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Davydov Splittings in Intense Transitions of Naphthalene and Anthracene

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Calculations of singlet exciton states of the molecular crystals naphthalene and anthracene have been performed by Craig and Walsh,[1] Craig and Hobbins,[2] and more recently by Silbey, Jortner, Vala and Rice[3] and Silbey, Jortner and Rice.[4] Theoretical treatments follow the original work of Davydov for the interaction of a molecule and the weak crystal field. Since intermolecular overlap in a molecular crystal is small, the interaction between molecules may be represented as a multipole expansion. For an intense transition ($f > 1.0$) the Craig method retains only dipole terms in the expansion. These dipole sums are evaluated by the Ewald Kornfeld procedure or by direct summation over a sphere of 20–30 Å. Silbey *et al.*, however, compute the intermolecular interactions to 55 Å using π-electron wavefunctions or dipole summation, and beyond 55 Å using dipole sums. The main differences in the results of the treatments are due to the contributions of these long range interactions.

The two methods of calculation predict very different values of the Davydov splitting of an intense transition. We wish to compare these results with some experimental values available for naphthalene and anthracene.

Naphthalene shows intense absorption in the vapour at 2100 Å. The observed intensity in this region may arise from one or several electronic transitions.[5] Calculations of the crystal spectrum have previously been performed using solution spectral values rather than free molecule energies and intensities.† The calculations made on the basis of vapour spectral values[5] are shown in Table 1. Interaction integrals are calculated using the crystal dipole sums of Craig and Walmsley.[6] The calculation of Silbey *et al.* using dipole sums is also given.‡ Second order effects are not included since for an intense transition there is only slight alteration in the calculated splitting. The difference in the calculation by using vapour data ($f = 1.3$, $\bar{\nu} = 47530$ cm^{-1}) rather than solution data quoted by Silbey *et al.* ($f = 1.7$, $\bar{\nu} = 45500$ cm^{-1}) may be seen from Table 1 (ii) and (iii). The predicted Davydov splitting is considerably reduced on using vapour spectral values, but is still much greater than that derived from the simpler calculation of Craig and Walsh. This is seen in Fig. 1 where (i) and (iii) from Table 1 are compared with experiment. If the free molecule intensity arises partially from a further (short-axis polarized) transition in this region as has been suggested,[5] the calculated splitting will be reduced. For an f value of 1.0 the splitting would be 5346 cm^{-1} rather than 6770 cm^{-1} (Table 1 (i)).

Previous experimental data is that of Bree and Thirunamachandran[7] who observed a b-polarized component at 44850 cm^{-1}, $f = 0.13$. From our investigation§ qualitative information only has been obtained. There is a region of absorption from 45000 cm^{-1} ($\|b$) and 50000 cm^{-1} ($\perp b$) extending to shorter wavelength. The intensity of absorption appears slightly greater $\perp b$ than $\|b$.

These results alone are inadequate in definitely assessing which

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† Table II of the paper of Silbey *et al.*[3] gives the solution value for both f and E for the intense transition (β-band)—not the vapour phase value as stated. The difference between the transition energies of absorption between vapour and solution is 2180 cm^{-1}. The f value of 1.70 should be 1.30.[5]

‡ Results obtained from using π-electron wave functions to compute the interactions directly are not very different from those by the dipole method.

§ Polarized crystal spectra were obtained using a 0.5 m Jarrell Ash Seya Namioka vacuum grating monochromator fitted with external optics. Crystal samples were sublimation flakes grown from zone refined naphthalene. Difficulty in obtaining and preserving thin crystals (< 0.1 microns), necessary for penetration of the crystal band by the light, limited observations to below 52000 cm^{-1}.

Table 1 Naphthalene—Calculated Crystal Bands and Intensities.
Energy in cm^{-1} relative to $(\Delta w^r + D^r)$[a]

Calculation	Symmetry	Molecular transitions		Crystal bands		
		Δw^r $\bar{\nu}_{\text{vapour}}$	$\Delta w^r + D^r$ $\bar{\nu}_{\text{solution}}$	$\Delta E^{\alpha}(\text{B}_u)$ $(\perp b)$	$\Delta E^{\beta}(\text{A}_u)$ $(\parallel b)$	$\Delta E^{\alpha} - \Delta E^{\beta}$ Davydov splitting
A. Method of Craig and Walsh	(i) $^1\text{B}_{2u} \leftarrow {}^1\text{A}_g$	47530	45350	+4834	−1936	6770
	$f = 1.3$			$f = 0.247$	0.058	
B. Method of Silbey *et al.*	(ii) $^1\text{B}_{2u} \leftarrow {}^1\text{A}_g$	—	45500	+32000	−4400	36400
	$f = 1.7$			$f = 0.32$	0.076	
	(iii) $^1\text{B}_{2u} \leftarrow {}^1\text{A}_g$	47530	45350	+16780	−2540	19320
	$f = 1.3$			$f = 0.247$	0.058	

[a] The term $(\Delta w^r + D^r)$ would be expected to be more closely approximated by solution spectral values.

method of calculation is the more applicable although the predictions of Silbey *et al.* appear more at variance with experiment.

The corresponding system in anthracene has been more closely studied by Lyons and Morris[8] from 36000 cm^{-1} to 60000 cm^{-1}. The

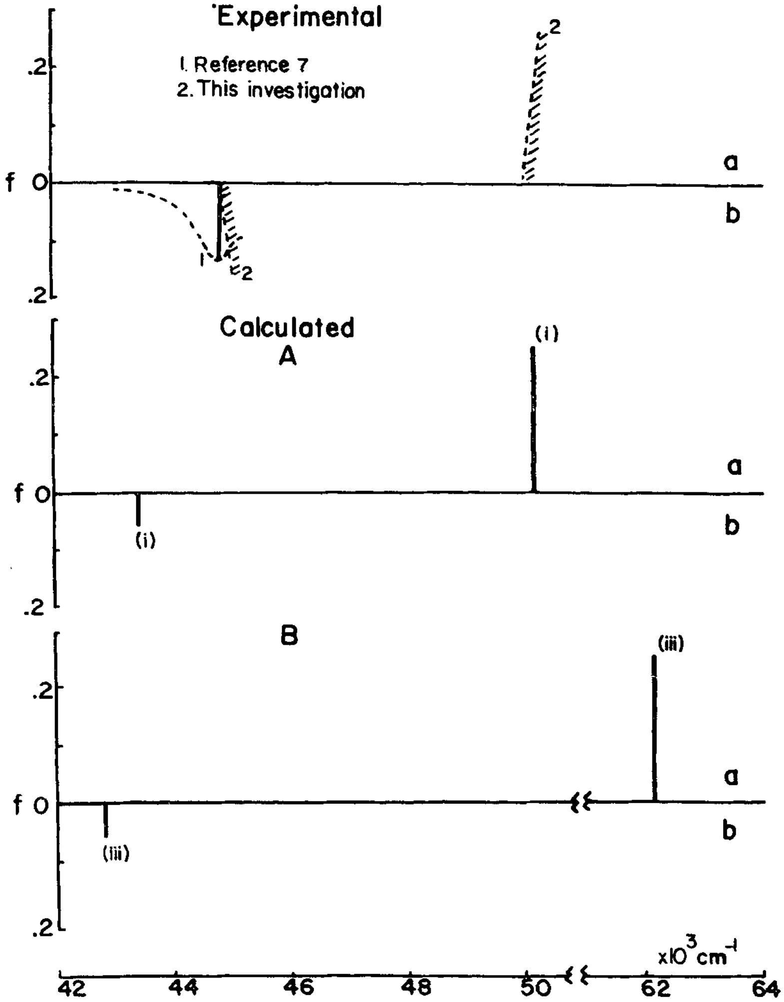

Figure 1. Experimental and calculated crystal bands of naphthalene. (A) Method of Craig and Walsh; (B) Method of Silbey, Jortner, Vala and Rice.

TABLE 2 Anthracene—Calculated Crystal Bands and Intensities.
Energy in cm^{-1} relative to $(\Delta w^r + D^r)$

Calculation	Symmetry	Molecular transitions		Crystal bands		
		Δw^r $\bar{\nu}_{\text{vapour}}$	$\Delta w^r + D^r$ $\bar{\nu}_{\text{solution}}$	$\Delta E^\alpha(\mathrm{B_u})$ $(\perp b)$	$\Delta E^\beta(\mathrm{A_u})$ $(\parallel b)$	$\Delta E^\alpha - \Delta E^\beta$ Davydov splitting
A. Method of Craig and Hobbins	(i) $^1\mathrm{B_{2u}} \leftarrow {}^1\mathrm{A_g}$	42270	39000	+7810	−1850	9660
	$f = 1.6$			$f = 0.40$	0.03	
	(ii) $^1\mathrm{B_{1u}} \leftarrow {}^1\mathrm{A_g}$	—	45200	−475	−525	50
	$f = 0.2$			$f = 0.02$	0.16	
	(iii) $^1\mathrm{B_{1u}} \leftarrow {}^1\mathrm{A_g}$	—	54000	−680	−752	72
	$f = 0.4$			$f = 0.04$	0.32	
B. Method of Silbey *et al.*	(i) $^1\mathrm{B_{2u}} \leftarrow {}^1\mathrm{A_g}$	42270	39000	+18700	−2080	20780
	$f = 1.6$			$f = 0.40$	0.03	
	(ii) $^1\mathrm{B_{1u}} \leftarrow {}^1\mathrm{A_g}$	—	45200	−397	−1535	1138
	$f = 0.2$			$f = 0.02$	0.16	
	(iii) $^1\mathrm{B_{1u}} \leftarrow {}^1\mathrm{A_g}$	—	54000	−569	−2203	1634
	$f = 0.4$			$f = 0.04$	0.32	
Results from Ref. 4, Table II	$^1\mathrm{B_{2u}} \leftarrow {}^1\mathrm{A_g}$	39000	39000	+29094	−3578	32762
	$f = 2.3$			$f = 0.575$	0.04	

For calculations of (ii) and (iii) above, first order calculation only is used. Second order effects could possibly be significant.

calculated crystal spectrum using vapour spectral data[9] ($\bar{\nu}$ = 42270 cm^{-1}, f = 1.6) is shown in Table 2 for the methods of Craig and Hobbins[2] and of Silbey, Jortner, Vala and Rice.[4] Again the

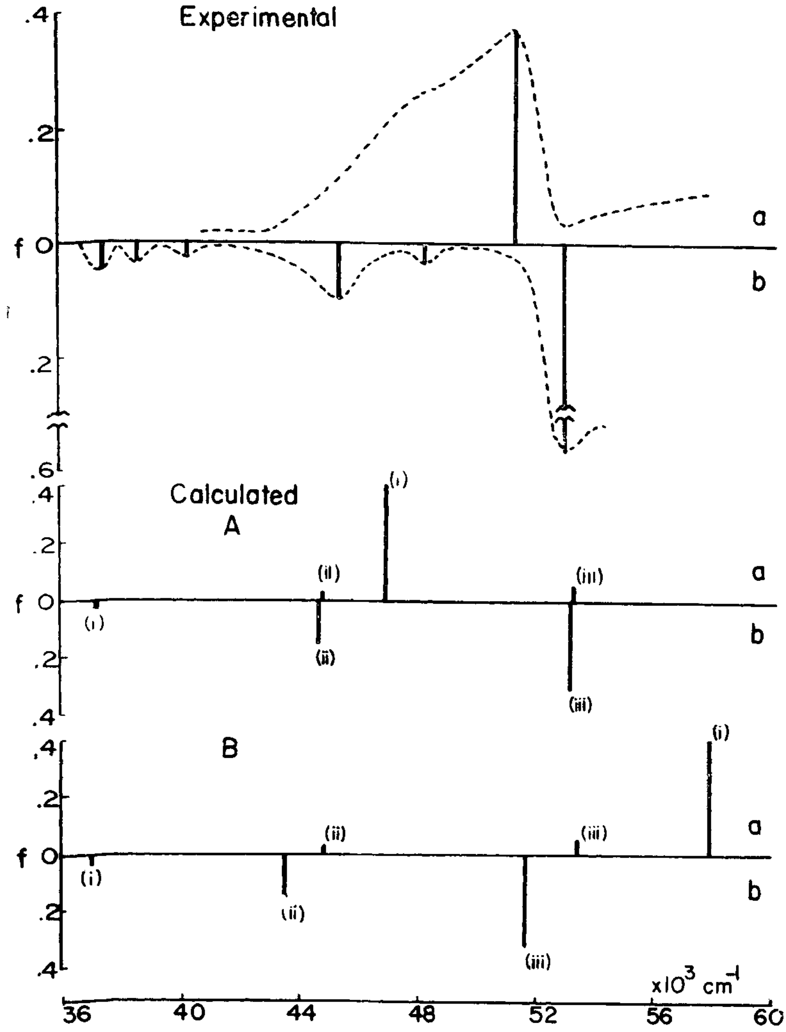

Figure 2. Experimental and calculated crystal bands of anthracene. (A) Method of Craig and Hobbins; (B) Method of Silbey, Jortner and Rice.

Davydov splitting using the method of Silbey *et al.* is considerably reduced when vapour values are used. Calculations for other electronic transitions in this region observed in solution[8] are also shown (Table 2 (ii) (iii)).† Theory and experiment are compared in Fig. 2.

Free molecule transitions in this region are expected to interact to produce a broad crystal spectrum but certain inferences are possible. The crystal spectrum from 36000 cm^{-1} to 56000 cm^{-1} can be accounted for in broad outline using either theory applied to the appropriate free molecule transition. In particular, the a-component observed experimentally near 50000 cm^{-1} can only arise from the free molecule transition at 42270 cm^{-1}. The inclusion of long range interactions in calculating crystal spectra does not appear necessary for an intense molecular transition. The method of Craig *et al.* predicts the spectrum more closely than does the method of Silbey *et al.* In particular their predicted a-crystal band lies in the region of experimentally observed intense absorption. The predicted a-crystal band of Silbey *et al.* lies outside this observed region.

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† Such transitions should occur in the vapour spectrum, of course. But the band expected at about 45000 cm^{-1} in the vapour would be masked by the intense broad band centred at 42270 cm^{-1} and spread over 4000 cm^{-1}. The band expected at 54000 cm^{-1} probably underlies the intense Rydberg series seen in this region.[9] The exact position cannot be obtained, but the solvent shift in solution would be small.

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