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Raman Scattering in Semiconductor Structures Based on Monophthalocyanine and Triphthalocyanine Molecules Incorporating Erbium Ions

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Abstract—Semiconductor structures of the type of butyl-substituted erbium monophthalocyanine and triphthalocyanine are studied by Raman spectroscopy. It is shown that, when the sandwich-like structure of the molecule incorporating two complexing atoms between the ligands is considered instead of the planar molecular structure with one ligand and one metal atom, a series of lines appears in the Raman spectrum. In this series, the wave numbers of the lines represent an arithmetic progression with the arithmetical ratio $\sim 80 \text{ cm}^{-1}$. It is suggested that this feature is due to the larger number of organic molecules per metal atom in the triphthalocyanine complex, and the four Raman peaks at the frequencies 122, 208, 280, and 362 cm^{-1} are the manifestation of slight out-of-plane vibrations of the phthalocyanine ligands.

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1. INTRODUCTION

At the present time, molecular compounds based on phthalocyanines are promising materials for organic microelectronics.

These heterocyclic compounds exhibit high thermal resistance and do not decompose when heated up to 600°C in air and 900°C in vacuum [1]. Thermal stability of phthalocyanines allows the production of bulk organic molecular crystals by sublimation when deposited on substrates heated to various temperatures, as well as by sputtering from the gas phase [2]. The high sensitivity to changes in the composition of the surrounding environment has been beneficial for using phthalocyanines as one of the basic components to develop gas sensors [3, 4].

The ability of macrocyclic phthalocyanine molecules to form compounds with almost all elements of the periodic table makes it possible to synthesize a large family of semiconductor structures referred to as metal phthalocyanines [5]. Metal phthalocyanine complexes can serve as active catalysts of mild and selective oxidation.

It is now known that lanthanide phthalocyanine complexes can form sandwich-like “three-deck” structures composed of two atoms of the complexing agent and three phthalocyanine ligands. Such compounds are referred to as triphthalocyanines [6].

The purpose of this study is to investigate erbium monophthalocyanine and triphthalocyanine by Raman

spectroscopy over a wide frequency range of Raman shifts.

2. EXPERIMENTAL

The butyl-substituted erbium monophthalocyanine samples to be studied were produced from ligands in the course of chemical reaction by boiling in orthodichlorobenzene with erbium acetate. The erbium-tripphthalocyanine-type structures were synthesized from free ligands in boiling alcohol [7]. The structural formulas of the samples without peripheral butyl substitutes are illustrated in Fig. 1. For the illustration of the molecules of phthalocyanine complexes, we used the Gauss View 3.07 graphics software package.

The samples of erbium phthalocyanine complexes were deposited on quartz substrates by the spin-coating technique.

To record the Raman spectra, we used a Jobin Yvon HR800 Raman spectrometer. For the source of excitation, we used a He–Ne laser emitting radiation at the wavelength 632.82 nm .

3. RESULTS AND DISCUSSION

Figures 2 and 3 show the Raman spectra of butyl-substituted erbium monophthalocyanine and triphthalocyanine (curves 1, 2).

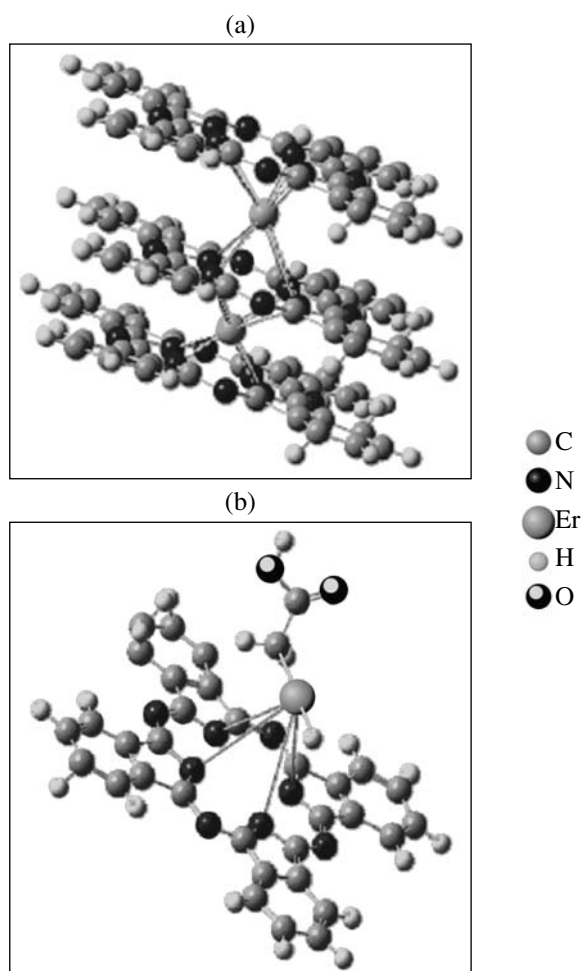


Fig. 1. Structural formulas of the erbium phthalocyanine complexes: (a) erbium triphthalocyanine and (b) erbium monophthalocyanine.

For these complexes, in the region of large Raman shifts, the Raman peaks are observed against the background of a broad photoluminescence (PL) band resulting from electron transitions in the erbium ions from the $^4G_{11/2}$ state [8]. In the case of erbium-monophthalocyanine-type planar structures, this PL band peak is at a wave number of about 2450 cm^{-1} . In a sandwich-like structure, when considered instead of the planar structure, the number of ligands is three times larger, and the PL band is shifted to larger wave numbers. For erbium triphthalocyanine, the maximum of the PL band is close to 3300 cm^{-1} .

The narrow 1676 , 1609 , and 1551 cm^{-1} Raman peaks in erbium monophthalocyanine correspond to stretching vibrations of benzene rings [9, 10]. One more type of vibration of benzene rings manifests itself in the vicinity of 945 cm^{-1} . These are the out-of-plane vibrations of benzene rings [9]. Such vibrations become apparent mainly in sandwich-like structures of the type of bisphthalocyanine and triphthalocyanine

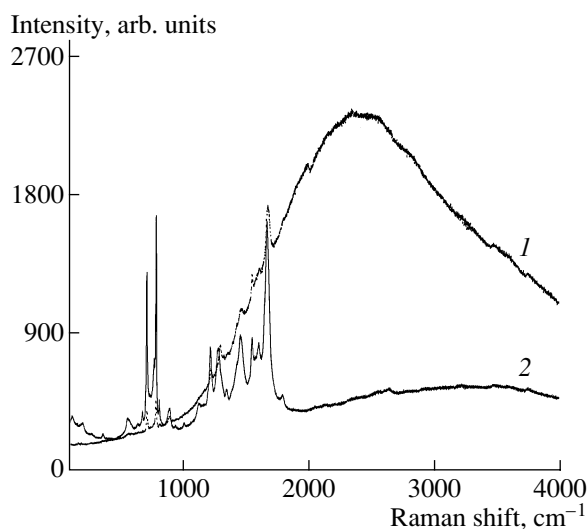


Fig. 2. Raman spectra of the butyl-substituted erbium phthalocyanine complexes in the range $100\text{--}4000\text{ cm}^{-1}$. Curves 1 and 2 refer to (1) erbium monophthalocyanine and (2) erbium triphthalocyanine.

[10]. In the spectra of the erbium monophthalocyanine complexes (curves 1 in Figs. 2, 3), these peaks are lacking.

When we pass to smaller wave numbers, we record the Raman lines at the frequencies 1461 and 1350 cm^{-1} typical of the --C=C-- vibrations of pyrrole rings [10]. In the triphthalocyanine-type structures, we observe a 1130 cm^{-1} peak corresponding to the out-of-plane vibrations of pyrrole rings. According to [10], the 1350 cm^{-1} peak can be also attributed to the bending vibrations of benzene rings.

Vibronic properties of the isoindole group are manifested as the 1432 cm^{-1} peak typical of stretching vibrations [10].

The in-plane bending vibrations of the carbon-hydrogen bonds are observed as the 1302 , 1222 , and 1112 cm^{-1} lines. The 1302 cm^{-1} peak is observed only for the planar monophthalocyanine-type structures. In erbium triphthalocyanine, the 1302 cm^{-1} line is unobservable [10].

The bending vibrations of the carbon-hydrogen bonds can present a series of peaks in the regions around 1285 and 897 cm^{-1} . However, these lines are most likely due to the vibronic properties of the molecules of peripheral substitutes, i.e., erbium monophthalocyanine and triphthalocyanine in the complexes under study. A contribution to the above Raman lines in this region of wave numbers can be also made by the butyl substitutes [9].

The bridge-like vibrations characteristic of the --C=N atomic combination manifest themselves as three Raman peaks at the frequencies 788 , 775 , and 718 cm^{-1} [9, 10].

The out-of-plane vibrations of phthalocyanine rings show themselves as the 816 , 683 , 643 , 561 , and

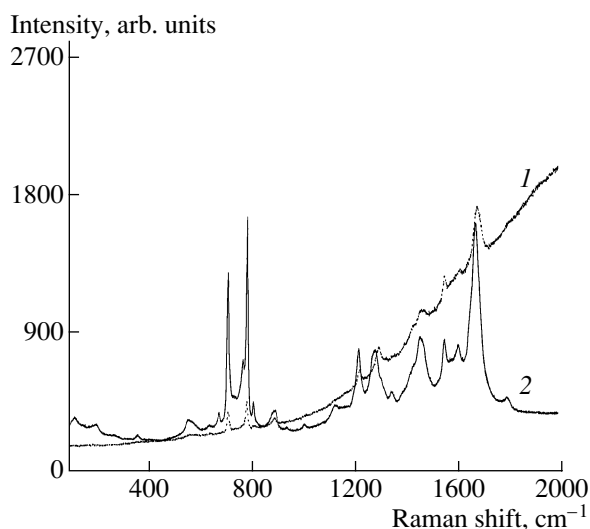


Fig. 3. Raman spectra of the butyl-substituted erbium phthalocyanine complexes in the range 100–2000 cm^{-1} . Curves 1 and 2 refer to (1) erbium monophthalocyanine and (2) erbium triphthalocyanine.

570 cm^{-1} lines [10]. The latter peak is evident in the spectra of the planar erbium monophthalocyanine structures. In the erbium-tripthalocyanine-type structures, the 570 cm^{-1} peak is unobservable.

In the spectra of erbium triphthalocyanine, in the region of large Raman shifts (Fig. 3, curve 2), a series of four peaks is observed at 366, 279, 208, and 122 cm^{-1} . These peaks are nearly equidistant. The average frequency separation between the peaks is $\sim 79 \text{ cm}^{-1}$. For the last three peaks in the series, the intensity is higher for smaller wave numbers. For each of the four peaks of the series, we estimated the ratio between the maximal intensities. For the 208 and 366 cm^{-1} lines, the ratio of the intensities is 1.27; for the 122 and 208 cm^{-1} , the ratio is 1.29; and for the 208 and 279 cm^{-1} , the ratio is 1.14.

In [11], it was shown that the Raman spectra of sandwich-like structures of the type of rare-earth-metal bisphthalocyanines could show a pair of lines separated from each other by 70 cm^{-1} . The frequencies of these lines are at the boundary between the middle and far infrared regions. Such lines correspond to the small-amplitude out-of-plane vibrations of phthalocyanine rings. In the Raman spectra of the planar erbium-monophthalocyanine-type structures, the above series of peaks is unobservable (Fig. 3, curve 1). This fact suggests that the position of the four peaks observed in this study does not depend on the type of peripheral substitutes or on the method of synthesis of the samples. The intensity and position of the four peaks can be dependent only on the larger number of organic ligands and complexing agents.

Thus, we can conclude that the 122, 208, 279, and 366 cm^{-1} peaks in the Raman spectra of erbium phtha-

locyanine complexes are characteristic of sandwich-like structures of the type of erbium triphthalocyanine.

4. CONCLUSIONS

Raman spectroscopy is applied to the experimental studies of the planar butyl-substituted erbium phthalocyanine structures of the type of monophthalocyanines and the sandwich-like structures of the type of erbium triphthalocyanine. For the two types of erbium-incorporating phthalocyanine structures, detailed identification of the features of the Raman spectra is carried out. The analysis of the results show four peaks in the region of large Raman shifts. These spectral features are observable only for the erbium triphthalocyanine structures. No such Raman bands are observed in the spectrum of erbium monophthalocyanine. From the analysis of the published data, it can be concluded that the four experimentally observed Raman lines correspond to the out-of-plane vibrations of phthalocyanine rings.

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