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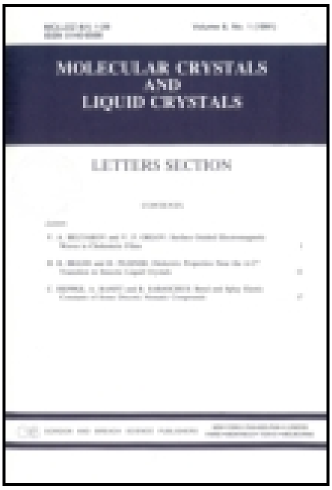

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The Peculiarities of the Optical Absorption of Monocrystalline Fluorene and Its Heteroanalogues in the Energy Range Between 3.5 eV and 8.5 eV

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The Peculiarities of the Optical Absorption of Monocrystalline Fluorene and Its Heteroanalogues in the Energy Range Between 3.5 eV and 8.5 eV

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Electronic absorption spectra of carbazole, dibenzofuran and fluorene were obtained in all three crystallographic directions (energy range 3.5-8.5eV). All electronic transitions with transition dipoles at oblique angles to a and b crystallographic axes can be traced to parental molecular states.

Crystal transitions with parallel transition dipoles can be traced to parental molecular states for thin (0.1-0.2μ) crystals, slow crystallized from melt under uniaxial pressure. For sublimation flakes and crystals fast crystallized from melt, these transitions cannot be traced to parental molecular states since their spectra have continuous, essentially uniform intensity distribution except for such transition at the onset of absorption.

Introduction

Organic π −conjugated crystals and polymers are extensively studied for their uses in optoelectronic devices and for prospective uses in solar cells. Understanding the electronic properties of these crystals is crucial from a fundamental point of view and for optimizing the performance of such devices.

It is widely accepted that electronic excitations in organic crystals lead to formation of *electron-hole pairs,* which are localized on a single molecule (Frenkel excitons) or on nearby molecules in the crystal (charge transfer excitons). Current theoretical models presume that excitonic states in π- conjugated crystals can, to a certain extent, be traced to parental molecular states. This perception is based on experimental studies of electronic absorption spectra of numerous organic crystals in the transmittance or reflectance mode but, in most cases, in *transmittance* mode only transitions to low energy states were investigated.

One of the reasons for this lack of comprehensive information in the scientific literature and in text books on absorption spectra (in *transmittance* mode) of organic π −conjugated crystals is the difficulties of obtaining sufficiently thin and appropriate size monocrystals necessary for measuring transmittance spectra in a large energy range.

Thin highly unisotropic mono-crystals tend to grow in the crystallographic plane of strongest interactions, and the transitions polarized perpendicular to this plane are inaccessible at normal incidence of light on such samples. To circumvent this difficulty we

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*Address correspondence to linanakh@yahoo.com employed measuring spectra of the crystals studied at oblique incidence of light on the sample.

Another difficulty is that in the crystals extensively studied in the literature (e.g., acenes, oligothiophenes) the optical indicatrix axes do not coincide with the crystallographic axes, thus complicating symmetry assignment of the electronic bands in the crystal spectra. As a result the comparison of crystal spectra polarized in all three crystallographic directions in a large energy range with corresponding transitions in the molecular spectra is hindered. Crystals studied in this work do not have this limitation, since at normal incidence of light on thin (0.1-0.2 μ) samples only transitions of one allowed (molecular) symmetry are accessible and transitions of the other allowed symmetry can be obtained from spectra measured at oblique incidence of light on the sample.

Molecular structures of compounds studied in this work – dibenzofuran, fluorene and carbazole are very similar, as are their crystalline structures. The molecular symmetry is C_{2v}; therefore transitions of two symmetry types - $\mathbf{A_1}$ (along the short axis of the molecule) and $\mathbf{B_2}$ (along the direction perpendicular to the latter axis) - are allowed in their molecular electronic absorption spectra. The crystals of these compounds are orthorhombic with four molecules per unit cell [1-4] - space group P_{nma} (Figure 1, panel I). Molecular transitions dipoles of $\mathbf{A_1}$ symmetry lie in the ab (herring bone) plane of the crystal. In the crystal absorption spectra $\mathbf{A_1}$ symmetry molecular states give rise to two Davydov [5] components (B_{3u} and B_{2u} symmetry). Molecular transitions dipoles of $\mathbf{B_2}$ symmetry in the crystal are parallel to the c crystallographic axis and to each other; therefore this state produces only one Davydov component (B_{1u} symmetry).

Molecules in these crystals form parallel layers (Figure 1, panel I) within which the closest distance between molecules is around 4.1 Å, while the closest distance between molecules in adjacent layers is around 10Å. Thus excitonic coupling in the crystals studied is highly anisotropic, with coupling between molecules within the ab layer an order of magnitude stronger than between layers; therefore, these crystals can be considered quasi-two-dimensional, as was previously shown for anthracene and other oligocenes [6, 7]. The molecular packing of the crystals studied in this work is denser in the ab plane than in the crystals of iso-π-electronic anthracene, since the areas of the ab plane in the former are smaller than that in iso-π-electronic anthracene and phenanthrene; the molecular structure of hetero-analogues of fluorene is closer to that of phenanthrene. It is interesting that alkali-metal-doped phenanthrene is shown to be a superconductor at 5 K [8].

The denser crystal packing and other structural distinctions of crystals of fluorene and its hetero-analogues might lead to not yet discovered electronic properties of these compounds and have led to intriguing preliminary theoretical and experimental results concerning the electronic spectra of transitions with *parallel transition dipoles* (c-polarized, B_{1u} symmetry), namely:

(a) in the *experimental* absorption spectra of carbazole *sublimation flakes* transitions of B_{1u} symmetry could not be traced to parental molecular states, since they formed a continuous, essentially uniform intensity background in the energy range of four electronic transitions of this symmetry; thus individual electronic transition of B_{1u} symmetry could not be identified in the spectrum of our previous work [9] and corrigendum.

(b) local field theory calculations [9] predict that in the carbazole crystal the two lowest energy electronic transitions of $\mathbf{B_2}$ (B_{1u}) symmetry should retain only around 20% of the parental molecular oscillator strength, with the missing oscillator strength found in higher energy transitions (in agreement with the sum rule for oscillator strengths). This prediction could not be tested in Ref. 9 because of the result described in (a).

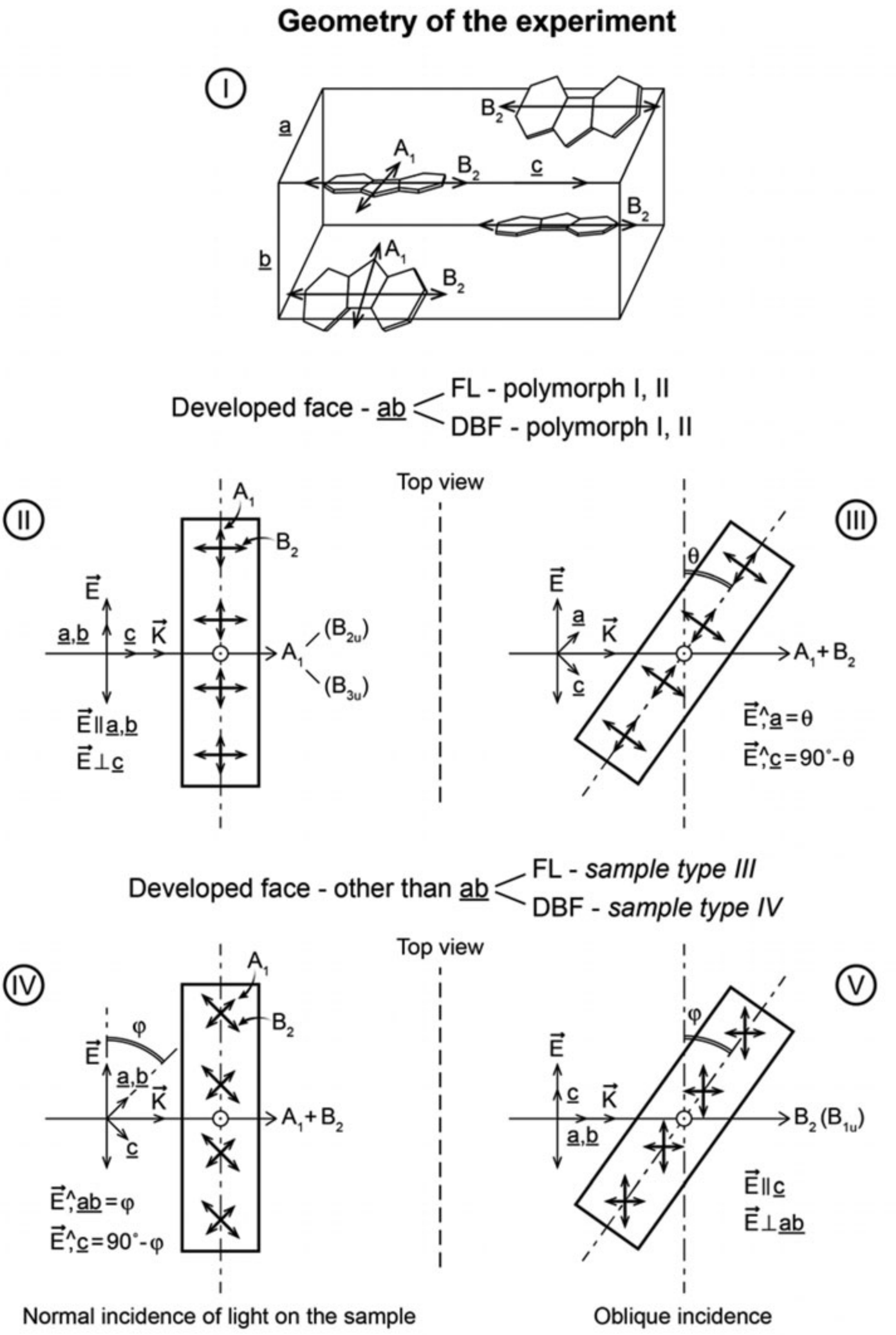

Figure 1. Geometry of the experiment. I- crystalline structure of fluorene and its heteroanalogues; II- normal incidence of light on the ab plane of a sample; III- oblique incidence of light on the ab plane; IV- normal incidence of light on a developed plane containing a projection of the c crystallographic direction; V- oblique incidence of light on such plane.

In view of these preliminary findings the current work has three major objectives:

i. attempting to ascertain crystallization conditions under which the spectra of B_{1u} symmetry transitions in these crystals can be traced to parental molecular states so that prediction (b) can be tested in these crystals;
ii. determining under which crystallization conditions and sample thicknesses multiple B_{1u} symmetry transitions form a continuous uniform intensity distribution, as was observed in the near UV energy region for these transitions in carbazole thin sublimation flakes [9];
iii. to include in the study two other compounds with molecular and crystalline structures similar to those of carbazole (dibenzofuran and fluorene) in order to investigate how common the experimental effect observed in (a) is, and also if intensity redistribution between multiple electronic transition predicted in (b) can be observed experimentally (see above).

There are numerous theoretical and some experimental studies of intensity redistribution between multiple electronic transitions in the spectra of molecular associations such as biopolymers, polymers with aromatic pendants, dimers, and higher aggregates of aromatic compounds (hypochromism - diminished intensity, and hyperchromism - increased intensity of an individual transition in question) [10-17]. We do not know of works in which hypo/hyperchromic effects were convincingly demonstrated for π-conjugated organic crystals. We have observed hypo/hyperchromic effects in the spectra of molecular associations of dibenzofuran in fast-frozen normal alkanes (compare pgs. 246 and 249 of Ref. 18). It is therefore of interest to ascertain whether these effects are observable in single crystals of dibenzofuran and other fluorene heteroanalogues, and whether existing theories on intensity redistribution between multiple electronic transitions account for the experimentally observed properties.

The aforementioned distinctions of the crystalline structures of fluorene and its heteroanalogues, and preliminary theoretical and experimental findings on the electronic properties of carbazole sublimation flakes [9] indicate that these compounds present fascinating models for studies of electronic properties of π-conjugated organic crystals.

In work [19] electron energy loss (EEL) spectra of fluorene vapor and single crystals were obtained. The EEL crystal spectrum is measured up to 25 eV, and the authors of [19] conclude that distinct $\pi - \pi$ electronic transitions in these crystals, and also in phenanthrene and anthracene, are observable up to around 9.0 eV; thus, according to their conclusion our spectra cover the complete energy range of such $\pi - \pi$ electronic transitions.

The aim of this project is to obtain information on all photo-excitable π electronic states of fluorene and its hetero-analogues in the solid state, and discern their correlation with corresponding molecular states. To this end we present electronic absorption spectra (in *transmittance* mode) of fluorene, dibenzofuran and carbazoe in all three crystallographic directions, in the energy range of distinctly observable $\pi - \pi$ electronic transitions, and for samples obtained under different crystallization conditions.

Experimental

Fluorene (Supelco #48568) and dibenzofuran (OEKANAL, analytical standard) were obtained from commercial sources. We have measured the electronic spectra of four different types of samples of fluorene and dibenzofuran, which presented at least three modifications (polymorphs) with distinct transmittance spectra.

Type 1 samples were obtained by melting the material between LiF plates and applying strong uniaxial pressure in the direction perpendicular to the surface of the sample during the crystallization of melt under a nitrogen stream. These samples grow in the ab plane (see ***Results*** section, the end of first paragraph) with thicknesses around 0.1-0.2 μ. To avoid evaporation of samples in the vacuum sample chamber they were sealed with Duco cement.

Type 2 were sublimation flakes of thickness around 0.20-0.35 μ, about 1.3-1.5 mm wide obtained by heating the material in an oven in a sealed Petri dish in the presence of N_2 gas; this sample also had a developed ab plane [20]. As reported in the literature, thin sublimation flakes develop pinholes in open air (and more so in our experiments in a vacuum sample chamber). To prevent formation of pinholes the flakes were hermetically sealed between LiF plates using Duco cement.

Type 3 were sublimation flakes of smoky color (which implies large birefringence) around 1.0μ thick and 2.0-3.0 mm wide. Birefringence in the ab plane of these crystals is several times smaller than in the ac or bc plane; therefore unusually large birefringence could mean that the developed plane contains a projection of the long crystallographic axis.

Type 4 samples were obtained from melt under fast crystallization conditions (thickness around 0.40 μ).

The two extinction directions of light transmitted through the crystal were marked under a polarizing microscope; the crystals were diaphragmed and attached to a sample holder so that one of the extinction directions was parallel to the direction of the electric field. The sample holder was equipped with a goniometer, allowing rotation of crystals around an axis perpendicular to the direction of the electric field. The sample holder was equipped with a goniometer, allowing rotation of crystals around an axis perpendicular to the direction of the electric field. The crystal structure of very thin sublimation flakes and their orientation with respect to the crystallographic axes was determined by X-ray diffraction [20]. The structure corresponds to that reported in the literature, and the thin sublimation flakes of compounds studied were found to grow in the ab crystallographic plane.

The thicknesses of samples were estimated (i) from measurements of birefringence, using a polarizing microscope fitted with a U-CSE Olympus compensator, (ii) from an atomic force microscope thickness measurement, and (iii) utilizing spectroscopic data from Refs. 28 and 29. The discrepancy in thickness values between different methods was about 20%.

The spectra were recorded at the Synchrotron Light Source at Brookhaven National Laboratory. Synchrotron radiation is delivered to the sample position using a modified Wadsworth monochromator, which scans through the wavelength region of interest. The photomultiplier tube has a magnesium fluoride window transparent to about 120 nm. The signal from the PMT is converted to voltage using a transimpedance amplifier (ORIEL). The computer interacts with a lock-in amplifier, the samples, the high voltage and synchrotron ring signals. Neglecting reflectance, the data for the sample and the respective baseline allow the calculation of *Absorbance (log 1/T)* of the crystal as a function of wavelength.

To establish if the observed spectra can be traced to molecular states, crystal spectra were compared with the corresponding synchrotron radiation linear dichroism (SRLD) spectra from Ref. 21.

To insure that no changes occurred in the sample during the time of measurements we repeatedly measured the spectrum at normal incident of light and compared it to the original spectrum.

Results

Dibenzofuran Spectra

Depicted in Fig. 2 are absorption spectra (log 1/T) of synchrotron radiation linear dichroism (SRLD) *molecular* spectra from our previous work [21], and *crystal* spectra of sample 1 (polymorph I) of dibenzofuran, crystallized from melt under uniaxial pressure (thickness around 0.2 μ). In Ref. 22 it was shown that the lowest energy transition (to the $2\boldsymbol{A_1}$ state) of the dibenzofuran *molecule* borrows a substantial part of its intensity from the closely positioned higher energy $1\boldsymbol{B_2}$ symmetry transition via non-totally symmetric vibrations with frequencies around 400 and 700 cm^{-1}. As a result, these *non-totally* symmetric vibronic bands in molecular spectra have intensities comparable to that of the pure electronic band, while the *totally* symmetric vibronic bands are three times weaker (see *Inset* on top of Fig. 2, reproduced from Ref. 18, pg. 250). When a dibenzofuran *crystal* grows in the ab plane, non-totally symmetric vibronic (and electronic) bands cannot be observed at normal incidence of light on the sample (Fig 1, panel II), and the ratio of the average intensity in the vibronic band area (290-300 nm) to that in the pure electronic band in the crystal ($2B_{3u}$ -306 nm, 4.1 eV) is expected to be ~1.0:3.0. This is the case for *polymorph I* of dibenzofuran (Fig. 2, spectrum II); we therefore assumed that this sample has a developed ab crystallographic plane.

At normal incidence of light on this plane five B_{2u} (and B_{3u}) symmetry transitions at 4.10, 5.46, 6.10, 7.14 and possibly 8.28 eV are detected (Fig. 2, spectrum II, where only the **E**lla (B_{3u}) component is shown); the energies of both components are listed in *Table 1*. Comparison of this spectrum with the corresponding Synchrotron Radiation Linear Dichroism (SRLD) *molecular* spectrum (Fig 2, panel I, dashed line) shows that the excitations to several B_{3u} states can be traced to parental molecular $2\boldsymbol{A}_1$, $3\boldsymbol{A}_1$, $4\boldsymbol{A}_1$, and possibly $5\boldsymbol{A}_1$ states, in agreement with the prevailing view on the subject in textbooks and scientific literature.

Electronic transitions polarized in the c-crystallographic direction (B_{1u} symmetry) were obtained by employing oblique incidence of light on the sample. Rotating the sample by 35^0 around the axis perpendicular to the electric field vector **E** produced a spectrum consisting of electronic transitions of both symmetries (Fig. 2, spectrum III). In order to separate the transitions of different symmetries, the properly scaled b-component of the spectrum was subtracted from the spectrum of the tilted crystal. As a result we obtained an absorption spectrum of four (4.57, 4.96, 5.84, and 6.57 eV) B_{1u} symmetry transitions of the dibenzofuran crystal (Fig 2, spectrum IV and *Table 1*), which can all be traced to parental molecular $\boldsymbol{B_2}$ states (Fig. 2, compare spectrum IV with the SRLD molecular spectrum IVa, reproduced from our previous work [21]). Comparison of the *intensities* of these B_{1u} transitions with corresponding transitions in the SRLD spectrum shows that the intensity distribution in the spectrum of *polymorph I* of dibenzofuran is different from that in the SRLD spectrum; specifically, in the latter the lowest energy transition ($1\boldsymbol{B_2}$) is comparable in intensity to those of the $3\boldsymbol{B_2}$ and $4\boldsymbol{B_2}$ symmetry transitions, while in the corresponding *crystal* spectra the $1B_{1u}$ transition is substantially weaker than the $3B_{1u}$ and $4B_{1u}$. Thus, hypochromism (diminished intensity) is observed in the lowest energy $1B_{1u}$ transition of dibenzofuran and hyperchromism is observed in higher energy transitions in *qualitative* agreement with theory [9-12].

At normal incidence of light on a thin (~0.15 μ) s*ublimation* flake of dibenzofuran (*sample 2*) the spectra reveal four B_{2u} (and B_{3u}) electronic transitions - at 4.10, 5.46, 6.1, and 7.58 eV (Fig. 3, spectra I and II, and *Table 1*), which are similar to those of polymorph

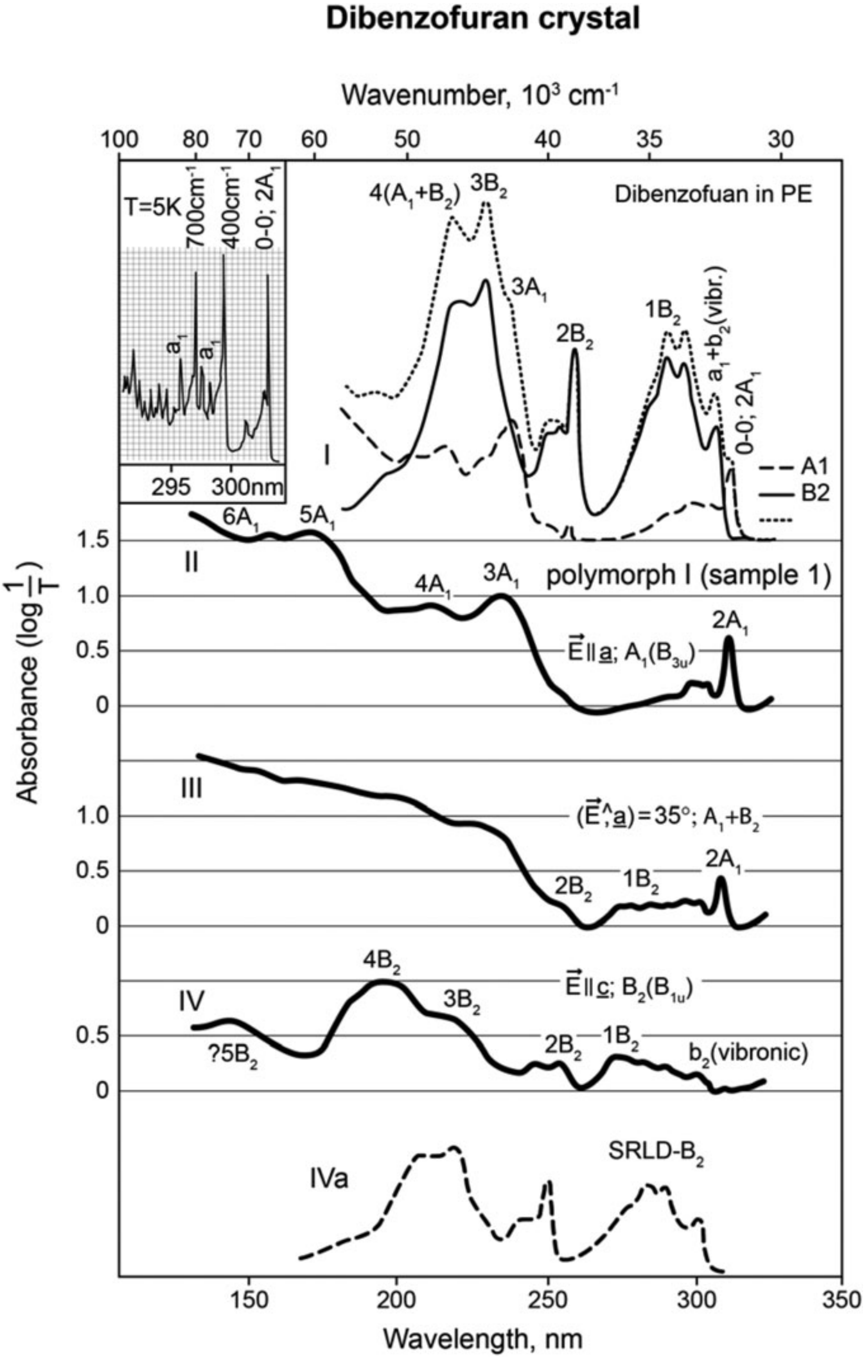

Figure 2. Electronic absorption molecular and crystal spectra of dibenzofuran. I- SRLD (molecular) spectrum: _ _ _ A_1 symmetry. ____ B_2 symmetry, ... combined spectrum. Inset- spectrum of the onset of the $2A_1$ transition of dibenzofuran in fast-frozen heptane at 5 K. Electronic transmittance spectra of a thin (0.2 μ), slow-crystallized from melt dibenzofuran crystal (polymorph I): II- Ella; III- Eˆa= 35^0; IV- Ellc (see text); IVa- SRLD B_2 symmetry molecular spectrum.

Table 1. Electronic absorption spectra of fluorene and dibenzofuran polymorphs I and II. (In parenthesis the maximum value of Absorbance (log 1/T) of each electronic band is shown)

Electronic transition ***Symmetry***	Dibenzofuran						Fluorene					
	Polymorph I			***Polymorph II***			***Polymorph I***			***Polymorph II***		
	nm	***eV***	*A*	nm	***eV***	*A*	nm	***eV***	*A*	nm	***eV***	*A*
$2A_1$ (B_{3u})	306	***4.10***	*(0.63)*	306	***4.10***	*(0.43)*	282	***4.43***	*(0.01)*	282	***4.43***	*(0.25)*
(B_{2u})	306		*(1.29)*	306		*(0.94)*	282		*(0.08)*	282		*(0.45)*
$3A_1$ (B_{3u})	229	***5.46***	*(0.98)*	229	***5.46***	*(0.56)*	218	***5.73***	*(0.50)*	229	***5.46***	*(0.55)*
(B_{2u})	229		*(1.86)*	229		*(1.26)*	218		*(0.45)*	229		*(1.00)*
$4A_1$ (B_{3u})	205	***6.09***	*(0.90)*	205	***6.09***	*(0.70)*				195	***6.41***	*(0.85)*
(B_{2u})	205		*(1.85)*	205		*(1.16)*				195		*(1.90)*
$5A_1$ (B_{3u})	175	***7.14***	*(1.53)*	165	***7.58***	*(1.57)*	172	***7.26***	*(0.65)*	166	***7.53***	*(1.35)*
(B_{2u})	175		*(1.81)*	165		*(2.31)*	172		*(0.49)*	166		*(1.90)*
$6A_1$ (B_{3u})	151	***8.28***	*(1.51)*									
(B_{2u})			*(2.31)*									
	nm	***eV***	*A*				nm	***eV***	*A*			
$1B_2$ (B_{1u})	273	***4.57***	*(0.29)*				303	***4.13***	*(0.24)*			
$2B_2$ (B_{1u})	252	***4.96***	*(0.24)*				248	***5.04***	*(0.70)*			
$3B_2$ (B_{1u})	214	***5.84***	*(0.63)*				225	***5.56***	*(0.65)*			
$4B_2$ (B_{1u})	190	***6.57***	*(0.94)*				185	***6.76***	*(0.80)*			

I in the pre-vacuum UV region and somewhat different in the vacuum UV (compare Fig. 2 spectrum II with Fig. 3, spectrum I and II). We assume that sample 2 of dibenzofuran is polymorph II. Comparison of the spectrum of B_{2u} and B_{3u} symmetry of the sublimation flake (Fig. 3, spectra I and II) with the corresponding SRLD spectrum (Fig 2, panel I, dashed line) shows that, similar to polymorph I, the excitations to four B_{2u} and B_{3u} states in the crystal can be traced to respective $2A_1$ **$3A_1$**, **$4A_1$** and possibly **$5A_1$** molecular states. The Davydov splitting [5] of all transitions in polymorphs I and II is within experimental error.

No spectrum of the B_{1u} symmetry transitions was obtained for polymorph II of dibenzofuran in this round of experiments.

Dibenzofuran samples *fast* crystallized from melt between LiF plates (*sample type 4*) consisted of several monocrystals. Spectra of two diaphragmed mono-crystals were measured. At normal incidence of light, the spectra of *monocrystals* 1 and 2 resemble those of polymorph II of dibenzofuran but reveal an essential difference: for monocrystal 1 the ratio of vibronic-band average intensity to that of the pure electronic band in the B_{3u} (and B_{2u}) symmetry transition is ~1.0:1.7, (Fig. 3, spectrum III) and for monocrystal 2 it is ~1.0:1.4, while in crystals grown in the ab plane this ratio is 1.0:3.0. This difference indicates a strong presence of $\boldsymbol{b_2}$ vibronic bands in the lowest energy $2B_{3u}$ (and $2B_{2u}$) transition, which also implies the presence of B_{1u} symmetry *electronic* transitions in the spectra of these monocrystals, although the exact orientation of these mono-crystals with respect to the crystallographic axes is not known. Rotation of each of the monocrystal (1 and 2) of *sample type 4* of dibenzofuran by 60^0 around the axis perpendicular to the electric field vector almost entirely eliminated B_{2u} (and $B_{3u)}$ symmetry transitions, revealing predominantly B_{1u} transitions (Fig.3, spectra IV and VI). All transitions of latter symmetry, including the lowest energy one (which is not the onset of absorption), form an almost

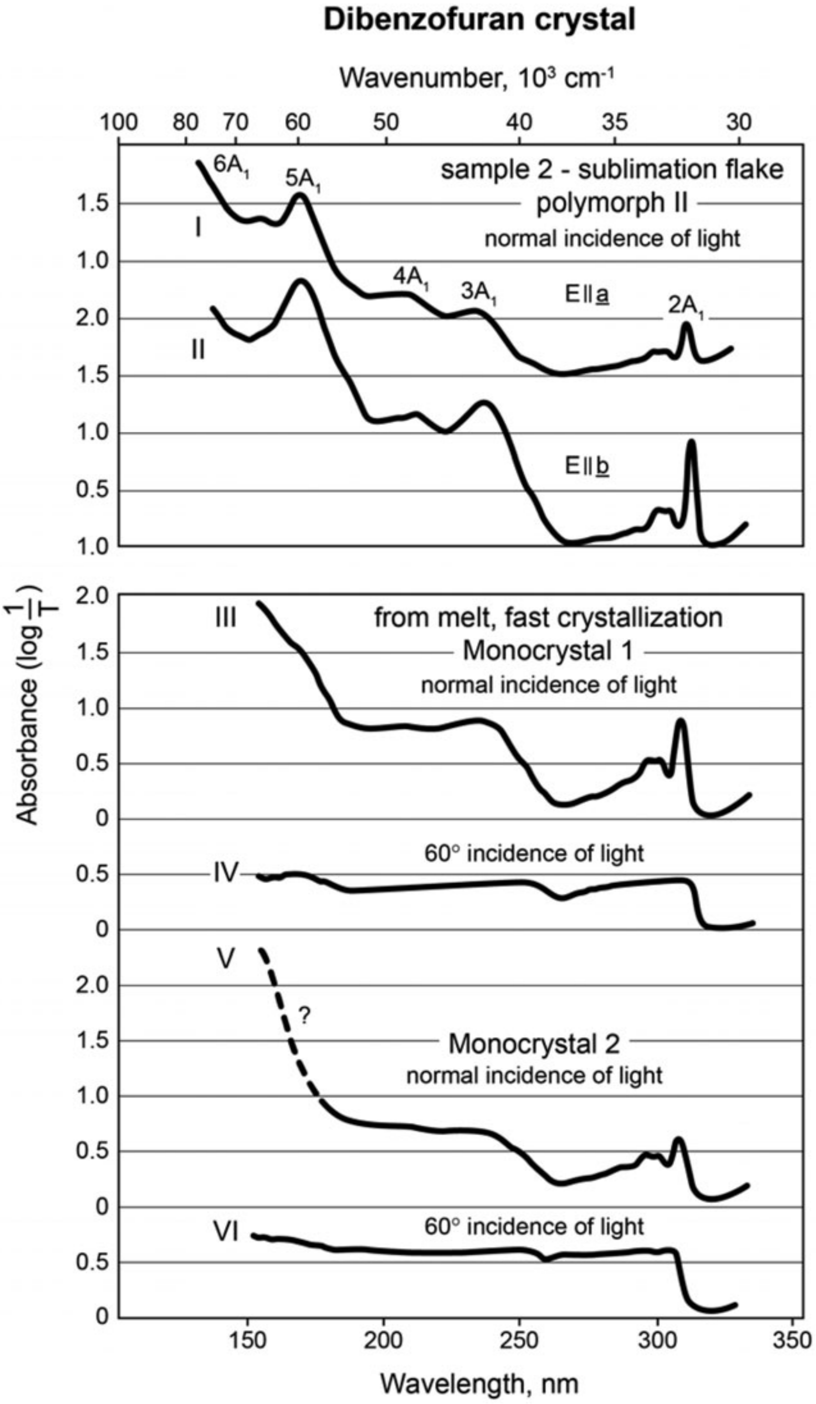

Figure 3. Electronic absorption spectra of dibenzofuran crystals. Polymorph II (sublimation flake): I- Ella; II- Ellb; Sample fast crystalized from melt—monocrystal 1: III- normal incidence of light, IV- 60^0 incidence of light; monocrystal 2: V- normal incidence, VI- 60^0 incidence of light on the sample.

continuous uniform intensity background in the energy range of four different electronic transitions - a type of spectrum not reported before for organic π-conjugated crystals.

Fluorene Spectra

Sample 1 of fluorene is a very thin crystal ($<0.10\ \mu$) obtained by slow crystallization from melt between LiF plates under strong uniaxial pressure. In Figure 4 (spectra I and II) the B_{3u} and B_{2u} symmetry Davydov components of polymorph I of fluorene are shown. As suggested in Ref. 21, the two closely spaced bands near 210 nm (5.95 eV) in the *molecular* SRLD spectrum of fluorene (Fig. 4, spectrum Ia) correspond to convoluted $3\boldsymbol{A_1}$ and $4\boldsymbol{A_1}$ transitions. Similarly, in polymorph I of fluorene $3B_{3u}$ is convoluted with $4B_{3u}$, and $3B_{2u}$ with $4B_{2u}$; they form two bands of different polarizations at 5.73 eV. The spectrum of the three lowest energy bands (four transition) of this symmetry (at 4.43, 5.73, 7.26 eV) can be traced to parental molecular states, since these spectra are almost identical with the spectrum of the $\boldsymbol{A_1}$ symmetry transitions of the SRLD spectrum of *molecular* fluorene (compare Fig 4, spectrum I and II with spectrum Ia). The Davydov splitting of all states is within experimental error. The peculiarity of these spectra is an enormously large polarization ratio $I_b/I_a \sim 8$ for the lowest energy $2B_{2u}$ and $2B_{3u}$ symmetry transitions of this polymorph, while the oriental gas model predicts it to be around 1.5. This anomaly does not take place in the higher energy transitions. Since the thickness of sample 1 of fluorene is less than $0.10\ \mu$ and the sample was obtained under *strong uniaxial* pressure, there is a possibility that the structure of the crystal has changed under this condition of sample preparation. In work [23] the effect of pressure on crystalline structure of fluorene was studied experimentally, and it was shown that the a crystallographic direction is the most sensitive to changes under pressure. It was also found that under pressure the structure of the crystal changes from herring-bone to π-stacking. If there is a similar stacking effect under uniaxial pressure, then the orientation of B_{3u} of transition dipoles in the ab crystallographic plane would be closer to being parallel and the orientation of B_{2u} symmetry transitions closer to head-to-tail. According to hypo/hypercromy theory this would result in diminished oscillator strength of the lowest energy $2B_{3u}$ transition (hypochromy) and corresponding increase in higher energy transitions of this symmetry (hyperchromy). Since the oscillator strengths of the former transition is very small as compared to that of higher energy transitions, the increase in the oscillator strength of the latter would not be noticeable. For the lowest energy B_{2u} symmetry transition the hypo/hyperchromy effect predicts increase of the oscillator strength, which might explain the enormously high polarization ratio in the lowest energy transition, while the polarization ratio of all higher energy transitions is close to that predicted by the oriental gas approximation.

The spectrum of B_{1u} symmetry transitions was obtained by a procedure similar to that employed for the dibenzofuran polymorph I. The spectrum of the tilted crystal, consisting of transitions of both allowed symmetries, is shown in Fig 4, spectrum III. The resulting spectrum of four B_{1u} symmetry transitions - at 4.13, 5.04, 5.56, 6.76 eV, is shown in Fig. 4, spectrum IV and is recorded in *Table 1*. Comparison of these B_{1u} transitions with the SRLD (molecular) spectrum of the $\boldsymbol{B_2}$ symmetry (Fig. 4, spectrum IVa) shows that for each of the four electronic transitions of $\boldsymbol{B_2}$ symmetry in the SRLD spectrum there is a corresponding B_{1u} symmetry transition in the spectrum of polymorph I of fluorene. Thus the excitations of all $\pi-\pi$ electronic states of B_{1u}, B_{2u} and B_{3u} symmetries in the spectrum of polymorph I of fluorene can be traced to parental molecular states.

In the spectrum of a *thin sublimation flake* of fluorene four B_{3u} (and B_{2u}) symmetry electronic transitions at 4.43, 5.46, 6.41and 7.53 eV are detected (Fig. 4, spectra V and VI

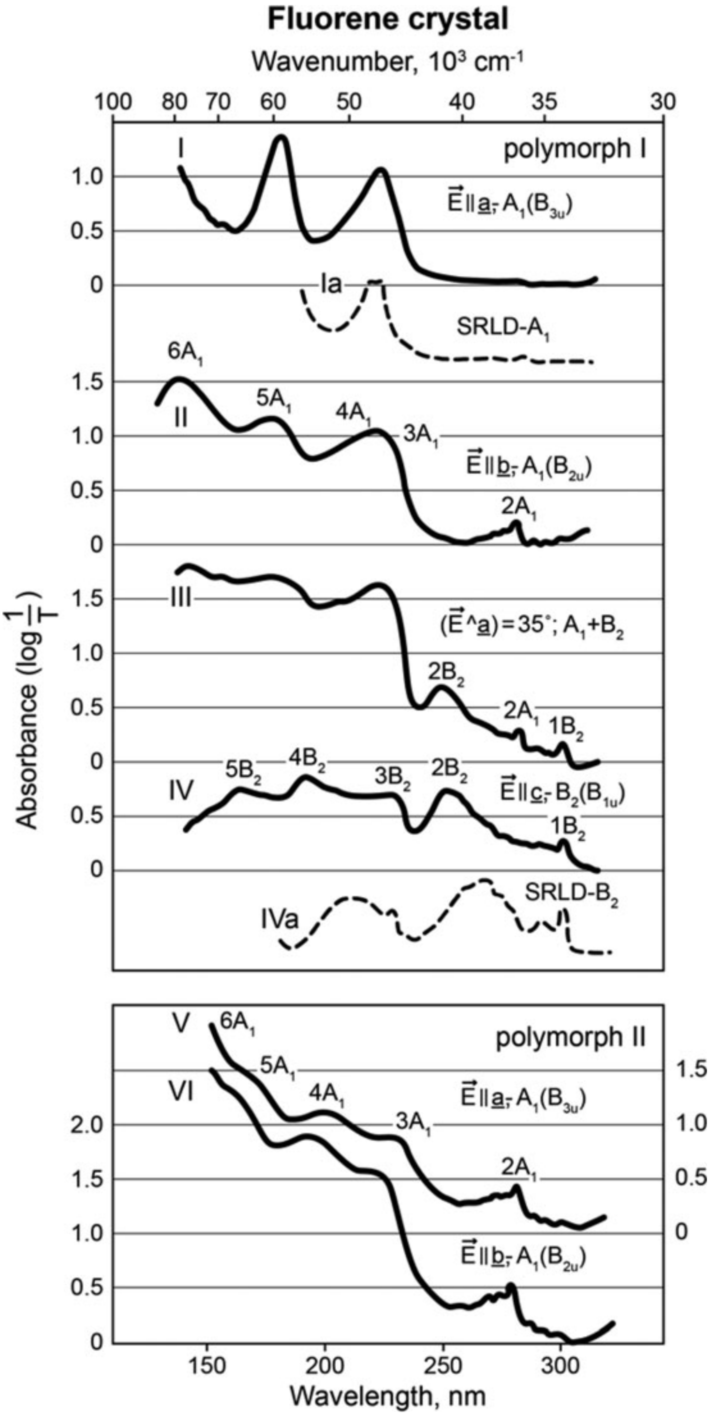

Figure 4. Electronic absorption spectra of fluorene crystals. Polymorph I, slow crystalized from melt sample $<0.1\ \mu$ thick: I- Ella; (compare with Ia- SRLD A_1 symmetry molecular spectrum); II- Ellb; III- Eˆa= 35^0; IV-Ellc; (compare with IVa- SRLD B_2 symmetry molecular spectrum. Polymorph II ($0.15\ \mu$ thick sublimation flake): V- Ella; VI- Ellb.

and *Table 1*), but the positions of maxima and intensity distribution between transitions in samples 1 and 2 are substantially different (compare spectra I and II with spectra V and VI in Fig. 4). Therefore, we assume that sample 2 presents polymorph II of fluorene. The drastic differences in positions of electronic bands in these two polymorphs of fluorene could be due to the hypothesized in the previous paragraph changes in the structure of the very thin samples of fluorene slow crystallized from melt under strong uniaxial pressure. The Davydov splitting for all the $\mathbf{A_1}$ (B_{2u} and B_{3u}) symmetry transitions in polymorph II is again within experimental error. We were unable to obtain the spectrum of the B_{1u} symmetry transitions for polymorph II of fluorene probably due to the malfunctioning of the goniometer.

The unusually large birefringence of *sample 3* of fluorene, a smoky-colored sublimation flake approximately 1.0 μ thick, led us to assume that the developed plane of this sample contained a large projection of the c crystallographic direction, in which case the geometry of the experiment at normal incidence of light on the sample is that of Fig. 1, panel IV. Alignment of the c crystallographic axis with the electric field vector **E** was attempted by rotating sample 3 of fluorene around the axis perpendicular to the electric field vector (Fig. 1, panel V).

The corresponding spectra are shown in Figure 5. Spectrum I in Fig. 5 was obtained at normal incidence of light on the sample with the electric field vector **E** parallel to one of the extinction directions in the crystal; spectra II, III and IV are a result of rotating sample 3 by 15^0, 30^0 and 40^0 around the direction perpendicular to the electric field vector. Rotating the sample 40^0 seems to position the ab crystallographic plane almost perpendicular to the electric field vector (Fig. 1, panel V), so that only a minute intensity of the $2\boldsymbol{A_1}$ symmetry transition is present (Fig. 5, spectrum IV). Thus this spectrum consists predominantly of $\mathrm{B_{1u}}$ symmetry transitions (Fig 1, panel V), but no bands resembling *molecular* $\boldsymbol{B_2}$ transitions or the corresponding $\mathbf{B_2}$ (B_{1u}) transitions of *polymorph I* of fluorene could be detected in polymorph III of fluorene, *with the exception of the transition of this symmetry at the onset of absorption.* All other transitions of this symmetry form a continuous, almost uniform intensity background.

The spectrum of a different smoky-colored sublimation flake obtained at *normal incidence* of light on the sample is shown in Fig. 5, spectrum V. The spectrum is similar to that of the previous sample at 30^0 rotation (compare with Fig. 5, spectrum III), which illustrates that these spectra (in which $\mathbf{B_2}$ (B_{1u}) symmetry transitions are not traceable to corresponding molecular states) are not an artifact due to oblique incidence of light on the sample. As discussed for polymorphs I of fluorene and dibenzofuran *oblique incidence* of light on the latter samples allowed to obtain spectra with $\mathbf{B_2}$ (B_{1u}) symmetry transition traceable to corresponding molecular states.

Carbazole Sublimation Flake Spectra

In Ref. 9 the absorption spectra of a carbazole sublimation flake 0.17 μ thick were obtained only in the near UV region. Here we present spectra of a sublimation flake 0.35 μ thick extended to higher energy.

The spectrum of the carbazole sublimation flake at normal incidence of light on the sample with the electric field vector parallel to one of the extinction directions in the crystal is shown in Fig 6, panel II. Comparison of this spectrum with the $\mathbf{A_1}$ symmetry SRLD spectrum (Fig 6, panel I, dashed line) shows that the transition in the crystal spectrum can be traced to *molecular* states of $\mathbf{A_1}$ symmetry, thus the a (or b) crystallographic direction of the crystal was close to the direction of the electric field **E** of incident light.

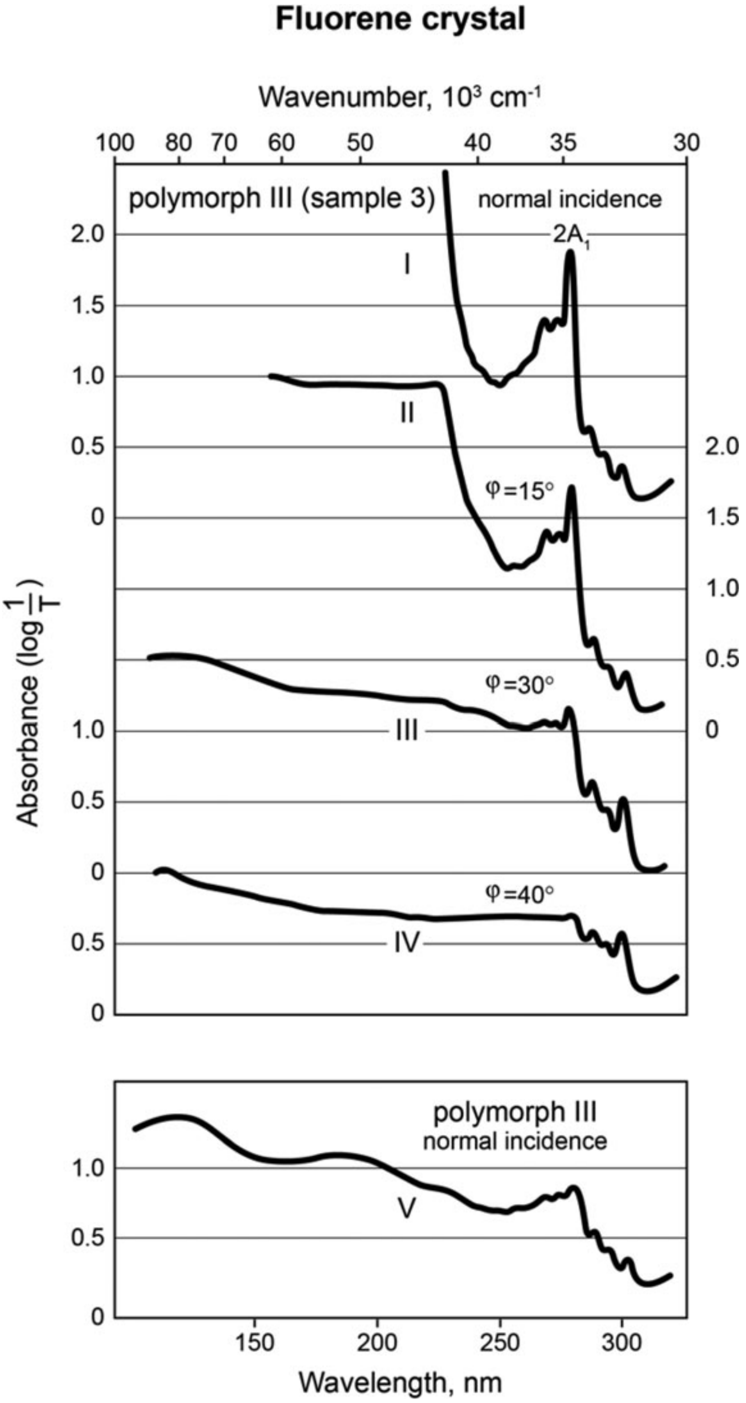

Figure 5. Electronic absorption spectra of a thick (~1 μ) sublimation flake. I- normal incidence of light on the sample; II- oblique incidence at 15^0; III- at 30^0; IV- at 40^0 rotation around an axis perpendicular to the direction of the electric field E of incident light.

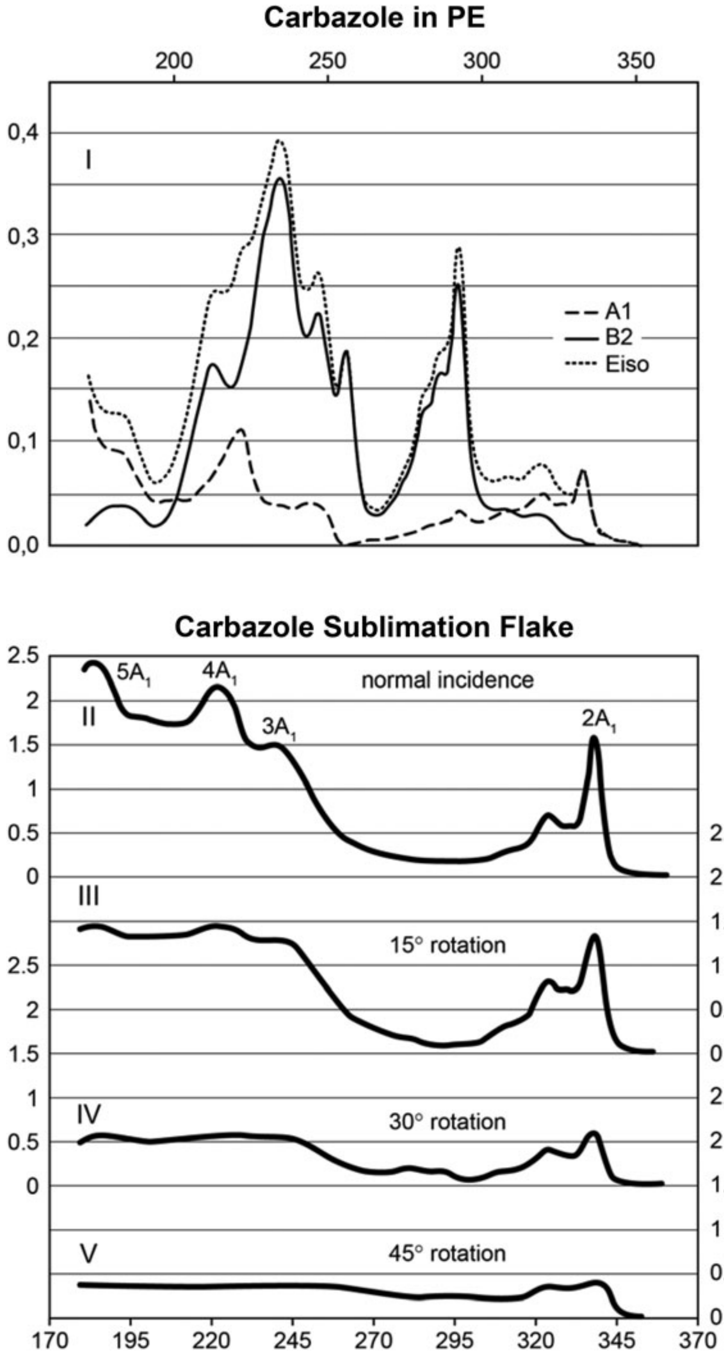

Figure 6. Electronic absorption spectra of SRLD sample and a thin sublimation flake of carbazole. I- SRLD spectrum; II- thin sublimation flake (0.35μ), normal incidence; III- oblique incidence at 15^0; IV- at 30^0; V- at 40^0 around an axis perpendicular to the electric field E of incident light.

It can also be seen that transitions of $\mathbf{B_2}$ symmetry (solid line) dominate the *molecular* spectrum.

Rotating the crystal 15^0 and 30^0 and 45^0 around an axis perpendicular to the electric field vector leads to dramatic decrease of the intensity of all $\mathbf{A_1}$ (B_{2u} and/or B_{3u}) transitions, but transitions corresponding to the molecular $\mathbf{B_2}$ symmetry transitions cannot be identified in these rotated sublimation flakes (Fig. 6, panels III, IV and V). At 45^0 rotation of the 0.35 μ sublimation flake only a small fraction of the intensity $\mathbf{A_1}$ symmetry transition remains, indicating that at this geometry of the experiment (Fig 1, panel 5), the transition dipoles of $\mathbf{B_2}$ (B_{1u}) symmetry are almost parallel to the electric field vector, in which case the $\mathbf{B_2}$ (B_{1u}) transitions should dominate the spectrum. Nevertheless similar to results of [9], individual bands of B_{1u} symmetry cannot be identified in the spectrum of this sublimation flake, since all of them seem to form a low intensity, almost continuous background.

Discussion

Davydov splitting

As distinguished from the acenes group, in the crystals of which there is substantial Davydov splitting in the lowest energy transition (which increases dramatically with increasing length of the acene molecule) [7], in π-conjugated aromatic crystals with phenantrenoid arrangement of rings factor-group (Davydov) splitting in the lowest transition of phenanthrene at 5K was found to be 47 cm^{-1} [25], and at higher transitions at the same temperature no such splitting was found. In EEL spectra of chrysene and picene at 20 K for a small momentum transfer of 0.1 Å^{-1} (optical limit) no Davidov splitting was detected at 20 K [26]. Compound studied in this work also have phenantrenoid arrangement of rings, and no Davidov splitting was detected in all three compounds studied in this work at room temperature, or in the 5 K spectrum of a free-mounted carbazole sublimation flake [27].

Effect of Crystallization Rate and Thickness of Samples on Spectra

Electronic absorption spectra of dibenzofuran and fluorene *thin* (~0.10 - 0.20 μ) crystals *slow crystallized* from melt under uniaxial pressure (polymorph I), polarized in all three crystallographic directions (B_{1u}, B_{2u} and B_{3u} symmetries), can be traced to parental molecular states in the energy range of all discernable $\pi-\pi$ transitions (~3.5-9.0 eV).

In contrast, the spectra polarized in the c-crystallographic direction (*parallel transition dipoles, B_{1u}* symmetry) of relatively *thick* (0.40 μ) dibenzofuran crystals (Fig 3, spectra IV and VI) and fluorene crystals (data not shown), *fast crystallized* from melt, *cannot* be traced to parental molecular states. In the latter spectra multiple B_{1u} symmetry transitions fuse together forming a continuous, almost uniform intensity background.

The dramatic difference in spectra of samples produced by the two crystallization rates can be explained by assuming that it is a manifestation of two different types of excitonic states. In very thin crystals, *slow* crystallized from melt, surface (substrate influenced) states predominate. This interpretation is in agreement with our previous study [27] of 5 K spectra of the lowest transition of the carbazole crystal where it was shown that in crystals slow crystallized from melt between silica plates approximately 60 molecular layers (thickness ~0.06 μ) adjacent to the silica plates are responsible for spectra of substrate influenced states. *Fast* crystallization and relatively large thickness of samples minimizes the influence of substrate on the spectra of these crystals; therefore we presume the corresponding spectra to be due to *bulk* excitons.

Spectra of Sublimation Flakes

Spectra of B_{1u} symmetry of carbazole thin ($\sim$0.17 μ) sublimation flakes [9] and spectra of carbazole sublimation flakes of thickness of 0.35 μ, obtained in this work, are similar in character to those of thick ($\sim$1.0 μ) sublimation flakes of fluorene; thus the character of B_{1u} symmetry spectra (parallel transition dipoles) of *sublimation* flakes are independent of the thickness of the flakes (and similar to the spectra of fast crystallized from melt samples). Transitions in these spectra fuse together forming a low, almost uniform intensity distribution in the energy range of four electronic transitions. We therefore assume that the spectra of sublimation flakes are also predominantly due to *bulk* excitons since the structure of crystals grown by sublimation cannot be influenced by substrates. For these reasons we suggest that the spectra of thin sublimation flakes of dibenzofuran and fluorene are also presumably due to bulk excitonic states, although we were unable to obtain their B_{1u} experimental spectra in this round of experiments.

To summarize, we propose that spectra of all sublimation flakes of fluorene and its hetero-analogues, irrespective of their thickness, are due to *bulk* excitonic states; the spectra of sufficiently thick, fast crystallized from melt samples are also due to *bulk* excitonic states. In the B_{1u} symmetry spectrum of these samples multiple electronic transitions fuse together forming a continuous almost uniform intensity background, and thus they *cannot* be traced to parental molecular states. This unusual result requires confirmation by an independent method capable of discerning the electronic properties of *bulk* excitonic states in organic crystals.

Comparison of the Results of This Work With Literature Data

Polarized electronic absorption spectra of fluorene and dibenzofuran single crystals in the near UV region in the a and b crystallographic directions (B_{3u} and B_{2u} symmetry) were reported by Bree et al [28, 29]. In transmittance mode these spectra were measured in the energy range from $\sim$ 4.0 to 5.5 eV. As a result only one maximum was detected in the spectrum of B_{3u} (and B_{2u}) symmetry transitions. In the current work absorption spectra were measured in all three crystallographic directions in the whole energy range of distinct $\pi-\pi$ transitions, which according to Ref. 19 extends from the onset of absorption to about 9 eV. The positions of the pure electronic bands in the crystal spectrum of the lowest energy transition (B_{3u} and B_{2u}) of fluorene and dibenzofuran in works 28 and 29 coincide with those in our spectra. The polarization ratio I_b/I_a of the lowest transition of the *dibenzofuran* crystal in [29] is the same as for polymorphs I and II of dibenzofuran in our spectra, and close to the oriental gas value of 2.0. The polarization ratio I_b/I_a of the lowest transition of fluorene in [28] is $\sim$1.0, which is dramatically different from that in our spectra - in polymorph I of our spectra it is $\sim$8.0 and in polymorph II $\sim$ 1.6, the latter close to the oriental gas value of 1.5. No *single crystal* spectra of transitions polarized in the c (long) crystallographic direction were measured in works [28] and [29]. Qualitative spectra of *dibenzofuran powder* in KBr discs were presented in Ref. 29. The maxima of the $1B_1u$, $2B_1u$ and $3B_1u$ transitions in the dibenzofuran powder spectra of [29] are close to those in our spectra of polymorph I of dibenzofuran.

In Ref. [30] the low temperature absorption spectrum of a fluorene thin crystal was measured in the energy range from 4 eV to 4.8 eV. The energy of the pure electronic band of the lowest transition approximately coincides with that in polymorph I of fluorene in our spectra. It was not clear to us whether the authors of [30] identified one or two electronic transitions in their spectra; we could not follow the reasoning of the authors concerning symmetry assignments of transitions in their spectra, nor did we understand what the proposed assignments were.

Reflection spectra of fluorene and dibenzofuran in the pre-vacuum UV were measured in all three crystallographic directions in Ref. [31]. Only the maxima of two transitions ($3\mathbf{A_1}$ and $1\mathbf{B_2}$) out of ten measured in the reflection spectra of the fluorene crystal and *no* transition in the spectra of dibenzofuran crystals are close in energy to those in our absorption spectra of polymorphs I or II of these compounds. We do not know the reason for these discrepancies, but we believe that measuring absorption spectra in transmittance mode is a much more sensitive method than in reflectance mode.

Theoretical calculations of response to photo-excitation of the fluorene crystal by light polarized in three crystallographic directions is presented in Ref. 23. The theoretical approach is based on the supposition that crystal excited states can be traced to parental molecular states, so this approach in principle cannot account for the unusual character of B_{1u} spectra of sublimation flakes or fast crystallized dibenzofuran, fluorene and carbazole crystals. Density functional theory was used for calculation of density of states. The work corroborates the results of [21] and of the current work that $\pi-\pi$ transitions of B_{3u} (and $B_{2u)}$ symmetry extend to higher energy in the vacuum UV than those of B_{1u} symmetry. The onset of absorption in [23] for B_{3u} (and B_{2u}) transitions is shifted to lower energy by $\sim$ 0.5 eV, and for B_{1u} by ~0.7eV with respect to our experimental spectra. This result is common when DFT is applied to calculation of the electronic structure of crystals. Also the intensity distribution in the theoretical spectra of B_{3u} transitions is different from that in B_{2u} symmetry transitions, which is unlike our experimental spectra, in which these intensity distributions are similar. There is no correspondence either between relative positions of maxima or the intensity distribution in the experimental spectra with those in Ref. 23. The theoretical spectra of B_{1u} symmetry transitions do not agree with the corresponding experimental spectra for any of the experimentally obtained spectra of this symmetry.

Concluding Remarks

- For the first time electronic absorption spectra of *highly anisotropic* π-conjugated organic crystals were obtained in *transmittance* mode in all three crystallographic directions and in the total energy range of discernable $\pi-\pi$ transitions.
- Analysis of these spectra shows that
- electronic excitations, polarized in all *three* crystallographic directions of thin crystals of dibenzofuran and fluorene, grown from melt by *slow* crystallization under uniaxial pressure, can be traced to parental molecular states;
- strong hypochromism is observed in the lowest energy ($1B_{1u}$ symmetry) transition of dibensofuran in *qualitative* agreement with theory;
- in samples, obtained by *sublimation* or under *fast* crystallization conditions, all transitions of B_{1u} symmetry (parallel transition dipoles) fuse together forming a continuous, essentially uniform intensity distribution (except when the $1B_{1u}$ transition is the onset of absorption). We do not know of a model or a phenomenon explaining these unusual spectra;

- transitions at the *onset of absorption* of all three allowed symmetries can be traced to parental molecular states irrespective of crystallization conditions;
- all transitions of B_{2u} and B_{3u} symmetry (transition dipoles are at oblique angles to the a and b crystallographic axes) can be traced to parental molecular states irrespective of crystallization conditions.

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