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Lattice Vibrations of Potassium Oxalate Monohydrate and the Bound State of Water of Crystallization

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A normal coordinate treatment of the potassium oxalate monohydrate crystal as a whole was carried out. On the basis of the results of the calculation, the nature of the lattice vibrations and the bound state of the water of crystallization were discussed.

Recent investigations of the crystal structure of potassium oxalate monohydrate by Pedersen[1] and by Chidambaram *et al.*[2] have concluded that it is a monoclinic structure belonging to the $C2/c$ space group. The IR spectra of the substance have also been measured by Collman and Holtzclaw,[3] Schmelz *et al.*,[4] Pedersen,[5] and the present author.[6] In the region of 300—4000 cm^{-1}, no remarkable differences are not found among the spectra obtained by the various investigators except for the differences ascribed to the different resolving powers of the spectrometers. Pedersen measured a powder X-ray diagram for the sample used for the measurement of the IR spectra, and identified it with the sample which he had used for structural determination.[1] From these facts, it may be concluded that the samples used for the IR measurements by the other investigators have the same crystal structure as that of Pedersen's sample or that differences in IR spectra due to differences in crystal structure do not appear in the 300—4000 cm^{-1} region even if these are differences in crystal structure due to crystal modification among the samples. Therefore, in the present investigation, I calculated the lattice vibrations for the crystal structure obtained by Pedersen[1] and Chidambaram *et al.*,[2] using the observed frequencies,[6] in order to make clear the bound state of the water of crystallization and also to elucidate the nature of the lattice vibrations.

Normal Coordinate Treatment

A normal coordinate treatment was carried out for the crystal structure obtained by Chidambaram *et al.*;[2] the lattice parameters were $a=9.236$ Å, $b=6.190$ Å, $c=10.694$ Å, and $\beta=110°47'$. The Bravais unit lattice, which has a cell containig $2K_2C_2O_4 \cdot H_2O$ and belonging to each lattice point, is the monoclinic lattice (C), and the cell-repeating vectors are $(\boldsymbol{a}+\boldsymbol{b})/2$, $(\boldsymbol{a}-\boldsymbol{b})/2$, and $(\boldsymbol{a}-\boldsymbol{c})$. The numbering of the atoms and ions in the chemical units and a part of the crystal lattice is shown in Fig. 1.

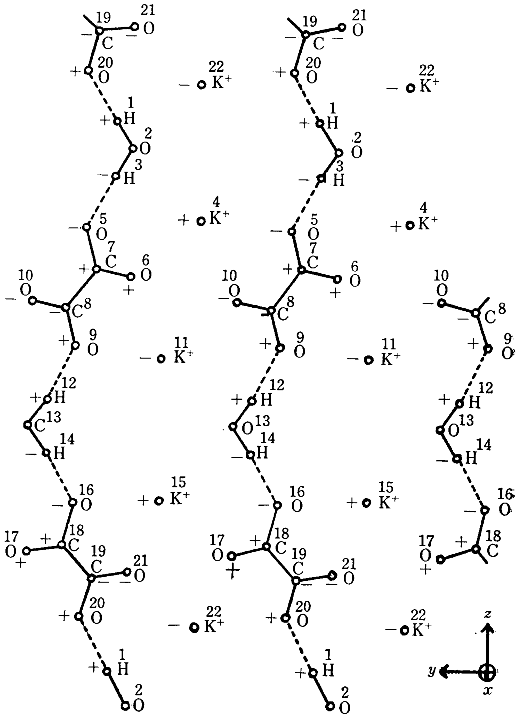

Fig. 1. A part of crystal lattice of potassium oxalate monohydrate (+and−represent "above the paper plane" and "below the plane," respectively)..

Optically-active lattice vibrations were calculated according to the $\boldsymbol{G}\,\boldsymbol{F}$ matrix method developed by

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[1] B.F. Pedersen, *Acta Chem. Scand.*, **18**, 1635 (1964).

[2] R. Chidambaram, A. Sequeira and S.K. Sikka, *J. Chem. Phys.*, **41**, 3616 (1964).

[3] J. P. Collman and H. F. Holtzclaw, Jr., *J. Amer. Chem. Soc.*, **80**, 2054 (1958).

[4] M. J. Schmelz, T. Miyazawa, S. Mizushima, T.J. Lane and J.V. Quagliano, *Spectrochim. Acta*, **9**, 51 (1958).

[5] B. F. Pedersen, *Acta Chem. Scand.*, **21**, 801 (1967).

[6] K. Fukushima, This Bulletin, **43**, 39 (1970).

TABLE 1. CARTESIAN SYMMETRY COORDINATES (ELEMENTS OF THE VECTOR, $(X_s)^{i,j,k}_{\text{Bravais}}$)*

A_g	$x_{s1} = \Delta(x_1-x_3+x_{12}-x_{14})/2$
	$x_{s2} = \Delta(y_1+y_3-y_{12}-y_{14})/2$
	$x_{s3} = \Delta(z_1-z_3+z_{12}-z_{14})/2$
	$x_{s4} = \Delta(y_2-y_{13})/\sqrt{2}$
	$x_{s5} = \Delta(x_5-x_9+x_{16}-x_{20})/2$
	$x_{s6} = \Delta(y_5-y_9-y_{16}+y_{20})/2$
	$x_{s7} = \Delta(z_5-z_9+z_{16}-z_{20})/2$
	$x_{s8} = \Delta(x_6-x_{10}+x_{17}-x_{21})/2$
	$x_{s9} = \Delta(y_6-y_{10}-y_{17}+y_{21})/2$
	$x_{s10} = \Delta(z_6-z_{10}+z_{17}-z_{21})/2$
	$x_{s11} = \Delta(x_7-x_8+x_{18}-x_{19})/2$
	$x_{s12} = \Delta(y_7-y_8-y_{18}+y_{19})/2$
	$x_{s13} = \Delta(z_7-z_8+z_{18}-z_{19})/2$
	$x_{s14} = \Delta(x_4-x_{11}+x_{15}-x_{22})/2$
	$x_{s15} = \Delta(y_4-y_{11}-y_{15}+y_{22})/2$
	$x_{s16} = \Delta(z_4-z_{11}+z_{15}-z_{22})/2$
A_u	$x_{s1} = \Delta(x_1-x_3-x_{12}+x_{14})/2$
	$x_{s2} = \Delta(y_1+y_3+y_{12}+y_{14})/2$
	$x_{s3} = \Delta(z_1-z_3-z_{12}+z_{14})/2$
	$x_{s4} = \Delta(x_5+x_9-x_{16}-x_{20})/2$
	$x_{s5} = \Delta(y_5+y_9+y_{16}+y_{20})/2$
	$x_{s6} = \Delta(z_5+z_9-z_{16}-z_{20})/2$
	$x_{s7} = \Delta(x_6+x_{10}-x_{17}-x_{21})/2$
	$x_{s8} = \Delta(y_6+y_{10}+y_{17}+y_{21})/2$
	$x_{s9} = \Delta(z_6+z_{10}-z_{17}-z_{21})/2$
	$x_{s10} = \Delta(x_7+x_8-x_{18}-x_{19})/2$
	$x_{s11} = \Delta(y_7+y_8+y_{18}+y_{19})/2$
	$x_{s12} = \Delta(z_7+z_8-z_{18}-z_{19})/2$
	$x_{s13} = \Delta(x_4+x_{11}-x_{15}-x_{22})/2$
	$x_{s14} = \Delta(y_4+y_{11}+y_{15}+y_{22})/2$
	$x_{s15} = \Delta(z_{12}+z_{11}-z_{15}-z_{22})/2$
	$x_{s16} = \Delta(y_2+y_{13})/\sqrt{2}$
B_g	$x_{s1} = \Delta(x_1+x_3-x_{12}-x_{14})/2$
	$x_{s2} = \Delta(y_1-y_3+y_{12}-y_{14})2$
	$x_{s3} = \Delta(z_1+z_3-z_{12}-z_{14})/2$
	$x_{s4} = \Delta(x_2-x_{13})/\sqrt{2}$
	$x_{s5} = \Delta(z_2-z_{13})/\sqrt{2}$
	$x_{s6} = \Delta(x_5-x_9-x_{16}+x_{20})/2$
	$x_{s7} = \Delta(y_5-y_9+y_{16}-y_{20})/2$
	$x_{s8} = \Delta(z_5-z_9-z_{16}+z_{20})/2$
	$x_{s9} = \Delta(x_6-x_{10}-x_{17}+x_{21})/2$
	$x_{s10} = \Delta(y_6-y_{10}+y_{17}-y_{21})/2$
	$x_{s11} = \Delta(z_6-z_{10}-z_{17}+z_{21})/2$
	$x_{s12} = \Delta(x_7-x_8-x_{18}+x_{19})/2$
	$x_{s13} = \Delta(y_7-y_8+y_{18}-y_{19})/2$
	$x_{s14} = \Delta(z_7-z_8-z_{18}+z_{19})/2$
	$x_{s15} = \Delta(x_4-x_{11}-x_{15}+x_{22})/2$
	$x_{s16} = \Delta(y_4-y_{11}+y_{15}-y_{22})/2$
	$x_{s17} = \Delta(z_4-z_{11}-z_{15}+z_{22})/2$
B_u	$x_{s1} = \Delta(x_1+x_3+x_{12}+{}_{14})/2$
	$x_{s2} = \Delta(y_1-y_3-y_{12}+y_{14})/2$
	$x_{s3} = \Delta(z_1+z_3+z_{12}+z_{14})/2$
	$x_{s4} = \Delta(x_5+x_9+x_{16}+x_{20})/2$
	$x_{s5} = \Delta(y_5+y_9-y_{16}-y_{20})/2$
	$x_{s6} = \Delta(z_5+z_9+z_{16}+z_{20})/2$
	$x_{s7} = \Delta(x_6+x_{10}+x_{17}+x_{21})/2$
	$x_{s8} = \Delta(y_6+y_{10}-y_{17}-y_{21})/2$
	$x_{s9} = \Delta(z_6+z_{10}+z_{17}+z_{21})/2$
	$x_{s10} = \Delta(x_7+x_8+x_{18}+x_{19})/2$
	$x_{s11} = \Delta(y_7+y_8-y_{18}-y_{19})/2$
	$x_{s12} = \Delta(z_7+z_8+z_{18}+z_{19})/2$
	$x_{s13} = \Delta(x_4+x_{11}+x_{15}+x_{22})/2$
	$x_{s14} = \Delta(y_4+y_{11}-y_{15}-y_{22})/2$
	$x_{s15} = \Delta(z_4+z_{11}+z_{15}+z_{22})/2$
	$x_{s16} = \Delta(x_2+x_{13})/\sqrt{2}$
	$x_{s17} = \Delta(z_2+z_{13})/\sqrt{2}$

* Underscripts in the left side of the equations represent coordinate numbers, while those in the right side represent atom (or ion) numbers.

Shimanouchi *et al.*[7] The optically-active cartesian symmetry coordinate vector, X_{op}, and the optically-active internal symmetry coordinate vector, R_{op}, are expressed as follows.

$$X_{\text{op}} = \lim\,(n_1n_2n_3)^{1/2}\sum_{i=0}^{n_1}\sum_{j=0}^{n_2}\sum_{k=0}^{n_3}(X_{\text{s}})^{i,j,k}_{\text{Bravais}}$$

$$n_1,\ n_2,\ n_3 \to \infty$$

$$R_{\text{op}} = \lim\,(n_1n_2n_3)^{1/2}\sum_{i=0}^{n_1}\sum_{j=0}^{n_2}\sum_{k=0}^{n_3}(R_{\text{s}})^{i,j,k}_{\text{Bravais}}$$

$$n_1,\ n_2,\ n_3 \to \infty$$

In these equations, $(X_s)^{ijk}_{\text{Bravais}}$ and $(R_s)^{ijk}_{\text{Bravais}}$, respectively, are the cartesian and internal symmetry coordinate vectors associated with the three-dimensional Bravais cell, (i,j,k). The components of the vectors are shown in Tables 1 and 2. The optically-active B matrix, B_{op}, is defined as: $R_{\text{op}}=B_{\text{op}}X_{\text{op}}$.

The optically-active F matrix, F_{op}, constructed from the diagonal matrix with respect to each Bravais cell, F_{000}, and the interaction matrices, F_{100}, F_{010}, F_{001}, *etc.*, are as follows.

$$F_{\text{op}} = F_{000} + F_{100} + \tilde{F}_{100} + F_{010} + \tilde{F}_{010} + F_{001} + \tilde{F}_{001} + \cdots$$

The lattice vibration frequencies were calculated by the secular equation, $|M^{-1}F_{\text{xs}}-\lambda E|=0$. In this equation, M is the diagonal matrix constructed from the masses of the atoms and ions, and $F_{\text{xs}}=\tilde{B}_{\text{op}}F_{\text{op}}B_{\text{op}}$.

The following potential was assumed:

$$V = V_{\text{C}_2\text{O}_4}^{2-} + V_{\text{H}_2\text{O}} + V_{\text{Inter}}$$

$V_{\text{C}_2\text{O}_4{}^{2-}}$ and $V_{\text{H}_2\text{O}}$ represent the Urey-Bradley force fields associated with $C_2O_4{}^{2-}$ and H_2O respectively, and V_{Inter} is the interaction potential of H_2O, $C_2O_4{}^{2-}$, and K^+. In the case of deuterated potassium oxalate monohydrate, the same potential function

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[7] T. Shimanouchi, M. Tsuboi and T. Miyazawa, *J. Chem. Phys.*, **35**, 1597 (1961).

TABLE 2. INTERNAL SYMMETRY COORDINATES (ELEMENT OF THE VECTOR, $(\mathrm{R_S})^{\mathrm{i,j,k}}_{\mathrm{Bravais}}$) *

$\mathrm{A_g}$ $\varDelta R_{si} = \varDelta(R_i^{\mathrm{I}}+R_i^{\mathrm{II}}+R_i^{\mathrm{III}}+R_i^{\mathrm{IV}})/2$

$i = 1$ to 36 excluding 5, 28, 34, 35

$\varDelta(R_i^{\mathrm{I}}+R_i^{\mathrm{III}})/\sqrt{2}$

$i = 5, 28, 34$

$\mathrm{A_u}$ $\varDelta R_{si} = \varDelta(R_i^{\mathrm{I}}-R_i^{\mathrm{II}}-R_i^{\mathrm{III}}+R_i^{\mathrm{IV}})/2$

$i = 1$ to 36 excluding 5, 28, 34, 35

$\varDelta(R_i^{\mathrm{I}}-R_i^{\mathrm{III}})/\sqrt{2}$

$i = 28, 34, 35$

B_{g} $\varDelta R_{si} = \varDelta(R_i^{\mathrm{I}}+R_i^{\mathrm{II}}-R_i^{\mathrm{III}}-R_i^{\mathrm{IV}})/2$

$i = 1$ to 36 excluding 5, 28, 34, 35

$\varDelta(R_i^{\mathrm{I}}-R_i^{\mathrm{III}})/\sqrt{2}$

$i = 5, 28, 34$

$\mathrm{B_u}$ $\varDelta R_{si} = \varDelta(R_i^{\mathrm{I}}-R_i^{\mathrm{II}}+R_i^{\mathrm{III}}-R_i^{\mathrm{IV}})/2$

$i = 1$ to 36 excluding 5, 28, 34, 35

$\varDelta(R_i^{\mathrm{I}}+R_i^{\mathrm{III}})/\sqrt{2}$

$i = 28, 34, 35$

$\varDelta R_{28}^{\mathrm{I}} = \varDelta\alpha_{\ 1\ (i,j,k)\ 2\ (i,j,k)\ 3\ (i,j,k)}$

$\varDelta R_{29}^{\mathrm{I}} = \varDelta\alpha_{\ 5\ (i,j,k)\ 7\ (i,j,k)\ 6\ (i,j,k)}$

$\varDelta R_{30}^{\mathrm{I}} = \varDelta\alpha_{\ 5\ (i,j,k)\ 7\ (i,j,k)\ 8\ (i,j,k)}$

$\varDelta R_{31}^{\mathrm{I}} = \varDelta\alpha_{\ 6\ (i,j,k)\ 7\ (i,j,k)\ 8\ (i,j,k)}$

$\varDelta R_{32}^{\mathrm{I}} = \varDelta\alpha_{\ 1\ (i,j,k)\ 2\ (i,j,k)\ 4\ (i,j,k)}$

$\varDelta R_{33}^{\mathrm{I}} = \varDelta\alpha_{\ 1\ (i,j,k)\ 2\ (i,j,k)\ 22\ (i,j,k+1)}$

$\varDelta R_{34}^{\mathrm{I}} = \varDelta\alpha_{\ 4\ (i,j,k)\ 2\ (i,j,k)\ 22\ (i,j,k+1)}$

$\varDelta R_{35}^{\mathrm{I}} = \varDelta t\ (7\text{–}8)$ (internal rotation angle coordinate around the bond, 7–8)

$\varDelta R_{36}^{\mathrm{I}} = \varDelta\pi(7\text{–}568)$ (out- of -plane bending coordinate regarding the plane formed by atoms, 5,6,7 and 8)

$\varDelta R_i^{\mathrm{II}} = \mathbf{i}\ (\varDelta R_i^{\mathrm{I}}),\ \varDelta R_i^{\mathrm{III}} = \boldsymbol{\sigma}\ (\varDelta R_i^{\mathrm{I}}),\ \varDelta R_i^{\mathrm{IV}} = \mathbf{C}_2\ (\varDelta R_i^{\mathrm{I}})$

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* In this table, $\varDelta R_i^{\mathrm{I}}$'s for $i=1$ through 27 correspond to R_{i}'s in Table 3. The symbols, **i**, $\boldsymbol{\sigma}$ and $\mathbf{C}_2$ represent symmetry operations associated with inversion, glide plane and 2-fold axis, respectively.

was assumed:

$$
\begin{aligned}
2V_{\mathrm{inter}} = {} & \sum_i f_i(\mathrm{O\cdots H})(\varDelta q_i(\mathrm{O\cdots H}))^2 \\
& + \sum_i f_i(\mathrm{O\cdots K^+})(\varDelta q_i(\mathrm{O\cdots K^+}))^2 \\
& + \sum_i f_i(\mathrm{O\cdots O})(\varDelta q_i(\mathrm{O\cdots O}))^2 \\
& + \sum_i H_i(\mathrm{H\text{-}O\cdots K^+})\, r^i_{\mathrm{O-H}}\, r^i_{\mathrm{O\cdots K^+}} (\varDelta\alpha^i_{\mathrm{H-O\cdots K^+}})^2 \\
& + \sum_{(i,j)} 2a(\varDelta\alpha^i_{\mathrm{H-O\cdots K^+}})(\varDelta\alpha^j_{\mathrm{H-O\cdots K^+}}) \\
& + \sum_{(k,l)} 2b(\varDelta\alpha^k_{\mathrm{H-O\cdots K^+}})(\varDelta\alpha^l_{\mathrm{H-O\cdots K^+}})
\end{aligned}
$$

TABLE 3. ATOM-ATOM AND ATOM-ION INTERACTIONS *

	Atom or ion number		Atom-atom (atom-ion) distance (Å)
R_1	$2(i,j,k)$	$3(i,j,k)$	0.962 (O-H)
R_2	$3(i,j,k)$	$5(i,j,k)$	1.792 (H···O)
R_3	$5(i,j,k)$	$7(i,j,k)$	1.273 (C-O)
R_4	$6(i,j,k)$	$7(i,j,k)$	1.234 (C-O)
R_5	$7(i,j,k)$	$8(i,j,k)$	1.555 (C-C)
R_6	$2(i,j,k)$	$4(i,j,k)$	2.933 (O···K⁺)
R_7	$4(i,j,k)$	$5(i,j,k)$	2.762 (O···K⁺)
R_8	$4(i,j,k)$	$6(i,j,k)$	2.849 (O···K⁺)
R_9	$5(i,j,k)$	$4(i+1,j-1,k)$	3.486 (O···K⁺)
R_{10}	$6(i,j,k)$	$10(i-1,j+1,k)$	3.789 (O···O)
R_{11}	$6(i,j,k)$	$11(i-1,j+1,k)$	2.813 (O···K⁺)
R_{12}	$2(i,j,k)$	$5(i,j+1,k)$	3.699 (O···O)
R_{13}	$2(i,j,k)$	$10(i,j+1,k)$	3.792 (O···O)
R_{14}	$4(i,j,k)$	$9(i,j+1,k)$	2.795 (O···K⁺)
R_{15}	$2(i,j,k)$	$6(i+1,j,k)$	3.687 (O···O)
R_{16}	$5(i,j,k)$	$6(i+1,j,k)$	3.338 (O···O)
R_{17}	$5(i,j,k)$	$9(i+1,j,k)$	4.149 (O···O)
R_{18}	$6(i,j,k)$	$10(i\text{-}1,j,k)$	4.445 (O···O)
R_{19}	$2(i,j,k)$	$4(i+1,j,k)$	3.304 (O···K⁺)
R_{20}	$2(i,j,k)$	$6(i,j+1,k)$	3.592 (O···O)
R_{21}	$4(i,j,k)$	$6(i,j+1,k)$	2.966 (O···K⁺)
R_{22}	$4(i,j,k)$	$10(i+1,j+1,k)$	2.813 (O···K⁺)
R_{23}	$4(i,j,k)$	$20(i-1,j,k+1)$	3.025 (O···K⁺)
R_{24}	$4(i,j,k)$	$21(i-1,j,k+1)$	2.988 (O···K⁺)
$R_{25} =$	$5(i,j,k)$	$6(i+1,j,k)$	3.338 (O···O)
$R_{26} =$	$5(i,j,k)$	$9(i,j+1,k)$	3.721 (O···O)
$R_{27} =$	$5(i,j,k)$	$10(i,j+1,k)$	4.138 (O···O)

* In this table $m(i,j,k)$ represents atom or ion, m, in the Bravais cell, (i,j,k). Regarding atom or ion number, m, refer to Fig. 1.

TABLE 4. RESULT OF FACTOR GROUP ANALYSIS

	$\mathrm{K_2C_2O_4\cdot H_2O}$ (C^6_{2h}) or $\mathrm{K_2C_2O_4\ D_2O}$ (C^6_{2h})				
	N	T	T'	R'	n
$\mathrm{A_g}$	16	0	4	4	8
$\mathrm{A_u}$	16	1	6	1	8
$\mathrm{B_g}$	17	0	5	5	7
$\mathrm{B_u}$	17	2	6	2	7

N; number of the total freedom,
T; number of the translations,
T'; number of the translational lattice vibrations,
R′; number of the rotational lattice vibrations,
n; number of intramolecular vibrations of $\mathrm{C_2O_4}^{2-}$ and $\mathrm{H_2O}$ (or$\mathrm{D_2O}$).

In the above potential, only those interactions between atoms and ions with an atom-ion or atom–atom distance of less than 4.5 Å were taken into account. The atom-ion and atom–atom distances are shown in Table 3. The force constant, a, is the interaction force constant between two bond angles, $\alpha^{\mathrm{i}}_{\mathrm{H-O\cdots K^+}}$ and $\alpha^{\mathrm{j}}_{\mathrm{H-O\cdots K^+}}$, which share a H–O bond, and the force constant, b, is the interaction force constant between two bond angles, $\alpha^{\mathrm{k}}_{\mathrm{H-O\cdots K^+}}$ and $\alpha^{\mathrm{l}}_{\mathrm{H-O\cdots K^+}}$, which share a O···K⁺ bond.

I also treated the optically-active lattice vibrations of A_g, A_u, B_g, and B_u species of potassium oxalate monohydrate and deuterated potassium oxalate monohydrate shown in Table 4. Based on the observed frequencies⁶⁾ of IR active vibrations (A_u and B_u species), the force constants marked

TABLE 5. FORCE CONSTANTS (in mdyn/Å)**

	Set I	Set II
K(O-H)*	5.640	5.839
K(O···H)*	0.150	0.122
K(C-O)*	7.200	7.500
K(C-C)	2.500	2.500
f (O···K$^+$)	$f=10.803\exp(-1.413r)(1.413-(2/r))$	
f (O···O)	$\ln f=7.070-2.820r$	
H(H-O-H)*	0.640	0.568
H(O-C-O)*	0.150	0.100
H(O-C-C)*	0.150	0.300
F(H-O-H)*	−0.100	−0.258
F(O-C-O)*	3.000	2.500
F (O-C-C)*	0.500	0.850
t (C-C)	0.250	0.250 mdyn.Å
H^1(H-O···K$^+$)*	0.040	0.125
H^2(H-O···K$^+$)*	0.040	0.102
H (K^+ ···O···K$^+$)*	0.000	0.026
F^1(H-O···K$^+$)	0.000	0.000
F^2(H-O···K$^+$)*	0.000	0.010
F(K$^+$···O···K$^+$)	0.000	0.000
a*	0.000	0.110 mdyn. Å
b*	0.000	−0.180 mdyn. Å

** H^1, F^1 relate to $\Delta R^{\mathrm{I}}_{32}$ in Table 2, while H^2, F^2 relate to $\Delta R^{\mathrm{I}}_{33}$ in the table.

with * in Table 5 were adjusted by the method of least squares.[8] The numerical computations were carried out by making use of the Computation Center, Tokyo University, and the programs, BGLZ and LSMB, set up at the Shimanouchi Laboratory, Department of Chemistry, Faculty of Science, University of Tokyo, and also a program made by the author. The force constants, Set I, in Table 5 were obtained by the following equations. The O···O force constant, f_i (O···O), was assumed to be $f_i=A\cdot\exp(-Br)$, and the parameters, A and B, were determined by the method of least squares, using seven values of the O···O force constant (5.14 mdyn/Å, 3.02 mdyn/Å, 3.03 mdyn/Å, 1.74 mdyn/Å, 1.05 mdyn/Å, 0.76 mdyn/Å, and 0.555 mdyn/Å, corresponding to the interatomic distances of 2.09 Å, 2.20 Å, 2.21 Å, 2.27 Å, 2.36 Å, 2.47 Å, and 2.48 Å),[9] while the K$^+$···O force constant, f_i(K$^+$—O), was assumed to be $f_i=C\cdot\exp(-Dr)$ $(D-(2/r))$ and the C and D parameters were determined using two values of the K$^+$···O force constant (0.11 mdyn/Å and 0.14 mdyn/Å, corresponding to the atom-ion distances of 3.05 Å and 2.83 Å).[10] In the above equations, represents the atom-atom or atom-ion distance.

Here, the expressions of the force constants, f_i(O···O) and f_i(K$^+$···O), were obtained from the second derivatives of an assumed repulsive potential, $a\cdot\exp(-br)$, and an electrostatic attractive potential, c/r. The potential for K$^+$···O was assumed to be $a\cdot\exp(-br)+(c/r)$, and the first derivative of the potential was set at zero, while the potential for O···O was assumed to be $a\cdot\exp(-br)$. The other force constants were transfered from related compounds. In Table 5, the force constants, Set II, are the force constants obtained by the method of least squares,[8] which gives the calculated frequencies shown in Tables 6, 7, 8 and 9.

Discussion

I. Assignment of IR Bands. Tables 6, 7, 8, and 9 show the significant terms of potential

TABLE 6. CALCULATED FREQUENCIES (in cm^{-1}) AND SIGNIFICANT TERMS OF POTENTIAL ENERGY DISTRIBUTIONS (A_u species)

$K_2C_2O_4$ H_2O

ν_{obs}	ν_{calc}	Significant terms of p.e.d.
3200	3154	$R_1(97)$
1608	1638	$R_{28}(61)$, $R_{33}(19)$, $R_{32}(17)$
1580	1598	$R_3(65)$, $R_4(63)$
1303	1356	$R_4(47)$, $R_3(43)$
758	762	$R_{29}(71)$, $R_{31}(17)$
	520	$R_{32}(80)$, $R_{33}(15)$
524	518	$R_{36}(95)$
	309	$R_{31}(35)$, $R_{30}(29)$
	232	$R_{35}(34)$
210	224	$R_6(56)$, $R_2(11)$, $R_{20}(10)$
190	175	$R_9(32)$, $R_8(17)$, $R_7(11)$
	141	$R_{11}(20)$, $R_{14}(18)$, $R_{23}(13)$, $R_8(12)$
115	135	$R_{14}(29)$, $R_{23}(21)$, $R_{24}(14)$
92	95	$R_{23}(22)$, $R_{21}(12)$, $R_{11}(12)$
	79	$R_2(24)$, $R_6(17)$, $R_{22}(16)$

$K_2C_2O_4$ D_2O

ν_{obs}	ν_{calc}	Significant terms of p.e.d.
	2286	$R_1(96)$
1595	1598	$R_3(65)$, $R_4(63)$
1305	1356	$R_4(47)$, $R_3(43)$
1225	1192	$R_{28}(61)$, $R_{33}(19)$, $R_{32}(17)$
760	762	$R_{29}(71)$,$R_{31}(17)$
505	518	$R_{36}(96)$
358	371	$R_{32}(79)$, $R_{33}(16)$
	309	$R_{31}(35)$,$R_{30}(29)$
	232	$R_{35}(34)$
215	215	$R_6(55)$, $R_2(10)$
165	174	$R_9(31)$,$R_8(17)$, $R_7(11)$
	141	$R_{11}(19)$, $R_{14}(18)$,$R_{23}(13)$,$R_8(11)$
125	135	$R_{14}(28)$,$R_{23}(21)$,$R_{24}(14)$
93	94	$R_{23}(22)$,$R_{21}(12)$,$R_{11}(11)$
	78	$R_2(24)$,$R_{22}(16)$,$R_6(16)$

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TABLE 7. CALCULATED FREQUENCIES (in cm^{-1}) SIGNIFICANT TERMS OF POTENTIAL ENERGY DISTRIBUTIONS (B_u species)

$K_2C_2O_4$ H_2O

ν_{obs}	ν_{calc}	Significant terms of p. e. d.
3370	3296	$R_1(98)$
1608	1600	$R_3(64),R_4(64)$
1303	1361	$R_3(45),R_4(45)$
758	789	$R_{29}(65),R_{31}(15)$, $R_{30}(14)$
718	691	$R_{32}(133)$
614	601	$R_{33}(151)$, $R_{32}(28)$
524	518	$R_{36}(96)$
351	351	$R_{30}(37),R_{31}(33)$
	232	$R_{35}(32),R_{22}(13),R_{11}(13),R_{24}(13)$
210	208	$R_2(32),R_6(31),R_{19}(14)$
190	199	$R_{23}(25),R_{14}(22)$
160	164	$R_8(28),R_{21}(22),R_{19}(12)$
129	144	$R_9(21),R_2(20),R_{14}(17)$
115	103	$R_{19}(48),R_{20}(22)$
56	56	$R_2(21),R_6(20),R_{24}(19),R_{20}(12)$

$K_2C_2O_4 \cdot D_2O$

ν_{obs}	ν_{calc}	Significant terms of p.e.d.
2460	2417	$R_1(98)$
1595	1600	$R_3(64),R_4(64)$
1305	1361	$R_3(45)$, $R_4(45)$
760	789	$R_{29}(65),R_{31}(15),R_{30}(14)$
	530	$R_{32}(119)$
505	518	$R_{36}(96)$
432	443	$R_{33}(154),R_{32}(40)$
358	351	$R_{30}(37),R_{31}(34)$
215	232	$R_{35}(32)$, $R_{22}(13)$, $R_{11}(13),R_{24}$ (13)
	201	$R_6(22),R_9(17),R_2(14)$
195	197	$R_2(20),R_{14}(17)$, $R_{23}(17)$
165	162	$R_8(24),R_{21}(22),R_{19}(14),R_6(11)$
…	142	$R_9(22),R_2(21),R_{14}(18),R_7(10)$
93	96	$R_{19}(50),R_{20}(22)$
54	56	$R_2(21),R_6(20),R_{24}(19),R_{20}(12)$

energy distributions. From the terms, it is clear that the calculated frequencies, 691 cm^{-1} and 601 cm^{-1} (B_u species), are related to the R_{32} and R_{33} coordinates. Therefore, they are due to the rotational lattice vibrations of the water of crystallization and correspond to the bands at 718 cm^{-1} and 614 cm^{-1}. The vibration having the calculated frequency 520 cm^{-1} (A_u species) is also due to another lattice vibration associated with the water of crystallization, as the significant terms of the potential energy distributions show.

In the region below 250 cm^{-1}, it is interesting that the calculated frequencies correspond well with the observed frequencies despite the fact that the assumed potentials of $a \cdot \exp(-br)$ and $a \cdot \exp(-br)+(c/r)$ were used for the O···O and K^+···O interactions respectively.

TABLE 8. CALCULATED FREQUENCIES (in cm^{-1}) AND SIGNIFICANT TERMS OF POTENTIAL ENERGY DISTRIBUTIONS (A_g species)

$K_2C_2O_4$ H_2O

ν_{obs}	ν_{calc}	Significant terms of p.e.d.
	3154	$R_1(97)$
	1701	$R_4(56),R_3(55),R_{30}(13),R_{31}(12)$
	1638	$R_{28}(61),R_{33}(19),R_{32}(17)$
	1408	$R_5(47),R_3(39),R_4(38),R_{29}(12)$
	992	$R_5(48),R_{29}(22)$
	805	$R_{36}(99)$
	575	$R_{30}(38),R_{31}(37)$
	520	$R_{32}(80),R_{33}(15)$
	484	$R_{29}(39),R_5(16)$
	232	$R_{11}(22),R_{22}(22),R_{24}(18),R_6(11)$
	207	$R_{14}(22),R_9(21),R_{26}(18),R_{23}(16)$
	179	$R_6(31)$
	166	$R_{21}(27),R_8(21),R_9(13),R_{14}(11)$
	131	$R_9(21)$
	87	$R_{26}(25),R_{20}(19),R_{19}(17),R_{24}(10)$
	57	$R_6(21),R_{20}(21),R_{26}(14),R_{27}(12)$

$K_2C_2O_4 \cdot D_2O$

ν_{obs}	ν_{calc}	Significant terms of p.e.d.
	2286	$R_1(96)$
	1701	$R_4(56),R_3(55),R_{30}(13),R_{31}(12)$
	1408	$R_5(47),R_3(39),R_4(38),R_{29}(12)$
	1192	$R_{28}(61),R_{33}(19)R_{32}(17)$
	992	$R_5(48),R_{29}(22)$
	805	$R_{36}(99)$
	575	$R_{30}(38),R_{31}(37)$
	485	$R_{29}(39),R_5(16)$
	371	$R_{32}(80),R_{33}(16)$
	230	$R_{11}(23),R_{22}(23),R_{24}(19)$
	206	$R_{14}(23),R_9(21),R_{26}(19),R_{23}(18)$
	174	$R_6(33)$
	166	$R_{21}(29),R_8(22),R_9(12)$
	130	$R_9(20)$
	86	$R_{26}(24),R_{20}(20),R_{19}(17)$
	57	$R_6(21),R_{20}(21),R_{26}(14),R_{27}(12)$

II. Bound State of the Water of Crystallization. The potassium oxalate monohydrate crystal contains one kind of water of crystallization molecule. Each oxygen atom in the water of crystallization molecule is on the symmetry element, the 2-fold axis, of the Bravais cell of the crystal, and it is accompanied by two nearest neighbor potassium ions at a distance of 2.93 Å. Each water of crystallization molecule is bound to the oxygen atoms of $C_2O_4^{2-}$'s by hydrogen bonds. If we assume sp^3 orbitals for the oxygen atom of the water of crystallization molecule, as in the case of ice, the orbitals of the lone-pairs do not point to the potassium ions; therefore, we can not expect a simple σ-bond for O···K^+. In order to obtain information about the bound state of the water of crystallization molecule, the force constants of rotation about the principal axes of the moment of inertia, *A*, *B* and

TABLE 9. CALCULATED FREQUENCIES (in cm^{-1}) AND SIGNIFICANT TERMS OF POTENTIAL ENERGY DISTRIBUTIONS (B_g species)

$K_2C_2O_4H_2O$			$K_2C_2O_4D_2O$		
ν_{obs}	ν_{calc}	Significant terms of p.e.d.	ν_{obs}	ν_{calc}	Significant terms of p.e.d.
	3296	$R_1(98)$		2417	$R_1(98)$
	1701	$R_4(56),R_3(55),R_{30}(13),R_{31}(12)$		1701	$R_4(56),R_3(55),R_{30}(13),R_{31}(12)$
	1408	$R_5(47),R_3(39),R_4(38),R_{29}(12)$		1408	$R_5(47),R_3(39),R_4(38),R_{29}(12)$
	992	$R_5(48),R_{29}(22)$		992	$R_5(48),R_{29}(22)$
	805	$R_{36}(99)$		805	$R_{36}(99)$
	691	$R_{32}(133)$		575	$R_{30}(38),R_{31}(37)$
	602	$R_{33}(149),R_{32}(28)$		530	$R_{32}(119)$
	575	$R_{30}(38),R_{31}(37)$		484	$R_{29}(39),R_5(16)$
	484	$R_{29}(39),R_5(16)$		443	$R_{33}(154),R_{32}(40)$
	217	$R_6(20),R_{11}(13),R_{22}(13)$		214	$R_{11}(19),R_{22}(19),R_6(12)$
	201	$R_{11}(19),R_{22}(19),R_2(18)$		198	$R_9(18),R_2(14),R_{11}(13),R_{22}(13)$
	188	$R_{23}(18),R_{26}(17),R_9(14),R_{14}(12)$		185	$R_{23}(19),R_2(14),R_{21}(12),R_{14}(10)$
	165	$R_{21}(30),R_8(21)$		164	$R_{21}(25),R_8(18),R_6(13)$
	144	$R_{14}(37),R_{24}(26),R_{19}(14)$		143	$R_{14}(37),R_{24}(27),R_{19}(11)$
	112	$R_{19}(31),R_{20}(19),R_2(19),R_{24}(18)$		107	$R_{24}(23),R_{19}(19),R_{20}(14)$
	105	$R_9(20),R_7(14),R_{26}(12),R_8(12),R_{23}(11),R_2(11)$		104	$R_2(28),R_9(15),R_{19}(12)$
	67	$R_{14}(26),R_{24}(21),R_{19}(14),R_{23}(12),R_6(12)$		65	$R_{14}(25),R_{24}(20),R_{19}(17),R_6(12),R_{23}(12)$

C, of the molecule were calculated.

Expressing the angle of rotation around the principal axis, *m*, and the force constant by $\Delta\theta_m$ and k_m respectively, we obtain the following equation:

$$k_m(\Delta\theta_m)^2 = \sum_n \tilde{\rho}_{mn}\tilde{B}FB\rho_{mn}$$

Here, ρ_{mn} represents the displacement of the atom, *n*, caused by the rotation around the axis, *m*, having an angle of rotation, $\Delta\theta_m$. B is the matrix transforming the displacements of the atoms in the water of crystallization molecule to the coordinates which change by the displacements, and *F* is the potential energy matrix having the coordinates as its bases. ρ_{mn} is expressed by the equation: $\rho_{mn}=e_m\times r_n\cdot\Delta\theta_m$. The vector, e_m, is a unit vector parallel to the principal axis, *m*, and r_n is a vector from the center of gravity of water molecule to the atom, *n*. The values of the k_m's obtained by the use of the force constants in Table 5 are as follows:

$$k_A=0.081 \text{ mdyn}\cdot\text{Å},\ k_B=0.237 \text{ mdyn}\cdot\text{Å},\ k_C=1.886 \text{ mdyn}\cdot\text{Å}$$

From these values, it can be concluded that the water of crystallization molecule is more strongly bound around the C axis than around the *A* and *B* axes. The contributions of the hydrogen bonds to k_A, k_B, and k_C were calculated to be 0.001 mdyn·Å, 0.002 mdyn·Å, and 0.002 mdyn·Å respectively. As the O···K⁺ interactions make as little contributions to the k_m's as the H···O interactions, most contributions to the k_m's are considered to arise from the interaction between the nearest neighbor potassium ions and the lone-pair electrons of the water of crystallization molecule. Each of the potassium ions is on the side of the plane passing the oxygen atom of the water of crystallization molecule and perpendicular to H–O–H plane at the same distance, 2.02 Å, from the plane. The relatively small values of k_A suggest that the rotation around the axis, *A*, does not seriously change the degree of the interaction between the potassium ions and the lone-pair electrons; the small change in the degree of the interaction may be realized when we note that the lone-pair orbitals extend along the above-mentioned plane separating the two potassium ions. The large values of k_B and k_C also suggest this type of extension of the orbitals.

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