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Charge carrier generation through photexcitation with strongly absorbed light and very weakly absorbed light has been compared for anthracene and phenazine crystals. No attempt was made to prepare clean surfaces, but purified crystals were used. The field dependence for strongly absorbed light was similar for both crystals, superlinear at low fields, linear at high fields. For weakly absorbed light, the photo generation of charge in anthracene could be described as Onsager type behavior, generation in phenazine could not. These results are discussed in terms of the charge generation process.

To date, the formation of free charge carriers without the involvement of defects or surface states has been discussed for molecular crystals in terms of the Onsager theory.[1] The experimental data is generally obtained through one-photon generation processes, i.e. excitation into a spectral region of high absorption. Obviously great care is needed to minimize surface effects. These experimental difficulties are relaxed in studies involving two or more photon carrier generation where the excitation occurs uniformly in the crystal bulk. It was therefore decided to study this multiphoton generation in phenazine, a material where to date, only one sign of mobile carrier has been observed, and no Onsager type behavior reported.[2]

The crystals were prepared from purified phenazine (chromatography and zone-refining) by Bridgman growth, which were subsequently cut and polished. Pulsed excitation 4500 and 5400A from a Molectron dye laser was used, the pulse power and transient photocurrent measured by typical time of flight techniques.[3] Anthracene crystal behavior was used for quality control experiments; 3371 and 4500A excitation.

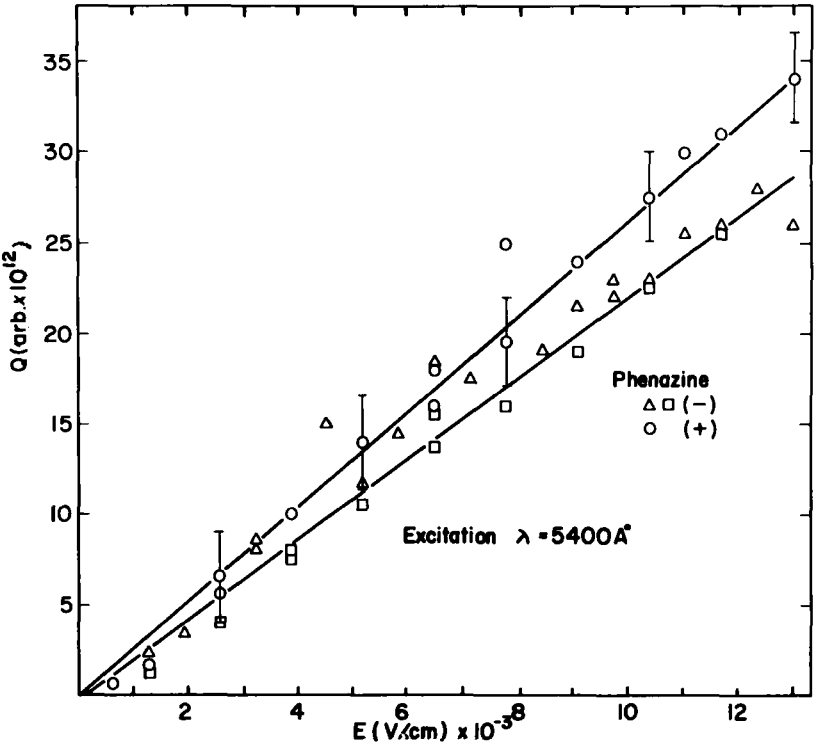

FIGURE 1 Dependence of the photogenevated charge following bulk excitation (5400A°) for a phenazine crystal as a function of the applied field. The effect of field reversal is also illustrated.

The anthracene crystals showed the expected behavior for the field dependence of both surface and bulk generation, namely with strongly absorbed light, 3371A°, a superlinear dependence at low fields and a linear dependence at high fields, and with weakly absorbed light, 4500A° and 5400A°,[4] a linear field dependence which extrapolated to a positive intercept at zero field. The results for phenazine with strongly absorbed light 4500A° paralled those of anthracene, but for weakly absorbed light, 5400A°, a linear field dependence was always observed with a zero intercept for zero field Figure 1. The collected charge was independent of the electrode polarity for all bulk excitation experiments.

Obviously for these phenazine crystals, a simple Onsager description for carrier generation does not apply. It has been suggested both that the microscopic anistropy of the crystal could dominate the carrier escape process in free carrier generation,[5] and the presence of a recombination region could modify carrier generation/field dependence behavior.[6] Indeed the latter model did give rise to a physical interpretation of the behavior observed.

However a detailed analyses would require a deconvolution of several interacting processes, and is thus highly questionable.

It is apparent that there is a fundamental difference between the behavior of anthracene and in this case, phenazine in bulk carrier generation. The band gap of phenazine can be estimated as ~4.1 eV.[8] Anthracene, the most probable impurity molecule which would be difficult to remove by physical methods of purification, would act as a deep hole trap, ~1.0 eV, and not influence electrons. The observed election mobility in phenazine was ~1cm^2/V sec, no free holes were observed. An anthracene "impurity" site could selectively prepare a change-transfer state, the electron density being centered on the neighboring phenazine molecule. A CT state has been suggested as a necessary intermediate for carrier generation.[9]

It would be expected that the activation energy for this bulk generation would not be the same as for surface (strong absorption) generation, but would be smaller. Indeed a lower activation energy for bulk generation compared to surface generation is found for phenazine. Onsager theory simply relates charge separation in an external field to separation with no applied field, it pays no attention to the initial excitation process. Considering its relationship to the Enstein Relation shows that any anisotropy in the crystalline medium cannot explain a zero intercept in a charge-generation/applied field plot. Therefore again one is led to the conclusion that the difference between anthracene and phenazine lies in the nature of the initial state prepared. Two photon and multiphoton carrier generation studies over the complete spectral range appear the only recourse to investigate the nature of these states and the fundamentals of the carrier generation process.

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