Host-Guest Interaction in Mixed Molecular Crystals

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Host-Guest Interaction in Mixed Molecular Crystals

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Polarized spectra of carbozole, anthracene and naphthacene doped in tolane host have been investigated. The polarization ratio of the successive vibronic peaks of the individual guests progressively diminishes for the higher member of the vibronic bands. This progressive decrement in the value of polarization ratio is not observed for pure crystal spectra. This result thus convincingly shows the effect of host environment on the guest transition.

INTRODUCTION

In a mixed crystal guest molecules fit themselves in the vacant site of the host lattice and, as a result, a considerable effect of the host environment on the guest is expected. It has been assumed that in some mixed crystals this environmental effect known as a host-guest interaction[1] causes mixing of the excited states of the guest molecules with the excited states of the surrounding host molecules. Due to the mixing of the excited states, there will be *transference of intensity from the host transition to the guest transition and* consequently the polarization ratio of the guest transition deviates much from oriented gas model value. Again if the host and guest are oppositely polarized, the lowering of the polarization ratio of the guest will be appreciable. A previous experiment was done on naphthacene in trans-stilbene crystals by Chaudhuri.[2] The observed appreciable lowering and gradual decrement in the polarization ratio of the successive band peaks was explained as being due to host-guest interactions.

To investigate the phenomenon more thoroughly, we have taken three *different guest molecules doped in a common host crystal.* The lowest energy state of all the guests (carbazole, anthracene and naphthacene) are short axis polarized while that of the host (tolane) is intense long-axis polarized one.

Experimental

The mixed crystals required for the present experiment were grown by evaporation of liquid solution of tolane containing traces of guest-molecules (carbazole, anthracene and naphthacene). The most developed face of the crystal grown in this way is (001) face. The axes of the crystal were identified by observing the isogyr pattern under a polarizing microscope. The absorption spectra of the mixed crystal were recorded spectrophotometrically. The detail procedure was described elsewhere.[3,5]

Results and Discussion

Figure 1, Figure 2 and Figure 3, represents the plots of optical density/wave number for a- and b-polarized absorption spectra for tolane crystal containing traces of carbozole, anthracena and naphthacene respectively in solid solution at 90°K. The peak positions and the values of polarization ratio for the different peaks of the individual guests are entered in Table 2. The a- and b-polarized band peaks of the individual guest occur in the same position within the limits of experimental error.

The O—O band of carbazole, anthracene and naphthacene appear at 29500 cm^{-1}, 25840 cm^{-1} and 20661 cm^{-1} respectively. The origin of all the guests are displaced towards the higher energy compared to that in pure crystal of the respective guest molecules. The 'O—O' band of the host crystal is at 32740 cm^{-1} and the integrated polarization ratio ($b:a$) is observed to be (2:1).

The sharp and intense origin with few other vibronic structures are the characteristic features observed in the absorption spectra of carbozole in tolane (Figure 1) while in anthracene and naphthacene spectra several vibrionic peaks are observed.

A mode with a frequency of 1410 cm^{-1} or its multiple arises due to c—c stretching vibration in the anthracene spectrum, and the main progression forming mode in naphthacene spectra has a frequency of 1400 cm^{-1}.

The tolane (Diphenyl acetylene) crystal is monoclinic[6] having space group C_{2h}^5 ($P_{21/a}$). The oriented gas model polarization ratios for different transition moment directions are entered in Table 1. Both a, - b- polarized spectra appear strongly in Figure 1, Figure 2, and Figure 3. That the b-polarized absorption is stronger than the a-polarized one signifies that the first electronic transitions of the guests are short-axis polarized.

The oriented gas polarization ratio ($b:a$) for a short axis transition in a tolane matrix is 4.3:1. However, the observed polarization ratio, even for O—O band, is much below the oriented gas model value and the observed polarization ratio decreases progressively and continuously for the higher members of the vibronic band series. This feature is common for all the guest spectra, even for the spectra of naphthacene whose first excited electronic
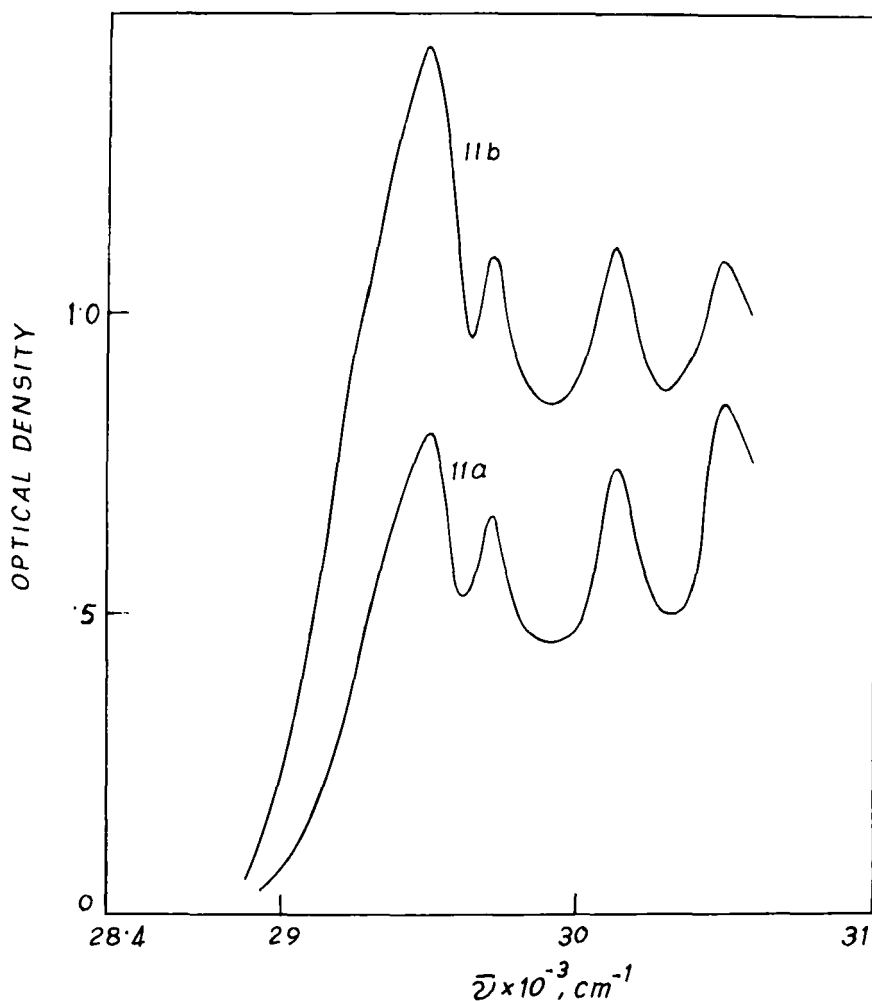
FIGURE 1   a- and b- polarized absorption spectra of carbazole in tolane at 90°K.

energy level is far lower than that of tolane. (Table 2), this effect is formidable. The last vibronic peak nearly depolarizes for all the guests.

Let us now consider the theory of host-guest interaction developed by Craig and Thirunamachandran.[1] The transition moment M to the excited state of the guest molecules is given by

$$M = C \left(\mathbf{m}'_{1S} + \frac{\Delta' H_{ip} \mathbf{m}^k_{ip}}{\Delta \omega^r_G - \Delta \omega^k} \right) \qquad (1)$$
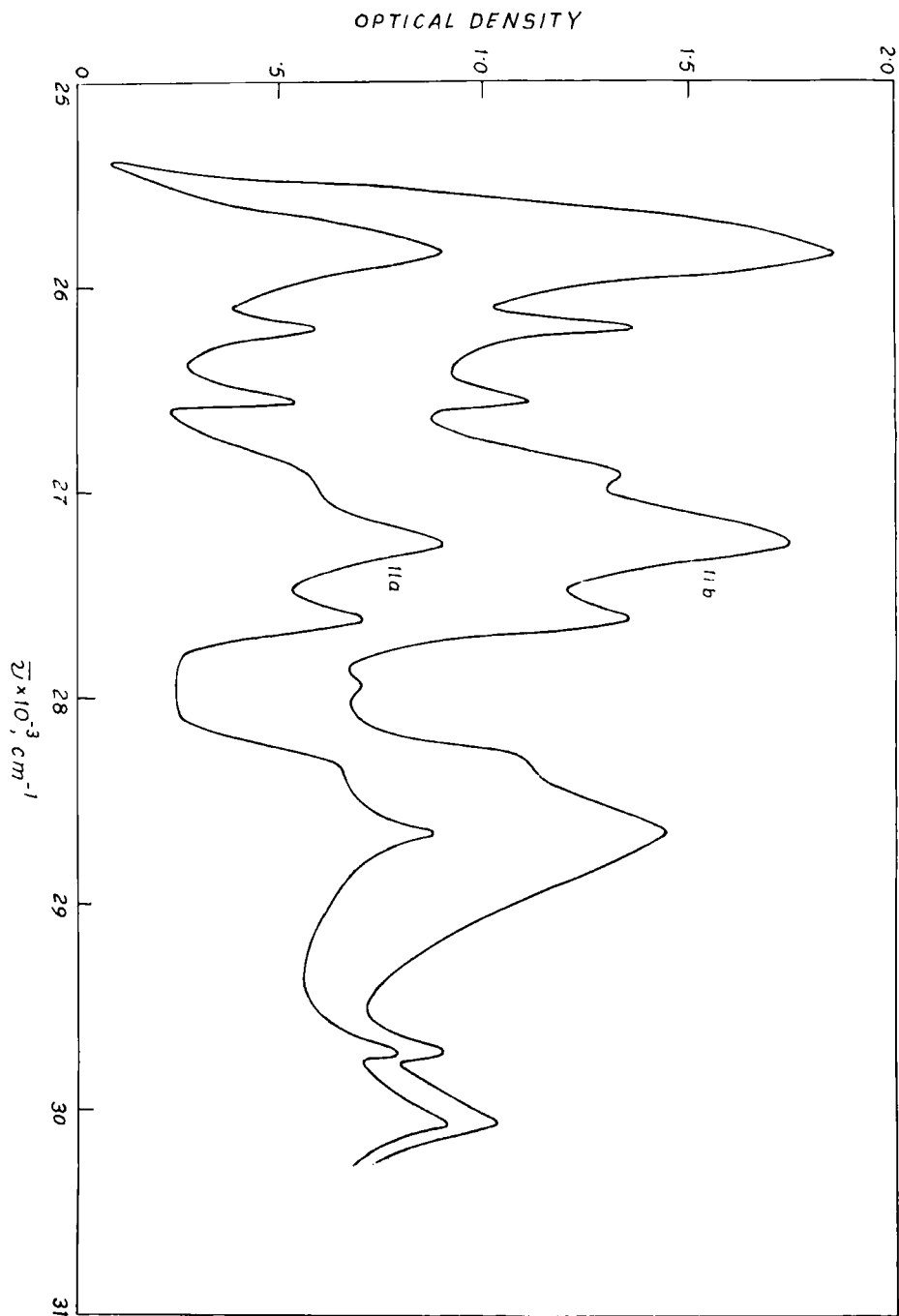
OPTICAL DENSITY

FIGURE 2   a-, and b- polarized absorption spectra of anthracene in tolane at 90° K.
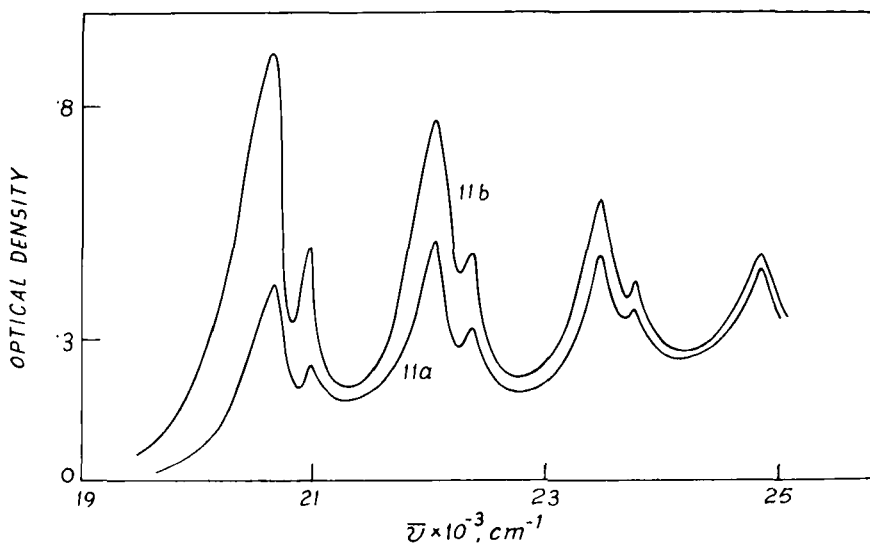
FIGURE 3   a- and b-polarized absorption spectra of napththacene in tolane at 90° K.

in which H_{ip} is the Hamiltonian of a host molecules corresponding to the ith unit cell and pth site, $\mathbf{m}_{ip}^k$ is corresponding free molecular transition moment of the host molecule excited to the kth excited states. $\mathbf{m}'_{ls}$ is the free molecular transition moment of the guest molecule to rth excited states. $\Delta\omega_G^r - \Delta\omega^k$ is the difference in electronic energy of host and guest, 'C' is the normalizing co-efficient. The primed sum omits $ip = 1S$. Thus, theoretically the contribution to the free molecular transition moment of the guest due to the mixing of the host-guest states depends (i) on the matrix element H_{ip}, (ii) on the strength of

TABLE I
Orientation of Tolane Molecule in Crystal Lattice

Transition direction		a	b	c	Polarization $(b : a)$
L	I	35.9°	75.3°	58°	1 : 18
	II	34.5°	84.5°	56.1°	
M	I	117.5°	33.8°	72.0°	4.3 : 1
	II	110.2°	29.8°	69.0°	
N	I	111.2°	119.7°	37.7°	1.6 : 1
	II	114.7°	119.9°	41.6°	

TABLE II

First Absorption System of Guests (Carbazole, Anthracene and Naphthacene)
in Tolane Crystal at 90° K.

Guest molecules	Band peaks $\bar{v}$ cm^{-1}	$\bar{v} - \bar{v}_0$ $= \Delta\bar{v}$ cm^{-1}	Analysis	Polarization ratio ($b : a$)
Carbazole	29500	0	O—O	1.812
	29710	210	210	1.65
	30140	640	640	1.51
	30500	1000	1000	1.28
Anthracene	25840	0	O—O	2.08
	26215	375	375	2.305
	26570	730	730	2.07
	26920	1080	1080	2.28
	27250	1410	1410	1.84
	27620	1780	1410 + 375	1.7
	28330	2490	1410 + 1080	1.7
	28650	2810	2 × 1410	1.65
	29720	3880	2 × 1410 + 1080	1.14
	30070	4230	3 × 1410	1.12
Naphthacene	20661	0	O—O	2.175
	20971	310	310	2.02
	22061	1400	1400	1.509
	22380	1719	1400 + 310	1.486
	23480	2819	2 × 1400	1.25
	23780	3119	2 × 1400 + 310	1.178
	24870	4209	3 × 1400	1.066

the individual host transition moment m_{ip}^k and (iii) inversely on the difference in electronic energy of host and guest states.

The polarization ratio of the guest molecules depend on this transition moment **M**. It is evident from the above discussion that when the lowest energy electronic transition of the host is fairly strong there can be transfer of intensity from this host transition to the guest transition due to host-guest interaction. Due to this transfer of intensity, the polarization ratio of the guest should deviate from its oriented gas model value. Again as this interaction depends inversely on the difference in the electronic energy of host and guest states, the higher member of the vibronic bands of the guest which are closer to the lowest excited state of the host must get greater contribution from the host transition moment. Consequently the polarization ratio of the successive higher members of the vibronic bands of the guest spectrum should change progressively and continuously.

In the case of bands which are purely electronic in origin, we should compare the polarization ratios of O—O bands of the hosts (Naphthacene, Anthracene and carbazole). It is observed that the P.R. value of these bands are also decreasing in the same order as the Craig's theory predicts. However,

in this case the effect of host-guest interaction appears to be far less pronounced than in the case of vibronic bands of the same individual guest. It can be emphasised here that P.R. of the guest molecule in the host lattice depend on the direction of the resultant transition moment M (Eq. 1) and therefore on the relative strengths of the two terms on the right hand side of Eq. 1. Of these the first term m'_{is} being the free molecular transition moment of the guest is different for different guests. It is difficult to claim without theoretical computation, the validity of Craig's theory of host-guest interaction purely from our experiments. But existence of this interaction is evident as one sees the considerable decrease of P.R. for O—O band of naphthacene which lies about 2000 Å higher than O—O band of tolane.

Let us now compare the results of our present investigation with those of others in which the lowest energy transitions of both host and guest are polarized in the same direction such as naphthacene in *anthracene*[4] and anthracene in *carbazole*.[5] The lowest energy transition of both host and guest in these mixed crystals are polarized along the short-axis of the molecule. In either case, the observed polarization ratio is less than the oriented gas model value and there is very little band to band variation in the polarization ratio of the guest absorption system. Whereas in the present investigation in which the lowest electronic transition of host and guest are oppositely polarized, the observed polarization ratio of the guest absorption is much below the oriented gas model value and there is an appreciable and systematic lowering in its value for the successive higher order vibronic bands.

From above discussion it can be concluded that for such system where the lowest energy transition of the host is fairly strong like tolane and is polarized opposite to that of the guest the progressive decrement in the polarization ratio for the higher members of the vibronic bands due to host-guest interaction is appreciable even when the lowest energy state of guest is far lower than that of host like naphthacene in tolane host. Thus our present investigation strongly supports the theory developed by *Craig.*[1]

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