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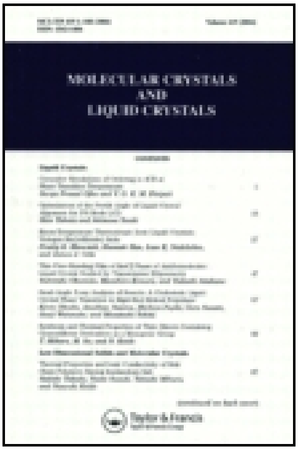

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Photoconductivity in Single Crystal Carbazole

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AC photoconductivity of single crystal carbazole has been studied a photoconductive response lag was observed with respect to the optical absorption spectrum. Spectral distribution of the photoconductivity is found to be dependent on the geometrical arrangements of the electrodes.

1. INTRODUCTION

The photoconductive properties of carbazole are of considerable interest in light of the high photoconductive sensitivity of poly N-vinil-carbazole. Carbazole forms orthorhombic crystals, with four molecules per unit cell (Fig. 1). The carbazole molecule has C symmetry. Therefore, two types of transitions, are allowed in the one photon absorption spectra of the carbazole molecule: transitions polarized along the short molecular direction (A1 symmetry) and those polarized along the long molecular direction (B1 symmetry). The molecular electronic states of carbazole have been extensively studied.[1–12] It is established that transitions near 340 nm and 240 nm are short axis polarized while transition at 290 nm, 250 nm, and 230 nm are "long axis" polarized (Fig. 2). In the crystal the long "axis" of the molecule lies exactly parallel to the c-axis in the crystal. The short molecular axis forms an angle of approximately 60 degrees with the a crystallographic axis.

Crystals grown by sublimation at thicknesses suitable for transmittance spectra measurements usually have a well-developed *ab* face. Hence, only transitions polarized along the short axis of the molecule will appear in the crystal spectra at normal incidence of light on the sublimation flake. It was shown[13] that in the crystal the absorption due to the low energy long axis polarized transition near 300 nm is greatly diminishes due to local field effect. The intensity distribution in the absorption spectra of the carbazole crystal can be obtained from transmission spectra of a carbazole polycrystalline powder or from transmittance spectra of a sublimation flake at oblique incidence of light on the surface of the flake (Fig. 3). As displayed in the figures the absorption starts near 340 nm, diminishes in the region between 320–260 nm and increases up to vacuum UV region.

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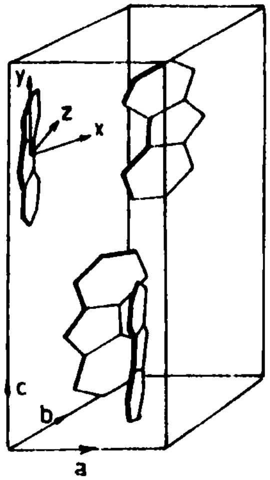

FIGURE 1 Unit Cell of Carbazole Crystal.

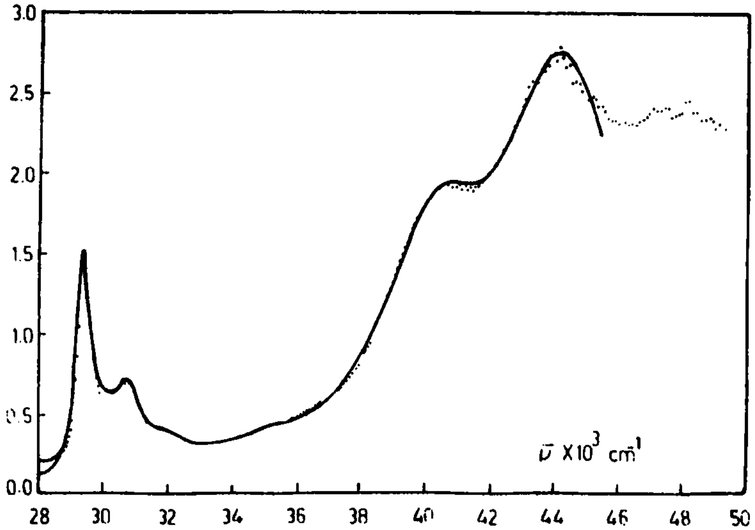

FIGURE 2 Long Axis Polarized Absorption.

2. EXPERIMENTAL

2.1. Sample Preparation

Carbazole single crystals were prepared by sublimation of purified sample at 175 °C and allowed to crystallize on the surface of a watch glass which is fitted on top of a

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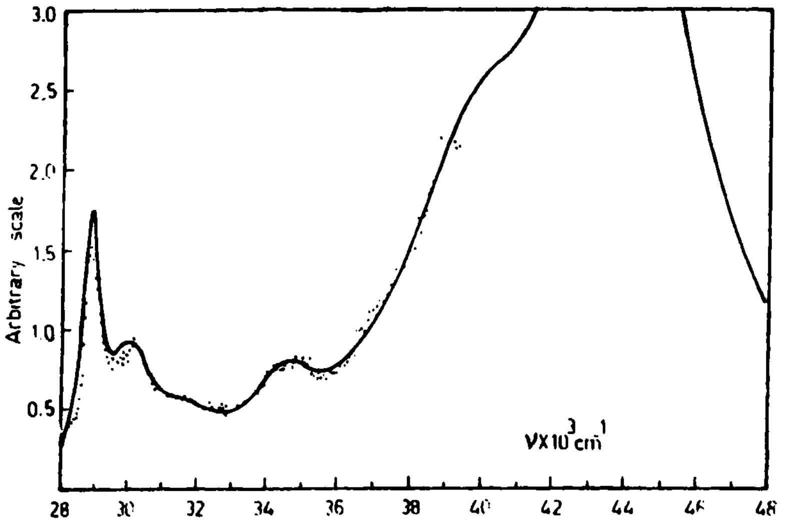

FIGURE 3 Oblique Illumination Absorption.

beaker. Crystal flakes grown in this method contain *ac* crystallographic directions. They were checked using polarized optical absorption measurements (Polycrystalline samples which are grown on top of metal electrodes show the same orientation).

Aluminum stripes 0.1 and 0.3 mm wide and 8 mm long were evaporated on top of Corning 7059 glass or quartz substrates with sample attached. Samples either used in this construction or Indium contacts with identical shape as aluminium stripes evaporated on top of the sample, under 2×10^{-6} torr base pressure.

Measurements were carried out at room temperature in air. Measurements were made at the field strengths of minimum 5×10^3 volts/cm and maximum 6×10^4 volts/cm. In a short term (3–7 days) no measurable changes were found between previous and later measurements. For periods about one month there were drastic decreases in both conductivity and photoconductivity.

2.2. Data Collection

A 60 W deuterium lamp with a quartz lens was used as a light source for measurements between 300–200 nm range. A 300 WXe lamp is used as a light source for measurements between 280–600 nm. The deuterium lamp with Oriel monochromator gives a flux of 2.1×10^{12} photons/cm^2 sec at 240 nm while Xenon with the same monochromator gives 5×10^{14} photons/cm^2 sec at 400 nm. Figure 4 shows the block diagram of the experimental setup used in photoconductivity measurements described in detail elsewhere.[14] Chopping frequency was 13 Hz. Figure 5a shows excitation source spectral intensity distribution for 300–700 nm wavelength interval while Figure 5b shows excitation source intensity distribution for 300–200 nm. Normalization of photoresponse is made using these values.

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3. RESULTS

3.1. Photoconductivity in the 300–400 nm Range

Figure 6 shows photoconductivity of polycrystalline carbazole with top and bottom (Al) electrodes. They follow the absorption curve but with somewhat broadened form and with an energy shift. When only top (Al) electrodes are used the knee at 340 nm

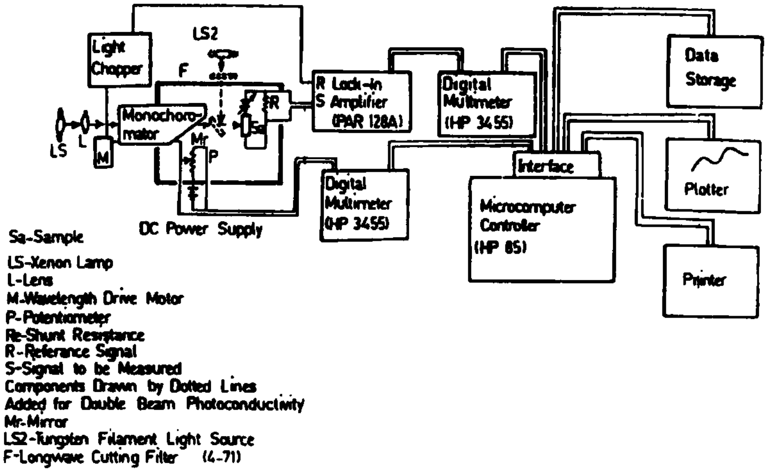

FIGURE 4 Experimental Setup Used in AC Photoconductivity Measurement.

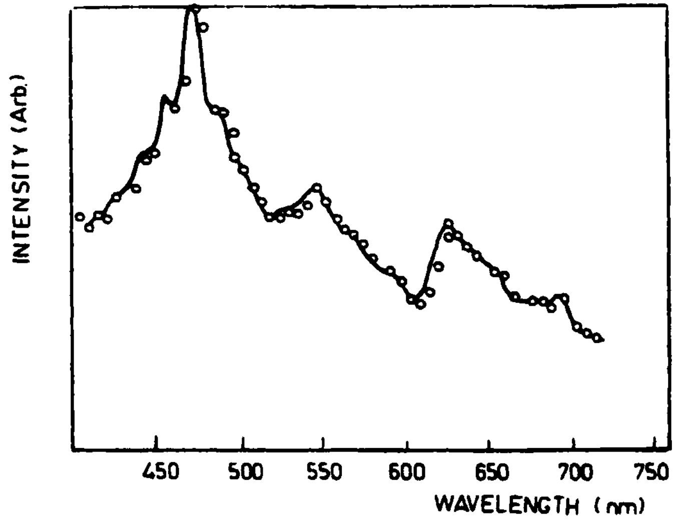

FIGURE 5a Deterium Lamp Source Spectral Energy Distribution.

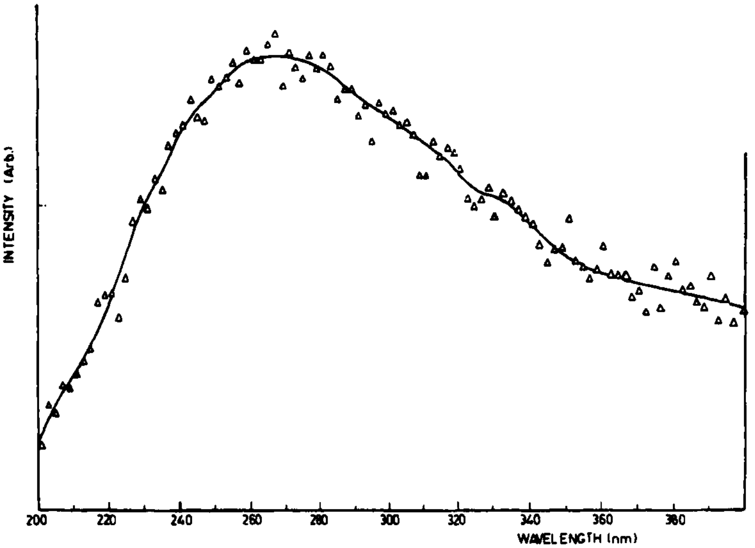

FIGURE 5b Xenon Lamp Source Spectral Energy Distribution.

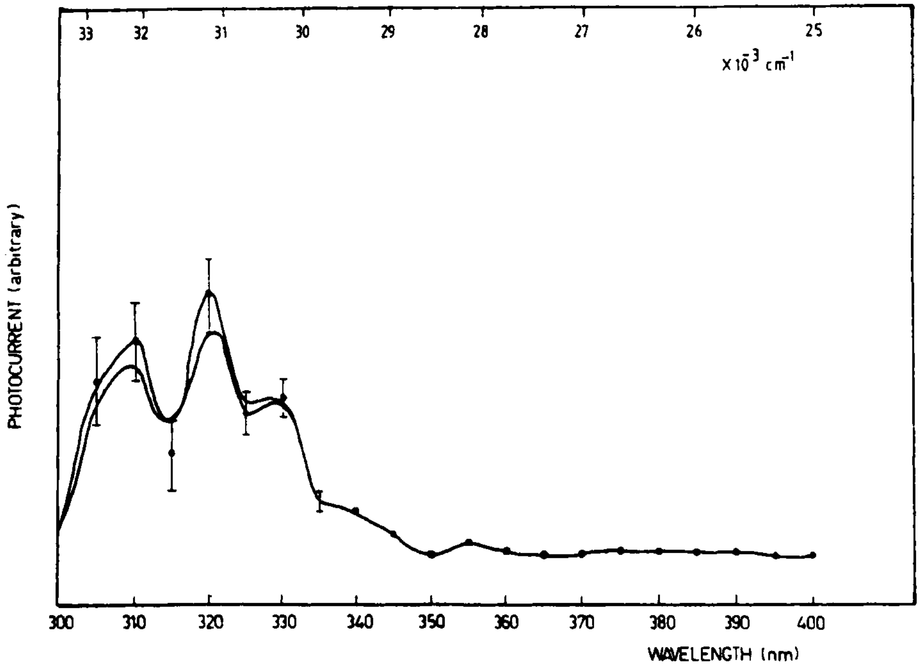

FIGURE 6 Photoconductivity in the 300–400 nm Region.

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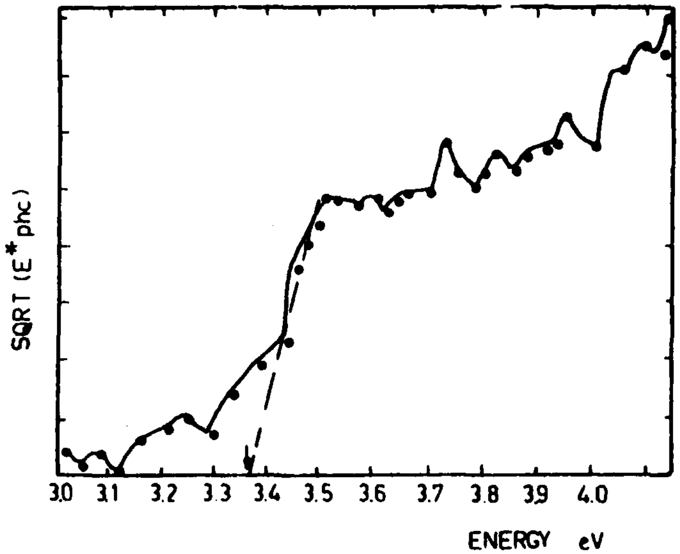

FIGURE 7 Energy Gap Determination.

becomes less pronounced and the ratio of peaks at 310 nm and 320 nm changes. Using single crystal carbazole does not effect the shape of photocurrent versus wavelength curve but it increases the photocurrent an order of magnitude. An interesting feature in this wavelength region at 300–280 nm interval is that even though the absorption coefficient is lower than 320 nm the photocurrent is higher. Figure 7 shows the square root of photocurrent times energy versus energy. From extrapolation of this using a Tauc[15] parabolic band approximation we observe an optical energy gap of 3.4 ± 0.2 eV.

3.2. Photoconductivity in the 30-50000 cm^{-1} Range

Between 30 and 50,000 cm^{-1}, photoconductivity rises steadily. There is a knee around 43000 cm^{-1} and rapidly rises around 42–43000 cm^{-1} and at 44–46000 cm^{-1} it reaches its maximum value. After this value, it decreases. As can be seen from Figure 8, it follows the absorption coefficient with an energy lag. This lag is also seen at higher wavelength as described in section 3.1 Figure 8 shows photoconductivity measurement made with top Indium electrodes. Using bottom electrodes shifted the photoconductivity maximum to higher values. With this configuration $I_{ph} = 0.5 \times 10^{-12}$ amps while the dark current is 7×10^{-12} amps at 100 volts across 0.3 mm gap (3×10^3 Volts/cm). These measurements were done with electrodes on the *ac* plane. Illumination of the sample is oblique (~46°). Excitation intensity was 10^{12} photons/cm^2sec. For the same group of samples with similar dimensions maximum the value of photocurrent ranged from 10^{-10} amps to 10^{-12} amps. High currents were obtained with electrodes which requires high temperature for evaporation (Al, Au).

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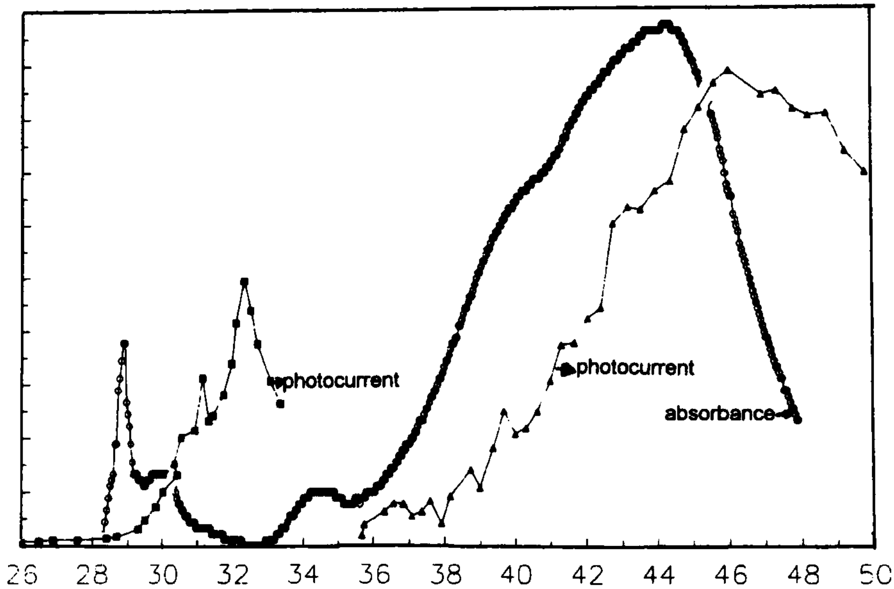

FIGURE 8 The Full Spectrum of Photoconductivity and Absorbance Data.

3.3. Intensity Dependence of Photocurrent

The intensity dependence of photocurrent was found by plotting the photocurrent on a log-log scale when photocurrent expressed as $I_{ph} = I_0 F^{\gamma}$ where I_{ph}:photocurrent, I_0: a constant, F: intensity of light, γ is the exponent. γ is found to be 1.0 ± 0.1. Indicating a monomolecular recombination.[16] We were not able to determine the majority carrier.

4. DISCUSSION AND CONCLUSIONS

From the experimental evidence we presented above, it has been shown that:

a) The spectral distribution of photocurrent follows the absorption coefficient of the carbazole with an energy lag. This lag may be due to the fact that in the order to observe the photocurrent, the excitation energy must be greater/equal to the required excitation energy for optical transition plus exciton energy.

b) Photocurrent vs. wavelength graph also shows broader peaks than the absorption peaks, which in turn can be explained if we accept that recombination of photocurrent occurs via extended states near the absorption edge.

c) Energy gap of carbazole crystals obtained with this method was found to be 3.4 ± 0.2 eV, which can easily be altered with the impurity in the crystal. Since experiments were done in the open atmosphere impurity adsorption/absorption is probable. This value must be taken with precaution.

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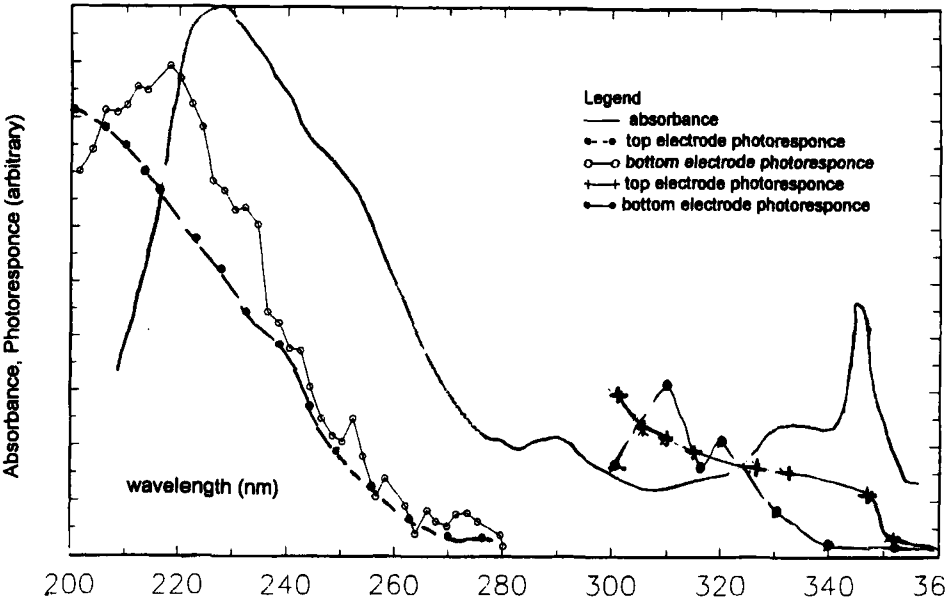

FIGURE 9 Electrode Effects on the Photoresponce of the Carbazole.

d) Electrode effects are shown to be important in obtaining the photocurrent vs wavelength curve and photocurrent magnitude. As expressed in section 3.2, the magnitude of photocurrent is dependent on the electrode solid interface formation. As Figure 9 shows even below the band gap top electrode and bottom electrode gives difference photoresponce. For the bottom electrode case since the sample is obtained on top of pre-evaporated aluminum stripes as a result different type crystallization may occur. Also another effect is oxidation of the electrode after evaporation. To obtain the correct value of photoresponce we suggest non-blocking liquid electrodes.

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