations of formic acid and acetic acid dimers was made using the rigid monomer model. The potential function was expressed in terms of the H· ·O stretching and the O–H· ·O and H· ·O═C–O bonding potential constants, which were calculated from the observed infrared frequencies and the entropy of dimerization. The H· ·O stretching force constant was found to be 0.33×10^5 dyne/cm., which is 5% of the H–O stretching force constant. The low frequency vibrations are described in terms of the translational and rotational amplitudes and the fractional potential energy associated with each potential constant. The assumption of the rigid monomer model was examined and found to be satisfactory. The value of atomic polarization calculated on the assumption of independent rigid monomers with the monomer dipole moment is somewhat too small but plausible changes in the dipole moment of each monomer unit yield agreement with the observed polarization.

A carboxylic acid monomer R–COOH has nine and the dimer $(R–COOH)_2$ twenty-four degrees of vibrational freedom other than the internal vibrations of the R groups. As the result of an electron diffraction study the dimer molecule was found to be planar[2] with the point group C_{2h}. Therefore those twenty-four vibrations of dimer molecules are grouped into nine a_g, eight b_u, four a_u and three b_g vibrations. Of these seven a_g, seven b_u, two b_g and two a_u vibrations can be correlated with the corresponding internal vibrations of two monomer units, while the remaining two a_g, one b_u, one b_g and two a_u vibrations may approximately be described as the translational and rotational vibrations of two monomer units against each other. In the present paper, the nature of the vibrations of the latter group will be discussed.

Due to their low frequencies, few measurements have been made of these vibrations of carboxylic acid dimers. Bonner and Kirby-Smith[3] observed a Raman line at 232 cm.$^{-1}$ of formic acid dimer in the vapor phase. Infrared absorption of trifluoroacetic acid dimer was studied by Oetjen,[4] but no strong band was observed in the region 90–250 cm.$^{-1}$. However, Millikan and Pitzer[5] observed two infrared bands of formic acid dimer at 237 and 160 cm.$^{-1}$ and a band of acetic acid dimer at 188 cm.$^{-1}$.

Normal coördinate treatments on these low frequency vibrations have been made by Halford[6] and by Slutsky and Bauer.[7] In each of their treatments approximations were made which, although appropriate at that time, should now be removed in order to allow more realistic comparison with the recently obtained spectral frequencies.

Low Frequency In-plane Vibrations.—The vibration frequencies and normal coördinates may be calculated by the GF matrix method of Wilson.[8] In ring molecules such as carboxylic acid dimer, however, the total number of internal coördinates exceeds that of the vibrational degrees of freedom, and it is preferable to express the inverse kinetic (G) and potential energy matrices (F) in terms of appropriate symmetry coördinates which are orthogonal to redundant coördinates. Redundant coördinates of carboxylic acid dimer in the a_g symmetry class are linear combination of the interbond angle coördinates only, while symmetry coördinates and redundant coördinates in the b_u class are to be expressed as linear combinations of the interbond angle coördinates as well as of the bond stretching coördinates and the coefficients are quite complicated and impractical to calculate. Accordingly it is more practical to deal with each monomer unit as a rigid body.

As a first approximation, then, the kinetic energy T^i of the in-plane low frequency vibrations may be expressed as

$$2T^i = M[(\Delta\dot{R}_A)^2 + (\Delta\dot{R}_B)^2] + I_Z(\dot{\omega}_A^2 + \dot{\omega}_B^2) \quad (1)$$

where M is the mass of each monomer unit, R the distance between the center of mass of the dimer and that of a monomer unit, ω the in-plane rotational displacement of an individual monomer unit around its own center of mass, I_Z the corresponding moment of inertia, and the subscripts A and B refer to the monomer units A and B, respectively (see Fig. 1). The internal symmetry coördinates in the a_g symmetry class are

$$S_1 = (\Delta R_A + \Delta R_B)/2^{1/2}$$

and

$$S_2 = (\omega_A + \omega_B)/2^{1/2} \quad (2)$$

and those in the b_u class are

$$S_3 = (\omega_A - \omega_B)/2^{1/2} \quad (3)$$

The coördinate $(\Delta R_A - \Delta R_B)/2^{1/2}$ is redundant.

The elements of the inverse kinetic energy matrix expressed in terms of these symmetry coördinates are

$$G_{11} = 1/M$$
$$G_{33} = 1/I_Z$$

and

$$G_{ij} = 0 (\text{for } i \neq j) \quad (4)$$

The symmetry coördinate $\dot{S}_2$ yields non-zero angular momentum of $2^{1/2}I_Z\dot{S}_2$, which is to be canceled out with an over all rotation of the dimer (I_Z': its moment of inertia) in the opposite sense with an angular velocity of $2^{1/2}I_Z\dot{S}_2/I_Z'$. The kinetic energy associated with S_2 is, then, equal to $a_Z I_z \dot{S}_2^2/2$ and the corresponding element of G is $G_{22} = 1/I_Z a_z$ where $a_z = 1 - (2I_Z/I_Z')$. If this correction is ignored, $G_{22} = 1/I_Z$. It may be mentioned here that the correction for non-zero angular momentum is necessary only for the symmetric vibrations and not for the antisymmetric vibrations since the symmetry coördinates in the latter case yield zero angular momentum.

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[1] This research was assisted by the American Petroleum Institute through Research Project 50.

[2] P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

[3] L. Bonner and J. S. Kirby-Smith, *Phys. Rev.*, **57**, 1078 (1940).

[4] R. A. Oetjen, quoted by N. Fuson and M. L. Josien, *J. Opt. Soc. Am.*, **43**, 1102 (1953).

[5] R. C. Millikan and K. S. Pitzer, THIS JOURNAL, **80**, 3515 (1958).

[6] J. O. Halford, *J. Chem. Phys.*, **14**, 395 (1946).

[7] L. Slutsky and S. H. Bauer, THIS JOURNAL, **76**, 270 (1954).

[8] E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

The potential function V^i for the in-plane vibrations is

$$2V^i = K[(\Delta r_{19})^2 + (\Delta r_{64})^2] + H_1'[(\Delta\alpha_{198})^2 + (\Delta\alpha_{643})^2] + H_2'[(\Delta\alpha_{019})^2 + (\Delta\alpha_{564})^2] \quad (5)$$

where r_{19} is the bond distance O_1–H_9, and α_{198} and α_{019} are the interbond angles O_8–$H_9 \cdot\cdot O_1$ and $H_9 \cdot\cdot O_1$–C_0, respectively (see Fig. 1). All the cross terms were neglected. The internal coördinates just given may be expressed in terms of the symmetry coördinates (see eq. 2 and 3). Then the elements of the potential energy matrix F are calculated as

$$\begin{aligned} F_{11} &= 4K\cos^2\delta + [4(H_1' + H_2')\sin^2\delta]/r_{19}^2 \\ F_{12} &= 4KR\cos\delta\sin\delta - [4(H_1' + H_2')R\cos\delta\sin\delta]/r_{19}^2 \\ F_{22} &= 4KR^2\sin^2\delta + [4(H_1' + H_2')R^2\cos^2\delta]/r_{19}^2 \\ F_{33} &= 4Ky_4^2 + 4(H_1'x_1^2 + H_2'x_4^2)/r_{19}^2 \end{aligned}$$

and

$$F_{23} = F_{13} = 0 \quad (6)$$

where $R = (x_A^2 + y_A^2)^{1/2}$ and $\delta = \tan^{-1}(y_A/x_A)$ and x_A and y_A give the position of the center of mass of the monomer unit A.

Low Frequency Out-of-plane Vibrations.—The first approximation to the kinetic energy T^0 of the out-of-plane low frequency vibrations may be expressed as

$$2T^0 = I_{XX}(\dot\chi_A^2 + \dot\chi_B^2) - 2I_{XY}(\dot\chi_A\dot\psi_A + \dot\chi_B\dot\psi_B) + I_{YY}(\dot\psi_A^2 + \dot\psi_B^2) \quad (7)$$

where χ and ψ are the rotational displacement of a monomer unit around axes through the center of mass of the monomer and parallel to the X- and Y-axes, respectively, and I_{XX}, I_{YY} and I_{XY} are the corresponding moments of inertia and product of inertia. The internal symmetry coördinates in the a_u symmetry class are

$$S_4 = (\chi_A + \chi_B)/2^{1/2}$$

and

$$S_5 = (\psi_A + \psi_B)/2^{1/2} \quad (8)$$

and those in the b_g class are

$$S_6 = [-(\chi_A - \chi_B)\sin\delta + (\psi_A - \psi_B)\cos\delta]/2^{1/2} \quad (9)$$

The coördinate $(\chi_A - \chi_B)\cos\delta + (\psi_A - \psi_B)\sin\delta$ is redundant. The elements of the inverse kinetic energy matrix expressed in terms of these symmetry coördinates are

$$\begin{aligned} G_{44} &= I_{YY}/(I_{XX}I_{YY} - I_{XY}^2) \\ G_{45} &= I_{XY}/(I_{XX}I_{YY} - I_{XY}^2) \\ G_{55} &= I_{XX}/(I_{XX}I_{YY} - I_{XX}^2) \quad (10) \\ G_{66}^* &= (I_{YY}\sin^2\delta - 2I_{XY}\sin\delta\cos\delta + I_{XX}\cos^2\delta)/(I_{XX}I_{YY} - I_{XY}^2) \end{aligned}$$

and

$$G_{46} = G_{56} = 0$$

The symmetry coördinate S_6 yields non-zero angular momentum and the apparent G_{66}^* must be corrected as in the case of S_2. In this case the derivation of the correction is much more complex;[9] the result is

$$G_{66} = \frac{I_{XX}'I_{YY}' - (I_{XY}')^2}{4MR^2(I_{XX}I_{YY} - I_{XY}^2)} \quad (11)$$

where I_{XX}', etc., are the moments and product of inertia of the dimer.

The potential function V^0 used for the out-of-plane vibrations is

$$2V^0 = H_1''[(\Delta\beta_{198})^2 + (\Delta\beta_{643})^2] + H_2''[(\Delta\theta_{01})^2 + (\Delta\theta_{56})^2] \quad (12)$$

where β_{198} is the interbond angle O_8–$H_9 \cdot\cdot O_1$ and

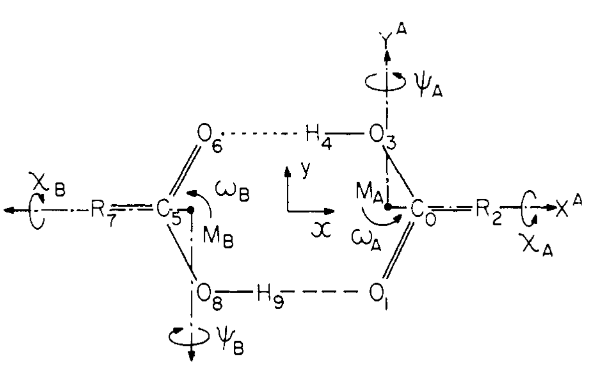

Fig. 1.—Coördinates of carboxylic acid dimer.

θ_{01} the internal rotation angle around the C_0=O_1 bond. All the interbond angles are assumed to be 120° except for $\alpha(O\text{–}H \cdot\cdot O) = 180°$. The internal coördinates, expressed in terms of the symmetry coördinates, are substituted into eq. 12 to obtain the elements of the potential energy matrix F.

$$\begin{aligned} F_{44} &= 4(H_1'' + 4H_2''/3)y_4^2/r_{19}^2 \\ F_{45} &= 4(H_1''x_1y_4 - 4H_2''x_4y_4/3)/r_{19}^2 \\ F_{55} &= 4(H_1''x_1^2 + 4H_2''x_4^2/3)/r_{19}^2 \\ F_{46} &= F_{56} = 0 \\ F_{66} &= 4(H_1'' + 4H_2''/3)R^2/r_{19}^2 \quad (13) \end{aligned}$$

Up to this point we have treated each monomer unit as a rigid body. This approximation is less satisfactory for the out-of-plane than for the in-plane vibrations because of the relatively low frequency and force constant associated with the O–H torsional motion. Consequently the validity of the rigid monomer model was investigated by a complete calculation for the out-of-plane motions. The mathematical details are given in Appendix I and the results are discussed below.

Entropy of Low Frequency Vibrations.—Since only a few of the low vibrational frequencies have been observed in spectra, it is necessary to use the entropy data to assist in determining potential constants. The dissociation equilibria of carboxylic acid dimers have been measured by many workers. Recently Taylor and Bruton[10] measured dimerization equilibria of formic acid and acetic acid over the temperature range 50–150° at relatively low pressures. The entropies of the low frequency vibrations of the two acids were calculated from the measured values of the entropy of dimerization. The results of these calculations are shown in Table I.

The translational and rotational entropies of formic acid monomer were calculated by the use of the bond distances and interbond angles determined by a microwave measurement.[11] The values for the dimer are given below. The vibrational entropies of the monomer and dimer of formic acid were calculated by the use of the frequencies observed by Millikan and Pitzer.[5,12] A similar calculation was made for acetic acid where the change in vibrational entropy on dimerization was assumed to be the same as in the case of formic acid. The bond distances and angles of acetic acid monomer

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(9) This formula was obtained by induction and verified numerically by appropriate reduction of the exact G matrix of Appendix 1.

(10) M. D. Taylor, THIS JOURNAL, **73**, 315 (1951); M. D. Taylor and J. Bruton, *ibid.*, **74**, 4151 (1952).

(11) R. G. Lerner, B. P. Dailey and J. P. Friend, *J. Chem. Phys.*, **26**, 680 (1957).

(12) R. C. Millikan and K. S. Pitzer, *ibid.*, **27**, 1305 (1957).

TABLE I

ENTROPY OF DIMERIZATION AT 373°K. (IN CAL./DEG. MOLE)

	Entropy: Monomer	Entropy: Dimer	Entropy: Dimerization
(A) Formic acid			
Translation + rotation	60.23	67.04	−53.42
High frequency vibration	1.81	2.46	− 1.16
Low frequency vibration	...	18.60	+18.60
Thermal			−35.98[a]
(B) Acetic acid			
Translation + rotation	63.72	69.50	−57.94
High frequency vibration			− 1.16[b]
Low frequency vibration	...	22.26	+22.26
Thermal			−36.84[a]

[a] Ref. 10. [b] Assumed to be the same as in the case of formic acid.

were assumed to be the same as the corresponding quantities in the dimer.

Entropy of Dimerization by Classical Mechanics.—At the temperatures of interest for carboxylic acids in the vapor state the low frequency vibrations may be treated by classical statistical mechanics in good approximation. For example at 373°K. the error of the classical calculation of the entropy of the six low frequency vibrations is only 0.1 cal./deg. mole for formic acid, and it would be less for any other carboxylic acid. The classical formulation of the entropy of dimerization explicitly cancels many extraneous factors such as masses and moments of inertia and shows the essential relationship to the force constants of the bonds connecting the monomer units.

The dimensions of the monomer are assumed to remain unchanged in the dimer; this is not exactly true in the case of formic acid, where data are available, but is a useful approximation.

The classical expression for the entropy of a vibrational mode

$$S_i = R[1 + \ln(kT/hc\nu_i)] \qquad (14)$$

is used together with the conventional equation for translational and rotational entropy. Also the product of the vibration frequencies is obtained from the product of the determinants of **G** and **F**, as

$$\prod_i (2\pi c\nu_i) = [\mathbf{G}]^{1/2}\cdot[\mathbf{F}]^{1/2} \qquad (15)$$

After extensive cancellation the entropy of dimerization is

$$\Delta S = \Delta S_v' + R(2 \ln T - {}^1/_2 \ln f) - 108.66 \qquad (16)$$

where $\Delta S_v'$ is the change in entropy of high frequency vibration on dimerization and f is the following function of potential function constants.

$$f = \frac{4}{3}\left(\frac{4}{r_{19}}\right)^6\left[\{KH_1''H_2''y_4^2(H_1' + H_2')\left(H_1'' + \frac{4}{3}H_2''\right) \times \{Ky_4^2 + (H_1'x_1^2 + H_2'x_4^2)/r_{19}^2\}\right] \qquad (17)$$

Without reference to the particular values of the quantities remaining in equation 16, it is apparent that the entropy of dimerization is independent of the mass and moments of inertia of the monomer units because these quantities have canceled (except possibly for a very small effect on high frequency vibrations in $\Delta S_v'$). Thus, if the dimensions and force constants associated with the hydrogen bonds remain the same for a series of carboxylic acids, the entropy of dimerization will remain constant also. The approximate constancy of the entropy of dimerization has been noticed by others,[7] but the explanation is much more apparent in these terms.

The values shown in Table I indicate that the hydrogen bonding in acetic acid is a little stronger than that in formic acid. Approximately a 13% average difference in the potential constants is indicated by the classical formula, but other approximations make it probable that the true difference is somewhat smaller. The heat of dissociation of the dimer is about 8% larger for acetic than for formic acid, hence this difference in potential constants seems very reasonable.

Evaluation of Potential Constants.—The potential function as expressed in equations 5 and 12 contains three force constants for in-plane motions and two for out-of-plane motions. Since there are only three observed frequencies for formic acid and but one for acetic acid and since the entropy yields but one additional datum, it is clearly impossible to evaluate five independent constants for each acid. In order to obtain a reasonable excess of data over adjustable constants, it was assumed that (1) the constants for acetic and formic acids are the same and (2) the bending constants H_1 and H_2 are the same for in-plane and for out-of-plane motion, *i.e.*, $H_1' = H_1''$ and $H_2' = H_2''$. It was shown in the preceding section that assumption (1) is in error by somewhat less than 13% on the average. If the constants are evaluated midway between the acetic and formic acid values, the expected deviations between calculated and observed frequencies are only 3% or less.

The bond distances adopted were: $r(C{=}O)$ = 1.25 Å., $r(C{-}O)$ = 1.35 Å., $r(O{-}H)$ = 0.95 Å., $r(O\cdots O)$ = 2.75 Å., $r(C{-}H)$ = 1.085 Å., and $r(C{-}CH_3)$ = 1.54 Å. The methyl group of acetic acid was treated as a point mass.

The value of $F_{33} = 4Ky^2 + 4(H_1x_1^2 + H_2x_4^2)/r_{19}^2$ of eq. 6 was calculated by the method of least squares from the observed frequency of 237 cm.$^{-1}$ (formic acid) and 188 cm.$^{-1}$ (acetic acid). The values of H_1 and H_2 were then adjusted so that the calculated ν_4 frequency of formic acid agreed with the observed value of 160 cm.$^{-1}$ and the calculated entropy of formic acid and acetic acid dimers fitted best with the observed values (Table I). The result of the calculation is shown in Table II. It will

TABLE II

OBSERVED AND CALCULATED FREQUENCIES AND CALCULATED ENTROPY AT 373°K. OF LOW FREQUENCY VIBRATIONS OF FORMIC ACID AND ACETIC ACID DIMERS

	$(HCOOH)_2$			$(CH_3COOH)_2$		
Vibration	Frequency Obsd.	Frequency Calcd.	S_{373} Calcd.	Frequency Obsd.	Frequency Calcd.	S_{373} Calcd.
$\nu_1(a_g)$	232[a]	221	2.36		193	2.62
$\nu_2(a_g)$		103	3.84		95	3.99
$\nu_3(b_u)$	237[b]	248	2.15	188[b]	180	2.74
$\nu_4(a_u)$	160[b]	160	2.98		80	4.33
$\nu_5(a_u)$		60	4.85		46	5.43
$\nu_6(b_g)$		243	2.19		128	3.40
Sum of entropy						
(calcd.)			18.37			22.51
(obsd.)			18.60 ± 0.3			22.26

[a] Ref. 3. [b] Ref. 5.

be seen that the calculated and observed entropy values agree within approximately the experimental error, even though the same values of force constants were used in both cases. The differences are, of course, in opposite directions. The force constants thus calculated are

$$K(\mathrm{H\cdot\cdot O}) = 0.33 \times 10^5 \text{ dyne/cm.}$$
$$H_1 = 0.043 \times 10^{-11} \text{ erg/radian}^2$$

and

$$H_2 = 0.027 \times 10^{-11} \text{ erg/radian}^2$$

Stretching Force Constant.—Halford[6] estimated the value of K as 0.41×10^5 dyne/cm. from the ratio empirically found between the values of force constant and of heat of dissociation. This is not too much different from the value of 0.33×10^5 obtained in the present study. Slutsky and Bauer[7] assumed a potential function

$$V = \Delta H[(r_0/r)^6 - 2(r_0/r)^3]$$

where ΔH is one-half the dissociation energy of the dimer and the variable r is the O · · O distance. They predicted a value of 0.12×10^5. This is much smaller than the value of 0.33×10^5. However, if the variable r is taken as the H · · O distance instead of the O · · O distance, a value of 0.29×10^5 results which approximates that calculated in the present study.

It is interesting to compare the value of K(H · · O) with that of K(O–H). The value of K(O–H) of formic acid monomer is 7.2×10^5 and so the ratio of K(O–H):(H · · O) = 1:0.05. This value of 5% is the same order of magnitude as the bond order of water–water hydrogen bond (3%) calculated by Coulson and Danielsson.[13]

Bending Potential Constant.—The potential constant H_2 is associated with the in-plane and out-of-plane angular displacement of hydrogen atom with respect to the · · O=C–O group with which it is hydrogen-bonded. Its value of $0.02_7 \times 10^{-11}$ is 4% of the value 0.7×10^{-11} of the bending constant H–O–C. The ratio of the OH stretching and bending constants is K(O–H):H(H–O–C) = $1:0.1_0 \times 10^{-16}$, while the ratio of the H · · O stretching and bending constants is nearly the same, K(H · · O):H(H · · O=C) = $1:0.12 \times 10^{-16}$.

Calculated Frequencies.—The calculated Raman frequencies of formic acid dimer are 243, 221 and 103 cm.$^{-1}$. The only Raman line observed at 232 cm.$^{-1}$ may be due to the two vibrations 243 and 221 cm.$^{-1}$. Raman lines of acetic acid dimer are expected at 193, 128 and 95 cm.$^{-1}$. As shown in Table I, all the infrared frequencies calculated above 160 cm.$^{-1}$ have been observed. The frequencies to be observed are $\nu_5(\mathrm{a_u})$ = 60 cm.$^{-1}$ for formic acid, and $\nu_4(\mathrm{a_u})$ = 80 cm.$^{-1}$ and $\nu_5(\mathrm{a_u})$ = 46 cm.$^{-1}$ for acetic acid.

Vibrational Amplitude.—The nature of the low frequency vibrations may be discussed in terms of the vibrational amplitude of each internal coördinate. Relative amplitudes in the ath normal vibration can be calculated from the **L** matrix defined by $R_i = L_{ia}Q_a$, where R_i and Q_a are the ith internal coördinate and the ath normal coördinate, respectively.[8] The calculated values of the **L** matrix elements are shown in Table III. The fractional potential energy associated with each force constant[14] is another measure of the nature of a normal vibration, and the calculated values are shown in Table IV. It may be pointed out that the number given in the table is equal to $(\partial(\nu_a^2)/\partial K_h)/\nu_a^2$, where K_h is the hth force constant.

TABLE III

ELEMENTS OF L MATRICES OF FORMIC ACID AND ACETIC ACID DIMERS[a]

	$(\mathrm{HCOOH})_2$			$(\mathrm{CH_3COOH})_2$		
	Q_1	Q_2	Q_3	Q_1	Q_2	Q_3
ΔR_A	$+0.08_1$	$+0.00_1$	0	$+0.07_1$	-0.00_0	0
ω_A	$-\ .00_2$	$+\ .09_4$	$+0.07_8$	$+\ .00_0$	$+\ .06_7$	$+0.05_7$
ΔR_B	$+\ .08_1$	$+\ .00_1$	0	$+\ .07_1$	$-\ .00_0$	0
ω_B	$-\ .00_2$	$+\ .09_4$	-0.07_8	$+\ .00_0$	$+\ .06_7$	-0.05_7
	Q_4	Q_5	Q_6	Q_4	Q_5	Q_6
χ_A	$+0.01_0$	-0.08_5	-0.00_2	$+0.06_8$	-0.05_2	$+0.00_0$
ψ_A	$+\ .19_6$	$+\ .05_3$	$+\ .20_9$	$+\ .04_1$	$+\ .06_4$	$+\ .08_4$
χ_B	$+\ .01_0$	$-\ .08_5$	$+\ .00_2$	$+\ .06_8$	$-\ .05_2$	$-\ .00_0$
ψ_B	$+\ .19_6$	$+\ .05_3$	$-\ .20_9$	$+\ .04_1$	$+\ .06_4$	$-\ .08_4$

[a] Numerical values in the first and third columns are in 10^{12} c.g.s. unit and others in 10^{20} c.g.s. unit. χ, ψ and ω are the rotational displacements around the X-, Y- and Z-axes, respectively (see Fig. 1).

TABLE IV

FRACTIONAL POTENTIAL ENERGY ASSOCIATED WITH EACH FORCE CONSTANT

	$(\mathrm{HCOOH})_2$			$(\mathrm{CH_3COOH})_2$		
	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3
K(H· ·O)	1.0	0.0	0.9_5	1.0	0.0	0.9_5
H_1'(O–H· ·O)	0.0	.6	.0	0.0	.6	.0
H_2'(H· ·O=C)	0.0	.4	$.0_5$	0.0	.4	$.0_5$
	ν_4	ν_5	ν_6	ν_4	ν_5	ν_6
H_1''(O–H· ·O)	0.9_5	0.0_5	0.5_5	0.8_5	0.1_5	0.5_5
H_2''(H· ·O=C–O)	$.0_5$	$.9_5$	$.4_5$	$.1_5$	$.8_5$	$.4_5$

As shown in these tables, ν_1 is the translational vibration of each monomer unit and ν_2 and ν_3 are the rotational vibrations in the dimer plane, however, as for the potential energy, ν_1 and ν_3 are the hydrogen bond stretching vibrations and ν_2 the hydrogen bond bending vibration.

The out-of-plane vibration ν_6 is essentially the rotational vibration around the Y-axis and its frequency depends on H_1''(O–H · · O) as well as on H_2''(H · · O=C–O).

The ν_4 vibration of formic acid is essentially the rotational vibration around the Y-axis, while in the case of the ν_5 vibration of formic acid and the ν_4 and ν_5 vibrations of acetic acid, the amplitudes of the rotational displacements around the X- and Y-axes are nearly the same. Referring to the fractional potential energy associated with each force constant, however, ν_4 may well be called the O–H · · O bending vibration and ν_5 the H · · O=C–O torsional vibration both in the case of formic acid and acetic acid.

Approximation in Calculating Low Frequency Vibrations.—In the preceding section, the vibrational frequencies were calculated using the rigid monomer model (method II). The validity of this approximation may be examined by a comparison of such frequencies with those calculated without separating high frequency vibrations (method III). The equations for the out-of-plane frequency calculation by method III are given in Appendix I. The values of the force constants $H_\Omega = 0.59 \times 10^{-11}$ and $H_\theta = 0.22 \times 10^{-11}$ erg/radian^2 were chosen so that the calculated high frequencies of formic acid dimer agreed with the observed values[5] for the vari-

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(13) C. A. Coulson and U. Danielsson, *Arkiv. Fysik*, **8**, 245 (1954).

(14) T. Miyazawa, *J. Chem. Soc. Japan*, **76**, 1132 (1955).

ous isotopic species. The low frequencies thus calculated are shown in Table V. The frequencies calculated using the rigid monomer model (method II) are higher than those calculated by method III, since the assumption of the rigid monomer model is physically equivalent with the neglect of the interaction with the high frequency vibrations. However, the resulting difference between the two methods is less than 8%, thus rendering support to the rigid monomer model.

As mentioned in a previous section, in the case of symmetric vibrations the actual center of the rotational vibrations of a monomer unit is shifted away from the center of mass of its own. Therefore if the center of the rotational vibrations is assumed to be at the center of the mass of the monomer (method I), it should lead to non-genuine vibrations. Even though this assumption is not valid physically, the frequency errors (see Table V) are 18% for ν_2 and 8% for ν_6 and thus are not too serious.

Atomic Polarization.—The atomic polarization P_A of formic acid dimer has been measured and found to be 15.5 cc. in the vapor phase[15] and 15.2 cc. in heptane solution,[16] while that of acetic acid dimer in heptane solution[16] is 17 cc. It is interesting to calculate P_A by the present rigid monomer treatment and see whether the calculated value comes out to be the same order of magnitude as that observed.

The atomic polarization P_A is related with the electric moments by the equation

$$P_A = \frac{4\pi N}{9}\left[\frac{2(\mu_x^2 + \mu_y^2)}{F_{33}} + \frac{2(F_{44}\mu_x^2 + 2F_{45}\mu_x\mu_y + F_{55}\mu_y^2)}{F_{44} - F_{55} - F_{45}^2}\right] \qquad (18)$$

where N is the Avogadro number and μ_x and μ_y are the x and y components of the dipole moment of a monomer unit. Insertion of the various potential constants yields

$$P_A = 2.2\mu_x^2 + 2.2\mu_x\mu_y + 2.0\mu_y^2 \qquad (19)$$

where the μ's are in Debye units and P_A is in cc. The direction of the dipole moment of carboxylic acid was measured for a series of substituted benzoic acids.[17] If the same direction is assumed for formic acid monomer ($\mu = 1.8\ D$ in non-polar solution),[18] $\mu_x = 0.5\ D$ and $\mu_y = 1.7\ D$. These values yield a value of $P_A = 8$ cc., which is about half of the observed value. Accordingly the independent rigid model using the monomer moment is not too satisfactory. It is, however, conceivable that the y component μ_y of a monomer unit increases on dimerization because of increased contribution of the polar electronic structure O^-–CH=OH^+. If μ_y is increased by 0.8 D, then the calculated value of P_A agrees with the experimental value of 15 cc.

Appendix I

Complete Inverse Kinetic and Potential Energy Matrices for Out-of-plane Vibrations.—The inverse kinetic and potential energy matrices were calculated for all out-of-plane vibrations of the dimer by the Wilson[8] GF matrix method. The internal coördinates[19] are: the out-of-plane skeletal deformation coördinates $\Omega_0(C_0O_1R_2O_3)$ and Ω_5, O–H torsional coördinates $\theta_{14}(O_1{=}C_0{-}O_3{-}H_4)$ and θ_{69}, $\theta_{24}(R_2{-}C_0{-}O_3{-}H_4)$ and θ_{79}, of each monomer together with the coördinates $\theta_{93}(H_9 \cdots O_1{=}C_0{-}O_3)$ and θ_{48}, and $\theta_{92}(H_9 \cdots O_1{=}C_0{-}R_2)$ and θ_{47}, and the interbond angle bending coördinates $\beta_{346}(O_3{-}H_4 \cdots O_6)$ and β_{891}. The symmetry coördinates were constructed from these internal coördinates so that the resulting potential energy matrix was appropriate for the approximate separation of the high and low frequency vibrations.

TABLE V

COMPARISON OF FREQUENCIES CALCULATED BY THE THREE METHODS

Vibration	$(HCOOH)_2$ I	$(HCOOH)_2$ II	$(HCOOH)_2$ III	$(CH_3COOH)_2$ I	$(CH_3COOH)_2$ II
$\nu_1(a_g)$	221	221		193	193
$\nu_2(a_g)$	86	103		81	95
$\nu_3(b_u)$	248	248		180	180
$\nu_4(a_u)$	160	160	145	80	80
$\nu_5(a_u)$	60	60	58	46	46
$\nu_6(b_g)$	235	243	222	116	128

Symmetry coördinates in the a_u class are

$$S_a = (\Omega_0 + \Omega_5)/3^{1/2} + (-\theta_{14} - \theta_{69} + \theta_{24} + \theta_{79} + \theta_{93} + \theta_{48} - \theta_{92} - \theta_{58})(3/64)^{1/2}$$

$$S_b = (\theta_{14} + \theta_{69} + \theta_{24} + \theta_{79})(3/16)^{1/2}$$

$$S_4 = (\theta_{93} + \theta_{48} + \theta_{92} + \theta_{58})(3/16)^{1/2}$$

and

$$S_5 = (\beta_{346} + \beta_{891})/2^{1/2}$$

and those in the b_g class are

$$S_c = (\Omega_0 - \Omega_5)/3^{1/2} + (-\theta_{14} + \theta_{69} + \Delta\theta_{24} - \theta_{79} + \theta_{93} - \theta_{48} - \theta_{92} + \theta_{58})(3/64)^{1/2}$$

$$S_d = (3\theta_{14} - 3\theta_{69} + 3\theta_{24} - 3\theta_{79} - \theta_{93} + \theta_{48} - \theta_{92} + \theta_{58})(3/192)^{1/2} - (\beta_{346} - \beta_{891})/12^{1/2}$$

and

$$S^6 = (-\theta_{93} + \theta_{48} - \theta_{92} + \theta_{58})/8^{1/2} - (\beta_{891} - \beta_{346})/6^{1/2}$$

S_a, S_b, S_c and S_d are those related with the internal vibrations of monomer units; S_a and S_c correspond to the out-of-plane deformation coördinates, and S_b and S_d to the internal rotation around the C–O bond. S_4, S_5 and S_6 are the coördinates for the low frequency vibrations which were defined in eq. 8 and 9.

The inverse kinetic energy matrix expressed in terms of these symmetry coördinates was calculated by the use of the B matrix[8] which is defined as $S_i = B_{ik}z_k$. (z_k is the out-of-plane displacement of the kth atom.)

$$B_{a0} = \tau_{01} + \tau_{02} + \tau_{03}$$
$$B_{a1} = -\tau_{01}$$
$$B_{a2} = -\tau_{02}$$
$$B_{a3} = -\tau_{03}$$
$$B_{a4} = 0$$
$$2B_{40} = \tau_{01} - \tau_{02} + \tau_{03}$$
$$2B_{41} = -\tau_{01} - 2\tau_{19}$$
$$2B_{42} = \tau_{02}$$
$$2B_{43} = -\tau_{03}$$
$$2B_{44} = 2\tau_{19}$$
$$2B_{b0} = -\tau_{01} + \tau_{02} - \tau_{03}$$
$$2B_{b1} = \tau_{01}$$
$$2B_{b2} = -\tau_{02}$$
$$2B_{b3} = \tau_{03} + 2\tau_{34}$$
$$2B_{b4} = -2\tau_{34}$$

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(15) I. E. Coop, N. R. Davidson and L. E. Sutton, *J. Chem. Phys.*, **6**, 905 (1938).

(16) H. A. Pohl, M. E. Hobbs and P. M. Gross, *ibid.*, **9**, 408 (1941); A. A. Maryott, M. E. Hobbs and P. M. Gross, *ibid.*, **9**, 415 (1941).

(17) C. S. Brooks and M. E. Hobbs, THIS JOURNAL, **62**, 285 (1940); M. E. Hobbs and A. J. Weith, Jr., *ibid.*, **65**, 967 (1943).

(18) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 304.

(19) T. Miyazawa, T. Shimanouchi and S. Mizushima *J. Chem., Phys.*, **23**, 408 (1956).

$$
\begin{aligned}
2^{1/2}B_{50} &= 0\\
2^{1/2}B_{51} &= -\tau_{19}\\
2^{1/2}B_{52} &= 0\\
2^{1/2}B_{53} &= -\tau_{34}\\
2^{1/2}B_{54} &= \tau_{19} + \tau_{34}\\
6^{1/2}B_{60} &= -\tau_{01} + \tau_{02} - \tau_{03}\\
6^{1/2}B_{61} &= \tau_{01} + 3\tau_{19}\\
6^{1/2}B_{62} &= -\tau_{02}\\
6^{1/2}B_{63} &= \tau_{03} - \tau_{34}\\
6^{1/2}B_{64} &= \tau_{34} + 3\tau_{19}\\
B_{ii} &= B_{i,j+5} \text{ (for } i = \text{a, b, 4 or 5)}\\
B_{ij} &= -B_{i,j+5} \text{ (for } i = \text{c, d, or 6)}\\
B_{aj} &= B_{cj}\\
2B_{bj} &= 3^{1/2}B_{dj}
\end{aligned}
$$

and

$$\tau_{kl} = 1/r_{kl}$$

The potential function for the out-of-plane vibrations was chosen to be

$$
\begin{aligned}
2V = {} & H\Omega(\Omega_0 + \Omega_5^2) + H_\theta\,[(\theta_{14} + \theta_{24})^2 + (\theta_{69} + \theta_{79})^2]/4\\
& + H_1''(\beta_{346}^2 + \beta_{891}^2) + H_2''[(\theta_{39} + \theta_{29})^2 + (\theta_{84} + \theta_{74})^2]/4
\end{aligned}
$$

Here H_Ω and H_θ are the force constants for the out-of-plane skeletal deformation and for the O–H torsion, respectively. The elements of the potential energy matrix expressed in terms of the symmetry coördinates are

$$
\begin{aligned}
F_{aa} &= 3H\Omega/8\\
F_{bb} &= 2H\theta/3\\
F_{44} &= 2H_2''/3\\
F_{55} &= H_1''\\
F_{cc} &= 3H_\Omega/8\\
F_{dd} &= H_\theta/2 + H_1''/6 + H_2''/18\\
F_{d6} &= -H_1''/18^{1/2} + 2^{1/2}H_2''/9\\
F_{66} &= H_1''/3 + 4H_2''/9
\end{aligned}
$$

and all other cross terms are equal to zero.

The approximate calculation of the low frequency vibrations may be made by the use of the **G** and **F** matrices now derived. For the calculation, the **G** matrix elements G_{44}, G_{45}, G_{55} and G_{66} were modified[8,20] so that they were in accord with the rigid monomer model, while the corresponding **F** matrix elements were used without modification. The rigid monomer model is physically equivalent with the assumption of infinite values for the force constants H_Ω and H_θ. The **F** matrix elements for the low frequency vibrations necessarily do not contain these constants.

(20) B. L. Crawford, Jr., and J. T. Edsall, *J. Chem. Phys.*, **7**, 223 (1939).

BERKELEY, CALIF.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

The Molecular Weight of Insoluble Sodium Metaphosphate[1]

BY ULRICH P. STRAUSS AND JEAN W. DAY

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The molecular weight of an "insoluble" sodium metaphosphate, $NaPO_3$ II, was determined from intrinsic viscosity measurements in aqueous lithium bromide. The necessary intrinsic viscosity-molecular weight relationships were obtained from viscosity measurements of several potassium Kurrol salts whose molecular weights ranged from 220,000 to 1,320,000. The results establish $NaPO_3$ II as a long-chain polyphosphate with a molecular weight of at least 280,000.

While much work has been done on the $NaPO_3$ system[2] there are considerable gaps in our knowledge of these compounds. X-Ray and microscopic studies have established the existence of at least three forms of crystalline $NaPO_3$ which are characterized as insoluble.[3] Two of these forms, $NaPO_3$ II and $NaPO_3$ III, have been denoted as Maddrell salts, and another form, $NaPO_3$ IV, has been called Kurrol salt. The Maddrell salts are believed to be high polymers[2,4]; however, proof of their structure is incomplete and their molecular weights apparently have not been determined.

This paper describes the determination of the molecular weight of $NaPO_3$ II. The problems were to identify the sample,[5] to select a solvent and to determine the molecular weight by means of viscosity measurements.

Results and Discussion

Identification of Sample.—The X-ray diffraction pattern identified the water-insoluble fraction, which constituted 95% of the sample, as $NaPO_3$ II.[6] No attempt was made to identify the water-soluble constituents. Six-tenths of a per cent. of the sample was volatile when it was heated at 600° for 18 hr. The sample was converted to the water-soluble Graham salt by heating at 600°,[7] and the Na/P ratio was determined by titrating the aqueous solution obtained to the first equivalence point[8]; the Na/P ratio was 1.03. The sample contained 9.69 meq. of phosphorus per gram of polymer,[9] calculated on a dry basis. The theoretical value for a sodium metaphosphate of this composition is 9.72. The agreement is within the accuracy attainable with the analytical technique.

Solubility Characteristics.—While the sample was insoluble in water it could be dissolved in aqueous LiBr. The dissolution probably involves an ion-exchange mechanism similar to that encountered with potassium Kurrol salt.[10]

Determination of Molecular Weight.—Several potassium Kurrol salts whose molecular weights ranged from 220,000 to 1,320,000 were used to prepare a calibration curve to estimate the mo-

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(1) The contents of this paper are contained in a thesis to be submitted by Jean W. Day to the Graduate School of Rutgers University in partial fulfillment of the requirements for the degree of Master of Science. This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1) 1018.

(2) B. Topley, *Quart. Revs.* (*London*), **3**, 345 (1949).

(3) E. P. Partridge, *Chem. Eng. News*, **27**, 214 (1949).

(4) E. Thilo, G. Schulz and E. Wichmann, *Z. anorg. allgem. Chem.*, **272**, 182 (1953).

(5) The sample was commercial IMP produced by Monsanto Chemical Co. (G. E. Taylor and A. G. Erdman, U. S. Patent 2,356,799, May 27, 1943).

(6) ASTM 2412, d, 2-0766.

(7) E. P. Partridge, V. Hicks and G. W. Smith, THIS JOURNAL, **63**, 454 (1941).

(8) U. P. Strauss and T. L. Treitler, *ibid.*, **77**, 1473 (1955).

(9) This was determined by potentiometric titration of the hydrolyzed polymer using NaOH as described by J. R. Van Wazer, *et al.*, *ibid.*, **72**, 639, 644, 647, 655, 906 (1950).

(10) R. Pfanstiel and R. K. Iler, *ibid.*, **74**, 6059 (1952).