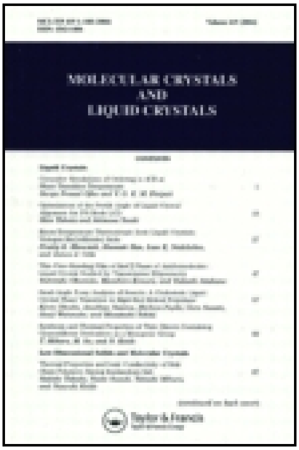

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Optical Properties of Carbazole Thin Monocrystalline Films

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Optical Properties of Carbazole Thin Monocrystalline Films

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Polarized transmission spectra of the 3400 Å system of carbazole monocrystalline films have been measured. Frequencies, oscillator strengths, and half-widths of the pure electronic and vibronic bands were found by fitting experimental spectra with theoretical expressions for transmittance through a film. No factor-group splitting for this transition was detected in free mounted sublimation flakes while for the same transition of films grown from melt between silica plates the factor-group splitting is 65 cm^{-1}. The more complex spectra of sublimation flakes on a silica substrate were interpreted as a superposition of a spectrum of a deformed region adjacent to the substrate and a spectrum of the undeformed remainder of the film. The thickness of the deformed region was found to be 0.06 μ.

INTRODUCTION

There has been a renewed interest in the spectroscopy of carbazoles due to the high photoconductivity of poly(*N*-vinyl carbazole). The photophysical processes in this and other polymers can be understood in terms of the spectral properties of the monomeric units which comprise the polymer.

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Much progress has been made in elucidating the characteristics of the lower lying molecular electronic states of carbazole.[1-12] It is established that the lowest (3400 Å) electronic transition of carbazole is of A_1 symmetry as is the fourth transition near 2400 Å. The second, third, and fifth transitions (near 2920, 2550 and 2320 Å respectively) are of B_2 symmetry.

Important insight into the interactions between the carbazole groups in its polymers could be gained from studies of interactions between molecules in the carbazole crystal. Nevertheless, little is known about its one-photon absorption spectrum. The low-temperature two-photon excitation spectrum of the carbazole crystal was studied by Bree and Taliani[4a]; the low-temperature one-photon absorption spectrum of carbazole in a fluorene matrix was analysed in detail by Bree and Zwarich.[4b] The only low-temperature (90 K) one-photon absorption spectrum of the carbazole crystal reported in the generally available literature refers to sublimation flakes placed on a silica substrate.[5] It was found that the polarization ratio of the *c* and *a* components of the 3400 Å absorption system is only slightly larger than 1.0 (at least two times smaller than that predicted by the oriented gas model), and from inspection of the reported spectra it can be seen that the absorption intensity in the region of the vibronic bands is comparable to that in the region of the pure electronic band. These results[5] are in contradiction to earlier studies of 77 and 20 K absorption spectra of carbazole thin films grown from the melt between silica plates[13] and with studies of carbazole single crystal absorption spectra at room temperature.[14,15] The spectra of free mounted carbazole monocrystalline films have not been reported in the literature. There is evidently a need for a careful examination of low-temperature absorption spectra of thin carbazole films obtained by different preparation methods.

It has been shown in numerous works that the optical characteristics of molecular crystals depend on the preparation method and the experimental conditions such as temperature and pressure. Broude et al.[16] reported that in the absorption spectra of naphthalene films of intermediate thickness (1 μ) grown from melt between silica plates and cooled to 20 K, the vibronic bands broaden with respect to the spectrum of the free-mounted crystal in both the *a* and *b* components, while the pure electronic *b* component becomes narrower. The whole spectrum shifts to higher energies (30 cm^{-1}); the so-called "M" bands shift somewhat differently in the two components, resulting in a 18 cm^{-1} splitting (there is no splitting of these bands in the spectrum of a free mounted crystal). Similar effects were noticed for sublimation flakes placed on a silica substrate.[16,17] On the other hand, in the spectra of an extremely thin film grown from melt[16] there is no splitting of the M-bands, but both components shift to higher energies by 100 cm^{-1}.

Prikhot'ko et al.[18] reported for a 1 μ naphthalene film grown from melt between silica plates that both the weaker (*a*) and the stronger (*b*) components of the pure electronic transition shift to higher energies as a result of deformation of the crystal. Since the weaker (low-energy) component shifts more than the stronger one, the factor-group (Davydov) splitting decreases in the deformed crystal. According to the authors of Ref. 18 this is a result of stretching strain induced by cooling due to the fact that the thermal contraction of quartz is smaller than that of naphthalene. As a consequence, at low temperature the distances between molecules in a film grown between silica plates is larger than in a free mounted film, which results in diminished resonance interactions.

Jetter and Wolf[19] found for an anthracene sublimation flake placed on a silica substrate and cooled to 4 K that both components of the absorption spectra shift to higher energies, with again the weaker (*b*) more so than the stronger one. In this case the weaker component lies at higher energy, so the Davydov splitting increases in the deformed crystal.

Lacey and Lyons[20] reported a thickness-dependent blue shift of the *b* component in anthracene films on a substrate, the shift increasing with decreasing thickness; however the position of the *a* component is thickness-independent. As a result, the Davydov splitting increases with decreasing thickness. Schipper[21] explained this behavior in anthracene assuming that compression strain occurs in the film "through strong attractive forces between the crystal and the plate which increases as the crystal approaches zero thickness."

The effect of compression (pressure) on the absorption spectra of naphthacene and pentacene polycrystalline films at room temperature was studied experimentally by Shirotani et al.[22] Contrary to the case of low temperature spectra of naphthalene and anthracene films on substrates the spectra of compressed films were shifted to lower energies, the low energy component shifting more than the higher energy one, so the Davydov splitting increased with increasing pressure.

In this study we report and discuss the transmission spectra of thin carbazole films (obtained by various sample preparation procedures) in the region of the first electronic transition of carbazole (3400 Å) at 6 K. These studies may elucidate the source of discrepancies between the results of Ref. 5 and those of Refs. 13–15, and will provide new experimental data for analysis of the effect of strain on spectra of molecular crystals.

EXPERIMENTAL

Carbazole purified by solvent extraction, zone melting, and sublimation was kindly donated by Dr. McGhie from the Laboratory of Materials Research of the University of Pennsylvania. A Cary-14 spectrophotometer equipped with polarizers and a liquid helium cryostat was employed for transmission spectra measurements. The samples were cooled by a flow of cold helium gas to a temperature of 6 K. To verify that the resolution of the instrument used is sufficient to ascertain the details of the transmission spectra, the spectrum of a free mounted carbazole flake was scanned on a high resolution instrument. No substantial difference between the spectra scanned on the two instruments was detected.

The optical properties of three types of samples were studied:

(i) Free mounted sublimation flake,
(ii) Thin film grown from melt between silica plates,
(iii) Sublimation flake placed on a silica substrate.

The method of free mounting involved attaching the opposite edges of the sublimation flake to small pieces of mica mounted on a thin brass diaphragm with an aperture of 0.3–0.6 mm, so that the unstrained center of the crystal was in front of the aperture. Similar diaphragms were used for transmission measurements of all other samples studied. The thickness was determined using a Bereck compensator fitted to a Leitz polarizing microscope, and the known birefringence of the crystal. The precision of thickness measurement is estimated to be ~10%. The thickness of the crystals varied between 0.08 and 0.18 μ (between 80 and 180 molecular layers).

The carbazole crystal belongs to the orthorhombic system, space group Pnma (D_{2h}^{16}) with four molecules in the unit cell[23] (Figure 1). The carbazole molecule has C_{2v} symmetry. Of all its symmetry elements, however, the molecule retains in the crystal only the plane of symmetry σ_s passing through the z axis perpendicular to the plane of the molecule. The long axis of the molecule y lies exactly parallel to the b axis of the crystal. The z molecular axis forms an angle of about 60° with the a crystallographic axis.

Investigation of the crystals (grown both by sublimation and from the melt) on a universal stage showed that for the thickness range

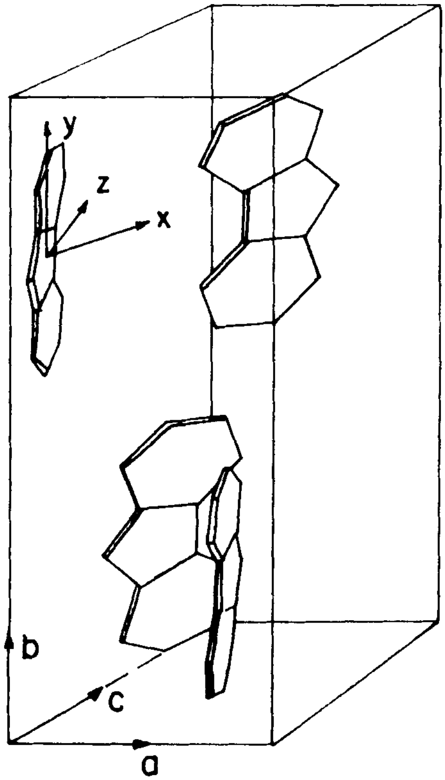

FIGURE 1 The unit cell of the carbazole crystal.[4b]

employed most of the crystals had a well developed *ac* face, containing the short and intermediate axes of the index ellipsoid.[14b] Therefore only electronic and vibronic bands corresponding to transitions of A_1 symmetry will appear in the crystal spectra at normal incidence of light on the *ac* face, as can be seen from the correlation table between molecular and crystalline states of carbazole (Table I).

Interpretation of the spectra

The temperature dependence of the *c*-component transmission spectrum of a sublimation flake on a substrate is shown in Figure 2. The peaks remain broad (half-width ~100 cm^{-1}) down to temperature 6 K. The polarized 6 K transmission (log 1/T) spectra of the carbazole films with $E\|a$ and $E\|c$ are presented in Figures 3, 4 and 5.

TABLE I

Correlation table showing symmetries and selection rules for molecule and crystal of carbazole.[4]

Molecular group C_{2v}		Site group C_s	Factor group D_{2h}	
			A_g	aa,bb,cc
xx,yy,zz;z	A_1	A′	B_{2g}	ac
xz;x	B_1		B_{1u}	c
			B_{3u}	a
	A_2		B_{1g}	ab
xy	B_2	A″	B_{3g}	bc
yz;y			A_u	
			B_{2u}	b

The frequencies, oscillator strengths and damping constants (half-widths) of pure electronic and vibronic bands at 6 K for free mounted sublimation flakes and for monocrystalline films grown from the melt were found by fitting the experimental log 1/T curves with the following expression.[24]

$$T = \frac{1}{4}\left|\frac{Z^{(1)} - 1}{Z^{(1)} + 1} - \frac{Z^{(2)} - 1}{Z^{(2)} + 1}\right|^2$$

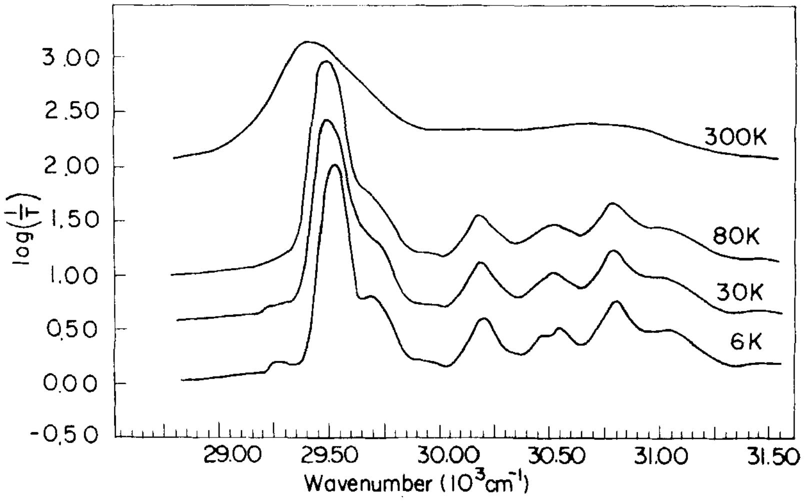

FIGURE 2 Temperature dependence of transmission (log 1/T) spectra of a carbazole sublimation flake on a silica substrate, $E \| c$, thickness 0.14 μ.

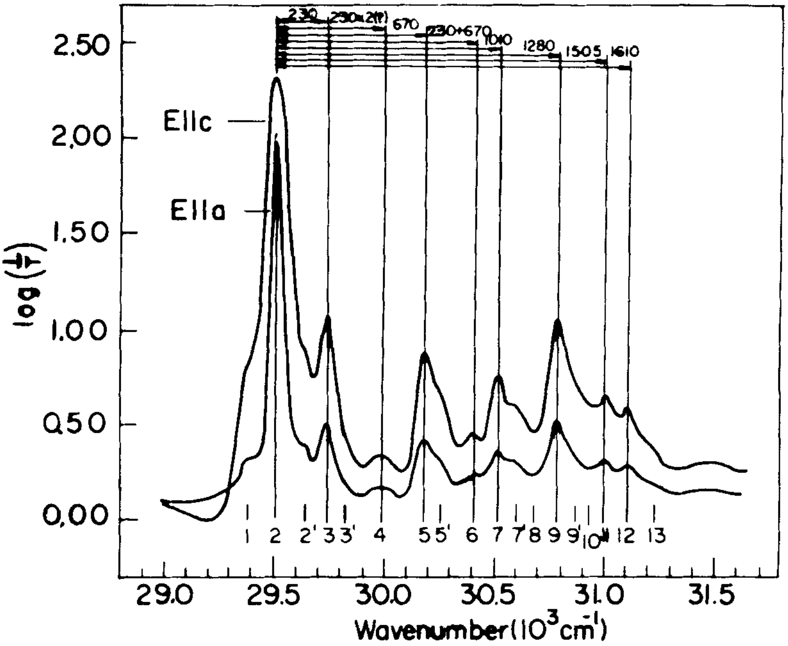

FIGURE 3 Transmission (log 1/T) spectra of a free mounted carbazole sublimation flake, thickness 0.18 μ.

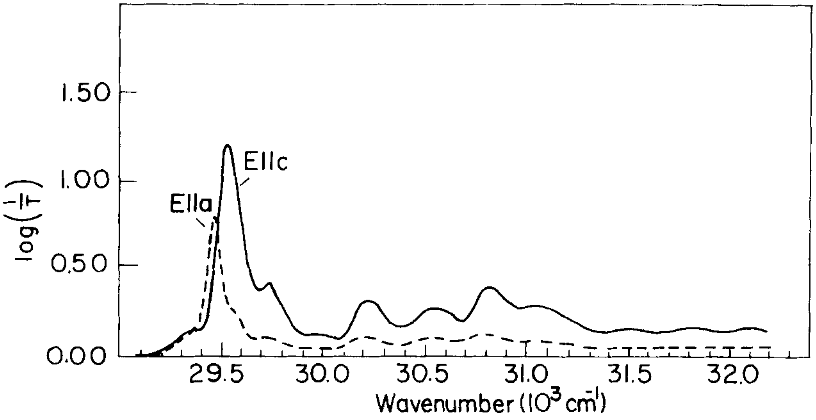

FIGURE 4 Transmission (log 1/T) spectra of a carbazole film grown from melt between silica plates, thickness 0.08 μ.

TABLE II

Wavenumbers ($\tilde{\nu}$), oscillator strengths (f), and damping constants (half-width, γ) of resonances in the 3400 Å system of carbazole monocrystalline films.

		Free mounted sublimation flake, thickness 0.18 μ				Monocrystalline film grown from melt between silica plates, thickness 0.08 μ				
m	n	$\tilde{\nu}$, cm^{-1}	f	$\gamma \times 10^3$cm^{-1}	Interpretation	$\tilde{\nu}$, cm^{-1}	f	$\gamma \times 10^3$cm^{-1}	p	q
1	a	29375	0.0005	0.10	X-traps	29325	0.0012	0.11	29315	
	c	29375	0.0032	0.14		29325	0.0006	0.09		
2	a	29510	0.0050	0.08	0–0	29455	0.0054	0.07	29452	29691
	c	29510	0.0085	0.10		29520	0.0120	0.10		
2′	a	29650	0.0003	0.12		29530	0.0020	0.12		
	c	29650	0.0018	0.12		29530	0.0030	0.11		
3	a	29740	0.0010	0.08	230 a_1	29730	0.0012	0.12	230 a_1	218 a_1
	c	29740	0.0020	0.08		29730	0.0030	0.12		
3′	a	29805	0.0005	0.10		29810	0.0006	0.13		
	c	29805	0.0010	0.12		29810	0.0016	0.13		
4	a	29990	0.0003	0.16	480 =	29990	0.0005	0.18	456 a_1	418 a_1
	c	29990	0.0018	0.18	230 × 2(?)	29970	0.0012	0.18		433
5	a	30180	0.0008	0.08	670 a_1	30190	0.0009	0.13	671 a_1	648 a_1
	c	30180	0.0018	0.08		30190	0.0025	0.13		
5′	a	30255	0.0008	0.12		30260	0.0009	0.13	766 a_1	717 a_1
	c	30255	0.0024	0.14		30260	0.0025	0.13		
6	a	30405	0.0004	0.12	905 =	30390	0.0006	0.16	900	864
	c	30405	0.0012	0.12	230 + 670	30390	0.0014	0.16		

7	a	30520	0.0006	0.08	1010 a_1	30510	0.0012	0.18	1015 a_1	983 a_1
	c	30520	0.0013	0.08		30510	0.0030	0.16		1014
7′	a	30600	0.0008	0.13		30600	0.0007	0.16		
	c	30600	0.0016	0.13		30600	0.0017	0.16		
8	a	30690	0.0003	0.12	1210(?)				1201	
	c	30690	0.0009	0.12						
9	a	30790	0.0012	0.08	1280 a_1	30780	0.0013	0.18	1277 a_1	1236 a_1
	c	30790	0.0020	0.08		30780	0.0030	0.18		1296 a_1
9′	a	30860	0.0008	0.13		30860	0.0010	0.16		
	c	30860	0.0028	0.13		30860	0.0030	0.16		
10	a	30930	0.0002	0.12	1420(?)	30950	0.0002	0.18	1426 a_1	1451
	c	30930	0.0003	0.12		30950	0.0006	0.18		
11	a	31015	0.0007	0.13	1505 a_1	31010	0.0016	0.18	1507	1511
	c	31015	0.0020	0.13		31010	0.0040	0.18		1551 a_1
12	a	31120	0.0006	0.12	1610 a_1	31120	0.0010	0.18	1621 b_2	1591 a_1
	c	31120	0.0012	0.12		31120	0.0019	0.18	1655 a_1	
13	a	31230	0.0003	0.14	1720(?)	31230	0.0016	0.18		
	c	31230	0.0010	0.14		31230	0.0016	0.18		

Captions to columns *m*, *n*, *p*, and *q* of Table II:

m Labels of bands.

n Components of our transmission spectra.

p Two-photon excitation spectrum of the carbazole crystal[4a].

q One photon absorption spectrum of carbazole in the fluorene matrix[4b].

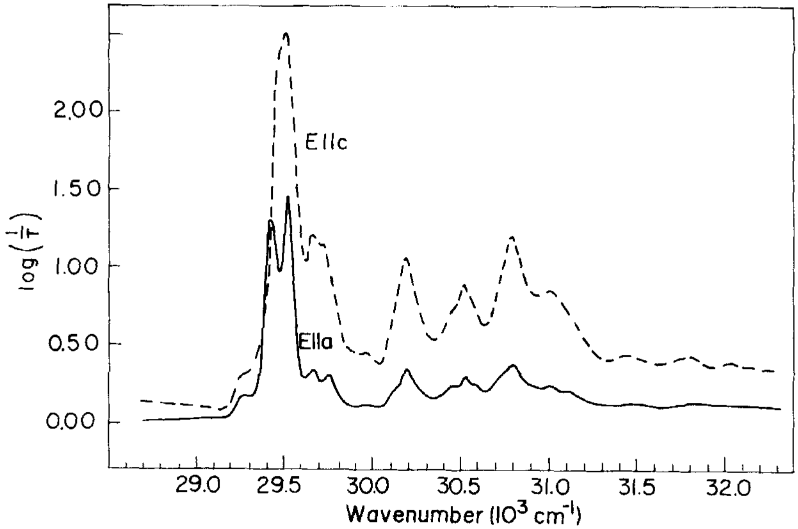

FIGURE 5 Transmission (log 1/T) spectra of a sublimation flake on a silica substrate, thickness 0.14 μ.

where

$$Z^{(1)} = \frac{-i}{\sqrt{\epsilon_{a,c}}} \tan\left(\frac{1}{2}\frac{\omega}{c}\sqrt{\epsilon_{a,c}}\, t\right),$$

$$Z^{(2)} = \frac{i}{\sqrt{\epsilon_{a,c}}} \cot\left(\frac{1}{2}\frac{\omega}{c}\sqrt{\epsilon_{a,c}}\, t\right),$$

$$\epsilon_{a,c} = 1 + \omega_p^2 \sum_{\text{all transitions}} \frac{f_{a,c}}{\omega_{a,c}^2 - \omega^2 - i\gamma_{a,c}\omega},$$

t = thickness of the film
$f_{a,c}$ = oscillator strengths of resonances,
$\lambda_{a,c}$ = damping constants (half-widths) of resonances,
$\omega_{a,c}$ = frequencies of resonances,
ω = $2\pi c\tilde{\nu}$-variable frequency,
c = speed of light
$\epsilon_{a,c}$ = principal dielectric constants in the a and c directions.
ω_p = $\left[\frac{4\pi N e^2}{m}\right]^{1/2}$ plasma frequency associated with a molecular concentration $N = 4.69 \times 10^{21}$ cm^{-3},

m = electronic mass,
e = electronic charge.

The results of this fitting are presented in Table II. The precision of the frequency determination is ± 5 cm^{-1} for stronger sharper bands and ± 10 cm^{-1} for weaker overlapped bands. The precision of oscillator strengths is estimated to be $\pm 10\%$ for bands with optical densities above 0.2 and below 1.5 and $\pm 20\%$ for other bands, and that of γ determination for the major bands is about $\pm 5\%$.

(i) Free Mounted Sublimation Flake

The spectrum of a free mounted carbazole thin crystal (Figure 3) can be interpreted in terms of six a_1 fundamentals: 230, 670, 1010, 1280, 1505, and 1610 cm^{-1}. The pure electronic band for both the a and c components is at 29510 cm^{-1} (Table II) so that Davydov splitting is undetectable (smaller than 10 cm^{-1}). The half-width of the 0–0 band a component (γ = 80 cm^{-1}) is slightly smaller than that of the c component (γ = 100 cm^{-1}, see Table II). The half-width of the vibronic bands are the same in both components and are equal to the half-width of the pure electronic a component. The polarization ratio f_c/f_a of the strongest vibronic bands is about 2.0; the polarization ratio of the pure electronic bands is found to be about 1.8 and is probably somewhat underestimated due to the high optical density of the c-component band. The pure electronic and each strong vibronic band has a broad shoulder (γ = 120–130 cm^{-1}) at higher energies with $\Delta\bar{\nu}$ = 140 cm^{-1} for the pure electronic and 70 cm^{-1} for vibronic bands. (In Table II and Figure 3 these shoulders are labeled as follows: 2′ for the 0–0 and 3′, 5′, 7′ and 9′ for the vibronic bands). The ratio of the intensity of the shoulder to that of the corresponding peak is around 0.15 for the pure electronic band, 0.5 for the first vibronic band (0–0 +230 cm^{-1}) and around 1.0 for all other bands. The Frank–Condon factor for the four strongest vibronic bands (0–0 +230, 670, 1010 and 1280 cm^{-1}) ranges between 0.2 and 0.3.

(ii) Film Grown From Melt Between Silica Plates

The general intensity distribution in the spectrum of a film grown from melt (Figure 4) resembles that of a free mounted flake but there are several important differences (Figures 3 and 4). Unlike for the free mounted flake, the pure electronic band in the a component of the spectrum (29455 cm^{-1}) is shifted to lower energies with respect to the corresponding band in the c component (29520 cm^{-1}), so the

Davydov splitting is 65 cm^{-1}. The *a*-component band has a high energy shoulder like as in the free mounted flake but with $\Delta\tilde{\nu} = 90$ cm^{-1} (as opposed to $\Delta\tilde{\nu} = 140$ cm^{-1} for the latter). The high energy shoulders of the vibronic bands are not clearly resolved but from the contour of the vibronic bands it can be deduced that each consists of two bands (as in the free mounted flake), the low-energy one being broader than in the latter (Table II). It can be seen from Table II and Figures 3 and 4 that the vibronic region of both the film grown from melt and the free-mounted flake consists of a similar set of resonances as far as energies and oscillator strengths are concerned. As mentioned before, the major differences occur in the region of the pure electronic transition and in the width of the vibronic bands. The Frank–Condon factors remain approximately the same and the polarization ratios are somewhat larger than in the free mounted film.

(iii) Sublimation Flake On a Silica Substrate

The spectrum of a strained sublimation flake is more complex (Figure 5), and can be interpreted as an approximate superposition of the spectrum of a free mounted flake and that of a film grown from melt between silica plates (Figures 6 and 7). Although the *a*-component 0–0 band at $\tilde{\nu} = 29430$ cm^{-1} resembles that of the film grown from

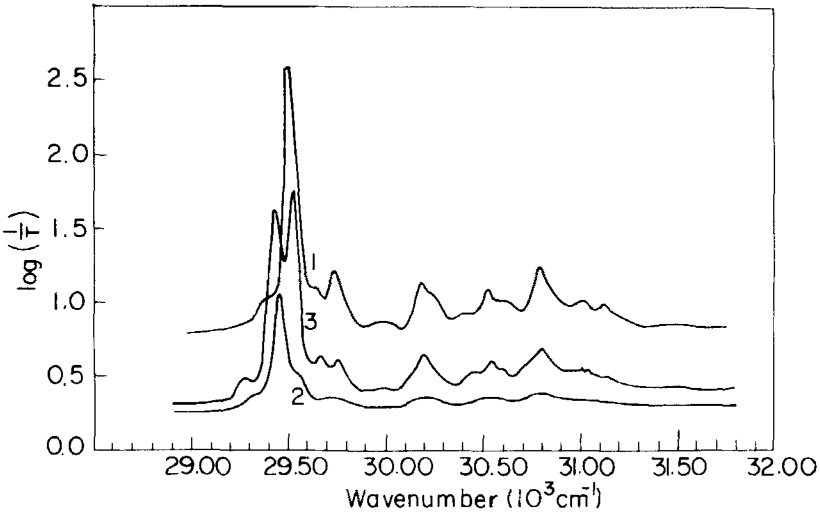

FIGURE 6 Comparison of the *a*-component carbazole spectra for samples: 1- free mounted sublimation flake, thickness 0.18 μ; 2- film grown from melt between silica plates, thickness 0.08 μ; 3- sublimation flake on a silica substrate, thickness 0.14 μ.

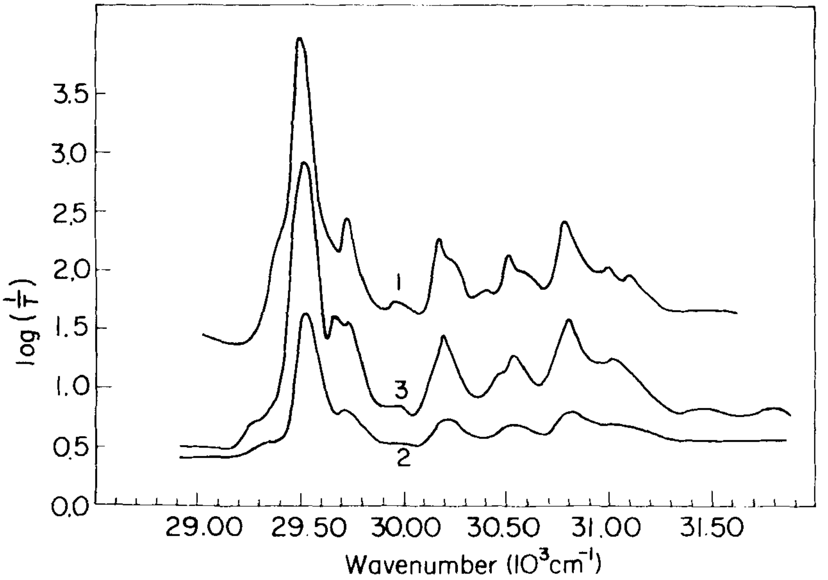

FIGURE 7 Comparison of the *c*-component carbazole spectra for samples: 1- free mounted sublimation flake, thickness 0.18 μ; 2- film grown from melt between silica plates, thickness 0.08 μ; 3- sublimation flake on a silica substrate, thickness 0.14 μ.

melt, the former is at lower energy. Another difference is that each major vibronic band has a low-energy shoulder not found in the spectra of the other two types of film. This shoulder is more strongly expressed in the *a* component of the spectrum but is also noticeable in the *c* component.

DISCUSSION

The intensity distribution of our 6 K one-photon absorption spectra of the carbazole thin crystals measured in the *ac* face differs from that reported by Chekravorty and Ganguly.[5] A possible reason for this difference is that the flakes studied in Ref. 5 were grown with faces at an angle to the *ac* crystallographic plane. We base this assumption on the following facts: (i) We observed an intensity distribution similar to that reported in Ref. 5 if light was obliquely incident on the *ac* face of the films. (ii) We also observed such an intensity distribution for some optically thicker sublimation flakes (as judged from interference colors under crossed polarizers). The transmittance of these flakes in the region of the first electronic transition was not higher than that of the *ac* face flakes implying that the optically thicker flakes had a larger birefringence rather than a larger physical thickness. Consequently their developed face had a component of the *b* direction of the unit cell for which the refractive index is larger than in the *a* and *c* directions. (iii) This intensity distribution is similar to a superposition of the *b* with the *a* or *c* components of the spectra reported in Refs. 14 and 15.

The bandwidth in the one-photon spectrum is much larger (half-width is about 100 cm^{-1}) than in the two-photon spectrum reported by Bree and Taliani[4a] where the half-width equals 14 cm^{-1}. The vibrational intervals are very close in the two spectra (see Table II), but differ considerably from those reported in Ref. 5.

A noticeable feature of the one-photon spectrum of a free mounted monocrystalline film is the absence of a measurable factor-group splitting between the B_{1u} and B_{3u} components. The splitting predicted in the dipole–dipole approximation[4a] is 4 cm^{-1} which is within our experimental error. (Bree and Taliani[4a] observed a moderate (14 cm^{-1}) splitting between the A_g and B_{2g} states in the two-photon spectrum.)

The relatively large Davydov splitting between the B_{1u} and B_{3u} states (65 cm^{-1}) observed in the carbazole crystal grown from melt between silica plates does not have a clear explanation although it does have precedents: the splitting of the M-bands in the low-temperature spectra of naphthalene films[16] grown from melt between silica plates, and the increased splitting in low temperature spectra of anthracene flakes placed on a substrate.[19] An increase of Davydov splitting is also observed for crystals under compression[22] which is in this latter case explained as due to smaller intermolecular distances.

The facts that the polarization ratios, Frank–Condon factors and the intensity distribution of the carbazole absorption spectra are temperature and deformation independent suggest that phase transitions involving noticeable rearrangements of molecules with respect to the crystallographic axes do not take place in carbazole under the conditions of our sample preparation. This implies that the observed large Davydov splitting in the spectrum of crystals grown from melt between silica plates is not due to a phase transition. It is possible,[21] that the substrate induces closer packing within the same crystalline structure.

The broadening of the vibronic bands in the deformed crystal is similar to that observed in the naphthalene M bands.[17,18] In the latter case it was interpreted as due to inhomogeneous strain. It is unclear though why this strain does not lead to broadening of the pure electronic band.

The complex spectrum of the sublimation flake on a substrate (Figure 4) can be interpreted as due to two regions in the film: a deformed region adjacent to the substrate and an undeformed remaining region (Figures 5 and 6). This interpretation is supported by the fact that the intensity of the low-energy (*a*-component) band associated with the deformed region is thickness-independent, while that of the band associated with the undeformed remainder of the film is thickness-dependent (Figures 4 and 8). A similar interpretation was suggested by Ferguson[25] to explain "doubled" lines in the fluorescence spectrum of an anthracene sublimation flake placed on a substrate.

The reason for the larger shift of the *a*-component of the deformed layer in the sublimation flake with respect to that in the film grown from the melt between silica plates is unclear. It might indicate that the substrate induces closer packing on the adjacent layer of a solid flake than when the substrate is originally in contact with liquid carbazole.

In accord with our interpretation, the spectrum of a sublimation flake on a substrate was fitted with the following expression for transmittance through a two-layer film:

$$T = \left[1 - \left(\frac{Z_3 - 1}{Z_3 + 1}\right)^2\right] \left|\frac{1 - m_1}{1 + m_1}\right|^2 \left|\frac{1 - m_2}{1 + m_2}\right|^2 \frac{Re\, Z_1}{Re\, Z_3},$$

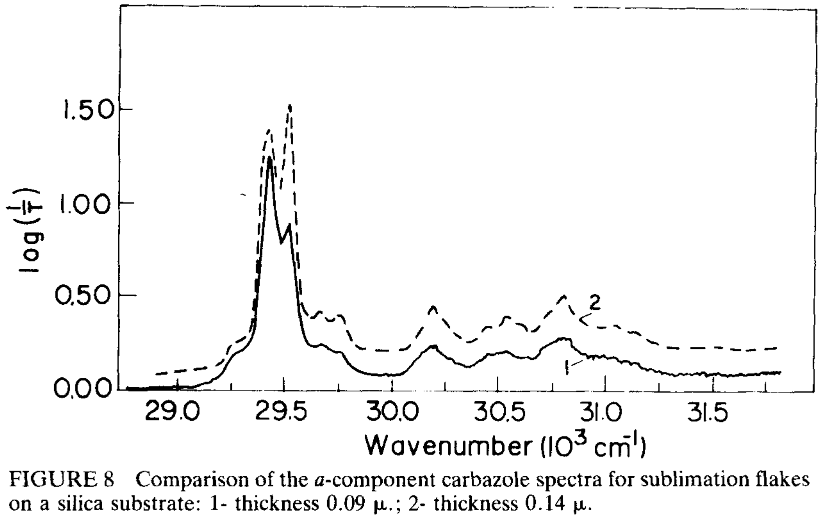

FIGURE 8 Comparison of the *a*-component carbazole spectra for sublimation flakes on a silica substrate: 1- thickness 0.09 μ.; 2- thickness 0.14 μ.

where

$$Z_3 = \frac{Z_2(Z_2^{(1)} + Z_2^{(2)}) + 2Z_2^{(1)}Z_2^{(2)}}{Z_2^{(1)} + Z_2^{(2)} + 2Z_2},$$

$$m_1 = \frac{Z_1 + Z_1^{(1)}}{Z_1 + Z_1^{(2)}},\ m_2 = \frac{Z_2 + Z_2^{(1)}}{Z_2 + Z_2^{(2)}},$$

$$Z_1 = \frac{1}{\sqrt{\epsilon_s}},\ Z_2 = \frac{Z_1(Z_1^{(1)} + Z_1^{(2)}) + 2Z_1^{(1)}Z_1^{(2)}}{Z_1^{(1)} + Z_1^{(2)} + 2Z_1}.$$

$Z_1^{(1)}$ and $Z_1^{(2)}$, $Z_2^{(1)}$ and $Z_2^{(2)}$ are similar to $Z^{(1)}$ and $Z^{(2)}$ in the expression for a one layer film, with $Z_1^{(1)}$ and $Z_1^{(2)}$ containing the dielectric tensor and thickness for layer 1 (adjacent to the substrate) while $Z_2^{(1)}$ and $Z_2^{(2)}$ contain the same for layer 2. The dielectric constant of the substrate is ϵ_s. It was assumed in this calculation that the oscillator frequencies and damping constants are different in the two layers, but the oscillator strengths are the same.

Fitting the experimental log 1/T curve with the theoretical expression allows one to find the thickness of the deformed layer. The value turns out to be 0.06 μ (sixty molecular layers).

It is interesting to note that we did not observe any measurable shifts (Davydov splitting) of vibronic bands due to deformation, contrary to all works cited in the introduction. This might be due to the much lower intensities of the vibronic bands as compared to that of the pure electronic band.

The higher-energy shoulders of the major vibronic bands observed for both the free mounted and deformed carbazole films could be thought of as due to two-particle excitations in the crystal. But if we consider the extremely small value of the Davydov splitting in the free-mounted film as evidence for small resonance interactions in the crystal, then bands associated with two-particle excitations should be weak in the crystal spectra.[26] The alternative explanation is that these strong shoulders are a result of vibron exciton-phonon transitions.

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