The Optically-active Vibration and Elastic Constant of Soda-niter[1]

Akio YAMAMOTO, Yuji SHIRO,* and Hiromu MURATA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730

**Shinonome Branch School, Faculty of Education, Hiroshima University, Shinonome-3-chome, Hiroshima 734*

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A force field which reproduces satisfactorily both the observed vibrational frequencies and the elastic constants has been determined for the sodium nitrate crystal using the short-range interaction model. In addition to the short-range interactions, the long-range interactions of the vibrationally-induced dipoles were also taken into consideration on the basis of the rigid-ion model; those effective charges which explain fairly well the observed TO–LO frequency splittings were obtained. The distribution of the effective charges on each atom was examined; the best set of effective charges has been found to be $Z_{Na}=0.87\ e$, $Z_N=0.17\ e$, and $Z_O=-0.35\ e$.

The crystal vibration of soda-niter ($NaNO_3$)[2] has been extensively studied in connection with that of the isomorphic crystals having the calcite structure. However, previous investigations[2] have dealt almost exclusively with the short-range interaction model, and little attention has been paid to long-range Coulomb interactions. In the present paper, we wish to call further attention to the effect of the charge distribution on the TO–LO frequency splittings.

First, the short-range interactions are taken into consideration, and the force constants are refined so as to reproduce both the observed vibrational frequencies[2] and the elastic constants.[3] Secondly, a detailed normal coordinate treatment is performed for the optically-active crystal vibration on the basis of the rigid-ion model.[4] The basic formulation of this model was mainly established by Born and his co-workers.[4] As is implied by the name, the interactions of vibrationally-induced dipoles are taken into account as those of rigid point dipoles; any influence of the electronic polarizability of the constituent atoms is implicitly neglected. This model was first applied to the vibrational analysis of relatively simple crystals, such as alkali-halide crystals.[5] The assumptions implicit in this model are, however, considered to be untolerably drastic in a sense; as a consequence, the reproducibility of the frequency dispersion relations, in particular, is found to be poor.[6] For rather complicated crystals, even rigid-ion analyses have been scarcely performed yet because of the long and tedious procedures required, together with the experimental limitations. In the course of a survey of the vibrational properties of complex crystals,[7] in the present study the rigid-ion model is applied to the normal coordinate analysis of the optically-active vibration (wave vector $\boldsymbol{y}=\mathbf{0}$), regarding all the atoms as ionizable.

Method of Calculation

Crystal Structure. Sodium nitrate crystallizes in the calcite structure. As is shown in Fig. 1, this structure is most easily visualized as a sodium chloride lattice distorted by the introduction of the disk-shaped nitrate groups. Although the calcite structure is also considered to be a hexagonal lattice, the primitive unit cell is trigonal and contains two formula units of $NaNO_3$. The space group of the trigonal cell is D_{3d}^6—$R\bar{3}c$, and the cell constants[8] are found to be $a_{rh}=6.3247$ Å and $\alpha=47°16'$. Each sodium atom is coordinated with six oxygen atoms of different nitrate groups, and each such oxygen atom is bound to two sodium atoms.

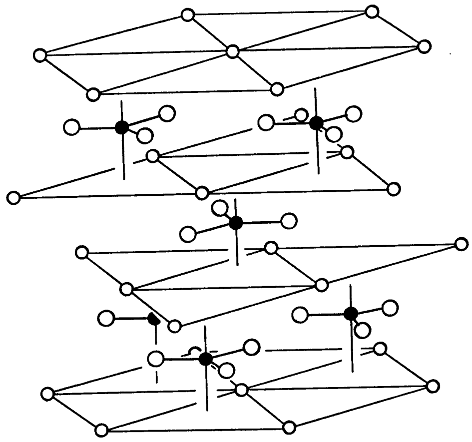

Fig. 1. Crystal structure of soda-niter. ○, Sodium; ●, Nitrogen; ○, Oxygen.

Normal Coordinate Treatments. In the present study, the normal coordinate treatments were performed in two steps, those based on the short-range interaction model and on the rigid-ion model.

Short-range Interaction Model: The application of Wilson's *GF*-matrix method to the analysis of the optically-active crystal vibration was previously reported by Shimanouchi *et al.*[9] In this study, the modified Urey-Bradley force field[10] was applied to the intramolecular vibrations of the nitrate groups, the correction terms of which were the bond interaction term, *p*, for the adjacent N–O bond pairs and the angle interaction term, *n*, for the adjacent O–N–O angle pairs in a single nitrate group. On the other hand, the central force field was used for the intermolecular (lattice) vibrations. With respect to the latter, only the pairs that lie within 3.5 Å were taken into consideration as effective short-range interatomic interactions. As Fig. 2 illustrates, there are six different kinds of pairs in this crystal. The corresponding interatomic distances are listed in Table 1. The dynamical matrix due to these short-range interactions will be designated as $\boldsymbol{D}^s$ hereafter.

Rigid-ion Model: In addition to the short-range interactions mentioned above, the long-range Coulomb interactions of vibrationally-induced dipoles are taken

Table 1. Force constants (mdyn/Å) and effective charges (electron unit) of soda-niter

FC	Coord.	NO	Pair	Dist.[a]	I $Z=0$	II $x=-1$	III $x=-1/2$	IV $x=-1/5$	V $x=0$	VI $x=+1/5$	VII $x=+1/2$	VIII $x=+3/4$
K	R	6	N O	1.2175	5.656	5.572	5.457	5.450	5.544	5.680	5.863	5.696
H[b]	θ	6	O N O	(120°)	0.581							
F[b]			O O		1.645							
α	ϕ	2	NO_3		0.485	0.492	0.513	0.509	0.493	0.469	0.438	0.428
p					−0.036	0.068	0.037	0.027	0.018	0.017	0.039	0.060
n[c]					0.145	0.107	0.110	0.107	0.130	0.150	0.170	0.184
f_1	q_1	12	Na N	3.2458	0.055	0.043	0.029	0.025	0.023	0.016	0.022	0.019
f_2	q_2	12	Na O	2.4178	0.118	0.162	0.188	0.172	0.191	0.211	0.210	0.204
f_3	q_3	12	Na O	3.4258	0.000[b]	0.000[b]	0.000[b]	0.006	0.008	0.007	0.007	0.005
f_4	q_4	6	O O	3.1638	0.054	0.026	0.028	0.076	0.068	0.052	0.036	0.030
f_5	q_5	12	O O	3.4116	0.050	0.003	0.014	0.014	0.004	−0.012	−0.033	−0.040
f_6	q_6	12	O O	3.4258	0.036	0.025	0.031	0.019	0.007	−0.008	−0.027	−0.031
Z_{Na}		2				0.77	0.74	0.86	0.90	0.87	0.74	0.62
Z_N		2				−0.77	−0.37	−0.17	0.00	0.17	0.37	0.46
Z_O		6				0.00	−0.12	−0.23	−0.30	−0.35	−0.37	−0.36

a) Unit of distance is Å. b) Fixed force constants. c) Unit of n is mdyn·Å.

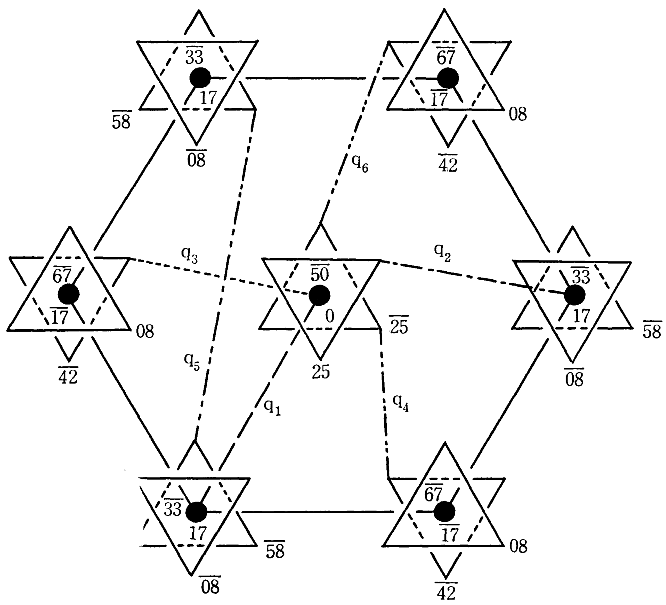

Fig. 2. Short-range interactions in soda-niter, projected on a plane perpendicular to the z axis of the hexagonal cell. The heights of atoms or nitrate groups are expressed in units of $100/c_0$.
(——), Na···N; (······), N···O; (—·—), Na···O; (—··—), O···O.

into account in this model. The additional interactions are considered to play an important role, especially in predominantly ionic crystals, and the frequency splitting between LO- and TO-frequencies is brought about through the interactions.[4]

According to Born and Huang,[4] the Coulomb part, $\boldsymbol{D}^c$, in the dynamical matrix near the Γ point is given by:

$$\begin{aligned}D^c_{ij}(k, k'; \boldsymbol{y}\rightarrow\boldsymbol{0}) = Z_k e^2(m_k m_{k'})^{-1/2}\{&4\pi v^{-1} \lim_{y\rightarrow 0} (y_i y_j/|\boldsymbol{y}|^2)\\ &- Z_{k'}Q_{ij}(k, k'; \boldsymbol{y}\rightarrow\boldsymbol{0})\\ &+ \delta_{kk'}\sum(k'')Z_{k''}Q_{ij}(k, k''; \boldsymbol{y}\rightarrow\boldsymbol{0})\},\end{aligned}$$

where **y** is the wave vector; Z_k, the effective charge of the k-th atom in terms of electronic charge, e; m_k, the mass of the k-th atom, and v, the unit cell volume. The $Q_{ij}(k, k')$ is a tensor of the second rank for the wave vector zero; it is most easily visualized as the tensor representing the gradient of the Coulomb field at the k site, which is spanned by the point dipoles at the k' site over the trigonal lattice. The numerical evaluation of the tensor elements can be carried out straight-forwardly by the Ewald method.[11] The summations were performed with the PEG0 computer program.[12] The values are constant for a fixed wave vector in the same lattice; therefore, it is sufficient to calculate the sums once for each crystal.

The overall dynamical matrix of the model is now obtained by superposing the Coulomb part, $\boldsymbol{D}^c$, on the short-range part, $\boldsymbol{D}^s$, *viz.*:

$$\boldsymbol{D} = \boldsymbol{D}^s + \boldsymbol{D}^c.$$

Since this crystal contains nitrate groups, there is another serious problem to be elucidated: the distribution of the effective charges on the groups cannot be known in advance. As is shown in Fig. 3, we have inevitably assumed several trial sets of charge distribution under electrically neutral conditions in the whole crystal. In this figure, x stands for the distribution parameter and Z denotes the magnitude of the effective

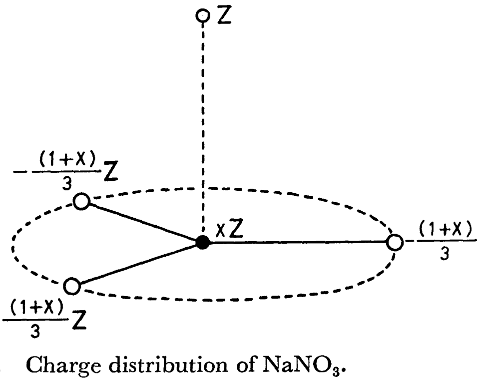

Fig. 3. Charge distribution of $NaNO_3$.
○, Oxygen; ○, Sodium; ●, Nitrogen;
z, magnitude of effective charge in terms of electronic charge e; x, distribution parameter.

charges. Supposing this distribution model, the distribution parameter, x, and the magnitude, Z, enter as independent parameters to be adjusted appropriately. Varying the parameter, x, little by little, both the magnitude, Z, and the short-range force constants were refined in order to obtain the best fit between the observed[2)] and calculated frequencies, both ν_t and ν_l, by the least-squares method.[13)]

If group theoretical analysis is performed on the basis of the crystal symmetry, much useful information can be obtained beforehand for the vibrational analysis. Generally, one must make the "k-group analysis" [14)] based on the symmetry of the wave vector. In the case of the vibration near the center of the Brillouin zone, however, the k-group analysis is reduced to the usual factor-group analysis.[2b)]

Refinement of Force Constants. As has been mentioned above, the Jacobians with respect to the frequency[13)] and to the elastic constant[15)] were obtained independently from the treatments of the short-range interaction model. Taking both Jacobians into consideration, the refinement of the short-range force constants was performed by the use of the following expression:

$$\Delta K = (\tilde{J}_h^{\nu} W_{\nu} J_h^{\nu} + \tilde{J}_h^{E} W_E J_h^{E})^{-1} \times (\tilde{J}_h^{\nu} W_{\nu} \Delta \boldsymbol{\nu} + \tilde{J}_h^{E} W_E \Delta \boldsymbol{E}),$$

where the suffixes ν and E attached to some matrices denote those which are related to the vibrational and the elastic properties respectively. The $\boldsymbol{W}$ matrices are the relative weight matrices of the observed vibrational frequencies or elastic constants. The $\Delta\boldsymbol{\nu}$ and $\Delta\boldsymbol{E}$ are the deviation column-matrices of the calculated eigenfrequencies and elastic constants respectively from their observed values.

In the case of the rigid-ion model, both the short-range force constants and the magnitude, Z, of the effective charges were adjusted with reference to the observed ν_t and ν_l values.

The actual calculation was carried out on a TOSBAC 3400 MODEL 41 electronic computer at the Computing Center of Hiroshima University.

Results and Discussion

Optically-active Vibration. According to the rigid-ion model, certain interactions are found to be brought about between the macroscopic field and the induced dipoles if any dipole moment is induced as a whole unit cell through the vibration of fictitious charged particles. Only the A_{2u} and E_u symmetric modes of the vibration are those which give rise to the polarization. Any vibrational frequencies, ν_l, of the longitudinal wave are higher than the corresponding frequencies, ν_t, of the transverse wave. The reason for the difference in the frequencies of the longitudinal and transverse waves is obvious: in a transverse wave, the

TABLE 2. DIPOLE LATTICE SUM, $Q_{ij}(k, k')$,[a)] OF SODA-NITER

	(1_x)	(1_y)	(1_z)	(2_x)	(2_y)	(2_z)	(3_x)	(3_y)	(3_z)
(1_x)	0.0427								
(1_y)	0.0000	0.0427							
(1_z)	0.0000	0.0000	0.0152						
(2_x)	0.0188	0.0000	0.0000	0.0427					
(2_y)	0.0000	0.0188	0.0000	0.0000	0.0427				
(2_z)	0.0000	0.0000	0.0630	0.0000	0.0000	0.0152			
(3_x)	1.1583	0.0000	0.0000	0.0031	0.0000	0.0000	0.0427		
(3_y)	0.0000	−0.5118	0.0004	0.0000	0.0150	−0.0221	0.0000	0.0427	
(3_z)	0.0000	0.0004	−0.5458	0.0000	−0.0221	0.0825	0.0000	0.0000	0.0152
(4_x)	−0.0943	−0.7232	−0.0004	0.0120	0.0052	0.0191	0.1812	−0.1269	−0.0004
(4_y)	−0.7232	0.7407	−0.0002	0.0052	0.0061	0.0110	−0.1269	0.0346	0.0002
(4_z)	−0.0004	−0.0002	−0.5458	0.0191	0.0110	0.0825	−0.0004	0.0002	−0.1151
(5_x)	−0.0943	0.7232	0.0004	0.0120	−0.0052	−0.0191	0.1812	0.1269	0.0004
(5_y)	0.7232	0.7407	−0.0002	−0.0052	0.0061	0.0110	0.1269	0.0346	0.0002
(5_z)	0.0004	−0.0002	−0.5458	−0.0191	0.0110	0.0825	0.0004	0.0002	−0.1151
(6_x)	0.0031	0.0000	0.0000	1.1583	0.0000	0.0000	−0.0223	0.0000	0.0000
(6_y)	0.0000	0.0150	−0.0221	0.0000	−0.5118	0.0004	0.0000	0.0121	−0.0502
(6_z)	0.0000	−0.0221	0.0825	0.0000	0.0004	−0.5458	0.0000	−0.0502	0.1109
(7_x)	0.0120	0.0052	0.0191	−0.0943	−0.7232	−0.0004	0.0120	−0.0052	−0.0191
(7_y)	0.0052	0.0061	0.0110	−0.7232	0.7407	−0.0002	−0.0052	0.0061	0.0110
(7_z)	0.0191	0.0110	0.0825	−0.0004	−0.0002	−0.5458	−0.0191	0.0110	0.0825
(8_x)	0.0120	−0.0052	−0.0191	−0.0943	0.7232	0.0004	0.0120	0.0052	0.0191
(8_y)	−0.0052	0.0061	0.0110	0.7232	0.7407	−0.0002	0.0052	0.0061	0.0110
(8_z)	−0.0191	0.0110	0.0825	0.0004	−0.0002	−0.5458	0.0191	0.0110	0.0825
(9_x)	0.0422	0.0000	0.0000	0.0422	0.0000	0.0000	0.0209	−0.0730	−0.0545
(9_y)	0.0000	0.0422	0.0000	0.0000	0.0422	0.0000	−0.0730	0.0506	0.0529
(9_z)	0.0000	0.0000	0.0162	0.0000	0.0000	0.0162	−0.0545	0.0529	0.0292
(10_x)	0.0422	0.0000	0.0000	0.0422	0.0000	0.0000	0.0209	0.0730	0.0545
(10_y)	0.0000	0.0422	0.0000	0.0000	0.0422	0.0000	0.0730	0.0506	0.0529
(10_z)	0.0000	0.0000	0.0162	0.0000	0.0000	0.0162	0.0545	0.0529	0.0292

Table 2. (Continued)

	(4_x)	(4_y)	(4_z)	(5_x)	(5_y)	(5_z)	(6_x)	(6_y)	(6_z)
(4_x)	0.0427								
(4_y)	0.0000	0.0427							
(4_z)	0.0000	0.0000	0.0152						
(5_x)	−0.0386	0.0000	0.0000	0.0427					
(5_y)	0.0000	0.2544	−0.0005	0.0000	0.0427				
(5_z)	0.0000	−0.0005	−0.1151	0.0000	0.0000	0.0152			
(6_x)	0.0120	−0.0052	−0.0191	0.0120	0.0052	0.0191	0.0427		
(6_y)	−0.0052	0.0061	0.0110	0.0052	0.0061	0.0110	0.0000	0.0427	
(6_z)	−0.0191	0.0110	0.0825	0.0191	0.0110	0.0825	0.0000	0.0000	0.0152
(7_x)	0.0035	0.0149	0.0435	0.0031	0.0000	0.0000	0.1812	−0.1269	−0.0004
(7_y)	0.0149	−0.0137	0.0251	0.0000	0.0150	−0.0221	−0.1269	0.0346	0.0002
(7_z)	0.0435	0.0251	0.1109	0.0000	−0.0221	0.0825	−0.0004	0.0002	−0.1151
(8_x)	0.0031	0.0000	0.0000	0.0035	−0.0149	−0.0435	0.1812	0.1269	0.0004
(8_y)	0.0000	0.0150	−0.0221	−0.0149	−0.0137	0.0251	0.1269	0.0346	0.0002
(8_z)	0.0000	−0.0221	0.0825	−0.0435	0.0251	0.1109	0.0004	0.0002	−0.1151
(9_x)	−0.0200	0.0493	−0.0186	0.1063	0.0236	0.0731	0.0209	−0.0730	−0.0545
(9_y)	0.0493	0.0915	−0.0737	0.0236	−0.0349	0.0207	−0.0730	0.0506	0.0529
(9_z)	−0.0186	−0.0737	0.0292	0.0731	0.0207	0.0292	−0.0545	0.0529	0.0292
(10_x)	0.1063	−0.0236	−0.0731	−0.0200	−0.0493	0.0186	0.0209	0.0730	0.0545
(10_y)	−0.0236	−0.0349	0.0207	−0.0493	0.0915	−0.0737	0.0730	0.0506	0.0529
(10_z)	−0.0731	0.0207	0.0292	0.0186	−0.0737	0.0292	0.0545	0.0529	0.0292

	(7_x)	(7_y)	(7_z)	(8_x)	(8_y)	(8_z)	(9_x)	(9_y)	(9_z)	(10_x)	(10_y)	(10_z)
(7_x)	0.0427											
(7_y)	0.0000	0.0427										
(7_z)	0.0000	0.0000	0.0152									
(8_x)	−0.0386	0.0000	0.0000	0.0427								
(8_y)	0.0000	0.2544	−0.0005	0.0000	0.0427							
(8_z)	0.0000	−0.0005	−0.1151	0.0000	0.0000	0.0152						
(9_x)	−0.0200	0.0493	−0.0186	0.1063	0.0236	0.0731	0.0427					
(9_y)	0.0493	0.0918	−0.0737	0.0236	−0.0349	0.0207	0.0000	0.0427				
(9_z)	−0.0186	−0.0737	0.0292	0.0731	0.0207	0.0292	0.0000	0.0000	0.0152			
(10_x)	0.1063	−0.0236	−0.0731	−0.0200	−0.0493	0.0186	0.0188	0.0000	0.0000	0.0427		
(10_y)	−0.0236	−0.0349	0.0207	−0.0493	0.0915	−0.0737	0.0000	0.0188	0.0000	0.0000	0.0427	
(10_z)	−0.0731	0.0207	0.0292	0.0186	−0.0737	0.0292	0.0000	0.0000	0.0630	0.0000	0.0000	0.0152

a) Unit of $Q_{ij}(k, k')$ is Å^{-3}. In this table, i, $j=x, y$ or z, and k and k' specify the particles in the primitive cell. Atom numbering is as follows:
1 N(1/4, 1/4, 1/4); 2 N(−1/4, −1/4, −1/4); 3 O(1/3−u, 1/4, u); 4 O(u, 1/2−u, 1/4); 5 O(1/4, u, 1/2−u); 6 O(u−1/2, −1/4, −u); 7 O(−u, u−1/2, −1/4); 8 O(−1/4, −u, u−1/2); 9 Na(1/2, 1/2, 1/2); 10 Na(0, 0, 0); u=0.4901.

vibrationally-induced dipole gives rise to the direction normal to the applying macroscopic field, while in a longitudinal wave, the dipole is induced parallel to the field; therefore, this field contributes an additional restoring force. A frequency splitting between ν_l and ν_t is called a "TO–LO splitting"; the splitting width depends entirely on the long-range Coulomb interactions.

The numerical values of the diagonal elements of the dipole lattice sums were examined by the use of the following relation:

$$\sum_1^3 (i) Q_{ii}(k, k'; \mathbf{y} \to \mathbf{0}) = 4\pi/v,$$

where v denotes the unit cell volume, where $i=x$, y, or z, and where k and k' specify the particles in the primitive unit cell. The calculated lattice sums are listed in Table 2. When the charges are distributed spherically or tetrahedrally, the tensor, $\boldsymbol{Q}$, becomes scalar and has the well-known value of $4\pi/3v$ (in Å^{-3}), like that of the Lorentz field.

Intramolecular Vibration: Factor-group analysis[2b)] predicts that the intramolecular modes near the center of the Brillouin zone will have the irreducible representation:

$$\Gamma_n = A_{1g} + A_{2g} + 2E_g + A_{1u} + A_{2u} + 2E_u.$$

The A_{1g} and E_g branches are Raman-active, and the A_{2u} and E_u branches are infrared-active, while the A_{1u} and A_{2g} branches are optically-inactive in both infrared absorption and Raman effect.

For the short-range interaction model, the observed[2)] and calculated frequencies and the tentative assignments are listed in Table 3. The results for the rigid-ion model are given in Table 4. The corresponding force constants and effective charges are also shown in Table 1. Each distribution parameter, x, is listed at the top of Table 1. Model I corresponds to the short-range interaction model, while Model II and below are based on the rigid-ion model. Apparently, the

TABLE 3. OBSERVED AND CALCULATED VIBRATIONAL FREQUENCIES (cm^{-1}) OF SODA-NITER

Sym.		Obsd[a]	Calcd	Assignment[b]
A_{1g}	ν_{11}	1068	1067	NO str.
A_{2g}	ν_{21}		836	NO_3 out-of-plane def.
	ν_{22}		200	NO_3 transl(z).
	ν_{23}		174	NO_3 rot(z).
E_g	ν_{31}	1385	1392	NO str.
	ν_{32}	727	726	ONO def.
	ν_{22}	184	178	NO_3 rot (x,y).
	ν_{34}	98	124	NO_3 transl (x,y).
A_{1u}	ν_{41}		1069	NO str.
	ν_{42}		148	Na transl(z).
A_{2u}	ν_{51}	831	831	NO out-of-plane def.
	ν_{52}	217	212	Na, NO_3 transl (z).
	ν_{53}	89	124	NO_3 rot (z).
E_u	ν_{61}	1405	1392	NO str.
	ν_{62}	692	725	ONO def.
	ν_{63}	214	209	Na, NO_3 transl(x,y).
	ν_{64}	173	173	Na transl(x,y).
	ν_{65}	145	118	NO_3 rot(x,y).

a) Ref. 2(f). b) str., stretching; def., angle deformation; rot., rotational lattice mode; transl., translational lattice mode.

vibrationally-induced dipoles are seen not to exert a critical effect on the intra-molecular vibration. Thus, the observed large frequency splittings between E_g and E_u symmetric N–O stretching modes were again poorly explained as in Model I. The rigid-ion model may, therefore, be considered not to be suitable for the vibration of strongly interacting systems, such as those coupled firmly with a co-valent bond. An analysis which is based on some models of a higher order might be essential for a satisfactory explanation of these experimental facts. These subjects have been discussed in part by Decius *et al.*;[16] however, apart from their background polarization model, the point dipole approximation may be unsuitable for the intramolecular vibration.

Lattice Vibration: The lattice modes of the crystal have the irreducible representation of:[2b]

$$\Gamma_l = A_{1u} + 2A_{2g} + 2A_{2u} + 2E_g + 3E_u.$$

Group theory reveals five distinct infrared-active frequencies, two of the A_{2u} symmetry and three of the E_u symmetry. There are also two Raman-active modes with the E_g symmetry. The observed[2] and calculated frequencies are given in Tables 3 and 4, together with the intramolecular ones. The contribution (%) of each

TABLE 5. CONTRIBUTION (%) OF POTENTIAL TERMS TO EACH NORMAL FREQUENCY[a]

Sym.		K	f_1	f_2	f_3	f_4	f_5	f_6	H	F	α	p	n
A_{1g}	ν_{11}	53	0	1	0	0	1	0	0	46	0	−1	0
A_{2g}	ν_{21}	0	1	0	0	1	0	0	0	0	98	0	0
	ν_{22}	0	3	35	0	9	12	39	0	0	1	0	0
	ν_{23}	0	2	5	0	47	42	4	0	0	0	0	0
E_g	ν_{31}	83	0	1	0	0	0	0	14	5	0	1	−3
	ν_{32}	5	0	2	0	1	3	0	46	53	0	0	−9
	ν_{33}	0	0	33	0	47	0	20	0	0	0	0	0
	ν_{34}	0	23	29	0	30	0	18	0	0	0	0	0
A_{1u}	ν_{41}	53	0	1	0	0	1	0	0	46	0	−1	0
	ν_{42}	0	21	79	0	0	0	0	0	0	0	0	0
A_{2u}	ν_{51}	0	1	0	0	0	0	0	0	0	99	0	0
	ν_{52}	0	7	70	0	0	20	4	0	0	0	0	0
	ν_{53}	0	20	11	0	0	58	11	0	0	0	0	0
E_u	ν_{61}	83	1	0	0	0	0	0	14	5	0	1	−3
	ν_{62}	5	0	2	0	0	3	1	46	53	0	0	−9
	ν_{63}	0	22	68	0	0	0	9	0	0	0	0	0
	ν_{64}	0	32	62	0	0	0	5	0	0	0	0	0
	ν_{65}	0	29	2	0	0	0	69	0	0	0	0	0

a) Notations are the same as those in Tables 1 and 3.

TABLE 4. OBSERVED AND CALCULATED LONGITUDINAL AND TRANSVERSE FREQUENCIES (cm^{-1}) OF SODA-NITER

Sym.	Observed		II		III		IV		V		VI		VII		VIII	
	ν_t	ν_l	ν_t	ν_l	ν_t	ν_l	ν_t	ν_l	ν_t	ν_l	ν_t	ν_l	ν_t	ν_l	ν_t	ν_l
A_{1g}	1068		1068		1069		1068		1069		1068		1068		1069	
A_{1u}			1069		1070		1070		1070		1069		1068		1070	
			192		194		192		199		202		195		186	
A_{2g}			847		844		843		842		842		843		845	
			191		199		215		205		179		139		126	
			110		107		123		117		117		113		103	
A_{2u}	838	843	834	850	839	841	840	840	839	841	837	844	835	846	835	851
	205	251	216	262	217	262	188	257	190	266	198	267	205	254	211	243
	51	89	50	90	52	85	52	80	53	76	53	75	53	73	53	72
E_g	1385		1377		1377		1376		1377		1376		1375		1376	
	727		727		725		728		727		728		728		727	
	186		166		157		183		184		185		187		188	
	98		101		101		115		110		104		98		95	
E_u	1357	1419	1375	1383	1377	1377	1376	1376	1377	1378	1376	1380	1375	1382	1376	1385
	727		727	729	726	726	726	726	725	725	726	726	726	727	725	726
	204	271	210	254	212	256	183	254	187	264	196	267	208	258	213	247
	175	185	167	180	175	183	161	166	169	171	175	178	182	184	183	185
	87	97	86	102	88	102	80	92	82	93	85	95	88	95	89	96

TABLE 6. CONTRIBUTION (%) OF POTENTIAL TERMS TO EACH NORMAL FREQUENCY; DISTRIBUTION PARAMETER $x=-1$[a)]

Sym.	Mode[b)]	K	f_1	f_2	f_3	f_4	f_5	f_6	H	F	α	p	n	Z[c)]
A_{1g}	ν_{11}	52	0	1	0	0	0	0	0	46	0	1	0	0
E_g	ν_{31}	83	0	0	0	0	0	0	14	5	0	−1	−2	0
	ν_{32}	6	0	2	0	0	0	0	44	53	0	0	−5	0
	ν_{33}	0	2	61	0	18	0	19	0	0	0	0	0	−1
	ν_{34}	0	23	33	0	48	0	10	0	0	0	0	0	−14
A_{2u}	ν_{51}(t)	0	1	0	0	0	0	0	0	0	100	0	0	−1
	ν_{51}(l)	0	1	0	0	0	0	0	0	0	96	0	0	3
	ν_{52}(t)	0	8	97	0	0	1	2	0	0	0	0	0	−7
	ν_{52}(l)	0	6	65	0	0	0	0	0	0	1	0	0	28
	ν_{53}(t)	0	58	2	0	0	29	65	0	0	0	0	0	−54
	ν_{53}(l)	0	7	18	0	0	11	26	0	0	2	0	0	35
E_u	ν_{61}(t)	83	0	0	0	0	0	0	14	5	0	−1	−2	−1
	ν_{61}(l)	82	0	0	0	0	0	0	14	5	0	−1	−2	1
	ν_{62}(t)	6	0	2	0	0	0	1	44	53	0	0	−5	0
	ν_{62}(l)	6	0	2	0	0	0	0	43	53	0	0	−5	0
	ν_{63}(t)	0	14	90	0	0	0	9	1	1	0	0	0	−15
	ν_{63}(l)	0	14	62	0	0	0	2	0	0	0	0	0	22
	ν_{64}(t)	0	30	92	0	0	0	1	0	1	0	0	0	−24
	ν_{64}(l)	0	19	78	0	0	0	7	1	1	0	0	0	−7
	ν_{65}(t)	0	51	9	0	0	0	87	0	0	0	0	0	−47
	ν_{65}(l)	0	27	11	0	0	0	66	0	0	0	0	0	−5

a) Notations are the same as those in Tables 1 and 3. b) t, transverse; l, longitudinal. c) Coulomb term.

TABLE 7. CONTRIBUTION (%) OF POTENTIAL TERMS TO EACH NORMAL FREQUENCY; DISTRIBUTION PARAMETER $x=+0.2$[a)]

Sym.	Mode[b)]	K	f_1	f_2	f_3	f_4	f_5	f_6	H	F	α	p	n	Z[c)]
A_{1g}	ν_{11}	53	0	1	0	0	0	0	0	46	0	0	0	0
E_g	ν_{31}	85	0	0	0	0	0	0	14	5	0	0	−2	−2
	ν_{32}	6	0	3	0	1	−1	0	44	53	0	0	−8	2
	ν_{33}	0	0	37	3	55	0	−3	0	0	0	0	0	8
	ν_{34}	0	10	132	6	6	0	−11	0	0	0	0	0	−42
A_{2u}	ν_{51}(t)	0	0	1	1	0	0	0	0	0	94	0	0	4
	ν_{51}(l)	0	0	1	1	0	0	0	0	0	93	0	0	6
	ν_{52}(t)	0	4	149	0	0	−2	0	0	0	0	0	0	−51
	ν_{52}(l)	0	3	72	0	0	0	0	0	0	1	0	0	24
	ν_{53}(t)	0	10	50	9	0	−133	−27	0	0	0	0	0	191
	ν_{53}(l)	0	1	128	5	0	−73	−15	0	0	0	0	0	54
E_u	ν_{61}(t)	85	0	0	0	0	0	0	14	5	0	0	−2	−2
	ν_{61}(l)	84	0	0	0	0	0	0	14	5	0	0	−2	−1
	ν_{62}(t)	6	0	3	0	0	−1	0	44	53	0	0	−8	2
	ν_{62}(l)	6	0	3	0	0	−1	0	44	53	0	0	−8	2
	ν_{63}(t)	0	9	140	0	0	0	−1	0	0	0	0	0	−48
	ν_{63}(l)	0	6	66	0	0	0	0	0	0	0	0	0	28
	ν_{64}(t)	0	10	110	0	0	0	0	0	0	0	0	0	−19
	ν_{64}(l)	0	9	115	0	0	0	−1	0	0	0	0	0	−23
	ν_{65}(t)	0	8	20	12	0	0	−46	0	0	0	0	0	106
	ν_{65}(l)	0	3	48	11	0	0	−40	0	0	0	0	0	78

a) Notations are the same as those in Tables 1 and 3. b) t, transverse; l, longitudinal. c) Coulomb term.

potential parameter to the frequencies was calculated for Model I; the results are shown in Table 5. Similar results were obtained for the rigid-ion model; examples are given in Tables 6 and 7 for only two distribution models. Note how the Coulomb term contributes to each lattice mode. Table 4 suggests that a good agreement is obtained over a wide range of charge distributions. Unlike the intramolecular vibration, the lattice vibration is mainly concerned with the relative motion of considerably separated groups; therefore, even with the point dipole approximation the dynamical properties of the system are described satisfactorily well.

Normal coordinate treatments have been made by several groups of authors[17)] using the short-range interaction model. In addition to these, both the interaction of the vibrating dipoles and the influence of the electronic polarizability were taken into account respectively as the rigid-ion model and the shell model[18)] by Plihal *et al.*[19] They regarded the nitrate group as one bulky ion, the charge of which is located at the center of the goup, and analyzed the optically-active vibrations of three crystals of the calcite structure. Their rigid-ion calculations essentially correspond to those of Model II in this study. If one assumes this charge distribution, the influence of the long-range Coulomb interactions appears mainly in the translational lattice modes, and as is illustrated in Figs. 4 and 5, the Z-dependence of the vibrational frequencies is found to be monotonic. In spite of their rather crude approximation, a good agreement was obtained between the calculated and experimental results in the same manner as in the present investigation.

As is shown in Table 1, certain short-range force constants gradually changed; however, the magnitude, Z, of the effective charges was seen to fall into the range from 0.8 e to 0.9 e, regardless of the distribution parameter, x. Though the calculated TO–LO splittings appear to depend critically on Z rather than on x under these circumstances, the x-dependence of the calculated frequencies differs slightly from model to model. Some typical behavior is illustrated in Figs. 4 and 5. As far as the present investigation is concerned, the charge distribution model of $x=+1/5$ has given the best results. In this distribution, the effective charges on the atoms are $Z_{Na}=0.87\ e$, $Z_C=0.17\ e$, and $Z_O=-0.35\ e$. Those distribution models which have larger values of the x parameter than unity were found to give poorer results in this work. Though the above distribution is considered to be the best in this rigid-ion treatment, both the distribution parameter, x, and the magnitude, Z, might be altered in the higher-order models.

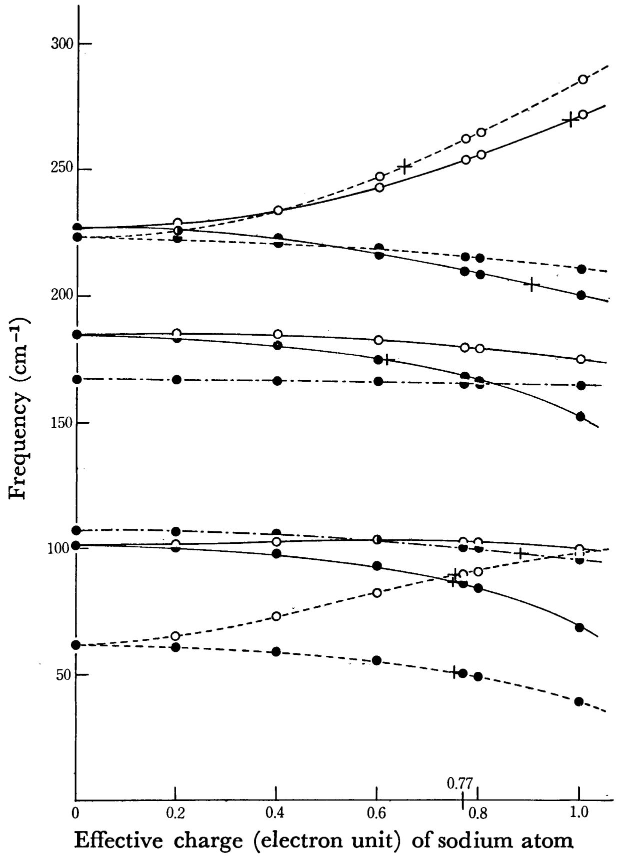

Fig. 4. Z-Dependence of optically-active lattice vibrations for $x=-1$.
(------), A_{2u}; (—•—), E_g; (——), E_u; ●, transverse mode; ○, longitudinal mode; +, observed frequency.

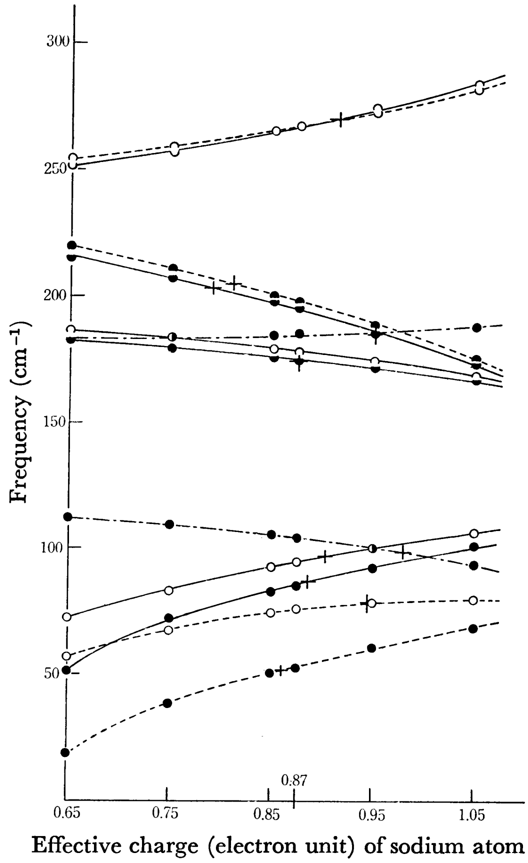

Fig. 5. Z-Dependence of optically-active lattice vibrations for $x=+1/5$. Other descriptions are the same as those in Fig. 4.

As to the short-range force constants, they have been considered in previous short-range interaction treatments to arise from the repulsive force; therefore, they must have positive values inherently. Because account was taken separately of the long-range Coulomb interactions in addition to the short-range ones, they do not necessarily have positive values. Therefore, the physical meaning of the force constants is considered to be essentially different from those in the previous treatments.

The charge distributions of various groups have been estimated from the studies of cohesive energy[20] and of electronegativity;[21] however, the results differ considerably both with the methods and with the investigators. Those obtained are, by nature, statical properties; consequently, they need not always coincide with those of the present dynamically-effective charges.

We wish to conclude this section by pointing out the following relation:

$$\sum_{1}^{n}(i)\omega_{i0}^{2} = \sum_{1}^{n}(i)\omega_{i}^{2}(\mathbf{y}\to\mathbf{0}),$$

where the left and right sides are concerned with the frequencies of the equilibrium crystal field[16] and of the

Table 8. Observed and calculated elastic constants (10^{10} dyn/cm^2) of soda-niter

	Obsd[a]	Calcd	Sym.
C_{11}	86.7	81.5	A_{1g}, E_g
C_{21}	16.3	25.5	A_{1g}, E_g
C_{31}	16.0	23.0	A_{1g}
C_{33}	37.0	43.1	A_{1g}
C_{41}	8.2	8.4	E_g
C_{44}	21.3	15.6	E_g

a) Ref. 3.

Table 9. Contribution (%) of potential terms to each elastic constant in soda-niter[a]

	C_{11}	C_{21}	C_{31}	C_{33}	C_{41}	C_{44}
K	1	1	1	0	0	0
f_1	17	17	18	4	52	27
f_2	23	35	44	17	47	31
f_3	0	0	0	0	0	0
f_4	1	0	10	36	14	23
f_5	51	49	-1	0	-2	0
f_6	6	-1	27	42	-14	19
H	0	-1	0	0	1	0
F	1	0	1	0	1	0
α	0	0	0	0	0	0
p	0	0	0	0	0	0
n	0	0	0	0	0	0

a) Notations are the same as those in Table 1.

rigid-ion approximation respectively, and where n is the number of the vibrational degrees of freedom.

Elastic Constant. The elastic constants of this crystal were determined long ago; the data of Bhimasenachar[3)] have been most commonly referred to. Since the space group of the crystal belongs to D_{3d}^6, the independent non-zero elements are the following terms; C_{11}, C_{21}, C_{31}, C_{33}, C_{41}, and C_{44}.[22)] Few attempts have been performed to make a theoretical calculation of the elastic constants of this crystal except for that by Shiro.[17c)] The calculated and observed elastic constants are compared in Table 8. The contribution of the potential parameters was also calculated; it is given in Table 9. This table suggests that the predominantly contributing terms to each element are in the following manner: C_{11} and C_{21}, f_5; C_{31}, f_2; C_{33}, f_6; C_{41}, f_1 and f_2; C_{44}, f_2. It is thus verified, by the way, that weakly-interacting parts are greatly responsible for the elastic properties of the crystalline state.

Since the mode of contribution to the elastic properties is considered to be essentially independent of that to the vibrational properties, the more reliable force constants are to be obtained with reference to the two types of properties complementarily.

Finally, the resulting elastic constants are identified as the mechanical part, because all interactions except for the short-range ones were neglected in this treatment. Therefore, further work will be required to take the contributions from the other interactions[4)] into consideration.

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