66. Vibrational Spectra of Anhydrous Lanthanum, Europium, Gadolinium, and Dysprosium Nitrates and Oxinitrates

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Summary

IR. and *Raman* spectra of $LnONO_3$ (50-4,000 cm^{-1}, Ln = La, Gd, Eu, and Dy) are reported and discussed. The low frequency region of the spectra reflects the cubic structure of these compounds. The dimensions of the cubic unit cells determined by X-Ray powder diagrams are: 12.81 ± 0.05 Å for $EuONO_3$, 12.69 ± 0.05 Å for $GdONO_3$, and 12.67 ± 0.05 Å for $DyONO_3$. The vibrational frequencies of the nitrato group are consistent with a bidentate nitrate of C_{2v} symmetry. The synthesis of anhydrous $Ln(NO_3)_3$ (Ln = La, Gd, Eu, and Dy) by dehydration of the corresponding penta- or hexahydrates is described. The IR. and *Raman* spectra (50-4,000 cm^{-1}) are analysed. Splitting of the bands point to a complex structure of these compounds. All six vibrational modes of the nitrato group are observed and the data are again consistent with bidentate NO_3^- moïeties. Finally, an analytical control of the purity of $Ln(NO_3)_3$ is suggested.

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1. Introduction. - We are currently investigating the solvation of lanthanide nitrates in nonaqueous solvents using both luminescence and vibrational spectroscopies. The assignment of the vibrational modes of anhydrous $Ln(NO_3)_3$ is not established with certainty in the literature and the *Raman* frequencies have not been reported. In this communication we thus present the results of a detailed study of the IR. and *Raman* spectra of the anhydrous lanthanide nitrates relevant to our solvation investigation, that is of $La(NO_3)_3$, $Eu(NO_3)_3$, $Gd(NO_3)_3$, and $Dy(NO_3)_3$. To assist the assignment of the vibrational modes we first report and discuss thoroughly the IR. and *Raman* spectra of the corresponding oxinitrates $LnONO_3$. Finally, a purity criterion for the anhydrous lanthanide nitrates is suggested.

2. Experimental. - 2.1 *Synthesis of the lanthanide oxinitrates.* The oxinitrates were obtained by thermal decomposition in an open vessel of the penta- or hexahydrated nitrates at 350-450° during 10-20 h [1] [2].

2.2 *Synthesis of anhydrous lanthanide nitrates.* 5 mmol of Ln_2O_3 (99.99%, *Glucydur*) were slowly dissolved in 28-29 mmol of concentrated nitric acid (analytical grade, *Merck*). The mixture was heated

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to 40-50° and stirred for 1-2 h. The excess of oxide was filtered off and the solution was evaporated to dryness. The nitrate was dried over KOH and then heated *in vacuo* (10^{-2} Torr) to *ca.* 80° for 1-3 days. The resulting product contained between 0.5 and 1.5 mol of H_2O per formula weight. This partially dehydrated nitrate was thoroughly ground and put into a pyrex tube attached to a vacuum line. When the pressure reached 10^{-5} Torr the sample was heated to 80° and kept at this temperature until the vacuum dropped below 10^{-5} Torr; this operation was repeated with heating temperatures of *ca.* 140, 180, and 200° (Ln = Eu, Gd, Dy, resp.) or 220° (Ln = La). When the final pressure reached $5 \cdot 10^{-6}$ Torr the pyrex tube was sealed off. This experimental procedure avoided manipulation of the very hygroscopic anhydrous nitrates. Nitrates of the lighter rare earths (La, Eu, Gd) were obtained in high purity after 2-3 days while $Dy(NO_3)_3$ required a longer dehydration time and was more easily contaminated with traces of oxinitrate.

2.3 *Chemical analysis.* The rare earth ion was determined by complexometric titration with EDTA (Titriplex III, *Merck*) in the presence of urotropine and xylene orange, and nitrogen by the *Kjeldahl* method. Values in % found for $Ln(NO_3)_3$: La 43.02 (calc. 42.75), N 13.08 (12.93); Eu 44.78 (44.96), N 12.43 (12.33); Gd 45.71 (45.81), N 12.12 (12.24); for $LnONO_3$: La 63.72 (64.04), N 6.52 (6.46); Eu 66.33 (66.08), N 6.14 (6.09); Gd 66.51 (66.84), N 5.88 (5.95); Dy 67.42 (67.57), N 5.78 (5.82). For $Dy(NO_3)_3$ only the N/Ln ratio was determined which was 2.980. However, the IR. spectra of all compounds confirmed the absence of water (no absorption at *ca.* 3,500 cm^{-1}).

2.4 *Spectroscopic measurements.* IR. spectra (4,000-250 cm^{-1}) were recorded as Nujol *(Fluka)* and C_4Cl_6 *(Merck)* mulls on a *Perkin-Elmer* 577 spectrometer (4,000-400 cm^{-1}: KBr windows; 400-250 cm^{-1}: polyethylene windows). Far IR. measurements for $Eu(NO_3)_3$ and $EuONO_3$ were performed with a *Bruker* IFS 113c *Fourier*-IR. spectrometer. *Raman* spectra of the finely powdered samples were obtained using a *Spex* Ramalog-4 spectrometer (excitation: Ar laser 514 nm (500 mW) or Kr laser 647 nm (250-300 mW). Sample preparation was conducted under strictly anhydrous atmosphere (*Lab-Con-Co* glove box, < 30 ppm H_2O).

X-Ray powder diagrams of the oxinitrates were recorded on a *Ital-Structures* spectrometer using the Cu K_a line.

3. Vibrational spectra of the oxinitrates.

– The IR. and *Raman* data for the studied oxinitrates are reported in *Tables 1* and *2*, and part of their *Raman* spectra is shown in *Figure 1.*

(i) The 50-600 cm^{-1} region of the spectra consists of lanthanide-oxygen and lattice vibrations [3]. The two (three in case of $LaONO_3$) *Raman* bands above 250 cm^{-1} appear at frequencies different from the four main IR. absorptions, which means that the *Raman* active modes are IR. inactive and *vice versa.* This rather simple situation, combined with the low number of observed transitions, implies that the unit cell of $LnONO_3$ possesses a high symmetry. The vibrations of the 250-600 cm^{-1} spectral range show a marked frequency shift towards higher wavenumbers with increasing atomic number of Ln. A similar situation is met with the cubic rare earth sesquioxides (Ln = Eu-Yb) and the observed shift has been correlated with the decrease in the Ln–O bond length [4] [5]. The more energetic vibration on the absorption region between 550 and 600 cm^{-1}, is typical of the cubic structure of the oxides: it is for instance absent in the IR. spectrum of La_2O_3 which is known to have a hexagonal structure [5] [6]. The presence of a band between 535 and 581 cm^{-1} in the IR. spectrum of the studied oxinitrates is thus consistent with the cubic structure of $LaONO_3$ [7] and it further suggests a similar structure for $EuONO_3$, $GdONO_3$, and $DyONO_3$. This suggestion is supported by the similarity of the *Raman* spectra in the range 60-190 cm^{-1} (see *Fig. 1*), and to check it further we have recorded the X-Ray powder diagrams of the oxinitrates (see *Fig. 2*). The cubic unit cell of $LaONO_3$ is found to have a size of 9.22 ± 0.02 Å, in excellent agreement with the published data of *Daire & Lehuede* [7]: 9.24 Å.

Table 1. *Observed IR. and* Raman *Frequencies of the Lattice and Lanthanide-Oxygen Vibrations for* $LnONO_3$ [cm^{-1}][a])

Ln	Lattice and lanthanide-oxygen vibrations												
La	[b])						265		315		347		535
		62		*115sh*	*144*	*178*		*287*		*326*		*437*	
		70sh		*120*	*154sh*	*192*							
						225							
Eu	72		98	119		186	282sh		349		365sh		567
							298sh				392		
							311						
		80		*126*	*144*	*186*				*353*		*492*	
		90				*208*							
						225sh							
Gd	[b])						285sh		365		380sh		574
							308sh				405		
							319						
		80		*115*	*143*	*186*				*370*		*515*	
		90		*126*		*210*							
						226sh							
Dy	[b])						310sh		373sh		417sh		581
							331		380		422		
		85		*115*	*143*	*184*							
				126		*210*				*380*		*535*	

[a]) Numbers are averages of 3-5 determinations on independent samples; sh denotes a shoulder; underlined numbers denote the strongest component of a multiplet; numbers in italic are *Raman* frequencies. [b]) IR. spectrum not measured below 250 cm^{-1}.

Table 2. *Observed IR. and* Raman *Frequencies of the* NO_3^- *Vibrations for* $LnONO_3$ [cm^{-1}][a])

Ln	$\nu_5(B_2)$[b])		$\nu_6(B_1)$[b,c])		$\nu_3(A_1)$[d])		$\nu_2(A_1)$[e])		$\nu_4(B_2)$		$\nu_1(A)$[e])	
La	689	*678*	711	*708*	821	*817*	1,040	*1,018*	1,219	*1,214*	1,596	*1,530*
			716					*1,036*				*1,577*
								1,068				*1,594*
Eu	675	*673*	717	*714*	822	*818*	1,034	*1,008*	1,202	*1,194*	1,615	*1,554*
	682		721					*1,028*				*1,614*
Gd	673	*671*	718	*712*	822	*818*	1,032	*1,008*	1,200	*1,192*	1,614	*1,556*
	680		720					*1,029*			1,621sh	*1,618*
								1,057				
Dy	675	*671*	718	*715*	824	*816*	1,031	*1,005*	1,197	*1,188*	1,620	*1,560*
	681		721					*1,027*				*1,624*

[a]) Numbers are averages of 3-5 determinations on independent samples; sh denotes a shoulder; assignment is made assuming bidentate C_{2v} nitrato groups: ν_1, ν_2 and ν_4 are stretching modes, ν_3 and ν_5 are bending modes and ν_6 is the out-of-plane rock; numbers in italic are *Raman* frequencies. [b]) For a discussion of the assignment of ν_5 and ν_6, see chap. 5. [c]) Extremely weak IR. absorption. [d]) Extremely weak *Raman* band. [e]) The underlined *Raman* band is very strong; the other components are weak or very weak.

The diagrams for $EuONO_3$, $GdONO_3$, and $DyONO_3$ are almost identical and the observed reflexions may be indexed in the cubic system with the following unit cells: 12.81±0.05 Å ($EuONO_3$), 12.69±0.05 Å ($GdONO_3$), and 12.67±0.05 Å ($DyONO_3$).

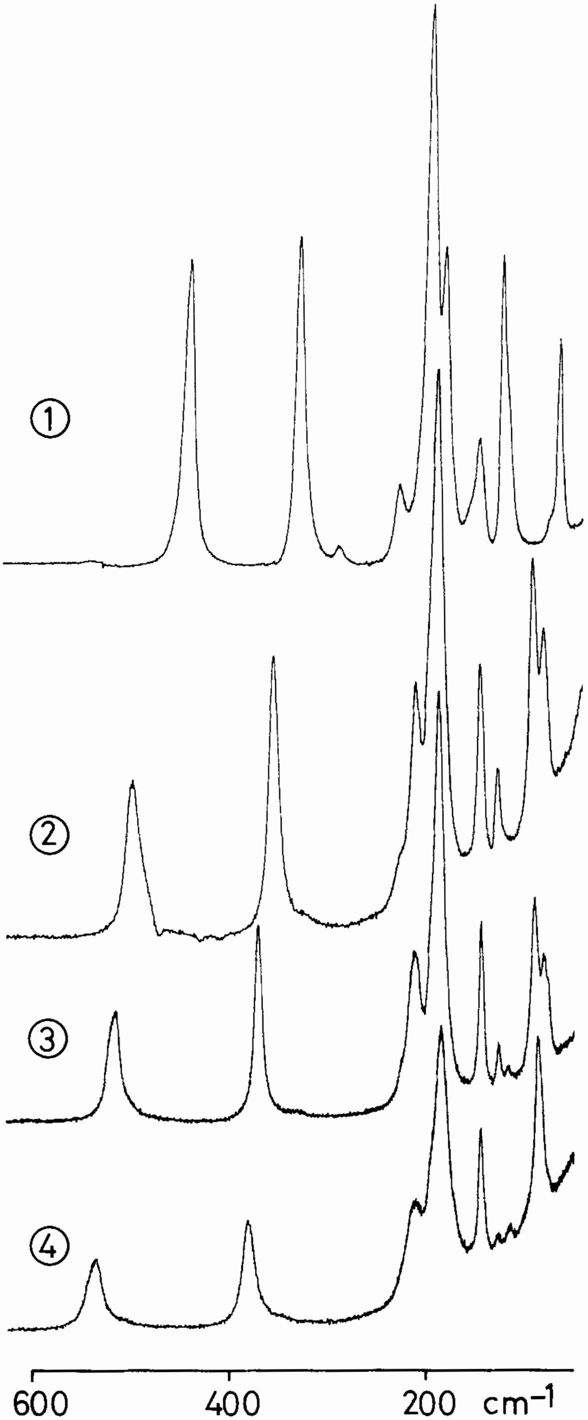

Fig. 1. *50–600 cm^{-1} region of the* Raman *spectra of $LnONO_3$* (1) Ln = La, (2) Eu, (3) Gd, (4) Dy

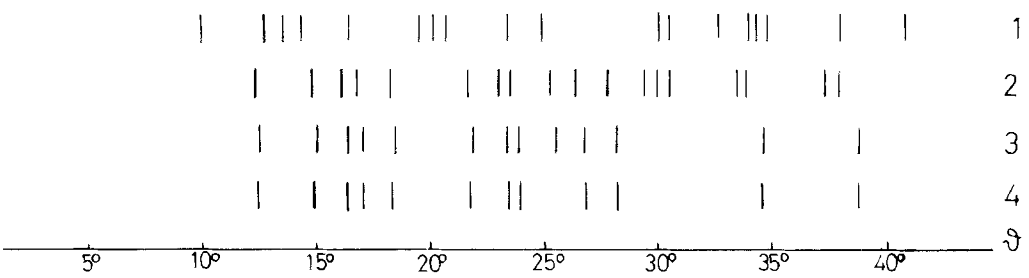

Fig. 2. *X-Ray powder diagrams of* $LnONO_3$ (1) Ln = La, (2) Eu, (3) Gd, (4) Dy

(ii) Coordinated nitrate has a lower local symmetry (C_{2v}, C_s or C_1) than ionic nitrate (D_{3h}), and therefore six vibrational modes are observed in both the IR. and *Raman* spectra (675-1,625 cm^{-1} range). Since the bands show little or no splitting the nitrato groups are probably equivalent in the lattice. The assignment of the six vibrational modes of coordinated NO_3^- to the observed transitions depends on both the local symmetry of the nitrato group and on whether NO_3^- acts as a monodentate, bidentate (or bridging) or even terdentate ligand [3] [9]. Crystal structure determinations [8] have shown that in many rare earth salts and complexes nitrato groups are usually bidentate ligands, and we thus rationalize our data in terms of bidentate NO_3^- groups possessing a local C_{2v} symmetry [3] *(cf. Table 2)*.

(iii) Overtone and summation bands are observed above 1,600 cm^{-1}. They correspond to the following symmetry allowed combinations. The sharp IR. absorption at 1,640 cm^{-1} is assigned to $2\nu_3$ (fundamental frequency $\triangleq$ 821-824 cm^{-1}); $2\nu_3$ is also observed in the *Raman* spectra (1,634-1,636 cm^{-1}, fundamental 816-818 cm^{-1}). The other combination bands are assigned as follows: 1,650-1,690 $cm^{-1} \triangleq \nu_4 + \nu(Ln-O)$; 1,700-1,730 $cm^{-1} \triangleq \nu_2 + \nu_5$ and $\nu_2 + \nu_6$; 1,910-1,930 $cm^{-1} \triangleq \nu_4 + \nu_5$; 2,200-2,230 $cm^{-1} \triangleq \nu_2 + \nu_4$.

Patil et al. [2] have reported the IR. spectra (700-1,600 cm^{-1}) of rare earth oxinitrates obtained as intermediates in the thermal decomposition of the nitrates (Ln = La, Pr, Nd, Dy, Yb, and Lu). Their data[2]) are in agreement with the frequencies listed in *Table 2*, except for the region of 1,300-1,600 cm^{-1}. They observe additional absorptions around 1,350 and 1,460 cm^{-1}, and they report a band around 1,600 cm^{-1} only for $LaONO_3$. All the oxinitrates we have studied exhibit a strong and broad band at *ca.* 1,600 cm^{-1}. We have followed the thermal decomposition of $La(NO_3)_3 \cdot 6H_2O$ by IR. spectroscopy in function of both the temperature and the heating time. The two strong and broad nitrate bands at *ca.* 1,335 and 1,460 cm^{-1} disappear on heating and, simultaneously, two similarly shaped bands appear at *ca.* 1,200 and 1,600 cm^{-1}. When heated too long or when overheated (450-500°) the oxinitrate decomposes: the IR. absorption at 1,200 cm^{-1} disappears, the band around 1,600 cm^{-1} becomes less intense and it is shifted to higher wavenumbers, and two fairly sharp bands appear at *ca.* 1,350 and 1,460 cm^{-1}. The chemical analyses after different heating times and the relatively poor horizontal levels observed in thermolysis curves [1] [7] also point to a limited thermal stability of the oxinitrate.

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[2]) *Patil et al.*'s assignment is based on a monodentate nitrate, which leads to an inversion of ν_1 and ν_4 and of ν_3 and ν_6.

4. Vibrational spectra of the anhydrous nitrates. - The IR. spectra of penta- and hexahydrated lanthanide nitrates and their interpretation are well understood [10] [11]; this is not the case for the anhydrous nitrates. Spectra of the latter (100-4,000 cm^{-1}, Ln = Pr-Lu) were first reported by *Walker & Ferraro* [12] who prepared the salts by direct synthesis from the corresponding metals. Their assignment is made assuming a local C_{2v} symmetry for NO_3^-, but these authors have observed only four of the six predicted vibrational modes. *Mironov et al.* [13] have isolated anhydrous europium nitrate by heating the hydrate *in vacuo*. These authors report an IR. spectrum (600-4,000 cm^{-1}) which exhibits six absorption regions; however most of the bands are shifted to higher energy compared to the data of [12]. The IR. and *Raman* data for the four investigated anhydrous nitrates are reported in *Table 3* and a typical IR. spectrum is shown in *Figure 3.*

(i) The lattice vibrations extend only up to 250 cm^{-1}. There is no systematic trend in the overall aspect of this low frequency region, which points to a rather complex structure of the nitrate with probably a mixture of differently bound molecules.

(ii) Six IR. active modes arising from the NO_3^- vibrations are observed and most of them are *Raman* active. The highest possible local symmetry for the nitrato group is again C_{2v}. The measured IR. absorptions are all split into two or more components. The fine structure of the lower frequency bands at *ca.* 1,030, 810 and 760/730 cm^{-1} is in fact very sensitive to the dryness of the nitrates; it disappears when the salts get hydrated. Our data show that the two additional bands reported by *Mironov et al.* [13] for $Eu(NO_3)_3$ at 755 and 725 cm^{-1} indeed belong to the vibrational spectrum of this salt. These bands are sometimes difficult to observe in complexes of lanthanide nitrates [11], but we also see them in the spectra of $Ln(NO_3)_3$ dissolved in anhydrous solvents and in the spectra of the oxinitrates.

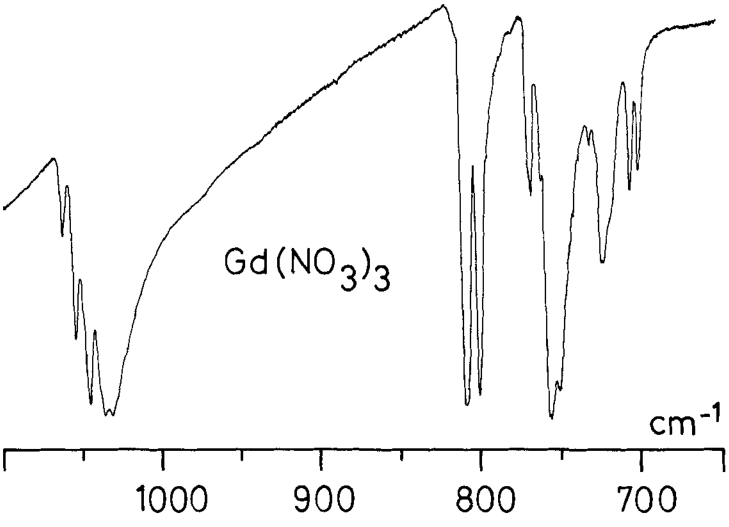

Fig. 3. *600-1,100 cm^{-1} region of the IR. spectrum of $Gd(NO_3)_3$* (as Nujol mull)

Table 3. *Observed IR. and* Raman *frequencies of anhydrous* $Ln(NO_3)_3$ [cm^{-1}][a])

Ln	Lattice and Ln – O vibrations				Nitrato group vibrations[b])											
					ν_5		ν_6		ν_3		ν_2		ν_4		ν_1	
La	[c])	*75*	[c])	*178*	729	*729*	745sh	*757*	805	[d])	1,032	*1,028sh*	1,306	*1,312*	1,436	[d])
		93		*230*	737	*737*	754		815		1,037	*1,037*	1,328	*1,346*	1,495	
		136		*249*							1,040		1,344		1,1510sh	
		149														
		163														
Eu	93	*55*	176	*180*	702	*727*	743sh	*750*	802	[d])	1,028	*1,042*	1,310sh	*1,320sh*	1,435	[d])
	113	*78*	192	*230*	709		750	*757*	810		1,034	*1,051*	1,325sh	*1,365*	1,510	
	154	*81*	238		720		758	*766*			1,042	*1,062*	1,345			
		107			728		770				1,050		1,370			
		125sh									1,060					
		139sh														
		155														
Gd	[c])	*76*	[c])	*181*	705	*720*	753	*750*	803	[d])	1,030	*1,042*	1,310	*1,360*	1,480	[d])
		92		*215*	710		759	*760sh*	811		1,036	*1,048*			1,550	
		105		*248*	725		766sh				1,046	*1,058*				
		129			735		771				1,054					
											1,062					
Dy	[c])	*67*	[c])	*182*	700	*695*	760	*757*	803	*805*	1,020	*1,031*	1,300sh	*1,336*	1,405	*1,395*
		90		*201*	709	*709*	771	*768sh*	809		1,030	*1,063*	1,325sh	*1,375*	1,430	*1,425*
		132		*250*	712	*724*		*776*	814		1,062	*1,070*	1,365		1,520sh	
		165			728				817		1,068					
											1,073sh					

[a]) Numbers are averages of 2-4 determinations on independent samples; sh denotes a shoulder; underlined numbers indicate the more intense component of a multiplet; numbers in italic are *Raman* frequencies. [b]) Same assignment as in *Table 2.* [c]) IR. spectrum not measured below 250 cm^{-1}. [d]) Too weak to be observed.

Our nitrates are completely anhydrous so that the absorption at 760 cm^{-1} cannot be assigned to a vibrational mode of water as determined for hydrated $Sm(NO_3)_3$ [3]: no transitions are observed at 3,500, 1,635, 645 and 437 cm^{-1}. Assignment of the absorptions is difficult to make since all the nitrato groups are not equivalent in the lattice as indicated by the extended splitting of the bands. *Zolin et al.* suggest that the IR. band at *ca.* 1,350 cm^{-1} is typical of terdentate nitrate [9]. Indeed, the frequency of the asymmetric stretch of bidentate NO_3^- is usually lower in transition metal complexes (*ca.* 1,250 cm^{-1} [3]) and in lanthanide oxinitrates (*ca.* 1,200 cm^{-1}, *cf. Table 2*). However, *Volodina et al.* [8a] have found by X-Ray crystallography that in $Pr(NO_3)_3 \cdot 6H_2O$ each Pr(III) ion is surrounded by ten oxygen atoms, six of them belonging to three bidentate nitrato groups. The IR. absorption of the asymmetric stretch of this hexahydrate is at 1,304-1,358 cm^{-1}, and similar frequencies (1,315-1,320 cm^{-1}) are observed for the other hexahydrates (Ln = Nd to Gd) having the same structure [11]. Moreover, available *Raman* data about aqueous solutions of $La(NO_3)_3$ [14] and $Gd(NO_3)_3$ [15] show that the bands at 1,344 and 1,299 cm^{-1} correspond to the ν_4 frequency of bidentate NO_3^-, respectively. Thus, in view of these experimental evidences we discuss the data of *Table 3* on the basis of bidentate nitrato groups, and to facilitate comparisons with the oxinitrates the fundamental frequencies are labelled assuming a local C_{2v} symmetry for NO_3^-.

As far as the results of solution measurements may be used to interpret solid state data, the assignment made in *Table 3* is confirmed by a study of the *Raman* spectra of $Eu(NO_3)_3$ in non-aqueous solvents (acetone, 2-propanol, acetonitrile, dimethylformamide) [16]. A band at 1,000 cm^{-1} ($\triangleq \nu_2$, A_1; solid state: 1,030) is polarized; the bands at 720 (730) and 750 (760) cm^{-1} are both depolarized and therefore correspond to ν_5 and/or ν_6. This study, together with the results obtained by *Ferraro et al.* [17] for lanthanide trinitrate complexes, proves that in such solutions the nitrato groups have a local C_{2v} symmetry rather than a C_s one.

(iii) Many overtone and summation bands are observed in the IR. spectra above 1,700 cm^{-1}, which is indicative of a fairly large anharmonicity of the NO_3^- vibrations [18]. They correspond to the following combinations: 1,740-1,850 $cm^{-1} \triangleq \nu_2 + \nu_5$ and $\nu_2 + \nu_6$; 2,020-2,080 $cm^{-1} \triangleq \nu_4 + \nu_5$ and $2\nu_2$; 2,330-2,430 $cm^{-1} \triangleq \nu_2 + \nu_4$; 2,460-2,610 $cm^{-1} \triangleq \nu_1 + \nu_2$. Similar combinations are found in the spectra of the oxinitrates (*cf.* chap. 3) and of uranyl nitrate [19].

5. Interaction between the nitrate and the lanthanide ions. - *Ferraro* [20] has suggested that the spread between ν_1 and ν_4 gives information about the polarization of the NO_3^- ion or about the covalent character in the metal-nitrate bond. *Hester & Grossman* [21] have shown, using normal coordinate calculations, that indeed the splitting ν_1-ν_4 for bidentate nitrato groups increases almost linearly with increasing metal-oxygen force constant k(M–O). The calculated ν_3-ν_5 splitting amounts to about half the ν_1-ν_4 value and its variation with increasing k(M–O) is less pronounced than for ν_1-ν_4.

In the case of the oxinitrates the splitting corresponding to ν_1-ν_4 (given in wavenumbers) increases from 370 cm^{-1} (average of IR. and *Raman* data for Ln = La) to 430 cm^{-1} (Ln = Dy), reflecting an increase in the NO_3^-/Ln^{3+} interaction. This splitting is large compared to the known values for transition-metal, lanthanide, and uranyl derivatives, which are usually smaller than 300 cm^{-1} [20]. However, a similarly large ν_1-ν_4 spread (375 cm^{-1}) is also observed for tin(IV) nitrate [22]. A possible explanation is that in compounds having highly symmetrical unit cells coupling of the vibrational modes between several NO_3^- groups may enhance the ν_1-ν_4 splitting [21]. According to the calculations of [21] an increase of ν_1-ν_4 should result in an increase of ν_3-ν_5. This is the case for $LnONO_3$ provided ν_5 is assigned to the transition at *ca.* 680 cm^{-1}: the splitting corresponding to ν_3-ν_5 (expressed in wave-numbers) varies from 135 cm^{-1} (average of IR. and *Raman* data for Ln = La) to 145 cm^{-1} (Ln = Dy). If ν_5 were assigned to the transition at *ca.* 715 cm^{-1}, the splitting corresponding to ν_3-ν_5 would decrease slightly from 108 cm^{-1} (Ln = La) to 103 cm^{-1} (Ln = Dy). An evaluation of ν_1-ν_4 for the lanthanide nitrates is difficult and values of the corresponding wave-numbers range from 40 to 240 cm^{-1} depending on which components of the multiples are considered. The NO_3^-/Ln^{3+} interaction seems, however, to be less strong than in the oxinitrates, as indicated by ν_3-ν_5, the corresponding value of which varies from *ca.* 70 cm^{-1} (Ln = La) to *ca.* 80 cm^{-1} (Ln = Dy).

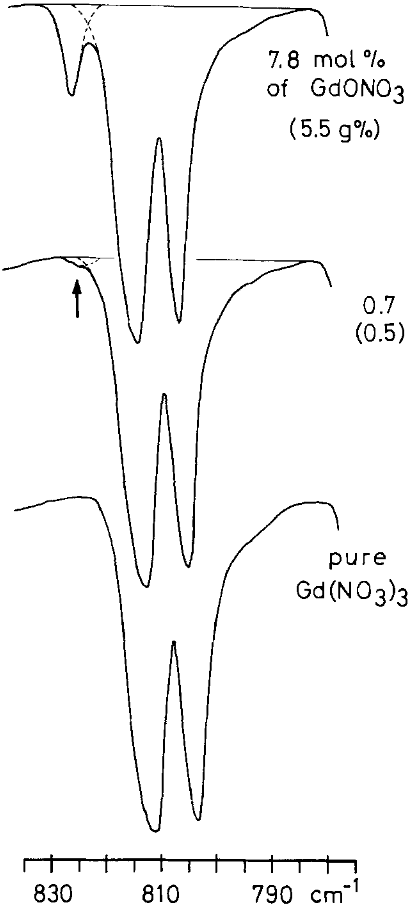

Fig. 4. *780-830 cm^{-1} region of the IR. spectra of some $GdONO_3/Gd(NO_3)_3$ mixtures*

6. Purity criterion for the anhydrous nitrates. - To avoid manipulations we synthesize the very hygroscopic anhydrous nitrates by heating the corresponding hydrates under high vacuum. This requires some care since a too low heating temperature results in an uncomplete dehydration and a too high one leads to the formation of oxinitrate. An analytical control of the reaction would thus be very helpful. The 790-830 cm^{-1} region of the IR. spectrum of $Ln(NO_3)_3/LnONO_3$ is especially well suited for this purpose: there the oxinitrate exhibits a sharp absorption well separated from the sharp doublet of the nitrate, and the baseline is fairly flat. In this way, about 0.5 weight-% of oxinitrate in the nitrate can be detected *(cf. Fig. 4)* by the appearance of a shoulder on the high energy side of the nitrate doublet. A plot of the ratio of the peak areas *vs.* the mol-% of $LnONO_3$ gives a straight line up to 40 mol-% oxinitrate.

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