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Abstract

Full Text

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INTERACTION OF INTRAMOLECULAR AND LATTICE VIBRATIONS OF CRYSTALS ACCORDING TO INFRARED SPECTRA

The study of questions concerning the excitation of vibrations and the redistribution of energy in crystal lattices—interest in which has increased considerably over the last ten years—is connected first of all with the spectroscopic method of investigation. A. S. Davydov ([1]-[3]) carried out several very interesting works concerning the theory of absorption of light by molecular crystals. R. Halford ([4], [10]), D. Hornig ([11]-[17]), and their collaborators carried out a number of investigations devoted to the study of vibrational spectra of molecules and complex ions in crystals.

Fig. 1. Infrared transmission spectrum of a single-crystal sample of $Ba(NO_3)_2$

However, at present there is still no quantitative theory of the influence of the crystal field and temperature on the width, position, and intensities of bands in the absorption spectra of crystals.

As is known, in a crystal lattice molecules have a fixed equilibrium position and orientation. Vibrations of particles about their equilibrium positions and orientations, i.e., lattice vibrations, have energies 10–100 times smaller than the energies of internal vibrations and, as a result, can be excited already at comparatively low temperatures.

According to theoretical concepts ([1], [2]), excitation of lattice vibrations should cause an increase in the probability of transitions in which excitation by light of internal vibrations occurs simultaneously with lattice vibrations. In addition, with increasing temperature the probability increases of excitation by light of molecules from already excited lattice levels. Both of these processes should appear in the absorption spectra of molecular crystals in the form of satellites near the bands of intramolecular excitation.

Figure 2

Figure 2: Figure 2

Up to the present time this question has been touched upon only incidentally in investigations of intramolecular vibrations in crystals, and no pri—

effort to obtain more clear-cut results: isolated cases have been described in the literature in which the combination of the properties of certain absorption bands in the spectra of crystals makes it possible to interpret them in the manner indicated above.

Fig. 2. Infrared transmission spectrum of a single-crystal specimen of $Pb(NO_3)_2$

Since the question of the interaction of phonons with intramolecular vibrations is of great interest, we carried out studies of the infrared absorption spectra of single-crystal specimens of barium nitrate $Ba(NO_3)_2$ and lead nitrate $Pb(NO_3)_2$. The purpose of these studies was to clarify the question of the presence and features of such "combination" transitions, whose intensities should depend noticeably on temperature, while their distances from the centers of the bands of internal excitation should be of the order of the frequencies of lattice vibrations. The probability of such transitions should also depend on the kind of internal excitation and on the type of lattice vibrations, while the width of the corresponding bands should be determined by the sum of the frequency-density distributions of both bands or branches of the excited states.

Table 1

Frequencies of absorption bands in the spectrum of a barium nitrate single crystal $Ba(NO_3)_2$ (in cm^{-1})

$t = 20°$	$t = -160°$	Assignment
717	716	ν_4
–	724	ν_4
730	732	ν_4
–	748	$\nu_2 - 70$
764	766	$\nu_4 + 34$
778	782	$\nu_2 - 36$
797	799	$\nu_4 + 67$
821	818	ν_2
–	841	$\nu_4 + 109$
–	853	$\nu_2 + 35$
–	877	$\nu_4 + 143$
896	889	$\nu_1 - 158$; $\nu_2 + 71$
–	902	$\nu_1 - 145$
935	928	$\nu_1 - 119$; $\nu_2 + 110$

$t = 20°$	$t = -160°$	Assignment
–	938	$\nu_1 - 109$
952	961	$\nu_2 + 143$
975	983	$\nu_1 - 64$; $\nu_2 + 160$
1013	1013	$\nu_1 - 34$
–	1028	$\nu_1 - 19$
–	1038	$\nu_1 - 9$
1047	1047	ν_1
1085	1085	$\nu_1 + 38$
1111	1112	$\nu_1 + 65$
–	1149	$\nu_1 + 102$
1158	1162	$\nu_1 + 115$
–	1192	$\nu_1 + 145$
–	1202	$\nu_1 + 155$
–	1258	
1190–1550	1300–1550	ν_3, $2\nu_4$

In the crystals selected, the role of structural units having internal vibrational degrees of freedom is played by the complex ions $NO_3{}^-$. These ions are planar equilateral triangles, at the vertices of which oxygen atoms are located, and at the center a nitrogen atom. Such a system has six normal vibrations with frequencies in the region 700–1500 cm^{-1}. The lead nitrate specimen was a plate measuring $0.30 \times 10 \times 20$ mm, and the barium nitrate specimen a plate measuring $0.56 \times 10 \times 20$ mm. The spectra obtained are shown in Figs. 1 and 2, where the upper curve corresponds to a specimen temperature of −160°, and the lower to a temperature of 20°. The analysis carried out of the selection rules for the investigated cry-

crystals belonging to the space group T_h^6, with the aid of group theory leads to the conclusion that all fundamental internal vibrations of the NO_3^- ions should be active in absorption, which is indeed observed. However, in addition to these transitions, the spectra reveal a considerably larger number of weaker absorption bands than the data available in the literature (10,18). A key to their interpretation may be provided by clearly expressed absorption maxima located symmetrically with respect to the absorption peak ν_1 (in the region 1050 cm^{-1}) on the red and violet sides. When the temperature of the specimens is lowered to −160°, the intensity of the "red" satellites decreases noticeably. Taking into account the magnitude of the separation of these bands from the fundamental transition ν_1 and their temperature dependence, similar satellites can also be found for the bands ν_2 and ν_4. Since the possibility of explaining these additional absorption maxima on the basis of purely intra-ionic vibrational transitions is completely excluded, the characteristic features noted above allow one to consider that these satellites are the result of combination transitions, in which the quantum numbers of internal and lattice levels change simultaneously.

Table 2

Frequencies of absorption bands in the spectrum of a single crystal of $Pb(NO_3)_2$ (in cm^{-1})

$t = 20^\circ$	$t = -160^\circ$	Assignment
714–734	~ 715	ν_4
714–734	~ 724	ν_4
758	761	$\nu_2 - 49$
–	~ 774	$\nu_4 + 50$
~ 779	779	$\nu_2 - 31$
788	787	$\nu_4 + 63$
809	810	ν_2
~ 835	~ 839	$\nu_2 + 29$
–	857	$\nu_2 + 47$
~ 876	~ 879	$\nu_2 + 70$
891	894	$\nu_2 + 84$
–	~ 914	$\nu_1 - 136$
920	926	
–	941	
–	965	$\nu_1 - 85$
979	980	$\nu_1 - 70$
997	998	$\nu_1 - 52$
1014	1016	$\nu_1 - 34$
–	1050	ν_1
1079	1079	$\nu_1 + 29$
–	1097	$\nu_1 + 47$
~ 1131	1131	$\nu_1 + 81$
–	~ 1150	
–	~ 1184	$\nu_1 + 134$
1185–1540	1250–1500	$\nu_3,\ 2\nu_4$

In other words, in the case of such transitions, upon absorption of a quantum of light an exciton is created with the simultaneous creation (or disappearance) of a phonon. A more careful study of the spectrum of $Ba(NO_3)_2$ shows that, relative to the band of the vibration ν_1, satellites are arranged symmetrically at distances of 109, 119, 145, and 158 cm^{-1} on the red side and at 102, 115, 145, and 155 cm^{-1} on the violet side from the fundamental frequency 1047 cm^{-1}. Some of these frequencies are very close in magnitude to the lattice frequencies of barium nitrate crystal, known from combination-scattering spectra ([19]).

Table 3

Distances between the center of the band of the fundamental internal excitation and absorption bands interpreted as combinations with the lattice for various internal vibrations in the spectrum of $Ba(NO_3)_2$ (in cm^{-1})

ν_4	ν_2	ν_1	Direction
$\sim (155)$	$\sim (160)$	(155)	To the violet side
143	143	145	To the violet side
(109)	$\sim (110)$	115	To the violet side
–	–	102	To the violet side
(67)	71	65	To the violet side
(34)	35	38	To the violet side
ν_4	ν_2	ν_1	From the fundamental vibration
···	36	34	To the red side
···	$\sim (70)$	64	To the red side
···	···	109	To the red side
···	···	119	To the red side
···	···	145	To the red side
···	···	158	To the red side

Note. Here and in Table 4, the numbers enclosed in parentheses refer to transitions as to whose existence no definite conclusions can be drawn. Dots indicate possible transitions falling outside the limits of the spectrum studied.

It is natural to expect that the character of the interaction of intramolecular vibrations with lattice vibrations depends on the features of intramolecular excitation. These differences should affect precisely the combination absorption bands under consideration, determining their different peak intensities, the distribution of intensity, and the different number of satellites around different fundamental vibrational bands. The considerations expressed are fully confirmed by the experimental results.

Table 4

Distances between the center of the band of the fundamental intramolecular excitation and the absorption bands interpreted as combinations with the lattice, for different internal vibrations in the spectrum of $Pb(NO_3)_2$ (in cm^{-1})

ν_4	ν_2	ν_1	Direction	From
–	131	134	Toward the violet side	–
$\sim (82)$	–	81	Toward the violet side	–
63	$\sim (70)$	$\sim (70)$	Toward the violet side	–
50	47	47	Toward the violet side	–

ν_4	ν_2	ν_1	Direction	From
~ (30)	29	29	Toward the violet side	–
. . .	31	34	Toward the red side	the fundamental vibration
. . .	49	52	Toward the red side	the fundamental vibration
. . .	(70)	70	Toward the red side	the fundamental vibration
. . .	(84)	85	Toward the red side	the fundamental vibration
. . .	. . .	136	Toward the red side	the fundamental vibration

The most probable, in our view, interpretation of the observed transitions is given in the third column of Tables 1 and 2, and also directly on the spectra themselves (Figs. 1 and 2).

Comparing the results obtained, one can see that, despite the overall complexity of the absorption spectra, most of the bands fit into the scheme following from the arguments presented. The similarity of the structure surrounding individual intramolecular vibrational transitions in the infrared spectra of single crystals of barium nitrate and lead nitrate is most clearly seen from Tables 3 and 4.

In several regions of the spectrum of the crystals studied, the combination structure of one vibrational band is superimposed on an analogous structure belonging to another band. The complication of the spectrum caused by this circumstance, in particular cases, substantially hinders an unambiguous interpretation of some absorption maxima.

In conclusion, it may be noted that in the spectra under discussion the closest-lying satellites of the absorption bands correspond to lattice vibration frequencies of the order of 30–35 cm^{-1}, whereas in the combination-scattering spectrum the lowest-frequency lines are separated from the exciting frequency by 80–90 cm^{-1}. Apparently, these satellites appear in the infrared spectrum owing to the participation of lattice vibrations that do not change the polarizability of the molecules.

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

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