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An Upper Limit to the Excited Electron-Cation Recombination Lifetimes of Trapped Electrons in Ethanol and 2-Methyltetrahydrofuran Glasses at 4 and 77 K

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N,N,N′,N′-Tetramethyl-*p*-phenylenediamine (TMPD) fluorescence lifetimes in 2-methyltetrahydrofuran (MTHF) glass at 77 K (13.5 ns) and in ethanol glass at 77 K (12.3 ns) and 4 K (11.5 ns) were measured using 347 nm excitation from a frequency doubled ruby laser. Trapped electrons and $TMPD^+$ were generated in these matrices by photoionization and the recombination fluorescence stimulated by 694 nm laser light was found, within an experimental limit of 1 ns, to occur with the same lifetime as the directly excited fluorescence. A convolution analysis indicates that the electron-cation recombination lifetimes are ≤ 1 ns in all these matrices at the temperatures given. It is also suggested that a lower limit for the electron mobility of 0.005 $cm^2\ V^{-1}\ s^{-1}$ is implied by these data.

Electrons have been trapped in a variety of organic glasses and their electronic and geometric structures have been extensively studied.[1] Both bound-bound and bound-continuum transitions seem to occur depending on the matrix and on the exciting light energy. However, little is known about the excited state lifetimes because no luminescence is observed. Indirect laser photobleaching methods suggest that the excited state lifetime is ≤ 6 ps in liquid water[2] and <10 ps in aqueous glass at 77 K.[3]

Another approach to obtain the excited state lifetime of trapped electrons is to measure the recombination lifetime of laser stimulated recombination luminescence. In this method the trapped electrons are produced by photoionization of an aromatic solute whose excited states luminesce.[4,5] The closest localized electrons to the solute cations recombine with them isothermally by tunneling[6] to produce isothermal recombination liminescence. More distant localized electrons can be optically stimulated to recombine with the solute cation. If the optical excitation of the trapped electron is energetic enough to excite the electron to the conduction state of the matrix, the total recombination lifetime will consist of four parts: (a) the lifetime of the localized continuum or quasi-continuum state of the electron, (b) the electron lifetime in the conduction state, (c) the lifetime of the localized continuum state of the excited solute, and (d) the lifetime of the fluorescent state of the solute. Contribution (b) can be estimated from electron mobility data if known. We expect (c) to be short compared to (d) because lifetimes are generally shorter for more highly excited states. Thus a delay of the recombination fluorescence lifetime beyond the directly excited fluorescence lifetime of the solute (contribution d) may yield information about the excited electron state lifetime.

This type of experiment was initially tried for *N,N,-N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) in 3-methylpentane (3 MP) glass at 77 K, although the focus was on an estimate of lifetime (c) and contributions (a) and (b) were not considered.[7] The recombination fluorescent lifetime and an upper limit of 1 ns on the electron-cation recombination step was deduced.

In the present work we have extended this type of experiment to polar matrices, 2-methyltetrahydrofuran (MTHF) and especially ethanol, and have made measurements at both 4 and 77 K in ethanol. New information is obtained on the natural fluorescent lifetimes of TMPD under these various conditions, but even in these polar matrices only upper limit for the electron-cation recombination step can be deduced.

Experimental

Chemicals were purified as described previously.[5,6] A Korad Pockel cell switched ruby laser was used for excitation. The 694 nm output energy was about 1 J per pulse of half-width 15—25 ns. For fluorescence lifetime measurements the laser output frequency was doubled to 347 nm. For recombination fluorescence, trapped electrons were first generated by photoionizing TMPD (7×10^{-4} mol/dm^3) with 320±20 nm light from a filtered mercury lamp; then within 3—10 min fluorescence was stimulated with a 694 nm laser pulse. Laser induced emission was detected through a Bausch and Lomb monochromator at 400±10 nm with a 1P28 photomultiplier for nanosecond response[8] and photographed on a 7904 Tektronix scope. Temperature at 77 K was controlled by cold helium gas in a Dewar. At 4 K the sample was in a Dewar for liquid helium in which the sample position was not shielded by liquid nitrogen. Samples were prepared in 3 mm i.d. pyrex tubes.

Results and Discussion

The directly excited TMPD fluorescence intensity *vs.* time is similar to the laser pulse profile but its peak is typically shifted by 7—10 ns from the laser pulse peak. Accurate fluorescence lifetimes thus required a deconvolution procedure. For greater accuracy a Laplace transform method was used.[9] The fluorescence lifetime τ_f was determined from

$$\bar{L}(p)/\bar{G}(p) = (p/I_0) + (I_0\tau_f)^{-1}, \qquad (1)$$

where I_0 is the initial fluorescence intensity after instantaneous excitation, p is the Laplace transform parameter $\bar{G}(p)$ is the Laplace transform of the observed fluorescence curve, $\bar{L}(p)$ is the Laplace transform of the 347 nm laser pulse and exponential decay for the fluorescence

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was assumed. The left side of Eq. 1 was calculated by a computer program and plotted *vs.* p to give a linear plot from which τ_f was obtained. The τ_f values obtained in this way are estimated to be accurate to $\pm 10\%$ which is thus the effective time resolution of the apparatus with the deconvolution procedure (*i.e.* $\approx$1 ns). The values of τ_f were checked by convoluting the exponential fluorescence decay with laser pulse to simulate the observed fluorescence curves; agreement was excellent in all cases. The fluorescence lifetimes are summarized in Table 1.

TABLE 1. FLUORESCENCE DECAY TIMES OF TMPD IN VARIOUS MATRICES

Matrix	T/K	Decay time[a]/ns
Ethanol	Room	9.3, 7.1[b]
Ethanol	77	12.3
Ethanol	4	11.5
MTHF	77	13.5
Cyclohexane	Room	4.3[b]
3-Methylpentane	77	7.4$\pm$1.1[c]

a) Estimated error $\pm 10\%$ except where noted. b) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," 2nd ed, Academic Press, New York (1971), pp. 168—169. c) Ref. 7.

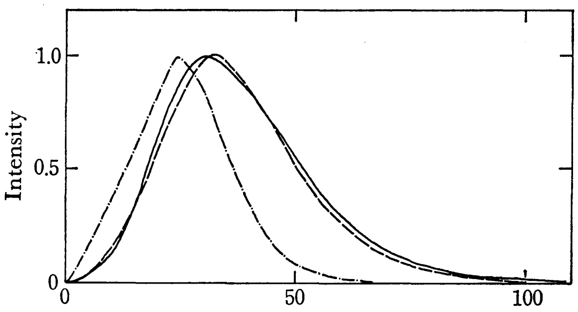

Fig. 1. Intensity *vs.* time profile of the 694 nm laser pulse (-•-) and the recombination fluorescence (——) in ethanol glass at 77 K containing 7×10^{-4} mol/dm^3 TMPD which was previously photoionized by UV light. The dashed curve is calculated TMPD fluorescence convoluted from the 694-nm laser pulse and an exponential fluorescence decay with a liferime of 12.3 ns.

The same deconvolution analysis gives recombination fluorescence lifetime within 10% of the direct fluorescence lifetimes. This is shown pictorially in Fig. 1. The laser stimulated recombination fluorescence for TMPD in ethanol at 77 K is shown in Fig. 1 as is the 694 nm laser pulse profile. The fluorescence calculated from the 694 nm laser pulse and the fluorescence lifetime is seen to coincide, within experimental uncertainty, with the recombination fluorescence. Similar results are obtained for TMPD in ethanol at 4 K and in MTHF at 77 K.

Excited TMPD$^+$ is not expected to contribute to the recombination fluorescence at 400 nm. This was verified by observing no emission from ethanol glass containing 4×10^{-5} to 2×10^{-4} mol/dm^3 TMPD$^+$ ClO$_4^-$ and excited by 694 nm light. Direct excitation of TMPD by 694 nm laser light *via.* double quantum absorption was negligible, since no emission was observed when ethanol glass containing 7×10^{-4} mol/dm^3 TMPD was irradiated by 694 nm laser pulse.

The coincidence of the directly excited and the recombination fluorescence lifetimes indicated that the electron-cation recombination process occurs within $\approx$1 ns which is our estimated time resolution with the deconvolution procedure. Thus the more polar matrices (MTHF and ethanol) show the same upper limit as the nonpolar 3-methylpentane (3MP) matrix.[7]

The upper limit of $\approx$1 ns corresponds to the upper limits for each of the three possible contributions: lifetime of localized continuum states of excited electron (a) and of excited solute (c) and lifetime of the electron in the conduction state (b). From the upper limit of the conduction state lifetime, cation field and recombination distance one can estimate the lower limit of the electron mobility. Assuming the average recombination distance of 10 nm the field independent electron mobilities in MTHF and ethanol matrices are $\mu > 0.005$ cm^2 V^{-1} s^{-1} based on the 1 ns upper limit and the increase in cation field as the recombination distance decreases.** This limit is consistent with the reported drift mobility of 0.055 cm^2 V^{-1} s^{-1} for MTHF glass at 77 K.[10]

The same lower limit on electron mobility is implied for ethanol glass at both 77 and 4 K unless tunneling recombination dominates (see below). This implication is particularly interesting at 4 K since it indicates that the electron mobility remains relatively high to quite low temperature.

In 3MP and MTHF the 694 nm light is energetic enough to excite the trapped electron to the conduction state as indicated by photoconductivity data.[1] However in ethanol the 694 nm (1.8 eV) light appears insufficient to excite the trapped electron to the conduction state since the photoionization threshold is 2.3$\pm$0.1 eV.[11] If the trapped electron is sufficiently close to the cation the Coulomb potential can distort the electron potential well and cause the recombination threshould to be less than the photoionization threshould. However, at separation distances of $\approx$3.0 nm this difference should be within the experimental uncertainty of $\pm$0.1 eV. In fact, the same threshold for electron loss is observed from photoconductivity, photobleaching and stimulated luminescence methods.[1]

Let us see whether tunneling recombination from an

** The average recombination distance can be estimated from a tunneling model for the recombination process[6] prior to laser stimulation. The tunneling rate constant k is given by the equation, $\log k = 15 - 0.44 d V_b^{1/2}$, assuming a simple one dimentional tunneling model with a square barrier of height V_b and width d. The V_b values can be taken as the electron trap depth in MTHF (1.6 eV) and in ethanol (2.3 eV).[1] Then at 200 s which is the average time between photoionization and laser excitation, one finds distances of 3.1 nm (MTHF) and 2.6 nm (ethanol). The average recombination distance will be several times greater than the minimum recombination distance thus estimated and we assume 10 nm. Assuming a dielectric constant of 2 the cation field at 10 nm is 7.2×10^4 V cm^{-1}.

excited state of the electron in ethanol can account for the observed recombination time. With a barrier height of $2.3 - 1.8 = 0.5$ eV, the simple tunneling model⁶⁾ predicts tunneling from 1.9 nm or less within 1 ns. However, the same tunneling model predicts that all electrons within 2.6 nm will have tunneled through the full 2.3 eV barrier in ethanol during the $\approx$200 s between photoionization and laser excitation. Thus there will not be any electron left within 1.9 nm of the cation at the time of laser excitation and the tunneling mechanism seems improbable. It is necessary to reduce the barrier height to 0.25 eV or less for the tunneling distance in 1 ns to be $>$2.7 nm and to make the tunneling mechanism a possible alternative.

A second possibility is that a few of the electrons constituting the 1 eV wide absorption band in ethanol are in shallow enough traps to be excited to the conduction state by 694 nm light. Since fluorescence is a more sensitive detection technique than photoconductivity it may be possible to observed such a small population of electrons if they exist. The observation that the stimulated fluorescence in ethanol glass is 1—2 orders of magnitude weaker than that in MTHF glass may support this suggestion.

We conclude that the localized continuum state lifetimes of trapped electrons and excited TMPD in 3MP and MTHF glasses are $\leq$1 ns at 77 K and in ethanol glass are $\leq$1 ns between 4 and 77 K. Likewise the electron conduction state lifetime is $\leq$1 ns which suggests a lower limit to the electron mobility of 0.005 $cm^2\,V^{-1}\,s^{-1}$ in these matrices.

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References

1) L. Kevan, *Adv. Radiat. Chem.*, **4**, 181 (1974).

2) G. A. Kenney-Wallace and D. C. Walker, *J. Chem. Phys.*, **55**, 447 (1971).

3) D. C. Walker and R. May, *Int. J. Radiat. Phys. Chem.*, **6**, 345 (1974).

4) A. C. Albrecht, *Acc. Chem. Res.* **3**, 328 (1970).

5) H. Mockel, J. Yuen and L. Kevan, *Int. J. Radiat. Phys. Chem.*, **7**, 251 (1975).

6) K. K. Ho and L. Kevan, *J. Phys. Chem.*, **81**, 1865 (1977).

7) D. S. Kliger, J. D. Laposa and A. C. Albrecht, *J. Chem. Phys.*, **48**, 4326 (1968).

8) J. W. Hunt and J. K. Thomas, *Radiat. Res.* **32**, 149 (1967).

9) W. P. Helman, *Int. J. Radiat. Phys. Chem.*, **3**, 283, (1971).

10) T. Huang and L. Kevan, *J. Chem. Phys.*, **61**, 4660 (1974).

11) A. Bernas, D. Grand and C. Chachaty, *Chem. Commun. (J. Chem. Soc., D)*, **1970**, 1667.