The Relaxation Time of the Orientation Polarization and its Influence on the Luminescence Intensity Distribution *

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Z. Naturforsch. **39 a,** 509–510 (1984);
received December 21, 1983

The characteristic relaxation time τ_R of the orientation polarization of polar solvent molecules around polar luminescent molecules influences the spectral emission distribution depending on $\tau_F > \tau_R$ or $\tau_F \leqq \tau_R$. This is shown on the luminescence of the polar molecules 4-isocyanate-4′-dimethylamino-transsstilbene (CDS), 4-isocyanate-4′-methoxy-trans-stilbene (CMS) and 4-isocyanate-3′,4′-dimethoxy-trans-stilbene (CDMS) (having a very short lifetime $\tau_F < 10$ ps) in chlorobenzene.

As known from the experiments and theoretical considerations of Galley and Purkey [1], the intensity distribution $I(\nu)$ within the fluorescence band and the band position of polar fluorescing molecules in frozen polar liquids are strongly influenced by the orientation polarization of the solvent molecules around the solute molecules. In this case the dependence of $I(\nu)$ on the excitation frequency ν_{exc} is due to the spectral heterogeneity of the medium. Such effects on stilbene derivatives in frozen and liquid mixed solutions have been observed previously [2]. An asymmetrical broadening of the fluorescence bands of indol and dimethylindol in mixed liquid solutions described in the papers [3, 4] can be interpreted in the same way.

Strongly polar solute molecules in different liquid polar solvents have different surroundings, and every surrounding fluctuates with a characteristic relaxation time τ_R [5]. If the lifetime τ_F of the solute molecule in the excited state is much longer than τ_R, the surroundings of all excited centres relaxe to a new statistical equilibrium before the emission. The solution appears to be homogeneous; the emission bands are homogeneously broadened. In this case, one expects a fluorescence emission band, the intensity distribution of which is independent of the excitation frequency ν_{exc}.

If, however, τ_F is comparable or shorter from τ_R, than the emission is expected to start partly before the relaxation, the emission bands should be broadened inhomogeneously and therefore the spectral emission intensity distribution should depend on ν_{exc}. Using short time pulse excitation, the spectral intensity distribution should be time dependent too.

Of special interest is the fluorescence of a class of substances (4-isocyanate-4′-dimethylamino-trans-stilbene (CDS), 4-isocyanate-4′-methoxy-trans-stilbene (CMS) and 4-isocyanate-3′,4′-dimethoxy-trans-stilbene (CDMS)), the mean lifetimes of which are very short. The lifetimes τ_F of these substances are less then 10 ps in chlorobenzene [6]. The relaxation time τ_R of chlorobenzene in dilute benzene solutions has been measured with cm waves to be 7.5 ps at 292 K [7] and 10.8 ps at 291.5 K [8], and using meter waves one gets 10.6 ps at 296 K [9]. Thus, for the polar CDS, CMS and CDMS molecules [10] in chlorobenzene, the condition $\tau_F \approx \tau_R$ is held.

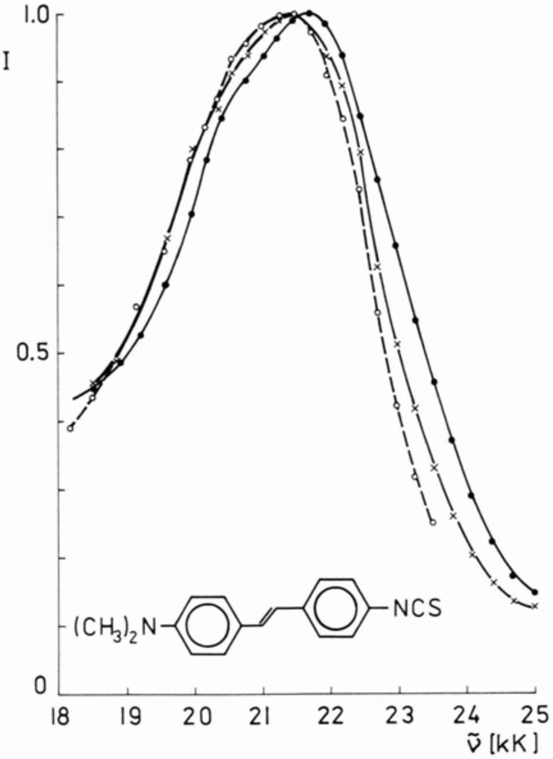

Fig. 1. Fluorescence spectra of CDS in chlorobenzene at 295 K: $\tilde{\nu}_{\text{exc}} = 28\,600\ \text{cm}^{-1}$ (●); $\tilde{\nu}_{\text{exc}} = 27\,000\ \text{cm}^{-1}$ (×); $\tilde{\nu}_{\text{exc}} = 24\,400\ \text{cm}^{-1}$ (○).

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* Carried out under Research Project M.R.I.5.

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In the unpolar benzene and cyclohexane the fluorescence intensity distribution $I(\nu)$ of CDS, CMS and CDMS was found to be independent of ν_{exc}. However, in chlorobenzene we observed for the three substances a marked dependence of $I(\nu)$ on ν_{exc}. As an example, the fluorescence spectra of CDS in chlorobenzene for three excitation wave numbers can be seen in Figure 1. They show clearly the excitation and emission of distinguishable centres by different excitation wave numbers.

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