Raman Effect in Ferroelectric Sodium Nitrite Crystal

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The Raman effect in sodium nitrite ($NaNO_2$) crystal has been observed by the use of the continuous helium-neon and ionized argon lasers as sources.[1] Several single crystals in the ferroelectric phase C_{2v}^{20}-*Im2m* of $NaNO_2$ were obtained through the kindness of Dr. S. Hirotsu and Mr. K. Suzuki, Tokyo Institute of Technology. The instruments used were a Perkin-Elmer Model LR-1 Laser-Excited Raman Spectrometer and a Spex 1400II Spectrometer.

In the first four columns of Table 1, a part of the result of our experiment is given. Here, the orientations of the crystal, directions of the incident and scattered beams, and the directions of the electric vectors of the incident and scattered beams were fixed so that all of the nine Raman-active fundamental frequencies (*i. e.* $3A_1+1A_2+2B_1+3B_2$) should be observed and that, for A_1, B_1, and B_2-type vibrations, frequencies of the pure transverse vibrations should be observed. In the fifth and sixth columns of Table 1, resonance frequencies are given, which were derived from the result of a recent measurement of the infrared reflectivity as the parameters characterizing the dielectric dispersion of this crystal.[2] On the basis of these data, all of the fundamental frequencies of the expected nine optically-active (in-phase), transverse vibrations have now been fixed. The translatory vibrations along the b and a axes are considered to cause only very small polarizability oscillation in the crystal in comparison with the rotatory vibrations of the NO_2^- ion. Therefore, it is probable that the Raman scatterings corresponding to these vibrations are not detected in our present experimental set up. This was taken into account in the assignments which are given in the last column of Table 1.

Besides what are given in the second column of Table 1, various orientations of the incident and scattered beams have been examined, and in many cases appreciably different frequencies from what are given in the third column of Table 1 have been observed. In the c(bc)a (instead of a(bc)b) orientation, for example, the B_2 frequencies are observed at 158, 172, and 1307 cm^{-1} (instead of 158, 191, and 1230 cm^{-1}). From such frequencies, we can obtain an information of the polarization forces[3] besides the elastic forces in the crystal.

TABLE 1. OPTICALLY-ACTIVE (TRANSVERSE) VIBRATIONS IN THE $NaNO_2$ CRYSTAL WITH THE C_{2v}^{20} SYMMETRY

Symmetry type of the vibration	Raman effect[a]			Resonance frequency[c]		Assignment
	Directions of the beams and their polarizations[b]	Frequency cm^{-1}	Intensity	Frequency cm^{-1}	Intensity	
A_1	a'(cc)b'	—	—	194	strong	Transl. along b
		830	medium	826	weak	NO_2^- scissor.
		1323	strong	1323	weak	NO_2^- sym. str.
A_2	a(ca)b	117	strong	—	—	Rot. around b
B_1	b(ab)c	—	—	149	strong	Transl. along a
		223	weak	223	weak	Rot. around c
B_2	a(bc)b	158	strong	157	strong	Rot. around a
		191	medium	188	strong	Transl. along c
		1230	medium	1235	strong	NO_2^- antisym. str.

a) Present experiment.

b) These directions are expressed by four symbols two inside a parenthesis and two out. The four mean, from left to right, the propagation direction of the incident light, the polarization direction of the incident light, polarization direction of the scattered light, and propagation direction of scattered light. a: 45° with a in the ab plane. b': 45° with b in the ab plane.

c) Derived from the infrared reflectivity (Ref. 2).

1) In 1959, André Tramer (*Compt. rend.*, **248**, 3546) observed Raman effect of this crystal by the use of mercury lamp as source. What he observed are mostly in accord with our results, but their assignments were not yet complete.

2) J. D. Axe, *Phys. Rev.*, **167**, 573 (1968).

3) M. Tsuboi and A. Wada, *J. Chem. Phys.*, **48**, 2615 (1968).