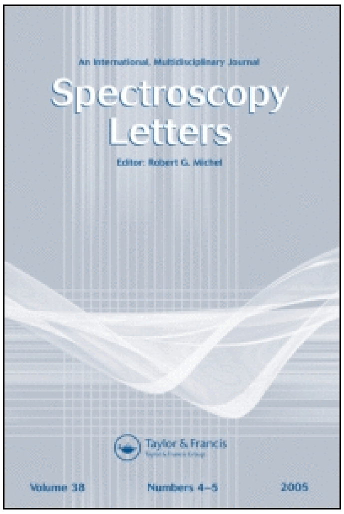

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Abstract: The n → π^* electron transitions in the binitrato-bis[*N*-(2-pyridylmethylene)-*N*′-benzoyl-hydrazone]R(III) nitrate complexes (R = Nd, Gd, Eu, Tb, Dy, Ho, Y, Er, and Yb), in the high-energy part of the visual range, have been investigated by the photoacoustic spectroscopy. The aim of this work was to analyze the n → π^* electron transitions and to evaluate the spectral parameters important in the nonradiative processes. The organic rare-earth(III) complexes are very useful for studying the above effects because the wavefunction of the rare-earth(III) ion is localized and the nonradiative processes in the visible region of electromagnetic radiation are dominated by the ligand electron transitions. The intensities of photoacoustic lines of the n → π^* transitions depend strongly on the electronic structure of the biogenic

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active compound, but the total intensity of nonradiative processes is almost independent of the type of rare-earth(III) ion. The fluorecsent properties of the samples were investigated.

Keywords: Photoacoustic spectroscopy, rare-earth complexes

INTRODUCTION

Photoacoustic spectroscopy (PAS) might serve as an excellent tool in the study of nonradiative processes in living systems. In Plato's *Symposium*, Aristotle observed that during a heated debate, the temperature in the room increases more than during not so lively discussion. As it is now well-known, metabolism is one of the most important processes of energy conversion in living systems. Could nonradiative processes take part in the transfer of intermolecular energy in living matter? The organic and organometallic substances active in biogenic compounds could take part in many nonradiative processes involving the electronic $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, d-d, and f-f transitions.[1–5] PAS has been applied directly to study of simple living-matter organisms (like cyanobacterium *Synechococcus*).[6] In our opinion, the photoacoustic phenomena could play a very important role in thermal stabilization processes. The energy of a quanta $h\nu$ is the smallest portion of energy taking part in the intermolecular interactions, but at the same time the $n = 10^{22}$ excitations (where n is the number of the nonradiative processes) could give an energy of about 1 kWh. It was suggested that, the $n \rightarrow \pi^*$ electron transitions could take part in an intermolecular energy transfer and they could play an essential role in thermodynamic processes within the living matter.[7] The organic complexes with rare-earth(III) ions could be very useful to study of the nonradiative processes by PA spectroscopy, because their wavefunctions are localized, and the intensities of the PAS line could be investigated as a function of a particular rare-earth(III) ion. The interest in the lanthanide complexes stems mainly from their low toxicity and their powerful paramagnetic and luminescent properties.[8] They are associated with important biological uses as diagnostic tools. A large number of papers has appeared on complexes with hydrazones due to their ability to chelate with metal ions.

Even everyday experience suggests the importance of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions for the living matter. Probably, the $n \rightarrow \pi^*$ transitions could play a very important role in thermodynamic stabilization of organisms. It is clear that the knowledge of the exact values for the intensities, linewidths, and positions of the PAS lines could be informative about the dynamical processes in the intermolecular interactions. During evolution of the living matter, the radiation from the Sun has played a crucial role and, thus, the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions must also be of equal importance in formation of the organic compounds. It is well-known that photoreceptors are very important in germination, seedling establishment, or shade avoidance. Especially, blue radiation photoreceptors exhibit great biological interactivity in the 300–500 nm range.[9] Hence, photoacoustic processes should participate strongly in the above-discussed processes.

The aim of this work is to analyze the $n \rightarrow \pi^*$ electron transitions in the binitrato-bis[*N*-(2-pyridylmethylene)-*N*′-benzoyl-hydrazone]R(III) nitrate complexes, designated as ROrg (R = Nd, Gd, Eu, Tb, Dy, Ho, Y, Er, and Yb), in the high-energy part of the visual region (R represents the lanthanide(III) ions). Preliminary experimental results have been already published.[5] Previously, it has been suggested that the $n \rightarrow \pi^*$ electron transitions could play a very important role in the intermolecular energy transfer in the living matter.[7] Our goal is to demonstrate the usefulness of PAS in obtaining and evaluating crucial spectroscopic parameters needed in the discussion of the nonradiative processes in that class of substances.

MATERIALS AND METHODS

The procedure of syntheses of the ROrg (R = Nd, Gd, Eu, Tb, Dy, Y, Ho, Er, and Yb) complexes has been presented elsewhere.[10] The PA spectra of polycrystalline powder samples have been obtained by using modification of the PAS method initially proposed by G.J. Papadopoulos and G.L.R. Mair.[11] A xenon arc lamp with 1-kW power and a 1/4 m ORIEL monochromator (Oriel Instruments, USA) 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 (Trevi, Italy). Only one chopper frequency was used because for lower frequencies, the measuring system displayed unstable behavior, and for greater frequencies, the signal to noise ratio decreased significantly. A dual SR830 lock-in amplifier measured amplitude and phase of the PA signal detected on the microphone. Data acquisition ensured that each final value was an average of 20 runs at the same wavelength of the incident light. A carbon black was used as a standard to recalibrate the final spectrum. The PA spectra of all the complexes were recorded at room temperature in the range 300–700 nm.

RESULTS AND DISCUSSION

Figure 1 presents, as an example, three obtained and simulated PA spectra for TbOrg, GdOrg, and EuOrg complexes in the near UV/blue region of electromagnetic radiation. The PA signals for the all ROrg complexes were obtained by detecting the heat generated through the nonradiative transitions in the samples after the absorption of periodically varying incident light. The PA absorption in the above region of electromagnetic radiation is the result of

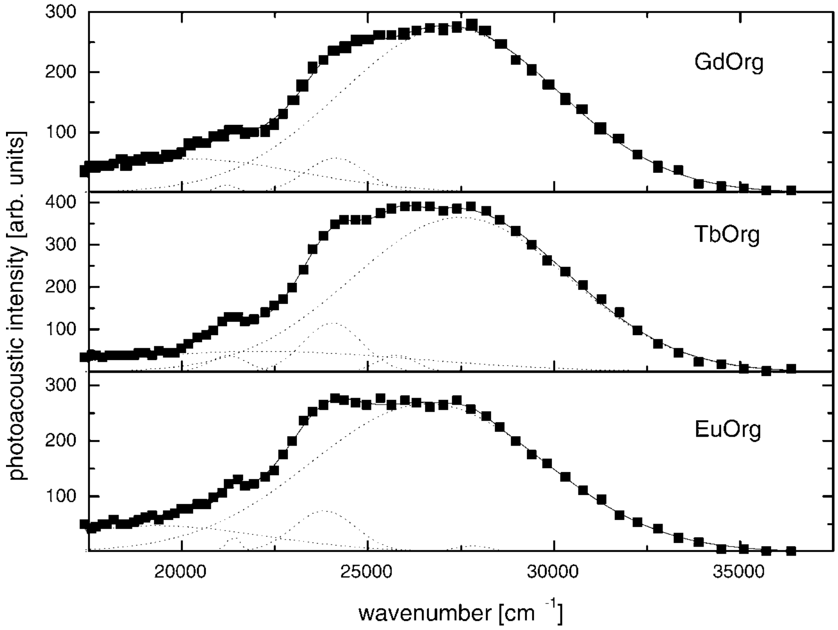

Figure 1. Photoacoustic absorption spectra of powder TbOrg, GdOrg, and EuOrg samples at room temperature. Solid (sum) and dotted (components) lines show the best fit curves with Gaussian line shape.

the n → π^* transitions. The f-f transitions are weaker and usually observed in the higher wavelength region.[5] The positions (ν), integrated intensities (I), and linewidths ($\Delta\nu$) of PAS signals of the ROrg (R = Nd, Gd, Eu, Tb, Dy, Ho, Y, Er, and Yb) complexes are given in Table 1. The spectral parameters were calculated by fitting the experimental spectra (PA intensity vs. frequency) by superposition of an appropriate number of Gaussian-type curves using the Origin computer program. The intensity and linewidth of PA spectrum of the ligand are the result of the nonradiative relaxation of the ligand, the intermolecular energy transfer, and the following nonradiative relaxation of the central R(III) ion.[12,13] The positions of the n → π^* transitions appear in the 28,000–22,000 cm^{-1} range. The intensities and linewidths are found to depend strongly on the type of the rare-earth(III) ion (Table 1). This indicates that the replacement of the R(III) ions could influence the relaxation and the parameters of the nonradiative processes of the complexes involved in the n → π^* transitions.

The electronic spectral data of the lanthanide(III) complexes and the ligand 2-pyridinecarboxaldehyde benzoylhydrazone both in the solid state (Nujol) and in solutions of DMF have been already investigated and discussed.[10] An intense absorption band in 38,000–45,000 cm^{-1} range is assign to the $\pi \rightarrow \pi^*$ transition of the five-membered chelate rings.

Table 1. The values of the parameters of the PA spectra of the binitrato-bis[*N*-(2-pyridylmethylene)-*N*′-benzoyl-hydrazone]R(III) nitrate (R = Nd, Gd, Eu, Tb, Dy, Ho, Er, and Yb) complexes

Complex	Frequency ν (cm^{-1})	Relative intensity I_i (arb. units)	Relative total intensity ΣI_i	Linewidth $\Delta\nu$ (cm^{-1})
NdOrg	27,548	1.00	1.00	6320
	24,691	0.48(5)		4290
	23,364	0.33(3)		1960
GdOrg	27,200	0.82(5)	0.66	5860
	24,130	0.12(2)		1580
	21,192	0.03(2)		537
	26,616	0.68(2)	0.55	3055
EuOrg	23,832	0.14(2)		2550
	21,386	0.07(1)		620
TbOrg	27,487	1.13(5)	1.23	5833
	25,600	0.27(3)		1000
	24,048	0.51(2)		1540
	21,237	0.28(3)		1000
DyOrg	27,472	0.65(3)	0.41	6520
	23,753	0.10(2)		2510
YOrg	28,653	0.92(2)	0.99	5200
	24,938	0.87(3)		8500
HoOrg	28,248	0.68(4)	0.76	5550
	25,000	0.43(3)		5940
	24,038	0.07(2)		2470
	22,935	0.10(2)		3200
ErOrg	27,855	0.87(4)	0.55	6200
	23,095	0.13(2)		4780
YbOrg	28,329	0.87(3)	0.75	5670
	24,038	0.12(2)		2950
	20,080	0.37(4)		8330

The accuracy of frequency and linewidth values is estimated to be within ±1% and ±5% range, respectively.

Another intense absorption band in the region ~33,000 cm^{-1} is attributed to intraligand transition of the $\pi \rightarrow \pi^*$ type located mainly on the C═N group. A third intense band appears in the 24,000–29,000 cm^{-1} region, which is assigned to the $n \rightarrow \pi^*$ transition located on the carbonyl group.[10]

The PA spectra are selectively sensitive only to the heat-producing de-excitation processes, and the intensity of thermally thick sample could be described by the following relation:[14]

$$I = b\,A_{abs}\gamma \tag{1}$$

where A_{abs} is the absorbance of the sample, γ is the probability of nonradiative transitions after excitation, and b is a coefficient that is determined by the thermal properties of the sample and by the spectrometer. Classically, the intermolecular energy-transfer efficiency of lanthanide complexes depends mainly on the two energy-transfer processes, one of which is from the lowest triplet state of organic ligand to the resonant level of lanthanide ion by the resonant exchange interaction. The energy transfer rate P could be given by the relation obtained from Dexter's theory:[15]

$$P = (2\pi Z^2)\int F_s(E)\varepsilon_a(E)dE \tag{2}$$

where Z is the charge of the central ion, $F_s(E)$ represents the observed shape of the emission band of the energy donor (the triplet state of the ligand), and $\varepsilon_a(E)$ is the shape of the absorption band of acceptor (the excited state of the central ion). Therefore, P depends on the overlap between the triplet state of organic ligand and the resonant level of lanthanide ion. If the energy gap is too large, the energy-transfer rate constant will be decreased due to the decrease in the overlap between the donor and acceptor.

The second process is the inverse energy transfer by the thermal de-excitation mechanism. The thermal de-excitation rate K(T) could be given by the following relation:

$$K(T) = A\exp(-\Delta E^{3+}_{T-R}/kT) \tag{3}$$

where $\Delta E^{3+}_{T\text{-}R}$ is the energy difference between the ligand triplet state and the resonant level of rare-earth(III) ions, k is the Boltzmann constant. If the energy gap is too small, the efficiency of energy transfer will decrease after the thermal de-excitation process. These additional processes could have an influence on the intensities of PA signals.

In the Rosencwaig-Gersho model of PAS for solids, it has been assumed that the relaxation process in the sample is purely nonradiative and instantaneous within the period of the light modulation.[16] When a system simultaneously includes nonradiative and radiative process, the excitation or absorbed energy ($E_{ex} = h\Omega$) is not fully converted to heat, and the photoemissive effects have sometimes been taken into account in the analysis of the PAS signals.[9]

It has been supposed that the area below the PA line could be used for an estimation of the relative intensity of nonradiative processes. The spectrum of NdOrg has been taken as a reference, and the relative intensity of the $n \rightarrow \pi^*$ transitions for other rare-earth complexes have been calculated in respect to the reference (Table 1). For the nonmagnetic sample of YOrg, the PA spectrum has been simulated by using only two lines, centered at 28,653 cm^{-1} and 24,938 cm^{-1}, respectively. The integrated intensity of the high-energy PA line is greater than for the low-energy transition. For all other investigated samples, the same tendency is also observed (Table 1). The most intense PAS line of all the highest energy transitions is registered for the TbOrg complex followed by the NdOrg complex. The samples of DyOrg, HoOrg, and EuOrg have shown the lowest intensity of the highest energy PA line.

For all other samples, the integrated PA intensity of that transition is almost the same. Additionally, the total intensity taken as a sum of integrated intensities of all PAS lines has been calculated. The total relative intensity is roughly the same for all investigated samples, with the exception of DyOrg and ErOrg (Table 1), meaning that for these complexes the processes described by relations (2) and (3) are less probable than for other ligands.

The number of nonradiative processes is almost constant over the spectrum of the investigated complexes as evidenced by their relative intensities, but the linewidths are rather different and they strongly depend on the rare-earth(III) ion. The linewidth is governed by the relaxation processes. The linewidth of the PAS line of the highest energy $n \rightarrow \pi^*$ transition is similar for all investigated samples ($5200 \div 6500\,\mathrm{cm}^{-1}$), except for EuOrg complex ($3055\,\mathrm{cm}^{-1}$), meaning that the time of intermolecular energy transfer for that transition does not depend substantially on the rare-earth(III) ion. As the charge transfer is the main process involved in the formation of the stabilized organometallic compound, the relaxation processes are very important. In the case of the PAS lines for other observed $n \rightarrow \pi^*$ transitions, an essential spread of values of the linewidths is observed, from $537\,\mathrm{cm}^{-1}$ (YOrg) to $8500\,\mathrm{cm}^{-1}$ (GdOrg). In differently excited processes, the relaxation time of other $n \rightarrow \pi^*$ transitions is being critically influenced by the surrounding ions.

As the PA spectrum gives only response to nonradiative process, the PA signals of fluorescence energy levels will be relatively weak. The different intensities and positions between PA and electron absorption spectroscopy may indicate the fluorescent properties of energy levels. In this respect, all investigated complexes could be divided into three groups: with strong (NdOrg, TbOrg, ErOrg, YbOrg), medium (EuOrg, HoOrg) and weak (GdOrg, DyOrg, YOrg) fluorescent properties.

In summary, the existence of intense photoacoustic absorption by means of the $n \rightarrow \pi^*$ transitions has been proved in rare-earth complexes of organic compounds. The intensities, linewidths, and positions of PA absorption lines are strongly influenced by type of the rare-earth ion. Such effects become pronounced whenever the rare-earth ion possesses a more complicated electronic structure. The greatest changes are observed in the case of integrated intensity. It is proposed that PA effects related with these transitions are crucial in biophysical processes occuring in the living matter. By comparing the electronic spectral data and PA spectra, the strength of fluorescent properties of investigated samples has been estimated.

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