

# Destruction of the vibrational structure of the band of instantaneous fluorescence spectra of polar solutions with increasing delay time

V. S. Pavlovich and S. V. Zablotskiĭ

*Institute of Atomic and Molecular Physics, Belarus Academy of Sciences; B. I. Stepanov Institute of Physics, Belarus Academy of Sciences, 220702, Minsk, Belarus*

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The evolution of the instantaneous fluorescence spectra of polar compounds in alcohols has been studied at delay times  $t$  greater than the average lifetime in the excited state by a factor of 5, 6, or more. As  $t$  is increased, one observes a destruction of the vibrational structure, a coalescence of the less intense vibrational bands, and a compression of the spectrum. This compression then gives way to an expansion, and the structure is partially restored. It is suggested that the effects observed stem from nonadiabatic random perturbations of an excited molecule which result from an abrupt reorientation of the molecules of the medium and their polar fragments (OH groups) and from a reorientation of the fragments of the compounds themselves. Such perturbations modulate the phase and amplitude of the radiation and also alter the frequency, leading to a spectral "borrowing" and a redistribution of intensity in the electronic–vibrational emission spectrum.

The fluorescence spectra of polar compounds in polar media experience a pronounced nonuniform broadening because of fluctuations of intermolecular interactions. These spectra can be represented as a convolution of a distribution function and an elementary spectrum (Ref. 1, for example). The elementary spectrum is usually understood as an electronic–vibrational band of individual impurity centers with a fixed peak frequency or a purely electronic transition broadened by translational vibrations and librations of molecules of the surrounding medium. The Debye model is invoked to describe the kinetics of the displacement of the instantaneous spectrum under the assumption that the effect of the orientational relaxation of the interactions of the impurity center with the surroundings is described by an exponential or approximately exponential shift of the center of gravity of the distribution function. A monotonic long-wave shift of the instantaneous spectrum with slight changes in its shape has been detected both in the fluorescence<sup>2–4</sup> and in the phosphorescence<sup>5</sup> during excitation near the peak of the absorption band. Accordingly, the elementary spectrum is also assumed to remain constant in time, while certain variations in the half-width of the instantaneous spectra are attributed<sup>4</sup> to particular features of the transformation of the distribution function. The kinetics of the spectrum was measured in Refs. 2–4 for delay times comparable to the average lifetime in the excited state,  $\tau_e$ , or approximately equal to  $2\tau_e$ .

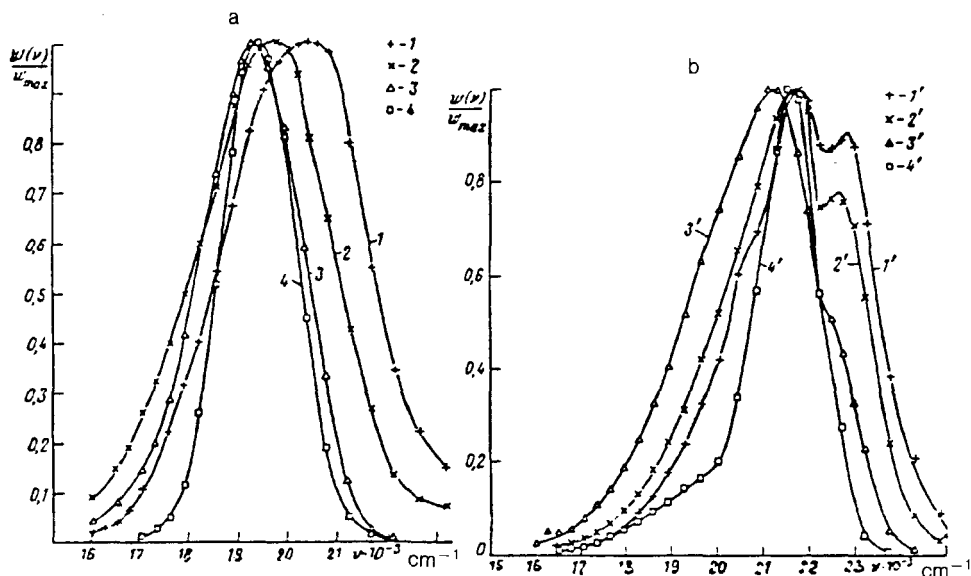


FIG. 1. Instantaneous fluorescence spectra. a: ZMMAMF in isobutanol at  $T=223$  K at delay times of 2.5, 5, 30, and 60 ns (curves 1-4). b: 2AA in isobutanol at  $T=196$  K at delay times of 10, 20, 40, and 100 ns (1'-4'). The duration of the exciting pulse is 0.5 (a) and 1.0 ns (b).

In an effort to learn about the effect of the orientational dynamics of the molecules of a medium in shaping of the fluorescence band, we have carried out detailed measurements of the instantaneous spectra for 2-acetylanthracene (2AA) and 3-monomethylamino-*N*-methylphthalimide (3MMAMP) in polar solutions which undergo a glass transition upon cooling, for delay times from 2.5 to 100 ns. The variation of  $t$  over a very broad range made it possible to obtain information on the evolution of the spectra over a time five or six times  $\tau_e$ . Measurements were also carried out at very long delay times, amounting to several microseconds. The excitation source was a nitrogen laser with a pulse length of 0.5 or 1 ns. For all entities studied, the excitation (337 nm) fell in the long-wave absorption band. We studied isobutyl, propyl, and ethyl alcohol solutions. The solution concentration was  $10^{-4}$ - $5 \times 10^{-5}$  M.

The results shown in Fig. 1 illustrate the evolution of the spectrum. With increasing delay time, the fluorescence band initially shifts in the long-wave direction; then it shifts in the opposite direction. More-detailed information on the change in the direction of the shift (the opposite shift) can be found in Ref. 6, where there are also citations of studies describing the measurement method which we used. In the present letter we wish to discuss some other, extremely characteristic features of the change in the shape of the instantaneous spectra: the disruption of the vibrational structure, the coalescence and collapse of the band, and the subsequent expansion as the delay time is increased.

A collapse of the fluorescence spectrum has been observed for all compounds studied. The contraction of the spectrum after the reverse short-wave shift is accom-

panied by a tendency of the spectrum to become symmetric, with a slight change in the position of the center of gravity of the band. This tendency can be seen particularly clearly in the diffuse spectra of 3MMAMP (Fig. 1a). The spectra of 2AA (Fig. 1b) undergo a collapse which is less symmetric. At a temperature of 196 K, the instantaneous spectrum of 2AA in isobutanol at  $t=100$  ns still has traces of the vibrational structure on the long-wave wing of the spectrum. However, even at  $t=200$  ns, the line is essentially completely symmetric with a half-width  $\Delta\nu=800$   $\text{cm}^{-1}$ . A further increase in the delay time is accompanied by a broadening of the band and—a slight unexpected result—a partial restoration of the structure. This effect, the opposite of a collapse, occurs at very long delay times: between 500 ns and 5  $\mu\text{s}$ . (Spectra are not shown in Fig. 1 for  $t>100$  ns, since in this letter we wish to stress the extremely characteristic changes in the structure of the band in the region in which the signal can be detected reliably, in which the measurement error is 10–15%.)

At room temperature, the instantaneous spectra of 2AA in isobutanol change for  $t$  between 10 ns and 5  $\mu\text{s}$ . For delay times  $t\leq 40$  ns, these spectra consist of a broad, asymmetric band peaking at 21 150  $\text{cm}^{-1}$  with a half-width of 3300  $\text{cm}^{-1}$ . At  $t>50$  ns we also see a contraction and a symmetrization of the spectrum (at  $t=200$  ns,  $\Delta\nu=1000$   $\text{cm}^{-1}$ ), which gives way to an expansion of the spectrum at microsecond delay times. The position of the peak of the instantaneous spectrum remains essentially the same, implying a very fast (subnanosecond) relaxation to equilibrium in the structure of the solvate sheath. We wish to stress that the delay time at which the collapsed instantaneous spectrum has its minimum width depends only weakly on the temperature, at least for temperatures above the glass transition point of the solvent.

The behavior observed here requires further development of ideas regarding the role played by intermolecular interactions and the orientational dynamics of the molecules of the medium in shaping the bands of the instantaneous spectra. In a dynamically active medium, the strength of the electric field exerted on an excited impurity molecule by the surroundings is subject to fast, random changes because of activation jumps involving changes in the time-varying orientational equilibrium coordinates (changes in the time-varying settling positions). The interactions with vibrations of impurity molecules which arise in the process must be assumed to be of a nonadiabatic nature and to cause an amplitude–phase modulation of steady states. As a result of an interference of the steady states, there is a spectral “borrowing.” This borrowing is manifested as a transfer of intensity from the vibrational side bands to a more intense band, for which the vibrational overlap integral of the steady-state wave functions of the  $S_1$  and  $S_0$  states is at a maximum. By analogy with similar effects in IR spectra and Raman scattering spectra, discussed in Ref. 7, we can conclude that the collapse of the band of the instantaneous spectrum is evidence of a manifestation of a phase memory and a weak nature of a reorientational perturbation. Another important point is that in the course of the reorientation there is a rapid change in the frequency of the electronic-vibrational  $S_1 \rightarrow S_0$  transition, caused by a change in the stabilization energy of the levels of the  $S_1$  and  $S_0$  states.

The expansion of the instantaneous-spectrum band at very long delay times indicates a pronounced phase relaxation and a loss of memory. The system also appears to be asynchronous immediately after the excitation.

In addition to the abrupt reorientations of the solvent molecules, random changes in the intermolecular interactions as a result of activated reorientation motions of the OH group of the solvent and also intermolecular random perturbations caused by a change in the orientation of the acetyl-(2AA) and methylamino-groups (3MMAMP) of the impurity molecules themselves have an analogous and apparently even stronger effect on the shaping of the band in a dynamically active medium. All these types of motions are responsible for a broadening and overlap of vibrational bands in the elementary spectrum.

This explanation, however, does not mean that the collapse time of the instantaneous spectrum should depend strongly on the temperature. The spectral "borrowing" and collapse of the spectrum are determined by a correlation of an intramolecular vibrational motion with activation perturbations and apparently depend not so much on the reorientation frequency as on the time spent in the activated state; in other words, they depend on the time taken to cross the crest of the potential barrier. Also important are two other time-varying parameters; the length of the exciting pulse and the time over which the instantaneous spectrum is measured. Since the excited impurity molecule and the immediate surroundings of the medium constitute an autonomous system, it can be assumed that the collapse of the instantaneous spectrum is a consequence of an autocorrelation of spontaneous electronic-vibrational transitions and random reorientational motions in the medium and the impurity molecule itself.

<sup>1</sup>N. G. Bakhshiev, V. S. Libov, Yu. T. Mazurenko *et al.*, *Solvatochromism* (Izd. Leningr. Univ., Leningrad, 1989).

<sup>2</sup>W. R. Ware, P. P. Chow, and S. K. Lee, *Chem. Phys. Lett.* **2**, 356 (1968); W. R. Ware, S. K. Lee, G. J. Brant, *et al.*, *J. Chem. Phys.* **54**, 4729 (1971).

<sup>3</sup>T. Azumi, K. Itoh, and H. Shiraishi, *J. Chem. Phys.* **65**, 2550 (1976).

<sup>4</sup>V. T. Koyava, V. S. Pavlovich, V. I. Popechits *et al.*, *Zh. Prikl. Spektrosk.* **34**, 1017 (1981).

<sup>5</sup>V. S. Pavlovich, P. P. Pershukevich, and L. G. Pikulik, *Zh. Prikl. Spektrosk.* **39**, 779 (1983).

<sup>6</sup>V. S. Pavlovich, P. P. Pershukevich, L. G. Pikulik *et al.*, *Dokl. Akad. Nauk BSSR* **28**, 800 (1984).

<sup>7</sup>A. I. Burshtein and S. I. Temkin, *Spectroscopy of Molecular Rotation in Gases and Liquids* (Nauka, Novosibirsk, 1982).

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