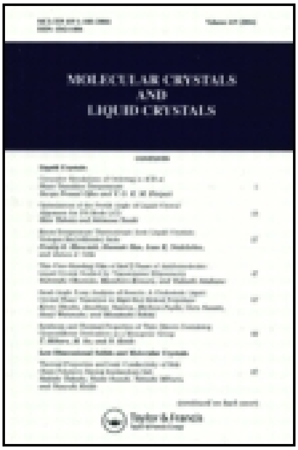

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Generation of Charge Carriers Through Excited States

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Charge carrier generation has been studied with two-color, two-step excitation. The complication associated with the penetration depth, which changes with the photon energy, can be eliminated with this technique. It has been found that in *p*-terphenyl and anthracene charge carriers are generated by photoionization of singlet excitons. Results of quantitative measurements of the photoionization cross section with additional information from transient absorption and fluorescence indicate that the initially created higher excited states relax rapidly to a lower-lying state which autoionizes. The capability of identifying the intermediate states with their lifetimes is demonstrated also with naphthalene and phenothiazine.

Photoconductivity is a phenomenon in which an otherwise insulating material exhibits a conductivity on irradiation with light of sufficient energy. It is a quantum effect, just as the external photoelectric effect, or the photoemission. Photoconductivity is an internal photoelectric effect and is closely related to photoemission. On absorption of light an electron with a certain kinetic energy is generated and thus a current can be observed when an electric field is applied. When the kinetic energy is sufficient to overcome the surface barrier the electron may appear in the vacuum and its kinetic energy can be analyzed by electron spectroscopic methods. When the kinetic energy does not allow the electron to leave the solid, its movement can still be studied through photoconduction.

Mobile electrons can be generated in an organic solid through various mechanisms. Which mechanism operates under a specific condition depends on the material, the photon energy, the excitation density, etc. It is possible that the state generated by the absorption of a photon is a pair of charge carriers: an electron and a hole (direct photoionization). It is also possible, however, that the final state of an optical transition is a neutral, electronically excited state. In many cases an action spectrum for photoconduction is quite similar to the absorption spectrum of the solid. This is an indication that exciton, which is the primary species created by the absorption of light, is involved in the generation of charge carriers. Steketee

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and de Jonge have noted a small but distinct difference between the action spectrum of photoconduction and the absorption spectrum of anthracene crystal and estimated the diffusion length of the singlet exciton in this material, assuming that excitons, generated within the absorption depth, diffuse to the surface where they dissociate into carriers.[1] The action spectrum would coincide with the absorption spectrum if the diffusion of the exciton is minimal and only the excitons generated at the surface give rise to a photocurrent. A finite diffusion makes the contrast between the peaks and valleys in the action spectrum of photoconduction smaller. The other extreme, the case where the diffusion length of the exciton is much larger than the penetration depth of the light, would give an action spectrum which has no wavelength dependence.

Energetically an exciton is located lower than an electron-hole pair. In the above case carriers of only one sign could be generated. This is also the case when dyes adsorbed on the surface of a crystal are excited and inject holes (dye-sensitized photocurrent).[2] Some more energy is necessary for an exciton to dissociate into a carrier pair. This additional energy can be supplied as the energy of another exciton in the case of the exciton–exciton annihilative ionization, or of a photon in photoionization of excitons. Exciton annihilation will be more important with strongly absorbed light, since a high local density of excitons favours the probability of excitonic bimolecular reactions. Irradiation with light can also give rise to the detrapping of carriers, either by direct photoexcitation[3] or through the interaction of excitons with trapped carriers.[4] It may be seen that the interpretation of an action spectrum can be quite complex, especially when it is obtained with d.c. measurements. The main difficulty arises from the fact that when the photon energy is changed the penetration depth of light also changes.

We have been trying to remove these complications by applying the multistep (and multiphoton) ionization technique which has been successfully used to study excited states of molecules and to combine with it measurements of fluorescence and transient absorption. The excellent energy and time (and polarization) resolution and high peak powers of pulsed lasers can be fully utilized.

Most of the experiments described here have been made with two-step excitation with pulsed lasers. Two-step excitation is a flexible method: The energy (and also the polarization) of each step can be independently varied. Also, the second step can be deliberately delayed. In our experiments excitons are generated in the bulk of a crystal by weakly absorbed light and photoionized with light for which the crystal is transparent. Excitation at the absorption edge is our choice as the first step. Two-photon absorption could also be used, but this is not always applicable for quantitative studies, since the two-photon absorption coefficient is often not known with sufficient accuracy. It is possible in this way to change the excitation energy without introducing difficulties associated with the changing penetration depth, encountered with one-photon (one-step) excitation. Figure 1 shows photocurrent waveforms observed with pulsed excitation with light of wavelengths from 308 nm to 355 nm. The change in the waveform results from the change in the penetration depth of the excitation light within the crystal. With strongly absorbed light carriers are generated within a thin surface layer and electrons (or holes) move across the whole thickness of the crystal in the form of a thin sheet, while

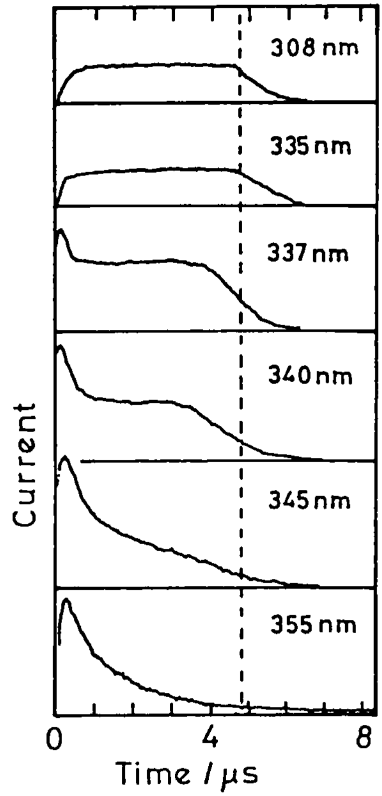

FIGURE 1 Photocurrent waveforms observed with various wavelengths (*p*-terphenyl), showing the effect of varying thickness of the excited region.

holes (or electrons) are confined in the generation region due to the applied field and hence do not contribute to the current. When the absorption coefficient is small and carriers are generated in the bulk of the crystal the waveform becomes a triangle. In an intermediate case the current pulse consists of an initial spike due to carriers of one sign which are moving to the front surface and a longer-lasting component coming from carriers of another sign which move to the rear surface. In this way the absorption coefficient can be known precisely from the current waveform.

It should be noted that a single photon of this energy is not capable of generating a carrier pair. This is indicated by the carrier yield which is proportional to the square of the pump intensity (Figure 2).[5] With higher excitation intensities the dependence changes from a quadratic to a linear one. This is the result of an efficient recombination of electrons and holes. The bimolecular recombination rate constant γ_{eh}, determined from the intensity at the break in Figure 2 is 1.3×10^{-6} $cm^3 s^{-1}$ and is in good agreement with that given by the Langevin formula

$$\gamma_{eh} = 4\pi e(\mu_e + \mu_h)/\epsilon$$

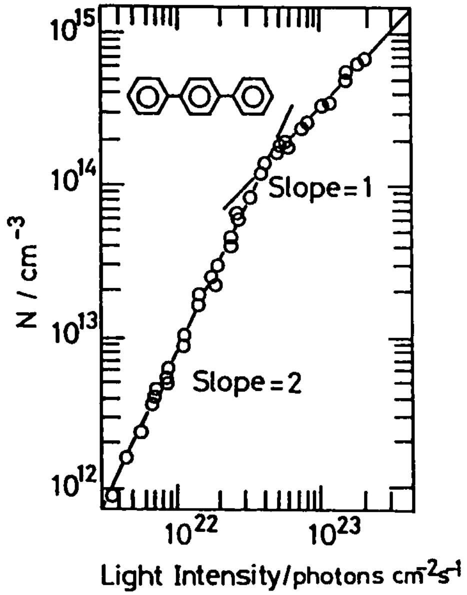

FIGURE 2 The number of generated carriers vs. the excitation intensity (at 337 nm). The break in the slope is caused by the electron-hole recombination which becomes increasingly important at higher excitation intensities.

with the mobilities measured with the same specimen. One more break in the slope can be observed at a still higher intensity. This is accompanied by a similar break in the fluorescence intensity, and is due to the exciton–exciton annihilation which, above this intensity, influences strongly the concentration of the singlet exciton, which is to be photoionized.

When a pulse of visible light is added which is not absorbed by the ground state crystal an increase is observed in the carrier yield (Figure 3). The increment can be attributed to the photoionization of excitons. As expected the increment is proportional to the intensity of the visible pulse (Figure 4), the proportionality constant being different for different wavelengths. The photoionization cross section can be determined from the density of the excitons (which can be calculated from the intensity of the UV pulse, the absorption coefficient at the wavelength and the lifetime of the exciton) and the number of the generated carriers which can be known directly from the magnitude of the photocurrent and the carrier transit times. The photoionization "spectrum" of exciton is obtained when the photoionization cross section σ_{PI} is plotted against the wavelength of the ionizing pulse.

Does the ionization occur with unit efficiency, if the excitation energy exceeds the threshold? The answer is yes in simple textbook cases like isolated atoms. In the condensed phase the efficiency is generally small. With one-photon excitation the experimental quantum yield of the carrier generation is 10^{-4} to 10^{-5}, and geminate recombination of electrons and holes is responsible for this small yield.[6]

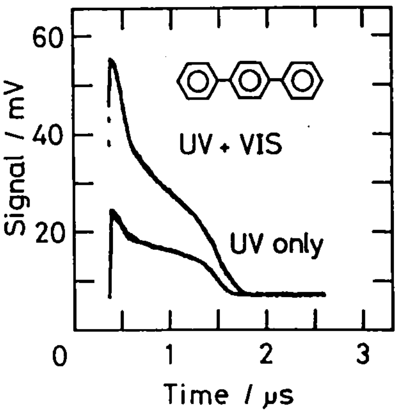

FIGURE 3 Photocurrent waveforms, observed with a UV (337 nm) pulse only (lower trace) and with simultaneous excitation with a 590 nm pulse and a UV pulse.

An attempt has been made to assess the ionization efficiency in the two-step excitation. For this purpose a transient absorption had to be measured.[7]

The method is straightforward. The transmission of a probe pulse in the visible is measured once with a pump pulse (in the UV) and then without it. The difference is taken as due to the absorption by excitons. This pump-and-probe type measurements have been quite popular in gas and liquid phase studies, but are generally considered to be difficult with organic solids: The sample specimen might not withstand the intense pump pulses, and the optical quality of the sample is often insufficient for transmission measurements. We have found that the damage can be avoided by a proper selection of the excitation condition so that the energy is deposited not in a very thin surface layer, but over an extended depth. (In solution studies this can be done by changing the concentration of the solution, but dilution is not applicable to crystals.) In order to assure the temporal coincidence of the pump and the probe pulses two pulsed dye lasers, pumped with a common laser (a nitrogen laser or an excimer laser), are used as the irradiation source. The results

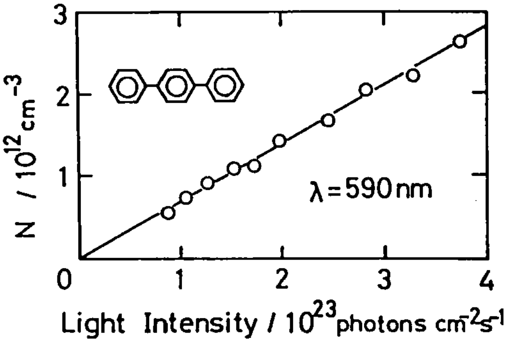

FIGURE 4 The number of carriers, generated by the photoionization of the singlet exciton, increases linearly with the intensity of the ionizing (visible) pulse.

with *p*-terphenyl is shown in Figure 5. Also shown in the figure is the transient $S_n \leftarrow S_1$ absorption of *p*-terphenyl in cyclohexane solution. It may be seen that they resemble each other quite well, indicating that the final state in the two-step excitation is a neutral excited state derived from a molecular higher excited state.

The intensity of the transient absorption is found to be proportional to the square root of the pump intensity. The measurement of the transient absorption requires a rather high exciton density. Accordingly the measurement is made with an intensity, at which the fluorescence decay is governed by the exciton–exciton annihilation. The square root dependence of the transient absorption on the pump intensity thus directly indicates that the mobile excitons are responsible for the absorption being observed.

The photoionization spectrum represents the cross section σ_{PI} with which an excited state is ionized while the absorption spectrum gives the cross section σ_A for all transitions starting from the lowest excited singlet state (Figure 6). The photoionization efficiency, i.e., the fraction of the transition which leads to the ionization, $\phi(E)$, is given by the ratio of the cross sections:

$$\phi\,(E) = \sigma_{PI}/\sigma_A.$$

The results are shown in Figure 7. It may be seen that the photoionization efficiency is a constant in the energy range between 5.8 eV and 6.4 eV (the energies are

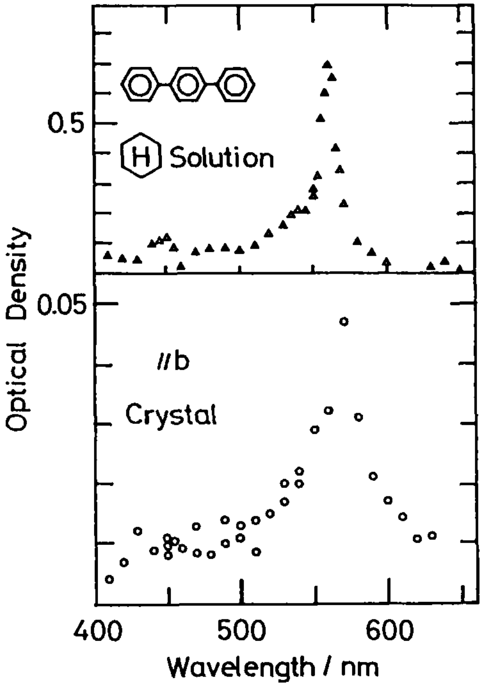

FIGURE 5 Transient absorption of *p*-terphenyl in cyclohexane solution (top) and in crystal (bottom). Note the close resemblance which indicates that the final states are similar in nature.

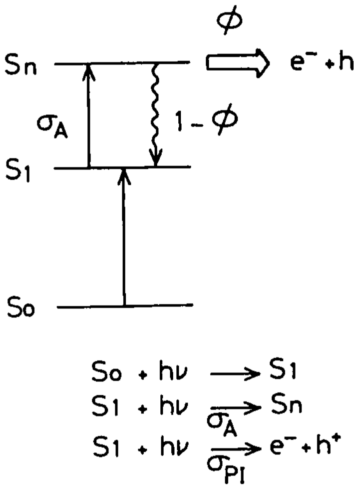

FIGURE 6 Two-color, two-step excitation for the study of photocarrier generation.

measured from the ground state). It has often been assumed that a higher excited state emits an electron which travels within the solid with a kinetic energy which is given by

$$E_{\mathrm{kin}} = h\nu - E_{th}$$

where E_{th} is the (internal) photoionization threshold. Photoelectron spectroscopy gives a direct support to this picture. The kinetic energy of an electron, emitted

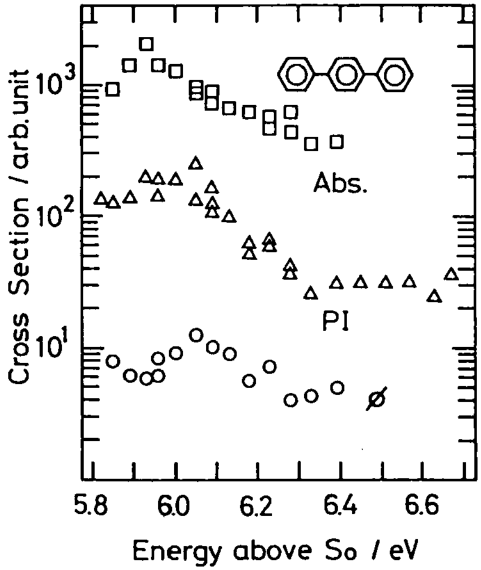

FIGURE 7 The ionization efficiency φ derived from the cross sections of the absorption and of the photoionization (*PI*). Note that φ does not increase with the photon energy.

into the vacuum is expressed as

$$E_{\mathrm{kin}} = h\nu - E_b$$

where E_b is the binding energy of the electron. The kinetic energy of the electron increases with the excitation energy. The results shown in Figure 7, on the other hand, seem to indicate that the kinetic energy of the electrons remains constant when the energy of the final state is changed between 5.8 and 6.4 eV. We interpret the results as indicating the presence of a state which is located below 5.8 eV and autoionizes with a high efficiency. The excess energy over this autoionizing level may be dissipated rapidly as energies other than the kinetic energy of the emitted electrons.

A distinct polarization dependence is observed with the second step excitation both in the photoionization and in the absorption. Excitation with *b*-polarized light gives a larger signal, irrespective of the polarization of the first step excitation. There seems to be a vibrational relaxation in the intermediate (lowest exciton) state and the "memory" of the polarization created by the first step excitation is lost before the system is excited further to a higher excited state.

A very similar behaviour has been observed with singlet excitons in anthracene.[8] Both the ionization and the absorption has been measured with a fairly good signal-to-noise ratio. Again, the photoionization efficiency $\phi(E)$ exhibits a plateau, in this case between 5.1 eV and 5.5 eV.

In the measurements described above irradiation with visible light only gives no detectable current. At much higher intensities, however, a current is observed which is proportional to the third power of the excitation intensity. This can be interpreted as due to the photoionization of the excitons, generated by two-photon absorption.[9] Since charge carriers can be collected quantitatively this offers a unique opportunity to measure a two-photon absorption coefficient, with the aid of a known photoionization cross section. With *p*-terphenyl crystal a coefficient of 6×10^{-29} cm s/photon is obtained for $\lambda = 590$ nm, which corresponds to a molecular two-photon absorption coefficient of 2×10^{-50} cm^4 s/photon.

When the second step excitation is delayed against the first step excitation both the transient absorption and the enhancement of the photocurrent decrease. By observing this decrease with various delays one can know the lifetime of an intermediate state and be sure whether singlet exciton or triplet, or some other state is involved. This capability has been exploited in the case of anthracene. With naphthalene the exciton lifetime of 78 ns could be measured using two UV pulses through a kind of correlation function measurement.[10]

Another example of the application of the two-step excitation is the study of the precursor state of the charge carrier generation in phenothiazine.[11] This is an interesting compound, with its low ionization potential ($I_P = 5.15$ eV in the crystalline state[12]). There is an indication of exceptionally low-lying CT states in phenothiazine which can be populated with light of 420 nm and is possibly long-lived.[13] With excitation with a short UV pulse the photocurrent rises instanteneously, as is normally the case with aromatic hydrocarbons, but exhibits a remarkably slow rise when excited with a 420 nm pulse. Its time constant is ~100 μs with a low intensity excitation and becomes shorter with increasing pump intensity. Obviously a long-lived intermediate state is involved when excited at this specific wavelength. Two-step excitation has been tried. The first step is made with a 420 nm (2.9 eV) pulse and the second step pulse, of a wavelength ranging from 450 nm to 560 nm, is delayed. The carrier yield is plotted against the delay. An exponential decrease with a time constant of 60 μs is observed with weak excitation. When the excitation intensity is increased the decay becomes faster at the initial part of the decay, which indicates the presence of a bimolecular process, and hence the mobile nature of the precursor state.

A single crystal of a high purity, free from excessive trapping, is a prerequisite for most of the measurements discussed above. A considerable effort has been invested in the purification and the crystal growth. Purification has been made with extensive zone-refining and single crystals were grown within a sealed tube, oxygen being rigorously excluded (oxygen is a well known quencher of the triplet exciton and acts also as a trap for electron). It may be said that a crystal is a reaction vessel, a flask, in which a variety of reactions proceed. A study of a reaction can be started when the flask has been thoroughly cleaned. Quite often, however, we find that what we are doing is, in effect, the characterization of a trace amount of impurities and defects in a high purity crystal.

Historically the dynamics of the excited states and the photoconductivity have been considered largely as a separate issue. They are, however, closely related and should be treated in a unified frame. Charge carriers themselves may be considered as an excited species in a crystal, just like singlet and triplet states. The only difference may be that they are a charged state, and hence susceptible to electrical detection.

Acknowledgments

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