

On the Intensity Distribution within Photoluminescence Bands in Rigid and Liquid Solutions*

A. Kawski

Luminescence Research Group, Institute of Experimental Physics, University of Gdańsk, Gdańsk, Poland

M. Stoń

Institute of Physics, Pedagogical High School, Słupsk, Poland

I. Janić

Institute of Physics, University of Novi Sad, Yugoslavia

Z. Naturforsch. **38 a**, 322–324 (1983); received October 29, 1982

The effect of the excitation light frequency on the intensity distribution within the fluorescence band and the band position of non-polar and strongly polar luminescent substances is investigated in pure and mixed liquid and glassy solvents. An interpretation concerning the intensity distribution in the emission band and the local temperatures determined by the method of Stepanov is given.

1. Introduction

Based on numerous experimental results [1–7], the intensity distribution $I(\nu)$ within the fluorescence band and the band position are generally assumed to be independent of the frequency ν_{exc} of the excitation light. Some authors [8–13], however, have found a measurable effect of ν_{exc} on $I(\nu)$.

The Franck-Condon principle leads to the conclusion that $I(\nu)$ is independent of ν_{exc} if thermal equilibrium between the luminescent centre (LC) and the surrounding initially disturbed is fully restored before the occurrence of the fluorescence emission [14–16]. Such an abrupt restoration can not be expected in every case [13]. An interesting interpretation of the observed marked effect of ν_{exc} on the intensity distribution and the band position for polar molecules in frozen solutions has been given by Galley and Purkey [12].

In the present paper, an attempt is made to verify the model proposed by Galley and Purkey [12] and to explain the results obtained so far with polymers in rigid media.

To this end, three donor-acceptor-substituted trans-stilbenes were selected: 4-dimethylamino-4'-nitrostilbene (DNS), 4-amino-4'-nitrostilbene (ANS) and diphenylenestilbene (DPS). DNS and ANS are strongly polar substances with electric dipole mo-

ments which in the excited state, μ_e , are about 3 times larger than in the ground state, μ_g , [17], whereas DPS is nonpolar. The investigations of the effect of microenvironment on the electronic spectra of the substances under study in mixed solvents [18] consisting of n-hexane and ethyl acetate enabled the determination of the mean solvation number (a so-called average co-ordination number), which for DNS and ANS amounts to 17. Thus, a considerable number of the solvent molecules gather in the solvation shells around these prolate molecules.

2. Experimental Results

Figures 1 and 2 show normalized fluorescence spectra of the non polar substance DPS in n-hexane and ethylacetate at room temperature and – for two different excitation frequencies – at 77 K. At room

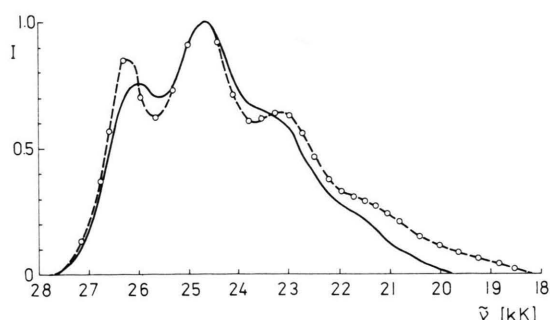


Fig. 1. Fluorescence spectra of DPS in n-hexane at 295 K ($\bar{\nu}_{\text{exc}} = 29410 \text{ cm}^{-1}$ – solid line) and at 77 K ($\bar{\nu}_{\text{exc}} = 30303 \text{ cm}^{-1}$ – broken line and $\bar{\nu}_{\text{exc}} = 28571 \text{ cm}^{-1}$ – \circ).

* Carried out under Research Project MR.I.5.

Reprint requests to Prof. Dr. A. Kawski, Instytut Fizyki Doświadczalnej, Uniwersytet Gdański, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

0340-4811 / 83 / 0300-0322 \$ 01.3 0/0. – Please order a reprint rather than making your own copy.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

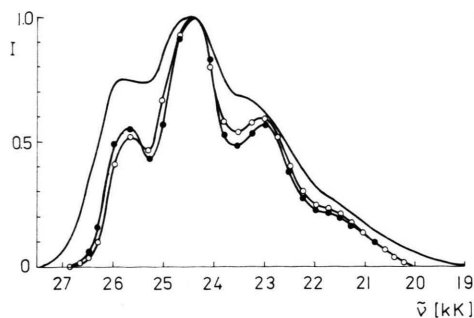


Fig. 2. Fluorescence spectra of DPS in ethyl acetate at 295 K; ($\tilde{\nu}_{\text{exc}} = 29412 \text{ cm}^{-1}$ – solid line) and at 77 K ($\tilde{\nu}_{\text{exc}} = 27778 \text{ cm}^{-1}$ – \circ and $\tilde{\nu}_{\text{exc}} = 27027 \text{ cm}^{-1}$ – \bullet).

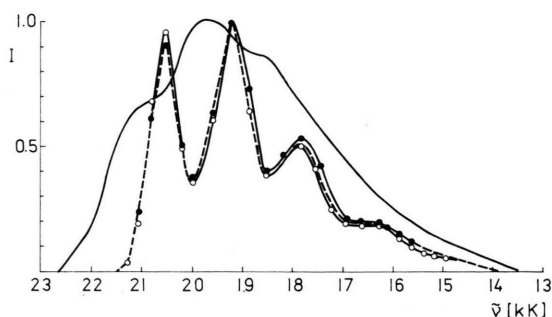


Fig. 3. Fluorescence spectra of DNS in n-hexane at 295 K ($\tilde{\nu}_{\text{exc}} = 23809 \text{ cm}^{-1}$ – solid line) and at 77 K ($\tilde{\nu}_{\text{exc}} = 25641 \text{ cm}^{-1}$ – broken line, $\tilde{\nu}_{\text{exc}} = 23809 \text{ cm}^{-1}$ – \circ and $\tilde{\nu}_{\text{exc}} = 23256 \text{ cm}^{-1}$ – \bullet).

temperature all three substances, DPS as well as DNS and ANS, have fluorescence spectra which are uninfluenced by ν_{exc} in n-hexane and ethylacetate.

At 77 K the fluorescence of the non-polar DPS shows a small dependence on ν_{ex} in ethylacetate only (Figure 2). The strongly polar DNS molecule ($\mu_g = 7.2 \text{ D}$, $\mu_e = 23.1 \text{ D}$) shows a very weak effect of this kind in n-hexane (Figure 3), but a strong effect in ethylacetate (Figure 4). A similar marked dependence of $I(\nu)$ on ν_{exc} has been observed with ANS ($\mu_g = 6.5 \text{ D}$, $\mu_e = 20.7 \text{ D}$) in acetylacetate and ethanol.

3. Discussion

The present as well as the previous studies [1–7] of nonpolar and polar luminescent molecules in liquid solvents satisfying the condition $\tau_F \gg \tau_R$ (τ_F —mean lifetime of the luminescent molecule, τ_R —orientation relaxation time of solvent molecules) confirm the independence of $I(\nu)$ from ν_{exc} . In

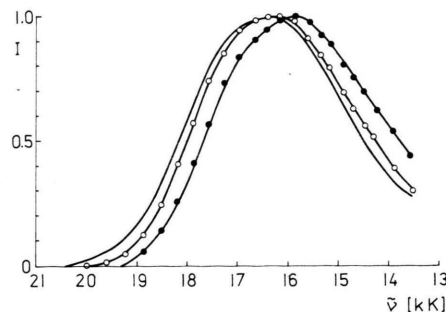


Fig. 4. Fluorescence spectra of DNS in ethyl acetate at 77 K; ($\tilde{\nu}_{\text{exc}} = 24390 \text{ cm}^{-1}$ – solid line, $\tilde{\nu}_{\text{exc}} = 22727 \text{ cm}^{-1}$ – \circ and $\tilde{\nu}_{\text{exc}} = 20618 \text{ cm}^{-1}$ – \bullet).

this case, fluorescence occurs from an equilibrated excited to the ground state Franck-Condon level [19, 20]. The effective temperatures T^* of the LC, determined using the universal Stepanov relation [21] between the absorption and fluorescence spectra, do not differ from the ambient temperatures T of the solvent [13, 22–25]. According to Bakhshiev *et al.* [26–28], the universal Stepanov relation holds only when configurational (to a high degree orientational) equilibrium exists between the excited molecule and the surrounding medium.

In frozen solutions, however, the condition $\tau_F \ll \tau_R$ is fulfilled. According to the model of Galley and Purkey [12], in rigid glassy solutions different LC's having different orientation of the solvent molecules in the solvation shell of the luminescent molecule are randomly distributed. Indeed, in this case the dependence of both the band position and the intensity distribution within the band on ν_{exc} is observed (Figure 4). In non-polar n-hexane (the orientation interactions are weak), however, the strongly polar DNS or ANS molecules show only a slight dependence of $I(\nu)$ on ν_{exc} (Figure 3).

One can also explain in this way the previous observations of Starkiewicz [8] concerning the change of the luminescence band shape in highly viscous solutions upon excitation in the anti-Stokes region.

In this context also our previous results concerning local temperatures T^* of the LC and a weak dependence of $I(\nu)$ on ν_{exc} require some explanations. For rigid solutions of non-polar (DPA, DBA, DCA)

* The preparation of rigid solutions and polymerization of methyl methacrylate and styrene are described in paper [30].

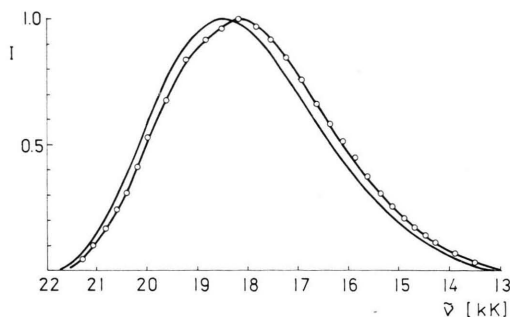


Fig. 5. Fluorescence spectra of DNS in a mixed liquid solvent consisting of n-hexane and 8 mol % ethyl acetate (8% mol fraction) at 295 K ($\nu_{\text{exc}} = 23809 \text{ cm}^{-1}$ — solid line and $\nu_{\text{exc}} = 22222 \text{ cm}^{-1}$ — \circ).

and polar (BBO) fluorescent substances in methyl polymethacrylate* the universal Stepanov relation gives $T^* > T$ but a weak dependence of $I(\nu)$ on ν_{exc} [13, 24]. A similar situation occurs with non-polar DPA, DPS and TPB in polystyrene [11]. The fluorescence polarization spectra show no change in the degree of polarization within the fluorescence band, which shows that in this case we deal with one kind of LC only. A temperature T^* higher than the ambi-

ent temperature T can be interpreted as a weak interaction between the luminescent molecules and the medium in methyl methacrylate and styrene polymers, thus indicating freedom of the luminescent molecules like in the gaseous phase or in Shpol'skii matrices. This conclusion is also confirmed by a low degree of polarization in such organic glasses. For molecules luminescing in gaseous phase under low pressure, $T^* > T$ is always observed [29].

A large difference $\Delta T = T^* - T$ was observed with luminescent molecules in liquid mixed (non-polar/polar) solvents when the mixture contained small amounts of the polar solvent component [31], whereas in pure non-polar or polar solvents $\Delta T \approx 0$ was obtained. This fact plainly evidences the formation of different LC's. Unsymmetric broadening of the fluorescence band of the solute is observed due to the formation of different LC's (the solute molecule with different numbers of polar solvent molecules in the solvation shell) contributing differently to the band shift [20, 32]. Intensity distribution and band position strongly depend on ν_{exc} in this case (Figure 5).

Thus, the universal Stepanov relation [21] is observed to be violated not only in frozen solutions but also in mixed liquid solvents at room temperature.

- [1] E. L. Nichols and E. Merritt, *Phys. Rev.* **18**, 483 (1904).
- [2] A. Jabłoński, *C. R. Soc. Pol. Phys.* **7**, 1 (1926).
- [3] A. Kowski and H. Wardziński, *Z. Naturforsch.* **20a**, 1354 (1965).
- [4] A. N. Sevshenko and E. K. Kruglik, *Internat. Conf. Luminescence, Budapest 1966, Preprints Supplement* (1966), p. 84.
- [5] A. Kowski, B. Pasztor, and H. Wardziński, *Acta Phys. Polon.* **29**, 71 (1966).
- [6] A. Kowski, B. Bartoszewicz, and G. Strzałkowska, *Acta Phys. Polon.* **A37**, 321 (1970).
- [7] A. Kowski, *Bull. Acad. Polon. Sci., Ser. Math., Astr. Phys.* **19**, 1141 (1971).
- [8] J. Starkiewicz, *C. R. Soc. Pol. Phys.* **4**, 73 (1929).
- [9] A. Kowski, *Bull. Acad. Polon. Sci., Ser. Math., Astro. Phys.* **11**, 567 (1963).
- [10] L. Kozma, L. Szalay, and J. Hevesi, *Acta Phys. Chem. Szeged*, **10**, 67 (1964).
- [11] A. Kowski and H. Wardziński, *Bull. Acad. Polon. Sci., Ser. Math., Astro. Phys.* **13**, 745 (1965).
- [12] W. C. Galley and R. M. Purkey, *Nat. Acad. Sci. USA*, **67**, 1116 (1970).
- [13] A. Kowski and J. Kukielski, *J. Luminesc.* **4**, 155 (1971).
- [14] A. Jabłoński, *Z. Phys.* **73**, 460 (1931).
- [15] A. Jabłoński, *Phys. Z. Sov.* **8**, 105 (1935).
- [16] A. Jabłoński, *Bull. Acad. Polon. Sci., Ser. Math., Astro. Phys.* **15**, 885 (1967); **16**, 835 (1968).
- [17] A. Kowski, I. Gryczyński, Ch. Jung, and K.-H. Hecken, *Z. Naturforsch.* **32a**, 420 (1977).
- [18] A. Kowski, B. Ostrowska, and M. Stoń, *Z. Naturforsch.* **36a**, 999 (1981).
- [19] L. Bilot and A. Kowski, *Z. Naturforsch.* **17a**, 621 (1962).
- [20] A. Kowski, *Chimia*, **28**, 715 (1974).
- [21] B. I. Stepanov, *Dokl. Akad. Nauk USSR* **112**, 839 (1957).
- [22] I. Ketskemety, L. Kozma, and J. Hevesi, *Acta Phys. Chem. Szeged* **12**, 83 (1966).
- [23] A. Kowski, *Acta Phys. Polon.* **A37**, 651 (1970).
- [24] A. Kowski and J. Kukielski, *Z. Naturforsch.* **25a**, 653 (1970).
- [25] A. Kowski, B. Bartoszewicz, and J. Kukielski, **A38**, 127 (1970).
- [26] N. G. Bakhshiev, I. V. Piterskaya, V. I. Studentov, and A. V. Altaiskaya, *Opt. Spectr.* **37**, 349 (1969).
- [27] N. G. Bakhshiev, I. V. Piterskaya, and A. V. Altaiskaya, *Opt. Spectr.* **38**, 897 (1970).
- [28] A. N. Rubinov and V. I. Tomin, *Opt. Spectr.* **30**, 859 (1971).
- [29] N. A. Borisevich, *Vosbuzhdeniye Sostoyaniya Sloznych Molekul v Oazovoj Fase, Isdat. Nauka i Tekhnika, Minsk* 1967.
- [30] A. Kowski, *Bull. Acad. Polon. Sci., Ser. Math., Astro. Phys.* **6**, 533 (1958).
- [31] A. Kowski and J. Kukielski, *Z. Naturforsch.* **25a**, 1380 (1970).
- [32] A. Kowski and J. Czajko, *Z. Naturforsch.* **29a**, 84 (1974).