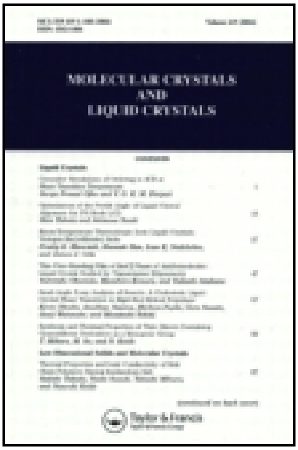

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Photoemission of Holes and Valence Band Structure in Anthracene

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Photoemission of Holes and Valence Band Structure in Anthracene

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Recent measurements of the Hall effect for volume-generated holes in anthracene and analysis of the differences between Hall and drift mobility values for electrons and holes suggest that both carriers move in a two-band system; a narrow band where the mobility is of the order of 1 cm^2v^{-1} sec^{-1} separated from a much wider band with high mobility by an energy of the order of 0.05 eV.(1) For electrons, the existence of wider bands has been well established by internal photoemission.(2,3) The conduction band system consists of a narrow band, less than 0.33 eV wide, separated by less than 0.05 eV from a higher band 0.3 eV wide.(3)

Internal photoemission of holes from a series of metals of varying work function has been measured by Williams and Dresner.(4) Although the curve of photoemission vs $h\nu$ fitted a Fowler plot, an additional structure with a regularity corresponding approximately to the principal ladder of vibrational states ($1400\ cm^{-1} = 0.175$ eV) led these authors to interpret the data as emission into a narrow band split by vibrational interaction. These measurements suffered from two defects: (a) Except for the case of Au, the spectral range near the photoemission threshold overlapped the region of triplet exciton generation, $h\nu > 1.8$ eV. (b) The sensitivity of the apparatus was not sufficient to permit measurements within 0.1 eV of the threshold, which was determined by extrapolation.

In this note the photoemission of holes has been studied using an anode of black colloidal platinum, which shifts the entire spectral range of the measurements well below the energy of the triplet bands. A cathode of D_2O was used, transparent for $h\nu > 0.67$ eV and the

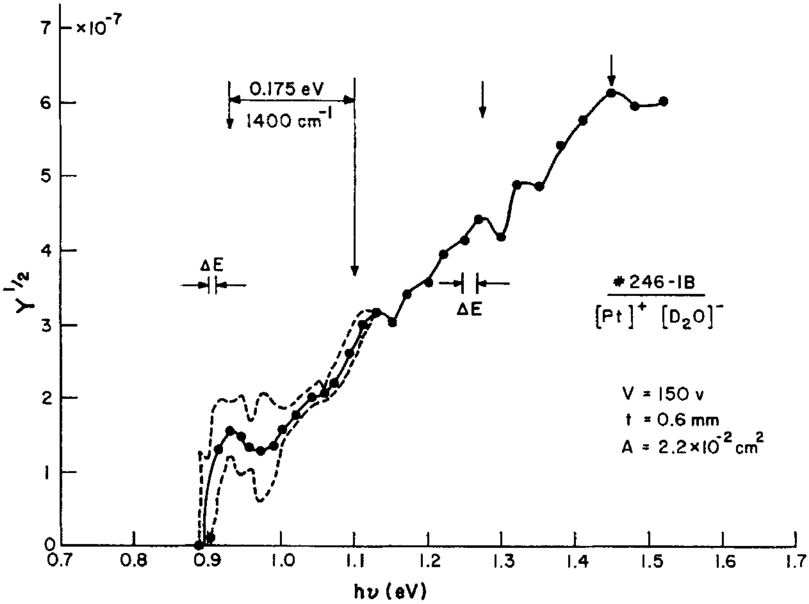

Figure 1. Internal photoemission of holes from an anode of colloidal platinum. The quantum yield Y is in arbitrary units. The dashed lines give the mean probable error of the measurements.

current sensitivity was one order greater than in Ref. 4. Figure 1 shows the results of a series of measurements on one crystal. The dashed lines give the mean probable error of the quantum yield curve. The monochromator resolution was 0.01 eV in the photoemission threshold region and 0.02 eV near $h\nu = 1.3$ eV. The threshold is found at 0.89 ± 0.01 eV, and the slope of the yield curve decreases sharply in the region between 0.96 and 1.00 eV. Using the fundamental assumption that the yield is proportional to the escape probability multiplied by the densities of initial and final states(4) this indicates a width for the highest valence band $0.025 < W \lesssim 0.6$ eV. For $h\nu > 0.99$ eV, the curve is close to linear on a Fowler plot [$Y^{1/2}$ vs $h\nu$], flattening out again at 1.45 eV. The curve shows an additional structure with peaks separated by approximately 0.175 eV as shown by the arrows. The sharp photoemission threshold as well as the plateaus at $h\nu \approx 0.96$ eV and $h\nu = 1.45$ eV favor interpretation of the data as emission into a two band system. The broader band is approximately 0.5 eV wide and separated from the narrow band by approximately 0.05 eV. This interpretation is also consistent with the transport data of Ref. 1. The structure of the yield curve indicates that the simultaneous excitation of a molecular vibration and hole photoemission may also occur, but the peaks are small and this effect is probably small compared to direct photoemission into the two band system.

To date, none of the calculations of the band structure of anthracene offer any support for the existence of the wider bands.(5–7) All make use of various refinements of the tight-binding approximation but concern themselves only with the highest V.B. and lowest C.B. Additional evidence for broader bands is available from optical measurements. Lyons and his co-workers(8) find absorption with structure at energies between the photoconductive band-gap at 4.4 eV and the ionization energy at 5.65 eV (determined by the external photoemission threshold). Further absorption is observed between 5.65 and 6.5 eV which, as in the case of the experiments of Geacintov and Pope,(9) must reflect the structure of the valence band. Note also that the density of states distribution in the valence and conduction band systems, derived from the internal photoemission experiments are symmetrical and almost identical.(3) It has been pointed out(5,7) that the wave functions to be used in calculating these band structures are those of the monopositive and mononegative anthracene ions. The optical absorption spectra of these two ions have been measured by Aalbersberg *et al.*(10) The two spectra show additional structure from that of the neutral molecule; they are identical except for a slight expansion of the energy scale, because of the smaller shielding factor, for the positive ion. The calculated band structure for the crystal might also be expected to reflect this symmetry.

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