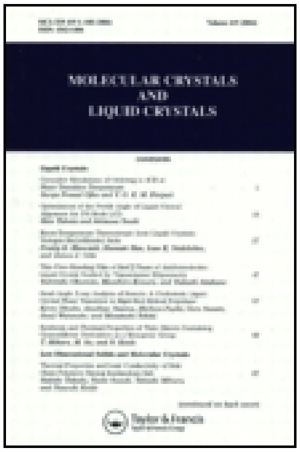

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On the Wavelength Threshold for Photoconductivity in Organic Solids

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In a previous publication[1] we reported on the photoconductivity of polystyrene for excitation in the vacuum ultraviolet. The threshold for the onset of this photoelectric effect was interpreted as indicating that photon energies which are close to the ionization energy of the free molecules (in this case, benzene) were necessary for the process to occur. In order to investigate whether this requirement holds in general we investigated the effect for a variety of other organic solids: polyethylene, anthracene, naphthalene, paraffin wax (m.p. 48 °C and m.p. 52 °C), cellulose and glucose. The results are shown in Fig. 1 which describes the variation of the photocurrent with excitation wavelength for the various materials. The curves have been normalized to the value 100 for excitation at 584 Å. The intensity of the exciting radiation was normalized by the fluorescence of sodium salicylate. It shall be pointed out that in order to obtain comparative current intensities the applied voltage for cellulose was 10 Volt, for glucose 1 Volt, while the necessary voltage for the other materials varied between 200–300 Volts. At 200 Volts, the dark current for glucose and cellulose was already greater than the photocurrent.

The results show that with the exception of naphthalene, all materials have the same wavelength-threshold for photoconductivity within the limits of our experimental arrangements; namely: for irradiation with light of 1220 Å the normalized current intensity lies between one and one tenth of a percent of the

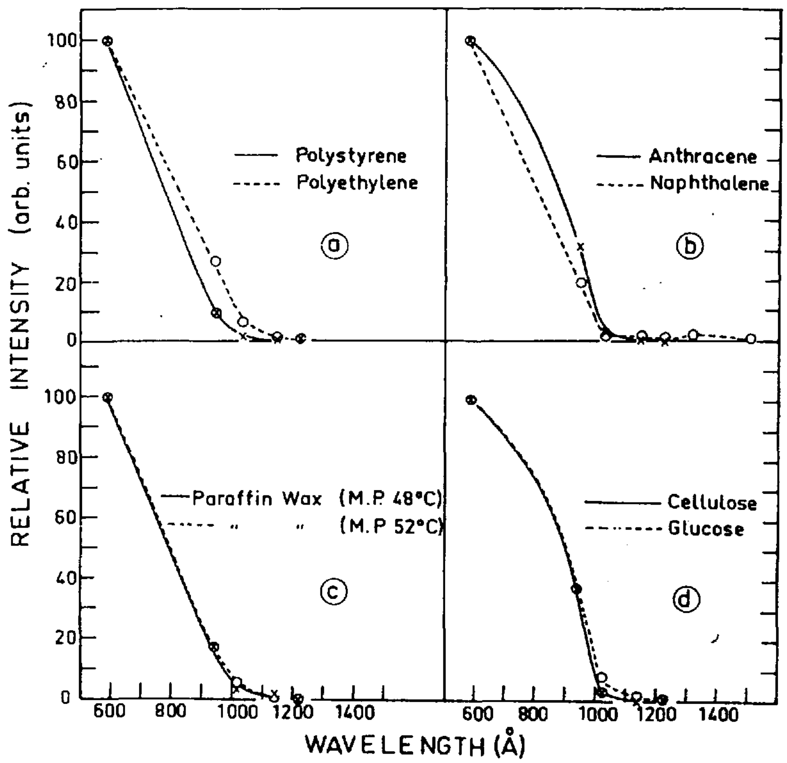

Figure 1. Variation of photocurrent as a function of excitation wavelength.

intensity which is obtained for irradiation at 584 Å. More accurately, when the logarithmic representation of the current-wavelength relation is extrapolated to 0.1% of the current intensity at 584 Å the wavelength varies from 1260 Å (9.8 eV) to 1330 Å (9.2 eV) for polystyrene, polyethylene and the paraffin waxes,‡ while for anthracene, cellulose and glucose the wavelength for the 0.1% intensity varies from 1180 Å (10.4 eV) to 1230 Å (10.0 eV). It is seen that the overall spread of threshold energies is not greater than 1.2 eV. These results may be com-

‡ For the paraffin waxes the current was actually measured by excitation with radiation of 1310 Å.

pared with the first ionization potentials of the free molecules as far as they were available to us. These are 12.2 eV for ethylene,[2] 9.6 eV for benzene,[2] 8.12 eV for naphthalene[3] and 7.38 eV for anthracene.[4] It is clearly seen that these values differ greatly from the threshold values for photoconductivity which are all close to 9.9 eV.

The results are particularly surprising for the case of anthracene which is well known to exhibit photoconductivity at *much longer* wavelengths.[5,6,7] We confirmed these results for excitation in the region 2700 Å–4000 Å. For wavelengths shorter than 2700 Å, however no photoconductivity is observed altogether, until the 10 eV region is reached. The photocurrent in this excitation region is by several orders of magnitude greater than for excitation in the near UV.

The behavior of naphthalene differs from that of the other materials investigated in this series. Small photocurrents are observed already for excitation energies as low as 7.4 eV. The photocurrent yield peaks around 9.5 eV and then decreases with increasing excitation energy. Beyond the minimum at about 10 eV the yield increases again with increasing excitation energy up to the highest measured values. We tend to identify the minimum at 10 eV with the threshold energy for photoconductivity found for the other materials. The lower energy band (7.4 eV–10 eV) may be the analogue of the near UV excitation band in anthracene.

The close proximity of the threshold values for a rather wide range of materials is not yet clearly understood. (The absolute values of the current differ by orders of magnitude for the different materials, due to their different conductivity properties). The existence of two excitation regions in anthracene (and probably also in naphthalene) may perhaps throw some light on the problem. It is possible that while the near UV conduction band of anthracene most likely belongs to the π-electron system, the photoconductivity which is observed for excitation in the vacuum UV originates in the σ-electron system of the material.‡ For

‡ The authors are indebted to Professor J. Jortner for this suggestion.

naphthalene the π-electron conduction band comes then already close to the σ-band and for polystyrene the two bands can not be differentiated any more.

The threshold was also investigated as a function of electrode material. A very slight increase in the threshold energy was observed by changing from silver to molybdenum to graphite.

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