

## ADSORBED MOLECULES AS PROMISING SYSTEMS FOR A SPECTRAL-SELECTIVE RECORD OF INFORMATION

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A central place in the scientific legacy of the late Academician G. P. Gurinovich is occupied by works concerned with the photophysics of complex organic compounds. The successes achieved in this field have been largely due to the variety of experimental techniques employed and to the creation of nontraditional objects that permitted one to reveal the studied regularities in the most distinct form.

The possibility of burning narrow stationary holes in inhomogeneously broadened vibronic absorption bands of complex molecules underlies an approach to increasing in the density of an optical record of information that is being intensely developed at the present time [1]. As is known, the ratio of the inhomogeneous band width to the homogeneous one (to the width of the burnt hole) may amount to  $10^3$ - $10^4$  at helium temperatures [2]. This value is used to estimate the potential multiplicity of an increase in the record density (in relation to the traditional bitwise record in spatial coordinates, where the density is limited by the diffraction limit and, in the two-dimensional version, is bounded by a value of the order of  $10^8$  bit/cm<sup>2</sup>). Due to the introduction of an additional "spectral coordinate" it is possible to write down  $10^3$ - $10^4$  bits in the form of narrow spectral holes in each spatial element.

It is evident, however, that the necessity of maintaining the recording medium at a low (helium) temperature is an obstacle to the practical use of this very tempting idea. In the absolute majority of cases, an increase in the temperature to 20-50 K in solid solutions of complex organic compounds in organic solvents is accompanied by a sharp increase in the electron-phonon interaction; the decrease in the Debye-Valler factor and the broadening of the phononless line lead to the impossibility of burning holes even at such relatively low temperatures. This point of view had been generally accepted, but the appearance of the work of G. P. Gurinovich and co-workers [3], in which fine-structure fluorescence spectra were obtained upon selective excitation for multiatomic molecules at 77 K, pointed to the possibility of the existence of systems with a relatively weak temperature dependence for electron-phonon bonding (EPB). From the viewpoint of the prospects for practical application, the search for molecular systems that permit the burning of holes at technologically more acceptable temperatures (for example, at the liquid nitrogen temperature) seems to be a very topical problem.

Thus far a number of results have been obtained pointing to the fact that adsorbed molecules look very promising as such systems. Thus, it is shown in [4, 5] that in the absorption spectra of hinizarine, sorbed chemically on alumina, at 77 K holes with widths of about  $15\text{ cm}^{-1}$  can be burned, and it is noted that the production of holes at such relatively high temperatures testifies to weak EPB of the adsorbed molecule with the matrix. Later, the same group of researchers investigated the burning of holes in spectra of octaethylporphin (OEP) physically sorbed on alumina [6], and they found that at 4.2 K holes with widths of  $2\text{ cm}^{-1}$  and a depth of up to 75% are burned. At 90 K holes were also burned, but they were much broader ( $54\text{ cm}^{-1}$ ).

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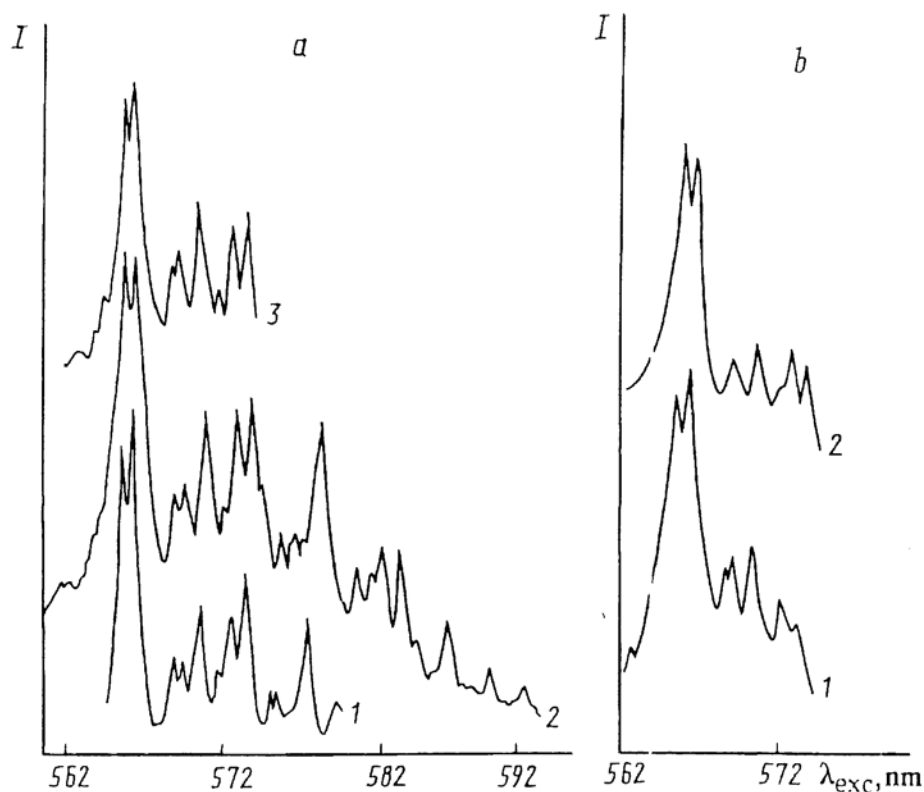


Fig. 1. Fluorescence excitation spectra of OEP in the case of narrow-band recording and selective laser excitation: a) OEP adsorbed on an industrial film of PE (1), spectrum from [8] (2), on a modified sample of PE (3); b) OEP adsorbed on paraffin (1), on polycrystalline anthracene (2).  $T = 77$  K.

We note that in recent years the possibility of burning holes at 77 K in spectra of organic compounds (mainly porphyrins) implanted in polymer matrices [7-9] has been shown. Thus, in [9] holes with a width of  $4 \text{ cm}^{-1}$  were obtained in an inhomogeneously broadened 0-0-band of OEP implanted in a polyethylene (PE) film by using the authors' technique of diffusion from the gas phase. We note that for OEP in a vitrified solvent (cyclohexane:toluene at 3:1) at 77 K holes were not detected, while the fluorescence excitation spectrum recorded in narrow-band recording had a very blurred structure compared to the spectrum of OEP in PE.

Thus, it was demonstrated experimentally that organic molecules sorbed on various kinds of matrices constitute systems characterized by relatively weak EPB at relatively high (77 K) temperatures. The force of EPB for a certain type of molecules in the adsorbed state is much smaller than for the case of being in a frozen solvent. As regards polymer matrices, one must take into account the presence of an appreciable fraction (several percent) of the so-called free volumes in the total volume of the polymer matrix [10]; moreover, depending on the type of polymer and the procedure for preparing a solid polymer sample, both the indicated fraction of these volumes (for PE, for example, only variations in the density depending on the preparation procedure go beyond the limits of 5-6%) and the mean dimensions of individual "elementary" volumes, which attain hundreds and thousands of angstroms, can be varied. In view of this, it seems reasonable to expect similarity in the properties of the microenvironment for organic molecules that are sorbed on traditional sorbents with a developed surface (alumina, silica gel, etc.) and implanted in a polymer matrix, interpreting this implantation as an analog of sorption, in the given case in the free volumes of the polymer matrix. What these two types of matrices have in common is the presence of relative "spatial freedom" in the microenvironment of the molecule; this radically distinguishes the microenvironment in the given systems from the densely packed one in frozen organic solvents. Evidently, the noted difference in the character of the microenvironment is the reason for the weaker EPB in systems of sorbed molecules.

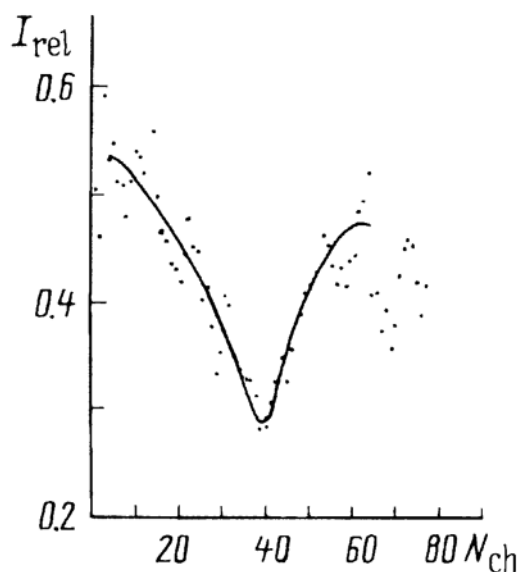


Fig. 2. Normalized spectral hole of OEP in a polyethylene film in the region of the 0-0-band (implantation from vapor, the time of burning is 20 min). The mean power of burning radiation is  $10^{-3}$  W (the first channel corresponds to  $1\text{ cm}^{-1}$ ).

The present work presents the results of an investigation of fluorescence excitation spectra in the case of narrow-band recording and also the contours of burnt holes for OEP (considered to be a convenient test object, on whose structural spectra vast experimental material is available) sorbed on different types of matrices: polymer (PE, polypropylene (PP), polymethyl metacrylate (PMMA), polyvinyl alcohol (PA)); alumina (A); disperse polycrystalline matrices (paraffin, anthracene; the latter were used as matrices-substrates onto which OEP was sputtered at 77 K from the gas phase). Various procedures for modifying the polymer matrices were developed: loosening of the structure by keeping polymer films in solvents up to their swelling with subsequent freezing of the object and removal of the solvent by lyophilic drying; production of polymer films from a solution with the use of various versions of drying (at room temperature, lyophilic). We tested various means of implantation of the dye: from the gas phase at different temperatures of the substrates, and from a solution. In essence, we performed primary screening of a rather wide range of objects with the aim of elucidating the effect of different kinds of factors on the spectroscopic characteristics of systems of "matrix-adsorbed molecule" type. The need for such work is dictated by the scarcity of available information on the fine-structure spectra of adsorbed molecules.

The fluorescence excitation spectra were recorded on a setup in which the excitation source was a tunable jet dye laser (Rhodamine 6G or phenalemine) pumped by radiation of the second harmonic of a YAG:Nd<sup>3+</sup> laser with continuous pumping and acoustooptical *Q*-switching (LTI-702). The repetition rate of the pulses was 5 kHz, and the spectral width of the radiation was  $2\text{ cm}^{-1}$ . The fluorescence radiation passed through a monochromator whose spectral width did not exceed  $4\text{ cm}^{-1}$ . The recording was done in the photon counting regime, and the signal was accumulated in a multichannel analyzer and was input to a personal computer for processing. The holes were burned by the pulsed dye laser radiation (the repetition rate was 10 Hz, and the spectral width was  $2\text{ cm}^{-1}$ ). The time-averaged power density ranged from 0.5 to  $5\text{ mW/mm}^2$ , and the time of burning varied from 2 to 15 min. The holes were probed by scanning the inhomogeneously broadened 0-0-transition band by radiation from a tunable laser; the contour was recorded in the form of the fluorescence excitation spectrum with wide-band (nonselective) recording. The results presented in the work relate to a temperature of 77 K.

As a preliminary criterion for estimating the properties of the matrix, we used the degree of structuring of the excitation spectrum (the widths of individual structural elements, the intensity of the structureless pedestal).

Fluorescence excitation spectra for OEP in PE (implantation from the gas phase) are presented in Fig. 1a. As is seen from the figure, the degree of structuring of spectra 1 and 2 differs: in spectrum 2 the pedestal is much higher. In this regard, we note that the degree of structuring depends on the concentration of OEP in the sample; the concentration could be varied by varying the time of exposure of the film to OEP vapor. Curve 1 corresponds to a low concentration; the possibility of a further decrease in it is limited by the sensitivity of the setup. With an increase in the concentration, the bands are broadened, the intensity of the structureless pedestal increases, and the spectrum starts to resemble that depicted by curve 2. For a sample loosened by structural modification (curve 3) it turned out to be possible to increase the concentration substantially without appreciable losses in the structure of the spectrum.

The noted changes in the spectra upon variation in the concentration are noncontradictorily explained by the lack of volumes ("loci of binding") that are acceptable for the sorption of OEP molecules in a polymer film. As the concentration increases, saturation of the acceptable volumes is attained, and contributions to the recorded spectrum start to come from centers that cannot be considered as isolated OEP molecules (associates, "quasi-associates" – microassemblies with energy transfer), which leads to blurring of the structure. In a modified (loosened) polymer, the fraction of volumes acceptable for sorption increases, which shifts the start of the manifestation of concentrational effects to the region of higher concentrations.

Results qualitatively similar to those described above were obtained for sorption of OEP in PP films. For PE and PP the widths of individual vibronic bands are  $15\text{--}20\text{ cm}^{-1}$ .

When OEP is sorbed on a "classical" sorbent (A), the width of the band in the excitation spectrum in narrow-band recording turns out to be substantially higher, i.e.,  $\sim 65\text{ cm}^{-1}$ . This result correlates with the aforementioned data on the burning of holes in the spectra of OEP sorbed on A [6]. We note that the frequency of the 0–0-transition (the maximum of the inhomogeneously broadened band) for OEP on A is shifted to the high-frequency region by 10 nm relative to the position for the OEP-PE system.

An argument in favor of the fact that the insertion of OEP from the gas phase into the matrix of a polymer can be justifiably considered to be an analog of sorption is results on the excitation spectra of OEP adsorbed from the gas phase on disperse polycrystalline samples. As such samples, we used paraffin and finely crystalline anthracene whose layer was produced by rapidly drying a solution of anthracene on a hot glass substrate. As follows from Fig. 1b, for such systems, in which the implantation of the large OEP molecules in the structure of a crystalline matrix is obviously out of the question (the sputtering of the dye from the gas phase was done on substrates cooled down to 77 K), the spectra turn out to be entirely similar to those obtained for OEP-PE and OEP-PP, i.e., sorption on "inert" nonpolar matrices gives similar results that depend little on the nature of the matrix. In connection with this, the noticeably large widths of the bands observed for OEP-A are explained by the strengthening of PFB due to the involvement of the "interior" of the tetrapyrrole cycle in the interaction for this kind of matrix, which contains, as is known, charged surface groups. In fact, the participation of the central groups of the tetrapyrrole cycle in the interaction with the charged structures of the surface (namely, the change in the distribution of the electron density upon electronic excitation is associated with excitation of cyclopolyene) should lead to stronger EPB compared to sorption of OEP, which contains in its structure a nonpolar "periphery" in the form of eight ethyl groups, on a nonpolar matrix. In the latter case, the interaction is determined by dispersion forces and exerts a weak effect on the characteristics of electronic transition (which also follows from the virtual coincidence of the frequencies of electronic transitions for OEP on various types of nonpolar matrices).

We note that in implantation of OEP in matrices of polar polymers (polyvinyl alcohol polymethyl metacrylate), the degree of structuring of the spectra turns out to be much lower than for nonpolar matrices; moreover, for example, for OEP-PVA one observes a high-frequency shift of the spectrum by 3 nm. These data agree with the remarks on stronger EPB for polar matrices.

For the OEP-PE systems we obtained holes in inhomogeneously broadened absorption spectra at 77 K and also investigated the kinetics of the disappearance of holes. The maximum experimentally recorded depth of a hole (Fig. 2) was as large as 40% (this is apparently the maximum depth attained to date for holes in spectra of organic molecules at 77 K). For such a depth, the holes are somewhat broader ( $10\text{ cm}^{-1}$ ) than those obtained in [9], where the depths were several percent.

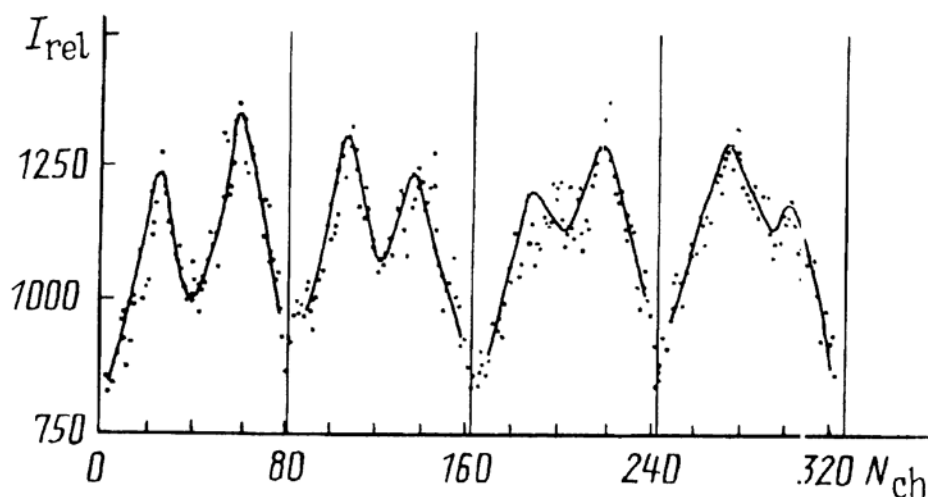


Fig. 3. Dynamics of the smearing of the spectral hole of OEP in a polyethylene film in the region of the 0-0-band. The spectra are separated by a 40-sec interval (the first channel corresponds to  $1 \text{ cm}^{-1}$ ).

The kinetics of the disappearance of a hole is presented in Fig. 3. The characteristic times of the disappearance are measured by units of minutes. Since the basic mechanism of the burning is NH-tautomerization [11], it is pertinent to attribute the smearing of a hole to the reversibility of the process at 77 K. At the same time it is found that there is also a "residual" hole not disappearing for dozens of minutes. The mechanisms responsible for its existence call for further investigation.

Thus, already the preliminary results permit us to consider adsorbed molecules as promising systems for a spectral-selective record of information at relatively high (77 K) temperatures. Further investigations should be directed toward finding systems with minimum widths for the holes and maximum ratio of inhomogeneous and homogeneous widths. (For the OEP-PE system, this factor, characterizing the potential increase in the information capacity, exceeds an order of magnitude.) As sorbents, it is promising to use, along with polymers, disperse nonpolar inorganic matrices characterized by a high Debye temperature (diamond, silicon). We note that preliminary results on the fine-structure spectra of OEP sorbed on a powderlike sample of synthetic diamond are very encouraging; however, to perform a detailed investigation of these systems, it is necessary to improve the signal-to-noise ratio by increasing the effective concentration of the dye molecules in the sample by using matrices with a more developed structure of the surface; works in this direction are being carried out at the present time. On the other hand, an increase in the inhomogeneous width can be attained by artificially increasing the heterogeneity of the structure of the surface by using different methods of modifying it. The state-of-art in the development of different types of modifications, in particular, in application to materials of semiconducting microelectronics, is a factor making it possible to ensure a high degree of flexibility in the variation of the properties of systems of "complex molecule-adsorbent" type.

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