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Second-Order Stark Shifts in the Optical Spectrum of Anthracene in a Naphthalene Crystal†

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The O—O band of the spectral transition to the $^1B_{2u}$ excited state of anthracene in a naphthalene host crystal has been studied by Stark modulation. The transition shifts to lower energy in the electric field with a quadratic field strength dependence. Stark shifts normalized to an applied field of 10^5 V/cm along the a^*, b, and c^* axes were measured to be 4.8 ± 1.3, 15.2 ± 1.7, and $44.1 \pm 3.0 \times 10^{-3}$ cm^{-1}. The elements of the polarizability difference tensor between the ground and excited states have been computed from these shifts for a series of local field approximations. The closest agreement between the resulting trace of the polarizability difference tensor and previous experimental measurements of this quantity is obtained with the less anisotropic local fields. The use of an "exact point dipole" local field yields the poorest agreement and this is suspected to result from the breakdown of the point dipole approximation. The most logical choice of the local field tensor (calculated from the ground state molecular polarizability and bulk crystal susceptibility) yields polarizability difference tensor elements of 42 ± 3, 24 ± 5, and 2 ± 2 Å^3 for the long, short, and normal symmetry axes of naphthalene.

1. INTRODUCTION

The Stark effect on the spectroscopic transition energy of guest molecules substitutionally oriented in host molecular crystals has been used in the past to extract information about the charge distribution in excited electronic states. The majority of these studies have focused on the determination of excited state dipole moments of polar guests dispersed in non-polar host crystals via the first order Stark splittings of their sharp vibronic transitions at cryogenic temperatures.[1,2] More recent experiments[3,4] on crystals composed of small non-polar molecular species that undergo changes of internal

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nuclear geometry upon excitation have similarly yielded excited state dipole moments. The latest extension of this technique has been the realization of earlier predictions[1] that the polarizability anisotropies in excited electronic states can be obtained from measurement of second order Stark shifts. Such measurements were reported recently in the spectra of pentacene and tetracene[5,6] in mixed crystals. The purpose of the present paper is to report observations of the electric field induced shifts of the O—O band of the $^1B_{2u}$ state of anthracene in a naphthalene host crystal at 1.6K.

Since anthracene is non-polar in both its ground and $^1B_{2u}$ excited state,[7] the first nonzero contribution in the field induced correction to their energies derives from their polarizabilities. Up to second order the shift in energy of the spectral transition, neglecting reaction field effects, is given by:

$$\Delta\varepsilon(B_{2u} \leftarrow A_g) = -\tfrac{1}{2}\mathbf{d}\cdot\mathbf{E}\cdot\Delta\boldsymbol{\alpha}(B_{2u} \leftarrow A_g)\cdot\mathbf{d}\cdot\mathbf{E}$$

where $\Delta\boldsymbol{\alpha}(B_{2u} \leftarrow A_g)$ is the polarizability *difference* tensor between the ground and excited states involved in the transition, **E** is the macroscopic electric field, and **d** is a local field tensor relating the macroscopic fields to the internal fields experienced by the guest molecule.

A proper analysis of the anisotropy of the Stark shifts along orthogonal crystal directions yields all of the diagonal components of the polarizability difference tensor in the chosen axis system. The diagonal components in the system of molecular symmetry axes can be obtained from the transformation: $\Delta\boldsymbol{\alpha}$ (molecular) $= \mathbf{R}\cdot\Delta\boldsymbol{\alpha}$ (crystal) $\cdot\,\mathbf{R}^t$ where $\mathbf{R}$ and $\mathbf{R}^t$ are the matrix of direction cosines and its transpose that rotate the crystal axes into the molecular axes.

In addition to the shift, a field induced alteration of the transition moment and subsequent change in the oscillator strength of the transition can possibly occur. In practice, observations of this effect have been limited to systems exhibiting closely lying states having appreciable oscillator strength between them.[8] Since the nearest opposite parity electronic state of anthracene ($^1B_{1g}$) has been calculated[9] to lie more than 10,000 cm^{-1} to higher energy than the $^1B_{2u}$ state, it was doubtful that this phenomenon would be observed. Electric field induced mixing with the closer lying $^1B_{1u}$ state is a higher order process whose spectral manifestations would be negligible.

2. EXPERIMENTAL

a. Sample preparation

High purity anthracene and naphthalene were prepared by potassium fusion of reagent grade material followed by extensive zone refining ($\approx$ 100 zone passes).

Mixed crystals were grown by the Bridgeman technique. During their growth considerable rejection of the anthracene occurred, necessitating the use of starting concentrations of approximately 10^{-3} mole/mole. Samples were taken from the lower portion of the boule where concentrations were estimated from the observed optical densities to be about 10^{-5} mole/mole.

All Stark measurements were performed with the applied field lying parallel to a principal axis of the dielectric tensor (and optical indicatrix). These directions were located with a polarizing microscope by identification of their conoscopic interference figures. In naphthalene (monoclinic, $P2_1/a$),[10] the principal dielectric axes (henceforth called a^*, b, and c^*) correspond to the acute bisectrix, optic normal, and obtuse bisectrix respectively.[11] The relation between the a^*, c^* and crystallographic a and c axes is diagrammed in the inset of Figure 2 and was determined from earlier measurements in this laboratory (see Ref. 11).

Only crystals possessing excellent cleavage characteristics and showing no signs of gross physical defects were used in this investigation.

From the quality of the observed interference figures along three mutually perpendicular directions of each sample, we estimate the maximum misalignment of the applied field from the stated directions to be 2°.

The oriented crystals were cut to form rectangular plates of the appropriate dimensions and inserted in the Stark capacitor between transparent SnO[12] coated quartz electrodes. This assembly was placed in an optical dewar, filled with liquid helium, and pumped below the lambda point to 1.6K.

b. Spectral measurements

Phase sensitive detection of the transmitted light intensity modulated by either a square wave bipolar electric field[13] or a mechanical chopper was used to determine the Stark and zero field spectra. This apparatus has been described in previous papers.[3,14] A modification employed in this experiment was the introduction of a computer interfaced Spex Ramacomp Spectrometer which enabled signal averaging to be performed. This was essential for the measurement of shifts of less than 10^{-3} cm^{-1}, otherwise instability in the xenon arc output intensity completely masked any modulated transmission signals.

The model 1402 double monochromator in this system contained two 1800 grove/mm holographically ruled gratings whose coupled angular rotation was controlled by a computer driven stepper motor. Signal averaging was accomplished by repetitively scanning over the spectral region of interest and adding the present modulation signal to the results of previous scans already acquired by the computer. A block diagram of this experimental apparatus is shown in Figure 1. The reproducibility of the spectrometer drive mechanism

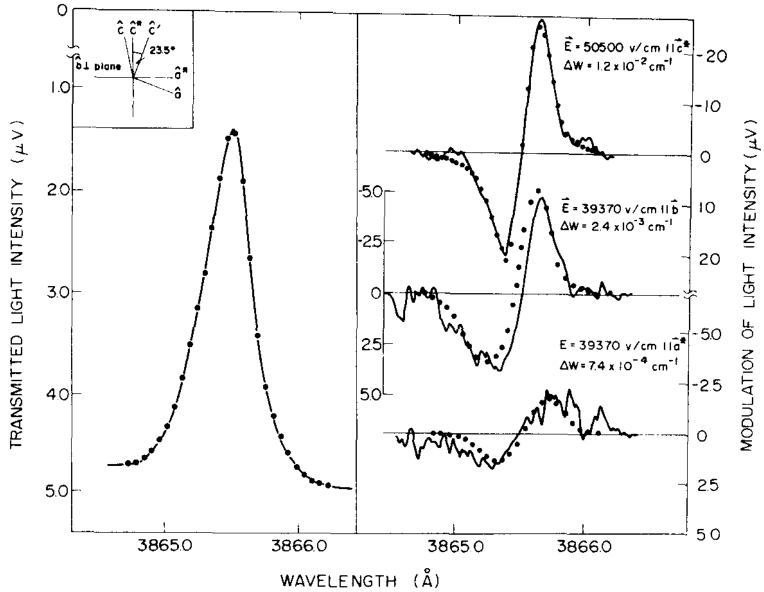

FIGURE 1 *Left Half*: Zero field spectrum of the electronic origin band of the ${}^1B_{2u}$ state of anthracene in a naphthalene host crystal. The orientation of the $\hat{a}^*$ and $\hat{c}^*$ axes in the *a,c* plane is shown in the upper left of the figure. *Right Half*: Stark modulation spectra of this band for each of the principal dielectric axes of the crystal.

in relocating the starting position of the spectral range was measured to be 0.02 cm^{-1}. This error is insignificant considering that the experimental spectral resolution was 0.3 cm^{-1}.

Of course the "effective" resolving power of the modulation technique is much greater than that set by the spectrometer slitwidth. With the above system the minimum discernable shift was calculated to be 3×10^{-4} cm^{-1}. This value was determined by assuming a signal to noise ratio of 2:1 in the modulation spectrum of a Gaussian contour having a fwhm of 1 cm^{-1}.

3. RESULTS

Illustrated in Figure 1 (solid lines) are a typical zero field spectrum and a Stark modulated spectrum for fields applied parallel to each of the three principal dielectric axes. The c^* axis modulated spectrum is the result of an individual scan while the a^* and b axis spectra represent the normalized sum of 100 and 25 scans respectively. These modulated signals mimic the shape of the first derivative of the transmission spectrum, indicative of a shift of the transition to lower energy. The integrated areas of their optical density counterparts are all zero within the uncertainty set by their signal to noise ratios. This is consistent with a conservation of transition oscillator strength in the field as expected for such a transition. Even with the assumption of transition moments of 1*D*, the calculated change of intensity due to mixing with the $^1B_{1g}$ is only 10^{-8} of the zero field intensity.

The field induced shifts were determined by two independent methods. In the first approach the shift was computed as the first moment of the modulated optical density normalized by the integrated area of the zero field optical density. A second method involved computer fitting the zero field lineshape to a functional form and then simulating the modulation spectrum under the assumption of a field induced shift. A least squares analysis (with the shift as a continuously adjustable parameter) was used to find the best agreement between computed and experimental spectra. Shifts thus obtained were found to be identical to those derived from the method of moments, indicating the absence of field induced broadening. The resulting fitted zero field and simulated modulation profiles are represented by the filled circles in Figure 1.

Stark shifts on the c^* axis obtained as a function of electric field strength are plotted in Figure 2 versus the square of the applied field. Over the range studied, the shift is seen to obey a quadratic field dependence as expected for a polarizability effect. From the slope of this plot and the fixed field measurements on the a^* and b axes we obtain the normalized results presented in Table I. These quantities reflect the accurately determined experimental shifts

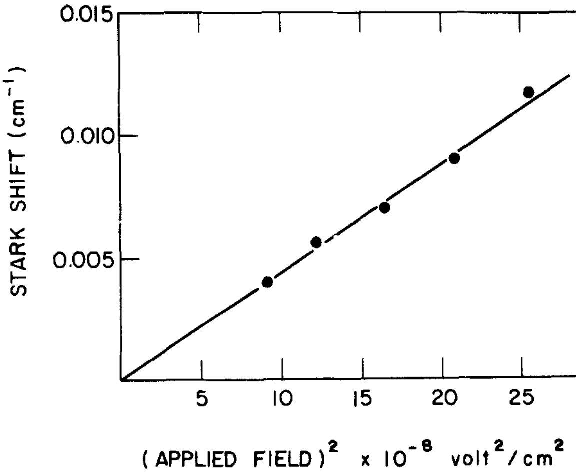

FIGURE 2 Plot of the Stark shift versus the square of the applied electric field parallel to the $\hat{c}^*$ direction of the crystal.

TABLE I

Observed Stark shifts quadratically normalized to an applied field of 10^5 Volts/cm for the O—O transition of the ${}^1B_{2u} \leftarrow {}^1A_g$ transition of anthracene in naphthalene

Electric field direction	Shift ($\times 10^3$ cm^{-1})
a^*	-4.8 ± 1.3
b	-15.2 ± 1.7
c^*	-44.1 ± 3.0

and are independent of any approximations used in the interpretation of the Stark effect in this system.

4. DISCUSSION

From the three shift measurements and certain assumptions, see below, one can determine the complete anisotropy of the polarizability difference tensor between the ${}^1B_{2u}$ and ${}^1A_g$ ground states. Such a quantitative interpretation of our results requires knowledge of both the orientation of the anthracene with respect to the crystallographic axes, and the local electric fields as a function of the macroscopic field. In addition the form of the polarizability for an anthracene molecule in a naphthalene host must be known.

Anisotropic EPR studies have accurately determined the direction cosines between the principal directions of the fine structure tensor of the anthracene guests and the crystallographic axes of naphthalene,[15] (see Table II). The guest orientation is found to differ only very slightly from that of the host suggesting only minimal distortion if any at all of the host lattice. However the absence of an exact relation between the applied field and that experienced at the molecular site prevents an unequivocal determination of the polarizability difference tensor. We will assume in this work that the principal

TABLE II

Direction cosines for anthracene in naphthalene

	a^*	b	c^*
L	0.0552	0.1167	-0.9921
M	0.4235	0.8965	0.1299
N	-0.9041	0.4274	0.0007

axes of the triplet anthracene fine structure tensor are also those of the polarizability of ground state anthracene in naphthalene. This amounts to assuming the oriented gas model or that the molecular symmetry is D_{2h}.

The main source of error in Stark effect studies of dense phases is in the estimate of the local field. A Lorentz field is valid only for the case of either a cubic array or a random distribution of induced dipoles. This latter fact justifies its use in the analysis of a Stark effect in a rigid glass. Of course such Stark measurements do not yield values for the individual tensor elements. Local field effects in anisotropic media are more difficult to predict. In the past a modified Lorentz approximation was employed in which it was assumed that the Lorentz formula was separately applicable for fields directed along each of the principal dielectric axes of the crystal. Recently "exact" calculations of local fields in non-cubic crystals have indicated that serious errors can result from the use of this approximation. However these calculations are themselves susceptible to an uncertainty caused by the assumption of point dipoles.

We have analyzed our data using several of the existing local field tensors so that we might obtain further insight into their reliability.

The results of recent theoretical and experimental studies of the polarizability of anthracene are given in Table III. Except where noted all quantities correspond to the trace of the difference between the polarizability tensors of the ${}^1B_{2u}$ excited and the ${}^1A_g$ ground state. The experimental values

TABLE III

Reported theoretical and experimental data on the polarizability difference between the ground and ${}^1B_{2u}$ state of anthracene

Technique	$\Delta\alpha_{LL}$	$\Delta\alpha_{MM}$	$\Delta\alpha_{NN}$	$tr(\Delta\alpha)$	Other
Theory (a)	—	—	—	84	
Theory (b)	—	—	—	101.4	
Theory (c)	63.0	0.38	−0.01	63.4	
Theory (d)	65.8	1.54	0.0	67.3	
Theory (e)	80.3	10.9	0.0	91.2	
Theory (f)	110	12.9	0.0	123.0	
Experiment (g)	—	6 ± 4	—	50.1 ± 3	
Experiment (h)	—	—	—	45	
Experiment (i)	—	8 ± 9	—	50 ± 7	
Experiment (k)					$tr(\Delta\alpha) - \frac{1}{2}\Delta\alpha_{MM} = 36 \pm 3$
Present work	42 ± 3	24 ± 5	2 ± 2	68 ± 4	$tr(\Delta\alpha) - \frac{1}{2}\Delta\alpha_{MM} = 56 \pm 3$

[g] Stark effect in fluid cyclohexane.[27]
[h] Solvent shift measurements.[24]
[i] Stark effect in 3-methyl pentane glass.[29]
[k] Stark effect in a polystyrene matrix.[34]

originate from solvent shift measurements and Stark experiments in rigid glasses and solutions. The traces obtained by Bakshiev (45 Å^3 – Stark effect in solution), and Mathies (50 ± 7 Å^3 – Stark effect in a rigid glass) are in excellent agreement. They are also reasonably consistent with the theoretical predictions of Mathies (63.4, 67.3 Å^3). These considerations based on experiments in isotopic media suggest that the trace of the polarizability difference tensor is likely within the range of 50 ± 10 Å^3.

The components and traces of the polarizability difference tensor obtained from our Stark shift data are presented in Table IV together with the local field tensors (transformed into the molecular principal axis system) from which they were computed. Considerable variation among the polarizabilities determined from these different approximations is found, but this is not surprising because the observed effect is quadratic in the applied field.

The polarizability of a species is strictly speaking a function of its local

TABLE IV

Components of the polarizability difference tensor and its trace calculated from several different local field approximations

Local field tensor	$\Delta\alpha_{LL}$	$\Delta\alpha_{MM}$	$\Delta\alpha_{NN}$	$T_r\Delta\alpha$
$\begin{pmatrix} 1.675 & & \\ & 1.675 & \\ & & 1.675 \end{pmatrix}$ M. F. Vuks *et al.*[16]	51 ± 4	20 ± 4	2 ± 2	73 ± 3
$\begin{pmatrix} 1.42 & & \\ & 1.62 & \\ & & 1.81 \end{pmatrix}$ Anisotropic Lorentz	48 ± 4	24 ± 5	5 ± 5	77 ± 4
$\begin{pmatrix} 1.59 & 0 & -0.54 \\ 0 & 1.89 & 0 \\ -0.28 & 0 & 1.13 \end{pmatrix}$ Ewald Sum + Susceptibility[35]	120 ± 10	18 ± 3	−3 ± 2	134 ± 5
$\begin{pmatrix} 1.44 & 0 & -0.45 \\ 0 & 1.64 & 0 \\ -0.27 & 0 & 1.93 \end{pmatrix}$ Molecular Polarizability and Crystal Susceptibility[23]	42 ± 3	24 ± 5	2 ± 2	68 ± 4
$\begin{pmatrix} 1.63 & -0.219 & -0.623 \\ 0.076 & 1.94 & -0.077 \\ -0.3 & -0.025 & 1.16 \end{pmatrix}$ Exact Point dipole calculation[17,18]	111 ± 10	20 ± 4	−5 ± 4	126 ± 6
$\begin{pmatrix} 1.32 & -0.006 & -0.020 \\ -0.01 & 2.02 & 0.095 \\ 0.023 & 0.071 & 1.53 \end{pmatrix}$ Averaged Lorentz Factor Tensors[21]	69 ± 5	14 ± 3	8 ± 5	91

environment. However intermolecular interactions in molecular crystals are usually sufficiently weak that individual molecular identities are retained. Consequently effective molecular polarizabilities in a crystal are not expected to differ radically from their vapor phase or solution values.[17] This concept is not borne out by the results presented in Table IV. In fact polarizabilities computed from the exact point dipole treatments of the local field exhibit the greatest deviation from the aforementioned values from isotropic experiments. These point dipole calculations of local fields have been criticized[21, 22, 32, 33] as being too highly anisotropic. This is evidenced by their failure to predict accurate effective ground state molecular polarizabilities.[22, 33] Additional support of this is found in their inability to predict directions of transition moments from polarized mixed crystal absorption spectra.[32] Excessive anisotropy in these calculated local fields has been suggested to result from the failure of the point dipole approximation.[22] In molecular crystals the size of the molecules is comparable to their separation and hence they are unlikely to respond to external fields precisely like an array of point dipoles.

Several theoretical attempts have been made to moderate the calculated local field anisotropy by using Lorentz factor tensors computed from the average of the individual sublattice Lorentz tensors.[21, 22, 32] This procedure resulted in a significant improvement in the calculation of effective molecular polarizabilities. Likewise in a reanalysis[21] of the Stark shift data for pentacene and tetracene the use of a local field derived from these averaged Lorentz factor tensors was suggested to yield better polarizability differences than either the anisotropic Lorentz, or the exact point dipole fields. The results of the analysis of our own data employing modified Lorentz factor tensors[22] is presented in the last row of Table IV. The resulting polarizabilities are close to those obtained from previous experimental studies in isotropic systems but nevertheless deviate from them by more than the experimental uncertainties. Closer agreement between our results and the isotropic ones is obtained with the Vuks isotropic and anisotropically modified Lorentz tensors. However neither of these local fields appear to have a firm theoretical basis.

The best agreement is obtained with the polarizabilities derived from a local field calculation of Munn and Williams[23] (using their corrected tensor of Ref. 33). In their analysis the local field is computed from the relations between the macroscopic and microscopic polarizations induced by an applied field. The polarizations are obtained from the measured dielectric permittivities, molecular polarizabilities, and unit cell volume. This technique accomplishes the spatial averaging (that was shown to be essential) without having to evaluate lattice dipole sums. In view of the fact that use of this tensor unifies experimental studies from isotropic and anisotropic media we propose it as the preferred internal electric field in the mixed crystal system.

CONCLUSIONS

The exact point dipole treatments of the local field prove to be inadequate in describing the effect of an electric field on the absorption spectrum of anthracene in naphthalene. Less anisotropic approximations yield polarizabilities that are much closer to previous experimental results from isotropic media. A local field tensor calculated solely from experimentally measured susceptibilities and molecular polarizabilities provides a reasonable description of the relevant manifestations of the internal field in naphthalene. We find that the components of the differences in polarizability between the ${}^1A_g$ ground state and ${}^1B_{2u}$ excited state of anthracene to be $\Delta\alpha_{LL} = 42 \pm 3$, $\Delta\alpha_{MM} = 24 \pm 5$, and $\Delta\alpha_{NN} = 2 \pm 2\,\text{Å}^3$.

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12. Objections have been raised concerning the use of SnO coated electrodes by the authors of the pentacene and tetracene work.[5,6] Their measurements with these electrodes yielded smaller shifts than those made after switching to stainless steel electrodes (see Figure 2 of Ref. 6). However in the present work no significant differences between these two electrodes were found. Our preference for the SnO electrodes was determined solely by consideration of light collection efficiency and signal to noise requirements.
13. Unipolar modulation was found to reduce the observed shifts by almost a factor of two. This phenomenon was likewise observed by the authors of Ref. 6, and it is presumably due to space charge buildup resulting in partial cancellation of the applied field. Bipolar modulation which altered the sign of the applied field upon successive periods of application appeared to overcome this problem.
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