INFRARED SPECTRUM AND LATTICE VIBRATIONS OF A SODIUM NITRATE CRYSTAL

1968

SovietRxiv

Abstract

Full Text

UDC 548.0:535.343

PHYSICS

S. V. KARPOV, A. A. SHULTIN

INFRARED SPECTRUM AND LATTICE VIBRATIONS OF A SODIUM NITRATE CRYSTAL

(Presented by Academician A. A. Lebedev, July 5, 1967)

Since the discovery of the complex structure of the infrared absorption spectrum in the vicinity of the fundamental stretching vibration of the OH ion in the crystal brucite, $Mg(OH)_2$, and also in $Ca(OH)_2$ and LiOH crystals, a discussion has arisen in the literature about the nature of these absorption bands. According to one point of view (^{1}), this structure is due to coupling of the stretching vibration of the OH ion with localized librations of noninteracting hydroxyl ions. Another point of view (^{2}) relates the observed picture to combinations of internal and external vibrations of the crystal lattice of $Mg(OH)_2$, $Ca(OH)_2$, and LiOH. In the opinion of Dows (^{3}), the librational theory has indicated the path toward understanding the phenomenon, but at present it is necessary to conclude that the idea of stronger interaction apparently can better explain the complex spectra of these crystals in the near infrared region.

Table 1

Selection rules for the IR spectrum of a $NaNO_3$ crystal

Symmetry	Normal coord.	Fundamental freq.	Polarization	Combination	Polarization	Combination	Polarization
A_{1g}	Q_1	ν_1	inactive	$\nu_1 \pm \nu_L\ (A_{1u})$	inactive	$\nu_2' + \nu_L\ (A_{1u})$	inactive
A_{1u}	Q_1'	ν_1'	inactive	$\nu_1 \pm \nu_L\ (E_u)$	x, y	$\nu_2' \pm \nu_L\ (E_u)$	inactive
A_{2g}	Q_2	ν_2	inactive	$\nu_1 \pm \nu_L\ (E_g)$	inactive	$\nu_2' \pm \nu_L\ (E_g)$	x, y
A_{2u}	Q_2'	ν_2'	z	$\nu_1 \pm \nu_L\ (A_{2u})$	z	$\nu_2' \pm \nu_L\ (A_{2u})$	inactive
E_g	Q_3, Q_4	ν_4	inactive	$\nu_1 \pm \nu_L\ (A_{2g})$	inactive	$\nu_2' \pm \nu_L\ (A_{2g})$	inactive

Symmetry	Normal coord.	Fundamental freq.	Polarization	Combination	Polarization	Combination	Polarization
E_u	Q_3', Q_4'	ν_4'	x, y	$\nu_1' \pm \nu_L\ (A_{1u})$	inactive	$\nu_4 \pm \nu_L\ (A_{1u})$	x, y
A_{1u}	Q_7	ν_7	inactive	$\nu_1' \pm \nu_L\ (E_u)$	inactive	$\nu_4 \pm \nu_L\ (E_u)$	x, y, z
E_u	Q_{10}, Q_{11}	ν_{10}	x, y	$\nu_1' \pm \nu_L\ (E_g)$	x, y	$\nu_4 \pm \nu_L\ (E_g)$	inactive
E_u	Q_{12}, Q_{13}	ν_{12}	x, y	$\nu_1' \pm \nu_L\ (A_{2u})$	inactive	$\nu_4 \pm \nu_L\ (A_{2u})$	x, y
E_u	Q_{14}, Q_{15}	ν_{14}	x, y	$\nu_1' \pm \nu_L\ (A_{2g})$	z	$\nu_4 \pm \nu_L\ (A_{2g})$	inactive
E_g	Q_{16}, Q_{17}	ν_{16}	inactive	$\nu_2 \pm \nu_L\ (A_{1u})$	z	$\nu_4' \pm \nu_L\ (A_{1u})$	inactive
E_g	Q_{18}, Q_{19}	ν_{18}	inactive	$\nu_2 \pm \nu_L\ (E_u)$	x, y	$\nu_4' \pm \nu_L\ (E_u)$	inactive
A_{2u}	Q_{21}	ν_{21}	z	$\nu_2 \pm \nu_L\ (E_g)$	inactive	$\nu_4' \pm \nu_L\ (E_g)$	x, y, z
A_{2u}	Q_{22}	ν_{22}	z	$\nu_2 \pm \nu_L\ (A_{2u})$	inactive	$\nu_4' \pm \nu_L\ (A_{2u})$	inactive
A_{2g}	Q_{23}	ν_{23}	inactive	$\nu_2 \pm \nu_L\ (A_{2g})$	inactive	$\nu_4' \pm \nu_L\ (A_{2g})$	x, y
A_{2g}	Q_{24}	ν_{24}	inactive	$\nu_2 \pm \nu_L\ (A_{2g})$	inactive	$\nu_4' \pm \nu_L\ (A_{2g})$	x, y

Note. inactive —not active. The vibration of the nitrate ion ν_3 and its combinations with lattice vibrations are not considered in the present work.

Recently, the complex structure of the IR spectra of a number of nitrate and carbonate crystals in the region of the fundamental internal vibrations of the NO_3^- and CO_3^{2-} ions was interpreted (^{4}) on the basis of the idea of librations of these ions about the trigonal axis. In light of the preliminary results of the discussion mentioned above, such an interpretation of the spectral structure of crystalline nitrates and carbonates is doubtful; and to assess its reliability, studies (^{5}) of the dispersion of the branches of external vibrations, knowledge of the special points of the Brillouin zone, and also a more careful study of the IR spectra are necessary. Since one of the most characteristic spectra presented in that work pertains to sodium nitrate, we

an attempt was undertaken at a more detailed study of the IR spectrum of oriented single-crystal samples of $NaNO_3$ in polarized light in the region 700-1300 cm^{-1} at temperatures of 80-560° K.

The $NaNO_3$ lattice has a calcite-type structure. The space group is D_{3d}^6—$R\bar{3}c$; the rhombohedral unit cell contains 2 "molecules" and has dimensions $a = 6.313$ Å, $\alpha = 47°15'$ at 18° C (^{6}). On heating above 200° C, $NaNO_3$ undergoes a

Fig. 1. External normal vibrations of the unit cell of a sodium nitrate crystal

Figure 1: Fig. 1. External normal vibrations of the unit cell of a sodium nitrate crystal

second-order phase transition, which is completed at 276° C (7) and, according to present-day data (8,9), is associated with orientational disordering of the anions and an increase in the migration rate of sodium ions.

The normal vibrations of the unit cell of the low-temperature phase of $NaNO_3$ were analyzed in (10,11). Kastler showed (12) that the real lattice vibrations are a superposition of translational and rotational vibrations belonging to the same symmetry type (Fig. 1).

Fig. 1. External normal vibrations of the unit cell of a sodium nitrate crystal

The spectroscopic selection rules (in the factor-group approximation) are given in Table 1. The internal vibrations of the nitrate ion have the following frequencies:

$$\nu_1(A_{1g}) = 1068 \text{ cm}^{-1};$$

$$\nu_2'(A_{2u}) = 838 \text{ cm}^{-1};$$

$$\nu_3(E_g) = 1385 \text{ cm}^{-1};$$

$$\nu_3'(E_u) = 1385 \text{ cm}^{-1};$$

$$\nu_4(E_g) = 720 \text{ cm}^{-1},$$

$$\nu_4'(E_u) = 726 \text{ cm}^{-1}.$$

Despite the splitting of the internal vibrational terms into two components, in the IR spectra and in the spectra of combinational scattering (c.s.) of the crystal there is no change in the number of the corresponding bands. The calculation carried out showed that the splitting of the components $\nu_2(A_{2g})$ and $\nu_2'(A_{2u})$ (according to (13), for this vibration the derivative of the dipole moment with respect to the coordinate is $\partial\mu/\partial q = 1.6$ debye per 1 Å), taking into account the interaction of the 80 nearest ions, does not exceed 0.5 cm^{-1}.

Fig. 2. Infrared absorption spectra of $NaNO_3$ crystal.

Figure 2: Fig. 2. Infrared absorption spectra of $NaNO_3$ crystal.

Experimental investigations of the c.s. of the $NaNO_3$ crystal have been carried out many times (see, for example, ([14])). In the low-frequency region of the spectrum there are 2 lines of type E_g with frequencies 98 and 185 cm^{-1}, and their intensities are approximately in the ratio $1:3$. Since the librational motion of the nitrate ions is accompanied by a strong change in the polarizability of the cell, the ratio of the intensities of these lines can serve as a measure of the participation of such motion in each of the two real vibrations.

The available information on the IR spectrum of $NaNO_3$ in the region of external vibrations is poorer and less reliable. From the reflection spectrum of a single crystal, Liebisch and Rubens ([15]) give for the E_u ensemble the frequencies 71, 133, and 217 cm^{-1}, and for the A_{2u} ensemble the frequencies 71 and 217 cm^{-1}. In ([16]), for a polycrystalline sample the frequencies 89, 173, and 217 cm^{-1} were obtained.

Absorption of $NaNO_3$ in the near IR region has been studied repeatedly (see, for example, ([17,18])); however, most of the results refer either to polycrystalline layers or to mica plates (plane $10\bar{1}1$). The spectra obtained in the present work are shown in Fig. 2,

from which it is seen that all absorption bands are sharply polarized. This fact makes it possible to assume that the selection rules for combination bands, derived in the factor-group approximation, are valid, at least, for part of each of the bands (19). In view of the fact that the available information on lattice vibrations pertains to $T = 300°K$, it is natural to begin the discussion with spectrum 3 (Fig. 2). In the polarization $\mathbf{E} \perp c$, the selection rules allow combination absorption with the participation of external vibrations of the types E_g and E_u. Therefore the bands 1004 and 926 cm^{-1} should be assigned to combinations ν_2' with the ensemble of external vibrations E_g, the first of which can be predominantly associated with the motion ν_{18} (Fig. 1). Similar combinations of ν_2 with the ensemble E_u give rise to the appearance of bands 1048, 978, and 954 cm^{-1}. Since librations of nitrate ions about the c_2 axes in antiphase should have a higher frequency than in librations in phase, the band 1048 cm^{-1} can be predominantly associated with the motion ν_{14}.

Fig. 2. Infrared absorption spectra of a $NaNO_3$ crystal. 1 $-\mathbf{E} \perp c$, 560°K; 2 $-\mathbf{E} \perp c$, 385°K; 3 $-\mathbf{E} \perp c$, 293°K; 4 $-\mathbf{E} \perp c$, 80°K; 5 $-\mathbf{E} \parallel c$, 293°K; 6 $-\mathbf{E} \perp c$, 80°K; (Spectra 1-4 were obtained on a sample cut perpendicular to the optical axis, spectra 5 and 6 on one cut parallel to it.)

The region of combination transitions of the internal vibration ν_1 becomes sufficiently transparent only when the sample is cooled. At $T = 80°K$ in this range (4 in Fig. 2) about 10 absorption maxima can be distinguished. The maxima 1167 and 1254 cm^{-1} should be assigned to combination transitions with external vibrations of the E_g ensemble, and the bands 1220-1229 cm^{-1} and 1189-1200 cm^{-1} to combination transitions with external vibrations of the E_u ensemble. The region corresponding to the 954 cm^{-1} band (spectrum 3), upon cooling, reveals a more complex structure. In this case the maximum 963 cm^{-1} can be interpreted as $\nu_2 + 115$ cm^{-1} (E_u), and the maximum 952 as $\nu_1 - 116$ cm^{-1} (E_u). The absorption bands 788 and 893 cm^{-1}, located in all spectra 1-4 symmetrically with respect to the band of the vibration ν_2, are apparently caused by combinations of this vibration with acoustic lattice vibrations of type E_u, whose density of frequencies is maximal near the boundary of the Brillouin zone. Librations of nitrate ions about the trigonal axis together with translations along this axis form the ensembles A_{2g} and A_{2u}, which in the approximation considered do not give IR-active combination bands with the vibrations ν_2 and ν_2'. The possibility of combination absorption in the region of the vibration ν_1 (or ν_1') with these ensembles can be realized only in the region of weak absorption 1140 cm^{-1} ($\mathbf{E} \parallel c$, spectrum 6). Therefore the argu-

the arguments presented in work (4) in favor of the librational concept seem unconvincing to us. The most probable interpretation of the remaining bands is given in Table 2. It may be noted that the inactive fundamental lattice vibration $\nu_7(A_{1u})$, according to spectra 5 and 6, has a frequency of about 175 cm^{-1}.

On cooling, many bands of combination absorption show splitting. However, because of the lack of sufficient information concerning the dispersion of the vibrational branches and the number of critical points in the Brillouin zone, it is difficult to indicate the actual cause of this.

Table 2

Frequencies of the bands of the IR spectrum of $NaNO_3$

80° K	300° K	Polarization	Assignment	80° K	300° K	Polarization	Assignment	80° K	300°K	Polarization	Assignment
727	726	x, y	ν_4'	946	927	z	$\nu_4+\nu_{14}$	1050		x, y	$\nu_2+\nu_{14}$
790	788	x, y	ν_2- acoustic	952		x, y	$\nu_1-\nu_{10}$	1066	1048	x, y	$\nu_2+\nu_{14}$
815	815	z	$\nu_2(N^{18}O_3)$	963	954	x, y	$\nu_2+\nu_{10}$	1141		z	$\nu_1+(A_{2u}, A_{2g})$
826	825	x, y	$\nu_4'+\nu_{16}$	981		x, y	$\nu_2+\nu_{11}$	1154		x, y	$\nu_1'+\nu_{16}$
838	838	z	ν_2'	987	978	x, y	$\nu_2+\nu_{12}$	1167		x, y	$\nu_1'+\nu_{16}$
840	840	x, y	ν_2'	1014		x, y	$\nu_2'+\nu_{18}$	1189	1185	x, y	$\nu_1+\nu_{10}$
873		z	$\nu_4+\nu_{12}$	1023	1004	x, y	$\nu_2'+\nu_{18}$	1200		x, y	$\nu_1+\nu_{10}$

80° K	300° K	Polarization	Assignment	80° K	300° K	Polarization	Assignment	80° K	300°K	Polarization	Assignment
893	889	x, y	ν_2+ acoustic	1035	1010	z	$\nu_2+\nu_7$	1220		x, y	$\nu_1+\nu_{11}$
906		z	$\nu_4+\nu_{18}$					1229		x, y	$\nu_1+\nu_{11}$
930	926	x, y	$\nu_2'+\nu_{16}$					1254		x, y	$\nu_1'+\nu_{18}$
937		x, y	$\nu_2'+\nu_{16}$					1265		x, y	$\nu_1+\nu_{14}$

Heating the sample leads to broadening of the bands and their shift (for some, up to 0.1 cm^{-1}/deg) toward lower frequencies. The intensity of the 1066 cm^{-1} band decreases noticeably already at $T = 385$°K. If it belongs to the E_u ensemble and, basically, corresponds to librations of nitrate ions about the c_2 axes (motion ν_{14}, Fig. 1), then this behavior reflects a decrease in the magnitude of the coupling of the vibrations within this ensemble as a result of the strongly anisotropic expansion of the crystal lattice on heating (20). With further heating, orientational disordering of the nitrate ions makes meaningless the choice of a cell with two "molecules." In view of the lowering of the site symmetry of the nitrate ions in a layer, the ν_1 band begins to appear in absorption (21).

The increase in the intensity of the combination bands in the region of 800 and 875 cm^{-1} is apparently due to an increase in the mobility of the ions in directions perpendicular to the trigonal axis.

Leningrad State University
named after A. A. Zhdanov

Received
2 VII 1967

CITED LITERATURE

1. R. M. Hexter, *J. Opt. Soc. Am.*, **48**, 770 (1958); *J. Chem. Phys.*, **34**, 941 (1961).
2. K. A. Wickersheim, *J. Chem. Phys.*, **31**, 863 (1959).
3. D. A. Daus, in: *Physics and Chemistry of the Solid State of Organic Compounds*, Moscow, 1967, p. 573.
4. R. A. Schroeder, C. E. Weir, E. R. Lippincott, *J. Res. Nat. Bur. Stand.*, **66A**, 407 (1962).

5. S. S. Mitra, *J. Chem. Phys.*, **39**, 3031 (1963).
6. J. Weigle, *Helv. phys. acta*, **7**, 46 (1934); H. Sajni, A. Mercier, *Helv. phys. acta*, **7**, 267 (1934).
7. F. C. Kracek, *J. Am. Chem. Soc.*, **53**, 2609 (1931); H. Miekk-Oja, *Ann. Acad. Sci. Fennicae*, AI, **7**, 7 (1941).
8. E. R. Andrew, R. G. Eades et al., *Proc. Phys. Soc.*, **79**, 954 (1962).
9. Y. Shinnaka, *J. Phys. Soc. Japan.*, **19**, 1281 (1964).
10. S. Bhagavantam, T. Venkatarayudu, *Proc. Ind. Acad. Sci.*, **9A**, 224 (1939).
11. J. Cabannes, *Rev. Sci.*, **80**, 407 (1942).
12. A. Kastler, *C. R.*, **227**, 1024 (1948); *Proc. Ind. Acad. Sci.*, **28A**, 349 (1948).
13. J. C. Decius, *J. Chem. Phys.*, **23**, 1290 (1955).
14. T. M. K. Nedungadi, *Proc. Ind. Acad. Sci.*, **8A**, 397 (1938); **10A**, 197 (1939).
15. T. Liebisch, H. Rubens, S. B. Preuss, *Akad. Wiss. Berlin*, **2**, 48, 876 (1919).
16. J. R. Ferraro, A. Walker, *J. Chem. Phys.*, **42**, 1273 (1965).
17. A. K. Ramdas, *Proc. Ind. Acad. Sci.*, **37A**, 441 (1953).
18. H. G. Häfele, *Zs. Phys.*, **148**, 262 (1957).
19. H. Winston, R. S. Halford, *J. Chem. Phys.*, **17**, 607 (1949).
20. J. B. Austin, R. H. H. Pierce, *J. Am. Chem. Soc.*, **55**, 661 (1933).
21. L. J. Slutsky, D. F. Eggers jr., R. A. Kluge, *Bull. Am. Phys. Soc.*, **10**, 108 (1965).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.