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NANOSECOND KINETICS OF THE PHOTOCONDUCTIVITY OF LIQUID TMPD SOLUTIONS IN METHYLCYCLOHEXANE

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The electric conductivity of N,N,N',N' -tetramethyl-*p*-phenylenediamine solutions in methylcyclohexane induced by a 347 nm laser pulse has been studied. At temperatures < 180 K a new transient photoconductivity effect has been revealed, a current peak whose duration (≈ 30 ns) equals the duration of the laser pulse. The current is attributed to the electric polarization of trapped electron-cation pairs before geminate recombination.

1. Introduction

Photoionization of solute molecules in organic matrices leads to generation of pairs (e_{tr}^- , A^+) of oppositely charged particles: the stabilized electron e_{tr}^- and the solute cation A^+ . Geminate pairs in such systems have been studied by various methods beginning with Albrecht et al. who showed that the geminate electrons could be excited by IR radiation to produce recombination luminescence [1]. Most of the pairs produced recombine geminately, but the pairs have a small probability to escape geminate recombination and separate into free charges. Only free charges are usually considered to explain photoconductivity data. Can geminate pairs contribute to the photocurrent at a constant external electric field?

Oppositely charged particles bound closely by Coulomb attraction are similar to dipoles which do not contribute to a steady direct current but give rise to a polarization current caused by a change of the dipole. The polarization of electron-cation pairs is supposed to be responsible for the transient current induced by radiation pulses in rigid non-polar organic matrices [2] and in particular for the photocurrent induced by IR radiation in the γ -irradiated 3-methylpentane glass [3, 4]. Recently Sauer et al. [5] assumed that the dc conductivity signals observed following pulsed photoionization of solutions of anthracene in dielectric liquids are due to geminate ions.

In the present work we attempt to observe the polarization current induced by photoionization of TMPD (N,N,N',N' -tetramethyl-*p*-phenylenediamine) solutions in liquid methylcyclohexane (MCH) at low temperatures, when the geminate recombination time of pairs (e_{tr}^- , $TMPD^+$) is commensurate with the current time resolution ($\approx 10^{-8}$ s). The photocurrent was generated by two successive light pulses: one pulse of a frequency-doubled ruby laser at 347 nm and the other of a ruby laser at 694 nm. Along with the usually studied photoconductivity induced by the two-photon ionization of aromatic molecules [6, 7] this method allows measurement of the photocurrent due to photoexcitation of e_{tr}^- .

2. Experimental

The experimental apparatus employed is shown in fig. 1. The 694 nm light of the ruby laser ($h\nu_1 = 1.79$ eV) producing 0.9 J in a 30 ns pulse was frequency doubled by a KDP crystal to deliver light of 347 nm ($h\nu_2 = 3.58$ eV). This light having a pulse energy $E_{347} \leq 10^{-2}$ J ionized the solution in the photoconductivity cell. A part (0.2 J) of the 694 nm laser beam was delayed by mirrors and could be directed into the same volume which had been illuminated by the 347 nm light. The delay time between the two pulses could be varied from 20 to 80 ns.

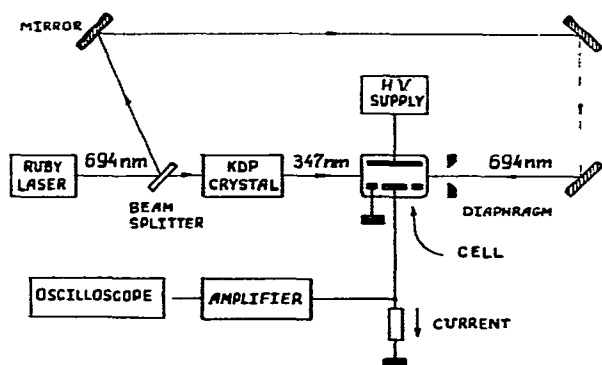


Fig. 1. Schematic diagram of the apparatus employed.

In the photoconductivity cell the collecting stainless-steel electrode $0.6 \times 1.3 \text{ cm}^2$ was supplied a guard and held 0.5 cm from the high-voltage electrode. A rectangular diaphragm $0.2 \times 0.3 \text{ cm}^2$ was used to protect the electrodes from the laser beam.

In pure MCH the excess mobility μ_e was measured by the time-of-flight method [8] using 3–5 MeV electron pulses to produce excess electrons. In this case the electron scavenging time was $\approx 10^{-3} \text{ s}$ in liquid MCH at 296 K and the distance between electrodes was 0.1 cm. It was found that $\mu_e = 0.07 \pm 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $T = 296 \text{ K}$ and the value of μ_e decreases with decreasing T down to $8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $T = 177 \text{ K}$ as $\mu_e = \mu_0 \exp(-E/kT)$, where $E = 0.17 \text{ eV}$.

For the photoconductivity experiments the TMPD concentrations ($< 1 \times 10^{-4} \text{ M}$) were chosen such as to eliminate strong light absorption.

3. Results

The insert in fig. 2 shows an oscilloscope trace of the photocurrent induced by the 347 nm pulse in a $4 \times 10^{-5} \text{ M}$ solution of TMPD in MCH at $T = 296 \text{ K}$. The signal decays with an initial half-life $\tau_e \approx 50 \text{ ns}$ to a longer one which has a half-life of $\tau_i \approx 30 \mu\text{s}$. Such current components have been commonly observed for the photo- and radiation-induced conductivity in non-polar liquids and interpreted as the electron and ion current, respectively. In our case the interpretation is verified by the ratio of the rapid component amplitude to the slow one (being equal to $\approx 10^2$) which agrees with the ratio of the electron and ion drift mobilities obtained for pure MCH.

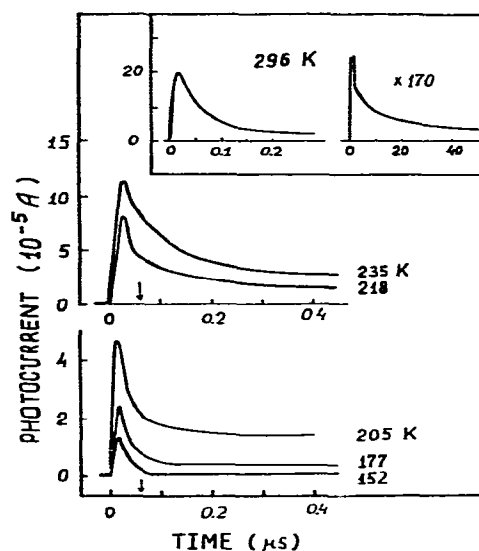


Fig. 2. Transient photocurrent induced by a 347 nm laser pulse in $4 \times 10^{-5} \text{ M}$ TMPD solution in MCH at the temperatures shown, $E_{347} = 4 \times 10^{-3} \text{ J}$ and the external field strength $F = 4 \times 10^3 \text{ V cm}^{-1}$. The arrow shows the end of the laser pulse. Insert: electron and ion components of the photocurrent at room temperature and $F = 1.2 \times 10^3 \text{ V cm}^{-1}$.

If the temperature decreases down to 230 K, the electron current amplitude decreases while τ_e increases. The electron current behaviour is in agreement with the known decrease of the ionization quantum efficiency [9], electron mobility and rate constant for electron scavenging and recombination in low-mobility liquids [10] when the temperature decreases.

A new transient photoconductivity effect occurs at temperatures below 220 K: a photocurrent peak whose duration about equals the duration of the laser illumination is observed (fig. 2). The amplitude of the fast current decreases with decreasing temperature more slowly than the end-of-pulse current I_e (figs. 2 and 3) and for $T < 180 \text{ K}$ the photocurrent amplitude I_{347} consists mainly of the fast current. At $T = 150 \text{ K}$ the amplitude I_{347} was proportional to the electric field strength in the interval $6 \times 10^3 - 3 \times 10^4 \text{ V cm}^{-1}$.

It should be noted that both I_{347} and I_e values for $4 \times 10^{-5} \text{ M}$ TMPD solutions are larger by a factor of $\approx 10^2$ than ones for the pure solvent. This suggests that the current observed was caused by action of light on TMPD molecules.

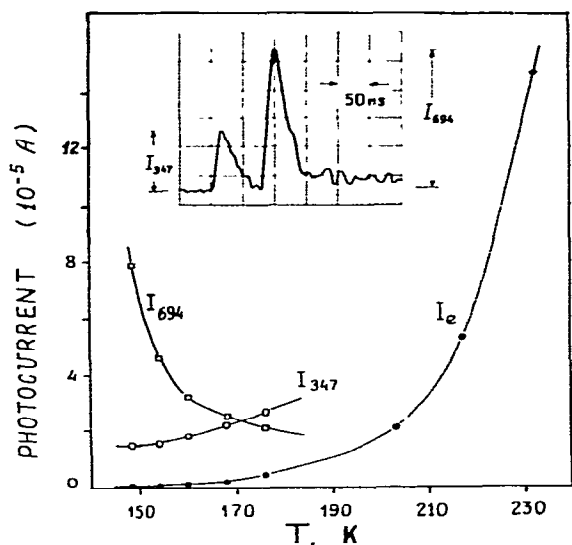


Fig. 3. Plots of the amplitudes I_{347} , I_{694} and the end-of-pulse current I_e (measured at the time marked by the arrow in fig. 2) against T for the 4×10^{-5} M TMPD solution at a light energy flux in the 694 nm pulse $Q_{694} = 2.2 \text{ J cm}^{-2}$, $E_{347} = 4 \text{ mJ}$, $F = 4 \times 10^3 \text{ V cm}^{-1}$ and a delay time 80 ns. Insert: the oscilloscope trace of the current upon combined excitation of the 1×10^{-4} M TMPD solution by the 347 nm and 694 nm pulses at 150 K. The delay time between the pulses is 80 ns, $E_{347} = 7 \text{ mJ}$, $Q_{694} = 1 \text{ J cm}^{-2}$, $F = 6 \times 10^3 \text{ V cm}^{-1}$, current scale $1.3 \times 10^{-5} \text{ A/div}$.

Photoexcitation of the TMPD solution by a 694 nm pulse after a 347 nm pulse results in the additional photocurrent transient $I_{694}(t)$ observed well at $T < 180 \text{ K}$, insert in fig. 3. (Upon only ruby-laser excitation, no appreciable photocurrent was observed.) At these temperatures the photocurrent amplitude I_{694} consists mainly of the fast current just as in the case of the photocurrent amplitude I_{347} . The value of I_{694} is approximately proportional to the flux of the 694 nm light energy Q_{694} and decreases when the delay time between 347 and 694 nm pulses increases. Fig. 3 shows that I_{694} increases with decreasing temperature.

4. Discussion

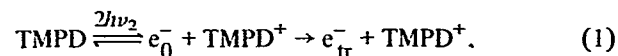
4.1. Nature of the fast current

It is not likely that the fast current observed is due to a capacitive effect based on the presence of photo-

excited molecules as has been considered by Schein et al. for photocurrent in anthracene [11]. Even if we assume that all TMPD molecules are photoexcited during the light pulse and acquire a polarizability of excited molecular states equal to that of a metallic sphere with a radius of 10 \AA , the value of the capacitive current will be less than the experimental one.

The fast current appears to be associated with short-lived species which have a larger mobility than the average mobility of excess electrons, μ_e . Such species are unlikely to be mobile holes MCH^+ because of the large difference between the ionization potentials of TMPD and MCH molecules (6.2 eV [12] and $10 \pm 0.2 \text{ eV}$ [13] in the gas phase).

Following the usual supposition that the precursor of an e_{tr}^- electron is a mobile or quasifree electron e_0^- , we suggest that both current peaks I_{347} and I_{694} are due to e_0^- electrons produced in the processes



for I_{347} and the process



for I_{694} , with localization of the electrons being very rapid on a time scale of $\approx 10^{-8} \text{ s}$.

It should be emphasized that the current peaks are registered on the timescale of $\lesssim 10^{-7} \text{ s}$ which is much shorter than the time of separation of pairs (e_{tr}^- , TMPD^+) produced by a 347 nm pulse into free charges $\tau_{sep} \approx r_c^2/D > 5 \times 10^{-6} \text{ s}$ at $T < 180 \text{ K}$. Here the average electron diffusion constant is calculated using the Einstein relation $D = \mu_e kT/e$ and the obtained value of $\mu_e < 10^{-3} \text{ cm}^2 \text{ V/s}$, $r_c = e^2/\epsilon kT$ is the Onsager radius, e is the electron charge, k and ϵ are the Boltzmann and dielectric constants. Using the relationship for τ_{sep} we assume that the initial distance between e_{tr}^- and TMPD^+ is much less than $r_c \approx 500 \text{ \AA}$ at $T \approx 150 \text{ K}$. This assumption seems to be right not only for prime e_{tr}^- produced in process (1) but also for e_{tr}^- formed by photoexcitation of e_{tr}^- in process (2) since a trapped electron is photoexcited less than once during a 347 nm light pulse ($\sigma Q_{347}/h\nu_2 \lesssim 1$ for the flux of the 347 nm light energy, $Q_{347} \lesssim 3 \times 10^{-2} \text{ J cm}^{-2}$ and the cross section of light absorption by e_{tr}^- , $\sigma \approx 10^{-17} \text{ cm}^2$ [14]) and the average length before localization of a photoliberated electron is thought to be much less than r_c .

The estimate of τ_{sep} agrees with data on the effect of photoexcitation of e_{tr}^- on the quantum yield of free charges in liquid MCH at $T < 180$ K [15] and allows interpretation of the increase of I_{694} with decreasing temperature (fig. 3) as a result of the time dependence of geminate recombination of e_{tr}^- .

Therefore, it should be expected that the majority of e_{tr}^- electrons produced by a 347 nm pulse at $T < 180$ K remain at the end of the pulse in the Onsager sphere, i.e. $N_{\text{gi}} \gg N_{\text{fi}}$, where N_{gi} is the number of e_{tr}^- electrons in volume between electrodes at the end of a light pulse, N_{fi} is that for electrons which are to escape geminate recombination. This gives rise to the following question.

4.2. Which e_0^- electrons, geminate or free, do mainly contribute to the fast photocurrent?

There are three reasons to consider not only free charges in the photocurrent observed.

(1) It is difficult to explain the value of the fast current I_{347} if we take into account only free e_0^- electrons. (We mean by free e_0^- those electrons the localization of which produces e_{tr}^- which will escape geminate recombination.) Indeed, in this case

$$I_{347} \tau_p = eF \mu_0 \tau_0 d^{-1} (1 + \sigma Q_{347} / h\nu_2) N_{\text{fi}}, \quad (4)$$

where τ_p is the 347 nm pulse duration, F is the external electric field strength, μ_0 is an average mobility of e_0^- during the time τ_0 before localization and d is the spacing of the electrodes. The two terms in parentheses on the right-hand side of eq. (4) correspond to the drift displacement of e_0^- electrons produced in processes (1) and (2). Eq. (4) gives $N_{\text{fi}} \approx 10^{15}$ if we use the data of fig. 2 ($I_{347} \tau_p \approx 2 \times 10^{-12}$ C at 177 K), $\sigma \approx 10^{-17}$ cm² and $\mu_0 \tau_0 = 4 \times 10^{-13}$ cm²/V as for liquid *n*-hexane at 175 K [16]. This value of N_{fi} seems to be too large: it means that the quantum yield of free charges is greater than $N_{\text{fi}}(2h\nu_2)/E_{347} \approx 0.1$, while experimental values for TMPD in low-mobility non-polar liquids do not exceed 10^{-6} at $T < 180$ K [9].

(2) Eq. (4) does not account for the proportional dependence of I_{347} on F . For the interval of F used ($6 \times 10^3 - 3 \times 10^4$ V/cm) one should expect a change of the escape probability and, consequently, N_{fi} several times. (The free ion yield in X-radiolysis of low-mobility liquids at $T \approx 150$ K increases more than twice with increasing F in the interval [17].)

(3) As has been noted [2-4], pairs of charged parti-

cles which geminately recombine, may contribute to the transient dc conductivity if their recombination time is of the order of the current time resolution or exceeds it. The contribution may be interpreted in terms of a polarization current caused by a change of the dipole $P = \sum N e r_i$ of all N pairs between the electrodes:

$$I(t) = d^{-1} dP_E/dt, \quad (5)$$

where r_i is the vector binding the negative and the positive charges of a pair, $P_E = (P \cdot F)/F$. The polarization current kinetics has been considered in some simple cases [3,4]. According to refs. [3,4], for an initial random distribution of pairs the initial current is approximately equal to the current of the same but free charged particles. It can be readily understood if

$$dr_i/dt = \mu(F_k + F), \quad (6)$$

where F_k and F are strength vectors of the Coulomb field and the external field, μ is the sum of the mobilities of charges of a pair. Since the average value of $(F_k \cdot F) = 0$ for all pairs at the initial time, we obtain from eqs. (5) and (6) $I(t=0) = e\mu FN/d$ as for free charges.

If we consider the fast photocurrent as an initial stage of polarization caused by a drift displacement of e_0^- produced in processes (1) and (2), we obtain

$$I_{347} \tau_p \approx e\mu_0 \tau_0 FN_{\text{gi}}(1 + Q_{347} \sigma / h\nu_2). \quad (7)$$

Though the average dipole momentum of an (e_{tr}^- , TMPD⁺) pair at the end of a 347 nm pulse may be small (≈ 1 e Å for $\mu_0 \tau_0 \approx 10^{-12}$ cm²/V s, $F = 10^4$ V/cm and $\sigma Q_{347} / h\nu_2 \lesssim 1$), eq. (7), in contrast to eq. (4), allows consistency between experimental values of I_{347} and $\mu_0 \tau_0$, since $N_{\text{gi}} \gg N_{\text{fi}}$. Moreover, it may account for the linear dependence $I_{347}(F)$ observed because the value of N_{gi} seems to depend weakly on F for $F < 3 \times 10^4$ V/cm.

5. Conclusions

Investigation of the electric conductivity of glassy hydrocarbons γ -irradiated at low temperatures [3,4] appears to demonstrate that the initial current induced by γ -irradiation as well as the initial photocurrent caused by photoexcitation of trapped electrons are determined by all electrons both those in geminate charge pairs and a far smaller fraction which are free.

The present experiment agrees well with this picture. We believe that measurement of the fast photocurrent associated with polarization of electron-cation pairs during formation of primary trapped electrons may give some new information on the early stages of photoionization in condensed media.

Acknowledgement

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