

**Charge Transfer and $f-f$ Transitions
Studied by Photoacoustic Spectroscopy
of $[\text{R}(\text{NO}_3)_2(\text{PicBH})_2]\text{NO}_3$
and $[\text{R}(\text{NO}_3)_3(\text{PicBH})_2]$ Complexes
(R – Rare Earth Ion)**

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High-resolution photoacoustic spectra of trinitrato-bis[N-(2-pyridylmethylene)-N'-benzoyl-hydrazine]R(III), (R = La, Ce, Pr), and binitrato-bis[N-(2-pyridylmethylene)-N'-benzoyl-hydrazine]R(III) nitrate (R=Y, Nd, Eu, Yb, Tb, Gd, Ho, Dy, Er) complexes, in the visual region, were studied for powder samples. Very intense photoacoustic spectra of various shapes were attributed to the intraligand transitions of the $\pi \rightarrow \pi^*$ type located mainly on the C=N group and the $n \rightarrow \pi^*$ transitions located on the carbonyl group. The intensity of these transitions essentially depends on the type of rare earth ions. The existence of $f-f$ electron transitions could influence the relaxation processes, which play an important role in intensity

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determination of the above transitions. For many investigated samples the energy levels of excited states of rare earth ions were identified ($f-f$ electron transitions). The radiation energy for some of the rare earth ions were compared with the $d-d$ electron transitions of certain copper(II) organometallic complexes, which are very important in biogenic systems. The correlation between ions with localized and extended wave functions is suggested.

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1. Introduction

The investigation of physical properties of new organometallic complexes with the trivalent lanthanide ions is rapidly expanding. Rare earth complexes studied by photoacoustic spectroscopy (PAS) together with luminescence spectroscopy allowed determination of the intramolecular energy transfer and the relaxation processes [1]. Much of the interest in the lanthanide's organometallic complexes is due to their promising technological and biological applications [2–4]. For example, gadolinium(III) chelates have been under intense scrutiny for their use as contrast agents for magnetic resonance imaging applications [5, 6]. Europium(III) complexes are used as probes for labeling of DNA [7] and proteins [8], and in luminescence resonance energy transfer studies [9]. Another use of lanthanide(III) complexes is in the sequence-specific cleavage of nucleic acids [10]. It is well known that local thermal processes during cancer play a very important role. Some of the organometallic compounds with rare earth complexes having $f-f$ electronic transitions could be used as the local probe of heat formed by light applied to destroy cancerogenic tissues. It is very important to study radiation and non-radiation transitions and their relaxation processes by the photoacoustic (PA) spectroscopy, especially if organic complexes of rare earth and transition metal ions are involved. Recently, the PAS method was used to study the spermidine copper(II) complexes [11, 12]. These complexes are very important in the living biological system, as they are involved in information transfer to DNA. In the visual region of the electromagnetic waves the absorption due to $d-d$ electron transitions and the splitting by the crystal field was observed and analysed. It will be very interesting to study the rare earth organic complexes by PAS in order to observe the $f-f$ electron transitions in the same region. The wave functions of rare earth ions are more localized than for transition metal ions and thus this radiation could play a very important role in biological processes in the living systems.

The aim of this work is to investigate PA spectra of two types of lanthanide chelates: trinitrato-bis[N-(2-pyridylmethylene)-N'-benzoyl-hydrazine]R(III), (R = La, Ce, Pr), designated as $[\text{R}(\text{NO}_3)_3(\text{PicBH})_2]$, and binitrato-bis[N-(2-pyridylmethylene)-N'-benzoyl-hydrazine]R(III)nitrate (R = Y, Nd, Eu, Yb, Tb, Gd, Ho, Dy, Er), designated as $[\text{R}(\text{NO}_3)_2(\text{PicBH})_2]\text{NO}_3$.

2. Experimental

The trinitrato-bis[N-(2-pyridylmethylene)-N'-benzoyl-hydrazine]R(III), (R = La, Ce, Pr), and binitrato-bis[N-(2-pyridylmethylene)-N'-benzoyl-hydrazine]R(III) nitrate (R = Y, Nd, Eu, Yb, Tb, Gd, Ho, Dy, Er) complexes were prepared under anhydrous conditions by the direct reaction of a solution of the ligand 2-pyridinecarboxaldehyde benzoylhydrazine (PicBH) with a solution of the lanthanide salt as described previously [13]. All synthesized complexes were crystalline solids, stable in dry air for at least one year. The crystal structure of two compounds, with Ce and Er ions, has been determined by the single crystal X-ray diffraction technique [14, 15].

The crystal of the Ce complex was monoclinic with space group $P2_1/n$ and cell constants $a = 18.6342(19)$ Å, $b = 11.1941(8)$ Å, $c = 34.734(2)$ Å, $\beta = 99.188(9)^\circ$, and $Z = 8$. The chemical structure of investigated complexes is presented in Fig. 1. There are two independent molecules of the complex compound in the asymmetric unit of the structure. The metal atom is twelve-fold coordinated by eight oxygen and four nitrogen atoms in an irregular icosahedral arrangement, which may also be described as a very distorted six-capped trigonal antiprism. The Ce–O distances range between 2.525(4) Å and 2.759(4) Å and the Ce–N distances between 2.725(4) Å and 2.848(4) Å [14].

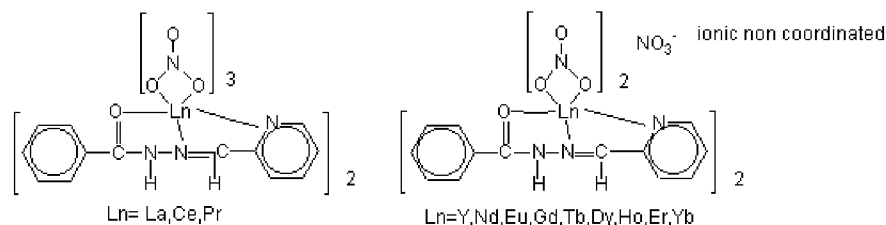


Fig. 1. Chemical structure of two kinds of the investigated complexes: $[\text{R}(\text{NO}_3)_3(\text{PicBH})_2]$ (left) and $[\text{R}(\text{NO}_3)_2(\text{PicBH})_2]\text{NO}_3$ (right).

The crystal of the Er complex is monoclinic with crystallographic $C2/c$ symmetry and cell constants $a = 26.902(1)$ Å, $b = 18.390(1)$ Å, $c = 15.259(1)$ Å, $\beta = 123.06(1)^\circ$, and $Z = 8$. The environment around the erbium atom can be best described as a distorted bicapped square antiprism. The erbium atom is 10-coordinate by linking to two tridentate 2-pyridinecarboxaldehyde benzoylhydrazine ligands and two bidentate nitrate ligands. The Er–O distances range between 2.361(3) Å and 2.465(3) Å. Similarly the Er–N distances range between 2.535(3) Å and 2.603(3) Å [13]. The linking of the hydrazone (Hdr) ligand to the metal atom is accomplished through the pyridine nitrogen, the azomethine nitrogen and the carbonyl oxygen in all complexes.

The PA spectra of polycrystalline powder samples have been obtained by using a modification of the PAS method initially proposed by G.J. Papadopoulos

los and G.L.R. Mair [15]. A Xenon arc lamp with 1 kW power and a 1/4m ORIEL monochromator were used as a light source, with bandpass width of 5 nm (at 500 nm). The light, intensity modulated with a chopper at frequency of 10 Hz, was directed into a photoacoustic cell equipped with TREVI EM27 microphone. A dual SR830 lock-in amplifier measured amplitude and phase of the PA signal detected on the microphone. Data acquisition ensured that each value was an average of 20 runs at the same wavelength of the incident light. A carbon black was used as a standard to re-calibrate the final spectrum. The PA spectra of all the complexes were recorded at room temperature in the range of 300–700 nm.

3. Results and discussion

Figures 2 and 3 present, as an example, PA spectra registered for the samples with La and Nd ions, respectively. In general, the PA spectrum could be seen as formed by three components: (a) in near UV range by very intense spectra arising

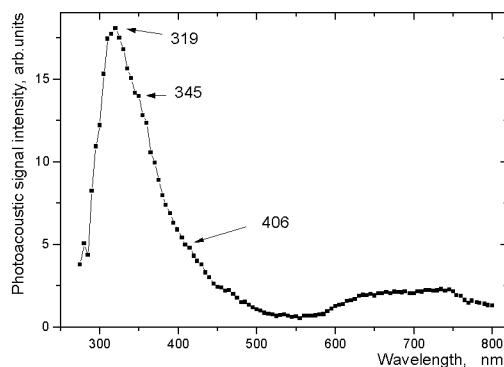


Fig. 2. Photoacoustic absorption spectrum of $[\text{La}(\text{NO}_3)_3(\text{PicBH})_2]$. The wavelengths (in nm) of three charge-transfer PA peaks are indicated.

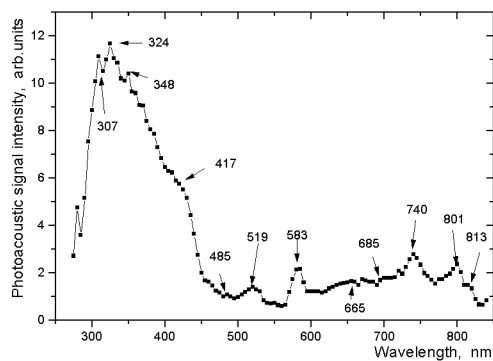


Fig. 3. Photoacoustic absorption spectrum of $[\text{Nd}(\text{NO}_3)_2(\text{PicBH})_2]\text{NO}_3$. The wavelengths (in nm) of charge-transfer (first on the left) and $f-f$ transitions are indicated.

from $\pi \rightarrow \pi^*$ transitions located on the C=N group and in near blue part coming from $n \rightarrow \pi^*$ transitions located on the carbonyl group; (b) in near IR by a very broad band; (c) $f-f$ transitions in some of the investigated samples.

The values of the positions of the absorption PA spectra together with their relative intensities are presented in Tables I and II. The PA spectra were obtained by detecting the heat generated through the non-radiative relaxation released by the sample absorbing the modulated incident light. The PA spectrum intensity (I) is given by the relation [16]:

$$I = kP_{\text{abs}}\gamma, \quad (1)$$

where P_{abs} is the absorbancy of the sample, γ is the probability for non-radiative transitions after excitation, and k is a coefficient which is determined by the thermal properties of the sample and the spectrometer.

TABLE I

The electronic PA spectra of charge transfer transitions for all investigated samples (band-multilevel electron transitions).

R^{3+}	$1/\lambda$ [cm^{-1}]	I_{max}/I	I_{max} [arb. units]	$1/\lambda_n(\text{opt})$ [cm^{-1}] [16]	I_{opt}	Band assignation
La	31300	1.00	100	33330	1.490	$\pi \rightarrow \pi^*$
	29000	0.78			27470	1.343
	21500	0.12				
	15300	0.12				band
	14000	0.13				band
	13400	0.12				band
Pr	31300	1.00	67	31250	2.007	$\pi \rightarrow \pi^*$
	29000	0.91				
	26000	0.42		26530	2.239	$n \rightarrow \pi^*$
	21500	0.12				
	16500	0.10				band
	14700	0.15				band
13600	0.15			band		
Nd	32570	1.00	65	33333	1.653	$\pi \rightarrow \pi^*$
	30860	1.00			30860	1.515
	28600	0.89				
	24000	0.52		24691	1.724	$n \rightarrow \pi^*$
	21700	0.14				
	~ 16000	0.13				band
	~ 13900	0.18				band

TABLE I (cont.)

R^{3+}	$1/\lambda$ [cm^{-1}]	I_{\max}/I	I_{\max} [arb. units]	$1/\lambda_n(\text{opt})$ [cm^{-1}] [16]	I_{opt}	Band assignment
Eu	31350	1.00	50	33560	1.618	$\pi \rightarrow \pi^*$
	30300	0.98				
	28740	0.95				
	24330	0.50		24690	1.732	$n \rightarrow \pi^*$
	21830	0.18				
	15700	0.13				
	14700	0.16				
	13800	0.19				
Gd	30860	1.00	59	33222	1.241	$\pi \rightarrow \pi^*$
	28650	0.88				
	24700	0.41				
	16000	0.11		29150	1.239	$n \rightarrow \pi^*$
	14900	0.14				
	13800	0.16				
Dy	31300	1.00	62	33112	1.156	$\pi \rightarrow \pi^*$
	29200	0.80				
	27300	0.20				
	21700	< 0.1		27777	1.586	$n \rightarrow \pi^*$
	16300	0.11				
	15000	0.13				
	13500	0.14				
Y	~ 33780		104	33230	1.112	$\pi \rightarrow \pi^*$
	31450	1.00				
	28900	0.85				
	25300	0.10		29590	1.010	$n \rightarrow \pi^*$
	21700	< 0.1				
	15600	0.11				
	14600	0.13				
	13600	0.12				
Ho	32370	0.90	62	33222	1.229	$\pi \rightarrow \pi^*$
	31180	1.00				
	28000	0.90				
	24250	0.86		26455	1.252	$n \rightarrow \pi^*$
	15800	0.12				
	14700	0.14				
	13600	0.15				
			24270	1.258	$n \rightarrow \pi^*$	
				1.272	band	
					band	
					band	

TABLE I (cont.)

R^{3+}	$1/\lambda$ [cm^{-1}]	I_{\max}/I	I_{\max} [arb. units]	$1/\lambda_n(\text{opt})$ [cm^{-1}] [16]	I_{opt}	Band assignation
Er	~ 33300			33333	1.716	$\pi \rightarrow \pi^*$
	31400	1.00	59	30770	1.589	
	~ 29940	0.80				
	~ 24100	0.15		24691	2.083	$n \rightarrow \pi^*$
	21500	< 0.1				
	~ 16000	0.12				band
	~ 14800	0.14				band
Yb	31200	1.00	72	33333	2.009	$\pi \rightarrow \pi^*$
	29300	0.89		31250	1.532	
	24500	0.14		24875	1.680	$n \rightarrow \pi^*$
	~ 22000	< 0.1				
	16500	0.10				band
	15000	0.15				band
	14000	0.14				band
Ce	31300	1.00	98			$\pi \rightarrow \pi^*$
	29000	0.85		27470	0.486	$n \rightarrow \pi^*$
	22700	0.15				
	15600	0.12				band
	14700	0.12				band
	13400	0.12				band
Tb	33800			33112	1.137	$\pi \rightarrow \pi^*$
	30300	1.00	73	29070	1.112	
	28500	0.92				
	24200	0.22		24272	1.019	$n \rightarrow \pi^*$
	16700	0.12				band
	15500	0.17				band
	14000	0.20				band
	13200	0.20				band

All PA absorption spectra were assigned based on the lanthanide spectra summarized by Dieke and Crosswhit [17]. The PA band in the region of $(30-32) \times 10^2 \text{ cm}^{-1}$ which is assigned to the $\pi \rightarrow \pi^*$ transition of Hdr is significantly stronger than that of the free-base Hdr. This is due to the fact that the π electron conjugated system of the complex is much larger than that of the free-base Hdr and has a higher molar absorptivity. The maximum of the values of PA spectra of $\pi \rightarrow \pi^*$ transition of C=N group could be different than the

TABLE II

The $f-f$ electron transitions.

R^{3+}	$1/\lambda$ [cm^{-1}]	$I_{\text{max}}(\text{La})/I$	$1/\lambda_n(\text{opt})$ [cm^{-1}]	I_{opt}	$f-f$ transitions
Nd	20600	0.10	20964	1.015	${}^4I_{9/2} \rightarrow {}^4G_{7/2}$
	19270	0.12	19493		${}^4I_{9/2} \rightarrow {}^4G_{7/2}$
	17150	0.19	17271	1.276	${}^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$
	15800	0.10	15950		${}^4I_{9/2} \rightarrow {}^4H_{11/2}$
	14600	0.12	14727		${}^4I_{9/2} \rightarrow {}^4F_{9/2}$
	13500	0.18	13553	1.625	${}^4I_{9/2} \rightarrow {}^4F_{7/2}, {}^2S_{3/2}$
	12500	0.20	12531		${}^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$
Ho	22300	0.38	22270	1.272	${}^5I_8 \rightarrow {}^3K_8$
	20620	0.21	20661		${}^5I_8 \rightarrow {}^5F_3$
	18620	0.09	18691	1.095	${}^5I_8 \rightarrow {}^5F_4$
	15550	0.17	15600	1.119	${}^5I_8 \rightarrow {}^5F_5$
Er	20490	0.10	20580	1.366	${}^4I_{15/2} \rightarrow {}^4F_{7/2}$
	19270	0.10	19305	1.963	${}^4I_{15/2} \rightarrow {}^2H_{11/2}, {}^4S_{3/2}$
	15400	0.12	15408	1.216	${}^4I_{15/2} \rightarrow {}^4F_{9/2}$

one obtained from UV spectroscopy and one of the reasons could be that the intensity of lamp light below 300 nm is very low. The higher values of PA spectra were impossible to record due to technical problems. The most intense PA line is observed at about 31000 cm^{-1} except for the sample with Tb ions (30300 cm^{-1}) while the ratio of the value of intensities is essentially different [100(La) : 67(Pr) : 65(Nd) : 50(Eu) : 59(Gd) : 62(Dy) : 104(Y) : 62(Ho) : 59(Er) : 72(Yb) : 98(Ce) : 73(Tb)]. From the above relation it is seen that for the rare earth(III) complexes with $f-f$ electron transition the PAS line is essentially less intense (Table I). The relation (1) shows that the intensity of PAS could be influenced by three different factors. The influence of the thermal process (k) and the absorbance (P_{abs}) on the intensity of the above PAS line are comparable and the non-radiative transition (γ) could be involved mainly in explanation of the observed differences in the PA spectra intensities.

It is clear that a compound in the excited state will relax by the two types of processes: radiative and non-radiative. The PA spectrum only responds to the non-radiative relaxation processes, whereas the PA signal of metastable energy levels, which relax by radiative processes, will be very weak or absent. The obtained values of electron transitions are given in Table I for molecular levels and in Table II from ionic levels ($f-f$ electron transitions). Three rare earth ions (La, Ce, and Y) do not have metastable ionic energy levels. Thus in the higher energy state they have the same absorption line and usually it is more intense than in other studied samples.

In Table II the values of $f-f$ electron transitions are shown only for three complexes with neodymium(III), holmium(III), and erbium(III) ions because for them they are more intense. The PA peaks of rare earth ions do not apparently shift in different hosts because the wave functions $f-f$ are well localized and the effect of environment on the bands $4f$ is very small.

Among the energy levels of Pr(III) ion, the luminescent levels are 1G_4 and 3P_0 and very weak absorptions at visible region of radiation are expected [16]. The electron could be in the excited levels 3P_2 and 1D_2 after radiation. For example, when electrons are excited to 3P_2 they could relax nonradiatively to 1I_6 and 3P_0 levels followed by the transition to 3H_6 level or 3H_4 [18, 19]. Some very weak absorption could be observed at lower and higher region of wavelength radiation but they are comparable to the absorption band from the molecular electron transitions.

The Nd(III) ion has the luminescent level ${}^4F_{3/2}$ and it could possess three different radiation processes like: ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$, ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$, and ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ [19]. The PA spectrum of neodymium ion is very rich in different transitions (Fig. 3 and Table I) inside of ionic levels. Table I shows the excited states, which take part in transitions to the ground state. The model of intermolecular energy relaxation processes for neodymium(III) salicylate complexes has been presented by Wu et al. [20]. In PA spectra, some intensities are very weak and other probably so weak or overlapping that we could not detect them. The PA measurements have given more information than UV measurements about physical processes for our materials. There are a lot of different relaxation transitions observed for this sample and PA spectrum is the most complicated in comparison with other samples in this series. The neodymium(III) ions in various hosts are often applied in lasers and the intensities of PA spectra of $f-f$ electron transitions are greater than for other rare earth ions.

The PA spectra of molecular electron transitions for the sample with Eu(III) are in good agreement with the energy levels of this ion in a large DTPA-like complex [8]. The ground state of Eu^{3+} ion is split into seven components (7F_0 – 7F_6) due to the first order spin-orbit coupling with $J = 0-6$. The first excited level of Eu^{3+} is 5D_0 situated at $\sim 17300 \text{ cm}^{-1}$ above the ground level 7F_0 . In the absorption spectrum of Eu^{3+} ion only very weak lines in the visible and in the ultraviolet regions are observed. In the region of free-base Hdr the absorption line is less intense than for other complexes because of the existence of many $f-f$ transitions arising in the UV region. Excitation of Eu^{3+} aqua ion with near UV light results in fluorescence originating not only from the 5D_0 level but also from the excited 5D_1 level. However, the intensities of the ${}^5D_1 \rightarrow {}^7F_J$ transitions are much lower than those of the ${}^5D_0 \rightarrow {}^7F_J$ transitions.

For the trivalent gadolinium ion the ground state is ${}^8S_{7/2}$ and it has the following nearest excited states: ${}^6P_{7/2}$, ${}^6P_{5/2}$, and ${}^6P_{3/2}$. For the sample $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ the fluorescence peak at 28570 cm^{-1} (with lifetime $\tau = 7.7 \text{ ms}$)

was identified to be the excited level ${}^6P_{7/2}$ [21] and at this region an intense band of PAS coming from the molecular transitions is observed, masking the $f-f$ transitions.

The excited energy level with the longest lifetime for Dy^{3+} is ${}^4F_{9/2}$. Optical characterization of Dy^{3+} in yttria stabilized zirconia single crystals has given the following values of the excited states: ${}^5F_{5/2} - 12563 \text{ cm}^{-1}$, ${}^6F_{3/2} - 13358 \text{ cm}^{-1}$, ${}^4I_{15/2} - 22200 \text{ cm}^{-1}$ and ${}^4G_{11/2} - 23745 \text{ cm}^{-1}$ [22] which are close to our energies obtained from very weak lines of PAS. The PA spectra for charge molecular transitions are similar to those observed in Ref. [4].

Among the energy levels of Ho(III) ion, the luminescent levels are: 5I_7 and 5S_2 . Ho(III) ion could have two radiative processes: ${}^5I_7 \rightarrow {}^5I_8$ and in the second case ${}^5S_2 \rightarrow {}^5I_8$. A lot of $f-f$ transitions are observed for this complex, similarly as for Nd^{3+} and Er^{3+} ions, and they could be very important in laser action application.

The trivalent cerium ion has the ground state ${}^2F_{5/2} (4f^1)$ and one excited state ${}^2F_{7/2}$ with the energy of 2200 cm^{-1} . Only charge transfer transitions are observed and they are very intense.

The trivalent erbium is one of most used lanthanides ion in laser applications. Er^{3+} ion in $\text{YAlO}_3:\text{Er}$ and $\text{YAG}:\text{Er}$ has two transitions: ${}^4S_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4I_{13/2}$. The obtained PAS has shown that the positions of $f-f$ transitions recorded for zirconia single crystals doped with Er^{3+} in optical measurements are shifted in the direction of lower wavelengths [23].

The trivalent ytterbium ion has the ground state ${}^2F_{7/2} (4f^{13})$ and one excited state ${}^2F_{5/2}$ with the energy of 10100 cm^{-1} . No PAS lines were observed in the visible region of the radiation.

PAS study of holmium oxide, erbium oxide and R^{3+} doped polyvinyl alcohol films ($\text{R}^{3+} = \text{Ho}^{3+}$ and Er^{3+}) have shown that $f-f$ transitions are in the same positions but their relative intensities are different [24]. This reveals that in other hosts the electronic-vibrational interaction is much stronger than in ionic oxides. In our matrix with holmium and erbium the essential differences are observed in the relative intensities of PAS as compared to the rare earth oxides [24]. These kinds of phenomena are very important especially for biogenic systems.

Large differences are observed between energies of charge transfer and $f-f$ transitions obtained from UV and PA spectroscopies. The UV spectra have been recorded for complexes in a solution. Usually the PAS lines are shifted towards lower energies. Probably the coupling energy between metal and ligand is stronger for these complexes in the solution. The charge transfer PA spectra are a few orders of magnitude more intense than spectra attributed to $f-f$ transition. As could be seen from the spectra the absorption PA lines of charge transfer transitions are most intense for complexes with lanthanum, itrium, and cerium ions. Relaxation processes that involve the intermediate $f-f$ transitions might be responsible for this effect. These kinds of processes could play a very important role in biological

TABLE III

The energies of $d-d$ electron transitions in polyamine copper(II) complexes [11, 12].

Compound	$1/\lambda_1$ [cm ⁻¹]	$1/\lambda_2$ [cm ⁻¹]	$1/\lambda_3$ [cm ⁻¹]
Spn323	20700	17600	14400
Spn333	19300	16400	13700
Spn343	22800	17700	14700
Spm323	20600	17700	14900
Spm333	17500	14300	12600
Spm343	20100	17200	14500

systems. Lanthanum(III) ion has no electron in $4f$ orbital and the ligand relaxes radiatively or non-radiatively directly to the ground state. The triplet state of the ligand is metastable, its lifetime is not reduced and the relaxation time has a greater value.

Table III shows the values of $d-d$ electron transitions for six copper(II) complexes playing a very important role in biogenic processes: three spermine copper dinitrate (Spn323, Spn333, Spn343) and spermine copper sulphate (Spm323, Spm333, Spm343) complexes. Surprisingly these values are in very good agreement with certain $f-f$ transitions of rare earth ions in organic complexes (Tab. II).

In our previous work it was shown that PAS could resolve the $d-d$ transitions of Cu^{2+} ions and they could be used for determination of the electronic structure for numerous copper complexes playing an important role in biological processes [11, 12]. The $d-d$ and $f-f$ transitions attracted particular attention due to their role in antitumor activity and in different pathological processes in living biological systems. In contrast to complexes with copper, in case of rare earth ions the non-radiation transitions should proceed inside ionic orbital. Comparison of PA spectra for the complexes with copper and rare earth ions reveals that the PAS lines of charge transfer bands are at different wavelengths and essential differences of intensity are observed. The PAS lines of Cu^{2+} ($d-d$ transitions) were broader and more intense than $f-f$ transition arising from the crystal field splitting. The relaxation processes involving copper ions are more complicated and suggest existence of probably another molecular orbital with lower energy transitions and thus cross relaxation processes. Some rare earth ions have a very complicated electronic structure and therefore there is much more combinations of $f-f$ transitions. They are thus more suitable for applications in laser actions.

4. Conclusions

In the present work PAS has been applied to determine the acoustic reaction to the electromagnetic radiation in the visual range of electromagnetic radiation. Except of charge transfer transitions for complexes with La, Y, Yb, and Ce ions, also intense $f-f$ peaks were registered for Nd, Ho, Er complexes and assigned to transitions between specific levels. This kind of studies by PA spectroscopy could give an important information useful for technological (e.g. laser) and biological applications. These will include the energies of charge transfer transitions and $f-f$ transitions in solid state. It would also help in explaining the mechanism of relaxation processes and the interaction between metal ion and ligands.

In most living systems, coexistence of different organic metal complexes with f configuration of the open shell metal ion can be evinced. From the PAS measurements it could be seen that beside intense spectra in the UV region, a weaker absorption occurs in the visual region. Two important physical phenomena for the organic metal complex compounds in living systems may be inferred from these observations. First, it is the radiation effect in the visual region and second, the thermal transports effect. It is not clear which their precise roles in the biological processes are. Now we wish to address and stress certain problems, which are difficult to study by the other well-known methods. We put forward an idea that the electron transitions between atomic levels (ground state and excited states) could play a role of a very sensitive "channel selector", especially for transition metals ions with extended wave functions. As copper(II) complexes in polyamines are important in the information transfer in DNA systems, a question arises about the role of the excited state of copper ions, e.g. in the carcinogenic processes. Does the existence of the excited states of copper ions make these processes faster? Electron transfer between metal complexes bound to DNA, especially with protein (polyamine is important here) is one of the most widely studied subjects in biophysics [25].

Additional resonance processes between rare earth ions (with localized wave functions) and transition metal ions (extended wave function) are present in the living system and are essential for the relaxation phenomena. The type of host for rare earth ions is very important and the electron-phonon interaction depends strongly on it. Intense absorptions connected with $f-f$ electron transitions have been reordered for the sample containing trivalent neodymium ions and these ions in other hosts are often used as lasing media. An essential role of the non-radiation transitions in the relaxation phenomena has been proved in these investigations. In a future work we will check the usefulness of these materials in laser applications.

References

- [1] W. Ronghu, S. Huiyu, S. Qingde, *Spectrochem. Acta A* **56**, 2073 (2000).
- [2] R. Reisfeld, C.K. Jorgensen, *Lasers and Excited States of Rare Earths*, Springer, Berlin 1977.

- [3] H.B. Kagan, J.L. Namy, *Tetrahedron* **42**, 6573 (1986).
- [4] K. Wang, R. Li, Y. Cheng, B. Zhu, *Coord. Chem. Rev.* **190-192**, 297 (1999).
- [5] J.A. Peters, J. Huskens, D.J. Ruber, *Prog. NMR Spectrosc.* **28**, 283 (1996).
- [6] S. Aime, M. Botta, M. Fasano, E. Terreno, *Chem. Soc. Rev.* **27**, 19 (1998).
- [7] H. Karsilayan, I. Hemmila, H. Takalo, A. Toivonen, K. Pettersson, T. Lovgren, V.M. Mukkala, *Bioconjng. Chem.* **8**, 71 (1997).
- [8] S.K. Saha, K. Kross, E.D. Kloszewski, D.A. Upson, J.L. Toner, R.A. Snow, C.D.V. Black, V.C. Desai, *J. Am. Chem. Soc.* **115**, 11032 (1993).
- [9] M. Li, P. Selvin, *Bioconjng. Chem.* **8**, 127 (1997).
- [10] L. Huang, L.L. Chappeli, O. Iranzo, B.F. Baker, J.R. Morrow, *JBIC* **5**, 85 (2000).
- [11] N. Guskos, G.J. Papadopoulos, V. Likodimos, G.L.R. Mair, J. Majszczyk, J. Typek, M. Wabia, E. Grech, T. Dziembowska, T.A. Perkowska, *J. Phys., Appl. Phys.* **33**, 1 (2000).
- [12] N. Guskos, G.P. Papadopoulos, V. Likodimos, J. Majszczyk, J. Typek, M. Wabia, E. Grech, T. Dziembowska, A. Perkowska, K. Aidinis, *J. Appl. Phys.* **90**, 1436 (2001).
- [13] D.G. Paschalidis, I.A. Tossidis, M. Gdaniec, *Polyhedron* **19**, 2629 (2000).
- [14] P. Christidis, I.A. Tossidis, D.G. Paschalidis, *Acta Crystallogr. C* **55**, 707 (1999).
- [15] G.J. Papadopoulos, G.L.R. Mair, *J. Phys. D, Appl. Phys.* **25**, 722 (1992).
- [16] M.J. Adams, J.G. Highfield, G.F. Kirkbright, *Anal. Chem.* **52**, 1260 (1980).
- [17] D.H. Dieke, H.M. Crosswhit, *Appl. Opt.* **2**, 657 (1962).
- [18] A.A. Kaminskii, *Laser Crystals*, Nauka, Moskva 1975 (in Russian).
- [19] A.A. Kaminskii, A.A. Pavliuk, P.V. Klevcov, *Optic and Spectroscopy* **28**, 292 (1970) (in Russian).
- [20] R. Wu, H. Zhao, Q. Su, *J. Non-Crys. Solids* **278**, 223 (2000).
- [21] S.P. Sinha, *Systematics and the Properties of the Lanthanides*, NATO ASI, Series C, Vol. 109, Eds. Shyama P. Sinha, D. Reidel Publ. Company, Dordrecht 1981, p. 451.
- [22] R.I. Merino, V.M. Orera, O. Povill, W. Assmus, E.E. Lomonova, *J. Phys. Chem. Solids* **58**, 1579 (1997).
- [23] R.I. Merino, V.M. Orera, R. Cases, M.A. Chamarro, *J. Phys., Conden. Matter* **3**, 8491 (1991).
- [24] M. Kumar, A.R. Dhobale, M. Kumar, M.D. Sastry, *J. Polymer Sci. B, Polymer Phys.* **35**, 187 (1997).
- [25] E.D.A. Stemp, R.E. Holmlin, J.K. Barton, *Inorg. Chim. Acta* **297**, 88 (2000).