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Femtosecond Transient Absorption Studies of Electrons in Liquid Alkanes

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The picosecond and femtosecond decays observed in earlier laser experiments on neat alkanes are consistent with the Onsager model of geminate recombination as well as previous experimental studies using γ -ray sources.

The motion of electrons injected into a liquid, e.g. by photoionization or pulse radiolysis, has been a subject of intense experimental¹⁻⁷ and theoretical⁸⁻¹³ interest. When there is only weak stabilization of the electron and its parent cation, as in nonpolar liquids such as alkanes, the dynamics has been described as the mutual diffusion of the electron-cation pair in the presence of a Coulomb field. In this spirit Onsager⁸ calculated the geminate ion-pair recombination kinetics, treating the electron as a classical Brownian particle in the Coulomb field of the cation. Picosecond experiments,² and in our laboratory femtosecond experiments,¹⁴⁻¹⁵ on the recombination dynamics in neat alkanes yielded excellent agreement with the Onsager model. Recently, however, there have been femtosecond dynamics studies¹⁶ of neat alkanes in which a different interpretation of the kinetic data has been proposed. Rather than the kinetics, as observed by transient absorption measurements, being controlled by the classical diffusion of the electron-cation pair, it was proposed that the observed kinetics are due to a fragmentation of higher excited singlet states.¹⁶ In this paper we discuss the reasons that we believe this interpretation to be incorrect and present data on both the linear and the branched alkanes, which exhibit different kinetics, and which together further support our original interpretation of the experimental data in terms of an Onsager recombination process.

One of the possible sources of the disagreement could be that the later studies¹⁶ were done with a single probe wavelength rather than the large wavelength range extending from the IR to the visible that we used.¹⁵ In the former experiment¹⁶ the single probe wavelength of 490 nm is used, whereas the earlier experiments¹⁵ included probe wavelengths from 500 to 1300 nm. This is an important element in analyzing the linear alkane data because of the strong wavelength dependence of the kinetics, as discussed by us in an earlier publication.¹⁵ By using a 1000 nm probe, we found that the background, which is constant on the picosecond time scale, was significantly smaller than the background obtained with a visible probe. In the IR, the background is approximately half the signal, while at 625 nm it is almost 90% of the total signal (Figure 1). We find that although the amplitude of the absorption is wavelength dependent, the observed decay rates are independent of wavelength. We concluded that there are two independent species contributing to the signals we observed in our experiments.¹⁵ One is a fast picosecond decay due to the electron-cation geminate recombination, and the second is a constant background signal due to absorption by the excited states of the neutral linear

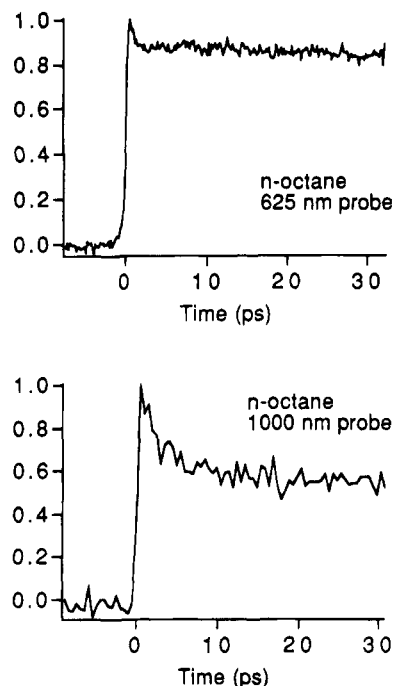


Figure 1. Femtosecond absorption in *n*-octane at room temperature following excitation with a 312 nm pump pulse and 625 and 1000 nm probe pulses.

alkanes. Linear alkanes such as *n*-octane are known to have excited state lifetimes on the order of nanoseconds,¹⁷ which consequently will appear nearly constant for the kinetics on the sub 100 picosecond time scale.

Picosecond studies by Sam and Scott, using low ionization potential solutes dissolved in linear alkanes, showed that the observed nonexponential time dependent signals were well-described by the Onsager model of geminate recombination.² We found similar agreement extended to the subpicosecond time scale. In Figure 2 we see that when including a constant background, which is due to the long-lived excited state of octane, excellent agreement with the Onsager model is obtained.¹⁵ Using the known electron mobility of the alkane solvents and a distribution of thermalization distances, the mean thermalization distance, $\langle r \rangle$, was found by us to be 48 Å.¹⁵ The mean thermalization distance is the average initial distance between the electron and the cation. Scott and Braun found a mean thermalization distance of 45 Å for a dilute solution of benzene in *n*-hexane.² These picosecond and femtosecond experiments are consistent with pulse radiolysis measurements of Schmidt and Allen,¹⁸ from which they calculated the mean thermalization distance to be 72 Å in *n*-octane.⁴ This increase in the thermalization distance is expected since the initial excess

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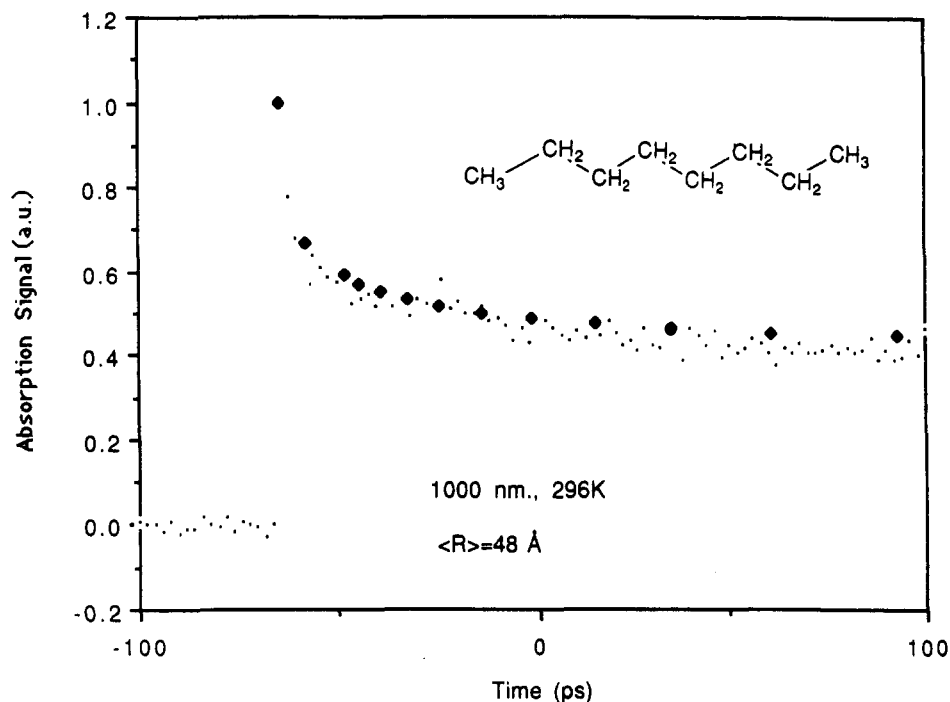


Figure 2. Electron-cation geminate recombination in *n*-octane following a 312 nm pump pulse and a 1000 nm probe pulse. Small dots are experimental data; large dots are theoretical fits to the Onsager model with an average thermalization distance of 48 Å.

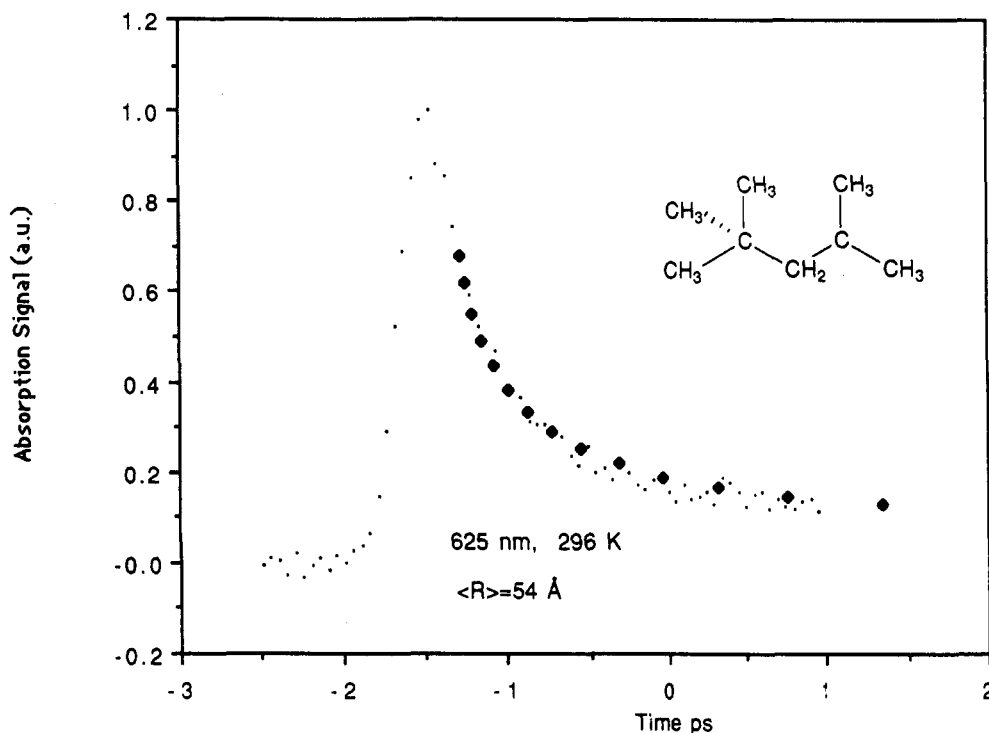


Figure 3. Electron-cation geminate recombination in isooctane following a 312 nm pump pulse and a 625 nm probe pulse. Small dots are experimental data; large dots are theoretical fits to the Onsager model with an average thermalization distance of 54 Å.

energy is much larger than the 2–3 eV of excess energy in our experiments and those of Scott and Braun. It is most likely that the electrons in the neat alkane experiments are produced by a three-photon process, as we noted earlier.¹⁵ These results on thermalization distances in *n*-octane together with observation of a strong IR absorption for the electron in alkanes, which is in agreement with pulse radiolysis measurements,¹⁹ are at odds with the claim¹⁶ that our experiments are inconsistent with traditional radiation chemistry.

We would like to consider now our results¹⁵ for the branched alkane, isooctane (2,2,4-trimethylpentane), which further support

the interpretation of the kinetics as due to a geminate recombination process. The branched alkanes, like isooctane, have much larger electron mobilities than their linear counterparts, and consequently the observed electron-cation geminate recombination is much faster than for the linear alkanes. No excited state absorption background is seen in the branched alkanes, which is consistent with their very short lifetime, as evidenced by a lack of observable fluorescence.²¹ The observed nonexponential kinetics also agree with the Onsager model of electron-cation geminate recombination (Figure 3). A thermalization distance of 54 Å was found in neat isooctane.¹⁵ An

increase in the electron thermalization distance between iso-octane and octane is also consistent with previous radiation chemistry measurements of escape yields.¹⁸ We therefore conclude that the success of the Onsager model to predict the observed nonexponential kinetics, of both *n*-octane and iso-octane, for which the electron mobility differs by 2 orders of magnitude, is strong experimental evidence for attributing the observed kinetics to a geminate recombination process.

In summary, the picosecond and femtosecond decays observed in earlier laser experiments are consistent with the Onsager model of geminate recombination as well as previous experimental studies using γ -ray sources.

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