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AMORPHOUS, VITREOUS, AND ORGANIC SEMICONDUCTORS

Vibronic States in Organic Semiconductors Based on Non-Metal Naphthalocyanine. Detection of Heterocyclic Phthalocyanine Compounds in a Flexible Dielectric Matrix

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Abstract—The vibronic properties of semiconductor structures based on non-metal naphthalocyanine molecules are studied using IR and Raman spectroscopy methods. New absorption lines in the transmission spectra of such materials are detected and identified. Three transmission lines are observed in the range 2830–3028 cm^{-1}, which characterize carbon–hydrogen bonds of peripheral molecular groups. Their spectral positions are 2959, 2906, and 2866 cm^{-1}. It is detected that the phthalocyanine ring can also exhibit its specific vibronic properties in the Raman spectra at 767, 717, and 679 cm^{-1}. The naphthalocyanine molecule in the organic dielectric matrix of microfibers is described using IR spectroscopy. It is shown that the set of vibrations characterizing the isoindol group, pyrrole ring, naphtha group, and C–H bonds, allows an accurate enough description of the vibronic states of the naphthalocyanine complex in complex heterostructures to be made. The spectral range with fundamental modes, characterizing a naphthalocyanine semiconductor in a heterostructure, is 600–1600 cm^{-1}. A comparison of the compositions of complex systems with a similar heterostructure containing lutetium diphthalocyanine demonstrated few errors.

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1. INTRODUCTION

Organic materials offer new methods and techniques for solving unusual design problems in modern industry and technology [1–8]. Among organic semiconductors, of particular attention are new phthalocyanine complexes. A wide class of materials including such heterocyclic compounds as subphthalocyanine [9] and supraphthalocyanine [10] which find wide use in modern micro- and optoelectronics. Naphthalocyanines, as well as erbium phthalocyanine complexes, strengthen the photovoltaic properties of multiwalled nanotubes [11, 12]. In particular, this is facilitated by an extra system of π electrons due to four additional benzene groups [13]. The ability of silicon naphthalocyanine complexes to form triplet states upon the absorption of light photons in the red spectral region and the reversible reaction with oxygen molecules allowed naphthalocyanines to be used as singlet oxygen generators [14]. Detailed description of the properties of naphthalocyanine complexes requires an analysis of their properties and their dynamics of change in that inorganic matrix whose characteristics can be modified or strengthened. In this research, the physical properties of naphthalocyanine complexes in an external matrix are studied by infrared (IR) spectroscopy. This method for examining the state of naphthalocyanine complexes has one important advantage over chemical and ion–plasma analysis methods: the system exposure does not lead to its destruction.

The main objective of this research is the detailed study of vibronic states in organic semiconductors based on non-metal naphthalocyanine using IR spectroscopy and Raman scattering (RS).

2. EXPERIMENTAL

Non-metal naphthalocyanine molecules were synthesized according to the standard method described in [15].

Finished phthalocyanine complexes were applied to silicon and quartz substrates by liquid-drop adsorption.

The vibronic properties of organic semiconductor structures based on phthalocyanine complexes were studied by RS and IR spectroscopy methods. The RS spectra excited to the wavelength 514 nm (Ar^+ laser)

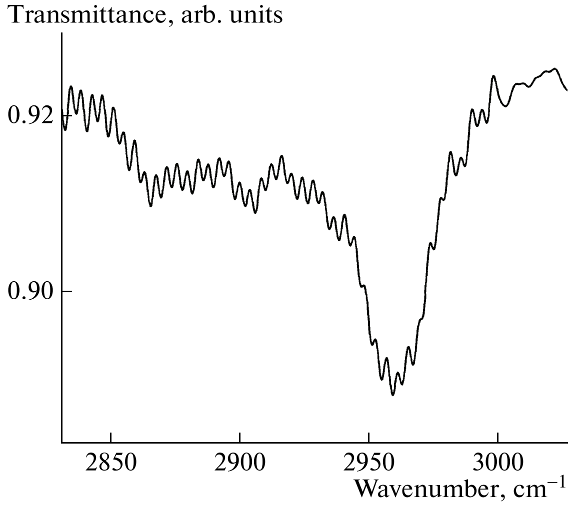

Fig. 1. Spectral characteristics of the transmittance for an organic semiconductor based on non-metal naphthalocyanines in the range 2831–3020 cm^{-1}.

were measured using a Horiba Jobin-Yvon T64000 micro-Raman spectrometer. The wave-number spectral resolution was 1 cm^{-1}. Measurements were performed using the geometry of backscattered light normally incident on the sample surface at room temperature.

The transmission spectra in the mid- and far-IR spectral regions were measured using Bruker IFS 113v and Tensor 26 Fourier spectrometers. The wave-number resolution was 2 cm^{-1}.

To study the behavior of phthalocyanine complexes in a flexible dielectric matrix, synthesized naphthalocyanine complexes were adsorbed within an organic porous matrix of microfibers. A tetrahydrofurane (THF) solvent was used.

3. EXPERIMENTAL RESULTS AND DISCUSSION

In the range 2830–3028 cm^{-1}, three transmission lines are observed, which characterize carbon–hydrogen bonds of peripheral molecular groups. As shown in Fig. 1, the spectral positions of these lines are 2959, 2906, and 2866 cm^{-1}. According to [16–20], two symmetric and two asymmetric vibrational modes can be located in this range, however, the low-frequency asymmetric mode may not appear (Fig. 1) in some semiconductor structures based on phthalocyanine complexes [16].

The line at 1943 cm^{-1} corresponds to C=C stretching vibrations of benzene rings closest to the molecule center. In the Raman spectrum at 1938 cm^{-1}, a low-intensity line may appear, which also characterizes this mode.

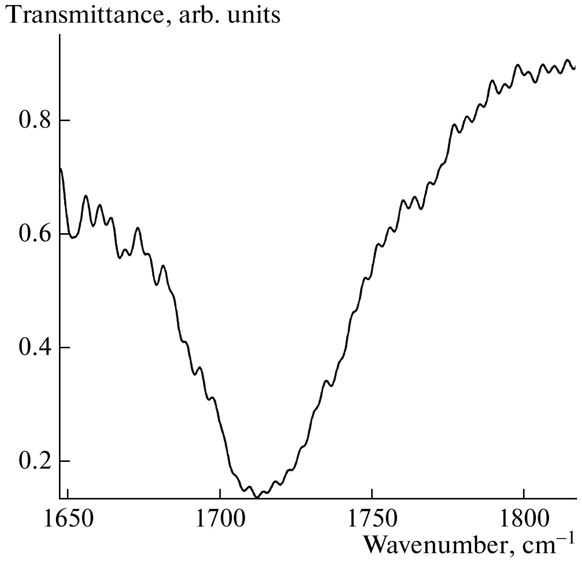

Fig. 2. Spectral characteristics of the transmittance for an organic semiconductor based on non-metal naphthalocyanines in the range 1647–1818 cm^{-1}.

The absorption lines at 1830 and 1803 cm^{-1} can correspond to vibrations of the naphtha group (an additional benzene ring attached to the isoindol molecular group). C=H bending vibrations and pyrrole ring stretching vibrations can also contribute to absorption lines.

In the region of 1770 cm^{-1} in the transmission spectra, we can see a low-intensity line corresponding to C=N stretching vibrations of the isoindol group and muonic atoms (Fig. 2). Absorption lines at 1761, 1751, and 1750 cm^{-1} can also appear in this region, which characterize the C=C stretching vibrations of benzene rings belonging to the naphtha group. It is difficult to unambiguously interpret these lines, since they are characterized by low intensity.

The naphtha-group vibrations also exhibit their vibronic properties, significantly contributing to the absorption line at 1720 cm^{-1}. C=N stretching vibrations of the pyrrole ring and bending vibrations of C=H bonds arranged along benzene rings also contribute to this line.

The absorption minima at 1712, 1669, 1651, and 1569 cm^{-1} correspond to stretching vibrations of benzene rings arranged closer to the molecular complex center. The absorption minima at 1545 and 1530 cm^{-1} characterize the coupled mode of muonic atoms and the isoindol group, and vibrations of the isoindol group itself.

In the range 1500–1400 cm^{-1}, isoindol stretching vibrations are observed, to which the lines at 1509, 1497, 1432, and 1415 cm^{-1} correspond. The absorption line at 1365 cm^{-1} corresponds to the same modes.

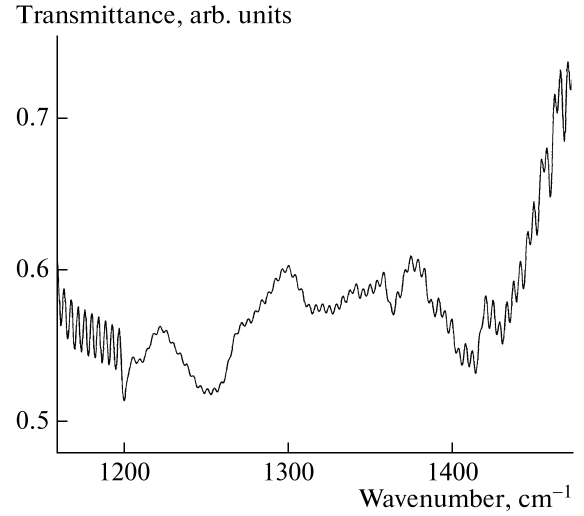

Fig. 3. Spectral characteristics of the transmittance for an organic semiconductor based on non-metal naphthalocyanines in the range 1160–1473 cm^{-1}.

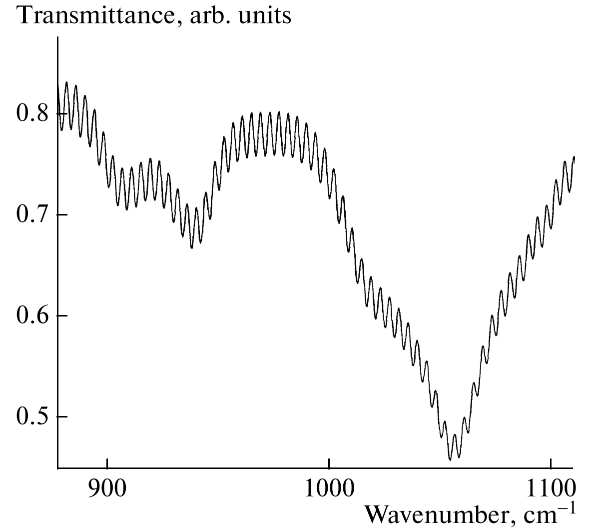

Fig. 4. Spectral characteristics of the transmittance for an organic semiconductor based on non-metal naphthalocyanines in the range 878–1111 cm^{-1}.

In the region of 1460 cm^{-1}, the transmission spectrum of the organic semiconductor based on non-metal naphthalocyanine contains an absorption line characterizing the stretching vibrations of isoindol and bending vibrations of C–H bonds. The low-intensity line at 1431 cm^{-1} is of the same origin (Fig. 3).

The line at 1415 cm^{-1} corresponds to the coupled mode of bending vibrations of the pyrrole ring, bending vibrations of C–H bonds, and C–N stretching vibrations of the isoindol group and muonic atoms (Fig. 3).

Isoindol stretching vibrations exhibit their vibronic properties at 1407 cm^{-1}.

The line at 1324 cm^{-1} characterizes the bending vibrations of all C–H bonds arranged along the perimeter of the naphthalocyanine molecule (Fig. 3).

The absorption minimum at 1253 cm^{-1} corresponds to the bending vibrations of all C–H bonds arranged along the perimeter of the naphthalocyanine molecule (Fig. 3).

In the region of 1211 cm^{-1}, we can see the contribution of naphtha-group stretching vibrations and C–H bond bending vibrations to the vibronic spectrum of the naphthalocyanine semiconductor (Fig. 3).

The mixed mode of naphtha group bending vibrations and pyrolle ring C–H and N–H bonds is in the region of 1058 cm^{-1} (Fig. 4).

Near this line, in the region of 1052 cm^{-1}, there can appear the mixed mode of naphtha group bending vibrations and isoindol and azo-atom bond stretching vibrations.

Stretching vibrations of the isoindol group are also present at 543 cm^{-1}.

The line at 936 cm^{-1} (Fig. 4) can correspond to bending vibrations of the isoindol group.

The line at 613 cm^{-1} characterizes stretching vibrations of the phthalocyanine ring.

In the region of 604 cm^{-1}, the mode of the isoindol and naphtha group torsional vibrations is observed. This mode can also manifest itself at 571, 568, 565, 562, 516, and 503 cm^{-1}.

The breathing mode of the phthalocyanine ring is responsible for the lines at 493, 484, 445, and 175 cm^{-1}.

The out-of-plane vibrations of the åðó-naphtha group are responsible for absorption lines at 439, 428, and 424 cm^{-1}.

In the Raman spectra, maxima at 1629, 1596, 1538, 1407, 1356, 825, 767, 717, and 679 cm^{-1} are detected, which also fully describe the pattern of vibrational and rotational transitions within the organic semiconductor under study (Figs. 5–8).

The maxima at 1629, 1596, and 1538 cm^{-1} correspond to stretching vibrations of benzene rings (Fig. 5).

The RS lines at 1407 and 1356 cm^{-1} correspond to stretching vibrations of the isoindol group. The signal at 1365 cm^{-1} is the mixed mode of the naphtha group and pyrrole ring stretching vibrations.

The RS lines at 1305 and 1321 cm^{-1} characterize the mixed mode of C=C stretching vibrations of the pyrrole ring and stretching vibrations of benzene groups (Fig. 6).

The maximum at 1278 cm^{-1} corresponds to the complex mode of stretching vibrations of the benzene group and bending vibrations of C–H bonds. Bending vibrations of C–H bonds also manifest themselves at 1219, 1178, and 1086 cm^{-1} (Fig. 7).

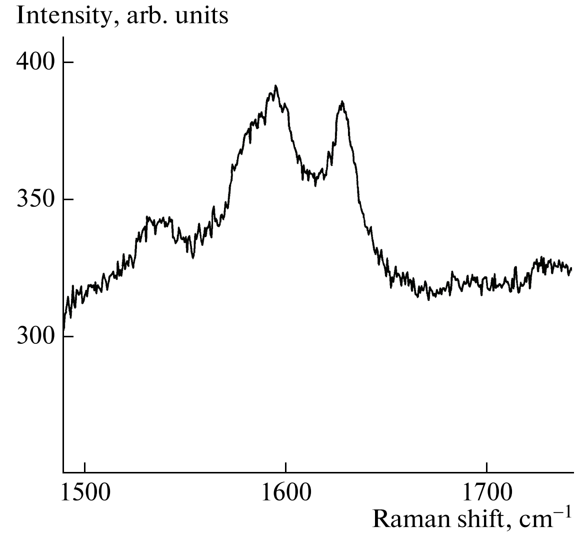

Fig. 5. Spectral characteristics of the Raman scattering signal for an organic semiconductor based on non-metal naphthalocyanines in the range 1490–1744 cm^{-1}.

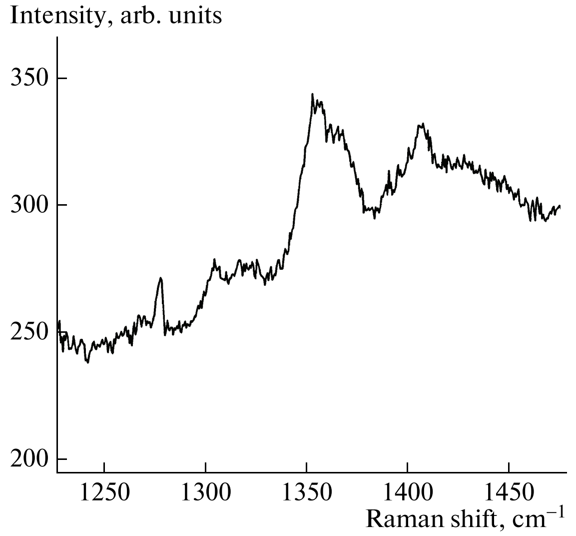

Fig. 6. Spectral characteristics of the Raman scattering signal for an organic semiconductor based on non-metal naphthalocyanines in the range 1227–1476 cm^{-1}.

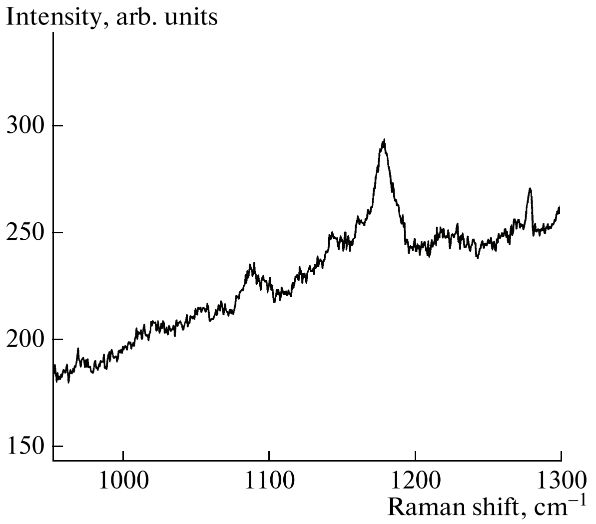

Fig. 7. Spectral characteristics of the Raman scattering signal for an organic semiconductor based on non-metal naphthalocyanines in the range 952–1200 cm^{-1}.

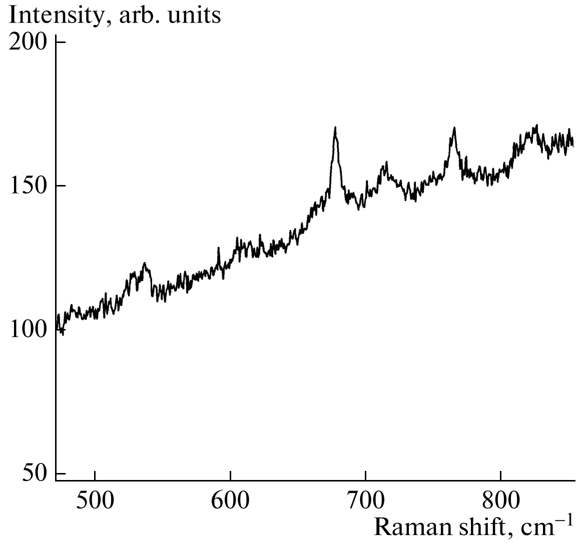

Fig. 8. Spectral characteristics of the Raman scattering signal for an organic semiconductor based on non-metal naphthalocyanines in the range 472–856 cm^{-1}.

At 1143 cm^{-1} (Fig. 7), the mode of breathing vibrations of the pyrrole ring is observed.

The RS line at 827 cm^{-1} corresponds to bending vibrations of C=H bonds out of plane.

The RS maximum at 767 cm^{-1} corresponds to stretching vibrations of the phthalocyanine ring.

The RS line in the region of 717 cm^{-1} corresponds to torsional vibrations of the phthalocyanine ring.

The RS signal at 679 cm^{-1} corresponds to the breathing mode of the naphthalocyanine rings.

All data obtained in this study are in good agreement with published data [21, 22].

Having used detailed information on the vibronic states of an organic semiconductor based on naphthalocyanines, we can give an informative [I'm not sure which adjective works best here] description on an organic heterostructure consisting of microfibers and phthalocyanine molecular complexes. As the main method for inspecting the heterostructure, IR spectroscopy is used. The reason for choosing this technique is the conventional geometry of the sample posi-

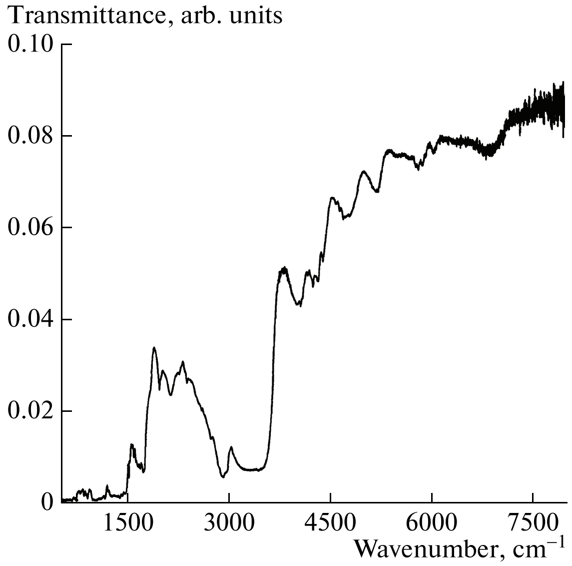

Fig. 9. Spectral dependences of the transmittance for the heterostructure based on microfibers in the range 500–7000 cm^{-1}.

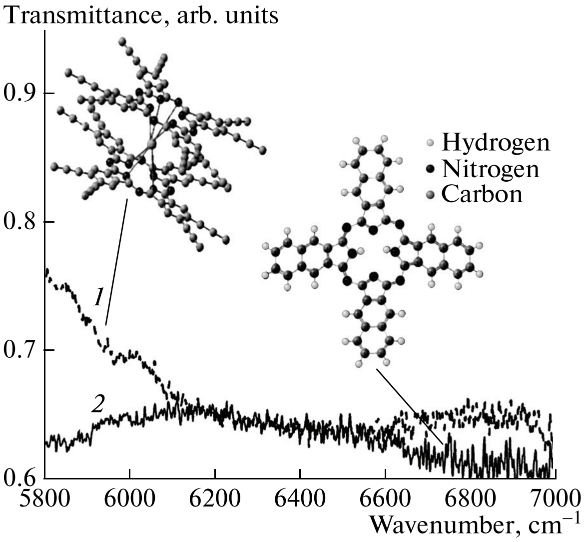

Fig. 10. Spectral dependences of the transmittance for the heterostructure based on microfibers and phthalocyanine complexes in the range 5800–7000 cm^{-1}: (*1*) lutetium diphthalocyanine and (*2*) non-metal naphthalocyanine.

tion with respect to the radiation source. Figure 9 shows the spectrum of the dielectric matrix consisting of microfibers. We can see that the dielectric matrix spectrum is quite difficult for analysis, since it contains many absorption lines in the range 7000 to 500 cm^{-1}. To prove that the choice of method for examining the heterostructure was the correct one, a structure of microfibers and lutetium diphthalocyanine is taken as a reference sample (Figs. 10–11). Figure 10 shows that IR spectroscopy allows the detection of intracenter transitions in the microfiber type matrix (6400 cm^{-1}) in the lanthanide shell (Fig. 10, curve *7*). A comparison of curves *1* and *2* shows that this method for analyzing the complex heterostructures makes it possible to avoid methodical error. In particular, in the study of a heterostructure containing a naphthalocyanine semiconductor, there is no absorption minimum at 6400 cm^{-1}, which correlates well with features of the chemical composition of the phthalocyanine complexes introduced into the matrix. An analysis of the presented spectra shows that the behavior of phthalocyanine semiconductors in the microfiber system can be quite accurately described using IR spectroscopy in the range 600 to 1600 cm^{-1} (Fig. 11). It appears that the main absorption lines characterizing this sample are a set of vibrations of the isoindol group, pyrrole ring, naphtha group, and C–H bonds. The range 600–800 cm^{-1} including vibrations of the phthalocyanine ring is not appropriate for interpretation, since absorption lines of a phthalocyanine semiconductor are modulated by intense absorption by matrix molecules.

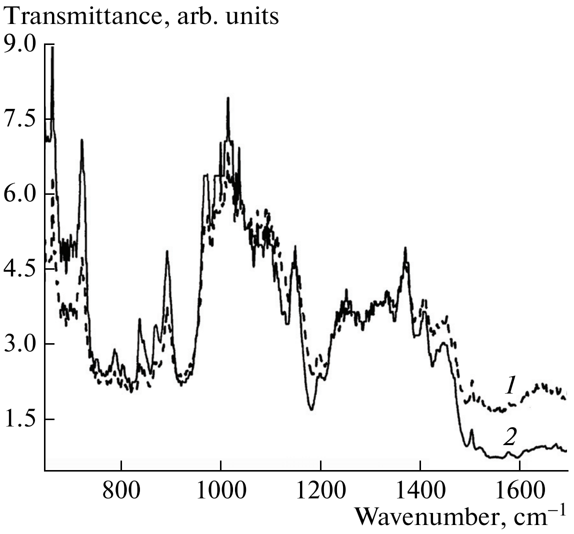

Fig. 11. Spectral dependences of the transmittance for the heterostructure based on microfibers and phthalocyanine complexes in the range 500–1700 cm^{-1}: (*1*) lutetium diphthalocyanine and (*2*) non-metal naphthalocyanine.

4. CONCLUSIONS

The spectral dependences of the absorption in the mid-IR region for organic semiconductors based on non-metal naphthalocyanine were measured and analyzed. It was shown that three transmission lines are observed in the range 2830–3028 cm^{-1}, which characterize carbon–hydrogen bonds of peripheral molecular groups. A series of lines, corresponding to torsional vibrations of the naphtha group was detected. Furthermore, the spectral dependence of Raman scattering was interpreted in detail; it was detected that the phthalocyanine ring exhibits its vibronic properties as lines at 767, 717, and 679 cm^{-1}.

It was shown that IR spectroscopy allows adequate analysis and examination of the state of complex heterocyclic molecules in heterostructures based on microfibers.

It was found that the main absorption lines characterizing the states of the phthalocyanine semiconductor in the complex matrix are in the range 600–1600 cm^{-1} and correspond to vibrations of the isoindol group, the pyrrole ring, the naphtha group, and the C–H bond.

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