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Optical Properties in Anthracene Films

A comparison between free and optical contact mounting

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V. L. Broude *et al.*[1] showed that optical contact mounting leads to a distortion of the optical properties of molecular crystals. The present paper compares and contrasts the true properties of freely mounted films of anthracene with those determined using the method of optical contact mounting. In addition, the temperature dependence of the polariton virtual mode absorption intensity has been determined for a freely mounted film and it is consistent with the mechanism of scattering (absorption) by acoustic phonons. From transmission and true absorption measurements with a very thin freely mounted film, it has been possible to determine for the first time the optical density profile of the surface exciton state previously observed by reflection and in fluorescence.

1. INTRODUCTION

Broude *et al.*[1] showed that a crystal in optical contact with a substrate experiences a considerable distortion of its optical characteristics. This work was enlarged upon by Prikhotko and Soskin,[2] but the optical contact procedure was used by Brodin *et al.*,[3] eleven years after the original Broude report, to measure the "absorption" spectrum of an extremely thin anthracene crystal.

At about the time of the original Broude report, Hopfield[4] and Pekar[5] showed that the stationary states of a crystal and the electromagnetic radiation field are mixtures of photons and excitons (photo-excitons or polaritons). These workers pointed out that true absorption by a crystal requires the participation of a third body, which might be a phonon, a defect, an impurity, an imperfection, etc.

The optical properties of a crystal should be discussed in terms of the three experimental quantities A (absorption coefficient), R (reflection coefficient) and T (transmission coefficient) which obey the following equation

$$A + R + T = 1.$$

There is particular importance attached to the reflectivity and this was quickly realised, culminating in the beautiful experiments of Turlet and Philpott.[6] Meanwhile, Philpott[7] had analysed the virtual polariton modes of slab-like molecular crystals within the polariton framework, unaware that Demidenko and Pekar[8] had considered the same problem previously.

The rapid increase of reflectivity as the wavelength of the light approaches the region of the exciton band (from a long wavelength direction), means that the conventional double beam technique for the measurement of absorption spectra gives an incorrect measure of the absorption spectrum. The usual alternative procedure involves determining the reflection coefficient and using the Kramers–Kronig relations to obtain the absorption profile. A much simpler, direct, method can be used for anthracene. This is the technique of measuring the excitation spectrum i.e., monitoring the fluorescence intensity as a function of the excitation wavelength. Regions of high reflectivity have, necessarily, low absorption intensity, so that the wavelength variation of the absorption coefficient (A) can be determined easily. In addition, if another photomultiplier is used to detect the transmitted light, then A and T can be measured simultaneously. With independent methods for the determination of both A and T, it is possible to characterize completely the optical properties of thin anthracene films by combining these results with the reflectivity data of Turlet and Philpott.[6]

The work of Broude *et al.*[1] established that optical contact distorts the optical characteristics of a molecular crystal such as anthracene. It is useful to compare and contrast the properties of films in optical contact with those which are freely mounted.

The optical properties of a slab-like crystal of anthracene are conveniently discussed in relation to three wavelength regions:

i) the region below the transverse frequency of the exciton,

ii) the region between the transverse and longitudinal frequencies of the exciton

iii) the region above the longitudinal frequency.

2. EXPERIMENTAL

The essential spectroscopic methods have been described earlier.[9] The method of mounting very thin crystals has not however, been clearly stated. It involves securing two opposite edges of a film by optical contact on small pieces of silica. The centre of the mounted film is then placed at the common focal point of a pair of reflecting objectives. These objectives allow sufficient working space for a silica flow tube to be placed between the two objectives and the sample can be cooled by a flow of cold helium gas to a temperature of between 5 and 6 K.

3. (i) SPECTRAL REGION

The interference properties of thin films are well known and the resultant colors seen by reflection and in transmission are well understood. Specifically, the transmitted light shows a wavelength variation of intensity with successive maxima and minima. The condition for transmission maxima is

$$nl = \frac{m\lambda}{2}, \qquad m = 0, 1, 2, \ldots \tag{1}$$

and for transmission minima is

$$nl = \frac{(m+1)\lambda}{4}, \qquad m = 0, 1, 2, \ldots \tag{2}$$

In these equations, n is the refractive index of the film at wavelength λ and l is the thickness of the film.

If the film transmission properties are determined by means of a double beam system in the visible region of the spectrum, it is relatively straightforward, providing the film is not too thick, to assign the m values of the interference maxima and minima by inspection.[11]

The wavelengths of the transition maxima have a special significance in polariton theory. They determine the so-called virtual modes, corresponding to standing waves of dielectric polarization induced by the electric field of the incident light wave. As the wavelength approaches that of the transverse exciton, the exciton component of the polariton increases and there is a corresponding increase of the refractive index of the light. The separation between adjacent maxima decreases as the wavelength decreases towards the wavelength of the transverse exciton and the interference maxima and minima converge to that point.

Demidenko and Pekar[8] applied earlier work by Demidenko[12,13] and Pekar[14] to the calculation of the true absorption by a thin film. Their model was based on the thermal scattering of the polariton by acoustic phonons as the source of intensity for the virtual modes. They showed that $A = 1 - R - T$ and the wavelengths of maximum absorption lie at the wavelengths of minimum reflectivity and maximum transmission.

Qualitative confirmation of the model of Demidenko and Pekar[8] was provided by the observation of the true absorption by freely mounted films of anthracene.[9,10] This absorption was found to be temperature dependent

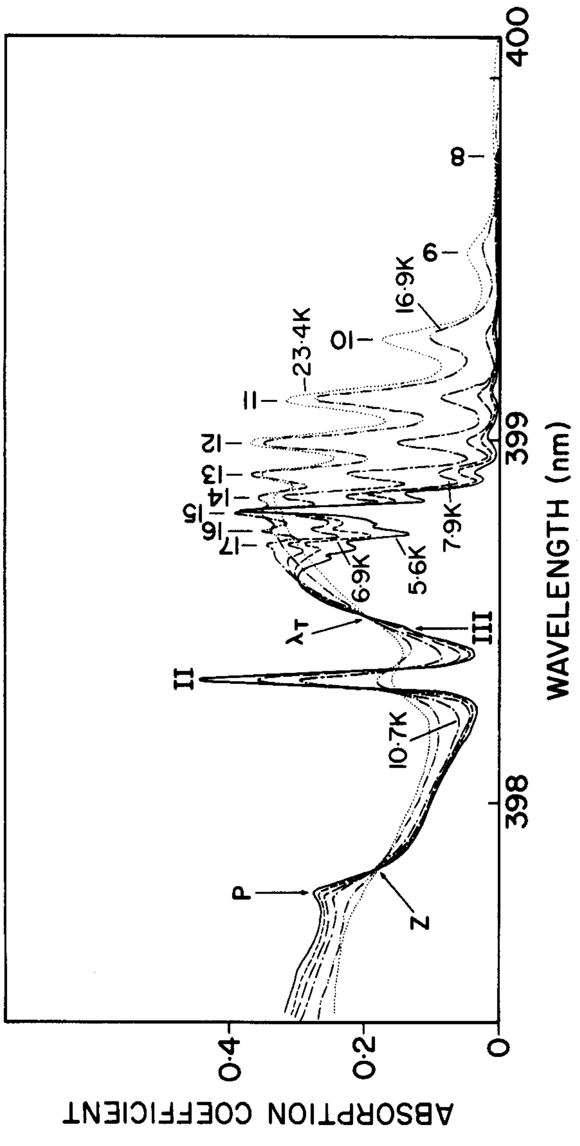

FIGURE 1 The absorption coefficient in the region of the transverse exciton (λ_T) measured at six temperatures. The m values are indicated by 8, 9, . . . , 17. II, III, P and Z are referred to in the text. The thickness of the freely mounted film was 410 nm.

as the example in Figure 1 shows. The *m* values of the virtual modes are given in the figure and they also correspond to the maxima observed in the transmission spectrum. The position of λ_T, the wavelength of the transverse exciton is also indicated in Figure 1. This value was derived from observations of a large number of freely mounted flakes of different thicknesses. The refractive index at λ_T was found,[10] by extrapolation, to be 15.5.

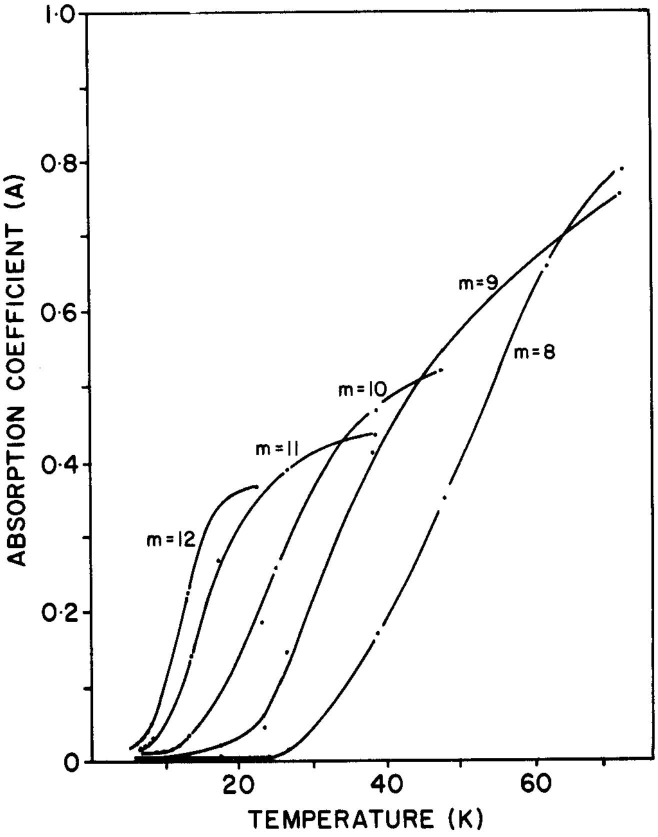

FIGURE 2 Temperature dependences of the absorption coefficients of the virtual polariton modes, $m = 8, 9, \ldots, 12$, of the same crystal as in Figure 1.

The temperature dependences of the absorption coefficients of some of the virtual modes are given in Figure 2. Note that each mode has a small temperature independent absorption intensity. The much larger temperature dependent intensity of each mode can be accounted for, empirically, by assuming that it is controlled by thermal activation, there being a critical thermal energy required before absorption of light will take place. A relationship of the form

$$A = A_0 \exp\left(\frac{-E_m}{kT}\right) \tag{3}$$

follows immediately and an analysis for $m = 8$ is shown in Figure 3. From the slope of the good straight line, the value $E_8 = 93 \pm 5\,\text{cm}^{-1}$ was obtained. Similar analyses for $m = 9$, 10, 11 gave the values $E_9 = 66 \pm 5\,\text{cm}^{-1}$, $E_{10} = 55 \pm 5\,\text{cm}^{-1}$ and $E_{11} = 39 \pm 5\,\text{cm}^{-1}$.

If the empirical values of E_m are added to the wavenumber positions of the corresponding virtual modes, the following wavenumber values are obtained: $\bar{\nu}_8(25004) + E_8(93) = 25097$; $\bar{\nu}_9(25030) + E_9(66) = 25096$; $\bar{\nu}_{10}(25045) +$

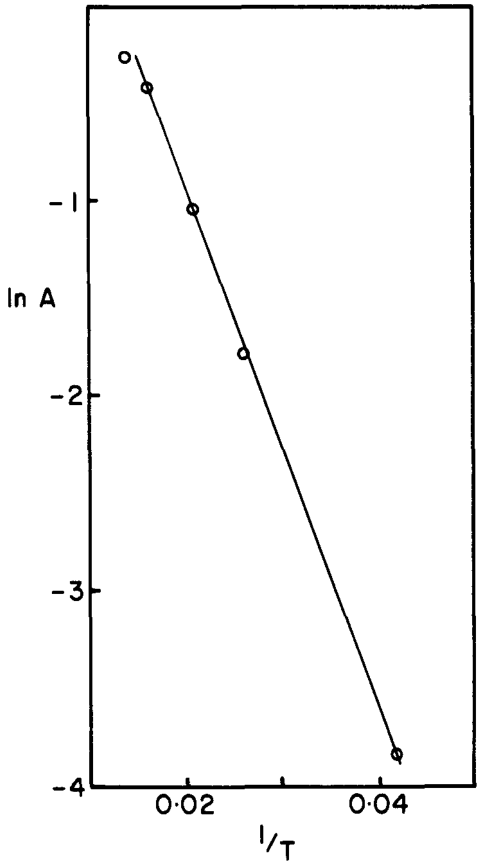

FIGURE 3 Arrhenius plot of the absorption coefficient of the virtual polariton mode $m = 8$ of Figures 1 and 2.

$E_{10}(55) = 25099$; $\bar{\nu}_{11}(25056) + E_{11}(39) = 25095$. Each of these values is, within the experimental error, equal to the wavenumber of the transverse exciton (25094).

The preceding analysis of the temperature dependent absorption intensity in the virtual mode region establishes with certainty that thermal energy is required to provide the energy mis-match between the energy of the virtual mode and the energy of the transverse exciton. This is the process of scattering of the polariton by thermal phonons (absorption) which is inherent in the polariton theories of Hopfield[4] and Pekar.[5] The data are consistent with scattering by acoustic phonons, rather than optical phonons, because their dispersion characteristics provide a continuous range of energies from zero, at the zone centre, to about 40 cm^{-1} at the zone boundary. It follows, for the lower values of m in the crystal considered above, that multiple phonon scattering is involved. There is no evidence for a change of mechanism for energies above about 40 cm^{-1}.

The virtual mode structure is also observed in the fluorescence spectrum, as shown earlier.[9] Here, the mechanism involves the emission of a photon and a phonon, the former matching the energy gap between λ_T and the wavelength of a virtual mode. Raman scattering can also be observed from the virtual modes by using a dye laser as excitation source.[9]

Let us compare the characteristics of freely mounted films with those of films in optical contact with silica. In the visible region we notice no difference between the two cases, there being essentially no contribution from the lowest energy b polarized exciton to the refractive index. However, as the wavelength approaches that of the transverse exciton, there is an increasing interaction between photon and exciton and the refractive index rises accordingly.

The effect of optical contact is to alter the homogeneity of the crystal. There is a shift of the energy of the transverse exciton for each layer of the crystal and therefore, a corresponding refractive index spread across the crystal, from layer to layer. The wavelength corresponding to a given m value is spread accordingly, so that the sharply defined virtual mode of a freely mounted film is no longer possible and the transmission (absorption) spectrum is smoothed out by the inhomogenous strain induced by the optical contact between one surface and the substrate.

The effect of strain is illustrated in Figure 4 for two crystals, each about 50 layers thick, one freely mounted and the other in optical contact with silica. The two full line curves give the measured optical density, uncorrected for reflection. The virtual mode structure on the absorption edge region of the freely mounted film is clearly seen, whereas it is broadened and nearly lost for the crystal in optical contact. Note also the extreme shift of the spectrum of the crystal in optical contact to lower wavelength. This shift

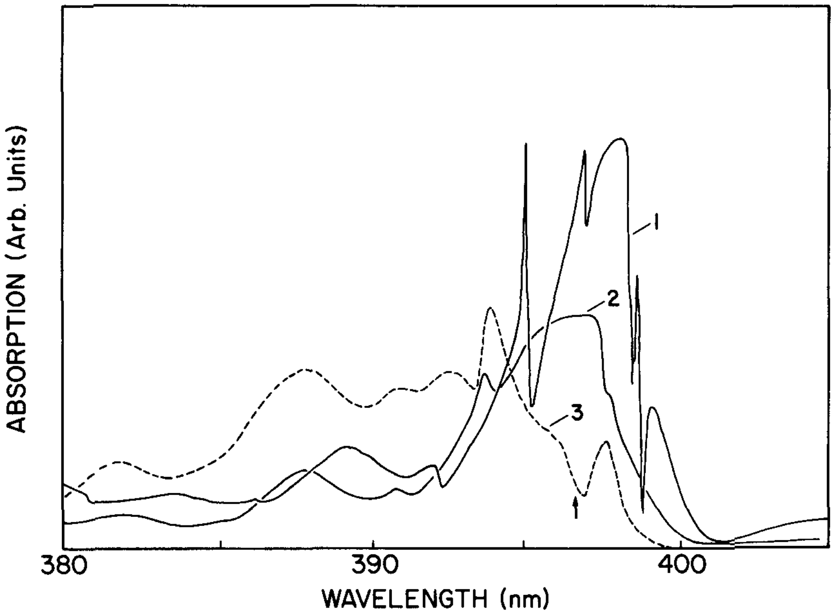

FIGURE 4 (1) Measured optical density spectrum of a freely mounted film 55 layers thick at 6 K. (2) Measured optical density spectrum of a film about 52 layers thick in optical contact with silica. (3) Excitation spectrum of the latter crystal for light incident on the free surface.

correlates with the thickness of the crystal, being largest for the thinnest crystals. The smaller shifts reported by Jetter and Wolf[15] apply to thicker crystals. There is also a corresponding shift of the fluorescence spectrum to lower wavelengths.[16]

4. (ii) SPECTRAL REGION

The wavelength of the transverse exciton is indicated by λ_T in Figure 1 and it can be seen that it marks a point for which the absorption coefficient is temperature independent, in the range 5 to 23 K. On the short wavelength side of λ_T there is a shoulder, indicated by III in Figure 1. This is followed by a narrow peak of absorption intensity, indicated by II. Beyond this peak there is another point for which the absorption coefficient does not change with temperature, shown by *Z* in Figure 1. Finally, there is another feature in Figure 1, a broader absorption peak marked by *P*.

The symbols II and III were chosen because the two features in Figure 1 correspond exactly to two dips of reflectivity observed by Turlet and Philpott[6] in the *b* polarized reflection spectrum of the (001) face of anthracene.

III lies 3 cm^{-1} above λ_T and it has been interpreted by Philpott[17] as the absorption (reflectivity) of the third layer of the crystal. The more intense absorption peak II has been assigned by Philpott[17] to the second layer of the crystal and to a surface induced state by the author.[9,10] It has been shown that it is the origin for the sharp line fluorescence observed from the purest crystals of anthracene,[9] that is the phonon frequencies are built on this line as origin and fluorescence was observed from very thin crystals at this wavelength.

The two wavelengths λ_T and Z are separated by 43 cm^{-1} and the absorption intensity at both points is temperature independent over the narrow region from 5 to 23 K. As λ_T represents the wavelength of the transverse exciton, the absorption mechanism corresponds to scattering by an acoustic phonon whose energy and wavevector are both zero. Wavelengths lower than λ_T correspond to scattering by acoustic phonons with increasing energy and non-zero wavevector. At the zone boundary the wavevector condition is analogous to that at λ_T and the two absorption coefficients should be the same which they very nearly are. The position indicated by Z then represents emission by a zone boundary acoustic phonon with an energy of 43 cm^{-1}. Turlet and Philpott[6] reported a small sharp minimum of reflectivity at this point.

The feature marked by P in Figure 1 lies 49 cm^{-1} to higher energy of λ_T. Examination of the Raman spectrum of crystalline anthracene shows a totally symmetric librational mode at 49 cm^{-1} at 4 K.[18] The absorption at P is therefore assigned to the emission of a lattice optical phonon. Turlet and Philpott[6] reported a broad maximum at this point.

The remaining feature of region (ii) to be considered is an anomaly present in transmission, absorption and reflection spectra which is associated with the first layer of the crystal, the surface layer. This anomaly was described first by Brodin *et al.*[3] from observations of reflection spectra and assigned to a surface exciton state.

Turlet and Philpott[6] repeated the work of Brodin *et al.*[3] and showed very elegantly that the reflection anomaly shifted to longer wavelength after deposition of various gases on the surface of the crystal.[19] Exactly the same phenomenon can be observed in the true absorption spectrum and in the transmission spectrum of a freely mounted anthracene film as shown in Figure 5, coated with air on both surfaces. The corresponding spectra of an uncoated film are shown for comparison. No other feature in the true absorption spectrum was found to shift as a result of the surface deposit of air. The phenomenon is therefore related to the surface layer of the crystal and the author interpreted it, qualitatively, using the early ideas of Hopfield and Thomas.[20] They showed that an anomaly should occur near the longitudinal frequency because of a difference between bulk and surface refractive indices.

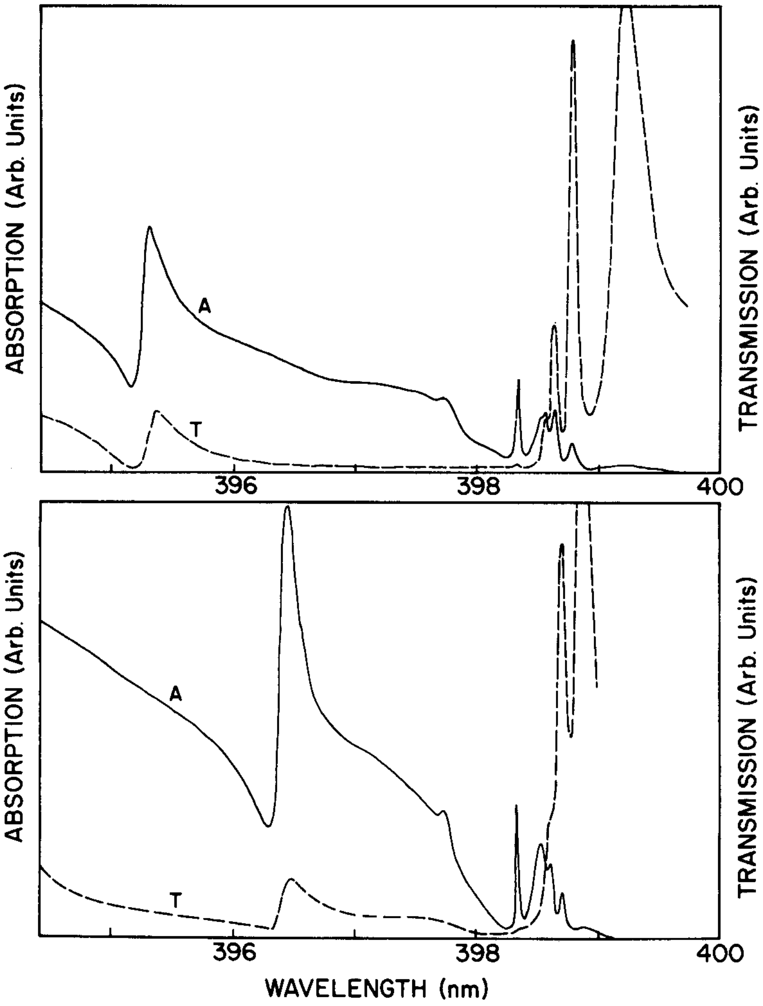

FIGURE 5 *Upper panel*: True absorption spectrum (*A*) and transmission spectrum (*T*) for a freely mounted film 110 layers thick with air on both surfaces, 8 K. *Lower panel*: True absorption spectrum (*A*) and transmission spectrum (*T*) of a freely mounted film 75 layers thick with no air on the surfaces, 8 K.

Philpott[17] has recently developed a quantitative description of the shift of the surface state energy for anthracene and he has shown that near the longitudinal frequency of the exciton there should be an interference-like structure in the reflection spectrum of the type observed. The wavelength of the longitudinal exciton is not known from experiment. The value calculated using the observed refractive index dispersion is 394.2 nm.[10]

Glockner and Wolf[16] reported the presence of a very weak emission line at 25,298 cm^{-1} (vac) i.e., 25,305 cm^{-1} in air. This coincides with the measured position of the reflectivity peak and it was interpreted by Brodin *et al.*[21] as emission from the surface exciton state. If this is correct then it should be possible to detect the associated absorption line. In order to do this it is necessary to work with an extremely thin film and measure two of the quantities A, R and T, so that the values of R and T can be fixed. In the present work both A and T were determined for a freely mounted film 47 layers thick and R was obtained by difference as shown in Figure 6. The variation of the true optical density was then determined and the resultant spectrum is shown in Figure 6. This must then represent the b polarized component of the surface exciton and on this basis an oscillator strength can be calculated by assigning the observed optical density to the two surface

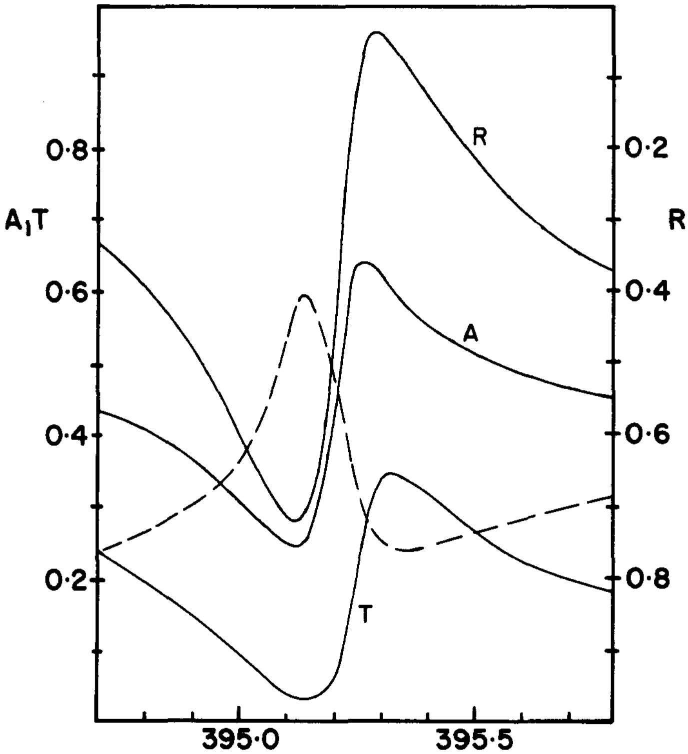

FIGURE 6 Measured true absorption spectrum (A) and transmission spectrum (T) of a freely mounted film 47 layers thick, 8 K. The reflectance spectrum (R) has been obtained from $R = 1 - A - T$. The broken curve is the calculated true optical density profile of the surface exciton state.

layers. This value is 0.014 in satisfactory agreement with a calculated oscillator strength of 0.023 for a *b* polarized exciton.[11] The dual observation of absorption and emission associated with the reflection anomaly then identifies it positively with the *b* polarized surface exciton of the anthracene crystal. The lifetime of this state is not known and picosecond studies are planned to try to measure it directly.

If we compare the optical properties of freely mounted films with those of films in optical contact we find immediately that the true absorption coefficients are higher for the latter. In addition, the magnitude of the true absorption coefficient depends on which surface is illuminated. The transmission coefficient does not change measurably so that the gain true absorption must be at the expense of reflectivity and hence there is a drop in refractive index.

Brodin *et al.*[3] determined the refractive index as a function of wavelength for a crystal about 50 layers thick, in optical contact with silica. Comparison of their results with those for freely mounted films[10] shows that the refractive index is lowered, by optical contact, close to the wavelength of the transverse exciton. This drop in refractive index is consistent with the observed increase of true absorption.

The strain induced by the optical contact produces an overall shift of the absorption spectrum to lower wavelengths as shown in Figure 4. The true absorption spectrum (curve 3) does not follow the spectral distribution of the apparent absorption spectrum (curve 2) in region (ii). In both cases the light was incident on the free surface and there is still an appreciable reflectivity which distorts the spectrum. The position of the vertical arrow in Figure 4 shows the position, given by Brodin *et al.*[3], of the *b* polarized absorption maximum for a crystal 75 layers thick in optical contact. It is not far from the position of the minimum absorption (maximum reflectivity) of the 50 layer thick crystal in optical contact.

There is no experimental control of the boundary between film and substrate so that variations of surface contact are to be expected which add to the inhomogeneity of the resultant optical properties. There is therefore rather poor reproducibility of experimental results, in contrast with those obtained using freely mounted films. The effect of the strain must diminish with distance away from the surface in optical contact and a transition from strained to strain free conditions must be envisaged for thicker crystals. This is evident in the observed differences in true absorption, being less for the surface not in optical contact. There is also another striking result which illustrates the pronounced differences between the two surfaces for crystals of an intermediate thickness. This is the observation of a fluorescence spectrum composed of "doubled" lines. One set, the lower energy set, has its emission lines at the wavelength positions observed in the fluorescence spectrum of

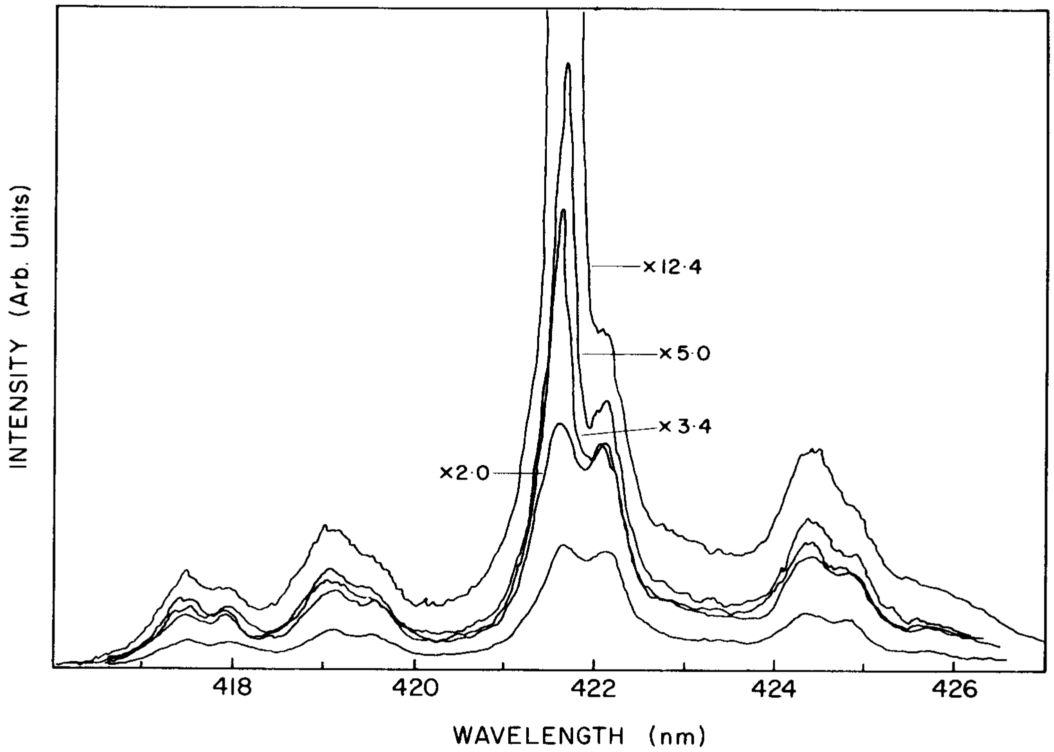

FIGURE 7 Portion of the fluorescence spectrum of a film about 1500 layers thick in optical contact with silica, excited by dye laser. Progressive increase of power density leads to stimulated emission from the 1403 cm^{-1} phonon mode at 416 nm, characteristic of the surface region at the optical contact, temperature about 8 K.

freely mounted films. The other set, at higher energy, has its lines at wavelength positions observed in the fluorescence spectra of very thin films mounted by optical contact with silica.

In one case where the phenomenon of "double" lines was observed, a dye laser was used to stimulate fluorescence (or Raman scattering) in the 1403 cm^{-1} phonon. This laser emission occurred from the surface state (II) in optical contact (the higher energy line) and not from the other surface. The results are shown in Figure 7 and they illustrate nicely the real difference between the two surfaces as a result of optical contact. It should be possible, with a freely mounted flake, to selectively coat one surface of a crystal with air and thereby observe the effect of removal of the surface degeneracy without straining the inner layers, as occurs with optical contact mounting.

5. (iii) SPECTRAL REGION

The interpretation of the features in this region are relatively straightforward. True absorption is expectedly high and the mechanism involves the emission of optical phonons. As a consequence, the reflectivity is reduced. Comparison between absorption and transmission spectra of crystals coated with air (freely mounted) and surface free crystals showed no features analogous to the anomaly in region (ii), which is puzzling. On the other hand, there are some features which can be recognized as phonon side-bands of the absorption spike II of region (ii).

The effect of optical contact mounting is shown in Figure 4. It leads to a displacement of the whole spectrum to lower wavelengths by an amount which is largest for the thinnest crystals. The features referred to in the previous paragraph are no longer distinguishable.

6. CONCLUSIONS

The original work of Broude *et al.*[1] pointed out the deficiencies associated with optical contact mounting of thin crystal films. For anthracene the distortion of the natural optical properties of thin films is so extreme that nearly all trace of the virtual polariton mode structure on the long wavelength side of the transverse exciton position is obliterated by optical contact mounting. For this reason alone the experimental manifestation of the elegant theoretical work of Hopfield, Pekar and others remained unknown until the properties of thin freely mounted films could be determined. Such studies have demonstrated that the mechanism of virtual mode absorption and emission involves the absorption and emission of acoustic phonons to provide the energy mis-match between the virtual mode energy and the energy of the transverse exciton.

Optical contact mounting provides a strain at one surface which is transmitted through the bulk of the film towards the other surface. As a result, the energy states of the crystal are moved upward by an amount which is largest for very thin films. The effect of the strain is non-uniform and the optical properties measured for light incident on the free face differ from those measured for light incident on the face in optical contact. In some cases fluorescence characteristic of both the free and the strained surface regions of the one crystal can be detected. The effect of the non-uniform strain in the crystal therefore adds to the distortion of the optical properties and helps explain much of the variation in the properties reported in the literature, particularly that centred around the magnitude of the Davydov splitting.[15,22,23]

Optical contact mounting virtually obliterates the effect of the interaction between the surface layer and the bulk, so that the reflectivity anomaly near 395 nm, evident in thick freely mounted flakes, is broadened substantially and weakened. On the other hand, freely mounted very thin films provide transmission data and true absorption data, in this region, which allow the determination of the absorption line shape of the surface exciton state.

The method of optical contact mounting should therefore not be used for any meaningful study of the optical properties of molecular crystals.

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