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Simple Mechanical Model Calculations of the Elastic Constants and Normal Frequencies of the $NaNO_2$ Crystal

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Synopsis. The optically-active vibration was analyzed for the $NaNO_2$ crystal on the basis of a simple mechanical model. Force constants which interpret fairly well both the observed elastic constants and the vibrational frequencies of the optically-active modes were determined.

In connection with the phase-transition phenomena, many investigators have taken part in the determination of the elastic constants[1] and in the spectroscopic study[2] of the crystal. In the present work, the elastic constants and the eigenfrequencies of the optically-active modes were calculated using a simple mechanical model.

The space symmetry of the sodium nitrite crystal is Im2m in the ferroelectric phase, and the cell constants are a_0=3.569 Å, b_0=5.563 Å, and c_0=5.348 Å.[3] Since two formula units are present in this crystallographic cell, the original lattice vector, **a**, has been transformed into a conventional lattice vector, $\mathbf{a}'=(\mathbf{a}+\mathbf{b}+\mathbf{c})/2$, in order to obtain the primitive unit cell in the vibrational analysis.[2a] The vibrational analysis was performed on the basis of the GF-matrix method,[4] in which vibrationally-induced dynamical effects[5] are implicitly neglected. In addition to the ordinary potential parameters of the NO_2 group, thirteen short-range interaction parameters were taken into account, as is illustrated in Fig. 1.

The elastic constants were microscopically calculated by the method established by Shiro.[6] In order to obtain the best fit, the potential parameters were

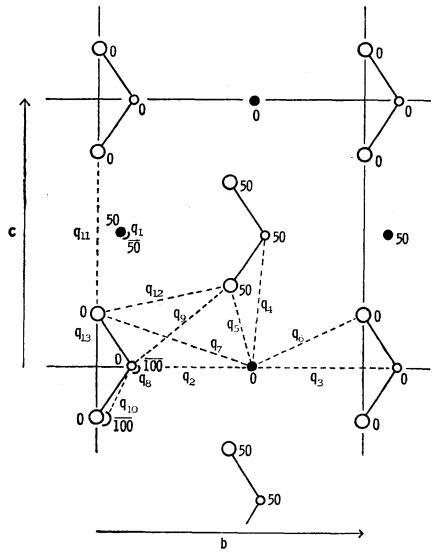

Fig. 1. Short-range interactions in $NaNO_2$ crystal. The heights of atoms are expressed in units of $100/a_0$.
●, Na; ○, N; ○, O.

Table 1. Internal coordinates and force constants in $NaNO_2$

Coord.	NO.	Distance[a]	Pair	Force Constant[b]
R	2	1.247	N O	6.946 K
q_1	1	3.569	Na Na	0.008 f_1
q_2	1	2.579	Na N	0.041 f_2
q_3	1	2.985	Na N	0.047 f_3
q_4	4	3.236	Na N	0.035 f_4
q_5	4	2.472	Na O	0.154 f_5
q_6	2	2.534	Na O	0.210 f_6
q_7	2	3.420	Na O	0.025 f_7
q_8	1	3.569	N N	0.008 f_8
q_9	4	3.212	N O	0.019 f_9
q_{10}	4	3.781	N O	0.010 f_{10}
q_{11}	1	3.289	O O	0.023 f_{11}
q_{12}	4	3.358	O O	0.018 f_{12}
q_{13}	2	3.569	O O	0.008 f_{13}
ϕ	1	(115°)	O N O	0.567 H
			O O	2.723 F
			(R, R')	0.595 P[c]

a) Distance in Å. b) Force constant in mdny/Å.
c) Correction term.

Table 2. Observed and calculated elastic constants (10^{10} dyn/cm^2) and contribution (%) of potential terms in $NaNO_2$

	Obsd[a]	Calcd	K	f_1	f_2	f_3	f_4	f_5	f_6	f_7	f_8	f_9	f_{10}	f_{11}	f_{12}	f_{13}	H	F	p
C_{11}	30.05	39.27	0	0	28	2	0	2	14	32	0	8	0	0	13	0	0	0	0
C_{21}	12.60	10.16	1	0	−10	3	−5	57	24	−12	0	31	0	0	13	0	−1	−1	0
C_{22}	54.79	54.07	0	0	0	0	21	52	2	0	0	4	0	19	0	0	0	1	0
C_{31}	10.60	33.30	0	0	−8	2	−3	46	20	−10	0	25	0	0	29	0	−1	−1	0
C_{32}	9.30	11.25	0	0	0	0	18	71	2	0	0	6	0	0	2	0	0	1	0
C_{33}	62.37	63.03	0	5	0	0	7	43	1	0	5	3	5	0	3	10	0	0	0
C_{44}	10.73	9.62	0	0	0	0	49	10	0	0	0	1	0	0	11	0	0	0	0
C_{55}	9.93	11.59	0	0	0	0	5	1	0	0	0	35	0	0	54	0	0	0	0
C_{66}	5.53	5.51	0	0	0	0	0	8	27	2	0	37	0	0	26	0	0	0	0

a) Ref. 1.

refined by the least-squares method with reference to the observed elastic constants[1c] and the vibrational frequencies[2c] complementally.

The best set of force constants was determined to be as is shown in Table 1. The observed[1c] and calculated elastic constants are compared in Table 2. Obviously, the observed elastic constants other than the C_{31} are reproduced fairly well. The contribution (%) of the potential parameters to the calculated elastic constants is also listed in Table 2. It is difficult on the basis of this model only to explain the relatively small value of the observed C_{31}, since the C_{31} constant is found to be considerably coupled with the C_{11} and C_{21} constants.

Table 3. Observed and calculated frequencies (cm^{-1}) of sodium nitrite crystal

Sym.		Obsd[a]	Calcd	Assignment[b]
A_1	ν_{11}	1330	1328	NO str.
	ν_{12}	826	821	ONO angle def.
	ν_{13}	217	235	transl (b).
A_2	ν_{21}	117	156	rot (b).
B_1	ν_{31}	242	209	rot (c).
	ν_{32}	169	124	transl (a).
B_2	ν_{41}	1316	1316	NO str.
	ν_{42}	286	248	rot (a).
	ν_{43}	160	151	transl (c).

a) Ref. 2(c). b) str, stretching; def, deformation; transl (a), translational (along the direction parallel to the a axis); rot (a), rotational (around the *a* axis).

The vibrational modes of the crystal have the following irreducible representations: $\Gamma=3A_1+A_2+2B_1+3B_2$. The calculated eigenfrequencies and the tentative assignments are given in Table 3. The observed frequencies cited here are the ones corrected by Tsuboi *et al.*[2c] to exclude conventionally the dynamical effects.[5] The simple Urey-Bradley force field has been found to give a somewhat poor agreement with the observed frequencies in a water-type molecule; therefore, we have introduced the correction term, p, between the stretching coordinates.[7] It is shown in Table 3 that the calculated frequencies reproduce the observed ones fairly well. Further investigations will, however, be required on the basis of some elaborated models, for a rigorous treatment is essential for the satisfactory explanation of the other dynamical properties.[2e] The degrees of the contribution of the potential parameters are considered to be independent of those from the elastic constants; therefore, the resulting force constants, which were obtained with reference to both properties complementally, seem to be reliable, at least in this idealized but simple model. The force constants obtained here may become a measure of the interatomic interactions due to repulsive forces.

The calculations were carried out on the TOSBAC 3400 TOPS 14 electronic computer at the Computing Center of Hiroshima University. The authors wish to express their thanks to Mr. Masaru Ohsaku of their laboratory for his useful suggestions.

References

1) a) K. Hamano, K. Negishi, M. Marutake, and S. Nomura, *Japan. J. Appl. Phys.*, **2**, 83 (1963); b) G. Hauret and A. Gharbi, *C. R. Acad. Sci. Paris, Ser. B*, **271**, 1072 (1970); c) K. Ota, Y. Ishibashi, and Y. Takagi, *J. Phys. Soc. Japan*, **29**, 1545 (1970).

2) a) E. V. Chisler and M. Shur, *Phys. Stat. Sol.*, **17**, 163 (1966); b) M. K. Barnoski and J. M. Ballantyne, *Phys. Rev.*, **174**, 946 (1968); c) M. Tsuboi, M. Terada, and T. Kajiura, presented at the Symposium on Molecular Structure, Tokyo, October (1968); d) Y. Luspin and J. P. Chapelle, *C. R. Acad. Sci. Paris, Ser. B*, **269**, 263 (1970); e) J. Sakurai, R. A. Cowley, and G. Dolling, *J. Phys. Soc. Japan*, **28**, 1426 (1970).

3) M. I. Kay and B. C. Frazer, *Acta Crystallogr.*, **14**, 56 (1961).

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

5) R. Frech and J. C. Decius, *ibid.*, **54**, 2374 (1971).

6) Y. Shiro and T. Miyazawa, This Bulletin, **44**, 2371 (1971).

7) T. Shimanouchi, *Pure Appl. Chem.*, **7**, 131 (1963).