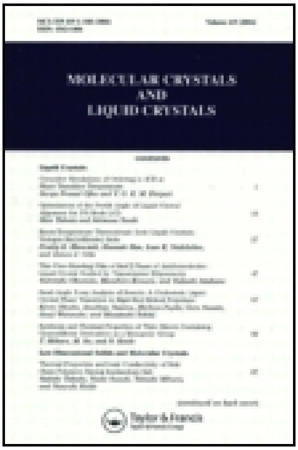

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Excitation Dynamics in Solutions, Films and Crystals of Indandione-1,3 Pyridinium Betaine

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Excitation Dynamics in Solutions, Films and Crystals of Indandione-1,3 Pyridinium Betaine

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The excitation decay kinetics of polar Indandione-1,3 Pyridinium Betaine (IPB) molecules in various environments: solvents, films and crystals, were studied using time-resolved luminescence and transient absorption measurements. A red-shift, depolarization and fast decay of the luminescence intensity were observed on a femtosecond time scale in dilute solutions and explained by excitation relaxation from the initially created intramolecular charge transfer state to the lower energy excited state of the indandione moiety. The first fast relaxation stage is followed by a slower one responsible for the relaxation to the ground state stage with the rate depending on the viscosity of the surrounding. By comparing the excitation properties of IPB in solution and those in the crystal form, the influence of the intermolecular interactions on the excited state dynamics is revealed. Excitation relaxation in the IPB deposited films of different thickness and in a single crystal is described as a competition between different relaxation paths of nonradiative recombination, these paths being the high lying Frenkel exciton states and the low lying intermolecular charge transfer states.

Keywords: molecular crystal; Indandione-1; 3-Pyridinium Betaine; ultrafast spectroscopy; charge transfer

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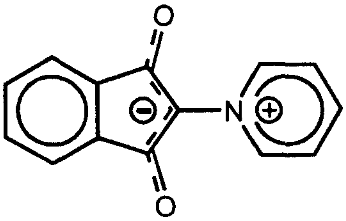
I. INTRODUCTION

Organic molecules containing electron-donor and electron-acceptor moieties attract much attention as model systems for investigation of the electron transfer reaction [1,2] and as an active medium for construction of non-linear optical materials [3,4]. Solids built up by dipolar organic molecules can be attributed to a new class of polar organic crystals [5]. Polar crystals often show significant photocurrent and well-pronounced non-linear-optical effects [6–9]. However, the origin of excited states and their relaxation mechanism in these materials are not well defined so far. Large dipole moments in the ground and excited states of the molecules evidently create strong intermolecular interactions and can enhance exciton-phonon coupling in polar organic solids. These interactions manifest themselves in the spectral and dynamic properties of excitons, which can be significantly different from those of excitations of separated molecules.

Solids of Indandione-1,3 Pyridinium Betaine (IPB) can be considered as a typical system of this class of organic crystals. IPB compounds belong to series of highly polar intramolecular salts in which the cation and anion are covalently bound in one molecule:



SCHEME 1

Quantum chemical calculations have shown that the IPB molecule itself is almost flat due to a strong π-electron conjugation [6,10]. Owing to the strong interaction between the donor and acceptor moieties, a partial intramolecular charge transfer from the indandione anion to the pyridinium cation takes place in the molecular ground state. As a result of the asymmetry of charge distribution, the IPB molecule possesses a considerable static dipole moment, $d_0 = 4.1$–4.5 D[6,11]. Such a permanent dipole moment can considerably enhance the coupling between molecules in comparison with that in classical organic crystals. After photoexcitation, the optically induced changes in the magnitude and sign of the dipole moment of the IPB molecule in the excited state ($d_{ex} = -3.6$ D[11] cause a large polarization effect of the surrounding. In accordance, an unusually large luminescence Stokes shift, reaching 1.0eV, which was attributed to the lattice reorganization effects was observed for IPB solids [12]. A large value of the exciton-phonon coupling constant, estimated for the IPB crystal of α-modification ($g = 1.91$)[13], allows us to expect peculiarities of IPB crystals characteristic for organic systems with a strong exciton-phonon interaction [14].

IPB crystals and deposited films may be regarded as excellent photoconductors. The quantum efficiency of photoconductivity (β) of thin IPB layers is electric field dependent and reaches the value of $\beta = 0.2 - 0.85$ el./phot. at $E \geq 10^4$ V / cm [9]. The top of the energy gap of the IPB ($E_G = 2.1$ eV) is found to be below the main long-wavelength electronic absorption band (at about 3.0eV [6]), in contrast with non-polar organic crystals, such as e.g. polyacenes, in which the E_G-value is usually larger than the energy of the first singlet $S_0 \rightarrow S_1$ transition [5]. This observation was accounted for high polarity of the IPB molecule and an essential intermolecular interaction [5].

The optically induced change in sign of the electric dipole moment of the IPB molecule is of a considerable interest to possible optoelectrical effects in molecular assemblies of these polar molecules. Reversible changes in the refractive index caused by light or an electric field have been observed in the IPB crystals [15,16]. Extended studies of linear and nonlinear optical properties of Langmuir-Blodgett films of the amphiphilic IPB molecules have demonstrated that films of the dipolar IPB molecules are promising candidates for possible applications in molecular optoelectronics [6, 17, 18].

A comparative study of the excited state relaxation dynamics of the IPB molecules in various environments, – dilute solutions, polymeric matrix, films deposited in vacuum and in the crystal form – is presented in this paper. Ultrashort excitation kinetics was examined by means of time-resolved luminescence and transient absorption measurements, briefly described in Sec.II. These two time-resolved methods supplement each other usefully, enabling us to distinguish different excited state relaxation stages. Excitation dynamics of IPB in solution and in a polymer matrix are considered in Sec.III. The ultrafast non-monotonous excited state deactivation process observed in IPB solutions is attributed to the relaxation within two molecular excited states. The origin of these states is discussed taking into account the results from quantum chemical calculations. A study of the exciton dynamics in IPB solids is presented in Sec.IV. By comparing the excitation properties of the IPB molecules in solution and those in the crystal form, the influence of the intermolecular interactions on the excited state dynamics is revealed. Excitation relaxation in IPB films of different thickness and in a single crystal is described by the competition of nonradiative relaxation of the Frenkel-like and of the low energy intermolecular charge transfer states. The properties of excited states of IPB in various environments are summarized in Sec.V.

II. MATERIALS AND METHODS

All samples have been prepared at the Institute of Physical Energetics in Riga (Latvia). The Indandione-1,3 Pyridinium Betaine was purified by the gradient sublimation technique [19]. All solvents used for preparation of the IPB solutions were reagent grade and used without additional purification. A polymeric film of IPB was prepared by dissolving polyvinylbutyral (PVB) in an ethanol-butanol mixture and then adding IPB/EtOH solution (10^{-4}mol/l). The solution was finally poured on a quartz substrate and left to dry. A polycrystalline IPB film was deposited in vacuum on a quartz substrate at room temperature and at $p = 10^{-5}$ Torr. The deposition rate was about 15 Å/s and the average thickness (*d*) varied from 0.1μm to 1.6μm. For photocurrent measurements the sandwich-type samples were prepared with Au bottom and Al top electrode.

Crystals of the most stable α-modification, having the form of rectangular flakes of dark yellow colour up to 2x3x5mm^3 in size, were obtained from solution according to the technique described in ref. [19]. According to the X-ray diffraction data, the α-modification of the IPB crystals belongs to the monoclinic system of the centrosymmetric space group $P2_1/a$, with 4 molecules per unit cell [20,21]. In the crystal structure, IPB molecules are almost flat and form molecular stacks (see Figure 1). There is a compromise between two typical molecular arrangement types in stacks. The first one is typical of weak donor-acceptor crystals, when a stacked structure is created by alternating donor and acceptor fragments of the molecules. The second one is similar to ion radical salts, when stacks are created by similar donor and acceptor fragments of the molecules [5].

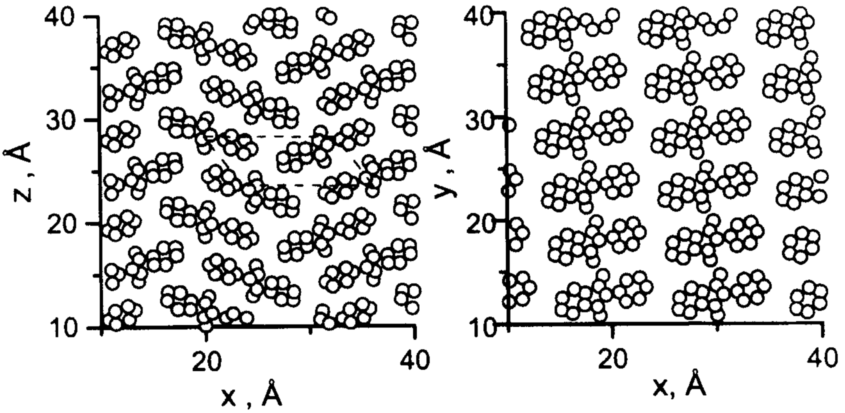


FIGURE 1 Structure of the IPB crystal α modification for different crystal planes depicted from X-ray diffraction data and molecular arrangement for different crystal planes (points reflect the center position of C, N and O atoms; lines denote the unit cell)

Steady state absorption spectra of the solutions, films and crystals were obtained by the Beckman spectrophotometer (UV 5270). Steady state luminescence spectra were obtained under cw Ar^+ laser excitation at 2.54eV by using a photomultiplier operating in photon-counting regime and a double grating monochromator DFS 52.

The spectral dependence of photoconductivity of the vacuum deposited thin film Au/IPB/Al were measured in the spectral range from 1.24eV to 4.27eV for irradiation applying a xenon lamp. The irradiation of the sample was a through bottom positive Au electrode. The intensity was of the order of 10^{14} phot/cm^{2}s. The value of the applied electric field was of the order of E=2 10^4V/cm, where the injection of charge carriers from electrodes did not occur [22].

Femtosecond time-resolved emission spectra and their kinetics were obtained by the luminescence upconversion technique. The experimental set-up has already been described [23]. The femtosecond laser source was a Ti:sapphire laser (Coherent MIRA 900) pumped by a 8W cw Ar^+ laser (Coherent INNOVA 310). The samples were excited at 3.15eV by the second harmonic of the Ti:sapphire laser radiation. After passage through a delay-line, the residual fundamental radiation was focused into a 0.2mm BBO upconversion crystal, thus serving as the gating pulse for sum-frequency generation. The luminescence was collected with a parabolic mirror and focused into the upconversion crystal together with the gating pulse. The upconverted UV-light was focused onto the entrance slit of a monochromator (Jobin-Yvon HR250) and the spectrally selected upconversion light was detected by a photomultiplier connected to a lock-in photon-counter. Time resolved luminescence spectra were recorded directly by simultaneously changing the monochromator wavelength, rotating the upconversion crystal and changing the delay line position in order to compensate for the group velocity dispersion. The luminescence kinetics was measured by changing only the delay line position.

The luminescence kinetics on a longer time scale were measured with a time-correlated single-photon counting system. The excitation light source was the second harmonic of a dye laser pumped by a mode-locked and frequency-doubled Nd^{3+}: YAG laser. The luminescence was detected by a micro-channel plate photomultiplier (Hamamatsu R1564U) using time correlated single photon counting. The FWHM of the instrumental response function was about 60ps, and the excitation photon energy was 4.22eV.

The picosecond transient absorption study was performed by using a pump-probe spectrometer based on a homemade low repetition rate Nd:Glass laser delivering pulses of 2ps duration. Second (2.33eV) and third (3.50eV) harmonics of the fundamental light were used for excitation, and a white light continuum was generated in a water cell to probe samples. The continuum light was split into two parts which passed through the sample at different positions, one overlapping with the excitation pulse, the second a few mm beside, serving as the reference. Both pulses were focused onto the monochromator entrance slit and their energies at selected wavelengths were measured using photodiodes positioned behind the exit slit. Transient absorption kinetics at a selected wavelength were measured by changing the delay time between the excitation and probe pulses. Transient absorption spectra at a fixed delay time were recorded by changing the monochromator wavelength and simultaneously changing the delay line in order to compensate for the group velocity dispersion.

III. EXCITED STATE DYNAMICS OF IPB MOLECULES IN SOLUTIONS

Steady-state absorption and luminescence spectra of IPB in ethanol are shown in Figure 2. Steady-state spectral properties of IPB in solvents of various polarities were studied in Ref. [24]. Analysis of the spectra and the quantum chemical calculations [25] have shown that the broad lowest energy electronic absorption band at 2.9–3.3eV is due to two transitions to different excited states of roughly similar energy. The main absorption band should be related to the intramolecular electron transfer from the indandione anion to the pyridinium cation reducing the dipole moment of the molecule [24]. This is in agreement with a blueshift of the absorption band of molecules in polar solvents. Hidden under this main absorption band is a weaker absorption band which is due to excitation of the indandione fragment of the IPB molecule [24,25]. IPB molecules in solutions show a very weak, broad, luminescence band, which is strongly Stokes-shifted ($\Delta E = 1.06$eV for IPB in ethanol). Excited state dynamics were monitored by time resolved luminescence spectroscopy. The time-resolved luminescence spectra of IPB in ethanol are presented in Figure 3. Here the high energy band at 2.78eV is caused by the Raman scattering of the excitation light in ethanol (CH_3 vibrations) thus, it is observable only in the presence of the pump pulse. The low energy band is due to the luminescence of the IPB molecules. In order to characterize the spectral dynamics of the luminescence, each time-resolved spectrum was fitted by two Gaussian bands, as shown in Figure 3. The energy position and the width of the Raman band as well as the width of the luminescence band were kept constant. This procedure reveals the time dependencies of the integral intensity and of the luminescence peak position. It is evident (Figure 4a) that during the first hundreds of fs after photoexcitation, a rapid shift of the luminescence maximum from 2.65eV at zero delay to 2.25eV occurs, followed by a slower shift on the picosecond time scale. It is worthwhile to note that the luminescence band has not yet attained the steady-state value, 2.145eV, after 8ps. Concurrently a rapid evolution in time of the integral luminescence intensity is observed: a rapid decay during the first hundred of fs is followed by a considerably slower relaxation process occurring on the picosecond time scale (Figure 4b). Figure 4c depicts the anisotropy decay of the luminescence obtained by measuring perpendicular and parallel polarized components of radiation at 2.58 eV photon energy. The luminescence anisotropy has the maximum value (0.4) at zero delay time and decays with the time constant of 0.6ps that is close to the characteristic redshift time of the luminescence. Qualitatively similar spectral dynamics were also obtained in dimethylsulfoxide solution (not shown).

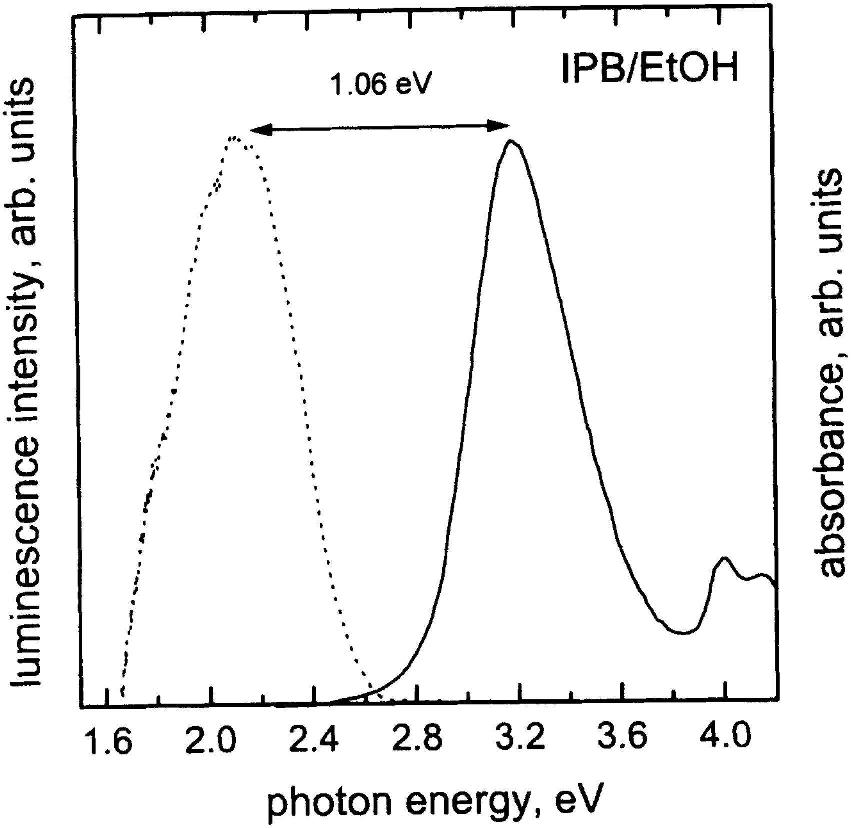


FIGURE 2 Steady-state absorption and luminescence spectra of the IPB solution in ethanol

Excitation relaxation studies of IPB in alcohols, dimethylsulfoxide, benzonitrile, toluene and benzene were also carried out by means of picosecond transient absorption spectroscopy. The transient absorption spectra of IPB in ethanol

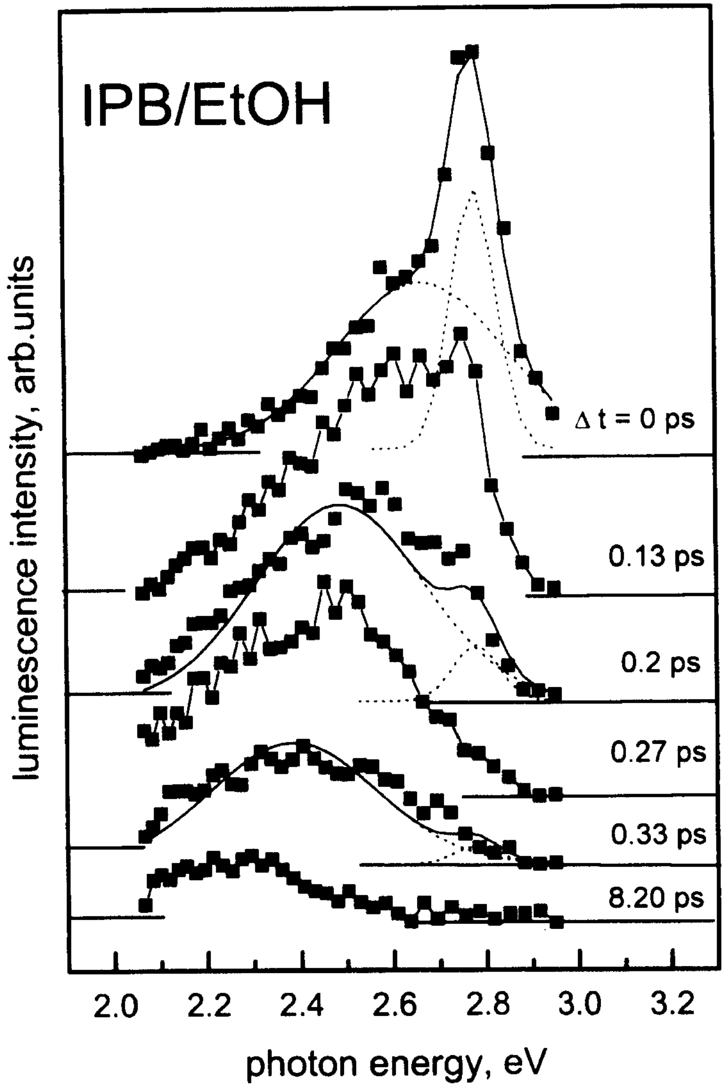


FIGURE 3 Time-resolved luminescence spectra of the IPB solution in ethanol. Lines display two Gaussian band fitting results

measured at various delay times after excitation at 3.5eV are shown in Figure 5. The broad band of the excited state absorption with a maximum at about 2.53eV dominates in the transient absorption spectrum at zero delay and blueshifts slightly in time. It is interesting that only induced absorption is observed in a spectral region of luminescence where the stimulated emission is expected. However, no indication of stimulated emission was observed. The transient absorption spectra of IPB in other solvents and in a PVB matrix are qualitatively similar (not shown). The time evolution of the transient absorption shows a short decay component of a few tens of ps, which is observed for all solvents, and a long-lived component of approximately 1ns, which is observed only in nonpolar solvents. The femtosecond process observed in the time-evolution of the luminescence spectrum is evidently too fast to be observed in transient absorption measurements. No distinct correlation between the relaxation rate and the solvent polarity was obtained. On the other hand, important changes in the excited state absorption decay were obtained by changing the solvent viscosity. The transient absorption evolution in time of IPB in various alcohols is shown in Figure 6. Relaxation times in alcohols increase with the viscosity, i.e. in methanol the induced absorption is characterized by 40ps decay time, while in decanol this decay time is about 140ps (see the insert in Figure 6). The induced absorption relaxation slows down to 200ps in the rigid PVB matrix. A solvent viscosity dependence of the relaxation rates implies that some solvent viscosity-controlled conformational reaction might be responsible for the excited state relaxation. Such a photoreaction leads to the ultrafast nonradiative excited state relaxation, which is often observed in organic charge transfer molecules. Usually it might be rationalized in terms of a twisted intramolecular charge-transfer reaction [26–28]. For the majority of simple organic molecules, containing electron donating and accepting parts, the charge separation is more favourable in the twisted conformation, where the two moieties involved in the charge transfer are orbitally decoupled, i.e. they are positioned in the nearly perpendicular planes. Our quantum chemical calculations indicate that such a process is possible for the IPB molecule as well. The IPB molecule in the excited state has a free energy minimum in a twisted configuration. Thus, the excited state twisting should lead to a decrease in the lowest transition energy (from 2.7 to 1.5eV) and in the relevant oscillator strength (from 0.55 to 0), what is in qualitative accordance with the observed luminescence dynamics (the details of the calculations will be published elsewhere). With this model in mind, it is tempting to attribute the fast relaxation component of less than 0.6ps, as obtained from the time-resolved luminescence experiment, to the twisting reaction. The slower relaxation component, of tens to hundreds of ps, observed both in the luminescence and in the excited state absorption decay may be attributed to the nonradiative decay from the twisted molecular configuration to the electronic ground state.

However, there are several arguments against the twisting model. First of all, a luminescence evolution with a characteristic time less than 0.6ps is too fast for the rotation of the large molecule fragment. Secondly, the viscosity dependence

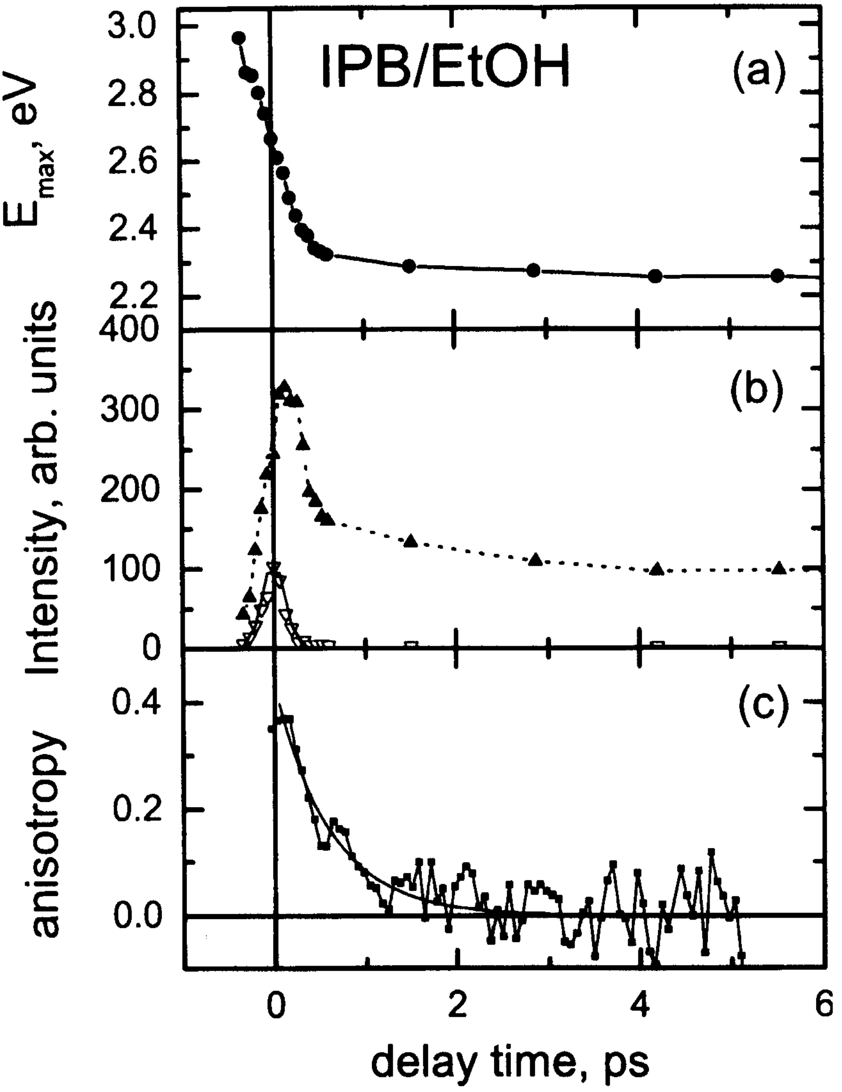


FIGURE 4 Time dependences of the luminescence peak energy position (a), luminescence and Raman signal intensity, solid and open points, respectively (b), and the anisotropy of the luminescence obtained at 2.58 eV photon energy (c) measured for IPB solution in ethanol

of the relaxation rate is relatively weak. In particular, the relaxation rate slows down too little in PVB matrix, where the large conformational changes should be strongly suppressed. Moreover, according to this model the observed large value of the Stokes-shift (about 1.0eV) for the luminescence of IPB in a PVB matrix, should be attributed to the twisted conformation, that hardly can be reached in a rigid matrix.

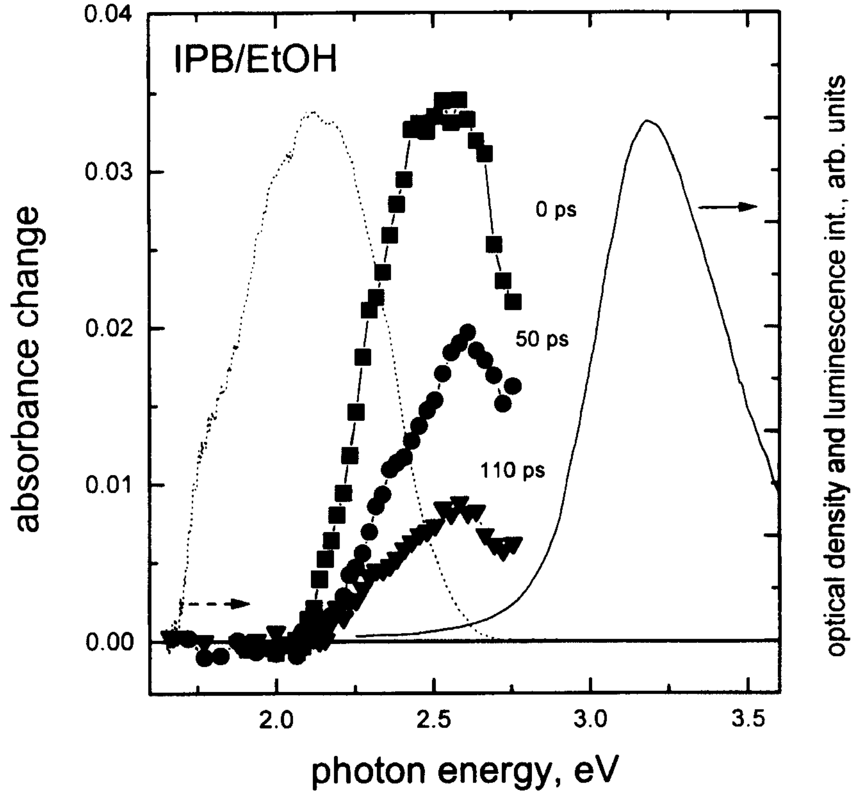


FIGURE 5 Transient difference absorption spectra measured at various delay times (0 ps, 50 ps and 110 ps) after excitation of the IPB solution in ethanol. The steady-state absorption and luminescence spectra are shown as a reference

Fast luminescence decay, much faster than the transient absorption relaxation, luminescence depolarization and the absence of the stimulated emission in the transient absorption indicate that the relaxation from the Franck-Condon excited state to another electronic state characterized by a lower value and differently oriented transition dipole moment takes place on the femtosecond time scale. As was pointed out above, an earlier study of the absorption spectrum of IPB indicates that another weak absorption band corresponding to the excitation of the indandione fragment of the molecule is present under the strong absorption to the

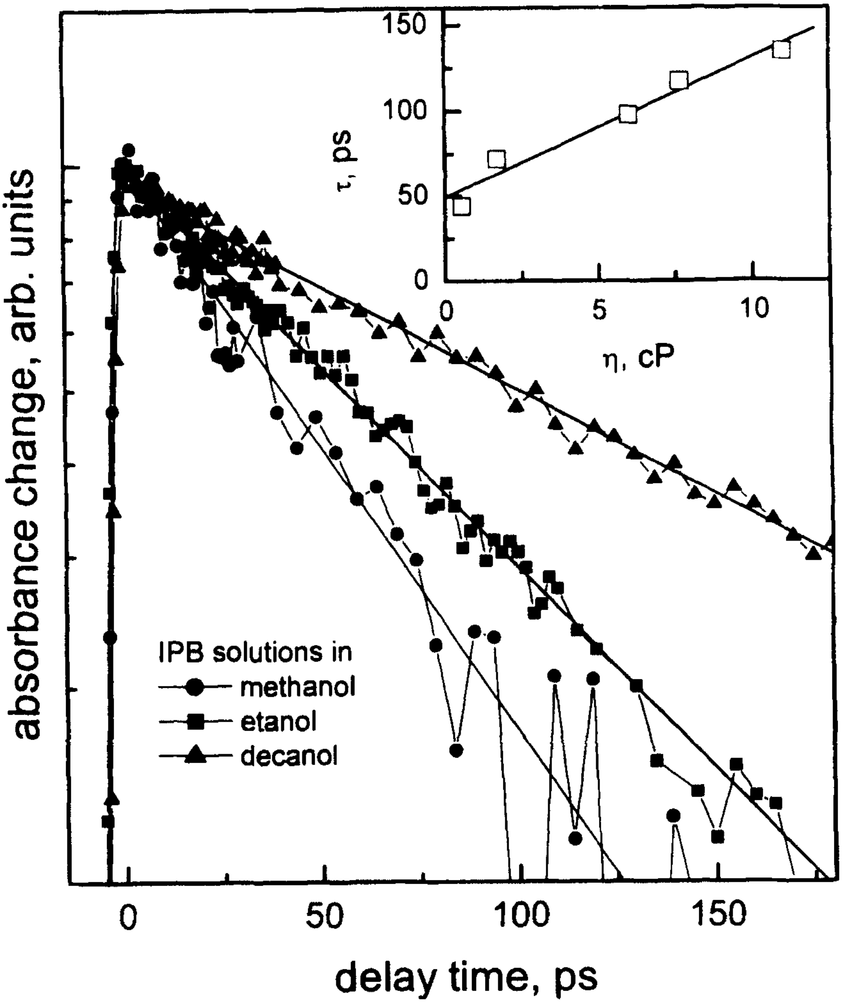


FIGURE 6 Transient absorption evolution in time of IPB in methanol, ethanol and decanol. The insert shows dependences of the relaxation times on the solvent viscosity in various alcohols

Franck-Condon charge transfer state [24]. Thus, the observed rapid red-shift, the decrease in the intensity and the depolarization of the luminescence occurring on the subpicosecond time scale, might be attributed to the energy transfer from the higher energy charge transfer state to the lower energy excited state localized on the indandione fragment state.

An alternative origin of the low energy excited state may be related with the proton transfer. A proton transfer from the pyridinium ring to the oxygen atom of the indandione moiety can probably occur in the excited state. Ultrafast proton transfer taking place on a femtosecond time scale has been observed in a number of simple organic molecules [29–31]. Further nonradiative relaxation to the ground state takes place on a time scale of tens of ps. Fast relaxation might be caused by the vibrational flexibility of the molecule. Such flexibility could probably also produce the observed viscosity dependence of the relaxation rate due to the solvent damping of the vibrational motion. Intramolecular twisting is very probably also involved in the relaxation process, which might explain the occurrence of the slow relaxation component observed for IPB in nonpolar solvents.

IV. EXCITATION DYNAMICS OF IPB FILMS AND A CRYSTAL

Steady-state absorption and luminescence spectra of IPB films and crystals were reported in Ref. [12]. Owing to the excitonic interaction, absorption bands of IPB solids are broadened and split into several overlapping Davydov components. Since the crystal of α-modification has four molecules in a unit cell (see Figure 1), up to four absorption components can be expected. Steady-state absorption and luminescence spectra of IPB films of various thickness (0.1μm, 0.5μm and 1.55μm) deposited in vacuum and of the crystal of α-modification are shown in Figure 7. Because of the high optical density of the crystal, it was only possible to measure the absorption spectrum in the low energy wing. The main absorption band of a thin IPB film is located at about 3.27eV and is blueshifted with respect to the molecular absorption of IPB in a nonpolar solvent, which is in line with the dependence of the charge transfer transition energy on the polarity of the environment. An increase in the film thickness results in a broadening and a redshift of the absorption band. A weak absorption shoulder might be resolved below the main absorption bands in the spectral region around 2.4eV and towards lower energies.

The luminescence efficiency is very weak for the IPB films (quantum yield $<10^{-6}$). The luminescence band is broad and strongly Stokes-shifted ($\Delta E = 1.02$ eV) with the maximum at about 2.25eV. The luminescence efficiency increases with the film thickness. The luminescence band of the crystal is even more redshifted with the maximum at about 2.12eV, which is very close to the luminescence band of the molecule in solutions. The excited state properties of the IPB solids are sensitive to the excitation photon energy. Figure 8 displays luminescence spectra of IPB crystal obtained for 3.5eV and 2.33eV excitation photon energies. It is evident that, although the luminescence bandshape is similar, the excitation in the low energy wing of the absorption of IPB solids enhances the efficiency of the luminescence dramatically (more than 100 times). The linear

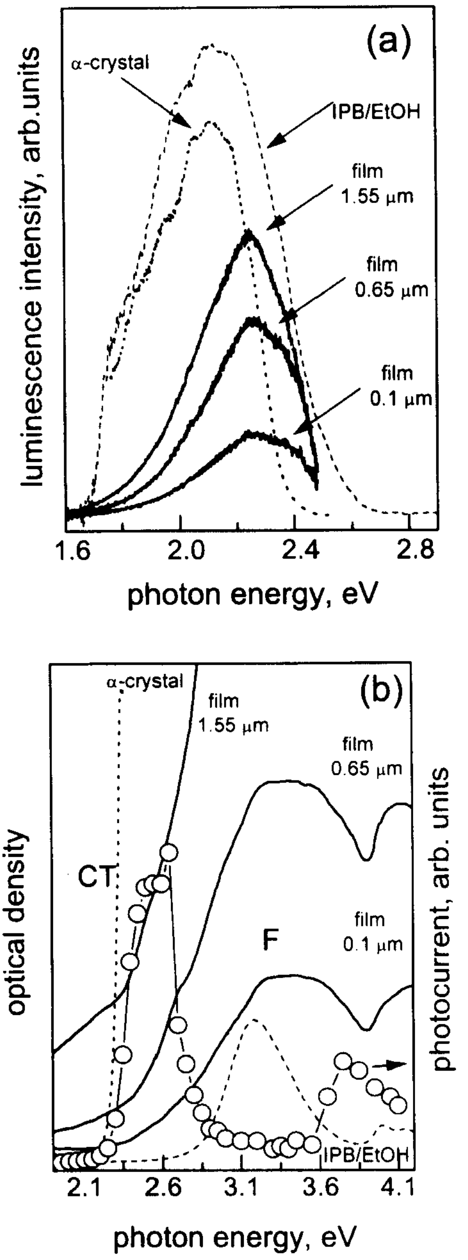


FIGURE 7 Steady-state luminescence (a) and absorption (b) spectra of IPB films of different thickness (solid lines), crystal (dotted lines) and IPB solution in ethanol (dashed lines). Points represent the spectral dependence of photocurrent measured for the Au/IPB/Al film

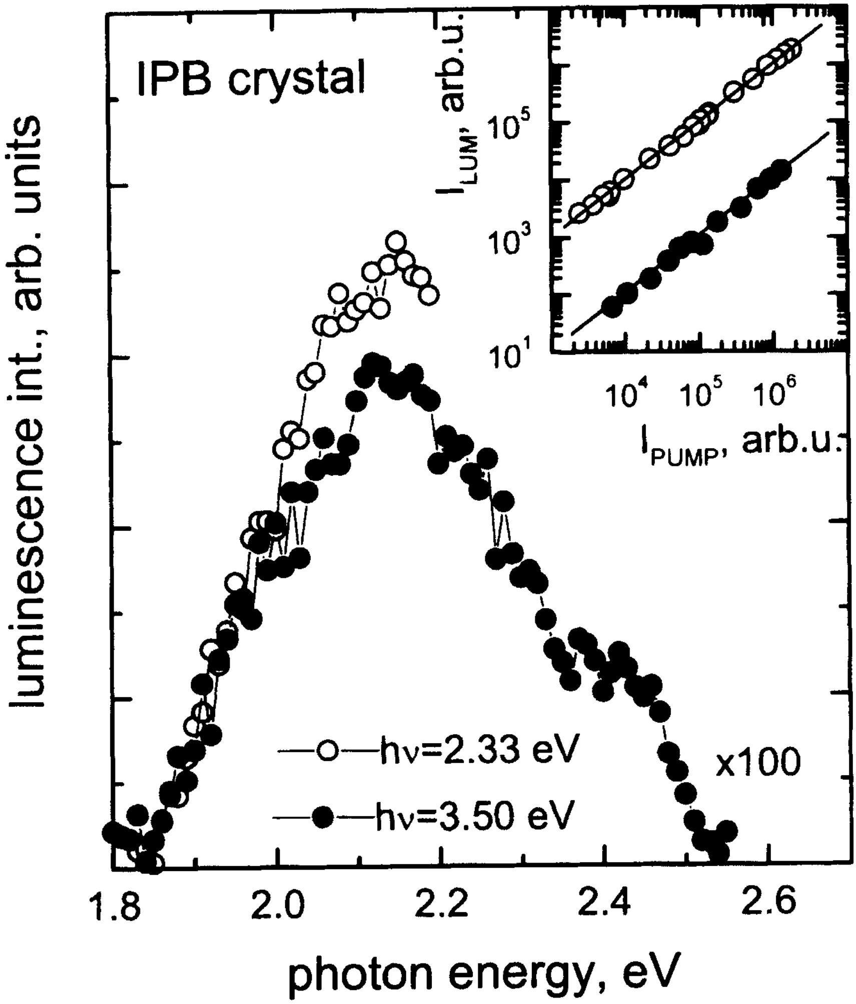


FIGURE 8 Luminescence spectra of the IPB crystal obtained for 3.5 eV and 2.33 eV excitation photon energy. The insert displays dependences of the luminescence intensity on the corresponding excitation intensity

dependence of the luminescence efficiency on the pump intensity for both 2.33eV and 3.50eV excitation quanta (see the insert in Figure 8) indicates that in both cases the excited states are created directly by a one photon absorption process, and a linear recombination is the dominant path. It should be noted that no significant luminescence was observed by excitation at 2.33eV of the IPB molecules in solutions and in a polymer matrix. Thus, the origin of the luminescence of the IPB molecules in solutions and in the solids is evidently different. The low lying excited state involved in the red-shifted absorption band (below 2.4eV) mentioned above is presumable responsible for the luminescence observed in the IPB solids. The mean lifetime of the luminescence decay in the IPB film and the crystal slows down to 470ps as is shown in Figure 9. It is almost the same for the film and the crystal and is independent of the monitoring photon energy. This is an indication of an intrinsic nonradiative recombination.

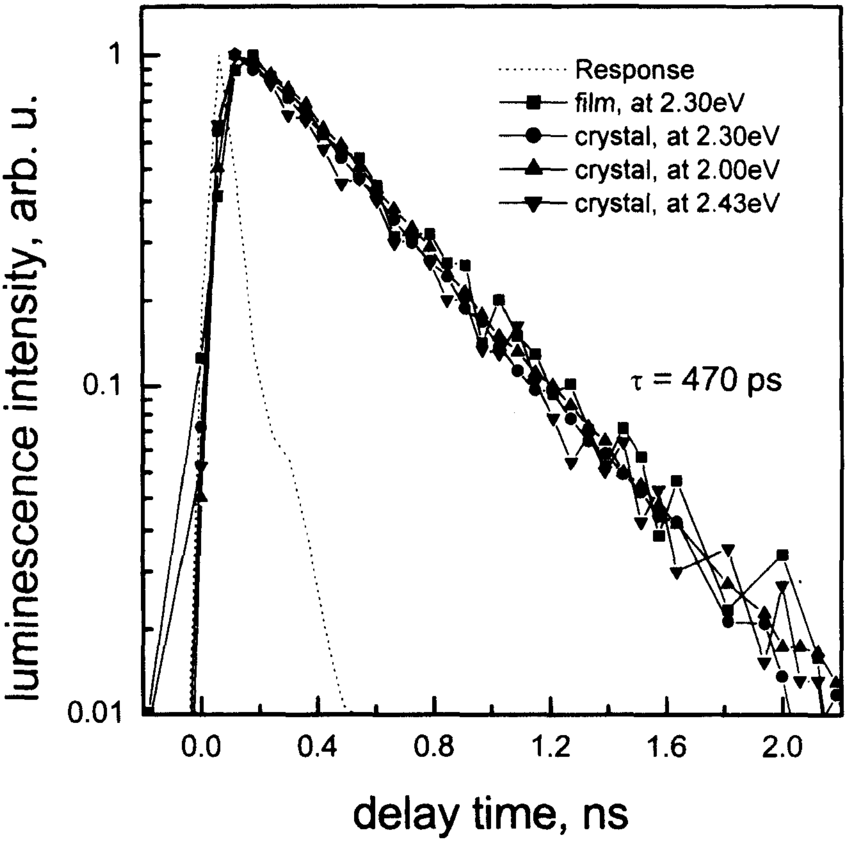


FIGURE 9 Luminescence decays of the IPB vacuum deposited film at 2.3 eV and the α-crystal at 2.3 eV, 2.0 eV and 2.43 eV photon energies. Dotted line shows a response function

The transient absorption spectral dependence reveals significant differences in the excited states of the IPB molecules and solids as well. Owing to the high optical density of the crystal it was impossible to measure induced absorption by excitation at 3.5eV. However, the crystal shows significant changes in the absorption spectrum by excitation on the absorption edge at 2.33eV, i.e. below the main absorption bands. The transient difference absorption spectra obtained at various delay times for the IPB crystal are presented in Figure 10. It should be noted that the transient absorption spectra of the IPB solids are completely different from those obtained in solution (cf. Figure 5). They show an induced excited state absorption in the red spectral region and a stimulated emission in the blue region, which coincides with the steady state luminescence spectra of the crystal. No substantial dynamics of the spectral shape is observed, only a decay of the entire spectrum, which takes place on the picosecond time scale with an average time constant of 280ps (see insert in Figure 10). Since the observed stimulated emission spectrum and its decay are similar to the luminescence of the crystal, one might again assume that the low-lying states situated at about 2.4eV, placing them below excited state reached in the main absorption band, are responsible for the luminescence.

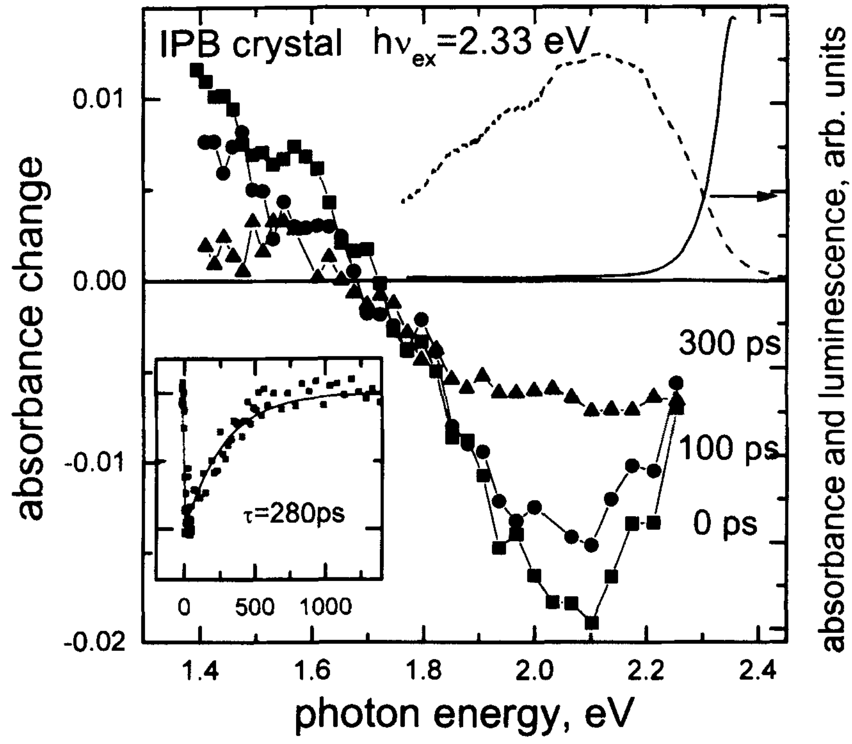


FIGURE 10 Transient difference absorption spectra of the IPB α-crystal measured at various delay times (0 ps, 100 ps and 300 ps) after excitation. The steady state absorption and luminescence spectra are shown as a reference. The insert depicts decay of the induced absorption signal at 2.07 eV

These low-lying states may be related to the charge separation and the generation of free carriers, since the spectral dependence of photocurrent observed in a Au/IPB/Al film shows a strong peak in the 2.55eV spectral region (see Figure 7). Such states may be the intermolecular charge transfer (CT) exciton states or some donor-acceptor CT complexes, which are very likely to appear in a stacked IPB crystal structure formed by polar molecular fragments (see Figure 1) [30,31]. The CT origin of these low-lying states is in line with observed quenching of the crystal luminescence by applying an electric field [12].

The photocurrent is significantly reduced in the spectral region 2.9–3.5eV, which is attributed to the formation of Frenkel exciton states. Because of the low optical density of the thin films of polycrystalline IPB, a measurable transient absorption signal can be obtained by excitation at 3.50eV (Figure 11). The spectrum of the induced absorption is very similar to the induced absorption spectra obtained for IPB molecules in solution. Owing to the excitonic interaction in the IPB film, the spectrum is slightly redshifted compared to that obtained in solution. The decay of the transient absorption signal is highly nonexponential. It has an efficient fast component (<30ps) and a slow one on the nanosecond time scale (see the insert in Figure 11). Thus, in accordance with the luminescence measurements, the excitation of IPB solids into Frenkel-like excitonic states (excitation at 3.5eV) leads to an enhanced nonradiative excited state relaxation. Since the spectral and the dynamic behavior of the transient absorption signal is similar for IPB solutions and films, one might assume that the nonradiative process responsible for the Frenkel exciton deactivation is determined by a intramolecular charge redistribution similar to that observed for IPB in solution. On the other hand, the direct excitation of the intermolecular CT states (excitation at 2.33eV) produces evidently a different charge redistribution between two IPB molecules leading to a relatively slow excitation relaxation. To get a more detailed energy scheme of the excitonic states, a careful analysis of the luminescence dynamics on the excitation photon energy is needed. This will be one of our future objectives on the studies of the excitons in the IPB crystals.

V. SUMMARY

We have investigated the excitation dynamics of Indandione-1,3 Pyridinium Betaine (IPB) intramolecular charge transfer molecules in various environments, – solution, films and crystals – using time-resolved luminescence and transient absorption measurements. A rapid nonradiative excited state relaxation is detected for IPB in solution. The observed spectral behaviors were attributed to a $S_2 \Rightarrow S_1$ excitation relaxation from the initially created intramolecular charge

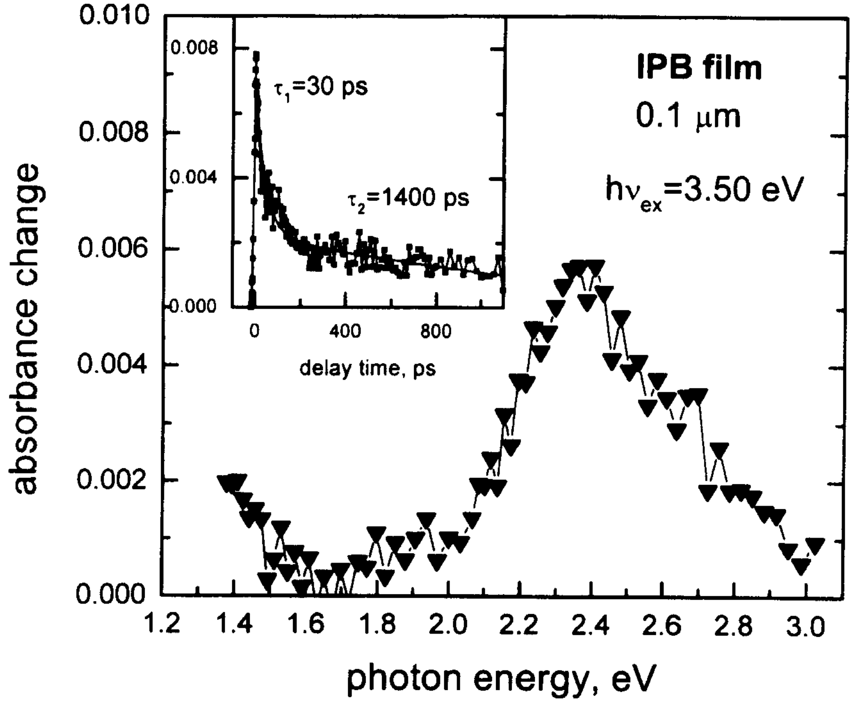


FIGURE 11 Transient difference absorption spectrum of the IPB film deposited in vacuum recorded at 0 ps delay. The insert depicts decay of the induced absorption signal at 2.3 eV

transfer state to a lower lying excited state of the indandione moiety. This electronic relaxation, takes place on the subpicosecond time scale. The first fast relaxation stage is followed by a slower one, corresponding to a relaxation to the ground state with a rate depending on the viscosity of the environment. In solvents, the average relaxation rate was in the range from 40ps to 150ps, and the excited state relaxation slowed down to 200ps in a polymer matrix.

The IPB molecules arranged in a regular crystal form also show a rapid nonradiative excitation relaxation with an average time constant of 500ps. The intermolecular charge transfer exciton states lying below the upper state involved in the main absorption bands (at about 2.4eV) are supposed to be responsible for the observed excitation dynamics. The resonance excitation of the CT states increases luminescence efficiency more than 100 times, indicating that the higher lying Frenkel exciton states are involved in the rapid nonradiative relaxation. The long-lived CT exciton states are probably responsible for the efficient photoconductivity in the IPB films and crystals.

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