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Photoconductivity in *p*-diiodobenzene†

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Castro and Hochstrasser[1] have measured the singlet-triplet absorption spectrum of crystalline *p*-diiodobenzene and interpreted their findings as evidence of strong vibronic coupling between molecular states. Within the band-theory model of excess charge transport this implies a wide conduction band in comparison to other molecular crystals and hence a relatively long mean-free path and high drift mobility of the excess charge. In light of these implications we have undertaken a preliminary study of *p*-diiodobenzene photoconductivity primarily to measure the drift mobilities. Such data are particularly important at this time because of the uncertain state of charge transport theory in molecular crystals as discussed recently by Glaeser and Berry.[2] Our study has indeed revealed relatively high drift mobilities. In addition we have found (1) that the action spectrum for charge generation bears no apparent relation to the known portion of the absorption spectrum of crystalline *p*-diiodobenzene, and (2) a discontinuity in the mobility *vs* temperature curve which is presently being investigated further.

Eastman 1102 *p*-diiodobenzene was purified by zone refining, recrystallization from absolute ethanol, and zone refining again in the dark. The purified material was crystallized from the melt under argon in a Bridgmann furnace. Two ingots were grown both of which consisted of several nearly-aligned crystals and which cleaved easily. Different crystal samples were prepared with surfaces normal to the three mutually perpendicular crystallographic

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axes. Orientation was done with a polarizing microscope and assignment of crystallographic direction by X-ray diffraction.[3] Most crystal samples were benzene polished which temporarily enhanced the charge carrier production. Photocurrents were generated by light pulses from a modified EG&G Model 49–11 Microflash unit and filtered through a Bausch and Lomb High Intensity grating monochromator. The crystal was mounted in the usual sandwich-type cell. The absolute light intensity was measured with an EG&G Model 580 Radiometer.

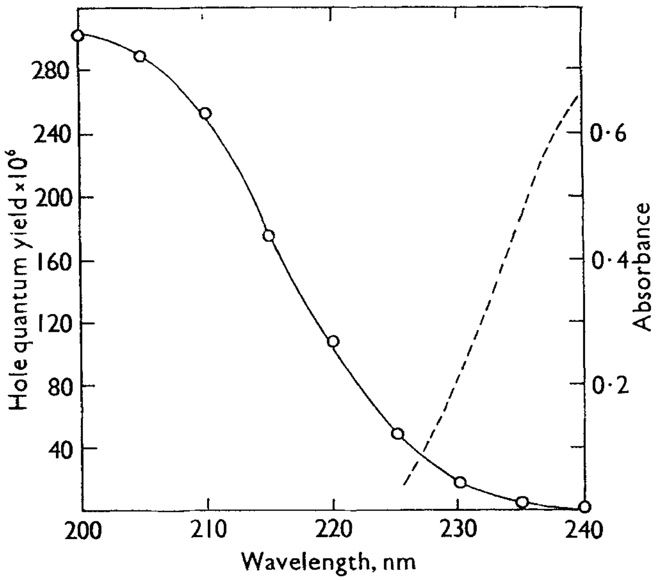

Figure 1. The solid curve is the *p*-diiodobenzene quantum yield for hole generation *vs* wavelength using light with spectral purity of ± 4 nm. The dashed curve is part of the absorption spectrum of *p*-diiodobenzene dissolved in methanol (2.0×10^{-3} M) taken through 0.1 mm of solution. The broad peak occurs at 243 nm.

Hole photocurrent was found at short wavelengths. Shown in Fig. 1 is the action spectrum for a crystal whose surface was an unpolished cleavage plane exposed to air. Although photocurrent was measured at wavelengths slightly below 200 nm, the peak of the action spectrum could not be located because of insufficient sensitivity of the radiometer in this range. No photocurrent was detected above 240 nm and no electron current at all was seen. The onset of photoconductivity at 240 nm is in the UV absorption region which is opaque to convenient spectroscopy. Absorption into the first triplet begins around 380 nm and the spectrum is known only to about 300 nm.[1, 4] The p-diiodobenzene molecular spectrum in dilute solution measured by Burawoy[5] and repeated in this laboratory has an intense peak centered at 243 nm, however. The tail of this peak is shown in Fig. 1.

The shapes of the current pulses were considerably distorted by trapping and detrapping effects. These varied from crystal to crystal and with temperature, but typical trapping times were 10–30 μsec. With such fast trapping and high mobilities it was

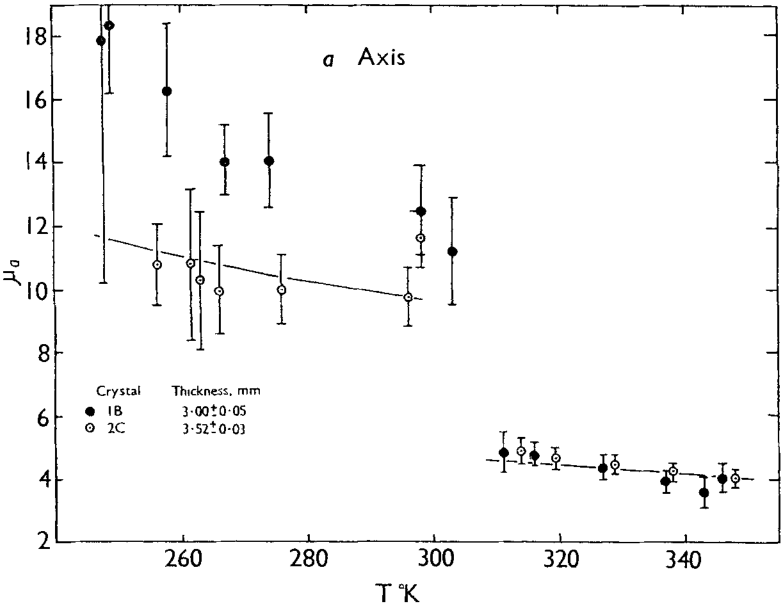

Figure 2a.

Figure 2. Hole drift mobility (cm^2/V-sec) *vs* absolute temperature. Figures (a), (b), and (c) show mobilities in the *a*, *b*, and *c* crystallographic directions, respectively.

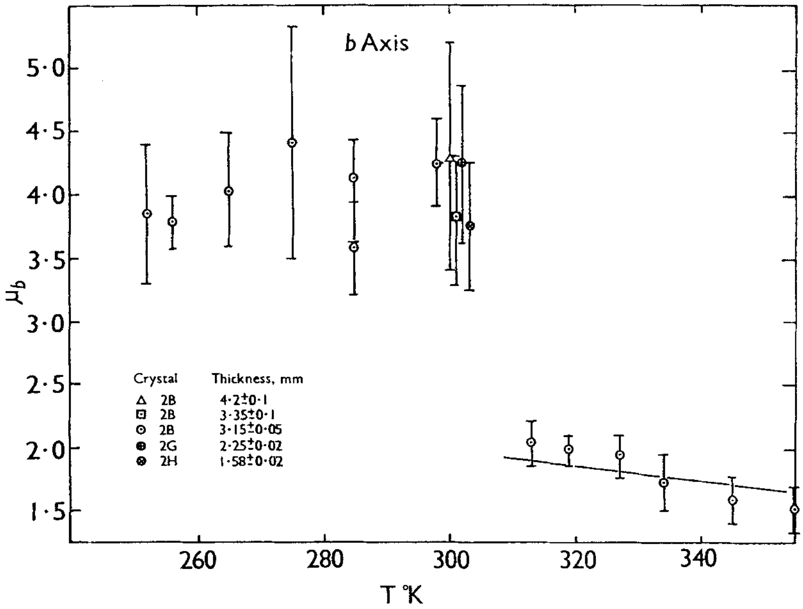

Figure 2b.

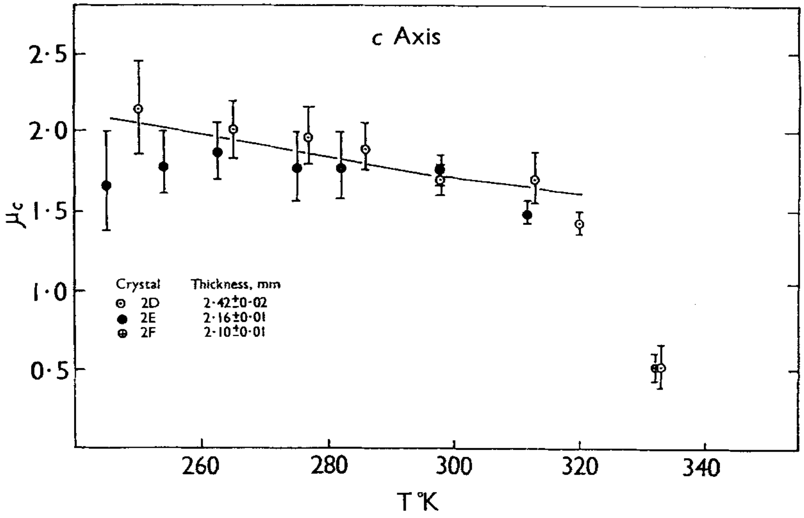

Figure 2c.

necessary to use crystals of 1.6–4.2 mm thickness and field strengths of 4000–14,000 V/cm to get resolvable transit times.

Drift mobilities measured from carrier transport times are shown in Figs. 2a, 2b, and 2c for photocurrents in the *a*, *b*, and *c* crystallographic directions, respectively. The error flags represent estimated uncertainty limits due to misalignment of crystal surfaces and to poorly defined carrier transit times. Any variation of mobility with applied field was generally well within these limits. The solid lines are theoretical plots of reciprocal absolute temperature.

Room temperature drift mobilities are about 12, 4, and 1.7 cm^2/V-sec in the *a*, *b*, and *c* directions, respectively. These numbers are to be compared with drift mobilities in other molecular crystals shown in Table 1. In the *a* and *b* directions in *p*-diiodobenzene the mobilities are above those measured to date in this type of solid. Although the molecular axes do not coincide with the crystallographic axes, the long iodine–iodine molecular axis has its largest projection, corresponding to a 32° angle, on the *a* axis.[11] This implies significant orbital overlap through the iodines on adjacent molecules along this axis.

TABLE 1 Experimental drift mobilities in molecular crystals (cm^2/V-sec)

Compound	Crystallographic direction	Holes	Electrons
p-Diiodobenzene	*a*	12	—
	b	4	—
	c	1.7	—
Anthracene[6]	*a*	1.2	1.7
	b	1.8	1.1
	c′	0.8	0.4
Naphthalene[7]	*a*	0.9	0.7
	b	1.4	0.7
	c′	0.4	0.4
Iodine[8]	*a*	2.3	—
	b	0.72	—
	c	2.1	—
Orthorhombic sulfur[9, 10]	normal to 111 plane	2.0	7×10^{-4}

The most surprising result of these experiments was the precipitous decrease in mobility noted at higher temperatures in all crystal samples. The effect is reversible but with hysteresis; several hours seem to be required for a crystal cooled to room temperature to regain the higher mobility. This may be due to a change in crystal structure and is being studied further.

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