Energy Level Structure of Trapped Electrons in 3-Methylhexane Glass from Photoconductivity and Optical Bleaching Studies

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Abstract: Electrons are trapped in γ-irradiated 3-methylhexane (3MH) glass at 77°K. Monochromatic photoexcitation produces photoconductivity and optical bleaching with a threshold near 1240 nm (1.0 eV) and a peak near 1000 nm (1.24 eV). This transition is linear in light intensity and independent of temperature between 77 and 4.2°K, so it is interpreted as a one photon transition directly to the conduction band or to an autoionizing state. Photoexcitation near 1650–1700 nm discloses a two photon transition which depends on the light intensity squared. The first photon corresponds to the well-known optical absorption of trapped electrons in 3MH at 1650 nm. This transition is interpreted as a 1s $\rightarrow$ 2p type. The 2p state then presumably crosses to an intermediate 2s-type state from which the second photon is absorbed. The threshold of the second photon transition was not determined but the transition appears to have a peak near 1700 nm. The temperature dependence of both optical bleaching and photoconductivity under photoexcitation with $\lambda > 1400$ nm shows that population of the intermediate 2s-type state involves an activation energy $\sim$0.001 eV. The deduced energy level structure of trapped electrons in 3MH is remarkably similar to the structure in the more polar matrix, methyltetrahydrofuran.

Efficient electron trapping occurs in a variety of polar and nonpolar glassy matrices. These electrons can be detected by electron paramagnetic resonance (epr) and by optical absorption. In these matrices it is clear that the ground state of the trapped electron (e_t^-) is a stable bound state. However, only recently has the energy level structure of e_t^- up through the conduction band level been delineated.[1] In 10 *M* NaOH–H_2O glass at 77°K, e_t^- has no stable bound excited state,[2,3] while in pure single crystal ice a stable bound excited state does exist.[1,4] A more complex energy level structure has been found for e_t^- in the slightly polar methyltetrahydrofuran (MTHF) glass.[5] There, both one and two photon pathways to promote e_t^- to the conduction state were found. The two photon pathway was postulated to proceed *via* an intermediate configurationally relaxed 2s type state,[6] and this postulate has been supported by theoretical calculations[7] based on a semicontinuum model for trapped and solvated electrons.[8,9]

In this paper we elucidate the energy level structure of e_t^- in the nonpolar glassy matrix, 3-methylhexane (3MH). Previous studies of this type have concerned e_t^- in polar matrices and it is of interest to assess the effect of matrix polarity on the e_t^- energy level structure. The wavelength and light intensity dependence of the photoconductivity and optical bleaching associated with e_t^- disclose both one and two photon pathways to the mobile state. Also, from the temperature dependence of the photocurrent and optical bleaching rate, it is found that the two photon path involves a small activation energy. The overall energy level structure deduced for e_t^- in 3MH is surprisingly similar to that for e_t^- in MTHF.

Experimental Section

3-Methylhexane from Baker Chemical Co. was purified by shaking with sulfuric acid to remove olefins, rinsing with water, drying over Drierite, and fractional distillation below 90°. Finally, the solvent was degassed and passed over sodium mirrors as described previously for MTHF.[5] A small amount of naphthalene was added to increase the drying efficiency of the sodium mirrors in the final drying stages. Irradiations were carried out at 77°K at a nominal dose rate of 0.3 Mrad/hr in a Co^{60} γ source. Actual doses were corrected for the Co^{60} decay rate. The radiation dose was typically 0.7 Mrad except in the dose dependence measurements. The photoconductivity cell has been described.[5] The cell had a circular Pyrex or quartz window diameter of 16 mm and brass mesh electrodes.

The photocurrent magnitude in γ-irradiated 3MH is much smaller than that in γ-irradiated MTHF, and the dc measurement method used for MTHF[5] was not sufficiently sensitive. Therefore, an ac method with phase sensitive detection was used to measure the photocurrent in 3MH. A dc electric field was applied to the sample, but the exciting light was chopped at 90 Hz with a PAR Model 222 light chopper. The photocurrent was amplified by a Keithley 610 B electrometer and by two PAR Model 210 selective amplifiers before entering a PAR Model JB-6 lock-in amplifier which was referenced to the light chopper. The output from the lock-in amplifier was recorded on a strip chart recorder. The response time of the system was limited by the lock-in amplifier and was usually set at 3 sec.

The visible light source was a 500-W slide projector plus a focusing lens. The intensity measured by a YSI Model 65 radiometer was 5.1×10^5 ergs/(cm^{2}sec). The infrared (ir) light source was a 250-W General Electric heat lamp, Model R 40, plus a Corning No. 2540 filter which cuts off light below 950 nm. The ir light intensity was 3.0×10^5 ergs/(cm^2 sec). The spectral distribution of the visible and ir light sources has been given previously.[5] In some experiments "ir light" is designated. This refers to the ir lamp plus an Optics Technology No. 63 longwave pass filter which cuts off below 1400 nm. The intensity of the "ir light" was 1.7×10^5 ergs/(cm^2 sec). A Bausch and Lomb high intensity monochrometer set for a 20-nm bandpass was used to make wavelength dependence measurements in the visible range, while a differential filter method[5] was used in the ir range. This method consists of using a series of longwave pass filters and subtracting the signals from two filters at adjacent cuff-off wavelengths.

The temperature at 77 and 4.2°K was controlled as described

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(1) L. Kevan, *J. Phys. Chem.*, 76, 3830 (1972).

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(6) A 2s state and analogous terminology used in this paper refer to the type of hydrogenic wave function used to calculate the energy of a given state within the framework of the semicontinuum model.

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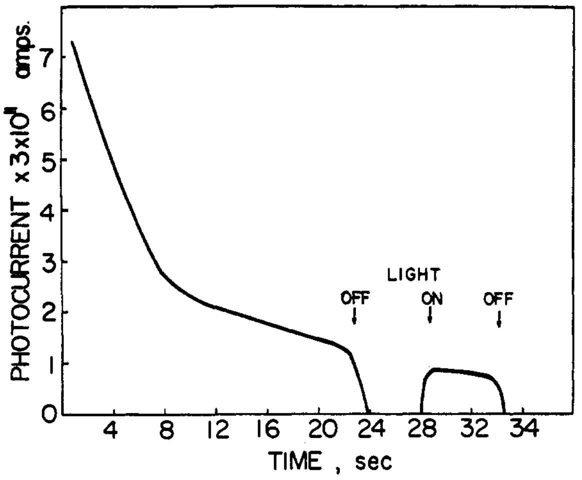

Figure 1. Photocurrent profiles for γ-irradiated (0.7 Mrad) 3MH at 77°K. The sample thickness was 0.05 cm; the applied field was 16 kV/cm; and ir light plus a Corning Filter No. 2540 which cuts off below 950 nm was used.

earlier,[2] and below 77°K cold helium gas boiled off from liquid helium was used. Variable temperatures could be obtained by varying the boil off rate.

Optical bleaching measurements were done with epr detection. Epr samples were prepared with 0.14 ml of 3MH in 3-mm i.d. Spectrosil quartz tubes. A Model 4500 Varian epr spectrometer with 100-kHz modulation was used. Measurements at 4.2 and 77°K were made in the same double dewar. For other temperatures the helium flow system mentioned above was used. The light sources were the same as described above.

Results

A. Phenomenology of Photocurrent and Photobleaching. A typical photocurrent profile photoexcited by ir light after 0.7 Mrad of irradiation and under a 16 kV/cm electric field is presented in Figure 1. The phenomenology is similar to the alkaline ice[2] and MHTF[5] matrices with visible light photoexcitation. Decay occurs due to combination with trapped cations, possibly with radicals, and to retrapping. The decay profile remains essentially the same for 400- to 1500-nm monochromatic light excitation. This is different from the behavior of the MTHF matrix.[5] The voltage dependence of the photocurrent, measured at 15 sec after the start of illumination, is strictly ohmic from 8 to 20 kV/cm for illumination between 400 and 2000 nm.

The epr signals for the photobleaching of the trapped electrons by near-infrared monochromatic light (1400 nm) can be seen in Figure 2. The upper and lower parts of the epr derivative curve are not symmetric in their bleaching behavior. After complete bleaching of e_t^-, the underlying radical spectrum is obtained, so the single line of e_t^- is superimposed on the radical signal. Since the g factor of both e_t^- and the radical are not exactly the same, the observation of asymmetry of the e_t^- epr line is attributed to the difference of g factors. The e_t^- signal height has been obtained by subtracting the height of the underlying radical signal from the observed total signal height. The height of the underlying radical was determined from the residual signal after the e_t^- was completely bleached. This peak-to-peak amplitude of the first derivative curve is proportional to the spin concentration of unbleached trapped electrons. The radical signal does not change during bleaching.

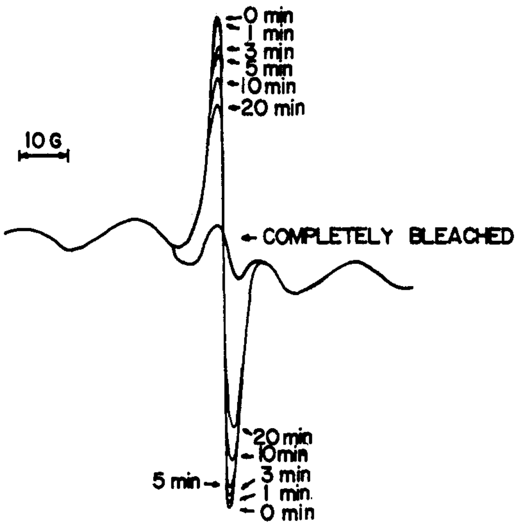

Figure 2. Typical epr spectra of progressive optical bleaching of e_t^- in 3MH (0.7 Mrad) at 77°K by monochromatic light at λ 1400 nm with $I = 0.75 \times 10^3$ ergs/(cm^2 sec).

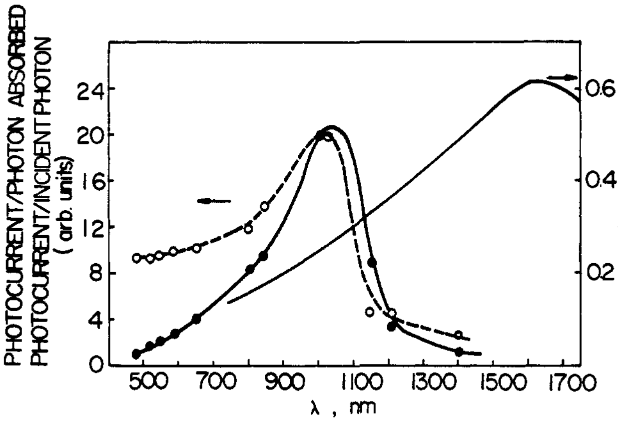

Figure 3. The wavelength dependence of photocurrent in γ-irradiated 3MH at 77°K at 16 kV/cm determined by the differential filter method: (●) photocurrent/incident photon; (○) photocurrent quantum efficiency curve; and (——) optical absorption curve.

B. Wavelength Dependence of the Photocurrent and of Optical Bleaching. The optical absorption spectrum of e_t^- in 3MH is a broad asymmetric band with a peak at 1650 nm. The wavelength dependence between 400 and 1400 nm of the photoconductivity per absorbed photon and per incident photon was measured by the differential filter method. The results are shown in Figure 3 and indicate only one photocurrent peak with a maximum at 1000 nm. We could not extend this measurement to longer wavelengths (*i.e.*, 1400 nm), because of the weak light intensities in this region.

The wavelength dependence of the rate constant for optical bleaching of e_t^- at a dose of 0.7 Mrad was carried out by epr measurements. This bleaching rate constant should be proportional to the number of electrons photoexcited to the conduction band per incident photon. The optical absorption and bleaching rate are shown at both 77 and 4.2°K in Figure 4. This bleaching rate has a maximum near 1000 nm, and there appears to be another peak below 1600 nm. The first peak (*i.e.*, 1000 nm) is coincident with the photocurrent peak in Figure 3 and the second sug-

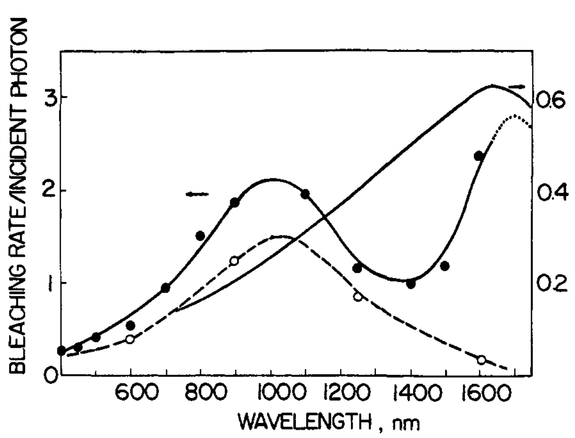

Figure 4. The relative optical bleaching rate constant of e_t^- in 3MH at 4.2°K and 77°K *vs.* bleaching wavelengths: (——) optical absorption curve at both 77 and 4.2°K; (●) optical bleaching rate at 77°K, the dotted extension is conjectured; (○) optical bleaching rate at 4.2°K.

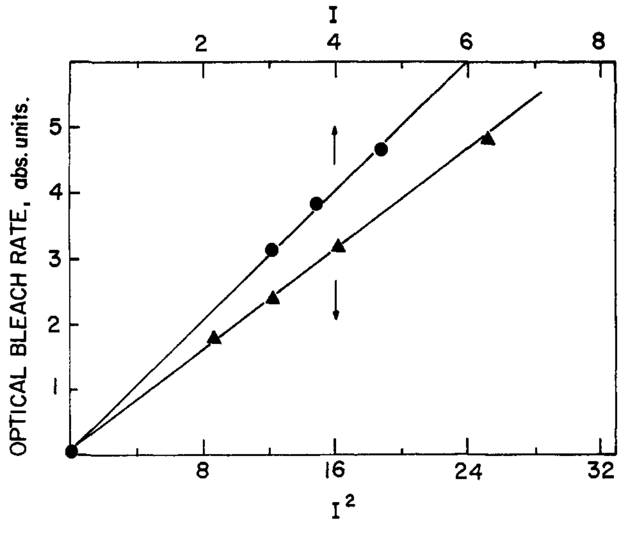

Figure 5. The light intensity dependence of the optical bleaching rate in γ-irradiated 3MH at 77°K with visible light (400–900 nm) (●) and with infrared light (1400–2000 nm) (▲).

gested peak should be a two-photon transition by analogy to the energy level structure of e_t^- in MTHF.[5] Since monochromatic light was used for the optical bleaching experiment, the energies of the two photons required for the two photon transition must be very close to each other. Otherwise, we would not see this peak as is the case of optical bleaching in the MTHF matrix where the two photons required for the two-photon transition are somewhat different in energy. Definite evidence for this two-photon process is found by light intensity measurements.

It is worth noting that there is a strong matrix absorption in 3MH glass between about 1160 to 1240 nm. This same matrix band also appears at nearly the same wavelength in MTHF glass. However, the wavelength dependence of photoconductivity and photobleaching is very different in MTHF[5] compared to 3MH. Thus, it does not appear that the matrix absorption leads to any spurious effects, like heating or photon depletion, on the photoexcitation of e_t^- in these two matrices.

C. Effect of Light Intensity on Photocurrent and on Optical Bleaching. The light intensities can be reduced with different size brass meshes. The visible light source was the slide projector with a peak intensity near 600 nm. The measurements with ir light were done with the ir lamp plus an Optics Technology Inc. Filter No. 63 to limit the wavelength region between 1400 and 2000 nm. The optical bleaching results are plotted in Figure 5. With visible light the optical bleaching rate is linearly proportional to the light intensity, but with ir light the optical bleaching rate depends on the square of the light intensity. The photocurrent magnitude shows the same results; with visible light the photocurrent is linear with light intensity, while with ir light the photocurrent depends on the square of the light intensity. These results confirm the existence of a two-photon process in the ir region of 1400–2000 nm for promoting e_t^- to the conduction state.

The optical absorption of e_t^- in 3MH shows a peak near 1650 nm, and there also appears to be a peak for the optical bleaching rate with monochromatic light. Together with the evidence for a two-photon process, we interpret the 1650-nm transition as occurring from the ground state of e_t^- to a bound excited state of e_t^-. Then the second ~1700-nm transition (from the optical bleaching results) is interpreted to occur from an excited state of e_t^- to a conduction band. The details of this analysis will be mentioned later. Since the energies of these two photons are so close to each other, we are able to observe the occurrence of this process with monochromatic light excitation.

D. Temperature Dependence of Optical Bleaching and Photocurrent. The temperature dependence of optical bleaching of e_t^- probes the existence of temperature-dependent pathways to the conduction band as observed in the MTHF matrix.[5] If optical bleaching were temperature independent, only direct transitions from the ground state to the conduction state or to states which autoionized to the conduction state would be indicated. However, temperature-dependent bleaching indicates weakly bound excited states near the conduction state or an activation barrier between two intermediate states.

The bleaching rates at 77 and 4.2°K as a function of the wavelength of the bleaching light are shown in Figure 6. These measurements are for samples irradiated to 0.7 Mrad and analyzed by epr. At a certain wavelength, such as 1600 nm, the bleaching rate follows the Arrhenius activation law and gives a linear plot of log k *vs.* $1/T$. There is little temperature dependence of the bleaching rate at shorter wavelengths (*i.e.*, 900 and 1250 nm), and direct transitions to the conduction band, possibly *via* autoionizing states, are indicated in this wavelength region. At longer wavelengths, the bleaching process is temperature dependent. If we interpret the bleaching temperature dependence in terms of an activation energy, we find at 1600 nm that $E_{ob} \sim 1.25 \times 10^{-3}$ eV, where ob refers to optical bleaching.

The temperature dependence of the photocurrent should give similar information about the optical excitation process. However, the photocurrent depends on the mobility as well as on the number of charge carriers excited to the conduction band.[2] The drift mobilities of photogenerated electrons in 3-

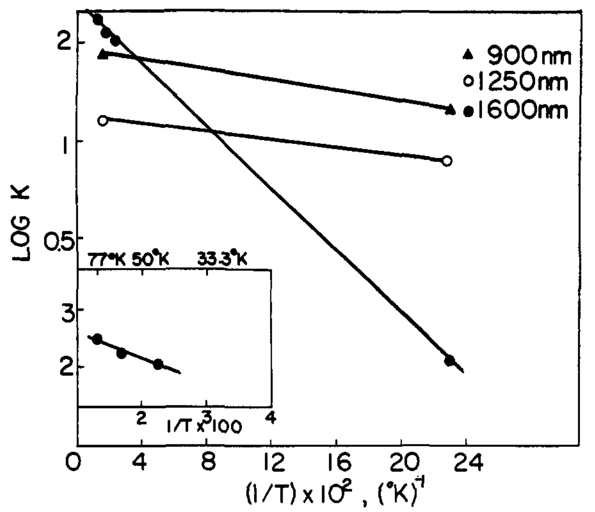

Figure 6. The determination of Arrhenius activation energy at different bleaching wavelengths for temperatures between 77 and 4.2°K for e_t^- in 3MH.

methylpentane (3MP)[10] and in MTHF[1] have recently been measured by a time-of-flight method between 4.2 and 77°K. In both matrices the mobility is temperature activated between 77 and 40°K and is approximately independent of temperature below 40°K. Between 77 and 40°K the apparent activation energy is 0.01 eV in 3MP and 0.0035 eV in MTHF.

For 3MH the temperature dependence of the photocurrent associated with e_t^- photoexcited by ir light (1400–2000 nm) is shown in Figure 7. At temperatures between 77 and 40°K the photocurrent is activated with an apparent activation energy of 0.0058 eV, and below 40°K the photocurrent is nearly temperature independent. This is the same behavior with temperature as observed for the electron drift mobility. If we estimate the electron drift mobility in 3MH as ~0.005 eV, as seems reasonable from the measured values in 3MP and in MTHF, the photocurrent activation energy minus the mobility activation energy yields ~0.001 eV for the activation energy associated with promoting e_t^- to the conduction state. This is at least consistent with the activation energy found by optical bleaching for this process. This small temperature dependence can be reasonably associated with the population of the intermediate state in the two-photon excitation of e_t^- in 3MH with ir light.

E. Dose Dependence of Photocurrent. The dose dependence of the photocurrent is shown in Figure 8. Each point represents a fresh sample and the measurements are for visible excitation only. The photocurrent rises linearly to about 0.72 Mrad and then decreases as the radiation dose is further increased. This particular dose dependence is consistent with the e_t^- yield *vs.* dose measured by epr.[11] The decrease of e_t^- at high dose has been interpreted in terms of reaction of trapped electrons with trapped positive ions and radicals.

Discussion

From the above results, we may analyze the energy level structure of e_t^- in 3MH matrix as follows.

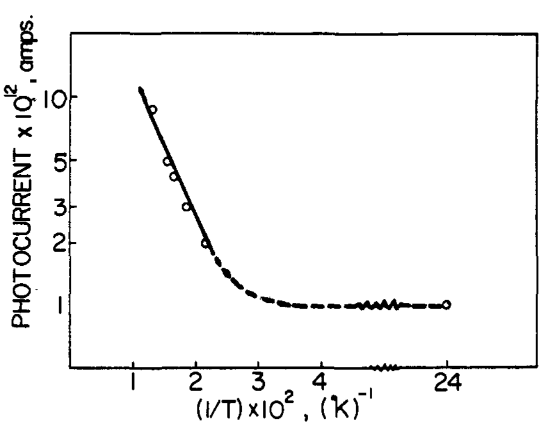

Figure 7. The plot of photocurrent *vs.* T^{-1} for the photoexcitation of e_t^- in 3MH at 16 kV/cm with ir light (1400–2000 nm). The photocurrents are those measured 20 sec after illumintion begins.

(1) The optical absorption maximum at 1650 nm = 0.75 eV = $h\nu_1$ appears to be a transition from the ground state to a stable bound excited state. This transition is presumably optically allowed.

(2) The wavelength maximum of both the photocurrent and the optical bleaching rate at 1000 nm = 1.24 eV = $h\nu_2$ must also correspond to a transition from the ground state. Since both photocurrent and optical bleaching result from this transition, the upper state must be the conduction band, a state that autoionizes to the conduction band, or a bound state close to the conduction band. The last possibility is eliminated by the lack of temperature dependence for optical bleaching and photoconductivity in this wavelength range. The optical absorption associated with this transition is not observed and is presumably weak. It could well be buried in the tail of the strong 1650-nm transition.

The threshold energy of the 1000-nm transition should correspond to the bottom of the conduction band and is about 1.0 eV = $h\nu_2$ (1240 nm) from both optical bleaching and photoconductivity data. The peak at 1000 nm can be interpreted as associated with a maximum in the density of states about 0.24 eV above the bottom of the conduction band. This is conjectural because there is no independent experimental information on how the density of states varies with energy in the conduction band. Mott[12] has discussed the density of states in glassy media from a theoretical viewpoint and postulates that the density of states typically reaches a maximum near the center of the delocalized conduction state; for example, see Figure 2.7 in ref 12.

The peak beyond the photoconductivity threshold can also be interpreted by analogy to photoionization of atomic hydrogen.[13] Delahay[14] has discussed this picture with reference to photoelectron emission from solutions. Within the framework of the semicontinuum model for trapped electrons,[7-9] we may equate the relative cross section for photoionization from a 1s hydrogenic wave function with variational

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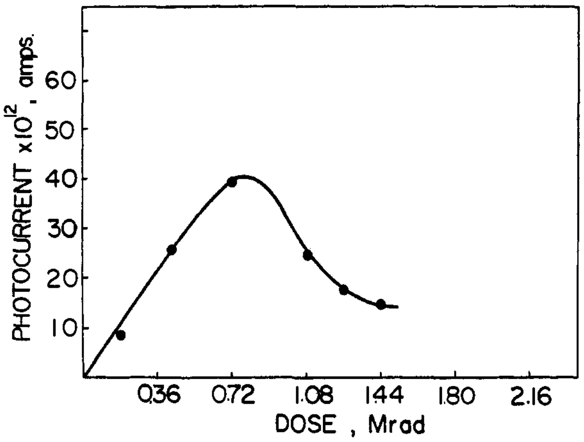

Figure 8. The photocurrent *vs.* the radiation dose for photoexcitation of e_t^- in 3MH at 77°K and 16 kV/cm with visible light.

parameter α to a plane wave conduction state wave function to the normalized differential of the oscillator strength, f, with respect to excitation energy, ϵ, above the ionization threshold[15] as given by $df/d\epsilon = (8\sqrt{2}/3\pi)\alpha^5\epsilon^{3/2}[(\alpha^2/2) + \epsilon]^{-5}$. For e_t^- in MTHF, where the semicontinuum model, ground state wave function is known,[7] the differential oscillator strength reaches a maximum ~0.6 eV above the photoionization threshold, which is in good agreement with experiment.[5] We cannot make a similar calculation for e_t^- in 3MH because the semicontinuum model is not directly applicable to nonpolar matrices like 3MH. However, it is clear that the atomic photoionization model will also predict a maximum for e_t^- photoionization in 3MH.

On the basis of the experimental data above, we do not feel it is possible to clearly distinguish between these two possible interpretations of the maximum above the conduction band threshold. However, to be consistent with the isolated trapped electron model interpretation of e_t^- energy levels, we feel that the atomic photoionization interpretation is to be preferred.

(3) The optical bleaching measurements indicate a second wavelength maximum beyond 1600 nm = 0.77 eV. The two-photon nature of e_t^- excitation to the conduction state in this wavelength region suggests a transition from an intermediate excited state to the conduction band. The threshold of this transition was not determined since 3MH matrix absorption precluded measurements from being carried out to longer wavelengths. So, we can only set a limit of $h\nu_3 < 0.7$ eV as the energy difference from the intermediate excited state to the bottom of the conduction band.

(4) Since a small temperature dependence was observed in both optical bleaching with 1600-nm light and ir photoconductivity ($\lambda \geq 1400$ nm) measurements, we interpret this small temperature dependence to be associated with the population of the intermediate state. The temperature dependence can be assigned to an activation energy for crossing from the excited state, to which the 1650 nm ($h\nu_1$) transition occurs, to an intermediate state from which the 1700 nm ($h\nu_3$) transition occurs. Alternatively, the temperature dependence could be at least partially atrributable to a temperature-dependent lifetime of the intermediate state. The intermediate state must be optically forbidden with respect to the ground state in order to achieve a sufficient population in it to allow an observable two-photon transition. So the intermediate state will have a different symmetry from the optically allowed excited state to which the 1650-nm transition occurs.

We may summarize the above interpretation of the energy level structure of e_t^- in glassy 3MH by an energy level diagram shown in Figure 9. We identify the ground state E_0' as described by a 1s type wave function. The optical transition $h\nu_1$ must occur to an unrelaxed 2p-type state, E_2, due to the Franck–Condon principle. This unrelaxed state is one in which the orientational polarization of the matrix is determined by the ground state 1s-type wave function as denoted by the 1s subscript. The unrelaxed 2p state then relaxes as the matrix nuclei respond to the new 2p charge distribution and the orientation polarization of the matrix then becomes consistent with the 2p charge distribution. Unrelaxed and relaxed states are discussed from a theoretical viewpoint in ref 8. The orbital subscript in parentheses for each energy level denotes the electron charge distribution with which the matrix nuclei are in equilibrium; these are all unrelaxed states. The relaxed states are denoted by a prime and do not show an orbital subscript. We propose that the electron in the unrelaxed 2p state crosses with a small activation energy to the relaxed 2s state (E_1'). This temperature-dependent crossing presumably involves interaction with lattice vibrations of the 3MH matrix. This same interaction could also cause the intermediate state lifetime to be temperature dependent. Transitions from the E_1' state to the ground state are optically forbidden by orbital symmetry but a nonradiative path (NR) may exist. Also an allowed optical transition $h\nu_3$ from E_1' to the conduction band $E_{c(2s)}$, which is consistent with the charge distribution of the E_1' state, is interpreted as the origin of the two-photon photocurrent and optical bleaching processes. In addition to $h\nu_1$, another transition from E_0' given as $h\nu_2$ is interpreted to occur directly to the conduction band $E_{c(1s)}$ which is consistent with the charge distribution of the E_0' state. If autoionizing states are involved in the transitions to the conduction state, the qualitative features of Figure 9 will still be retained.

The energy level structure deduced for e_t^- in 3MH is remarkably similar to that deduced for e_t^- in MTHF.[5] Thus the difference in polarity between 3MH and MTHF does not affect the qualitative features of the e_t^- energy level structure; only the energy differences between the levels are changed. Theoretical calculations on e_t^- in MTHF glass support the energy level structure deduced in that matrix.[7] In particular the calculations show that the relaxed 2s state lies above the relaxed 2p state by about 0.1 eV. This supports the postulate that electrons excited to the unrelaxed 2p state cross to a relaxed 2s state. Similar calculations cannot be carried out for 3MH because the theoretical semicontinuum model[8,9] is not directly applicable to nonpolar matrices like 3MH. However, the ordering of the e_t^- levels in MTHF and 3MH is probably the same because the experimental results are so similar.

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(15) K. Fueki, private communication, 1972.

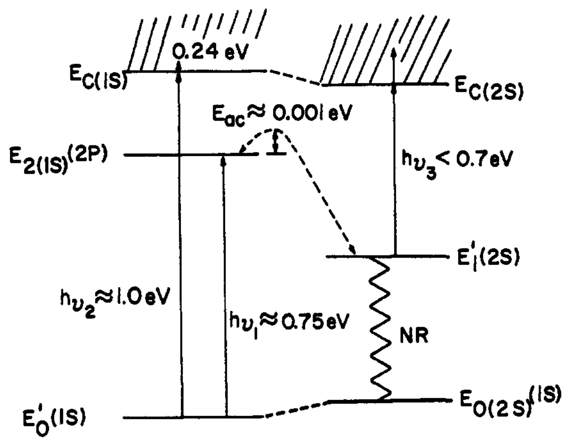

Figure 9. The energy level diagram for trapped electrons in 3MH glass at 77°K. 1s, 2s, and 2p refer to hydrogenic type wave functions; for vertical transitions to unrelaxed states the orbital in the subscript refers to the wave function which determines the orientational polarization of the matrix. Primes denote relaxed states. NR refers to a possible nonradiative transition.

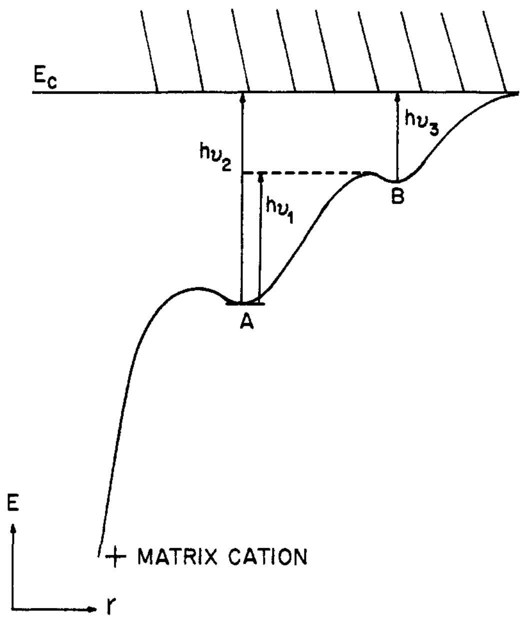

Figure 10. A schematic diagram of electron traps in the Coulomb field of a matrix cation and possible optical transitions. E_c is the conduction band.

Although the above model is attractive in its simplicity, there is one major flaw. Namely, it is difficult to believe that a 2s-type state can have a lifetime long enough (>0.1 sec) to build-up sufficient concentrations of electrons to give an observable two-photon transition. Certainly, within a single molecule in the condensed phase, no spin-allowed transitions with lifetimes of the order of 10^{-1} sec are known. For an electron bound by a matrix potential, the situation may possibly be different; the answers as to excited state lifetimes in such a case simply are not known yet. It may be better to regard the nature of the intermediate state involved in the two-photon transition as unspecified. However, we find it convenient to think in terms of the hydrogenic wave function model at present. Another model is discussed below, but it does not seem to be obviously preferable.

An alternative explanation for the two photon transition of e_t^- to the conduction band in both MTHF and 3MH matrices is to postulate two e_t^- traps of different depths in a Coulomb well associated with a positive ion as shown in Figure 10. In this model it is assumed that the electrons are trapped within the Coulomb well of a matrix cation. This model has been used with some success to understand the characteristics of e_t^- produced by photoionization of *N,N,N′,N′*-tetramethylphenylenediamine (TMPD) in 3MP glass at 77°K.[16] The Coulomb well model can account for the two-photon photocurrent as follows. One photon may excite e_t^- from trap A to trap B which is located farther away from the matrix cation and is subject to less distortion by the Coulomb field. A second photon may excite the electron from trap B to the conduction band at a distance sufficiently far from the matrix cation that the externally applied electric field drives the electron in the conduction band to produce photocurrent. It is not obvious, however, that the Coulomb well model accounts for the temperature activated population of trap B as seems to be required from the experimental results. Also, the optical bleaching process in the Coulomb well model would not be expected to show two-photon character. Optical bleaching of e_t^- in trap A is expected to be predominately a one-photon process since recombination with the matrix cation would be expected for most of the e_t^- upon photoexcitation from A. However, optical bleaching with ir light >1400 nm seems to be entirely a two-photon process. Finally, one would probably expect the spectrum of the wavelength dependence of photobleaching to be somewhat red shifted from the spectrum of the photoconductivity wavelength dependence on the basis of the Coulomb well model. The experimental results do not appear to support this.

The Coulomb well model differs from the isolated trapped electron model only in whether the matrix trapping potential for the electron is significantly distorted by the Coulomb field of nearby matrix cations or not. From the discussion above it appears that the Coulomb well model is not as appropriate as the isolated trapped electron model in γ-irradiated 3MH. The same conclusion applies to γ-irradiated MTHF. In the earlier work on the energy level structure of e_t^- in MTHF the light intensity dependence of the optical bleaching process was not reported. These experiments have since been done and show the same results as for e_t^- in 3MH. The optical bleaching rate of e_t^- in MTHF was measured by epr. For visible light photoexcitation, the bleaching rate is linear in light intensity. For ir light (λ >950 nm) photoexcitation, the bleaching rate is dependent on the light intensity squared. However, when e_t^- is produced by photoionization of TMPD in MTHF glass at 77°K, ir light photoexcitation yields a bleaching rate which is linear in light intensity. This indicates a one-photon process in contrast to the γ-irradiated matrix. The characteristics of ground state e_t^- in MTHF (*i.e.*, optical absorption spectrum and epr spectrum) show no difference when produced by γ- irradiation or by photoionization of TMPD. However, it appears that the ir photobleaching process is different for e_t^- produced by the two methods. The two photon photobleaching

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in γ-irradiated MTHF is consistent with an isolated trapped electron, while the one-photon photobleaching of e_t^- produced by TMPD photoionization in MTHF is consistent with the Coulomb well model. This difference sugggests that e_t^- produced by photoionization is trapped somewhat closer to a cation than e_t^- produced by γ irradiation. Further studies on this point would be of interest. This difference also suggests that the energy level structure illustrated in Figure 9 for e_t^- in γ-irradiated 3MH is at least a possible working model at present.

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Flash Photolysis Study of 4-*N*-Dimethylaminopyridine

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Abstract: A flash photolysis study of 4-*N*-dimethylaminopyridine in different solvents has led to the assignment of three transient species, together with their corresponding absorption maxima: (a) neutral radical, $\mathrm{Py{-}\dot{N}{-}CH_3}$ (λ_{max} 315 and 395 nm); (b) radical cation resulting from photoionization (λ_{max} 500 nm); and (c) triplet–triplet absorption (λ_{max} 500 nm). The radical–radical recombination is a second-order process occurring at room temperature with a value of $k/\epsilon_{395\ \mathrm{nm}} = 2.58 \pm 0.2 \times 10^5$ cm sec^{-1} in 2-propanol, $4.5 \pm 0.5 \times 10^5$ cm sec^{-1} in acetonitrile, and $1.8 \pm 0.4 \times 10^6$ cm sec^{-1} in ethyl ether. The triplet–triplet absorption is only observed at low temperatures ($<-55°$ in IPA, $<-90°$ in ethyl ether, and $<-150°$ in EPA). The lack of triplet–triplet absorption in 3-MP to temperatures of $-185°$ is probably due to significant variation of the triplet yield with solvent. A short-lived transient ($\tau \approx 50$ μsec) attributed to the radical cation with λ_{max} 500 nm was observed at room temperature only in acetonitrile. The energy of activation for the triplet decay rate constant in EPA was determined to be 3.5 kcal/mol.

Recent interest in the flash photolysis literature has been directed toward the elucidation of electronically excited states in aromatic heterocyclic molecules. The triplet–triplet absorption of acridine has been reported by several groups.[1–5] Qualitative observations of T–T absorption in pyrimidine, pyridazine, quinoxaline, and phenazine in hydrocarbon glassses at 77°K have also been performed.[6] With the use of steady-state cross illumination, Henry and Kasha[7] investigated T–T absorption of quinoxaline, phenoxazine, phenothiazine, and carbazole. Hadley[8] has used the flash photolysis technique to show that internal conversion from the singlet may be important in quinoxaline. Other flash photolysis studies of aromatic heterocyclics include phenoxazine,[9] thymine, uracil,[10,11] and orotic acid.[12] Although no triplet–triplet absorption has been observed in pyridine, we recently reported the T–T absorption of 4-*N*-dimethylaminopyridine in EPA at $-180°$, which exhibits a maximum at 500 nm.[13] This molecule is particularly interesting since we have previously demonstrated that its phosphorescence polarization changes sign on going from a polar solvent such as EPA to a nonpolar solvent such as 3-methylpentane.[14] Since this was the first reported T–T absorption for a pyridine derivative, it became of interest to study the flash photolysis behavior of 4-*N*-dimethylaminopyridine (4-DMAMP) in different solvents with the aim of better understanding the interaction between $^3n,\pi^*$ and $^3\pi,\pi^*$ states. Accordingly, this investigation was performed in isopropyl alcohol, EPA, acetonitrile, ethyl ether, methylcyclohexane, and 3-methylpentane with the temperature varied from room temperature down to 77°K, depending upon the solvent system selected.

Experimental Section

Materials. 4-*N*-Dimethylaminopyridine was obtained from EGA Chemie, West Germany, and purified by recrystallization. The solvents used in this investigation did not produce any absorbing transients upon flashing. Solutions of 4-*N*-dimethylaminopyridine were generally in the range 2×10^{-4} *M*.

Apparatus. All flash measurements were made with 10-cm path length cylindrical Suprasil cells (15-cm o.d.). Solutions were first vigorously degassed at 10^{-6} mm and then flame sealed under vacuum. An energy input of approximately 150 J/flash was employed using an apparatus described elsewhere.[15] A signal of 10-V was used to cover the range between 0 and 100% absorption, and kinetic

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