

Luminescence dynamics of an impurity center with a two-well adiabatic potential

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A study reveals that the anomalies in the spectra and decay kinetics of the luminescence of thioindigo molecules in a benzoic acid crystal stem from a two-well adiabatic potential. The interwell relaxation time has been found. The structure of the adiabatic potential undergoes a transformation as time elapses.

The low-temperature absorption and fluorescence spectra of organic molecules in frozen solutions and crystals frequently have a multiplet structure, which stems from the multiwell shape of the adiabatic potential.¹ The reasons for the appearance of several minima in the adiabatic potential of molecules with nondegenerate electron states differ from case to case, but the primary reasons appear to be the existence of mobile fragments in the molecular structure, the relatively low symmetry of organic molecules, and thus the pronounced anisotropy of their elastic properties. The experimental information available on impurity centers in crystals with a multiwell adiabatic potential is extremely scanty.² The intrawell and interwell relaxation of excitations has not been studied thoroughly, although this relaxation has attracted interest in connection with the study of new low-temperature mechanisms for the dephasing of optical transitions of impurity centers in crystals.^{2,3}

In this letter we are reporting a study of the steady-state luminescence spectra, emission kinetics, and time-resolved emission spectra of thioindigo molecules in a benzoic acid crystal over the temperature range 1.5–77 K. The spectral and kinetic measurements were carried out on a picosecond spectrofluorimeter, whose key parts are an argon laser with active mode locking and a time-correlated photon counting system.

The luminescence spectrum of these crystals at 77 K consists of a broad, structureless band (Fig. 1). The luminescence decay kinetics is a single-exponential process with a decay time which is independent of the measurement wavelength over the entire spectrum (Fig. 2).

During steady-state excitation, the low-temperature luminescence of thioindigo molecules has a line spectrum consisting of nonphonon lines of purely electronic and electronic-vibrational transitions (Fig. 1). For several of the nonphonon lines corresponding to electronic-vibrational transitions with intramolecular vibration frequencies 233.6, 496.1, 724.5, and 989.7 cm^{-1} , a doublet structure is observed. We are thinking of a spectral satellite on the high-frequency side of the nonphonon line. For the electronic-vibrational transitions which form in a process involving the vibration at 1528.2 cm^{-1} , on the other hand, there is no doublet structure (Fig. 1).

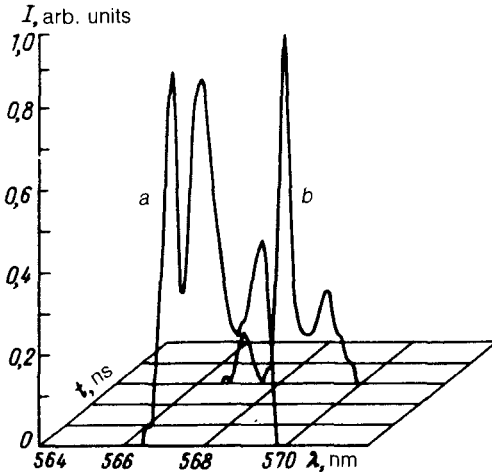


FIG. 1. Luminescence spectra during steady-state excitation. a—77 K; b— $T=1.5$ K.

A study of the luminescence with the help of a tunable narrow-band laser in crystals with various concentrations of thioindigo molecules has made it possible to eliminate concentration effects from consideration. This study has also established unambiguously that the doublet structure observed in the luminescence spectrum is due to the emission of thioindigo molecules.⁴

A study of the emission kinetics in the spectral components of the doublet showed that the luminescence kinetics is described by a decay law more complex than that detected at 77 K, regardless of the vibrational frequency (Fig. 2). An exceptional result is the clearly defined two-exponential decay. The time constant of the long exponential corresponds to that found at 77 K, while the time constant of the short one is $\tau=1.5$ ns. This component appears with opposite signs in the decay kinetics

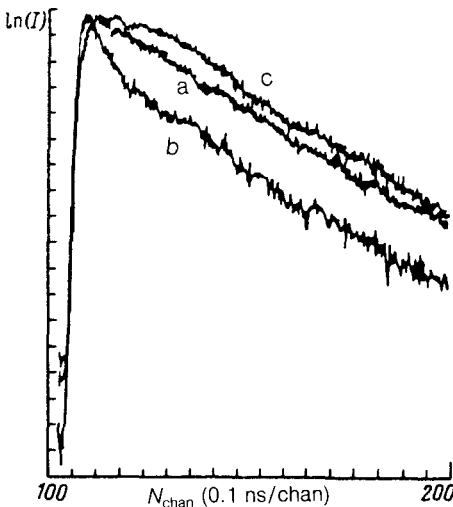


FIG. 2. Luminescence decay kinetics. a— $T=77$ K, $\lambda=570$ nm, $\tau=11.6$ ns; b— $T=1.5$ K, $\lambda=567.1$ nm, $\tau_1=11.6$ ns, $\tau_2=1.5$ ns; c— $T=1.5$ K, $\lambda=568.1$ nm, $\tau_1=11.6$ ns, $\tau_2=1.5$ ns.

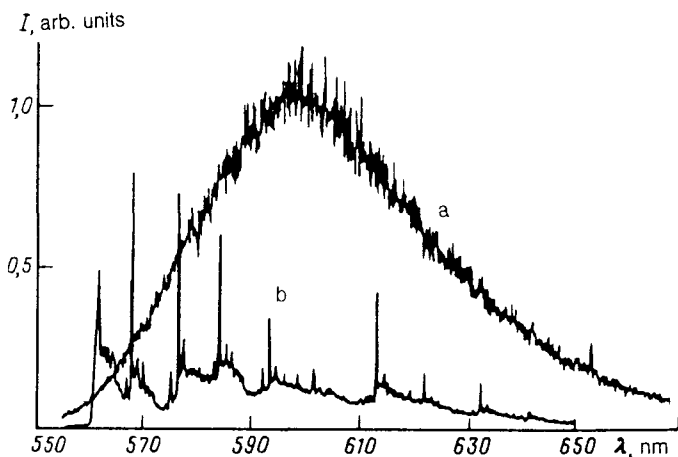


FIG. 3. Fragments of luminescence spectra recorded with a time resolution. a—Time resolution of 0.2 ns; b—15 ns.

recorded for the two components of the doublet. It is positive for the higher-frequency component of the doublet, describing a relaxation of the excitation, while it is negative for the low-frequency component.

It follows from the time-resolved luminescence spectra (Fig. 3) that the intensities of the constituent doublets become more nearly equal with decreasing time interval over which the spectrum is detected after the time of excitation. However, we also observe a decrease in the frequency interval between the components of the doublet, a broadening of the low-frequency component of the doublet, and a change in the intensity of the phonon wing.

On the basis of a study of the absorption spectra⁴ and the data of Ref. 5 it can be suggested that the ground and excited electronic states of the thioindigo molecule in a benzoic acid crystal are described by a two-well adiabatic potential. The absence of doublet structure from the electronic-vibrational transitions which are formed with the help of the intramolecular vibration at 1528.2 cm^{-1} in the luminescence spectrum may be due to two factors: Either the two-well adiabatic potential does not prevail for all vibrational degrees of freedom, or the vibrational frequency of 1528.2 cm^{-1} is above the potential barriers separating the wells. The exponential function with the shorter time constant detected in the luminescence decay kinetics is directly related to the interwell relaxation of population in the excited state of the thioindigo molecule. It follows from the time-resolved luminescence spectra that the probability for interwell relaxation can vary with the time, since the structure of the adiabatic potential (the depth of the wells and the potential barrier separating them) varies in time. This conclusion is supported by the spectral shifts between the components of the doublet and by the transformation of the structure of the low-frequency component of the doublet.

If this temporal transformation of the adiabatic potential is fairly general in

nature, then this fact can apparently play an important role in an analysis of the tunneling mechanism for the dephasing of optical transitions.³ It may also give rise to a time dependence of the homogeneous width of a spectral transition, since it is completely clear that the homogeneous widths which have been found by the nanosecond and picosecond photon-echo methods will differ (without even going into a comparison of these widths with experimental data on hole burning). A detailed explanation of these features will require further research.

¹ V. M. Agranovitch and R. M. Hochstrasser (eds), *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems* (Elsevier, New York, 1983).

² O. N. Korotaev, I. P. Kalmykov, M. F. Shchanov *et al.*, *JETP Lett.* **55**, 424 (1992).

³ I. S. Osad'ko, *Phys. Rep.* **206**, 45 (1991).

⁴ A. N. Lebedenko and Yu. V. Malyukin, Preprint IMK-92-28, 1992.

⁵ I. S. Osad'ko and S. A. Kulagin, *Opt. Spektrosk.* **49**, 290 (1980) [*Opt. Spectrosc. (USSR)* **49**, 156 (1980)].

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