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THE SECOND-ORDER STARK EFFECT ON THE $^1B_{2u}$ ELECTRONIC ORIGIN OF TETRACENE AND PENTACENE IN p-TERPHENYL

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The electric field induced shift of the electronic origin of the lowest B_{2u} singlet state of tetracene and pentacene in p-terphenyl at 1.8°K has been measured. From this shift we calculate the difference in polarizability of this state and the ground state along the long molecular axis to be 4.5 ± 0.5 Å³ for tetracene and 19.8 ± 1.0 Å³ for pentacene ($F_{c'} = 0.505 F_{eff}$). The ratio of these tensor elements $(\Delta\alpha)_{zz}$ for pentacene and tetracene is found to be 4.4 ± 0.6 and is independent of the local field approximation.

1. Introduction

Electric field effect measurements on polar molecules in oriented solids at 4.2°K have been very successful in probing the electron density distribution in excited states of organic molecules [1]. These measurements have shown that dipole moment changes of individual vibronic states can be determined very accurately and that such studies can be helpful [2, 3] for the assignment and analysis of such states as well. Another quantity extractable from electro-optical measurements are excited state polarizabilities (if ground state polarizabilities are known) and a great deal of work has been done in obtaining such quantities [4–7].

From a theoretical point of view these quantities are also of some interest as they provide testing material for molecular wavefunctions. Up to now, electro-optical studies for determining polarizabilities only have been reported on solutions, glasses and films. Such studies therefore can only provide *traces* of the quantities of interest. Such a situation is unsatisfactory to some extent, as one is really interested in the anisotropy of the polarizability and transition polarizability tensor of each vibronic level of a particular electronic state.

In this paper we report the first high-resolution electro-optical measurement of these anisotropic quantities on the electronic origin of the lowest $^1B_{2u}$ state of tetracene and pentacene in a mixed crystal with terphenyl at 1.8°K. Our experiments yield the difference in polarizability of the $^1B_{2u}$ state with the ground state along the long molecular axis. No indication of electric field induced intensity of this state has been observed.

Finally we discuss experimental conditions for and future prospects of these high-resolution electro-optical experiments.

2. Experimental

The p-terphenyl used as a host crystal was purified by zone refining and single crystals doped with tetracene and pentacene (10^{-6} molar) were grown from a temperature controlled Bridgeman furnace. p-terphenyl crystals are monoclinic [8] ($P2_1/a$) at room temperature with 2 molecules in the unit cell. The quality and orientation of the crystals was checked with a polarizing microscope. Crystals of about 1 mm thickness were mounted on their cleavage planes (ab) between transparent electrodes (pyrex discs coated with tin oxide on one side). The optical measurements were performed on a 3/4 meter 1702 Spex with a resolution of about 0.5 cm⁻¹ at 17 000 cm⁻¹ in the second order under the conditions used.
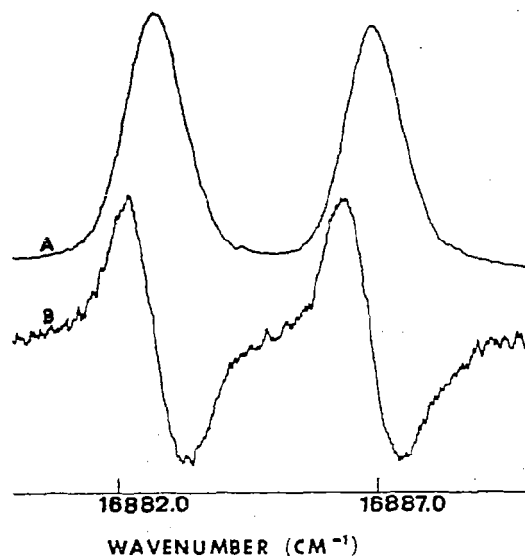
Fig. 1. Unpolarized absorption spectrum of a mixed crystal of pentacene in p-terphenyl (10^{-6} molar) at $1.8°$K. Fig. 1A shows the doublet origin near 16 884 cm^{-1} without electric field. Fig. 1B shows the absorption spectrum as detected by a lock-in amplifier at twice the Stark modulation frequency. The ac field was 65 kV/cm parallel to c'.

We have used two different techniques in detecting the second-order Stark effect.

(1) ac modulation (118 Hz) of the electric field with detection at twice the modulation frequency.

(2) A photoncount technique where the number of photons at a certain fixed frequency in the absorption is counted in and out of an electric field. These numbers are added to a plus—minus counter. The electric field being of a bloc form, was driven by a 1 Hz modulator (stability better than $1:10^6$) that also commanded the counter.

3. Results and discussion

In fig. 1A the origin absorption spectrum of pentacene in a p-terphenyl crystal at $1.8°$K is shown. The doublet splitting is 4.2 cm^{-1} and we find other lines at 123.0 and 181.9 cm^{-1} to the blue from the lowest observed absorption at 16 882.7 cm^{-1}. As fluorescence is observed from all these lines we have interpreted them as electronic origins of different pentacene sites in a p-terphenyl crystal lattice. The site

splittings observed here are really enormous and, further, it is surprising that the absorption spectrum is totally avoid of the phonon sidebands which are so common in other mixed crystal systems of this kind [9, 10].

The lines observed are also very sharp (0.9 cm^{-1}) so that electron—phonon coupling seems to be very small in this case. We feel that this point deserves further examination. Comparing molecular sizes of pentacene and p-terphenyl we expect that pentacene will enter p-terphenyl substitutionally with the long axes of the molecules being parallel. Polarized absorption measurements on the bc' crystal face indicate that all electronic origins are almost exclusively b-polarized, in accordance with the expected short-axis (B_{2u}) polarization of the lowest spin-allowed electronic transition in pentacene [11]. These measurements thus also confirm the expected alignment of the pentacene molecules in the p-terphenyl crystal lattice. This fact is pertinent to the interpretation of our electric field effect measurements.

Introducing now the electric field as a perturbation on molecular wavefunctions of a nonpolar molecule we find that two things happen.

(1) An energy shift of each vibronic level

$$\Delta E = -\tfrac{1}{2} F \cdot \alpha(\kappa\mu) \cdot F ,$$

with $\alpha(\kappa\mu)$ being the (symmetric) polarizability tensor of level $|\kappa\mu\rangle$ and F the local electric field.

(2) A change in the transition moment. This is normally expressed as a perturbation series in F in the following way

$$m_{\kappa\mu}(F) = m_{\kappa\mu}(0) + A \cdot F + F \cdot B \cdot F ,$$

where A and B are the transition polarizability and transition hyperpolarizability tensors of second and third rank, respectively. Expressions for A and B, correct up to second order in the electric field, have been obtained from perturbation theory and can be found in ref. [4]. In general one thus expects a shift and a change in intensity of a vibronic line under the influence of an electric field.

We have studied the effect of an electric field on the sharp absorptions of tetracene and pentacene in a p-terphenyl crystal at $1.8°$K. In this paper we only report results for the electric field parallel to the crystal c' axis, which is almost parallel to the long axes of the host (and guest) molecules (L $\wedge$ C' = $16°$).
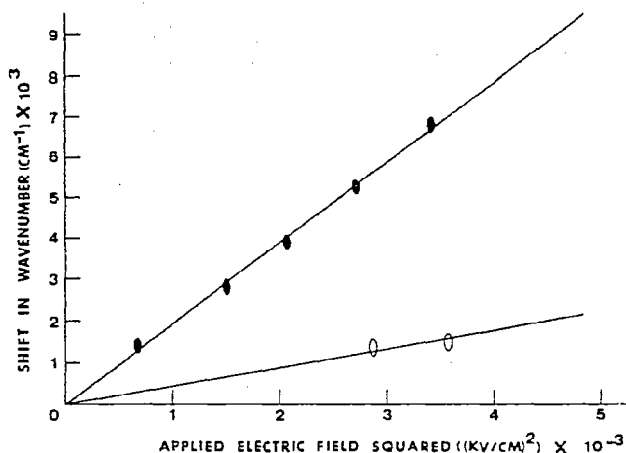
Fig. 2. Stark shifts of the pentacene $^1B_{2u}$ origin (solid ellipses) at 16 883 cm^{-1} and tetracene $^1B_{2u}$ origin (open ellipses) at 20 274 cm^{-1} as a function of the square of the applied electric field. The electric field is applied parallel to the crystal c' axis.

In fig. 1B we see the effect of an electric field on the pentacene absorption spectrum as detected by a lock-in amplifier. These signals were produced with an ac field of 65 kV/cm (top−top) applied along the crystal c' axis and detected at twice the modulation frequency. These signals are interpreted as being due to electric field induced shifts and the intensity of the signals corresponds for both lines to a shift of 8×10^{-3} cm^{-1}. With the photon-count technique we have verified the quadratic nature of the shift with applied electric field and this is shown in fig. 2. This result has been obtained at the high-frequency side (at half height) of the absorption at 16 882.7 cm^{-1}. We observe at this wavelength an increase in the number of photons transmitted in an electric field. The absorption thus shifts in an electric field to lower energy. This is also confirmed by counting the number of photons on the low energy side. By comparing both numbers we conclude that at this moment we are unable to detect variations in the transition moment induced by the electric field.

From fig. 2 we calculate with the Lorentz approximation ($F_{eff} = 1.98\,F_{c'}$, where $F_{c'}$ is the applied field along c')

$$(\Delta\alpha)_{c'} = (18.3 \pm 0.9) \times 10^{-24} \text{ cm}^3 \,.$$

Assuming that $(\Delta\alpha)_{yy} < (\Delta\alpha)_{zz}$ [$y(B_{2u})$ short axis, $z(B_{1u})$ long axis] we find for

$$(\Delta\alpha)_{zz} = (19.8 \pm 1.0) \times 10^{-24} \text{ cm}^3 \;(F_{eff} = 1.98\,F_{c'}) \,.$$

This value of $(\Delta\alpha)_{zz}$ for pentacene is much smaller than the corresponding quantity in tetracene* $(\Delta\alpha)_{zz} = (59 \pm 6) \times 10^{-24}$ cm^3) obtained from room-temperature electro-optical studies by Liptay et al. [7]. Simple π-electron calculations performed by Trsic et al. [12] also yield a much higher value for $(\Delta\alpha)_{zz} \approx 100$ Å^3 for the lowest $^1B_{2u}$ excitation of pentacene.

These facts prompted us to also study the electric field effect on the $^1B_{2u}$ electronic origin of the tetracene absorption in p-terphenyl. The optical absorption spectrum of this mixed crystal system at 4.2°K has been analyzed by Kruse and Small [9] and this study confirms the expected alignment of the tetracene molecule in the p-terphenyl crystal lattice. We have only analyzed the effect of an electric field on the doublet electronic origin near 20275 cm^{-1}. The results of this study are also shown in fig. 2. From these data we calculate $(\Delta\alpha)_{zz} = (4.5 \pm 0.5) \times 10^{-24}$ cm^3 for tetracene using the Lorentz approximation ($F_{eff} = 1.98\,F_{c'}$). The ratio of the values $(\Delta\alpha)_{zz}$ for pentacene and tetracene is found to be 4.4 ± 0.6 and this number is independent of the local field approximation.

We hope to obtain a much more accurate value for this ratio by growing mixed crystals of terphenyl that simultaneously contain tetracene and pentacene.

Our results on tetracene thus do not agree with previous results obtained from room temperature electro-optical experiments [5, 7]. At this moment we cannot offer an explanation for this discrepancy. It should be realized, however, that inherent to all electric field experiments the following side-effects occur.

(1) Electrostrictive effect: the application of an electric field results in a volume contraction [13]. This in turn will lead to a change in concentration. By the photon-count technique we have been able to show (see text) that such an effect is of no importance in our mixed crystal system.

(2) Internal pressure effect: this effect, intimately related with the electrostrictive effect, arises through

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* We have assumed here that the out-of-plane change in polarizability on excitation is negligible.

the volume contraction in an electric field. As pressure is known [14] to shift a spectral line to lower energy, this effect thus only tends to *increase* the value of $(\Delta\alpha)_{zz}$.

Without additional knowledge about the size of these effects it is difficult to eliminate them as a possible source of the existing discrepancy. It seems that our method of determining Stark effects on a single vibronic line of a particular state is the most direct one. The only approximation involved in this method, is the Lorentz local field approximation. In a following publication we hope to present the results of a much more detailed determination of *all* the tensor elements of $\Delta\alpha$ for tetracene and pentacene in a mixed crystal with *p*-terphenyl.

4. Conclusion

We have demonstrated the feasibility of detecting second-order Stark effects under high optical resolution on oriented single crystals at low temperature. At present our set up is able to detect light intensity variations of about 0.1% but with some improvements we hope to increase our sensitivity by a factor of ten.

Such a sensitivity and the use of polarized light will enable us to determine all the difference-elements of the polarizability and transition polarizability tensors of a particular state with the ground state.

In the case of nonpolar organic molecules, second-order Stark effects might be dominated by electric field induced mixing with nearby molecular g-states. Such effects might especially become important in azines and ketones with molecular inversion symmetry.

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