

Contraction of, and hole burning in, a phosphorescence line corresponding to the forbidden $T_1 \leftrightarrow S_0$ transition in the spectrum of pyrene in a glassy matrix

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(Submitted 20 November 1982)

Pis'ma Zh. Eksp. Teor. Fiz. **37**, No. 5, 201–204 (5 March 1983)

For the first time, a hole has been burned photochemically in the inhomogeneously broadened 0-0 spectrum of the $T_1 \leftarrow S_0$ transition of a complex organic molecule, specifically, the system of pyrene in a glassy matrix of butyl bromide (Py-BrBu), at 1.8 and 4.2 K. The results are compared with the resonant laser excitation of the phosphorescence spectrum.

PACS numbers: 33.50.Dq

1. Since the low-lying triplet level T_1 of organic molecules is metastable and plays an important role in energy conversion and photochemistry, it is interesting to use the spin-forbidden $T_1 \leftarrow S_0$ transition to observe the photochemical hole burning in inhomogeneously broadened spectra which is a well-known effect on $S_n \leftarrow S_0$ transitions.^{1,2} Primarily because of a spin-spin magnetic interaction, the triply degenerate T_1 state of the molecules splits into the three sublevels T_x , T_y , and T_z (Fig. 1a): "zero-field splitting."³ This splitting is characterized by the parameters E and D , whose values for pyrene (of symmetry D_{2h}) are $|E| = 0.017 \text{ cm}^{-1}$ and $|D| = 0.086 \text{ cm}^{-1}$ (Ref. 4). In the case of inhomogeneous broadening, there are three types of centers which are at resonance with the excitation line at the frequency ν_0 ; these centers absorb through T_x , T_y , and T_z , respectively. If a photochemical reaction occurs as a result of excitation to the state T_1 , three holes form in the inhomogeneous energy distribution of, for example, the $T_x \leftarrow S_0$ transition (Fig. 1b). When measurements are subsequently taken, each of the holes in the distribution function is manifested by three holes in the absorption or excitation spectrum (Fig. 1c). Since three of these nine holes occur at the frequency ν_0 , the spectrum will contain a multiplet of seven holes. The intensity distribution in a multiplet in the absence of saturation⁵ is determined by the probabilities for radiative transitions from the individual sublevels, is independent of the rates of spin-lattice relaxation, and is symmetric with respect to¹⁾ ν_0 .

A fine structure was observed previously⁶ in the spectrum of laser-excited phosphorescence. This fine structure is similar to the multiplet of holes only in the case of a fast spin-lattice relaxation, when a thermal equilibrium can be reached during the state lifetime T_1 (Fig. 1d). In the complete absence of relaxation, the phosphorescence spectrum has only a single line, at ν_0 (Fig. 1e), which is the sum of the transitions in the three distinct centers.

2. To burn a hole and then detect it in the phosphorescence excitation spectrum, we use a CR-699-21 single-frequency ring laser with the dye Rh 6G. The width of the output line is 10^{-4} cm^{-1} . The stability is monitored with a spectrum analyzer and

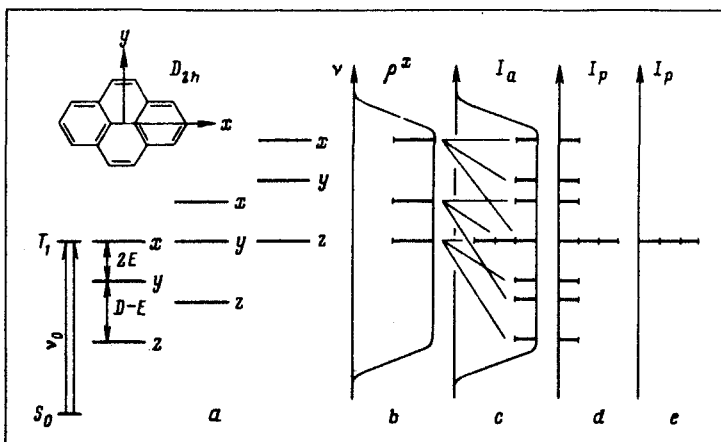


FIG. 1. a—Structure of the T_1 state of pyrene; b, c—holes in (b) the inhomogeneous frequency distribution in the frequencies of the $T_1 \leftarrow S_0$ transition and (c) in the absorption or excitation spectrum; d, e—phosphorescence line in the cases of (d) fast spin-lattice relaxation and (e) no spin-lattice relaxation.

found to be no worse than 10^{-3} cm^{-1} over the burning and measurement cycle. A 200-mW laser beam is focused to a spot 0.3 mm on the sample. The phosphorescence is detected with a spectrometer at the frequency of the intense vibron transition, ν_0 -404 cm^{-1} . The parasitic background of the laser beam and fluorescence from the sample are cut out by a single-disk phosphoroscope. The pyrene concentration is $7 \times 10^{-3} \text{ M}$. The measurements are taken at 1.8 and 4.2 K.

3. The inhomogeneously broadened 0-0 band of the $T_1 \leftarrow S_0$ transition in the Py-

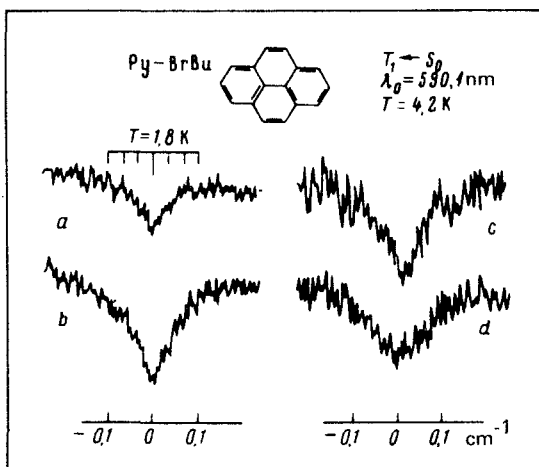


FIG. 2. Holes in the phosphorescence excitation spectrum. a, b—After burning for 10 min (a) or 30 min (b) at 1.8 K; c—immediately after burning at 4.2 K; d—after a hold in darkness for 30 min at 4.8 K. The positions of the fine-structure components calculated from the data of Ref. 4 are shown above spectrum a.

BrBu phosphorescence spectrum excited at the $S_1 \leftarrow S_0$ transition ($\lambda = 371$ nm) has a maximum at $\lambda = 587$ nm and a half-width of 180 cm^{-1} . Bombardment by the laser line $\lambda_0 = 590.1$ nm gives rise to a stable hole in the phosphorous excitation spectrum (Fig. 2) because of a photochemical reaction that goes through the T_1 state. The nature of this reaction will be discussed in a separate paper. After 10 min of bombardment, about 15% of the molecules which have absorbed at the laser frequency react, so that the shape of the hole is distorted only slightly by saturation⁵ (Fig. 2a). Increasing the bombardment dose deepens and broadens the hole (Fig. 2b). Illumination with "white" light near the $S_1 \leftarrow S_0$ transition fills in the hole and restores the original spectrum. The width of the unsaturated hole at 1.8 K is $\delta_h = 0.07$ cm^{-1} ; no fine structure is observed. Measurements at other points of the inhomogeneous band and also at a lower impurity concentration (10^{-3} M) yield similar values of δ_h .

To determine why the hole does not have a fine structure, we measured the phosphorescence spectrum during laser excitation, taking measurements in the after-glow at the same wavelength, $\lambda_0 = 590.1$ nm. These measurements were taken with a scanning Fabry-Perot interferometer; the scattered laser beam was cut off by a two-disk phosphoroscope. The spectrum was constructed through multiple scanning and by repeated measurement-restoration cycles; the interferometer was stabilized with respect to the laser line (Fig. 3). In the phosphorescence spectrum we see an intense central peak with faint satellites, at the noise level. The peak width, corrected for the instrumental line, is $\delta_p = 0.01$ cm^{-1} .

4. The observation of an isolated line in the phosphorescence spectrum indicates a freezing of the spin-lattice relaxation in the Py-Bru system at 1.8 K. This interpretation is supported by the fact that the side components intensify at 5 K, making it possible to estimate the relative probabilities for the radiative transitions: 1:0.3:0.1. This conclusion is consistent with data for pyrene derivatives.⁷ The homogeneous width of the 0-0 line of the $T_1 \rightleftharpoons S_0$ transition is $\Gamma = \delta_p/2 = 0.0005 \pm 0.001$ cm^{-1} at

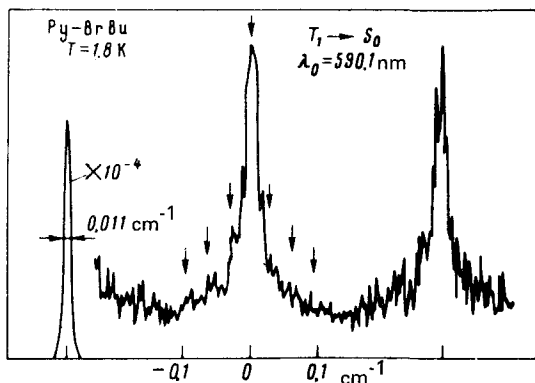


FIG. 3. Interferometric recording of the 0-0 phosphorescence line during laser excitation. The free dispersion is 0.28 cm^{-1} . The first-order line is the reference point of the stabilization system; its width is a measure of the instrumental width. The second order is smoothed. The number of measurement-restoration cycles is 8; the number of scanings is 560. The arrows show the calculated positions of the fine-structure components.

1.8 K. Because of the slight hyperfine interaction, the low probabilities for spin-lattice relaxation, the decay $T_1 \leftrightarrow S_0$, and the photochemical reaction, the homogeneous width is determined primarily by a phase relaxation through a modulation mechanism²⁾ and agrees in order of magnitude with the 0-0 broadening of the $S_1 \leftrightarrow S_0$ transition in crystalline matrices.²

5. The symmetric shape of the hole in the spectrum under conditions corresponding to a frozen spin-lattice relaxation indicates that the photochemical reaction is nonselective in the spin. The absence of a fine structure can apparently be explained on the basis of the relatively low probability for absorption at two of the three sublevels of the triplet and by an additional broadening of the individual components of the hole in comparison with the phosphorescence line. This broadening can be estimated to be at least equal to the distance between the fine-structure components, $\delta'_h \gtrsim 2|E| = 0.034 \text{ cm}^{-1}$. This result, $\delta'_h/\delta_p \gtrsim 3$, suggests that even at liquid-helium temperatures changes are occurring in the matrix in the glassy system which substantially change the energy of the 0-0 transition during the burning time, $\sim 10^3 \text{ s}$; these structural changes do not have a major effect on the lifetime of the triplet state, 80 ms. These structural changes can be attributed to (a) changes in the surroundings of the impurity as a result of the participation of matrix molecules in the photochemical reaction⁸ and/or (b) structural relaxation of the glass, e.g., in a transition to a stabler phase. The latter possibility is supported by the significant change in shape of the hole at 4.2 K during the dark pause (Figs. 2c and 2d): The width increases, while the depth decreases.

6. Measurements at 4.2 K yield $\delta_h \approx 0.1 \text{ cm}^{-1}$ and $\delta_p \approx 0.06 \text{ cm}^{-1}$. We see that the hole is broadened only slightly, while the phosphorescence line broadens significantly more rapidly. These results are typical of modulation broadening and confirm the results obtained at 1.8 K. At 1.8 K, because of the very different scale times, the width of the hole is thus determined by the fine splitting of the T_1 state and also (apparently) by a structural change of the matrix (scale time $\sim 10^3 \text{ s}$), while the width of the phosphorescence line is determined by modulational broadening (the scale time is the lifetime of the T_1 state, $\sim 0.1 \text{ s}$).

We wish to thank L. A. Rebane for suggesting the topic and K. K. Rebane and J. V. Kikas for useful discussions.

¹⁾If the photochemical reaction is selective in terms of the spin, the shape of the multiplet depends on the rate of the spin-lattice relaxation. For example, in the absence of relaxation we are left with only three components in the spectrum, which are generally in asymmetric positions with respect to ν_0 .

²⁾The short-range nature of the exchange-resonant interaction suggests that the contribution of triplet-triplet migration to Γ is only slight at this concentration.

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Translated by Dave Parsons

Edited by S. J. Amoretty