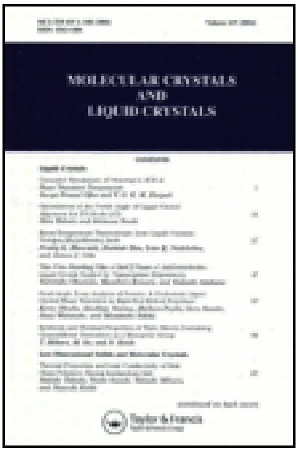

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Non-linear Spectral Effects in Films and Crystals of Polar Molecules

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NONLINEAR SPECTRAL EFFECTS IN FILMS AND CRYSTALS OF POLAR MOLECULES

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Abstract

The paper addresses the spectroscopic peculiarities of polar molecular crystals and films of dimethylaminebenzylidene-1,3-indandione (DMABI). Specific visible fluorescence bands for various modifications of the system are discovered. They are identical for all excitation conditions and seem to be correlated with the structural organization of the media. The infrared excitation of these bands is shown to be a two-step process which turns into the saturating regime at higher intensities.

INTRODUCTION

A steady dipole moment of a polar molecule in the ground state and its essential change during optical excitation create a strong electron-phonon and electron-vibrational mode interaction which cannot be treated within the perturbation procedure and, moreover, the applicability of the excitonic picture for crystals of polar molecules becomes far from being obvious. Due to these interactions, the spectral properties of such systems become very sensitive to structural changes, temperature and excitation intensities, and those systems can express optically nonlinear behavior in some spectral regions. Therefore, new possibilities of their application to nonlinear optics and molecular electronics are expected.

The compounds under investigation are α and γ modifications of dimethylaminebenzylidene-1,3-indandione (DMABI) crystals and films (see insert of Fig.1). The crystal structure of both modifications are determined in[1,2] . The molecules being in ground states, the structural differences of both crystal structures are well known. However, due to the strong interaction of the molecules with the surrounding, the electronic excitation state of the molecule could cause the structural changes distinctly influencing the spectral properties of the systems under investigation.

MATERIALS AND METHODS

Both modifications of the crystal were grown at Institute of Physics and Energetics in Riga (Latvia) using the methods from^3 . α-modification is violet-blue and γ-one is bright red. Films were created by precipitating the aqueous solution of the red crystal on a glass substrate or thermally deposited from vapor phase.

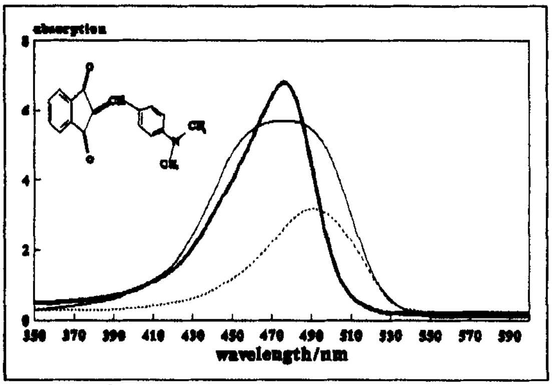

FIGURE 1. Absorption spectra of DMABI solutions in acetone (thin solid line), benzene (thick line) and ethyl alcohol (dashed line).

Absorption spectra of the film and DMABI solutions were obtained by means of the Beckman Uv-5270 spectrophotometer. The fluorescence spectra were recorded by means of spectrometer with double-monochromator (DFS-24, DFS-52 or Jobin Yvon HRD-1), multi-alkali photomultipliers FEU-79 or FEU-136 and DC amplifier (Soviet construction) or photon counter using a box-car. The fluorescence excitation in the visible region of the was provided by cw He-Ne laser (excitation at 633nm, 15 mW/mm^2 of intensity), quasi-cw copper gas laser (excitation at 510.2 nm and 576.4 nm, 900 mW/mm^2) and in infrared spectral region by Q-switched YAG:Nd^{3+} laser (excitation at 1064 nm, 10 ns pulses of 20 MW/cm^2 intensity).

The investigations were mainly provided at room temperature and at 4 K the spectra were obtained as well.

RESULTS

Absorption Spectra. The absorption spectrum at room temperature of 10^{-3} M of DMABI in acetone contains a single band with the maximum at λ=475*nm*. (see Fig.1). In solvents of a higher polarity, the absorption band shifts to the red as far as 0.5 eV. The absorption spectrum of the film, as it is seen in Fig.2, differs from this of the solution. Alongside with the absorbance in the visible ($\lambda\approx$520*nm*), the infrared absorption band at $\lambda > 1000nm$ appears.

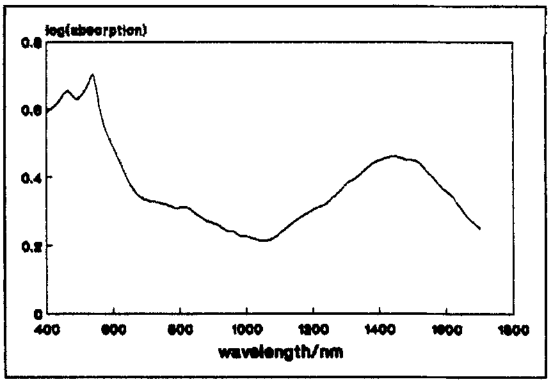

FIGURE 2 Absorption spectrum of DMABI film.

Fluorescence Spectra. Fluorescence spectra of both modifications of the crystal and that of the film in the visible have been measured using the excitation at wavelengths of 510.2 nm, 576.4 nm and 632 nm. The same luminescence spectra were observed after excitation by the first two wavelengths. Three characteristic bands are general, that occur at 620nm (I), 655nm (II) and 715nm (III).

The investigation of fluorescence quantum yield dependence on the excitation intensity shows the fluorescence bands of α- modification of the crystal and the film being independent. However, γ-modification of the crystal indicates the anomalous fluorescence quantum yield dependence on the excitation intensity (see Fig.4).

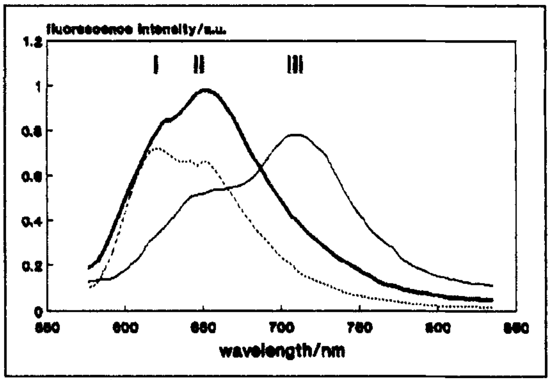

FIGURE 3. Luminescence spectra of the solid DMABI: α-modification crystal (thin solid line), γ-modification crystal (thick line) and film (dashed line).

The visible fluorescence, excited by YAG:Nd^{3+} laser (excitation at 1064nm in the infrared band) measured for both crystals and the film, yields the same spectra as that obtained by direct excitation in the visible region (see Fig.3). The fluorescence intensity shows a square dependence at low excitation intensities which changes into a linear dependence at high intensities (see Fig.5).

Low Temperature. The fluorescence spectra measured at 4 K by the excitation at 1064nm, have the same shapes for γ modification of the crystal and for the film (see Fig.6). However, α modification of the crystal indicates no fluorescence. The excitation intensity increasement in order to stimulate the fluorescence changes its phase into γ modification before starting to emit in the visible region of the spectra.

DISCUSSION

The absorption spectrum of the film virtually differs from the molecular solution one (see Fig. 1) indicating the crystal field influence on the spectral properties of the condensed matter. That statement is confirmed by the molecular absorption changes observed at different polarities of the solvent. Essential shifts of the absorption maximum (up to 0.5 eV to the red at the most polar media) prove the effect of the reorganization of the nearest surrounding of the excited molecule and can not be treated within the terms of perturbation.

The fluorescence spectra (Fig. 2) represent the direct connection of the spectral properties with the crystal structure. The spectra of γ-modification and of the film contain only bands I and II, while band III is characteristic to the crystal of α-modification alone. The structure of α-modification is constructed by the alternating sequence of electron-donor and electron-acceptor parts of the DMABI molecules [1] and γ-modification is build up of the stacks of molecules [2]. Here the alternating sequence of electron-donor and electron-acceptor parts of molecules due to differences in the relative orientation of them [4], evidently gives the larger energy of the polarization in α modification than in the other cases. Therefore, the structural buildup

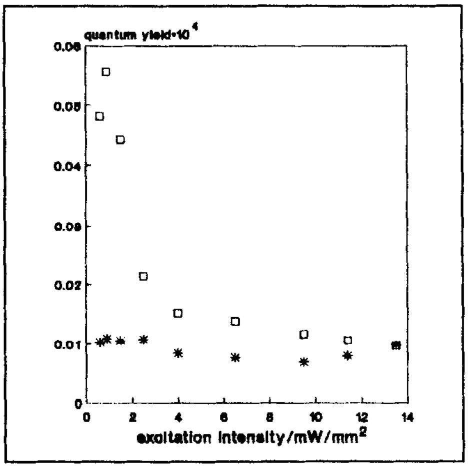

FIGURE 4. Quantum yields of the DMABI crystals fluorescence: α-modification - stars and γ-modification - squares.

confirms the origin of the fluorescence bands determined by the repolarization of the media after molecular excitation.

The presence of the absorption of the condensed media in the infrared spectral region (λ>1200 nm) is evidently due to the intermolecular interaction. This is directly confirmed by the infrared excitation of the visible fluorescence which is present in the condensed phase and absent in the solutions. Intramolecular charge transfer (CT) states are most probably responsible for the infrared absorption in the condensed matter. The visible fluorescence excited by the infrared pulses show the same spectra as in the case of visible excitation, once more confirming that the fluorescence bands are correlated with the structural buildup. Quantum yield of the infrared excited fluorescence indicates the square law dependence for all bands at low intensities transforming into linear dependences at higher intensities (see Fig. 5). Such a behavior refers to the two-step optical transition (via the state of the condensed matter responsible for the infrared absorption) which reaches the saturation threshold of the first (infrared) optical transition at higher intensities.

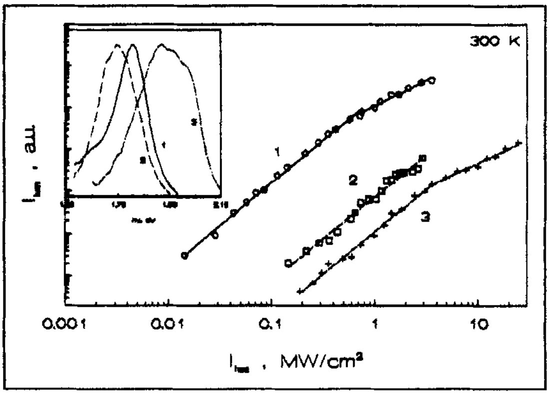

FIGURE 5. Luminescence intensity vs excitation intensity of α-crystal (1), γ-crystal (2), and the film (3).

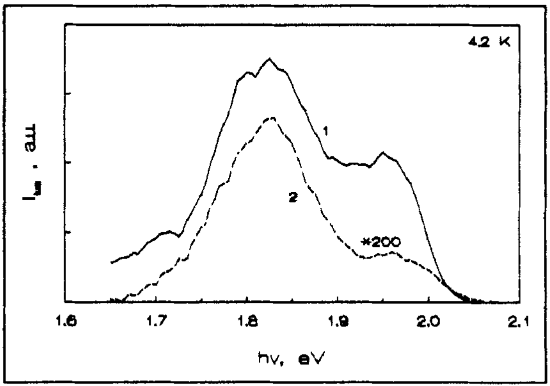

FIGURE 6. Fluorescence spectra of α-crystal (1) and γ-crystal at low temperature.

The low temperature fluorescence spectra excited by the infrared light indicate the similar bands for γ-modification of the crystal and the film. The absence of the visible fluorescence of α-modification at low temperatures can be explained by the freezing-out the molecular reorientation movement being the most significant in this case. It is remarkable that the visible fluorescence appears at the same time when the structural changes (and changes in the color of the crystal) are observed.

Quantum yields of the fluorescence excited in the visible region (Fig. 3), show no intensity dependence for α-modification. Meanwhile, for γ-modification, the anomalous quantum yield decrease is observed at low excitation intensities, which turns out by further increasing of the intensity. This effect is the evidence for the presence of two kinds of the crystal states (bands I and II). Besides, one of them has to be saturated at the low excitation intensities. However, this hypothesis needs more consecutive investigations.

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