Electronic spectroscopy, stimulated emission and persistent spectral hole-burning of cryogenic nitrogen matrices doped with tetrabenzoporphin

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This paper deal with our on-going work on the electronic spectroscopy of tetrapyrrole molecules embedded in cryogenic hosts. Under nanosecond laser excitation of the free-base tetrabenzoporphin molecules in a nitrogen matrix at 8 K, increasing the laser pulse energy results in essential enhancement of the intensity of one or several vibronic emission lines to take place in the fine-structure fluorescence spectrum. The observed intense monochromatic radiation possesses characteristics of stimulated radiation being realized as a result of a transition from the purely electronic S_1 level to a vibrational sublevel of the S_0 state, corresponding to excitation of stretching C–C vibrations of the tetrapyrrole methane bridges. We also report on persistent spectral hole-burning effects. The analysis of the holes and antiholes formation gives some insight on the photochemical properties of tetrabenzoporphin in a nitrogen matrix.

Introduction

Development of solid-state laser active media, based on dyes, remains one of the important problems of modern high technology. It is stimulated, first of all, by the need to create micron-sized lasers. The problem of miniaturization of solid-state elements enhances the interest for studying the spectral and kinetic characteristics of spontaneous and induced (stimulated) radiation of thin-film colored materials. The literature describes studies of thin 1 µm silica gel slabs doped with dyes of different classes (rhodamines, oxazole derivatives, coumarins, porphyrins, etc.) showing lasing characteristics [1–6]. It is important to note that in some experiments [3,5] external optical resonator mirrors were missing and stimulated emission (SE) was nevertheless detected due to light amplification in a single pass through the layer by just a "traveling wave" (traveling lasing wave).

We have performed spectroscopic studies of free base phthalocyanine (H_2Pc) and its zinc counterpart (ZnPc) [7], as well as of free base tetrabenzoporphin (H_2TBP) [8] in matrices of rare gases (Ne, Ar, Kr, Xe) at low temperature (8 K). We found that under the action of a pulsed laser excitation, SE was observed in guest molecules in these matrices and corresponds to transitions between the lowest singlet state S_1 to specific vibrational levels of the ground electronic state S_0 (S_1 (0–0) $\rightarrow$ S_0 (0–1) transition). The interest in porphyrins and phthalocyanines molecules as systems capable of SE is due to their high values of the fluorescence quantum yields, intense absorption bands in the visible spectrum, allowing carrying out effectively their excitation and localization of the fluorescence spectra in the red and near-IR region, as well as high thermal and photo stabilities. We recall that lasing emission from an organic molecule was observed for the first time in 1964 by Sorokin and Lankard [9,10]: stimulated emission was

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observed when a solution of chloro-aluminum phthalocyanine dissolved in ethanol was irradiated by the beam from a giant-pulse ruby laser. The wavelength of this stimulated emission was centered at approximately 755 nm.

The present work is in continuation of previously published results [7,8] in which the authors discussed the occurrence of the phenomenon of SE in H_2Pc, $ZnPc$ and H_2TBP molecules isolated in cryogenic matrices of rare gases, identifying so far a number of unsolved problems. For instance, a necessity arises to clarify the role of different parameters on the stimulated emission phenomenon by changing the nature of the host matrix, then changing the electron–phonon interaction. An important open question remains for understanding why the intensification of the light emission only occurs on a very limited number of vibronic transitions. Therefore, it appears necessary to establish what are the critical values for achieving the population inversion of levels taking into account the share of the fluorescence quantum yield between the vibronic transition (i.e., the intensity of vibronic lines), the value of the relaxation rate and the contribution of the different normal modes in the vibrational levels of the ground state S_0.

The purpose of the present paper is then to bring new information on the spectral characteristics of H_2TBP molecules embedded in a low-temperature matrix of molecular nitrogen (N_2). The choice of H_2TBP whose structural formula is shown in Fig. 1, is justified by two main reasons. First, the quasi-line fluorescence spectra of H_2TBP in n-octane Shpol'skii matrix at 4.2 K reveal lines assigned to individual vibronic transitions with exceptionally narrow spectral width. For example the components of the 0–0-doublet recorded in the fluorescence spectrum of H_2TBP in a single-crystal matrix of n-octane at 4.2 K have half-widths of 1.5 and 1.8 cm^{-1}, respectively [11]. Second, the role and the high speed of the photochemical NH-tautomerism in H_2TBP [12], which is the cause of efficient photoinduced interconversion of impurity centers in Shpol'skii matrices [13] needs to be studied further.

Experimental

For obtaining the low-temperature matrices of nitrogen doped with H_2TBP, a special device was designed and built to be attached to the cryostat. All details were fully described previously [8]. The temperature of the heater which could reach up to 300 °C, was adjusted for the powder of H_2TBP. Sublimated porphyrin molecules were carried by the flow of nitrogen, forming a gaseous mixture of $N_2 + H_2TBP$ which was deposited on a sapphire window in a closed-cycle helium displex cryostat at ~ 20 K to form a thin polycrystal film with a typical thickness of about 250 microns. Gas flow rates of 10 mmol/h allowed good matrix isolation of the tetrapyrrole molecules as monomers, as monitored by the absorption spectrum of the prepared sample, which allowed also an estimation of the re-

sulting concentration of the dye. Fluorescence, stimulated emission and fluorescence excitation spectra were produced with a pulsed dye laser at 10 Hz using DCM, Rh610 or Rh6G pumped by a frequency-doubled Nd^{3+}:YAG laser or an excimer XeCl laser. Fluorescence was recorded through a HRS 600 monochromator from Horiba-Jobin-Yvon, using a high-speed iCCD-camera (ANDOR, model DH-720). Most of the measurements were made at about 8 K.

Results and discussion

Absorption

The absorption spectrum of H_2TBP in pyridine at room temperature is shown by the dotted trace in Fig. 1 (curve *1*).

According to the Refs. 11, 14–16, the band at 663.4 nm belongs to the $S_1 \leftarrow S_0$ transition (Q_x band), while the bands at 432.5 and 417.0 nm are assigned to the $S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$ transitions (B_x and B_y bands), respectively. The 580–620 nm region is where the Q_y band is located and whose absorption spectrum shows the presence of three peaks. A careful analysis of the data taking into account the polarization of the quasi-line spectra, showed that the contour of this band results from the contributions of two different types of transitions: high-frequency vibronic transitions of the lowest S_1 electronic state and the pure electronic $S_2 \leftarrow S_0$ transition. Considering the nature of the violation of the mirror symmetry in frequencies as well as in the activity of individual normal modes in the S_1 and S_0 states of H_2TBP led to the conclusion that the purely electronic band assigned to the $S_2 \leftarrow S_0$ transition corresponds to the central maximum of the complex recorded contour [14,15]. Accordingly, the assessment of the energy difference $\Delta E_{S_2S_1} = E_{S_2} - E_{S_1}$ for H_2TBP in pyridine gives a value of ~ 1370 cm^{-1} [11,14,16]. The same value as well as a similar band shape were also observed for H_2TBP in DMSO. A noticeable change in the shape of the absorption band in the 580–620 nm region is observed in solvents such as n-octane ($\Delta E_{S_2S_1} \approx 1445$ cm^{-1}) [16], ethanol
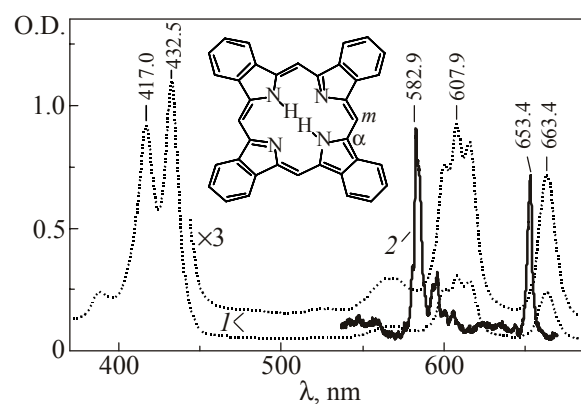

Fig. 1. Absorption spectra of H_2TBP in pyridine at 293 K (*1*) and in the nitrogen matrix at 8 K (*2*). The inset shows the structural formula of H_2TBP.

$(\Delta E_{S_2 S_1} \approx 1480$ cm$^{-1})$ [17] and in a mixture of tetrahydrofuran and ether [18], where the most intense feature is the short-wavelength component of the complex structure in the 580–620 nm range.

New information on the spectral characteristics is obtained from H$_2$TBP molecules whose inhomogeneous broadening is partially removed in their low-temperature absorption spectra in the solid N$_2$ matrix (Fig. 1, curve *2*). As can be noticed, significant changes in the absorption spectrum of H$_2$TBP/N$_2$ can arise when compared with the spectrum in pyridine. The blue-shift of $\sim$ 10 nm in the absorption bands (λ_{00} of $S_1 \leftarrow S_0$ = 653.4 nm) is indicative of the weakening of the interaction of molecules with the N$_2$ matrix environment as compared with pyridine. Also, the half-width of spectral bands decreased by an amount up to $\sim$ 3.5 times. For example, the band of the purely electronic $S_1 \leftarrow S_0$ transition becomes narrower, changing from $\sim$ 265 cm^{-1} in pyridine down to $\sim$ 75 cm^{-1} in N$_2$. However, an accurate localization of the $S_2 \leftarrow S_0$ transition of H$_2$TBP in N$_2$ is not well defined, in spite of a significant intensity of the absorption bands in the 570–600 nm region. Despite the fact that it cannot be exactly known, we can notice the similarity between the absorption spectra of H$_2$TBP in N$_2$ and in *n*-octane matrix as these two spectra have an intense band on the short wavelength 580–620 nm range. The spectral separation between this intense band and the band assigned to the $S_1 \leftarrow S_0$ electronic transition is equal to $\sim$ 1750 cm^{-1} in the *n*-octane matrix and $\sim$ 1850 cm^{-1} in the N$_2$ matrix. This observation allows us to infer that the exact $\Delta E_{S_2 S_1}$ for H$_2$TBP/N$_2$ should be slightly greater than for the *n*-octane Shpol'skii matrix for which $\Delta E_{S_2 S_1} \approx 1445$ cm^{-1}. Recent investigation of phthalocyanine in inert gas matrices [19] has similarly concluded that $\Delta E_{S_2 S_1}$ was slightly larger for H$_2$Pc/N$_2$ than for H$_2$Pc trapped in the *n*-decane Shpol'skii matrix.

Stimulated emission and excitation of the stimulated emission

Upon excitation in the Q_y absorption band at λ_{exc} = = 582.7 nm with the pulsed dye laser ($P_{exc} \approx 10$ mW, pulse length = 10 ns), the fluorescence spectrum of H$_2$TBP in N$_2$ at 8 K has the form shown in Fig. 2 (curve *1*). An intense band assigned to the pure electronic $S_1 \rightarrow S_0$ transition occurs at 653.8 nm, followed by low-intensity bands corresponding to vibronic transitions covering the 660–740 nm region. The resulting spectrum resembles the quasi-line fluorescence spectrum of H$_2$TBP in *n*-octane at 4.2 K [16], where the most intense vibronic band is a band corresponding to a low-frequency normal mode at $\sim$ 220 cm^{-1} (Fig. 2, see the band at 663.0 nm). As the power of pulsed laser excitation is increased from $P_{laser} \approx 30$ mW up to 100 mW, it is noticed that from the weak vibronic band at 731 nm of the normal fluorescence spectrum, two intense lines at 730.7 and 731.0 nm increase drastically (Fig. 2, compare curves *2* and *3*). Attention is drawn on the sharp narrowing
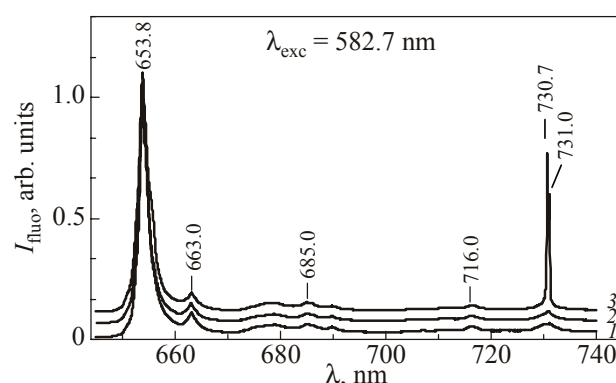

Fig. 2. Fluorescence spectra and stimulated emission from H$_2$TBP molecules in nitrogen matrix at 8 K (λ_{exc} = 582.7 nm, $P_{laser} \approx 10$ (*1*), 30 (*2*) and 100 (3) mW).

of these lines (up to $\sim$ 5 cm^{-1}, i.e., to the resolution limit of our spectrometer) and on their dependence with the relative intensities of the laser excitation power. These lines are assigned to SE. Changing the laser excitation wavelength in the region 580–585 nm does not lead to the appearance of other new SE lines in the recorded spectrum. There is only a slight difference in the relative intensities of the lines at 730.7 and 731.0 nm. By analogy with the observations reported in [7,8] we can conclude that the emission at these wavelengths is strongly enhanced when the exciting laser intensity exceeds a certain threshold value. This means that an inversion of population is achieved between the lowest electronic state S_1 and some vibrational sublevels of the ground state S_0. When such situation arises, then stimulated emission can occur and overpass any spontaneous fluorescence emission. In the case of H$_2$TBP/N$_2$, the analysis of the spectral data shows that SE takes place on a vibronic transition which involves a vibrational sublevel with an energy of about 1615 cm^{-1} from the ground S_0 state. This vibrational sublevel corresponds to the excitation of valence vibrations involving the C$_\alpha$C$_m$ methine bridges (see Fig. 1) with B_{1g} symmetry [11,20]. It is important to note that SE is observed under pulsed laser excitation with whose duration does not exceed the lifetime of the state S_1 (for example, in the case of H$_2$TBP in an ethanol-ether mixture, τ_S = 11 ns [21]) and at a repetition rate of 10 Hz, i.e., 100 ms between successive pulses. Such a situation precludes an effective population of the triplet state, which is well known for playing the role of "traps" for the active sites, which should be the case under steady-state photoexcitation, and then difficult to achieve conditions for population inversion.

In order to clarify the conditions under which SE occurs in H$_2$TBP/N$_2$, we have studied the excitation spectra of the stimulated emission. Figure 3,*a* shows such spectra for the Q_y band region at 8 K (curve *1*, monitoring the emission at λ_{obs} = 730.7 nm and curve *2* for λ_{obs}= 731.0 nm) which is compared with the absorption spectrum of H$_2$TBP/N$_2$ (curve *3*) in the same region. It can be seen that the contours of the bands in the excitation spectra of the SE —

Fig. 4. Fluorescence spectra and stimulated emission from H_2TBP molecules in nitrogen matrix at 8 K ($\lambda_{exc} = 652.7$ (*a*) and 654.0 (*b*) nm, $P_{laser} \approx 10$ (*1*), 30 (*2*) and 100 (*3*) mW).
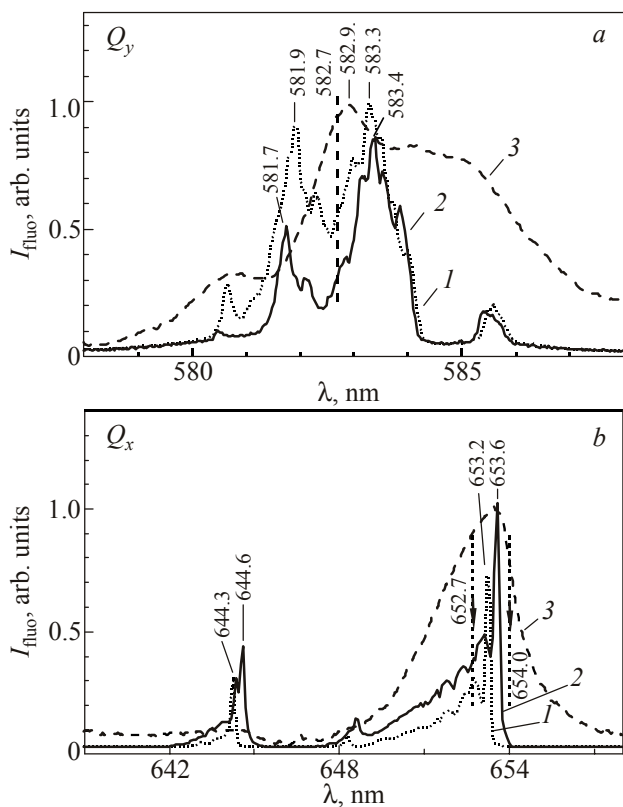
Fig. 3. Comparison of the excitation spectra of the stimulated emission (*1* and *2*) and the absorption spectrum (*3*) from H_2TBP molecules in nitrogen matrix at 8 K for $S_2 \leftarrow S_0$ ($\lambda_{obs} = 730.7$ (*1*) and 731.0 (*2*) nm) (*a*) and $S_1 \leftarrow S_0$ ($\lambda_{obs} = 730.7$ (*1*) and 731.1 (*2*) nm) (*b*).

with the detection of the emission in each of the two observed SE components — are almost identical and their spectral shift relative to each other is negligible. However, the maxima of the bands in the excitation spectra of the SE do not coincide with the maximum absorption spectrum at 582.9 nm in this area. This fact can be considered as a consequence of the population inversion induced at the wavelengths (580–585 nm) and the excitation powers (up to 100 mW) used for the two types of impurity centers. It should be noted that the SE intensity at 730.7 nm is higher than the SE intensity at 731.0 nm and this for almost all excitation wavelengths. An explanation of the observed features of the excitation spectra of the SE for each type of impurity centers requires a detailed analysis of the electronic and electronic-vibrational levels of the Q_x and Q_y states involved in the active transitions [11,16].

Stimulated emission in a range around 731 nm is also observed under pulsed laser excitation in the long-wavelength absorption Q_x band of H_2TBP/N_2 (Fig. 4). However, unlike the case of the excitation in the Q_y band, in this situation, there is a dependence of the number of SE components with a change of λ_{exc} within the Q_x absorption band (Fig. 3,*b*, the spectral position of the laser exciting radiation is shown by the arrows and vertical dotted lines).
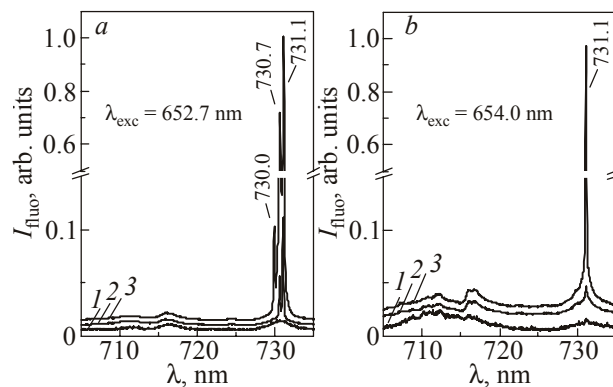
At $\lambda_{exc} = 652.7$ nm and under a gradual increase of the laser excitation power up to $P_{laser} \approx 100$ mW, four SE components appear in the emission spectrum (Fig. 4,*a*) while at $\lambda_{exc} = 654.0$ nm, only one SE component is intensified (Fig. 4,*b*). An explanation of this observed behavior for the spectral composition of the SE is provided by an analysis of the excitation spectra of the SE in the Q_x band absorption (Fig. 3,*b*). As shown in Fig. 3,*b*, the broad Q_x absorption band of H_2TBP/N_2 at 8 K (curve *3*) is transformed into a structured band in the SE excitation spectrum. For example, it can be noticed that for $\lambda_{obs} = 731.1$ nm, the SE emission line component on the long-wavelength side of the excitation spectrum of the SE (curve *2*), there is a narrow intense line at 653.6 nm and a broad and structured band on its short-wavelength side. Clearly, such a structure in the SE excitation spectrum is formed by the excitation (absorption) of the narrow zero-phonon line (ZPL) corresponding to the $S_1 \leftarrow S_0$ (0,0) transition and to its broad phonon side band (PSB). A similar observation can be made on the shorter-wavelength component of the SE spectrum recorded at $\lambda_{obs} = 730.7$ nm (curve *1*), while a slight blue shift can also be noticed. The observed SE excitation spectra may explain the dependence with λ_{exc} of the structured components. The excitation on the short-wavelength side within the Q_x band induces the simultaneous photoactivation of "red" (via their PSB) and "blue" (through their ZPL) kinds of impurity centers, whereas the excitation on the long-wavelength side affects only the "red" types of impurity centers through their ZPL. Indeed, in the first case, four types of impurity centers are identified, exhibiting SE at 731.1, 730.7, 730.3 and 730.0 nm, respectively (Fig. 4,*a*), while in the second case, only one SE component at 731.1 nm can be induced (Fig. 4,*b*). Notice that in the resulting SE excitation spectra shown (Fig. 3,*b*), not only SE is observed upon excitation in the Q_x (0–0) band of the purely electronic transition, but also in the vibronic Q_x (0–1) band at ~ 644 nm.

The results obtained demonstrate that under relatively high-power pulsed laser excitation in the Q_x and Q_y band

of H$_2$TBP/N$_2$, a sharp narrowing of lines is observed in the SE excitation spectra as compared with the normal fluorescence excitation spectrum. The former "exhibiting" thereby a greater selectivity of individual types of impurity centers in the matrix under study. These high-resolution SE spectra will allow more detailed studies of the spectral properties of certain types of impurity centers in a given matrix. The nature of the SE multiple components may be useful for identifying the main types of impurity centers of pigments in cryogenic matrices. Moreover, such studies have a methodological significance and are of great importance as a method for selective low-temperature molecular spectroscopy.

Hole-burning

In this work, we also carried out investigations on the photochemical properties of the H$_2$TBP/N$_2$ system via a method involving the photoburning of stable spectral holes (persistent spectral hole burning — PSHB) in the Q_x absorption band. The phenomenon of spectral hole-burning at low temperature is quite well known and largely studied in detail for the case of free base porphyrins (see [22] for a review). It is due to the intramolecular NH-tautomerism process, which in porphyrins implies only the displacement of the two central protons from one pair of opposite nitrogen atoms to the other (see structure in Fig. 1) [23].

The experimental results described previously have shown that the Q_x (0–0) band of H$_2$TBP/N$_2$ is structureless, i.e. inhomogeneously broadened due to the presence in the matrix of a large number impurity centers and to the superposition of their different individual spectral bands. This inhomogeneous broadening can be eliminated under the exposure with monochromatic laser light. Figure 5 presents the effect of such laser irradiation on the Q_x band (Fig. 5,*a*) and the difference spectrum obtained by subtracting the burnt spectrum from the unburnt one is also shown (Fig. 5,*b*). PSHB experiments then shows that burning at $\lambda_{burn} = 652.7$ nm (Fig. 5,*a*) forms a stable spectral hole corresponding to the zero-phonon line (zero-phonon hole) which can saturate with the increase of burning time. Typical laser exposure time for the observation of the spectral changes were chosen about 10 minutes with a laser excitation power for burning ~ 100 mW. This burning time was sufficient to achieve saturation of the zero-phonon hole, which then resulted in its broadening up to ~ 10 cm^{-1}. As can be seen from Fig. 5, where the effect of the laser excitation on the short-wavelength side of the ZPL is observed, a marked increase in absorption intensity due to the formation of a photoproduct (giving rise to an "antihole") on the high-energy side from λ_{burn}. The formation of an "antihole" during photoburning is associated with the formation of NH-tautomers of H$_2$TBP. This asymmetrical spectral distribution of the "antihole" due to the photo-transformation of H$_2$TBP symmetric molecules (point group symmetry D_{2h}) is a consequence of the existence of
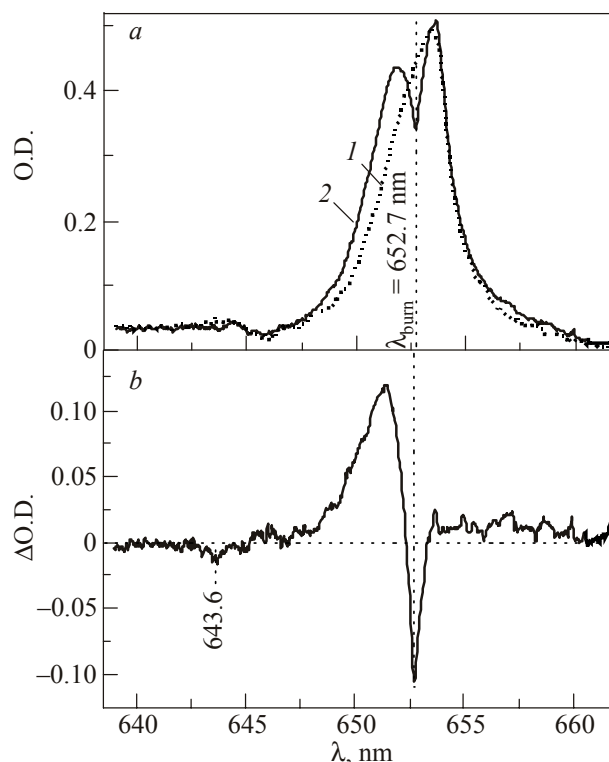

Fig. 5. Q_x (0–0) absorption band from H$_2$TBP molecules in nitrogen matrix at 8 K (*a*) before (*1*) and after burning (*2*) and (*b*) difference between both spectra showing the persistent spectral hole ($\lambda_{burn} = 652.7$ nm, $P_{burn} \approx 100$ mW, $t_{burn} \approx 10$ min).

a rather intense pseudo-phonon wing at long wavelength resulting from the burning of impurity centers, which absorb the laser radiation in the region of their phonon wing, i.e., centers with $\lambda_{ZPL} > \lambda_{burn}$. Naturally, at $\lambda_{exc} = 652.7$ nm, would be more excited centers through their extensive phonon band than centers excited through their ZPL. As a result, the long wavelength (respect to the selected λ_{burn}) photoproduct absorption and the intense pseudo-phonon wing at $\lambda > \lambda_{burn}$ almost cancel out each other. It is essential to notice that similar spectral changes were also observed for the Q_x (0–1) band located at ~ 643.6 nm, which means for the band that corresponds to the electron-vibrational transition.

As it was turned out in the case of H$_2$TBP/N$_2$, the intersystem conversion in impurity centers has a rather low efficiency, which is the reason for the almost complete lack of influence of the photochemical transformation on the efficiency of the SE phenomenon.

Conclusion

The main results obtained in the present work on absorption, fluorescence (stimulated emission) and persistent spectral hole-burning of matrix-isolated molecules H$_2$TBP in solid nitrogen can be summarized as follows:

It was found that the exposure to pulsed laser excitation in the Q_x and Q_y absorption bands of H$_2$TBP molecules

trapped in the low-temperature nitrogen matrix induces the occurrence of stimulated emission, together with normal spontaneous emission of fluorescent H_2TBP molecules. This stimulated emission is evidenced by the strong enhancement of the intensity of one or more vibronic fluorescence lines and it occurs when the intensity of the exciting laser radiation exceeds a certain threshold. The observation of such phenomenon means the achievement of a population inversion between S_1 (0–0) ground level and some vibronic sublevel of the ground electronic state. The vibronic transition involved in the process of stimulated emission corresponds to a vibrational level of S_0 state with an energy of ~ 1615 cm^{-1}, which is assigned to the stretching vibrations of $C_\alpha C_m$ methine bridges with B_{1g} symmetry.

The observation of stimulated emission was possible using pulsed laser excitation with nanosecond duration, not exceeding the lifetime of the lowest singlet S_1 state of H_2TBP, and a 10 Hz low repetition rate. In such a situation, the intersystem singlet-triplet conversion mechanism populating the lowest triplet state (a "trap" of the excited molecules) will only play a minor role, which is an important condition for creation of the population inversion in the system of singlet levels during the laser pulse.

The recorded spectra of the excitation of stimulated emission for individual impurity centers exhibit enhanced selectivity, which creates conditions for a more detailed study of the spectral properties of the molecules forming these impurity centers in the matrix.

The results obtained determine some scientific significance of these investigations. For instance, a practical significance of these results is to identify opportunities for application in the development of laboratory models of new thin-film materials based on low-temperature matrices colored with tetrapyrrole compounds for creating microlasers and light transformers devices (in the blue-green region) from the monochromatic radiation in the red or the near infrared range. The results obtained can be used to expand the search for new microlaser media based on organic dyes.

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