STUDIES OF OPTICAL ACTIVITY IN THE REGION OF VIBRATIONAL TRANSITIONS

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Abstract

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STUDIES OF OPTICAL ACTIVITY IN THE REGION OF VIBRATIONAL TRANSITIONS

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Optical activity (o.a.) in the region of vibrational transitions has until now been studied neither theoretically nor experimentally. At the same time, the very possibility of its occurrence is hardly in doubt. This also applies to that special type of activity which arises only in the crystalline state. In this region only quartz has been investigated (^{1}), the results for which proved doubtful (^{2}), and $NiSO_4$ (^{3}). O.a. in the IR region was observed for Te (^{4}) and Se (^{5}), but here, evidently, electronic transitions between bands are involved.

As for the theory of the question, we note that as early as (^{6}), from classical considerations, a suggestion was made concerning the contribution to o.a. made by vibrational transitions; one could only expect this contribution to be small because of the small oscillator strengths. The absence in this region of magnetic-dipole transitions is not an obstacle to the occurrence of o.a. (^{7}); in (^{8}) it was shown that neglect of magnetic interactions in the theory leads only to a change in numerical coefficients.

We have carried out measurements of the dispersion of rotation in the region under discussion for three crystals of dithionates: $SrS_2O_6 \cdot 4H_2O$, $CaS_2O_6 \cdot 4H_2O$, $K_2S_2O_6$ (symmetry classes respectively D_6^2, D_6^2, D_3^3). Their dispersions in the region 0.22–0.80 μ had previously been measured by one of us (^{9}). The results are shown in Figs. 1 and 2.

The data represent averages for 6 crystals of different thicknesses over 10 series of measurements for each. The thicknesses were chosen so that, for any wavelength, the smallest transmission was not less than 30–40%.

The measurements were made on the apparatus (^{10}) with an IKS-11 monochromator and a cooled InSb resistor. Particular attention was paid to monitoring scattered light and the so-called "false rotation" (^{11}). Our photoresistors are only weakly sensitive to radiation with $\lambda < 0.8\,\mu$; however, for control, measurements were made with a double DMR-4 monochromator with Si filters (transmission $> 1.5\,\mu$), SZS and ZS-6 (transmission $1 < \lambda < 2.5\,\mu$); the results agreed thanks

Figure 1. Rotatory dispersion of dithionate crystals at 77°K (a) and at 300°K (b) (—correction for slit width)

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Figure 2. Absorption spectrogram at 290°K for $SrS_2O_6 \cdot 4H_2O$ (1) and $CaS_2O_6 \cdot 4H_2O$ (2)

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to special measures against scattered light (^{10}). For further control of the influence of scattering and of some small nonlinearities possible in the amplification circuit, a specimen was measured consisting of a standard quartz plate of the All-Union Research Institute of Metrology and a cuvette with water, matched in thickness so that the absorption in the region studied was approximately equal to the absorption of the dithionate, using the data of (^{12}).

In the region of the rotation maxima, a correction was introduced for the slit width, determined by known theoretical and experimental methods. When the slit width was decreased, the rotation increased somewhat, whereas with "false rotation" the behavior would have been the opposite.

In our opinion, the observed o.a. bands should be attributed to water of crystallization (in $K_2S_2O_6$ they are completely absent in absorption; the intrinsic absorption of dithionates begins at $\lambda > 8\,\mu$). It is known (^{13}) that water has absorption bands in this region—the strongest of them are···

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in their vapors lie approximately at 1.5 and 2 μ and are, according to (13), overtones of $\nu_2 + \nu_3$ and $2\nu_2 + \nu_1$. For water of crystallization, the position of the bands in different crystals varies greatly.

The appearance of optical activity in the absorption bands of molecules that do not possess intramolecular optical activity, but are arranged in a definite manner (for example, along helices of polymer chains), has already been noted in the literature (^{14,15}) and seems natural; however, for water of crystallization this had not previously been observed.

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