

$N = 4-10$ can be characterized by a single peak at ~ 1031 cm^{-1} which steadily grows in intensity. For $N = 11-16$, the intensity of the 1031 cm^{-1} band is virtually constant with peak absorption cross section of $2.4 (2) \times 10^{-17}$ cm^{-2} . A second band for $N = 11-16$, grows from a shoulder at $N = 11$ to a resolvable separate peak at 1040 cm^{-1} for $N = 16$. No appreciable absorption was observed in the 9.6 μ R branch ($1070-1090$ cm^{-1}), the entire 10.6 μ region, or for $N = 1-3$. The depletion signals for each solvated ion were found to exhibit a linear dependence on laser intensity.

The C-O stretch at 1031 cm^{-1} in the $\text{Cs}^+(\text{CH}_3\text{OH})_N$, $N = 4-10$, solvated ions is shifted to lower frequency relative to gas-phase⁹ CH_3OH (1034 cm^{-1}) or methanol dimer¹⁰ (1045 cm^{-1}). The interaction between the methanol and the cesium cation is significantly different than the methanol-methanol interaction, although the constancy of the C-O stretch at 1031 cm^{-1} indicates a rather uniform environment. When more than ten solvent molecules are present, the cross section of the 1031 cm^{-1} band is unchanged. Clearly the interactions of the additional molecules are different from the first ten as demonstrated by the generation of a second C-O stretch band. Thus, it appears that the first solvation shell about the cesium cation is comprised of ten methanols. Although large, it is not inconsistent with thermodynamic ion-solvent association results for alkali cations. Data for Li^+ and Na^+ with NH_3 indicated a filled solvation shell of four molecules,¹¹ a number also inferred from Raman spectroscopy of Li^+ and Na^+ in liquid ammonia.¹² Data for K^+ and Rb^+ show no evidence for a filled shell at up to six ammonia molecules.¹¹ For larger Ca^+ and Sr^+ ions with water, evidence for filled solvation shells with six¹³ and eight¹⁴ molecules, respectively, is observed. The

Cs^+ ion is considerably larger than the above mentioned ions, thus an even larger solvation shell size would not be unexpected.

Additional investigations to understand the vibrational predissociation behavior for $\text{Cs}^+(\text{CH}_3\text{OH})_N$ as well as studies with different solvents and regions of the infrared ($\sim 3\mu$) are currently underway.

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Femtosecond study of geminate electron-hole recombination in neat alkanes

Robert M. Bowman, Hong Lu, and Kenneth B. Eisenthal

Department of Chemistry, Columbia University, New York, New York 10027

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The fate of an electron upon ejection into a liquid has been of great interest, both experimentally¹⁻⁷ and theoretically.⁸⁻¹³ In nonpolar liquids, where there is only weak stabilization of the parent cation and the electron, the dynamics are thought to be controlled by the mutual diffusion of the electron-cation pairs in a Coulombic field. If the electron thermalizes before it reaches the Onsager radius,⁸ the distance where the Coulombic binding energy equals the thermal energy of the electron, there is a high probability of geminate recombination. The rate of geminate recombination is determined by the electron's excess kinetic energy and scattering cross section in the liquid. Electron scattering is related to the packing and shape of the solvent molecules, which also determine the electron mobility. The main focus

of this letter is to study the influence of these solvent properties on the rate of geminate recombination.

There have been numerous picosecond studies of geminate recombination in hydrocarbon solvents.²⁻⁷ In these studies, geminate electrons are produced either by pulsed electron beam excitation or by the photoionization of a low concentration of solute molecules in the solvent of interest. These experiments have provided extensive information about the geminate recombination of electrons at low temperatures and in the presence of scavengers, but have only been able to give an upper bound (< 9 ps half-life in hexane²) on the scavenger free, room temperature geminate recombination time. Higher mobility solvents have not been studied thoroughly due to the lack of time resolution.

In this letter we present preliminary results on the first femtosecond study of geminate recombination of electrons in nonpolar liquids. Exciting results on electron solvation in water have been obtained recently using femtosecond techniques.¹⁴ The experiments reported here are done in two neat solvents, *n*-octane and iso-octane (2,2,4-trimethylpentane). These liquids highlight the very strong dependence of electron motions on the shapes of the constituent molecules, which in turn determines the structure and disorder in the liquid. This strong dependence on structure is revealed by the observation that iso-octane has a mobility nearly 200-fold greater than *n*-octane.¹⁵ It should be noted that their densities are the same (within 1.5%). In this study we ask how this large structural effect influences the recombination dynamics in these two isomeric liquids.

The dynamics were obtained from pump-probe experiments using an amplified colliding pulse mode-locked ring laser¹⁶ which produces 100 fs, 400 μ J, pulses with a center wavelength of 625 nm. The sample was multiphoton ionized by frequency doubled light at 312.5 nm and the resulting alkane cation is probed by monitoring the absorption^{17,18} of time-delayed 625 nm light. There are several advantages of these experiments over the ones previously performed. In addition to the improved time resolution, the high energy femtosecond pulses allows us to photoionize the neat solvents directly, making it unnecessary to add any solute to the

system which perturbs the microscopic environment. Also, we are probing the cation absorption not the electron absorption. As mentioned in previous work, excitation of the ionized electron changes its kinetic energy and can affect the recombination kinetics.²

The results of our experiments are shown in Fig. 1. The curves were fit to single exponential decays (solid lines). The decay times for *n*-octane and iso-octane are 2.2 ± 1.0 ps and 470 ± 40 fs, respectively. The fits to single exponential decays are not meant to imply any model for the geminate recombination. We are comparing this data and the data for several other neat alkanes¹⁹ to theoretical models.^{9,10,13} Assuming these decay times are equal to the geminate recombination times, which seems reasonable, there is a marked difference between the two octane isomers. As noted earlier, the molecular structure of hydrocarbons can strongly influence the electron mobility, with the mobility increasing as the shape of the molecule approaches a sphere.¹⁵ In the linear octane there is more disorder due to the entangling chains than in the more spherical iso-octane. Since the electron has a greater spatial extent in the more ordered iso-octane its corresponding motion, e.g., mobility, is greater than in the more disordered *n*-octane solvent.^{11,20} Consistent with this view, we find from this work that the recombination rate is much larger in iso-octane. An important point to note is that on these short time scales neither the iso-octane nor the *n*-octane decay curves level off to their negative time values. We interpret this to mean that a fraction of electrons have escaped from their parent cations. Therefore, we could have a method to measure directly the early time escape probabilities of electrons in different liquids. Finally, if the electron thermalizes before returning to its parent cation, then the thermalization time in iso-octane is very short, < 500 fs.

In conclusion, we have performed the first study of room temperature geminate recombination of an electron with femtosecond time resolution. The recombination times of the two octane isomers are consistent with the view that the electron motions in nonpolar liquids are strongly dependent on the liquid structure and, in particular, disorder. Further work is now in progress to try to quantify these results.

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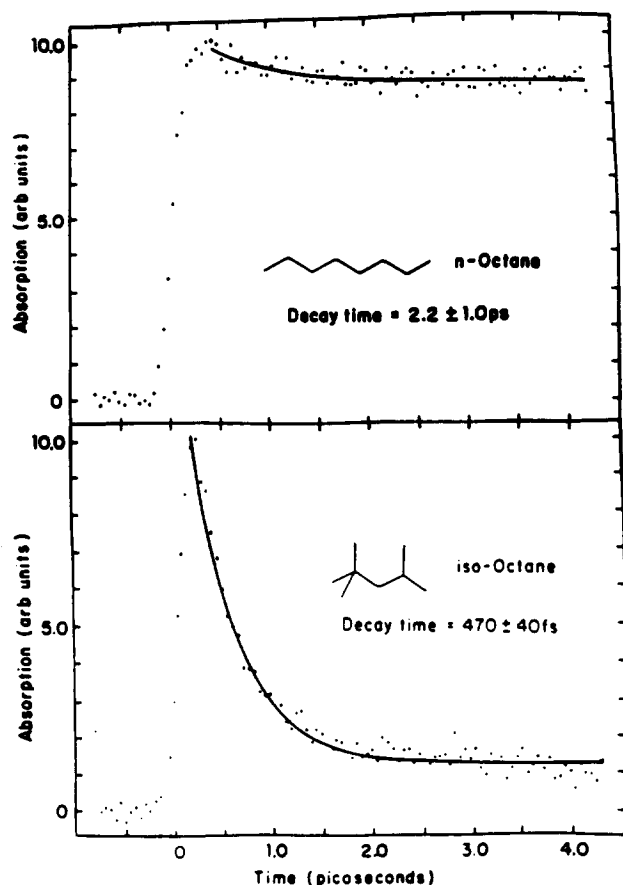


FIG. 1. Top: *n*-octane cation absorption vs the pump-probe time delay; the solid line is a fit to a single exponential decay; Bottom: Iso-octane cation absorption vs the pump-probe time delay; the solid line is a fit to a single exponential decay.

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Unimolecular dynamics following vibrational overtone excitation of HN_3 $\nu_1 = 5$ and $\nu_1 = 6$: $\text{HN}_3(\tilde{X}; \nu, J, K) \rightarrow \text{HN}(X^3\Sigma^-; \nu, J, \Omega) + \text{N}_2(X^1\Sigma_g^+)$

B. R. Foy, M. P. Casassa, J. C. Stephenson, and D. S. King

National Bureau of Standards, Molecular Spectroscopy Division, Gaithersburg, Maryland 20899

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We report measurements of the unimolecular vibrational predissociation lifetimes and $\text{HN}(X^3\Sigma^-)$ product state distributions following excitation of the fourth and fifth NH-stretching overtone transitions of HN_3 . These state-to-state photodissociation experiments provide an exceptionally detailed view of the dynamics of rovibrationally excited HN_3 and complement high resolution spectra and linewidth data for assigned rovibrational levels of $\nu_1 = 4, 5$, and 6 .^{1,2} The results build upon previous overtone excitation experiments³ on HOOH and tetramethyldioxetane, infrared multiphoton dissociation experiments⁴ on DN_3 , and theoretical calculations⁵ on the energetics and product spin selectivity of the ground state reaction $\text{HN}_3(\tilde{X}^1A') \rightarrow \text{HN}(X^3\Sigma^-) + \text{N}_2(X^1\Sigma_g^+)$, $\Delta H^6 = 5250 \text{ cm}^{-1}$, $E_{5,7}^{5,7} = 12\,600 \text{ cm}^{-1}$. The dissociation is spin forbidden, and the large barrier corresponds to the minimum energy singlet-triplet crossing.⁵

Our measurements were performed using a low pressure, thermal (293 K) HN_3 sample in a flow cell and two Nd:YAG-pumped dye lasers. The overtone pump laser operated at 575 ($\nu_1 = 6 \leftarrow 0$) or 662 nm ($\nu_1 = 5 \leftarrow 0$) with a spectral bandwidth $\approx 0.4 \text{ cm}^{-1}$ and energies 3 to 6 mJ. The HN fragments were probed by laser induced fluorescence of the $A^3\Pi-X^3\Sigma^-$ transition using a frequency-doubled dye laser with a bandwidth of 0.7 cm^{-1} and energy $5 \mu\text{J}$ (étalon-narrowed to 0.05 cm^{-1} for the measurement of Doppler profiles, energy $\approx 0.2 \mu\text{J}$). The lasers were collimated with beam diameters of $\approx 0.5 \text{ mm}$ and propagated anticollinearly. The observed LIF signals were linearly dependent on both pump and probe laser energy. The time delay between pump and probe was stepped electronically in 1 ns increments. Difference frequency generation in LiIO_3 gave a 10 ns FWHM cross correlation between the 575 nm pump and 336 nm probe lasers.

A portion of the nascent NH-fragment LIF excitation spectrum⁸ obtained exciting the ($5\nu_1$) Q_2 branch of H^{14}N_3 at $15\,103 \text{ cm}^{-1}$ is shown in Fig. 1. Results for a collisionally equilibrated sample are also shown. Under collisionless conditions there was no measurable population in the antisymmetric F_2 spin-rotation state, probed by transitions such as $Q_{32}(1)$. The experimental signal-to-noise ($S/N \approx 40$) and

relative line strengths [$R_1(1)$ vs $Q_{32}(1)$] put a limit on the ratio $F_2/F_1 \leq 0.06$. Since the populations of $F_1 \approx F_3$, less than 3% (and perhaps none) of the nascent fragment population is in F_2 levels. The rotational population distributions in the symmetric F_1, F_3 spin-rotation states, determined from more extensive excitation spectra, were approximately Boltzmann, characterized by $T_R = 280 \pm 50 \text{ K}$ for levels $N \leq 6$, corresponding to an average internal energy $\langle E_{\text{int}} \rangle = 200 \text{ cm}^{-1}$.

Doppler profiles were measured for $\text{HN } Q_1(3)$ and $R_1(3)$ transitions following $5\nu_1$ excitation. The observed profiles were essentially "top hat" in shape with $0.61 \pm 0.03 \text{ cm}^{-1}$ FWHM widths, independent of probe transition and

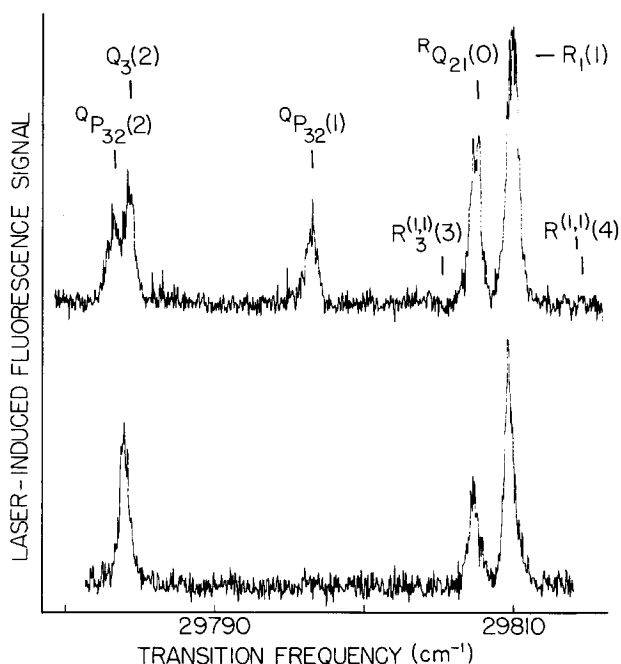


FIG. 1. Fluorescence excitation spectra of HN fragments following overtone photodissociation of HN_3 at the $5\nu_1 Q_2$ branch. Nascent population distributions were obtained at a 21 ns time delay for samples at 10 mTorr pressure (bottom spectrum); collisionally equilibrated samples (50 Torr of 5% HN_3 in Ar) were probed in control experiments (top spectrum).