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ANHARMONICITY OF NITRATE-ION OSCILLATION IN CRYSTALS AND MELTS OF SODIUM, RUBIDIUM, AND CESIUM NITRATE

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Second-order vibrational spectra (SOS) for certain nitrates of monovalent metals (mainly sodium) are already known [1-7], but have not been subjected to systematic study, and therefore it is often difficult to formulate an idea of the anharmonicity of their internal nitrate-ion vibrations. It is important to know the anharmonicity constants (AC) of nitrate-ion vibration not only from the viewpoint of its vibrational and rotational dynamics. Thus, new types of spectral manifestations of nitrate-ion disordering were recently observed in nitrate spectra [8, 9]. Brooker [7] confirmed these data, but expressed the opinion that these new bands, attributed to disordered particles, may be due to transitions from a nonzero level ("hot" transitions). Knowledge of AC is also necessary if these are to be localized. Therefore, the present work is an investigation of SOS in the IR region, with estimates of the limits of AC variation for sodium, rubidium, and cesium nitrates in crystalline and molten states.

The IR spectra were recorded on a Perkin-Elmer 180 unit in the region 500-4000 cm^{-1}, using an attachment for small samples. In the region up to ~1200 cm^{-1}, the spectral width of the slit was about 1 cm^{-1}; in recording SOS it was about 3 cm^{-1}. The investigation was carried out on polished chips of $NaNO_3$ (thickness 60 μ), $RbNO_3$ (50 μ), and $CsNO_3$ (55 μ) single crystals, of size about 2×2 mm. The heating-element setup is shown in Fig. 1. In studying the spectra of melts, the sample was held by surface-tension forces in hole 6. The temperature was held constant to an accuracy of up to ± 1°, and controlled by a Copel—Alumel thermocouple.

Some data on the Raman-scattering (RS) spectrum were obtained earlier, in [10, 11]. Examples of the IR spectra recorded are given in Fig. 2. The region of strongly polar vibrations ν_2 of the free ion in the IR

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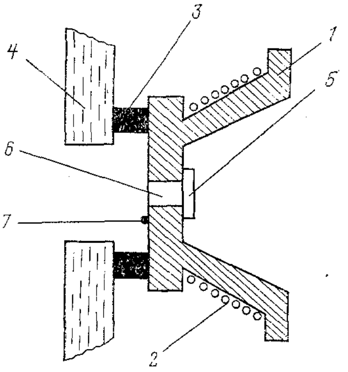

Fig. 1. Heater unit: 1) heater body; 2) heating element; 3) heat insulator; 4) main frame; 5) single crystal; 6) hole; 7) thermocouple site.

TABLE 1. Selection Rules for Overtones and Combination Tones of Sodium Nitrate

Vibration	Symmetry	ν_1		ν_3	
		A_{1g}	A_{1u}	E_g	E_u
ν_4	E_g^{RS}	E_g	E_u	$A_{1g}+E_g$	$A_{1u}+A_{2u}+E_u$
	E_u^{IR}	E_u	E_g	$A_{1u}+A_{2u}+E_u$	$A_{1g}+E_g$
ν_2	$A_{2g}^{(HA)}$	A_{2g}	A_{2u}	E_g	E_u
	A_{2u}^{IR}	A_{2u}	A_{2g}	E_u	E_g
ν_1	A_{1g}^{RS}	A_{1g}	A_{1u}	E_g	E_u
	$A_{1u}^{(HA)}$		A_{1g}	E_u	E_g
ν_3	E_g^{RS}			$A_{1g}+E_g$	$A_{1u}+A_{2u}+E_u$
	E_u^{IR}				$A_{1g}+E_g$

spectra was not investigated in the present work, and the position of the ν_2-band maximum with the relatively strong absorption in the layers used here was more accurately located using data on suspensions in mineral oil.

A "free" nitrate ion has the symmetry D_{3h} and is characterized by the vibrations ν_4 ($E' \sim 700$ cm^{-1}), ν_2 ($A_2'' \sim 800$ cm^{-1}), ν_1 ($A_1' \sim 1050$ cm^{-1}), and ν_3 ($E' \sim 1300$ cm^{-1}). Placing the ion in a crystal lattice leads to the splitting of all, or almost all, the vibrations by local and correlational fields. The crystal structure of nitrates in the temperature range investigated is as follows: for $NaNO_3$ (310-500°K), D_{3d}^6-$R\bar{3}C$, $Z = 2$, and the nitrate ion is in positions with local symmetry D_3 [12]; for $RbNO_3$ (310-437°K) and $CsNO_3$ (310-434°K), C_3^2–$P3_1$ or C_3^3–$P3_2$, $Z = 9$, and the nitrate ion occupies three sets of positions with local symmetry C_1 [13]; $RbNO_3$ (437-492°K) and $CsNO_3$ (434°K-T_m) have an unrefined cubic structure [12]. In a melt, the nitrate-ion symmetry is not D_{3h} but more likely C_{2v} or C_s [10, 11]. The selection rules for the SOS region presently of interest (wave numbers larger than ν_3, combination of all tones with ν_3 and ν_1) are simplest in the case of melts. If the nitrate ion is in the symmetry C_{2v}, then the symmetry of the vibrations is as follows: ν_1, (A_1); ν_2 (B_1); ν_3, ν_4 (A_1+B_2); all of them, separately and in combinations, are active in the IR spectrum. The same is true of the C_s structure of the nitrate ion, where ν_1, ν_3, and ν_4 belong to the class A' and ν_2 to A''. In the case of the high-temperature phases $RbNO_3$-III and $CsNO_3$-I, the lack of structural data hinders conformity to the selection rules for melts. For $RbNO_3$-IV and $CsNO_3$-II, all the internal IR tones are active (A and E) and give IR-active binary combinations (A, E, 2A + E); the presence of three sets of ions in the lattice should be borne in mind. Finally, the selection rule for the $NaNO_3$ crystal can be derived most rigorously (Table 1).

In considering all the spectra (see Fig. 2, for example), the regions of the following second-order bands are fairly clearly delimited: (a) $\nu_1+\nu_4$; (b) $\nu_1+\nu_2$, (c) $\nu_3+\nu_4$, or $\nu_2+\nu_3$, or $2\nu_1$; (d) $\nu_1+\nu_3$; (e) $2\nu_3$; in*

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* Line deleted in Russian original – Editor.

TABLE 2. Vibration Frequencies and Anharmonicity Constants of Nitrate Ion in Crystalline and Molten Nitrates

Vibration	$NaNO_3$		$RbNO_3$			$CsNO_3$		
	phase II	liquid	phase IV	phase III	liquid	phase II	phase I	liquid
ν_4	E_g 728 RS E_u 726 IR	721 IR 724 RS	707 IR 721 IR	707 RS [14] 718 IR	705 IR 710 RS	704,5 IR 715,5 IR	704 RS [15] 714 IR	707 IR 703 RS
ν_2	A_{2g} 838 IR A_{2u} 838	827 IR	837 IR	832 IR	829 IR	836 IR	832 IR	828 IR
ν_1	A_{1g} 1071 RS A_{1u} 1056	1056 RS	1057 IR	1052 RS	1045 RS	1047,8 IR 1050,4 IR	1050 RS	1043 RS
ν_3	E_g 1387 RS	1355 RS	1348 RS [14]	1340 RS [14]	1340 RS [14]	1348(*E*) RS [15] 1383(*A*) RS [15]	1340 RS [15]	1330 RS [15]
	E_u 1387 [16]	1445 RS	1420 RS [14]	1407 RS [14]	1405 RS [14]	1396(*A*) RS 1410(*E*) RS [15]	1400 RS [15]	1400 RS [15]
$\nu_1+\nu_4$	1787	1770	1760 1774	1757	1750	1753 1763	1751	1741
$\nu_1+\nu_2$	1899	1880	1892	1882	1875	1883	1878	1872
$\nu_3+\nu_4$	2101	2082	2060 2108	2058	2055	2047	2041	2035
$\nu_1+\nu_3$	2440	2421	2395	2392	2380	2382	2383	2365
$2\nu_3$	2762 2849	2790	2777	2743	2740	2736	2736	2730
$\varkappa_{33}$	−12	−10	+9	−5	−5	+8 −5	−4	±0
$\varkappa_{12}$	+5 −10	−3	−2	−2	+1	−1	−4	+1
$\varkappa_{13}$	−3 −8	+10	−10	±0	−5	−11	−7	−8
$\varkappa_{14}$	+3 −10	−5	−4 −3	−4	−2	±0	−3	−7
$\varkappa_{34}$	−14 −9[6]	+5	0	+9 ±0	+8	−2,5	−3 −13	±0

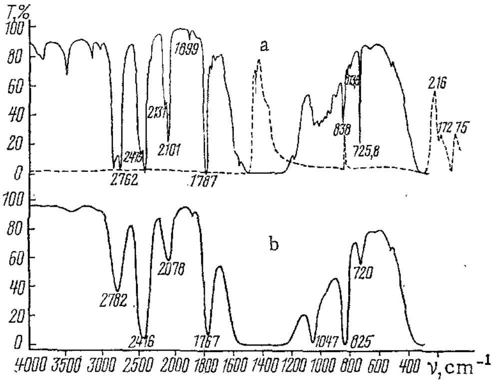

Fig. 2. IR spectra of sodium nitrate in crystalline and molten states; T = 310 (a) and 640°K (b). The dashed curve is the reflection spectrum for T = 310°K.

[1], and also according to the minimum-anharmonicity requirement, i.e., preference is given to the first combination.

The experimental data are given in Table 2. Note that in the case of low-temperature phases of rubidium and cesium nitrate the IR data obtained in the present work are in good agreement with the more accurate Raman data of [13-15]. The AC calculated from these data are shown in Table 2. These were calculated using specially selected and (in our opinion) more accurate literature data on inactive and Raman-active frequencies, and also ν_3. For melts, the calculated values $\nu_1+\nu_4$ are obtained with ν_4 taken as an average of IR and Raman. For $CsNO_3$-II, in finding $2\nu_3$, account was taken only of combinations of the type A × E, assuming that they relate to the vibrations of particles which are in the same position. Finally, where there were several possible calculated values $\nu_i+\nu_j$, $\varkappa_{ij}$ was calculated using min $(\nu_i+\nu_j)_{calc}$. Regrettably, the trend of AC variation on passing from one material to another or on changing the phase state remains unclear. Nevertheless, on average, for all the obtained results $\varkappa_{ij} < 0$. Adding to these data the values $\varkappa_{11} = -2$, $\varkappa_{22} = -3$, $\varkappa_{44} = -3.5$ cm^{-1} (overtone frequencies taken from [6, 7]) for NaNO$_3$-II and $\varkappa_{22} = -2$ cm^{-1} for CsNO$_3$-II,* it may be concluded that AC of the type $\varkappa_{ii}$ and $\varkappa_{ij}$ have the same effect on the observed frequencies. This conclusion is in good agreement with the calculations based on the IR spectra of a nitrate ion isolated in alkali-halide matrices [17].

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*In calculating this quantity, the data of [2] were used, but the 3-cm^{-1} shift of all the frequencies in [2] with respect to the more accurate data of [11, 13, 15, 16] was taken into account.