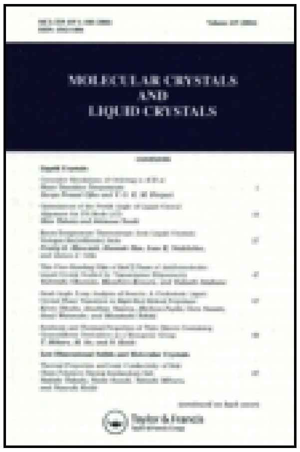

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Optical Properties of Chemically Mixed Molecular Crystals

Leigh B. Clark [a]

[a] Department of Chemistry, B-014, University of California, San Diego, La Jolia, CA, 92093

Version of record first published: 20 Apr 2011.

To cite this article: Leigh B. Clark (1984): Optical Properties of Chemically Mixed Molecular Crystals, Molecular Crystals and Liquid Crystals, 106:1-2, 21-29

To link to this article: http://dx.doi.org/10.1080/00268948408080176

Mol. Cryst. Liq. Cryst., 1984, Vol. 106, pp. 21–29
0026-8941/84/1062-0021/$18.50/0

Printed in the United States of America

Optical Properties of Chemically Mixed Molecular Crystals

LEIGH B. CLARK

Department of Chemistry, B-014, University of California, San Diego, La Jolla, CA 92093

(*Received September 27, 1983*)

The substitutionally mixed crystal system of tetracene as guest in an anthracene host lattice has been reinvestigated with perturbation theory calculations of intensity mixing. The effect of the actual misalignment of the guest molecules relative to the host lattice is appraised. Additional refinements in the calculations incorporate the higher energy host states and the initially mixed polarization of the free host and guest absorption bands. The results are compared to existing experimental data.

INTRODUCTION

Organic molecules often form mixed crystals in which chemically distinct guest molecules substitutionally replace individual host molecules. Such systems have been examined in order to probe the properties of the host crystal (transport phenomena, exciton band structure etc.) and to study the spectral properties of the guest molecules. In the latter regard the transition moment directions and excited state symmetries of the accessible guest states are obtainable from polarized absorption spectra of the now oriented guest sample. Additionally, information concerning the nature of the intermolecular interactions can be obtained by examining the differences between the experimental spectra and the predicted oriented gas spectra. It was toward this last consideration that the present work was initially directed.

When the transition energies to the excited guest states under study are well removed from the nearest host exciton band, then the effect of the host molecules on the guest spectral properties (e.g. energies, oscillator strengths along different crystal axes etc.) can be treated straightforwardly with perturbation theory. However, even in this deep trap limit actual comparisons between theory and experiment over the years have been less than satisfactory.

The 1963 paper by Craig and Thirunamachandran[1] spelled out the perturbation theory approach and led to a reexamination and improvement of the experimental data for the tetracene-anthracene system by Akon and Craig.[2] Fundamental to the perturbation theoretical approach is the expansion of the intermolecular perturbation in a multipole series whose leading term is dipole–dipole in nature. The results of calculations in the dipole–dipole limit, however, did not compare favorably with experimental findings and led to the suggestion that the inclusion of higher multipole terms of the intermolecular interaction was necessary. Unfortunately, all of these early calculations and comparisons were rendered invalid due to an incorrect dipole–dipole lattice summing procedure. The difficulty derived from the incorrect choice in the evaluation of the long range macroscopic part of the lattice summations, and the discrepancies were large.[3]

Another feature of the application of perturbation theory is a summation over all host excited states. Even though the magnitude of the coupling between guest and host excited states decreases inversely with the energy difference between such states all known high energy host state ought to be included. All calculations of state mixing using anthracene as the host lattice have included the first two excited electronic states only. There is available at present enough information (*viz.* energies, polarizations, oscillator strengths) for three additional higher energy states of anthracene to be included in the calculations.[4,5] In this regard there exist at present only a few hydrocarbons for which sufficient spectral data is available in order to serve as suitable host test cases.

Yet another important consideration in dealing with such mixed crystal systems involves defining the precise orientation of the guest molecules in the host lattice. An assumption of perfect positioning in which the guest assumes the exact orientation of the host (no misalignment) has always been made. However, the orientation of the dilute guest can be determined by ESR methods if a suitable number of guest molecules can be pumped to their lowest excited triplet level. An incomplete 1973 study of the tetracene-anthracene system was interpreted as suggesting a gross misalignment of 30°.[6] More recent measurements have defined the misalignment to be a few degrees at most.[7] With detailed orientation data available it is now possible to include the exact misalignment into the theoretical calculations. As we shall see, the effect is not insignificant.

The theory can be used to calculate corrections to the guest excited state energies and oscillator strengths for radiation polarized along the principal axes of the crystal face in question. The evaluation of the correction to the guest transition energy involves a ground state van der Waals term which is not calculable in the absence of good wavefunctions. Deductions based on the differences in say the energy between a particular guest state and various host lattices are founded on the assumption of similar ground state effects for the several hosts and are risky.[8] Intensity changes due to host-guest interactions do not carry the same type of difficulty as do the energy shifts. In particular the oscillator strengths (and their ratio, i.e. the polarization ratio or dichroic ratio) for the components of a given transition polarized along the two principal axes of a crystal face can be calculated without knowledge of the unknown crystal shift term. Here, however, a complication arises due to the "mixed polarization" of the electronic transitions of both free guest and free host molecules. There is ample evidence gained in recent years that the vibronic levels of at least the first excited state of the molecules considered here show an appreciable admixture of *L*-axis (long molecular axis) intensity into the nominally *M*-axis (short molecular axis) polarized transitions. The evidence comes from polarized fluorescence studies,[9,10] low temperature mixed crystal work,[11] stretched film results[12-14] and high resolution, super cold (seeded free jet expansion) gas spectra.[15] Again the actual mix of the polarized intensity must be adequately included in the calculations before observed crystal intensities can be interpreted properly.

In what follows new calculations of the system tetracene-anthracene are presented in which a number of important refinements and corrections have been made. The misalignment of the guest has been included not only in regard to the various projections onto the crystal axes but in the reevaluation of the two types of lattice sums utilized. The higher energy host states are included, and the appropriate mix of oppositely polarized band components are incorporated. The calculations permit the relative effects of such refinements and considerations to be appraised.

CALCULATIONS

The general theory of mixed crystal spectra given by Philpott[16] reduces in the deep trap limit to the perturbation theory of Craig and Thirunamachandran. The appropriate equations are available in the literature and will not be given here.[1,17] Basic input for the calculations are free molecule transition moment data for both guest and host, the host crystal structure and orientation of the guest in that structure and, finally, lattice sums of dipole–dipole interactions and dipole–dipole interactions squared for the various combinations of crystal sites and molecular transition moment polarizations. The calculations reported here are appropriate for the experimental arrangement in which radiation is incident perpendicularly to the (001) crystal face and polarized parallel to either the *a* or *b* crystal axis.

Free molecular spectra

We will be concerned here only with that part of the tetracene spectrum which appears at energies lower than the host absorption edge. The spectrum begins at about 4800 Å with a nominally *M*-axis polarized progression of vibronic bands showing a spacing of about 1400 cm^{-1}. In fact these bands are a superposition of many individual vibronic components which just happen to pile up to give the observed band contours.[15] In spite of the composite nature of the bands we label the series 0-0, 0-1 and 0-2. Pertinent spectral data is given in Table I. The energies listed have been obtained by subtracting an appropriate crystal shift term of 950 cm^{-1} from the transition energies found using alkane solvents.[18,19]

Five absorption systems are known for anthracene. The first system starting at about 3800 Å consists of a series of composite vibronic transitions much like the first system of tetracene. Transition data is

TABLE I

Free Molecule Spectral Properties

Tetracene		$\nu(\text{cm}^{-1})$	f_{total}	$\%_M$	f_M	f_L
I	0-0	20400	.0250	100	.0250	—
	0-1	21830	.0364	84	.0304	.0060
	0-2	23260	.0268	74	.0198	.0070
Anthracene						
I	0-0	26000	.0227	85	.0193	.0034
	0-1	27400	.0283	70	.0198	.0085
	0-2	28800	.0243	60	.0146	.0097
	0-3	30200	.0134	50	.0067	.0067
	0-4	31600	.0038	40	.0015	.0023
II		39000	1.6	0	—	1.6
III		44500	.108	100	.108	—
IV		54000	.404	100	.404	—
V		64500	.482	100	.482	—

given in Table I. Again the energies have been appropriately shifted in order to approximate the site shift of crystalline anthracene.

The vibronic components of system I of both anthracene and tetracene exhibit considerable and increasing mixed polarization (i.e. L polarization mixed into the nominally M polarized bands) as one proceeds away from the 0-0 region of each compound. The fraction of the total oscillator strength of each band which is polarized along the M axis together with the component oscillator strengths is given in the table. These fractions were estimated from published polarized fluorescence studies of anthracene and tetracene.[9,10] No absorption intensity polarized normal to the molecular plane has been observed. For calculations incorporating mixed polarization in the free molecules each vibronic envelope is considered to be composed of two superimposed, oppositely polarized, individual transitions. A slightly different set of Franck-Condon factors or relative oscillator strengths are used for the bands of anthracene system I from that which has been common. The new values are derived from cleanly resolvable low temperature hydrocarbon glass spectra.[20]

TABLE II

Molecular Orientations and Dipole Lattice Sums

Direction Cosines[a]				
Guest Site 1	M	.2823	.9128	.2957
	L	$-.5015$	$-.1219$	.8563
Host Site 1	M	.3234	.8919	.3161
	L	$-.4960$	$-.1248$	.8593
Lattice Sums[b]				
Dipole–Dipole (cm^{-1} Å^{-2})	M_{1h}	M_1L_h	L_1M_h	L_1L_h
host site $h = 1$	$-1836.$	1088.	1188.	2179.
	$(-1769.)$	(1165.)	(1165.)	(2100.)
host site $h = 2$	998.	1641.	1868.	2724.
	(967.)	(1832.)	(1832.)	(2661.)
Dipole–Dipole Squared (10^{-5} cm^{-2} Å^{-4})				
host site $h = 1$	13.29	1.93	1.94	6.50
	(12.36)	(1.97)	(1.97)	(6.50)
host site $h = 2$	1.77	14.27	14.70	8.32
	(1.63)	(14.43)	(14.43)	(8.46)

[a] Referred to the orthogonal a, b, c′ crystallographic axes. The direction cosines of site 2 are obtained by changing the sign of the *b* component.

[b] Guest is at site 1 (origin). Values for no misalignment are given in parentheses. The dipole-dipole sums are for $|\mathbf{k}| = 0$ and $\mathbf{k}$ perpendicular to (001).

Lattice Sums

Dipole–dipole lattice sums were evaluated by the Ewald–Kornfeld procedure for unit dipoles (1 Å) in the M or L directions.[21] The guest tetracene molecule is installed at site 1 of the host lattice with the misalignment indicated by the direction cosines shown in Table II. The remainder of the host lattice is considered to be undistorted. These lattice sums are given in Table II along with the corresponding sums for the case of no misalignment (i.e. pure host) for comparison. The sums of squared dipole–dipole interactions for which convergence is rapid were evaluated by direct summation to a spherical radius of 100 Å.

Results

The mixing calculations lead to calculated vibronic band component oscillator strengths along the a and b crystal axes. From these numbers the intensification factors (i.e. crystal f/oriented gas f) and the polarization ratios (f_b/f_a) can be obtained. The results of several calculations employing different input models are tabulated in Table III along with appropriate experimental data. The experimental data

TABLE III

Calculated Results for Intensity Mixing

		Polarization Ratios[a]		Intensification[b] Factors		Oscillators[c] Strengths	
		Oriented Gas	Mixed Crystal	I_a	I_b	f_a	f_b
Pure Polarization	0-0	7.61	2.82	4.01	1.49	.031	.089
No misalignment	0-1	"	2.74	4.33	1.56	.049	.136
	0-2	"	2.71	4.78	1.71	.040	.109
Pure Polarization	0-0	10.45	3.72	4.23	1.50	.025	.094
With Misalignment	0-1	"	3.60	4.59	1.58	.040	.144
	0-2	"	3.55	5.08	1.72	.033	.116
Mixed Polarization	0-0	10.45	3.34	4.43	1.42	.026	.088
With Misalignment	0-1	6.47	3.17	2.99	1.47	.035	.112
	0-2	4.97	3.03	2.58	1.57	.026	.078
Experimental[d]	0-0	—	3.6 ± .4	3.4	1.2	.020	.072
	0-1	—	3.7 ± .4	1.6	.9	.019	.069
	0-2	—	3.1 ± .3	1.2	.7	.012	.036

[a] Polarization Ratio, f_b/f_a.

[b] Intensification Factor, $f_{\text{crystal}}/f_{\text{oriented gas}}$.

[c] The oscillator strengths are one-dimensional values.

[d] See reference 2. The intensification factors have been recalculated to include mixed polarization effects in the free tetracene molecule spectrum.

are those given by Akon and Craig.[2] Their intensification values have been modified to include the observed mix of L and M axis intensity in the free molecule which effects these factors through changes in the oriented gas intensities. The quoted experimental uncertainties are ±13% for oscillator strengths and ±10% for the polarization ratios.

DISCUSSION OF RESULTS

The misalignment of the guest molecule shows up as a rather striking change (7.61 to 10.45) in the oriented gas polarization ratio for an M polarized transition. In addition, the effect of mixed polarization on the oriented gas polarization ratios is striking. Overall there is general agreement between the experimental results and all three calculations. However the agreement improves when the misalignment is included in the calculation, and a further improvement occurs when mixed polarization is also incorporated into the free molecule spectra.

The rapid fall off of the intensification factors along the a axis for the series 0-0, 0-1 and 0-2 seems to be related to the increasing mixed polarization found in the free molecule instead of through increasing host-guest coupling due to the decreasing energy gap between host and guest transitions. In fact the signs of the coupling terms between both L and M polarized host states and M polarized guest states is such as to shift intensity to the guest transition along the a axis. The effect is particularly strong for the intense host II (L polarized) system along the a axis. The result without consideration of the initial mixed polarization of the transitions is a steady increase along the sequence of transitions for the intensification factors for both axes and disagrees with the experimental results. When mixed polarization is included in the calculations, then the correct rapid drop off of intensification factors is reproduced along the a axis but not along the b axis. Along the b-axis the calculated intensity shifts very modestly from M polarized host states to M polarized guest states, however the reverse occurs when the host state is L polarized. The net effect in this latter case is very small. All calculations for the b axis intensification factors give substantially similar results, and none yield the observed modest decline for the series of bands. The quantitative nature of the above comments is indicated in Table IV which gives the cumulative effect of including successively higher host transitions into the calculation for the 0-0 band of tetracene.

The model calculations reported here ignore all terms of higher order than dipole–dipole in the intermolecular interaction. One of the

TABLE IV

Cumulative Effect on the Tetracene 0-0 Band
Due to the Successive Host Bands

		PR	f_a	f_b	I_a	I_b
Oriented Gas Values		10.45	.0060	.0625	—	—
I	(0-0)	10.69	.0062	.0667	1.04	1.07
	(0-1)	10.63	.0066	.0701	1.10	1.12
	(0-2)	10.47	.0069	.0721	1.15	1.15
	(0-3)	10.35	.0070	.0729	1.18	1.17
	(0-4)	10.31	.0071	.0730	1.18	1.17
II		2.79	.0254	.0708	4.25	1.13
III		2.90	.0256	.0743	4.28	1.19
IV		3.15	.0261	.0822	4.36	1.32
V		3.34	.0265	.0885	4.43	1.42

initial hopes of the present work was to gauge the importance and magnitudes of higher multipole terms. This goal has not been realized. Calculations using lattice sums which have been scaled in an effort to reflect more nearly the actual interactions modify the results somewhat, however due to the uncertainty in the experimental results it is not fruitful to pursue this tack at this time.[18] It seems that the experimental uncertainty for the system tetracene in anthracene needs to be narrowed before definite conclusions can be drawn. The quantitative examination of other mixed crystal systems which employ well-characterized host crystal systems (e.g. biphenyl,[22] diphenylacetylene[23]) should help to appraise the magnitudes of the neglected terms.

References

1. D. P. Craig and T. Thirunamachandran, *Proc. Roy. Soc.*, **271A**, 207 (1963).
2. C. D. Akon and D. P. Craig, *Trans. Faraday Soc.*, **63**, 56 (1967).
3. M. R. Philpott, *J. Chem. Phys.*, **50**, 5117 (1969).
4. L. B. Clark, *J. Chem. Phys.*, **53**, 4092 (1970).
5. L. B. Clark and M. R. Philpott, *J. Chem. Phys.*, **55**, 3790 (1970).
6. R. Ostertag and H. C. Wolf, *Chem. Phys. Letts.*, **22**, 65 (1973).
7. H. Dörner, R. Hundhausen and D. Schmid, *Chem. Phys. Letts.*, **53**, 101 (1978).
8. G. B. Talapatra and T. N. Misra, *Chem. Phys. Letts.*, **76**, 42 (1980)
9. H. Zimmermann and N. Joop, *Z. Elektrochem. Ber. Bunsenges. Physik. Chem.*, **64**, 1215 (1960).
10. D. M. Friedrich, R. Mathies and A. C. Albrecht, *J. Mol. Spec.*, **51**, 166 (1974).
11. N. J. Kruse and G. J. Small, *J. Chem. Phys.*, **56**, 2985 (1965).
12. J. Michl, E. W. Thulstrup and J. H. Eggers, *Z. Elektrochem. Ber. Bunsenges. Physik. Chem.*, **78**, 575 (1974).

13. J. J. Dekkers, G. Ph. Hoornweg, C. Maclean and N. H. Velhorst, *Chem. Phys.*, **5**, 393 (1974).
14. L. Margules and A. Yoger, *Chem. Phys.*, **27**, 89 (1978).
15. A. Amirav, U. Even and J. Jortner, *J. Chem. Phys.*, **75**, 3370 (1981).
16. M. R. Philpott, *J. Chem. Phys.*, **53**, 136 (1970).
17. L. A. Dissado and A. W.-H. Mau, *Chem. Phys. Letts.*, **31**, 588 (1975).
18. M. R. Philpott, *J. Chem. Phys.*, **59**, 4406 (1973).
19. G. C. Morris, *J. Mol. Spec.*, **18**, 42 (1965).
20. V. Hymowitz, Ph.D. Thesis, University of California, San Diego, 1975.
21. M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, England, 1954), p. 248.
22. T. G. McLaughlin and L. B. Clark, *Chem. Phys.*, **31**, 11 (1978).
23. L. B. Clark, *Chem. Phys.*, **5**, 484 (1974).