

## VIBRONIC SPECTRA OF EUROPIUM NITRATE HEXAHYDRATE

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In a previous work we reviewed briefly the factors influencing vibronic spectra of lanthanide compounds [1]. In the present work the origin of bands related to low-frequency metal-ligand vibrations is analyzed, and the origin of the fine structure of bands related to inner vibrations of the molecular anion in vibronic excitation spectra of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  is also considered. Previously published vibronic excitation spectra of the compound were measured with low resolution [2, 3] and also with high resolution but in a narrow spectral range when samples were excited by a rhodamine 6G laser [4]. Vibronic luminescence spectra have been published as well [5-7]. The quantum yield of luminescence of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  is low because of quenching by water molecules. The existence of lanthanide nitrates with different hydrate numbers hinders preparation of compounds that are isostructural over the lanthanide series [8] although investigation of them is desirable for justification of the approach to interpretation of the vibronic spectra [9]. Therefore, spectra of lanthanide nitrates activated by europium with heterocyclic diimines,  $\alpha, \alpha'$ -dipyridyl  $\text{Ln}(\text{NO}_3)_3 \cdot \text{dip}_2$  and *o*-phenanthroline  $\text{Ln}(\text{NO}_3)_3 \cdot \text{phen}_2$ , which are isostructural over the whole lanthanide series, including yttrium, and have a high quantum yield of luminescence, are taken for comparison in this work, as previously [5, 6]. These compounds and europium nitrate hexahydrate have the same coordination number, equal to ten, and the same structure of the metal coordination polyhedron [10].

The crystal structure of europium nitrate hexahydrate is the same as that of praseodymium nitrate hexahydrate [11, 12] and is centrosymmetric (spatial group  $C_i^1$ ) with two formula units in an elementary cell. <sup>1</sup>The compound consists of discrete  $\text{Eu}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  groups and isolated water molecules [11-14]. All water molecules are linked with each other by hydrogen bonds. The lanthanide ion polyhedron is a dodecahedron with bifurcated vertexes formed by four oxygen atoms of water molecules and six oxygen atoms of three bidentately bound nitrate groups. The position symmetry of all atoms of the compound under consideration is  $C_1$  [15].

**Methods and Objects of Investigation.** Isotopic substitution was widely used in [1, 4, 5, 9] for identification of vibronic satellites. Regions of water molecule vibrations were also determined using dehydration, i.e., through comparison of spectra of the compounds  $\text{Eu}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ , where  $n = 0, 1, 2, 4, 6$ . Detailed interpretation of the vibronic luminescence spectrum is hindered by overlapping vibronic wings of various  $^5D_0 - ^7F_j$  vibronic transitions and also comparatively intense transitions from the  $^5D_1$  level. Overlap of vibronic satellites of a transition, e.g.,  $^5D_0 - ^7F_0$ , with the region of zero-phonon lines region of another, e.g.,  $^5D_0 - ^7F_1$  or  $^5D_0 - ^7F_2$ , can lead to "anomalous" growth of the intensity of the of the aforementioned vibronic satellites which is due to intensity borrowing [1, 16]. Therefore, excitation spectra are suitable for studying the structure of vibronic bands.

Luminescence excitation spectra of both  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{D}_2\text{O}$  were measured with a resolution of  $\sim 0.1$  nm in the region of the  $^7F_0 - ^5D_0$ ,  $^5D_1$ ,  $^5D_2$  transitions. In addition, vibronic excitation spectrum

<sup>1</sup>V. B. Kravchenko established that europium nitrate hexahydrate and praseodymium nitrate hexahydrate are isostructural.

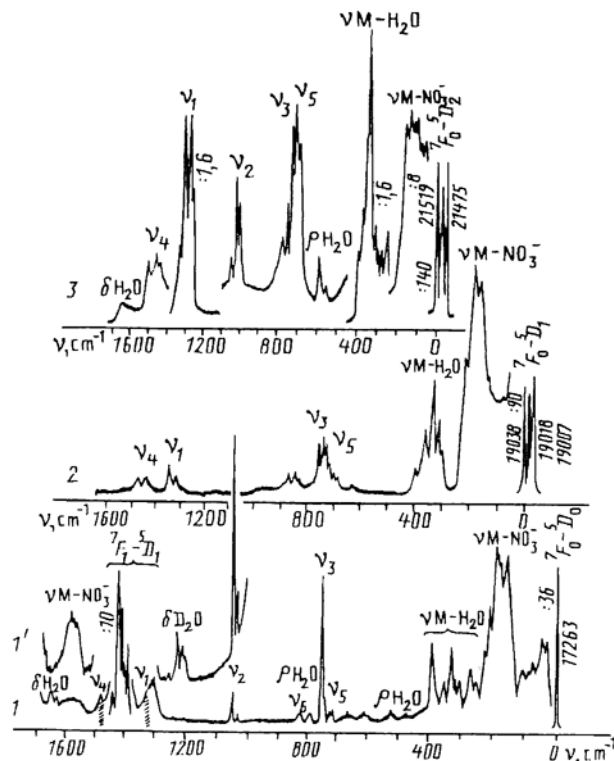


Fig. 1. Vibronic spectra of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in the region of the  ${}^7F_0-{}^5D_0$  (1),  ${}^7F_0-{}^5D_1$  (2),  ${}^7F_0-{}^5D_2$  (3) transitions and a fragment of the vibronic spectrum of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{D}_2\text{O}$  (1') at 77 K. Factors written on the spectra are the reduction in luminescence intensity upon placing neutral filters at the setup input.

of  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{D}_2\text{O}$  is analyzed in the region of the  ${}^7F_6-{}^5D_4$  transition. The spectra were measured at 77 K. A DkSSH-500 lamp or a filament lamp were used as an excitation source. A DFS-12 spectrophotometer was used to scan the luminescence excitation wavelength. The spectra were measured in the region of  ${}^5D_0-{}^7F_J$  ( $\text{Eu}^{3+}$ ) and  ${}^5D_4-{}^7F_J$  ( $\text{Tb}^{3+}$ ) transitions. The spectra were digitized using a computer with a digitizer. IR spectra were measured on IFS-113v and UR-20 spectrophotometers at 77 and 300 K.

At low temperatures, when the probability of population of the  ${}^7F_1$  level is low, there are no overlapping vibronic wings of various electronic transitions in the excitation spectra. However, the low quantum yield of the luminescence prevents measurement of high-resolution spectra of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  at 4.2 K. At 77 K the overlap of the zero-phonon transition  ${}^7F_1-{}^5D_1$  on the high-frequency portion of the vibronic wing of the  ${}^7F_0-{}^5D_0$  transition, including valence vibration bands  $\nu_1$  and  $\nu_4$  of the nitrate group, is substantial. The intensity of the latter bands was determined by evaluating the population of the Stark components of the  ${}^7F_1$  level at 77 K from the intensity distribution in the  ${}^7F_1-{}^5D_0$  transition. The intensity of vibronic satellites of the  ${}^7F_1-{}^5D_1$  transition, which can overlap the vibronic wing of the  ${}^7F_0-{}^5D_1$  magnetic dipole transition, is estimated to be an order of magnitude lower than the intensity of the wing. Therefore, they do not occur in the spectrum of the compound under investigation or in spectra of other nitrates, e.g., with dimethylsulfoxide,  $\text{Eu}(\text{NO}_3)_3 \cdot 4\text{DMSO}$ , and trimethylphosphine oxide,  $\text{Eu}(\text{NO}_3)_3 \cdot 2\text{TMPO}$ . For  $\text{Eu}(\text{NO}_3)_3 \cdot 2\text{TMPO}$ , having a high quantum yield of luminescence, the spectra of the vibronic wing of the  ${}^7F_0-{}^5D_1$  transition measured at 77 and 4.2 K were the same. We did not analyze the excitation spectra at 300 K because of overlapping intense lines of transitions from the  ${}^7F_2$  level.

**Metal-Ligand Vibrations and Justification of Use of a Molecular Model.** Figure 1 presents vibronic excitation spectra of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The position of lines in the spectrum and vibration frequencies for all Stark components of electronic transitions are given in Table 1. The bands in the range from 150 to  $400\text{ cm}^{-1}$  belong to metal-ligand vibrations. The relative contribution from vibrations of two types of ligands and the metal to the low-frequency bands



can be determined by means of isotopic substitution and variation of the metal mass. Upon replacement of H<sub>2</sub>O by D<sub>2</sub>O in Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O the bands in the range from 250 to 400 cm<sup>-1</sup> are shifted by 5-15 cm<sup>-1</sup> while the other low-frequency bands do not change their position [4], which makes it possible to assign them primarily to M–O(H<sub>2</sub>O) translational vibrations. These bands disappear upon dehydration of the compound. The bands in the range from 150 to 230 cm<sup>-1</sup>, which are not shifted upon deuteration and do not disappear upon dehydration, belong to M–O(NO<sub>3</sub><sup>-</sup>) vibrations. The slight change in reduced mass of the nitrate group upon replacement of <sup>14</sup>N with <sup>15</sup>N, leading to a negligible frequency change, precludes identification of the vibration bands by isotopic substitution.

We had no available samples of isostructural lanthanide and yttrium nitrate hexahydrates to identify bands with various contributions of motion of the metal, as was done, e.g., for lanthanide nitrates with heterocyclic diimines [9]. For example, upon passing from europium to yttrium, whose mass is much lower than that of europium, the bands 199, 220 cm<sup>-1</sup> are shifted to 222, 244 cm<sup>-1</sup> for the dipyriddy compounds and the band at 213 cm<sup>-1</sup> is shifted to 248 cm<sup>-1</sup> for phenanthroline compounds, which attests to the maximum contribution of motion of the metal to these vibrations. Replacing H-dipyriddy with D-dipyriddy demonstrates that the contribution of dipyriddy molecules to the 199, 220 cm<sup>-1</sup> vibrations is small. This makes it possible to assign these bands primarily to M–O(NO<sub>3</sub><sup>-</sup>) vibrations. The bond of NO<sub>3</sub><sup>-</sup> with the metal in Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O is of lower strength, which can be inferred from the frequency difference  $\nu_4 - \nu_1$  for the inner nitrate group vibrations [17, 18]. Consequently, the M–O(NO<sub>3</sub><sup>-</sup>) frequencies in this compound should be somewhat lower than those in compounds with heterocyclic diimines. As mentioned above, these are the lines grouped in the range of 150-230 cm<sup>-1</sup>, which include intense bands at 155, 190 cm<sup>-1</sup> and weaker bands at 207, 229 cm<sup>-1</sup> in the vibronic wing of the <sup>7</sup>F<sub>0</sub>–<sup>5</sup>D<sub>0</sub> transition.

Earlier [7] it was shown that upon increasing the temperature from 77 to 300 K the character of the Stark splitting of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O electronic transitions changes in the range from 200 to 280 K.<sup>2</sup> The electronic spectrum of the hexahydrate becomes similar to that of Eu(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O, having a weak temperature dependence, which attests to the similarity of the lanthanide ion shell symmetry in both nitrates. It is assumed that the weakening of the hydrogen bond skeleton in heating europium nitrate hexahydrate leads to free rotation of two water molecules of the outer sphere, which is the origin of partial averaging of the crystal field. The small difference in the structure of the metal polyhedrons in Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Eu(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O, leading to similarity of the vibronic [4] and IR spectra (Fig. 2) of these compounds in the low-frequency region, makes it possible to use longwave IR spectra of Eu(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O and Y(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O nitrates to identify bands of vibrations with a maximum contribution of motion of the metal. Among these are the intense bands in the range of 150-230 cm<sup>-1</sup> in IR spectra of Eu(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O and Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, which are shifted into the high-frequency region to 180-245 cm<sup>-1</sup> upon passing to Y(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O. Motion of the metal contributes little to M–O(H<sub>2</sub>O) translational vibrations.

Therefore, the frequencies of M–O(NO<sub>3</sub><sup>-</sup>) translational vibrations in spectra of europium nitrate hydrates and europium nitrates with heterocyclic diimines lie in the range from 150 to 230 cm<sup>-1</sup>. Metal-second-ligand vibrations of these two groups of compounds have, respectively, higher and lower frequencies relative to the M–O(NO<sub>3</sub><sup>-</sup>) frequency region. This is mainly due to inversion of the reduced mass ratio of the ligands as well as the character and magnitude of forces leading to formation of the crystalline lattice.

The different nature of the IR and vibronic spectra leads to different behavior of their bands upon variation of the metal mass for narrow-zone and wide-zone compounds [9]. IR spectra reflect directly the crystal lattice dynamics, whereas in vibronic spectra the lattice dynamics manifests itself through the luminescence of the impurity center. In IR spectra of compounds with a molecular structure that have narrow phonon zones, a dependence of the metal-ligand band position on the metal mass is observed, as, for instance, in Fig. 2. In contrast in vibronic spectra of the corresponding compounds activated with europium the position is constant. This fact attests to the weak interaction of adjoining molecules, which permits application of the molecular model to analysis of vibronic spectra of such compounds as europium nitrate hexahydrate. Apparently, Davydov splitting should not occur in vibronic spectra of compounds with a molecular structure. However, in IR spectra of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O measured with a

<sup>2</sup>An anomalous change in the conductivity of Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O crystals was also detected in the temperature range from 223 to 273 K [19].

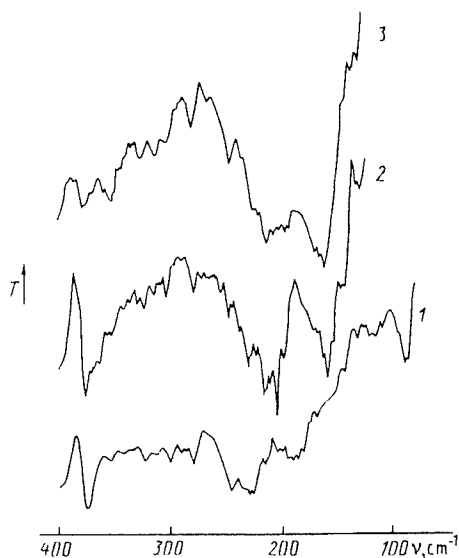


Fig. 2. Longwave IR spectra of  $\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  (1),  $\text{Eu}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  (2),  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (3) at 300 K.

resolution of approximately  $5 \text{ cm}^{-1}$  the splitting was also not observed. In particular, features characterizing variable dynamic interaction did not occur in IR spectra upon dilution of europium nitrate hexahydrate with the corresponding deuterated compound [15].

Within the framework of the molecular model one can limit consideration to one "molecule" consisting of the  $\text{Eu}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  complex and two isolated water molecules. Two water molecules of the outer sphere should not be neglected because they can contribute to the vibronic spectrum. We have shown that vibrations of anion of the outer coordination sphere of compounds such as  $[\text{Eu}(\text{AP})_6]\text{X}_3$  (AP is antipirin,  $\text{X}=\text{ClO}_4^-$ ,  $\text{BrO}_4^-$ ),  $[\text{Eu}(\text{HMPA})_6](\text{ClO}_4)_3$  (HMPA is hexamethylphosphortriamide), and  $[\text{Eu}(\text{H}_2\text{O})_9](\text{BrO}_3)_3$  occur in the vibronic spectrum. The erroneous statement of [9] was made because the vibration band intensity of units of the outer sphere is determined by several factors, in particular, by the nature of the electronic transition, and is not always sufficiently high.

**Inner Vibrations of Ligands.** In the high-frequency region of the vibronic spectrum (Fig. 1) splitting of inner vibration bands of nitrate groups and bands of water molecules is observed. In particular, deformation vibration  $\nu_3$  and the stretching vibration  $\nu_2$  of  $\text{NO}_3^-$  are split into two components, and deformation vibration  $\delta$  of  $\text{H}_2\text{O}$  into three components. These splittings are observed in IR spectra at 77 and 300 K as well (Fig. 3). An increase in temperature leads only to broadening and a low-frequency shift of librational vibrations  $\rho$  of  $\text{H}_2\text{O}$ . As noted above, the splitting should not be connected with dynamic interaction. In heavy metal compounds the probability of interaction of ligands in one "molecule" is also low because of the weak kinematic coupling between them. Therefore, the splitting should be caused by overlap of vibration bands of inequivalent nitrate groups and different molecules of water. The presence of the inequivalence is supported by x-ray data.

Let us compare results of group-theoretic analysis of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  vibrations in the "molecule" and "solid" approximations. It is known that the isolated planar trigonal anion  $\text{NO}_3^-$  has symmetry  $D_{3h}$  [20]. In most lanthanide compounds it is coordinated as a bidentate and its symmetry is  $C_{2v}$  and lower. Let give correlation relations for the types of symmetry of vibrations of the isolated nitrate groups and its position symmetry and factor-group in  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ :

	$D_{3h}$		$C_1$	$C_i$
$\nu_1$	1050	$A_1'$	$\nu_2$ 1050	$A$ $A_g + A_u$
$\nu_2$	830	$A_2''$	$\nu_6$ 830	$A$ $A_g + A_u$
$\nu_3$	1380	$E'$	$\nu_1$ 1300	$A$ $2A_g + 2A_u$
			$\nu_4$ 1470	$A$
$\nu_4$	725	$E'$	$\nu_5$ 710	$A$ $2A_g + 2A_u$
			$\nu_3$ 740	$A$

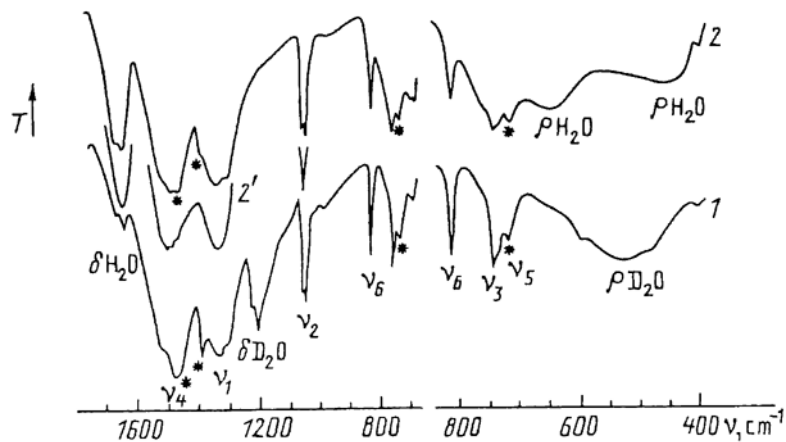


Fig. 3. IR spectra of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{D}_2\text{O}$  (1),  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (2, 2'). The samples were prepared with vaseline oil (1, 2) and hexachlorobutadiene (2'). Asterisks denote bands of vaseline oil.

The  $\text{Eu}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  molecule has 75 vibrations, 6 of which are outer vibrations of the whole molecule. The four coordinated water molecules have 12 inner and 24 "outer" vibrations (displacement relative to the nitrate groups and the metal). Two isolated water molecules have 6 more inner and 12 more outer vibrations. Six water molecules have 18 inner vibrations. Each of the three  $\text{NO}_3^-$  has 6 inner and 6 "outer" vibrations. The total number of inner vibrations of nitrate groups in the spectrum is equal to 18. Each inner vibration belonging to  $\text{NO}_3^-$  has three components, each inner vibration of coordinated water has four components, and of noncoordinated water two components.

When  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  is considered as a solid, each inner vibration of a nitrate group and a water molecule is to be split into  $3A_g + 3A_u$ - and  $6A_g + 6A_u$ -components, respectively. Owing to the alternative exclusion the  $3A_g$ - and  $6A_g$ -components should occur in Raman spectra, and the  $3A_u$  and  $6A_u$  components in IR spectra.

Therefore, in the first case the vibronic spectrum should contain three components ( $3A$ ) of each inner vibration of  $\text{NO}_3^-$  and six components of water vibrations. In the second case the number of the components of both types can be doubled. Analysis of the vibronic spectrum in the approximation of the molecular model makes it possible to explain why the number of components in the vibronic and IR spectra is the same.

Splitting of vibrations  $\nu_3$  and  $\nu_2$  into two components of different intensity apparently reflects the different activity of the three components of  $\text{NO}_3^-$  vibrations in the vibronic wing of the singlet electronic transition, which attests to different distortion of the three  $\text{NO}_3^-$  with symmetry  $C_1$ . In vibronic spectra of  $\text{Eu}(\text{NO}_3)_3 \cdot 2\text{TMPO}$  and  $\text{Eu}(\text{NO}_3)_3 \cdot 3\text{TBP}$  (TBP is tributylphosphate) [1], where the  $\text{Eu}^{3+}$  ion is situated on the fourth-order axis, there is one component of each of the vibrations  $\nu_5$ ,  $\nu_3$  and  $\nu_2$ , which attests to equivalence of nitrate groups without interaction between them.

When  $\text{Eu}^{3+}$  ion has position symmetry  $C_1$ , the Stark components of each electronic level have the symmetry  $A$ . Analysis of the vibronic spectrum in the region of the  ${}^7F_0 - {}^6D_2$  transition of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  shows that the intensity of vibronic satellites belonging to a certain vibration component and associated with different Stark components of the electronic transition are somewhat different. This can attest to a symmetry higher than  $C_1$  for the charge distribution about the  $\text{Eu}^{3+}$  ion. In [6] it has been noted that this symmetry is close to  $C_{1h}$ . In vibronic spectra of high-symmetry nitrates [1] the influence of symmetry selection rules on the intensity distribution of vibration bands of the nitrate group is more pronounced.

Deformation vibrations of water have the following frequencies in the vibronic and IR spectra:  $1630, 1650 \text{ cm}^{-1}$  -  $\delta \text{H}_2\text{O}$ ;  $1200, 1210, 1225 \text{ cm}^{-1}$  -  $\delta \text{D}_2\text{O}$ . Coincidence of the vibronic and IR spectra frequencies apparently attests to the appearance of two types of water molecules in the vibronic spectrum. The first is coordinated to the metal ion and the second is from the outer sphere, and they have different bond strengths. A low-frequency doublet is associated with the more strongly bound water molecules coordinated by the metal ion.

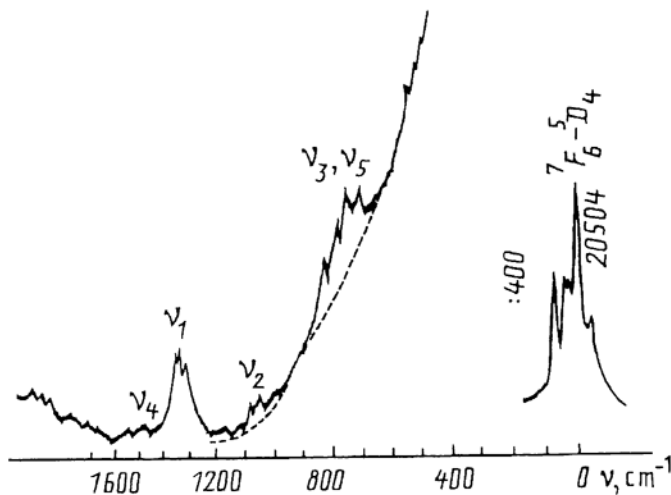


Fig. 4. Vibronic spectrum of  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{D}_2\text{O}$  in the region of the  ${}^7F_6 - {}^5D_4$  transition at 77 K.

In the vibronic wings of the  ${}^7F_0 - {}^5D_0$ ,  ${}^5D_1$  transitions the difference in integral intensities of vibration bands  $\nu_5$  and  $\nu_3$  is greater than that of vibration bands  $\nu_1$  and  $\nu_4$ . In contrast, in the vibronic wing of the  ${}^7F_0 - {}^5D_0$  transition the integral intensities of vibration bands  $\nu_5$  and  $\nu_3$  are close, but  $\nu_1$  band is much more intense than  $\nu_4$ . This intensity distribution is observed not only in vibronic excitation spectra of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  but also in excitation and luminescence (the  ${}^5D_0 - {}^7F_2$  transition) spectra of other nitrates of interest [1, 21], and is independent of the structure of the compound. This attests to the effect of the nature of the electronic transition (selection rules for  $J$ ) [22]. This factor is obviously more significant than the symmetry selection rules. A high intensity for band  $\nu_1$  relative to  $\nu_4$  is observed in the spectra of other lanthanide nitrates, e.g.,  $\text{Tb}^{3+}$  (the  ${}^7F_6 - {}^5D_4$  transition) (Fig. 4). The aforementioned transitions in the spectra of europium ( ${}^7F_0 - {}^5D_2$ ,  ${}^5D_0 - {}^7F_2$ ) and terbium ( ${}^7F_6 - {}^5D_4$ ) nitrates are electric dipole ones with  $\Delta J = 2$ .

Therefore, as a result of analyzing vibronic spectra of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and some other nitrates it has been shown that metal-ligand vibrations belonging to  $\text{NO}_3^-$  groups and water molecules have frequencies of  $150\text{--}230\text{ cm}^{-1}$  and  $250\text{--}400\text{ cm}^{-1}$ , respectively. Motion of the metal contributes mostly to the same low-frequency vibrations as  $\text{NO}_3^-$ . The fine structure of the inner vibration bands of  $\text{NO}_3^-$  and  $\text{H}_2\text{O}$  is due to inequivalence of these units. It has been demonstrated that the symmetry selection rules influence weakly the intensity distribution in the vibronic spectra compared to the effect of the nature of the electronic transition.

The results obtained justify the choice of a small structure unit that includes the metal ion and one  $\text{NO}_3^-$  group for modeling the vibronic spectrum [23]. A similar one-ligand model can apparently be used to calculate vibronic spectra of europium  $\beta$ -diketonates [24].

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