

MOLECULAR CLUSTERS: REAL-TIME DYNAMICS AND REACTIVITY

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ABSTRACT

In this chapter we present a review of the field of real-time chemical dynamics in clusters, with specific examples to illustrate the new level of understanding reached for microscopic solvation and reactivity. The experimental examples presented were chosen to represent a progression of chemical complexity, ranging from elementary bond breaking, to electron transfer, to proton transfer, and to bimolecular chemistry in aligned complexes. The chapter begins with a discussion of the fundamental processes of dissociation and recombination dynamics in solvent cages for the prototypical neutral and ionic cluster systems. We eventually discuss reactions in larger systems, elucidating the elementary steps of proton and double-proton transfer in acid-base and isomerization reactions. In describing recent work, we highlight the new experimental techniques designed to extract new dimensions in the chemical dynamics in clusters, namely time- and state-resolved measurements with product velocity and spatial angular resolutions.

1. INTRODUCTION

Experiments on molecular complexes and clusters formed in supersonic beam expansions are providing new levels of understanding of the effect that individual molecules have on the properties of chemical reactions in particular and on solvation in general. These aggregates can be studied by laser probes and their size-dependence sorted out by mass spectrometry and spectroscopy. A number of books and chapters have appeared on the subject (e.g. refs. 1, 2) and the excellent recent article by Castleman and Bowen gives an overview of the experimental progress made so far.³ Progress in lasers and molecular beams have allowed single-quantum state studies. Ultrafast lasers have reduced the time scale of study to that of elementary bond breaking and bond-making processes. Laser polarization techniques have been used to achieve molecular alignment, making possible measurements of angular distributions of products. And in sophisticated new experiments, all of these laser techniques have been brought to bear on molecular level samples. In fact, techniques to measure chemical properties of clusters have reached the point where direct comparisons with gas-phase and condensed-phase reactions can be made.

Solvation under controlled conditions of size and composition offers an opportunity to examine different phenomena of reactivity at the microscopic level. Some of the important new details being learned about solvent influence on reacting molecules include the following:

- Coherent motion of solvent molecules.
- Geometry and structure of the solvent about a solute molecule.
- Energies of interaction by individual molecules.
- Vibrational mode structure and dynamics.

- Solvent critical number in phenomena such as electron and proton transfer and caging.

Because such processes can be studied at the microscopic level, clusters are an ideal medium for understanding the connection between gas-phase and condensed-phase phenomena and in learning about the breakdown of bulk-phase properties as a system becomes increasingly smaller in size. The structure of the solvent about a reacting molecule is a longstanding issue and the interactions exerted by the solvent often determine the fate of chemical reactions. Learning about solvent interactions in microscopic detail could potentially lead to important advances in the understanding, and possibly control, of bulk-phase chemistry.

In this chapter, we present an overview of the rapidly expanding field of real-time dynamics in clusters. Measurements of cluster dynamics in the time domain began in 1983 with experiments probing excited-state lifetime (of isoquinoline) for various hydrogen bonding solvent molecules (Figure 1).⁴ To date, there are many groups conducting real-time measurements in clusters encompassing a large scope of interests; a number of reviews on time-resolved studies and on general topics in chemical dynamics in molecular clusters have been reported before.⁵⁻⁹ Metallic clusters represent a branch for different classes of phenomena, interesting in their own right. In keeping with the format of this book, we focus on more detailed accounts of case studies primarily from the authors' laboratories to illustrate the

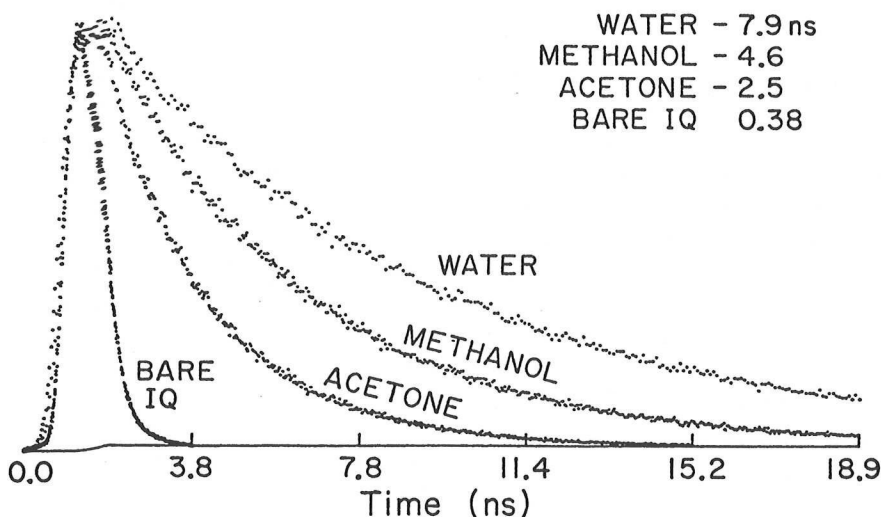


Figure 1. Excited state decay times of isoquinoline unsolvated and solvated as measured by time-correlated single-photon counting in a free-jet expansion (ref. 4).

new kinds of information being gained from these studies. We will present a series of studies chosen to illustrate a progression of chemical complexity ranging from elementary bond breaking, to electron transfer, to proton transfer, and to bimolecular chemistry in aligned complexes. This chapter centers largely on bimolecular solute-solvent chemical interactions; those time domain studies that do not fall under this main theme are summarized in Section 7.

In Section 2, we consider one of the most classic and fundamental problems in chemistry, namely what happens when a diatomic molecule dissociates in a solvent cage? Key insights have been provided by a history of time-resolved studies of I_2 dissociation/recombination in condensed phases. However, only recently have measurements been conducted in real time on solvated cluster systems such as I_2/M_n and I_2^+/M_n , where M_n is a solvent of n molecules of M , as a function of specific cluster size. These experiments have provided critical new understanding regarding the precise interaction of each solvent molecule, leading to cage escape vs. recombination probabilities, and measuring the actual coherent motions of bond breakage and caging in the solvent. In Section 3, we extend the discussion of I_2 to complexes I_2/Bz_n , Bz being benzene, wherein a competition between a charge transfer and a neutral channel to I_2 dissociation occurs. In these studies new multi-dimensional probes involving time-resolved angle-velocity measurements of products are introduced. In Section 4, we cover an extensive series of studies on a prototypical acid-base reaction $ROH^+ \cdot B_n \rightarrow RO^+ \cdot H^+ B_n$ (excited-state proton transfer), where ROH is an aromatic acid and B_n is a cluster of base molecules. Direct time domain studies have revealed that changing a single solvent molecule can lead to distinct chemical changes, sometimes affecting reaction rates by over 2 orders of magnitude. These results are making possible the validation of a quantum level model of proton tunneling involving solvent dynamics that may be extended to describe condensed-phase behavior.

Section 5 covers sophisticated new techniques building on earlier advances in studying bimolecular chemistry using alignments of molecules in van der Waals complexes. Recently, differential reactive cross sections in angle and velocity have been measured in photodissociation of van der Waals complexes with product quantum-state resolution and femtosecond time resolution. We focus on recent studies on $(CH_3I)_2$ and I_2/Bz_n . The quantum-state-resolved work on $(CH_3I)_2$ revealed a bimodal angle-velocity distribution for the I atom fragment, indicating an inequivalency of the two individual molecules, and rapid spin-orbit relaxation in I atom. The real-time measurements showed a 150 fs C-I bond scission and a build up of I_2 in less than 500 fs. The I_2/Bz_n work has led to direct observation of the time evolution of the transition state and products for the charge transfer reaction $Bz-I_2 \rightarrow [Bz^+ \cdots I^- \cdots I]^{\ddagger} \rightarrow Bz-I + I$, while monitoring the change in anisotropy and fragment translational energy.

The latest set of experiments described in Section 5, incorporating time-resolved and state-resolved differential cross-section measurements in aligned complexes, hold great promise of providing information needed to test quantum chemical

dynamics in these finite-sized systems. The van der Waals bond in a dimer complex helps to fix the geometry and limit the range of impact parameters under study. The full dimensionality of how molecules collide and break up into products can be followed in real time using femtosecond excitation and angular probing of product velocities. Section 6 describes the effect of microscopic solvation on isomerization reactions, and in Section 7 we conclude the chapter. An appendix has been added describing a state-to-state theory of proton tunneling appropriate to clusters and extendable to the condensed phase, thus helping to unify the connection between gas-phase and condensed-phase chemistry.

2. BOND DYNAMICS: DISSOCIATION AND CAGING

2.1. I_2/X_n

Vibrational Predissociation ($n = 1-4$)

Dimer systems offer the simplest picture of solute-solvent interactions. In a series of experiments Gutmann et al. directly measured state-to-state rates of vibrational predissociation for I_2 complexed to $X = \text{He, Ne, Ar, and } H_2$.¹⁰⁻¹² Questions of interest included: does the repulsive potential of the van der Waals bond determine the state-to-state rates of predissociation, and do vibrational and electronic predissociation have the same origin? The state-to-state process can be described by the following,



where excitation is to the B electronic state.

Experimental: Because of the picosecond time scale for these dynamics and the interest in probing state-specific effects, tunable picosecond duration pulses were used.¹⁰⁻¹² The 532 nm output of a Nd:YAG laser was split to synchronously pump two cavity-dumped, etalon-tuned dye lasers. The pump laser was operated in the visible in order to excite specific vibration levels in the B -excited electronic states of I_2 . The probe laser was operated in the ultraviolet in order to pump electronically excited I_2 to an ion-pair state, from which fluorescence was detected. Clusters were formed in a supersonic expansion using two arrangements. A continuous nozzle was used for Ar expansions to take advantage of the maximum repetition rate (800 Hz) of the laser. For H_2 , He, and Ne expansions, higher backing pressures were required, necessitating the use of a pulsed nozzle operated at about 100 Hz.

Excitation to a specific vibrational state ν_i' of the reactant I_2 stretching mode is followed by vibrational redistribution to the vdWs mode. In the case of Ne,

a single I_2 quantum exceeds the vdW binding energy hence the product I_2 is formed with $\nu_f' = \nu_i' - 1$ quanta. Real-time measurements of the rate of vibrational predissociation (VP) probe the coupling strength of the I_2 reactant vibration to the vdW's mode.^{10,11} Examples of the product formation times for different initial vibrational excitations are shown in Figure 2. The VP rates increase monotonically with increasing vibrational excitation for Ne. The situation for Ar was different in the following ways: (1) because the vdW's bond energy is much greater, the VP process was favored by the $\nu_f' = \nu_i' - 3$ channel, and (2) an electronic predissociation (EP) competes with VP.

Interesting questions arise when the number of solvent molecules is increased systematically.¹² For example, do the rare gas solvent molecules dissociate sequentially, each event being a VP (direct, sequential mechanism), or does intramolecular vibrational redistribution (IVR) to unreactive modes occur first, followed by sequential VP (indirect, evaporative mechanism)? The state-to-state time-resolved dissociation rates indicate that the onset to IVR occurs for just two Ne atoms. These

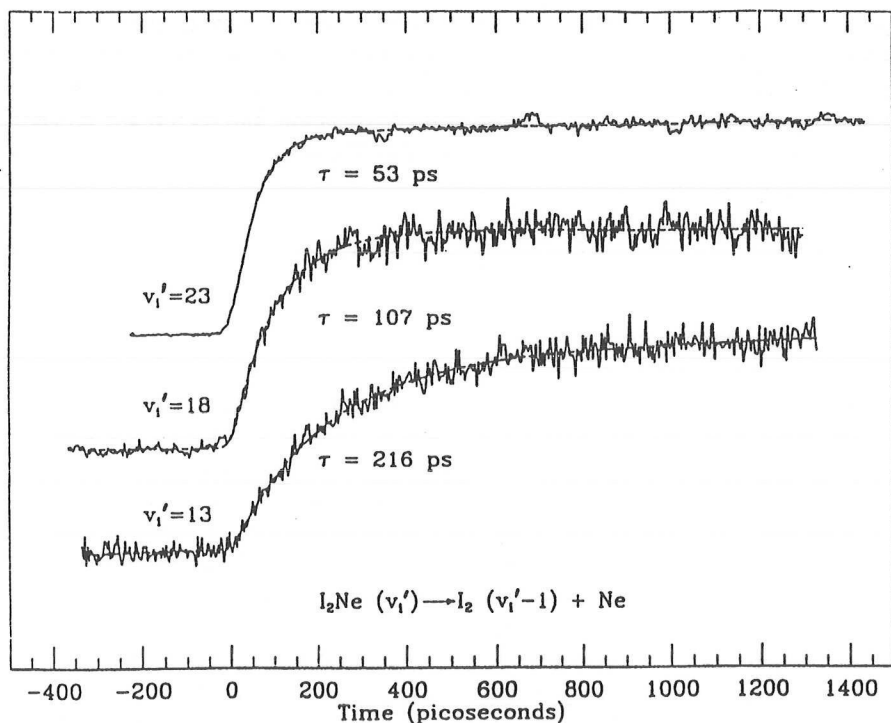


Figure 2. Representative pump-probe transients for vibrational levels $\nu_i' = 13, 18$, and 23 . The dashed line is the fit to an exponential rise function, from which the value of the state-to-state rate is given (refs. 10–12).

measurements were extended to $n = 3$ and 4 Ne atoms to test statistical theories for small cluster systems. Campos-Martinez et al. conducted time-dependent Hartree-type calculations on the VP of $\text{I}_2\text{-Ne}_2$ clusters.¹³ The computations indicate a sequential dissociation of Ne, although some behavior bordering on internal vibrational relaxation was observed for high initial vibrational states. The computed trend in the lifetime vs. initial vibrational state was in very good agreement with experiment (Figure 3).

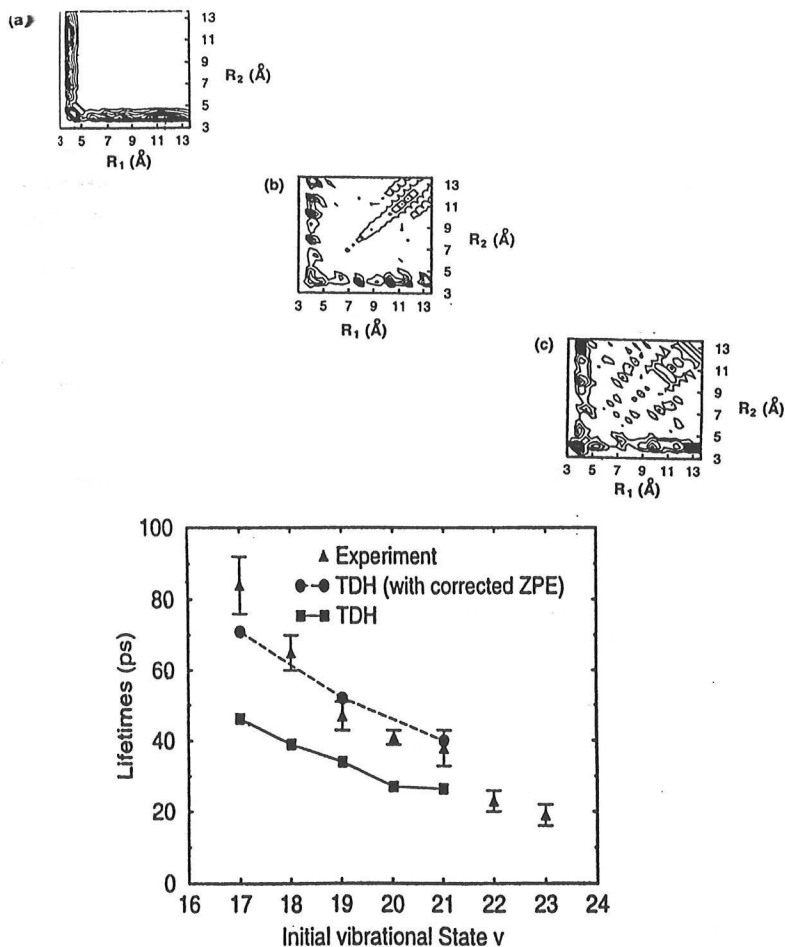


Figure 3. Snapshots at $t = 10$ ps when the initial state is $v = 17$ and for channels (a) $v = 16$, (b) $v = 15$, and (c) $v = 14$. The system is I_2Ne_2 and $R_1(R_2)$ is the distance from I_2 to Ne_1 (Ne_2). Comparison of computed lifetimes with experimental lifetimes is also shown (ref. 13).

Dissociation/Recombination in I_2/X_n Macroclusters

By increasing the cluster size new solvent dynamics can be probed. In the case of I_2 , direct measures of dissociation/recombination dynamics can be obtained and compared to the analogous measurements in bulk solvents and condensed phases.¹⁴ These events occur on much faster time scales than the predissociations described above for the smaller cluster systems. Experiments were conducted on clusters and on high-pressure gases.

Experimental: These experiments required femtosecond time resolution. The cluster experiments made use of a mode-locked Nd:YAG synchronously pumped linear, dispersion-compensated dye laser.¹⁴ The 615 nm output was passed through a Nd:YAG pumped, four-stage dye amplifier and then split into pump and probe pulses. The pump was used to generate a white-light continuum and the probe, frequency doubled to 308 nm. The continuum pulse was filtered and amplified by a 355-nm pumped three-stage dye amplifier to give tunable pump pulses (e.g. 480, 510, 520 nm for B state excitation and 614, 620, and 640 nm for A -state excitation of I_2). As above, the probe pulse excites an ion-pair state of I_2 , which is detected by fluorescence. For the high-pressure gas experiments, 60 fs pulses were generated in a colliding-pulse mode-locked ring dye laser and amplified in a four-stage dye amplifier system pumped by a Nd:YAG laser. The amplified pulses were recompressed in a double-pass, two-prism arrangement and then separated into pump and probe pulses using a 50:50 beam splitter. The fundamental at 620 nm and the frequency doubled output served as pump and probe, respectively. Other wavelengths were selected by using a continuum generation.

Macroclusters consisting of around 40–150 Ar atoms solvating I_2 were excited to the A state above its dissociative limit to $I + I$, and to B -excited electronic states at different energies above and below its dissociative limit to $I + I^*$.¹⁴ The A state undergoes direct dissociation whereas the B state predissociates from a bound to a repulsive potential. The direct dissociation of I_2 in the A state leads to a high-energy impact of the I atoms on the frozen solvent cage. The Ar solvent cage provides an outer potential barrier that causes the I atoms to oscillate back to a nearly molecular state. Initial geometries and snapshots of the structural changes for A -state excitation are calculated in Figure 4 for an I_2 solvated by 17 Ar atoms (two isomers presented) and 44 Ar atoms. These dynamics are manifested in the femtosecond transients in Figure 5 for 614 nm excitation. The rise and fall times for the first peak represent the formation of the excited-state wave packet and subsequent decay to I atom separations that no longer absorb the probe light. The signal reaches a minimum in about 250 fs followed by a prompt recovery to an optically absorbing state in about 300 fs. Molecular dynamics calculations show that the recovery represents a coherent bound motion involving

the solvent cage. The *B* state below the direct dissociative limit undergoes predissociation. The measured dynamics for 570 nm excitation in Figure 6 show a decay time of 15 ps, corresponding to the predissociation lifetime, followed by a 30 ps time scale recovery, due to recombination of solvent separated I atoms and vibrational relaxation.

These results provided the microscopic picture of the effect of solvation on dissociation and recombination. First, the time scale for direct dissociation, which was measured directly, is essentially unaffected by the solvent. Second, caging as

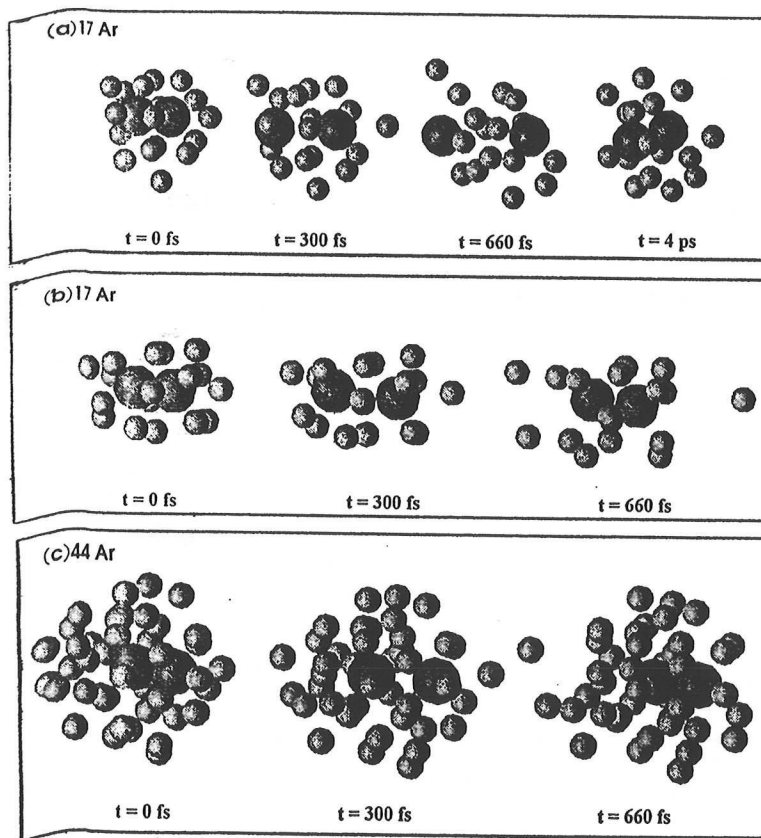


Figure 4. Snapshots of the structures of iodine (dark grey) in argon (light grey) solvent cages. (a) For 17 Ar atoms where one I atom is not capped, the subsequent recombination takes more than 4 ps. (b) For 17 atoms where I_2 is fully enclosed, recombination following dissociation is direct. (c) For larger clusters, the I_2 is almost always enclosed leading to caging that is direct and coherent (ref. 14).

a recombination process following direct dissociation, is a *coherent* process, with the solvent essentially frozen in configuration on this time scale. The wave packet motion is illustrated in Figure 7. The process is in a highly nonequilibrium dynamics with the solvent. Third, vibrational relaxation occurs on a much longer time scale. Finally, unlike the direct dissociation case (*A* state), the case of predissociation (*B* state) shows clearly the solvent involvement in the collision-induced predissocia-

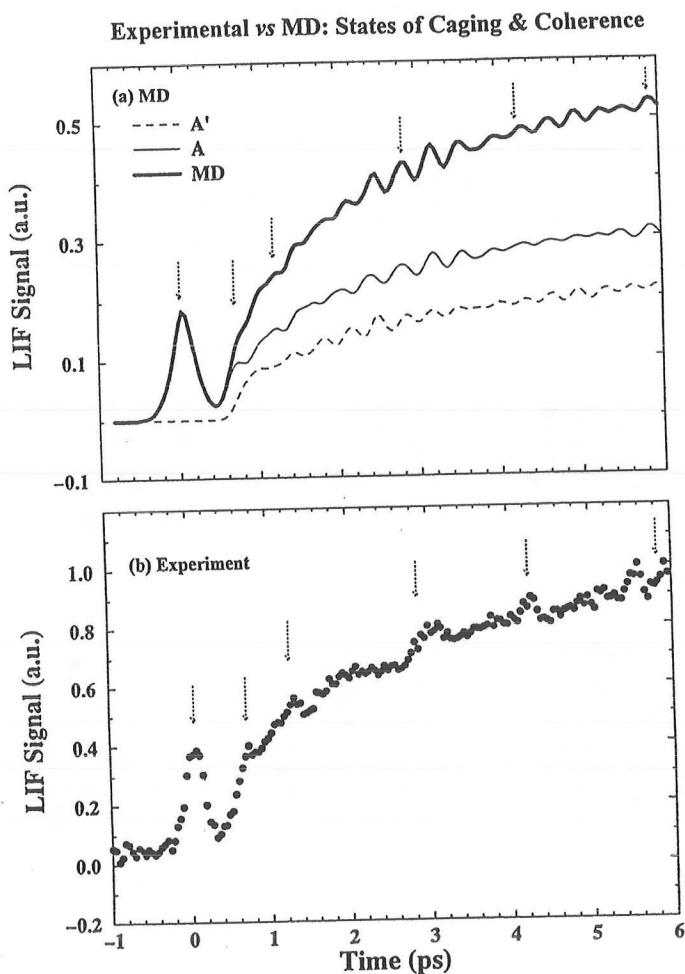


Figure 5. LIF transients following A-state excitation at 614 nm. (a) Simulations for I₂-Ar₄₄ with initial temperature of 30 K. (b) Experimental transient from monitoring red-shifted fluorescence (400 nm). Probe wavelength is 307 nm for both simulations and measurements (ref. 14).

tion and in the caging, but now on the picosecond time scale. The solvent reorganization being on the time scale of bond breakage.

I₂/X_n in the High-Pressure, Supercritical Region

To compare with condensed-phase behavior at solvent densities comparable to clusters and liquids, high-pressure, supercritical fluids were studied by Lienau et

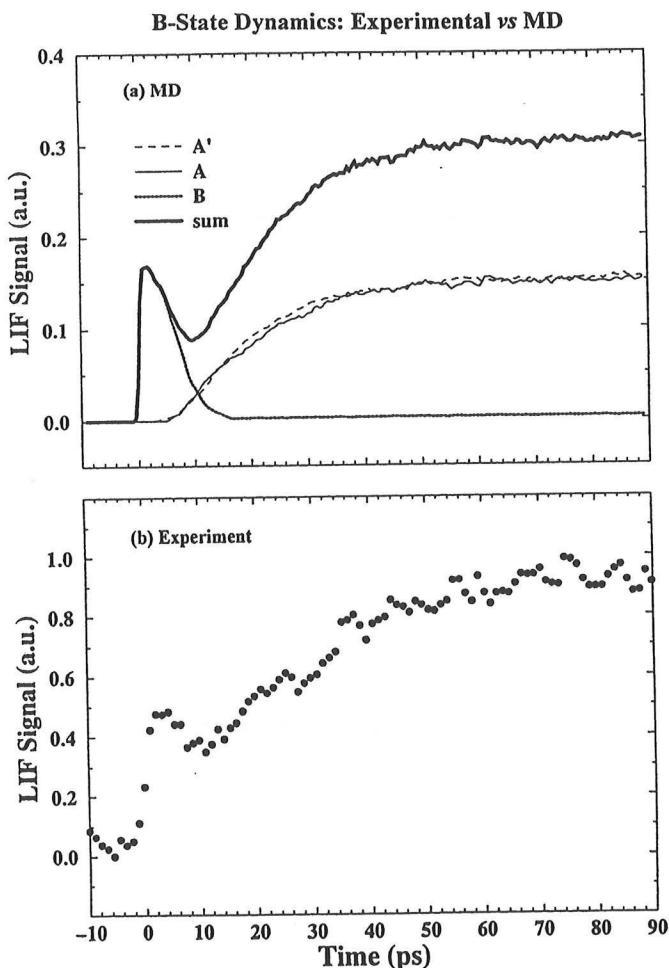


Figure 6. LIF transients following *B*-state excitation at 570 nm. (a) Simulations for I₂-Ar₄₄ for initial temperature of 30 K. (b) Experimental transient. Probe wavelength is 307 nm for both simulations and measurements (ref. 14).

al. to explore phenomena reflecting details of solute-solvent interactions.^{15,16} Femtosecond excitation of I_2 at the inner turning point of the B -state potential was achieved using 60 fs pulses from a CPM laser at 620 nm. Pressure was varied from 0 to a few thousand bar for the rare gases He, Ne, Ar, and Kr. The properties that were measured were: coherent nuclear motion of I_2 , rate of predissociation, and caging time and efficiency. Calculations of the solvent density and structure as a function of pressure for I_2/Ne_n are illustrated in Figure 8.

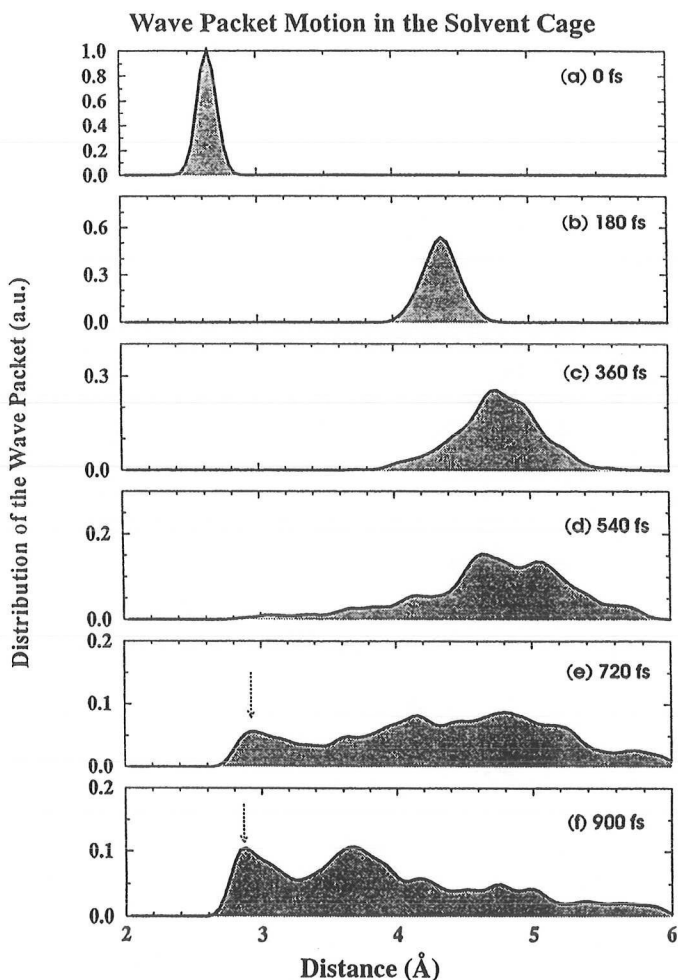


Figure 7. Wave packet motion as a function of time. The wave packet was treated classically for the spatial distributions of I-I distances at given times. The distributions were obtained by averaging over 1000 independent trajectories (ref. 14).

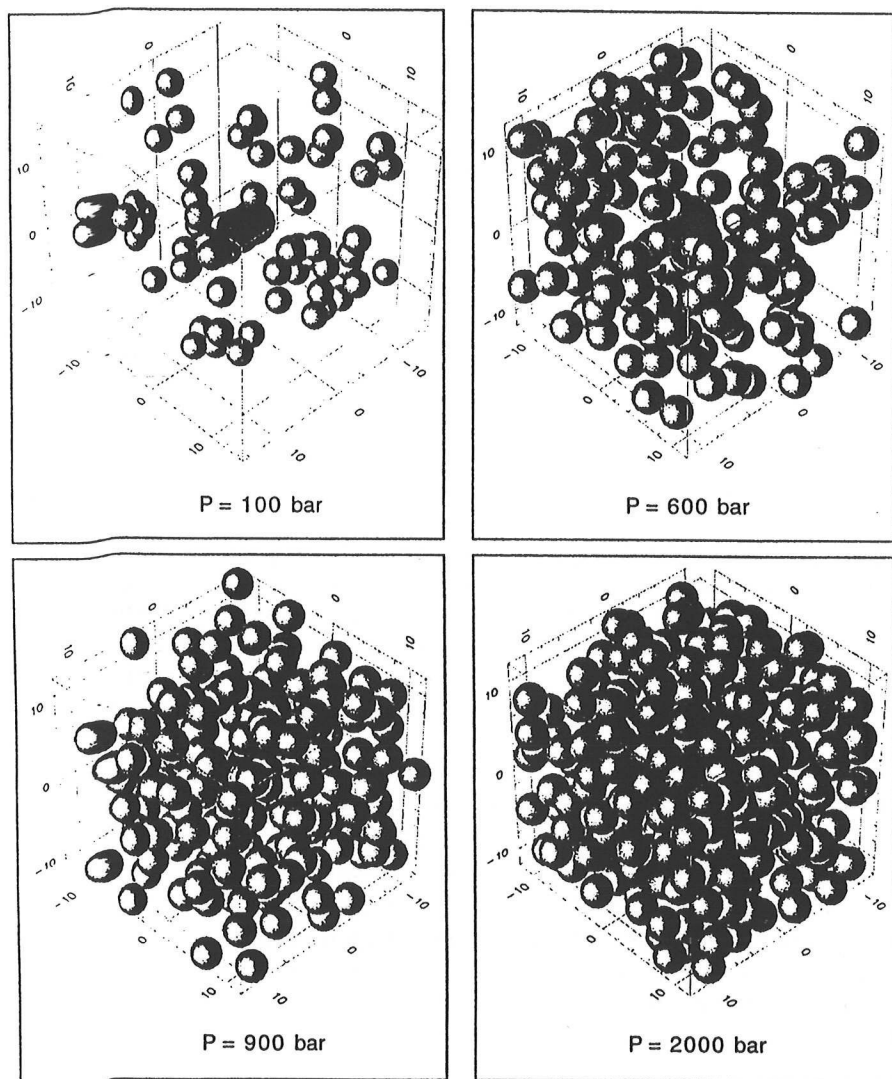


Figure 8. Snapshots of I_2/Ne_n system at four different pressures. The atom positions are in accordance with MD simulations. Coordinates are in angstroms (ref. 16).

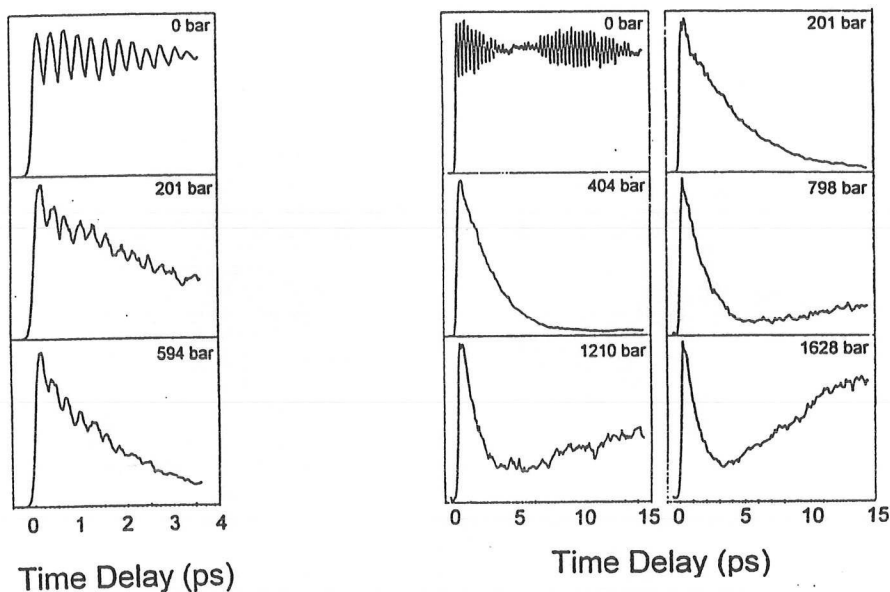


Figure 9. Femtosecond transients of iodine in compressed supercritical argon at 295 K. Left: experimentally observed transient at Ar pressures of 0, 201, and 594 bar using LIF detection at the "magic angle" (54.7°) between the pump and probe pulses. Fluorescence detection wavelength: 340 nm – 0 bar, 351 nm – 201 bar, and 360 nm – 594 bar. Right: the transient behavior at longer times, showing the onset of caging with density changes (ref. 15).

Femtosecond transients as a function of Ar pressure are presented in Figures 9 and 10.¹⁵ In Figure 9, I_2 vibrational coherence persisted for greater than 1.5 ps up to a pressure of 800 bar. Because the collision frequency between I_2 and the bath gas is about 4 ps^{-1} , these results indicate that at least 6 collisions are required to fully quench the vibrational coherence. At similar pressure, the I_2 signal decays on the same time scale as the vibrational coherence. The mechanism for this relatively fast decay is collision-induced electronic predissociation. At pressures of 400 bar and above, the transient decays are followed by a slower rise. This trend represents geminate recombination of I atoms by a cage effect. The onset of caging occurs at pressures where the bath gas density begins to deviate from ideal gas behavior. Above 1200 bar, the rise of the transient appears to be biexponential, which is consistent with similar studies in liquid Xe.¹⁷ These observations are assigned as fast vibrational relaxation with the A/A' states and slower curve crossing from the $A \rightarrow A'$ electronic states.

In the lighter rare gas solvents He and Ne, the vibrational coherence is only weakly affected by increasing pressure from 100 to 2000 bar. The transients for the

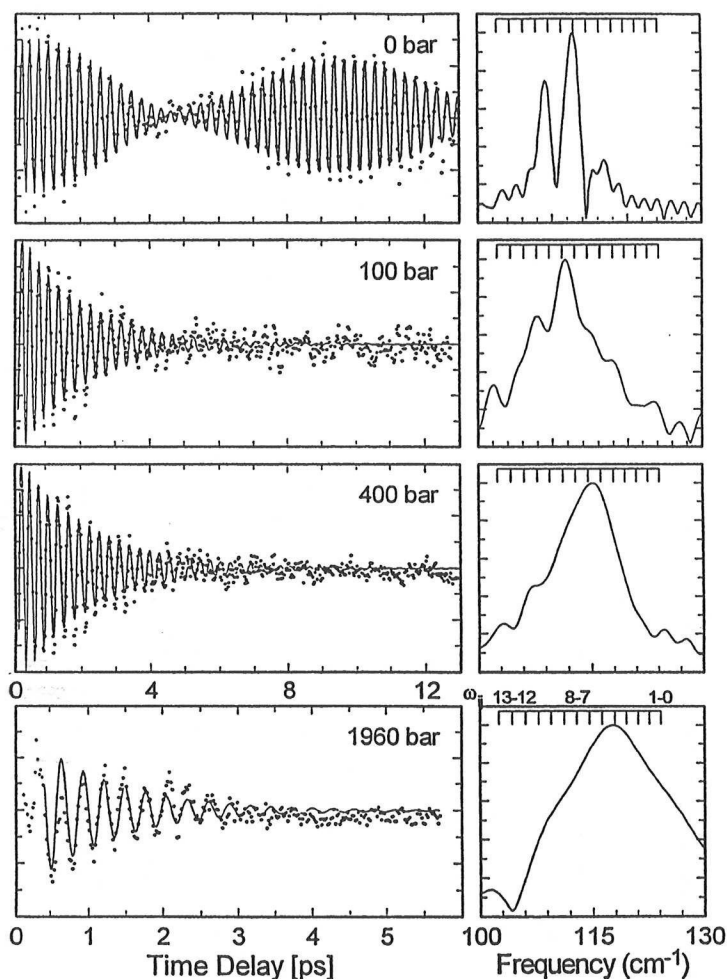


Figure 10. Vibrational dephasing in helium. Left: Oscillations on the femtosecond transients after subtraction of the underlying decay. Note the rapid dephasing at 100 bar compared to 0 bar, but the persistence at higher pressure (ref. 15).

I_2/He_n system, presented in Figure 10, indicate vibrational persistence of a few picoseconds at the highest pressures studied. The frequency spectrum for the I_2/He collisional interaction was examined by evaluating the Fourier transform spectrum of the oscillatory part of the transients obtained by subtracting away the decay component. The Fourier spectrum, plotted alongside the transients in Figure 10, show several interesting trends. At 0 bar, distinct vibrational eigenstates are ob-

served with the maximum corresponding to the frequency $\omega_{8,7} = 113 \text{ cm}^{-1}$. At a pressure of 100 bar He, the Fourier spectrum broadens significantly due to solvent-induced dephasing, and the intensity at higher frequencies increases. At 400 bar, the frequency spectrum is nearly completely broadened and shifted to higher frequency. The broadening and blue shifting increases at 1960 bar He.

Much of the underlying dynamics of solute-solvent interactions may be probed by measuring the correlation time for solute-solvent collisions and vibration-rotation couplings relative to the coherence or dephasing time T_2 and the energy relaxation time T_1 .¹⁶ Two regimes may be defined: slow modulation is when the correlation times are longer than T_2 , and fast modulation is when they are much shorter than T_2 . In the limit of very fast modulation, a motional narrowing of the properties of the solute may be observed. A measure of T_1 and T_2 as a function of

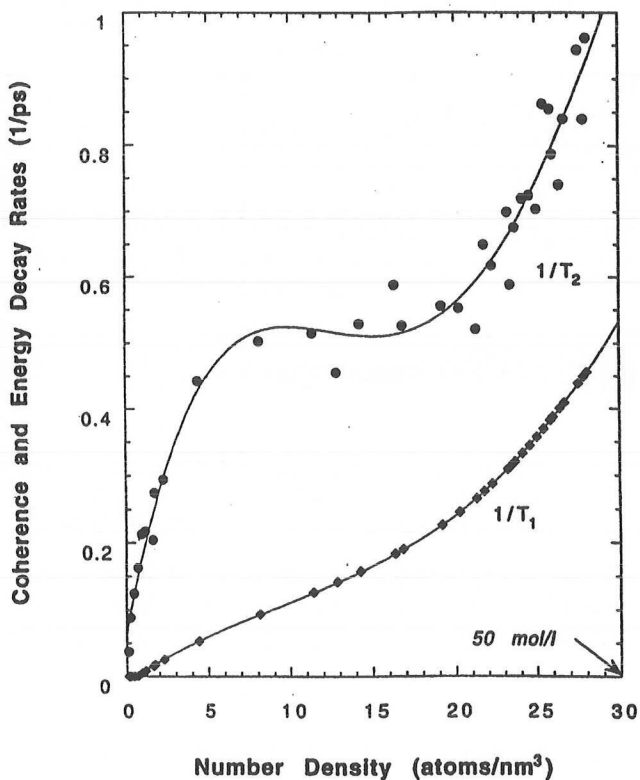


Figure 11. The behavior of the rates ($1/T_2$ and $1/T_1$) with solvent density for helium. The lines in this figure are polynomial fits to the experimental data. The densities were obtained from the known pressure-density conversion data reported elsewhere (ref. 16).

He pressure revealed interesting behavior as shown in Figure 11. The T_1 behavior can be explained by collision-induced predissociation. The T_2 results, however, break into three regions: (1) a low-density region where $1/T_2$ increases rapidly and linearly, (2) an intermediate-density region where $1/T_2$ is relatively constant, and (3) a high-density liquid-like region where $1/T_2$ increases again.

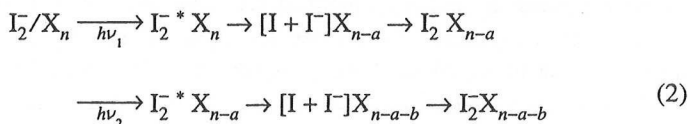
With the help of molecular dynamics (MD) simulations, the behavior of T_1 and T_2 with number density can be explained. The two principal forces involved are the real collisional force originating from the solute-solvent intermolecular interaction and a rotation-induced centrifugal force (i.e. vibration-rotation coupling).¹⁸ The motional narrowing regime begins at a number density of about 10 nm^{-3} . At this point the centrifugal force, which rises linearly at lower density, turns over and decreases (slowly) at higher density. This behavior is mirrored in the T_2 results up to about 20 nm^{-3} . At this higher density the collisional force dominates and $1/T_2$ increases again in rate.

2.2. I_2/X_n

The dissociation/recombination dynamics for a charged solute molecule in a neutral solvent is likely to differ markedly from that of a neutral solute/solvent system. Whereas the dynamics in the latter case are mostly dominated by thermally activated collisional interactions, the reaction dynamics in the former case will be driven more by Coulomb interactions between the solute and solvent. The Lineberger group carried out experiments on mass-selected cluster ions of I_2^+/X_n where X is CO_2 or Ar.¹⁹⁻²² These solvents have similar mass, but differ greatly in their polarity. The principal measurements were the caging fraction, and the recombination rates as a function of solvent cluster size.

Experimental: The Lineberger group employs a tandem mass spectrometer apparatus for time-resolved measurements of mass-selected cluster ions.^{19,20} Cluster ions are formed at the source of a pulsed valve by crossing the free jet expansion by a 1 keV electron beam. The cluster ions grow in size in the expansion and then are allowed to drift before being extracted into a tandem TOF mass spectrometer. In the linear TOF stage, the cluster ion masses separate and a pulsed mass gate allows a single mass through. Laser excitation occurs just beyond this region. The laser system is an Ar ion pumped Ti:Sapphire oscillator that is pulse-stretched and amplified in a regenerative amplifier, then recompressed, producing 150 fs, 1 mJ pulses at 790 nm.²¹ Some of the earlier work from this group used a mode-locked Nd:YAG synchronously pumped dye laser and pulsed dye amplifier.^{19,20} The dynamics of dissociation/recombination are probed by absorption recovery. Following pump excitation of I_2^+ , the ion dissociates to $I + I^+$ and no longer absorbs the probe pulse, which is of the same wavelength as the pump. If $I + I^+$ recombines to I_2^+ , and vibrationally relaxes, the cluster again can absorb the probe pulse.

This absorption recovery is detected in the following way:



The dissociation initiated by the pump causes some evaporation of solvent (designated as a in Eq. 2). Hence, the resultant mass spectrum leads to fragment ions, which are signatures for 1-photon absorption. If I_2^- reforms after dissociation, the cluster will absorb the probe pulse, dissociate, and lose additional solvent [designated as b]. Hence a second series of fragment ions are signatures for two-photon absorption, which is the absorption recovery signal.

The mass selection of I_2^-/X_n before pump-probe excitation enables a measure of the caging fraction as a function of solvent size n . The two product channels $\text{I}^-/\text{X}_{n-a}$ and $\text{I}_2^-/\text{X}_{n-a}$ in the first line of Eq. 2 are signatures for uncaged and caged dissociation, respectively. For CO_2 solvation, the first evidence of caging appears at $n = 4$, and the caging fraction increases monotonically reaching unity at about $n = 15$.²⁰ For Ar solvation, caging first appears at $n = 10$ and reaches a maximum caging fraction of about 0.50 at $n = 16$.²¹ The completion of the first solvation shell occurs at $n = 16$ for CO_2 , and presumably a similar value for Ar. The results of the caging fraction are consistent with the polarity of the solvent. CO_2 , having a larger charge separation (in form of an electric quadrupole moment) than Ar, forms a stronger ion-neutral bond as well as stronger solvent-solvent bonds than Ar. CO_2 , therefore, forms a more rigid solvent cage than does Ar, accounting for the greater caging efficiency.

Time-resolved measurements of $\text{I}_2^-(\text{CO}_2)_n$ dissociation revealed two interesting observations as shown in Figure 12.²⁰ (1) the absorption recovery times decrease with increasing solvent size over the range $n = 12$ –15; below and above these solvent sizes, the recovery times are asymptotic (≈ 40 ps for $n \leq 12$ and ≈ 10 ps for $n \geq 15$), and (2) a recurrence at about 2 ps is observed in the absorption recovery for cluster sizes $n = 14$ –17. These behaviors occur over a size range corresponding closely to the filling of the first solvation shell. The recurrence is attributed to coherent internuclear motion of I_2^- along the dissociative excited potential, which is now bounded by the solvent. This phenomena is analogous to the recurrence observed and discussed above for I_2^-/Ar_n .¹⁴ As with the I_2^-/Ar_n system, $\text{I}_2^-(\text{CO}_2)_n$ eventually recombines along the ground-state potential and undergoes vibrational relaxation to a distribution of states that are again optically active, accounting for the longer time dependence in the absorption recovery traces. The combination of experimental time-resolved measurements and theoretical support, particularly molecular dynamics, are providing key understanding of these fundamental processes.

The Neumark group recently conducted a femtosecond photoelectron study on size-selected I_2^-/Ar_n clusters.²³ They observed that the photodissociation of the

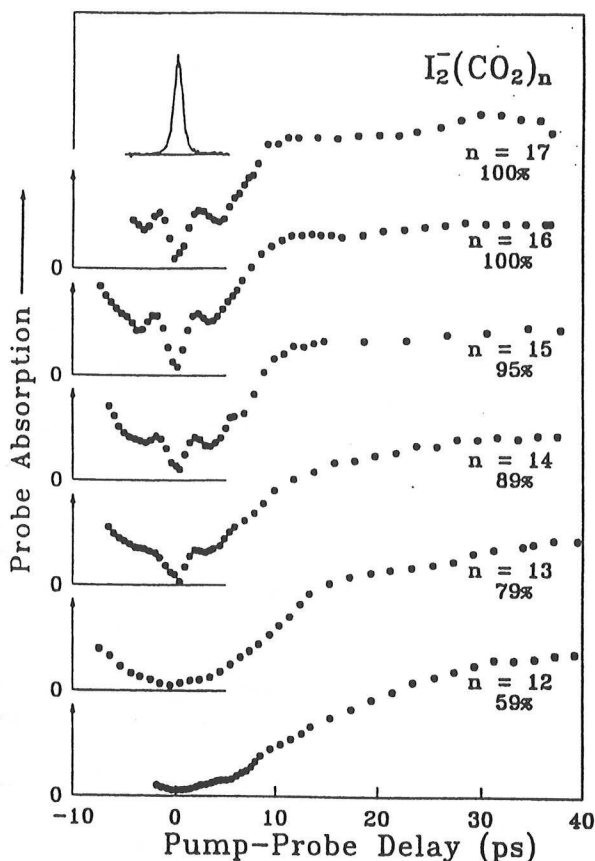


Figure 12. $I_2(CO_2)_n$ ($n = 12-17$) absorption recovery data obtained with 720 nm pump and probe pulses with parallel polarization. Percentage values are fraction of caged products. The top trace is the laser pulse autocorrelation (ref. 20).

I_2^- for $n = 6$ solvent molecules is complete in about 200 fs (same for bare I_2^-), but that the attractive interaction between the departing anion fragment and the solvent persists for about 1200 fs. For $n = 20$ cluster size, the photodissociated fragments are caged, leading to recombination and vibrational relaxation on the time scale of 35 ps and 200 ps, respectively, and that these processes occur on both the ground and excited electronic surfaces.

2.3. Comparison with Condensed-Phase Studies: Solids and Liquids

The above cluster experiments are especially valuable toward furthering the understanding of solvent interactions. They can also be directly compared to analogous studies in the condensed phase. The history of dissociation and cage

recombination studies of I_2 began in the condensed phase in the group of Eisenthal,²⁴ and many groups have subsequently contributed to the theoretical and experimental studies;^{17,25-27} for a review see the paper by Harris, Brown, and Harris.²⁷ For I_2 in liquids, caging was not resolved, but inferred to be occurring in less than 2 ps. The resolved coherent process in clusters indicate the microscopic, not bulk, role of the solvent. Furthermore, consistent with the theoretical analysis²⁸ of Hynes and Nesbitt, the time scales of caging and VR are much different—fs and ps, respectively. The effect of the solvent on electronic predissociation and dephasing has been studied thoroughly in dense fluids.¹⁵⁻¹⁷ Higher caging efficiencies are also observed for polar solvents in condensed-phase studies of neutral I_2 .²⁷ This behavior is consistent with the results for I_2/X_n studies described above. The comparison with liquid state studies by Fleming's group²⁹ and solid-state studies by Apkarian's group shows interesting behavior for the dependence on solvent density, polarity, and structure.^{30,31} Apkarian has recently provided a theoretical treatment of the effect of local symmetry on the predissociation in order to reconcile liquid- and solid-state results.³¹

For solids, Apkarian and coworkers measured the neutral I_2 dissociation/recombination with femtosecond resolution in rare gas matrices.³⁰ In these studies the solvent or matrix potential barrier is directly probed and the extent of lattice excitation measured. The rare gas matrix results show several recurrences as seen in Figure 13. The results exhibit behavior similar to that observed in the cluster results. The additional recurrences are also modulated by solvent-mode frequen-

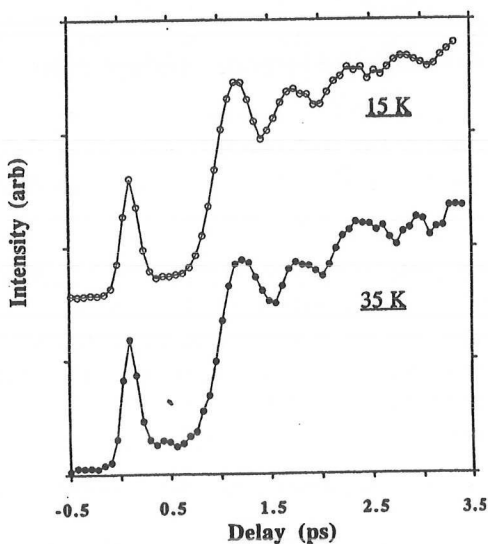


Figure 13. Temperature dependence of transients, recorded for a 704 nm pump. Simulations account for the major oscillations in the transients (ref. 30).

cies, attesting to the stiffness of the matrix. In a series of beautiful experimental and MD theoretical studies by the Apkarian and Martens groups, they have discussed the detailed nature of the recombination process and coherence.

Barbara and coworkers measured I_2^- dissociation/recombination dynamics in liquid solvents.³² In a related experiment, Ruhman and coworkers observed coherent vibrational motion of I_2 resulting from I_3^- photodissociation in the condensed phase.³³ These experiments have revealed the coherent nature of the dissociation/recombination process, thus providing a microscopic picture with connection between bulk liquid and cluster and solid phase phenomena.

3. ELECTRON TRANSFER

Charge transfer (CT) reactions are of fundamental interest in chemistry and biology. Because of the large change in charge density involving a coupling of ionic and covalent potentials, it is especially interesting to investigate the transition state, which presumably must have some hybrid structure intermediate between ionic and covalent configurations. We first consider a generic CT reaction $A^* + BC$. In the entrance channel of the potential energy surface, the reactants can undergo a long-range CT that modifies the subsequent dynamics of the reaction. This very fast interconversion to an ionic-like transition state is referred to as a harpooning mechanism, and exhibits characteristic properties in the reactive scattering cross sections,³⁴ in the absorption spectra of CT complexes,³⁵ and in the femtosecond dynamics.^{36,37} The separation of the transition state into products can then proceed along an ionic or a covalent potential. These properties are illustrated for the particular problem of $Bz-I_2$ in the potential energy diagram in Figure 14A.

Charge transfer, bimolecular reactions have been studied by femtosecond excitation of aligned van der Waals complexes. This method offers two principal benefits in detecting the transition state: (1) the collision time is precisely defined, and (2) the range of impact parameters is specified by the vdW geometry.^{37,38} In Section 5 we discuss in more detail experiments that measure real-time and state-resolved angle-velocity properties of products from cluster photoexcitation. However, we introduce the technique of kinetic energy time-of-flight (KETOF) here because the experimental system studied Bz_n/I_2 falls into the progression of reactions that we have outlined in the Introduction (i.e. from elementary to complex reactions).

3.1. Bz_n/I_2

Overview and Results

The $Bz-I_2$ complex in solution has been a prototype for studying charge transfer for many decades.^{39,40} The reaction may be viewed as a bimolecular reaction between benzene and I_2 of the form:

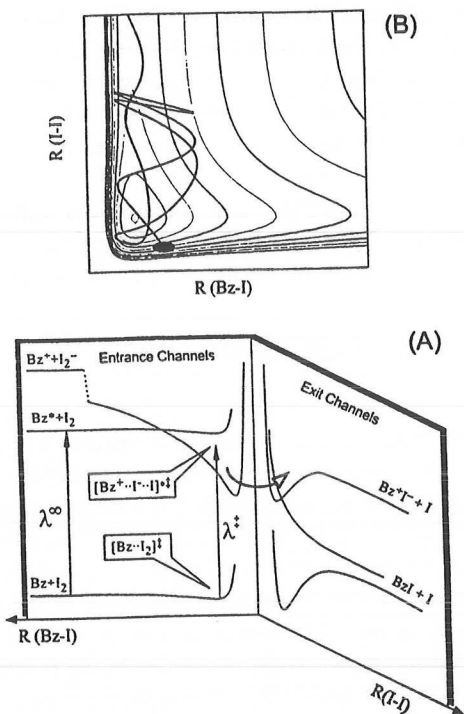
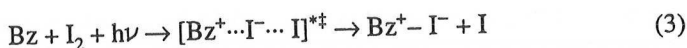


Figure 14. (A) A schematic diagram showing the cuts on the potential energy surface (PES) along the Bz-I and I-I coordinates. The CT transition state is directly reached by the $t = 0$ fs pulse ($\lambda^{\ddagger}$). The reaction proceeds through the exit channels either on the same CT PES shown in (A) or through nonadiabatic transitions, which lead to the I-I bond breakage. (B) A PES contour map of the Bz-I₂ CT state and a representative trajectory of the reaction on this PES (ref. 37).



In the cluster experiment discussed here, excitation takes place directly to the collision complex as illustrated in Figure 14. The pump pulse excites the neutral ground-state complex to an excited CT state that induces a prompt electron transfer. This starts the Coulomb field attraction and subsequent collision that leads to products. The products are either Bz⁺ - I⁻ + I or Bz - I + I. In either case, measuring the appearance of free I atom is a measure of the total rate from the harpoon region.

Experimental: The CT state was excited at 275 nm and other wavelengths. Reactions and products were probed by resonance ionization in a time-of-

flight mass spectrometer (TOFMS). Iodine atoms from reaction were probed by 2+1 REMPI at 304 nm. As the pulse had a bandwidth of 2 nm, both the $^2P_{3/2}$ (I) and $^2P_{1/2}$ (I*) spin-orbit states are simultaneously detected. The laser system is similar to the one described in Section 2.1.2.

The transient for the appearance of free I atom is given in Figure 15; a time constant of 750 fs is observed. A schematic is also presented in Figure 15 to illustrate the change in structure and charge as the complex evolves from neutral to CT state to transition state, and then to final products. The excitation to the CT state produces a vibrationally excited, but bound I_2 anion. An excursion involving nuclear coordinates for Bz and I_2 then takes place before break up into final products. The time constant of 750 fs indicates that the transition state lives for a few vibrational

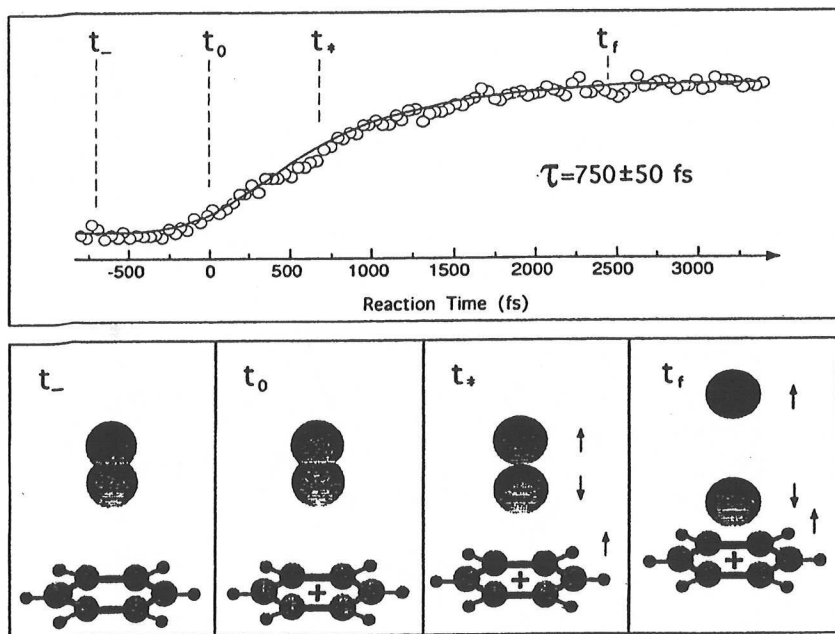


Figure 15. The fs transient of free iodine atoms (open circles) following the Bz- I_2 complex excitation to its CT state by the 275 nm fs ($t = 0$) laser pulse under the 1:1 complex condition (0.5 torr Bz). A single exponential fit (solid line) to this data with a response function convolution gives a rise time of 750 ± 50 fs. The four panels at the bottom describe the structural changes of the axial geometry, illustrating the complex before $t = 0$ (t_-), at $t = 0$ (t_0), in the harpoon region of the PES (t_*), and following the final breakage to Bz^+I^- and I products (t_f) (ref. 37).

periods. An example trajectory illustrating the quasibound oscillations in the transition state is presented in Figure 14B.

A powerful added dimensionality to the experiment is the measurement of the product angle-velocity distribution. Figure 16 presents measurements of the 1D product velocity-component distributions for I atom recoil detected at specific angles. The complex here is *o*-xylene-I₂. The series of plots represent the velocity distribution as a function of delay time after excitation. One should note that the total signal increases with time, which is a measure of the rate of decay of the transition state to product. Examining more closely, one notices that the relative distribution of slow and fast I atoms changes with time. At longer time, the lower velocity component, which peaks at a translational energy of about 900 cm⁻¹, increases relative to the fast component, which peaks at a translational energy of

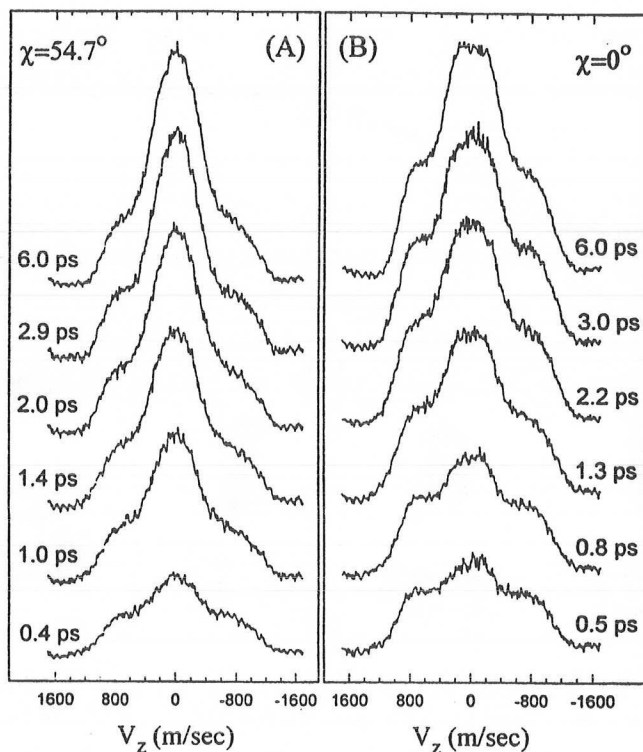


Figure 16. Time-resolved, KETO F distributions of iodine atoms resulting from the *o*-xylene-I₂ reaction measured at a series of pump-probe delay times. Pump laser polarization is (A) at the magic angle and (B) at 0° (parallel) with respect to the TOFMS axis. The pump-probe delay times are indicated for each distribution (ref. 37).

about 5000 cm^{-1} . In terms of formation rates, the high- and low-velocity components rise with time constants of about 450 ps and 1.4 ps, respectively. The anisotropy of the low- and high-velocity components is about 0.2–0.3 and 0.7–1.0, respectively.

Transition-State Geometry

An interesting issue is the structure of the transition state at the instant of excitation by the pump pulse. There is now strong experimental and theoretical evidence that I_2 lies perpendicular to the aromatic ring in what is called the axial geometry.^{41,42} This is to be compared to the “resting” or parallel geometry originally suggested by Mulliken.⁴⁰ The measured I atom recoil anisotropy, however, tells a different story. For a strictly axial geometry, there is no transition moment perpendicular to the benzene ring. In this case, the transition moment, in the plane of benzene, would be perpendicular to the recoil direction of the I atom, which would then have a limiting anisotropy value for β of -1 . The measured values of β , however, were positive. For the resting, in-plane geometry, the transition moment can be shown to also be perpendicular to the recoil direction, again in contradiction with the measured anisotropy.

The experimental results are understood by considering an oblique geometry. In simple terms, the two transition moments μ_{01} and μ_{11} , which are parallel and perpendicular to the benzene ring and associated, respectively, with the axial and resting structures, form a linear combination that can give a positive anisotropy for a specific range of oblique angles. For instance, an I_2 tilt angle of $30\text{--}35^\circ$ between the μ_{11} transition dipole and the recoil direction is $30\text{--}35^\circ$ corresponds to a predicted anisotropy of $\beta \approx +1$. The oblique angle occurs because of the large vibrational amplitude for the $\text{I}_2\text{--Bz}$ torsion, even for the vibrationless level. The Wiersma group has noted that μ_{11} is typically much greater than μ_{01} , except at precisely the axial geometry where it goes to zero.⁴³ Hence the excitation probability increases dramatically for tilt angles away from axial. This means that the transition state is formed at an oblique angle. The velocity distributions for both the I and I^* have recently been studied by Young’s group and are consistent with those of the Caltech group.⁴⁴

Dynamics and Mechanism

The transition-state entrance channel may be described as follows: At time zero, the system is excited to a CT state creating an instantaneous Coulomb potential along the Bz--I coordinate that launches the reaction (Figure 14A). The sudden charge separation creating the attractive force is what is referred to as the harpoon mechanism. The Bz and I_2 reactants undergo large amplitude collective vibrational motion (Figure 14B). The I_2 also begins to vibrate to reach a new equilibrium bond length for I_2^- .

The transition state, in less than 1 ps, enters the exit channel where it then branches into two major product channels: the ionic route $\text{Bz}^+\text{I}^- + \text{I}$ and the neutral route $\text{BzI} + \text{I}$ (there are other minor channels relating to different spin-orbit states of BzI and I , etc.). There have been many observations of the ionic channel in bimolecular encounters in the gas phase and in weakly bound complexes. Good examples include $\text{Rg}^* + \text{X}_2$ (Rg : rare-gas atom; X_2 : molecular halogen)⁴⁵ and the harpoon reactions $\text{M} + \text{X}_2$ (M : alkali metal atom).⁴⁶

For the Bz-I_2 system, the neutral product channel lies about 2.6 eV lower in energy than ionic channel. A determination of the branching channel was made by an analysis of the I atom recoil velocities. At 277 nm excitation, the available energy in the ionic channel is about 0.4 eV (3200 cm^{-1}). Based on recoil kinematics, the maximum translational energy available to the I atom is about 2000 cm^{-1} . The peak translational energy would lie below this value due to internal excitation of the Bz^+I^- product. The experimental translational energy distributions for product iodine atom gives peaks at about 1000 cm^{-1} and 5000 cm^{-1} . The high-energy component is inconsistent with an ionic channel, as it exceeds the allowable energy available. These results suggest that the neutral reaction channel dominates and occurs as a result of back electron transfer. The low translational energy component is assigned to a one-molecule caging product. The basis for this conclusion is: (1) the recoil anisotropy is much lower than that for the high translational energy I -atom component, and (2) the low-energy component has a much slower rate constant for formation than the high-energy component, at least for *o*-xylene- I_2 , the system studied by time-resolved KETOF.

Bz_n/I_2

The effect of further solvation of I_2 was investigated by increasing the pressure of Bz in the gas mixture. In Figure 17, the *ab initio* structure for Bz_n/I_2 indicates that for relatively small solvent clusters the I_2 lies on the surface of a Bz_n cluster; in other words an incomplete solvent shell. For larger solvent clusters, a complete solvation of I_2 eventually ensues. The time dependence for I atom release was recorded for increasing cluster size distributions and exhibits behavior consistent with the *ab initio* structure calculations. In Figure 18, transients are shown next to the corresponding TOFMS. There is a distinct trend with increasing solvation for the I atom escape to slow down and for a second longer time component to grow in. In 1:1 complexes, the fast time component was found to be a composite of two dynamical events that are distinguishable by monitoring the I atom rise as a function of translational energy. The rise time for high- and low-energy I atoms was measured to be 450 fs and 1.4 ps, respectively. The high-energy I atom represents uncaged prompt dissociation, whereas the low energy indicates a collision or a caged dissociation, albeit a one-molecule cage effect for the 1:1 complex. For larger clusters this caged dissociation increases only moderately in Figure 18, indicating

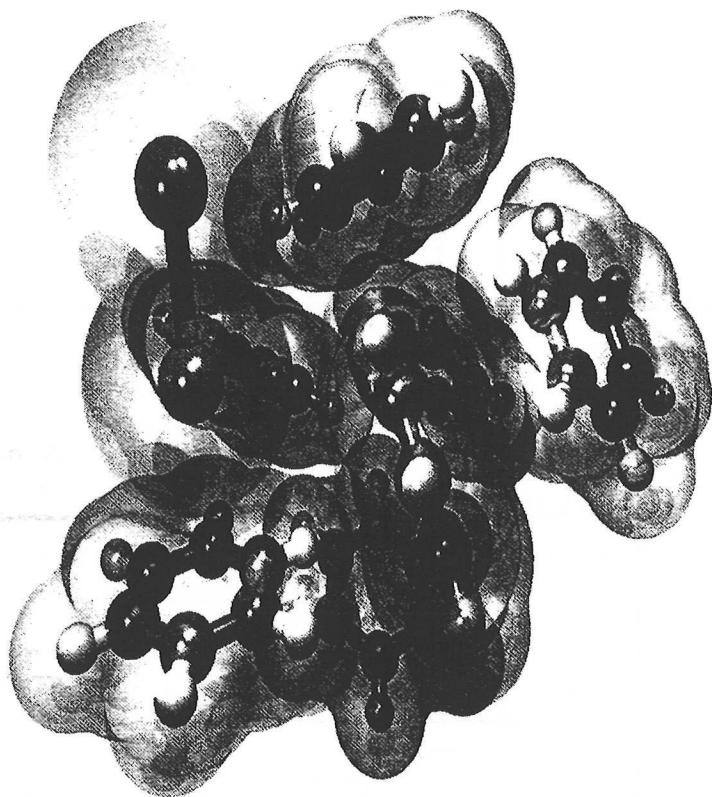


Figure 17. Molecular structure of I_2/Bz_n based on the results of ab initio (1:1 complex) and empirical (1: n) potential calculations (ref. 116).

that some I_2 lies on the surface of the solvent cluster, consistent with the calculated structure in Figure 17.

As the cluster size increases, a second long-time component becomes evident, increasing in intensity and time (from 19 to 75 ps in the examples in Figure 18). These dynamics are consistent with an I atom that is completely solvated. Caging of the dissociated I atom involves a cluster of solvent molecules, significantly slowing the escape of an I atom. For these larger clusters, the I atoms can become trapped and recombine. The different time constants measured in small and large clusters using kinetic energy analysis provide important insights into solvent structure, collisional interactions, and cage escape dynamics. Molecular dynamics simulations support the microscopic picture.

A

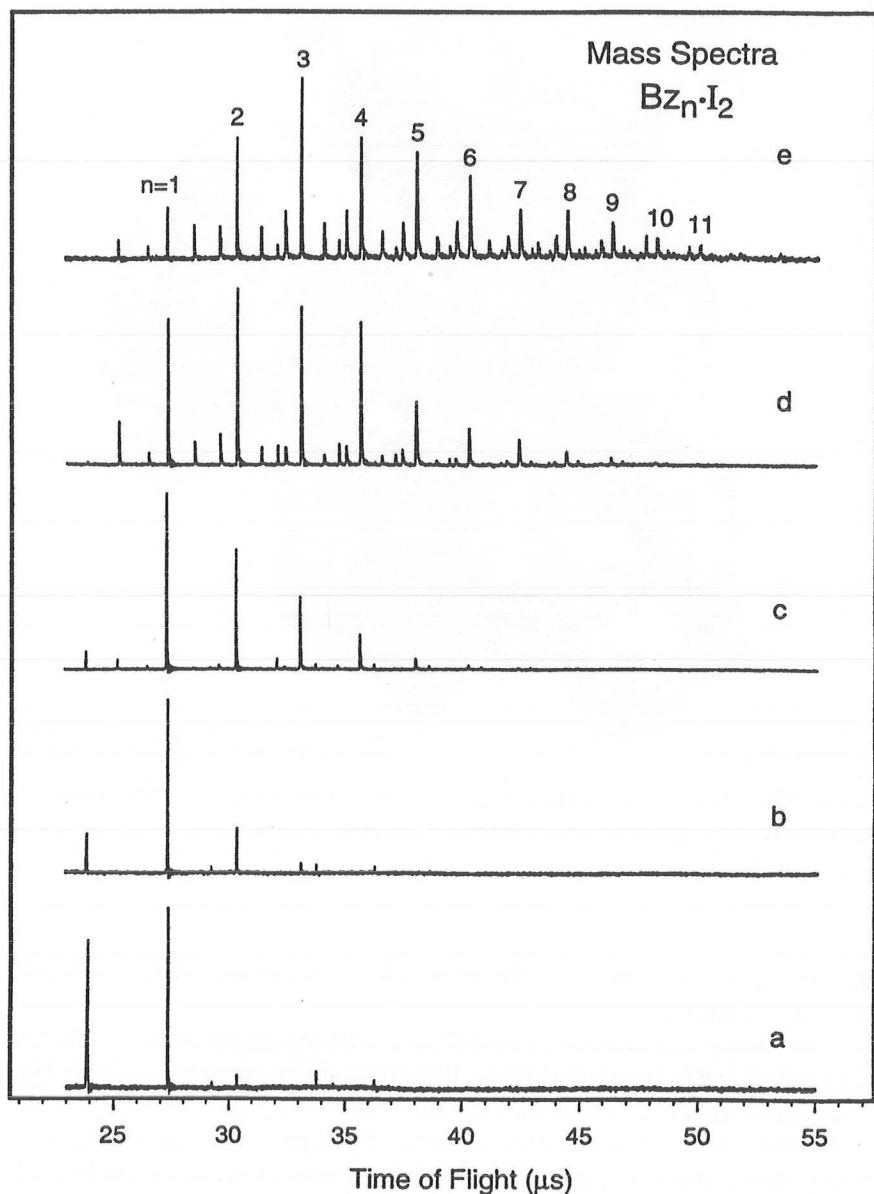


Figure 18. (A) TOFMS and corresponding transients for I atom detection as a function of benzene vapor pressure in the gas mixture: (a) 0.5 torr, (b) 1.3 torr, (c) 3.3 torr, (d) 9.5 torr, and (e) 24 torr. (continued)

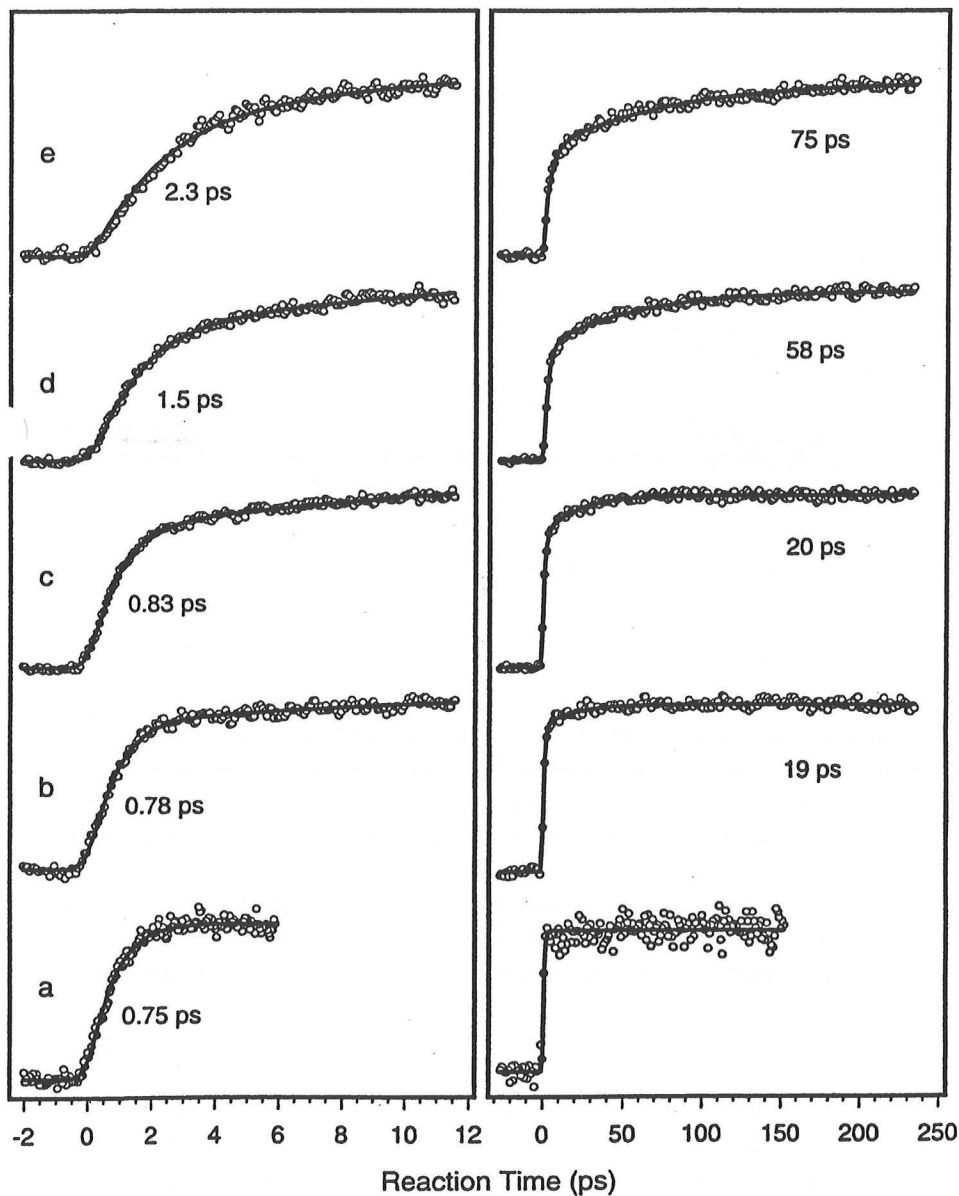


Figure 18. (Continued) The experimental transients were fitted to a biexponential function (ref. 37).

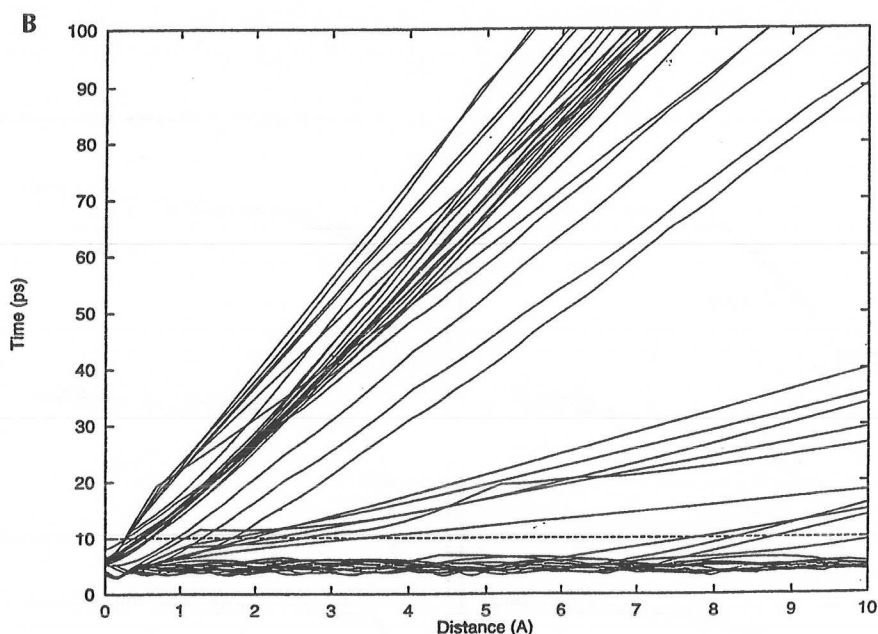


Figure 18. (B): MD simulations based on the results in Figure 17.

Comparison with Liquid Phase

Femtosecond measurements of the dynamics in liquids have been conducted by the groups of Wiersma^{43,47} and Sension.⁴⁸ The former group focused on I_2 /mesitylene and I_2 /toluene excitation at 310 nm (blue edge of the CT band) and the latter group on I_2 /mesitylene at 400 nm (the red edge). Both groups recorded transient absorption spectra over the range of about 400–700 nm. The Wiersma group measured a 25 fs transients assignable to the D–I photoproduct (where D is the aromatic electron donor) and to I_2 . The ratio of D–I to I–I bond breaking was reported to be about 1:3. The Sension group observed similar transient absorptions that were fully developed by 500 fs and had a time scale of ≤ 250 fs. The slower time scale for reaction in the latter work may be due to the longer wavelength excitation.

At comparable excitation energies, the transient absorption signal in liquid appears faster than does the high-energy I atom product in the results on the vdW complex. The different time scale can be partly explained by the D–I transient absorption signal which develops before complete I–I bond breaking that is required to detect free I atom. Bulk solvent–solute interactions may also account for faster dissociation. Transient absorption spectra in the liquid and gas phase

assign the product to D-I and not D^+-I^- , which is consistent with the conclusions of Bz-I₂ from I atom recoil velocity measurements.

Some information on solvent caging is obtained from a comparison of the results from the Caltech group³⁷ and the Wiersma group.⁴⁷ The latter liquid work revealed a slower rise following the initial 25 fs rise in the transient absorption traces. This was attributed to solute-solvent geometries in which the product I atom was launched into another solvent molecule to form D-I. The analog in isolated complexes is the low energy I atom that rises with a longer time constant than the high-energy I atom. The low-energy I atom results from an interaction with a second solvent molecule (e.g. Bz₂-I₂). Translational energy is lost and cage escape is delayed in the collision process. In liquid, the presence of many solvent molecules further cools the translational energy of the I atom to the point that it then combines with an aromatic solvent molecule.

4. PROTON TRANSFER

Excited-state proton transfer is a prototypical "large chemical system" that has been studied in clusters and condensed phase. The first spectroscopic study of ESPT in a cluster was reported by Leutwyler, Cheshnovsky, and coworkers for 1-naphthol(NH₃)_n.^{49,50} These experiments were important because they showed that it is possible to investigate how individual solvent molecules progressively stabilize the product states.

The dynamics in real time were first reported for naphthol^{51,52} and phenol⁵³⁻⁵⁹ complexed to a variety of solvents. The Syage lab reported on picosecond dynamics of ESPT of phenol (PhOH) complexed to various solvents.⁵³⁻⁵⁹ Several issues have been investigated: solvent dependence on rate,^{7-9,53} cluster ion properties,^{54,55} ESPT in phenol dimers,⁵⁶ structural effects,⁵⁶ photoelectron studies of solvent reorganization,⁵⁸ and the mechanism of proton tunneling.^{7,59} The Zewail group^{51,52} and the Bernstein and Kelley group⁶⁰ have been studying similar properties for naphthol (NpOH). These studies have recently been extended by Caltech group to the femtosecond domain.⁵² These investigators found that for 1-NpOH(NH₃)_n the minimum number of solvent molecules necessary to observe ESPT is $n = 3$. Our measurements for PhOH(NH₃)_n gave a corresponding value of $n = 5$. The difference in the critical ammonia solvent size for ESPT for phenol vs. 1-naphthol is consistent with the difference in acidity of the two S₁-excited aromatic acids (pK_a of 4.1 and 0.5, respectively).⁶¹

In a related series of experiments, Brucker and Kelley measured proton transfer rates in small solvent complexes formed in cryogenic argon matrices.⁶² They observed similar solvent-size dependences for 1-naphthol-ammonia; however, the rates differed from that of the isolated clusters formed in molecular beams, presumably due to the polarizability of the Ar matrix. The above studies, which we discuss in more detail later in this review, are important because they can be related

to the large literature of ultrafast studies of ESPT in solution by the groups of Robinson,⁶³ Barbara,⁶⁴ Huppert,^{65,66} Clark,⁶⁷ Kelley,⁶⁸ and others.

4.1. ROH^*/B_n

Background

Aromatic alcohols are more acidic in their S_1 state than in S_0 . Photoexcitation, therefore, increases acidity giving rise to the term pH jump.⁶⁵ Excited-state proton transfer (ESPT) reactions have been studied extensively in the condensed phase including several time-resolved experiments.^{63–68} These reactions are strongly solvent-dependent, largely because of the neutral acid AH (or AH^*) and the conjugate base A^- (or A^{*-}) which tends to be stabilized differently by the solvent. Hence, the acidities of the ground and excited states can change markedly with different solvents.

We represent proton transfer from the aromatic acid ROH (R = naphthyl or phenyl) by,



which corresponds to a conversion from a locally excited S_1 state with a covalent O–H bond to an excited ion-pair state. B_n refers to the solvent cluster consisting of n molecules of base B. A qualitative picture of the cluster potential energy curves for ground, excited, and ionic states is given in Figure 19 along with the pump-probe excitation/detection scheme used to measure the chemical rates. Figure 19 also shows representative ion energy distributions, measurable by photoelectron spectroscopy. Representative excited-state reactant decay and product formation are shown in the insert. The product formation signal is due to dissociative ionization of the excited-state product to giving a detectable yield of $\text{NH}_4^+(\text{NH}_3)_m$. This channel is minimal for reactant, and for some unknown reason does not occur for excited reactant or product for NpOH B_n clusters.

Basicity and Solvent Size Dependence

There is now a fairly large collection of rate measurements for phenol and 1-naphthol in a variety of solvent clusters from which to learn about fundamental interactions of solvent molecules. Figures 20 and 21 show a series of excited state reactant decay curves for the phenol and 1-naphthol systems. The phenol results in Figure 20 show a distinct onset to reaction at $n = 5$ ammonia molecules.^{7–9,53} The 1-naphthol results in Figure 21 show a threshold at $n = 3$.^{51,52} A similar conclusion in the latter case was reached for measurements by Bernstein, Kelley, and coworkers.⁶⁰ The $\text{p}K_a^*$ values (i.e. the negative logarithm of the equilibrium constant K_a for acid dissociation) of excited state 1-naphthol and phenol are 0.5 and 4.1, respectively, which converts to an enthalpy difference of 0.22 eV.⁶¹ Thus, additional ammonia solvent molecules are required to stabilize ESPT in phenol compared to

1-naphthol. If the rates of ESPT for NH_3 solvation in Figures 20 and 21 are plotted versus n , the resulting curve takes on a shape and inflection that is suggestive of an acid–base titration curve. Indeed, mass-specific, time-resolved cluster experiments correspond to single molecule titration measurements.

Measurements of ESPT in other solvents show striking differences compared to ammonia solvation. In Figure 20 no reaction is observed for $\text{PhOH}(\text{CH}_3\text{OH})_n$ up to $n = 11$. Water is also inactive for these moderate cluster sizes for phenol and for 1-naphthol. Knochenmuss et al. report reaction occurring in $1\text{-naphthol}(\text{H}_2\text{O})_n$,⁶⁹ but the thresholds are several hundred water molecules and the rates are on the nanosecond, not picosecond, timescale. For more basic solvent molecules, small

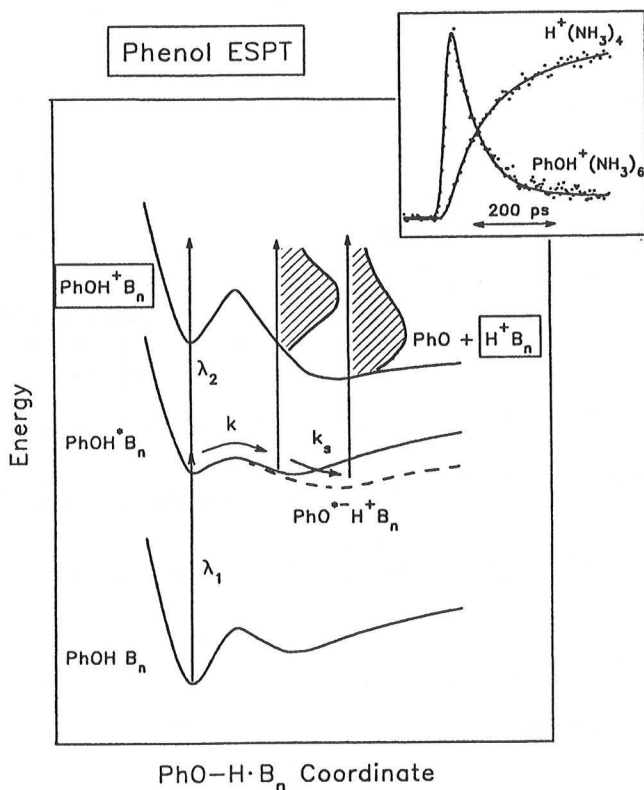


Figure 19. Schematic energy diagram for $\text{PhOH}(\text{NH}_3)_n$ (consistent with $n \approx 5$). The pump and probe pulses are denoted as λ_1 and λ_2 , and the excited-state proton transfer and solvent reorganization rate constants are given by k and k_s , respectively. Approximate photoelectron band shapes are shown by the shaded areas. The ion signals for reactant and product are given in the insert and show matching kinetics (ref. 7).

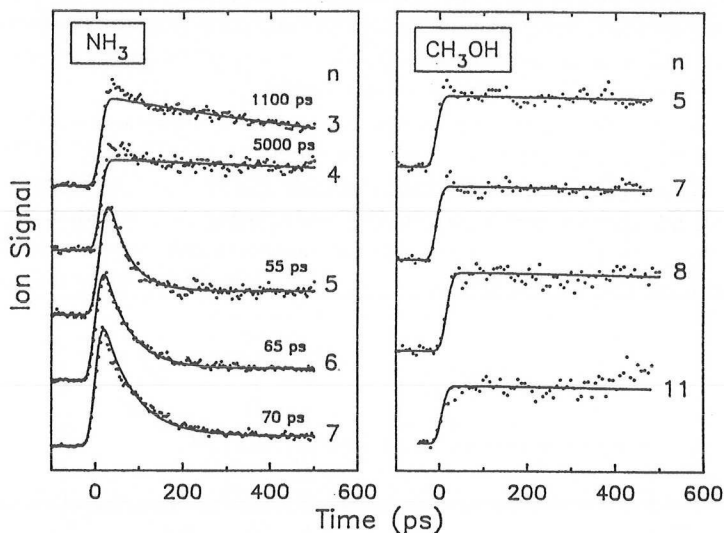


Figure 20. Picosecond measurements of $\text{PhOH}^* B_n$ for $B = \text{NH}_3$ and CH_3OH using 266-nm pump and 532-nm, probe. The calculated curves for CH_3OH solvation assumes a lifetime of 10 ns (ref. 53).

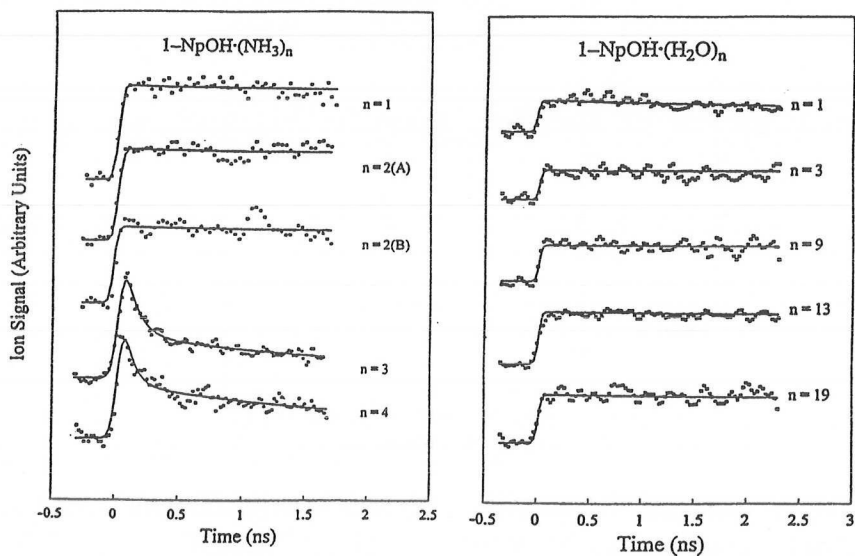


Figure 21. Picosecond measurements of $1\text{-NpOH}^* B_n$ for $B = \text{NH}_3$ and H_2O . 2A and 2B refer to different geometries for $n = 2$ ammonia molecules. Pump excitation was near the S_1 origin and probe excitation was near the ionization threshold (refs. 51, 52).

solvent-size thresholds for reaction are observed. In phenol, ESPT was observed for trimethylamine solvent at $n=3$, and for hydrazine at $n=5$.⁵³ In 1-naphthol a reaction was observed at $n=2$ for piperidine solvent and not for water up to $n \approx 20$.⁵²

How do these cluster rates compare to condensed-phase measurements? The ESPT lifetimes in PhOH and 1-NpOH in ammonia are in the 20–100 ps range depending on vibrational energy. No measurements in bulk ammonia have yet been made. In water solution, the groups of Robinson and Clark measured room temperature lifetimes of about 40 ps for 1-NpOH.^{63,67} In other condensed-phase systems, the ESPT rate is over an order of magnitude slower for 2-NpOH in water or for 1-NpOH in methanol or ethanol.

A mixed solvent system that strongly governs phenol reactivity is $\text{NH}_3/\text{CH}_3\text{OH}$.⁵³ Reaction rates for different solvent distributions of similar cluster size are presented in Figure 22. The substitution of a single CH_3OH molecule for an NH_3 molecule causes a substantial decrease in reaction rate. Excited phenol in neat NH_3 solvent cluster $(n,m) = (6,0)$ reacts in 65 ps whereas the $(5,1)$ cluster reacts in 750 ps. Considering that the $(5,0)$ cluster reacts in 60 ps (cf. Figure 20), the $(5,1)$ result indicates that the addition of a single CH_3OH molecule quenches the reactivity of the $(5,0)$ cluster. This is surprising because it implies that the aggregate proton affinity of the solvent is somehow reduced by the addition of CH_3OH . These results

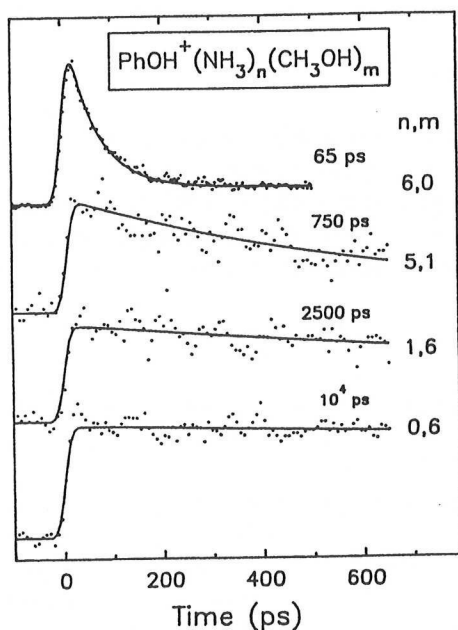


Figure 22. Picosecond measurements of $\text{PhOH}^+(\text{NH}_3)_n(\text{CH}_3\text{OH})_m$ using 266-nm pump and 532-nm probe (ref. 53).

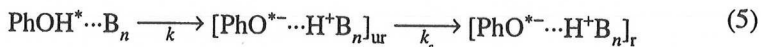
highlight the importance of solvent structure. The concept of critical solvent structures in ESPT reactions has been investigated in the solution phase by Robinson and coworkers.⁶² Their picosecond measurements and theoretical analyses on aromatic acids (e.g. 1- and 2-naphthol) in H₂O and alcohol (CH₃OH and C₂H₅OH) support the notion that a critical solvent cluster core is necessary to act as an efficient proton acceptor. For 2-naphthol in H₂O, the critical solvent-core size is reported to be about four.⁶³

Energetics

A simple description of the energetics of ESPT can be visualized by starting from CT states in gas-phase molecules.⁵³ CT states generally occur at high energy. In phenol and naphthol, the relevant states are expected to lie at very high energy relative to the covalent S_0 and S_1 states because of the large energy required to form a free proton (the H atom ionization potential is 13.6 eV. The ion-pair state(s), which has large proton character, is stabilized strongly by complexation of phenol to molecules with high proton affinity. The lowering in energy of the ion-pair states by the first solvent molecule is comparable to the proton affinity of the solvent molecule (which is 8.8 eV for NH₃⁷⁰). Each additional solvent molecule contributes less and less stabilization (the stepwise proton affinity^{71,72}); however, the cumulative stabilization by a few solvent molecules can lower the ion-pair state to energies comparable to that of the S_1 state, thus making ESPT thermodynamically allowed.

Solvent Reorganization

Here we consider what happens to the solvent structure after reaction occurs and, in so doing, consider the dynamical properties of the solvent. When proton transfer occurs, the solvent is no longer at equilibrium. The formation of a large product dipole is expected to exert a force on the solvent leading to further dynamics. For simplicity, we consider that reaction and solvent dynamics are separable, that is,



where the subscripts ur and r denote unrelaxed and relaxed solvent configurations and k_s is the solvent reorganization rate constant (cf. Figure 19).

Time-resolved ionization efficiency. The product formation curves for NH₄⁺ (NH₃)_n in the phenol/solvent_n studies showed two time dependences: a rapid rise matching the decay of the PhOH⁺(NH₃)_n signals (55–70 ps), and a much slower growth component of about 300 ps.^{7–9,53,58} The fast time response is due to the ESPT reaction. The slow time response is ascribed to solvent cluster reorganization. For 1-NpOH(NH₃)_n a two component time dependence is observed for the excited state decay, which is attributed similarly to ESPT and solvent reorganization. The

reorganization time varied from 200 ps to 3 ns depending on excitation energy and number of NH_3 molecules.^{51,52,60}

Time-resolved photoelectron spectroscopy. A more detailed probe of geometry change is obtained by monitoring the individual FC components to ionization by time-resolved photoelectron spectroscopy.⁵⁸ Photoelectron spectra are plotted in Figure 23a for different probe delay times. The spectra are broad because of the distribution of cluster sizes, large density of low-frequency modes, rapid vibrational redistribution, and large geometry change upon ionization. However, there is a general shift in the band with time reflecting the change in Franck–Condon factors for ionization as the solvent geometry in the excited-state product evolves. This method is analogous to the time-dependent Stokes shifts of emission bands in studies of solvent relaxation in the condensed phase.^{73–76}

The time dependence for the low-energy and high-energy photoelectron bands (gates A and B) is plotted in Figure 23b. The low-energy band (ions of high internal energy) increases rapidly in intensity and then decays at a slower rate. The high-energy band (ions of low internal energy) shows a corresponding slow rate of increase. These observations support the interpretation of a Franck–Condon distribution that changes with time due to solvent reorganization.

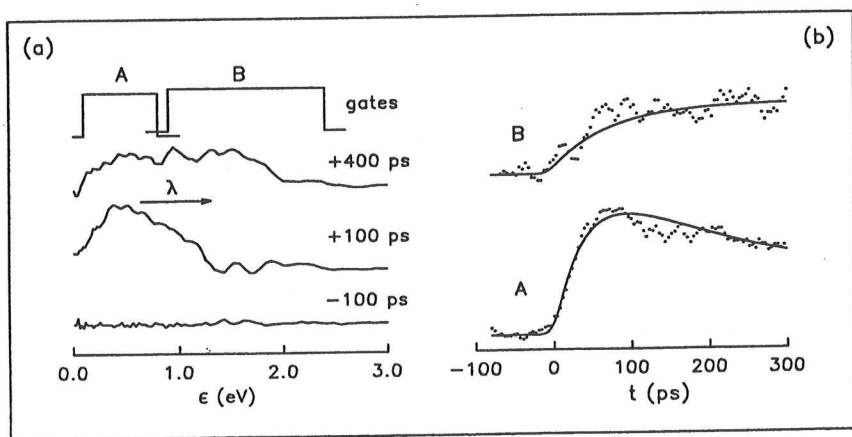


Figure 23. Time-resolved photoelectron spectra as a function of pump-probe delay time t . (a) Difference spectra corresponding to (pump + probe) – (pump). Gate widths are constant in time. (b) Observed time-dependences of the low-energy (gate A) and high-energy (gate B) photoelectron bands are plotted. Fitted curves were calculated for rate constants $k = (50 \text{ ps})^{-1}$ and $k_S = (300 \text{ ps})^{-1}$ and spectral parameters discussed elsewhere (ref. 7, 58).

Barrier Properties and Tunneling Mechanism

The barrier properties for ESPT are especially interesting in small clusters because it is not known whether a few solvent molecules act in a manner similar to condensed-phase solvents in facilitating tunneling. This raises the question whether tunneling is expected to occur at all in cold clusters, and if so, by what mechanism. Syage recently investigated this question and obtained evidence that proton tunneling does occur in small clusters of phenol-(NH₃)_n.^{7,59,77} Similar behavior has been reported by the Bernstein and Kelley group and by the Zewail group for 1-NpOH(NH₃)_n.^{51,52,60} The principal evidence in both systems is the observation that

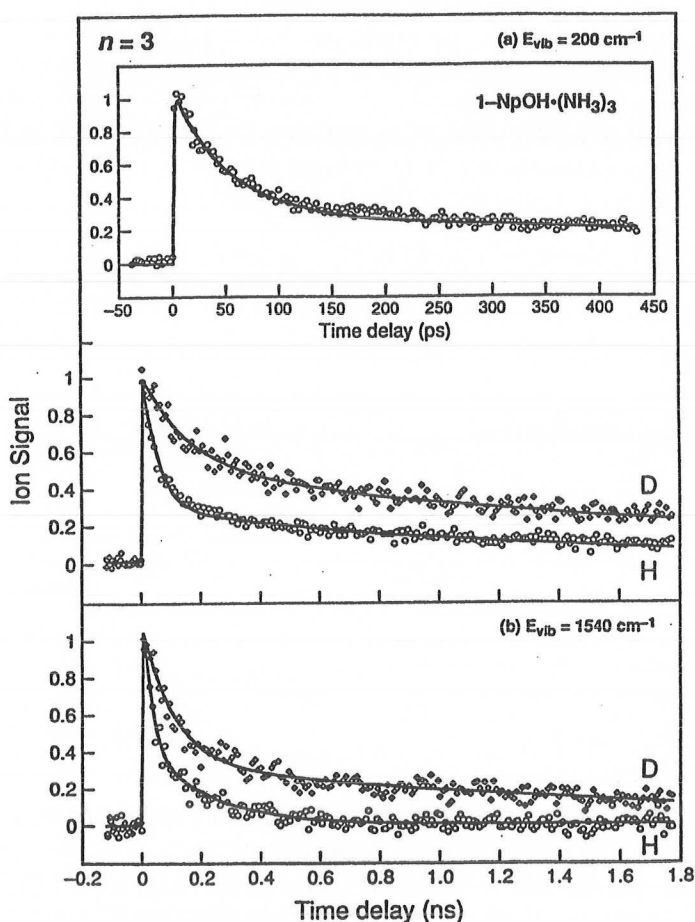
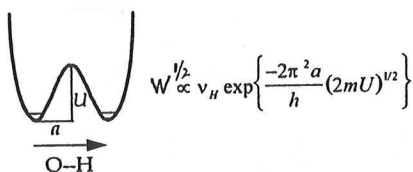


Figure 24. Femtosecond measurements of 1-NpOH*(NH₃)₃ and 1-NpOD*(ND₃)₃ (ref. 51, 52).

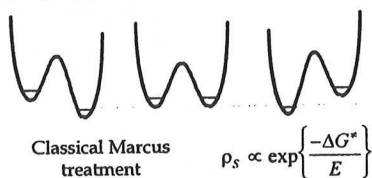
the transfer rate for a deuteron is nearly an order of magnitude slower than for a proton, as seen in Figure 24.

Work is in progress to develop a model of proton tunneling in clusters that can be made applicable to condensed-phase systems in order to draw direct comparisons between these two very different solvent systems. A proton tunneling model in clusters has been described in detail elsewhere^{7,59,77} and an abbreviated treatment is presented in the Appendix. In essence, it adapts the concepts of condensed-phase tunneling⁷⁸⁻⁸⁰ to a state-to-state treatment based on radiationless transition theory.⁸¹ For the present chapter it suffices to understand qualitatively what elements are in the theory and why they are important. These are summarized in Figure 25. A minimum of four nuclear coordinates is needed: (1) the O-H coordinate q_H , which is the reaction coordinate, (2) the O-N coordinate Q_N , in which the O...N symmetric stretch modulates the internuclear distance between potential minima, which in turn modulates the barrier height and width,^{78,79} (3) the solvent coordinate S , in which solvent modes cause fluctuations in the relative energies of reactant and product,⁸⁰ and (4) coordinates corresponding to product accepting modes that reduce the electronic energy gap between reactant and product.⁸¹ All coordinates, except for S are treated quantally. One does not expect quantitative agreement between theory

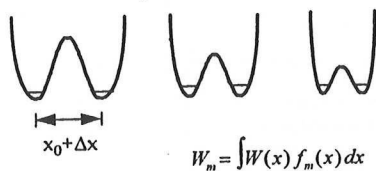
• **O-H Coordinate**



• **Solvent coordinate**



• **O - - - N symmetric stretch**



• **Product vibrational coupling**

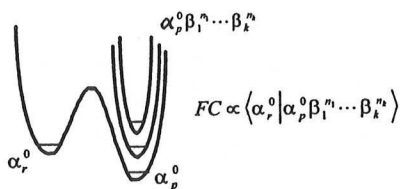


Figure 25. Diagrams that qualitatively show the important nuclear coordinates used in the present tunneling model. Terms not defined in the text are as follows: ν_H , a , m , and U are O-H frequency, barrier width, reduced mass of tunneling particle, and barrier height, respectively. FC are Franck-Condon factors for a vibrationless reactant where α is for the O-H vibration, and β_i are for all other modes i . m and n are quantum numbers for reactant and product, respectively (ref. 77).

and experiment for such large systems; however, the model successfully describes the three main qualitative trends on measured rate: the deuteron/proton ratio, the vibrational energy dependence, and the reaction free-energy dependence as varied by the number of solvents.^{7,59,77} This consistency may be taken as evidence that the theory is capturing the major physical processes governing microsolvation of proton tunneling.

One of the interesting observations for the $\text{PhOH}^*(\text{NH}_3)_n$ and $\text{NpOH}^*(\text{NH}_3)_n$ is the apparent insensitivity of ESPT rates with increasing n , when presumably the reaction free energy ΔG_0 is becoming more exothermic. This behavior may be a result of being in the Marcus inverted region. The tunneling theory above is compared to the measured size-dependent rates of ESPT in $\text{PhOH}(\text{NH}_3)_n$ and to other theories that are subsets of the above treatment in Figure 26. The ability to model tunneling rates as a function of ΔG_0 is a challenge to tunneling theories. The treatment of tunneling is represented by the curve (---) in Figure 26 and corresponds to considering the first three nuclear coordinates outlined above and in Figure 25. A model that ignores both product vibrations and the Marcus concept of activated solvent, but which instead assumes a continuum of product states, predicts

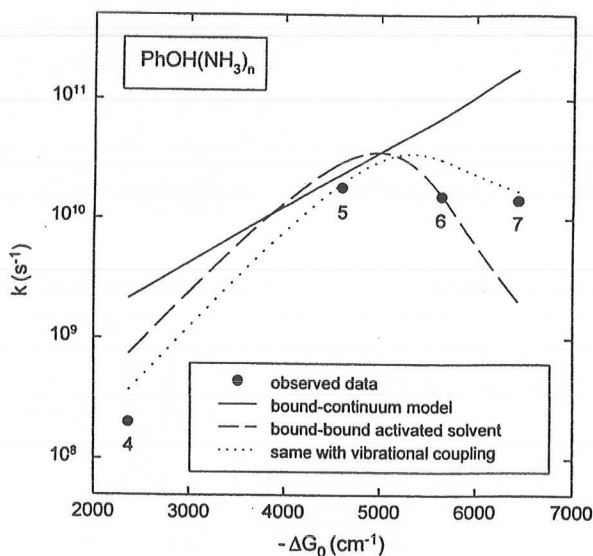


Figure 26. Calculated dependence of k on cluster size n and ΔG_0 by three models of tunneling and comparison to measurements for $\text{PhOH}(\text{NH}_3)_n$. Some parameters for calculations ($n = 4-7$, respectively) are: $\nu_{\text{H}} = 3500 \text{ cm}^{-1}$; $\nu_{\text{N}} = 140 \text{ cm}^{-1}$; $U_0 = 0.54, 0.40, 0.335, 0.285 \text{ eV}$; $a_0 = 0.349, 0.30, 0.275, 0.253 \text{ \AA}$, $\Delta G_0 = -2360, -4600, -5640, -6440 \text{ cm}^{-1}$ (cf. ref. 7, 59).

a continuously increasing tunneling rate with $-\Delta G_0$. This calculation is represented by the curve (—) in Figure 26 and corresponds to considering the first two coordinates outlined above. The model that includes all four nuclear coordinates is represented by the curve (· · ·) in Figure 26 and gives the best agreement with experiment. This treatment is also consistent with experimental measurements of the dependence of k on internal vibrational energy and on deuteration.

The phenol/ NH_3 cluster systems have been the subject of some theoretical investigations. Yi and Scheiner carried out *ab initio* calculations of the potential energy surfaces for ground and excited and ionic electronic states of PhO-H-NH_3 that has helped elucidate the barrier properties for ESPT.⁸¹ The calculated S_1 potential barrier is in reasonable agreement with the barrier deduced above for relating the experimental rates with a tunneling model. Siebrand and coworkers conducted structure calculations on the $\text{PhOH}(\text{NH}_3)_n$ system to help understand the buildup of the solvent shell, particularly to understand if there is a special structure at five solvent molecules to explain the onset to reaction.⁸² They generally find that the solvent bonds in chains and loops and that the loops are arranged to maximize the bonding between the reactive and the rest of the molecule. These results are in accord with experiment that indicates that up to 5 NH_3 form bonds off the reactive site by solvent-solvent bonds as opposed to some solvent molecules bonding independently to the aromatic ring. The structure calculations further show that the geometry for the reactant and product clusters (i.e. pre- and post-proton transfer) differ markedly. The slow solvent relaxation measured by time-resolved photoelectron spectroscopy is in agreement with their calculations.

4.2. Double Proton Transfer

The 7-azaindole dimer (7-AI) has been extensively studied because its structural specificity can serve as a model for DNA base pairing. A particularly interesting topic is whether excitation conditions that might change the hydrogen-bonding properties can disrupt base pairing to the extent that errors occur in DNA replication. In particular, 7-AI dimer is known to undergo a double-proton transfer upon electronic state excitation. The pioneering work by Taylor, El Bayoumi, and Kasha in the condensed phase revealed red-shifted fluorescence indicative of a tautomer structure.⁸³ Picosecond, then femtosecond measurements have been made of this fast process in solution; an excited-state lifetime of 1.4 ps was measured for 7-AI excitation in hexadecane solution at room temperature.⁸⁴

In a series of papers, Fuke and Kaya and coworkers measured fluorescence excitation spectra of 7-AI dimer and other analogs in free-jet expansions.⁸⁵ One of the more remarkable observations was an apparent mode specificity to the rate of ESPT wherein the N···N intermolecular mode showed dramatically enhanced line intensities in the excitation spectra recorded when monitoring the tautomer fluorescence. These observations are consistent with vibrational barrier compression discussed in the tunneling model above. We describe this further shortly.

The dynamics of bond breaking have only recently been measured. The Zewail group measured jet-cooled 7-AI dimer excited-state decay in a time-of-flight mass spectrometer using femtosecond pulses; 305–310 nm for excitation and 620 nm for ionization from the excited-state surface.⁸⁶ One of the principal questions regarding double-proton transfer, and more generally for all reactions involving multiple-bond reformation, is whether the reaction proceeds in a concerted, simultaneous manner, or whether it occurs in a series of steps. The latter possibility is illustrated in the sequence shown in Figure 27. The femtosecond transients recorded for the 7-AI dimer are presented in Figure 28. There is a distinct double-exponential decay that occurs at two different excess energies. These results are consistent with a stepwise proton transfer (i.e. an asymmetric reaction coordinate). The transients in Figure 28 were described as representing a fast single proton transfer to an intermediate state shown in Figure 27 that is asymmetric, followed by a second, slower proton transfer leading to the final, long-lived tautomer state.

Measurements were also conducted on deuterated species to test for the involvement of a tunneling mechanism. At 1 kcal/mol excess energy, the protonated dimer gave time constants of 360 fs and 1.7 ps, compared to 3.0 ps and 25 ps for deuterated dimer.⁸⁶ These values are consistent with a tunneling process through a double-well potential. Based on this model, a lower limit to the barrier height of 2.6 kcal/mol was derived for the second step. The barrier height for the first step is assumed to be less than the second step. Some interesting questions that remain are: (1) why is the ionization efficiency from the tautomer significantly less than from the reactant excited state, which leads to a transient decay, rather than a plateau or even a rising signal, and (2) is there any time-resolved evidence for the apparent mode-specific rate of tautomer formation reported by Fuke and Kaya?

In an attempt to answer these questions, Soep, Syage, and collaborators measured photoelectron spectra of 7-AI following subpicosecond excitation.⁸⁷ With regard to the first issue, it was observed that the tautomer excited state has poor Franck–Condon overlap with the corresponding dimer ion, consistent with the time-resolved data. The reason for this behavior is not yet known. The second question requires a sufficiently narrowband short pulse to resolve the bands

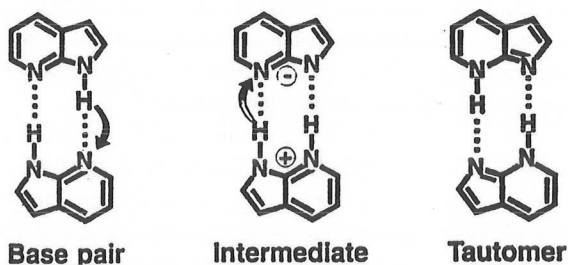


Figure 27. Molecular structures showing two-step, or one-step, cooperative double proton transfer of the base-pair 7-azaindole dimer (ref. 86).

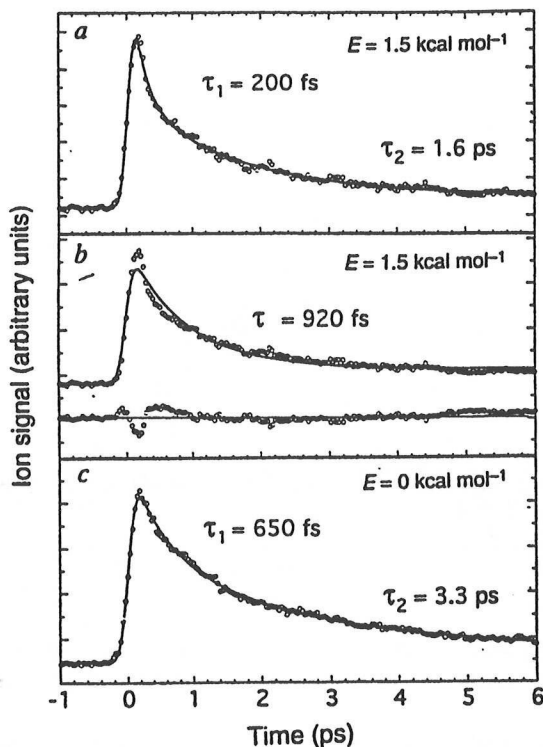


Figure 28. Femtosecond transients of 7-AI dimer: (a) excess energy of 1.5 kcal/mol, fitted to a double-exponential decay, (b) same data fitted to a single-exponential decay, (c) excess energy of 0 kcal/mol, fitted to a double-exponential decay (ref. 86).

that have components of the N...N mode. This requires using pulse durations that are similar to the time constant of the event being measured. Consequently instead of scanning the delay between ultrashort pump and probe pulses, an alternative method was invoked. By varying pulse duration, the competition between reaction and ionization of reactant excited state can be varied, resulting in different ionization yields. In the photoelectron spectrum of 7-AI dimer, a 10–20 fold decrease in intensity was observed for 5 ps vs. 800 fs excitation/ionization pulses of the same pulse energy when exciting the origin band as shown in Figure 29. A model for deriving time constants from the intensity changes has been developed. These methods should enable a determination whether the reaction rates exhibit mode-specificity.⁸⁷ The results in Figure 29 are consistent with the femtosecond rates measured⁸⁶ (see Note Added in Proof, page 56).

Experimental evidence for mode-specific ESPT may be found in the work by Fuke, Kaya and coworkers on the double proton transfer systems involving dimers

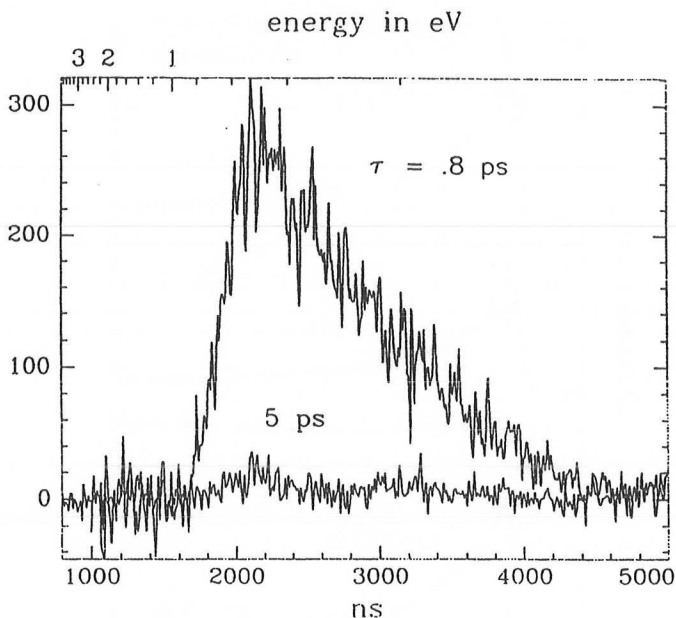


Figure 29. Photoelectron spectra of 7-AI dimer by pump-probe ionization at 310.1 nm for two different pulse durations, 0.8 ps and 5.0 ps (ref. 87).

of 7-azaindole (7AI) and 1-azacarbazole (1AC).⁸⁵ In these cases, the active mode Q_N is an N...N symmetric stretch. These frequencies are 120 and 114 cm^{-1} , respectively, in the $(7\text{AI})_2$ and $(1\text{AC})_2$ dimer excited states. Reaction times for $(7\text{AI})_2$ are typically longer than 1 ps for all modes except the Q_N mode where lifetimes of 0.5 and 0.2 ps were determined for 1 and 2 quanta, respectively. The double-proton transfer rates are much slower in $(1\text{AC})_2$ dimers, but a strong mode-specificity is still observed. Reaction times of 330, 130, and 65 ps were measured for 0, 1, and 2 quanta, respectively. Other modes had lifetimes of about 300 ps. In both the 7AI and 1AC dimers, a strong deuterium effect was observed, which is further evidence of a tunneling mechanism.

The tunneling model outlined in Section 4.1 supports the apparent mode-specificity observed for 7-AI dimer. Excitation of a single quanta of the N...N stretch predicts a nearly order of magnitude increase in rate relative to the origin. Vibrational relaxation is not included in the calculation, which may diminish the calculated mode enhancement.

4.3. $(\text{NH}_3)_n$ and $\text{Na}(\text{NH}_3)_n$

As an example of the important progress being made in ultrafast measurements of cluster chemistry involving bimolecular processes, we mention the work from

the Castleman group on the protonation reaction in $(\text{NH}_3)_n$ clusters following electronic state excitation.⁸⁸ Since this work is presented elsewhere in this book, we describe it only briefly. A considerable amount of work has been reported on the mass spectra of $(\text{NH}_3)_n$ cluster from single-photon,⁸⁹ multiphoton,⁹⁰ and electron ionization.⁹¹ The formation of protonated clusters $(\text{NH}_3)_m\text{H}^+$ clusters is prevalent in each case. From the single-photon and the electron ionization work, it is clear that an ionic proton transfer reaction occurs, namely $(\text{NH}_3)_n^+ \rightarrow (\text{NH}_3)_{n-m-1}\text{H}^+ + \text{NH}_2 + m(\text{NH}_3)$, with some evaporation. However, resonance multiphoton ionization opens up a pathway for neutral hydrogen transfer followed by ionization. The former and latter processes are reminiscent of the studies of ladder climbing vs. ladder switching which dominated studies in the early days of multiphoton ionization of molecules. For the specific case of ammonia, Castleman refers to the two paths as absorption–ionization–dissociation (AID) and absorption–dissociation–ionization (ADI), respectively. For long-lived electronically excited intermediate states, one would expect the AID mechanism to dominate. However, for very short-lived states, such as the directly dissociative A state, the ADI mechanism may be operative.

By measuring various ionic products as a function of femtosecond pump-probe delay time, the Castleman group could deduce that indeed, for long-lived states, such as the C' Rydberg state, only the AID pathway occurred.⁸⁸ This is evident in

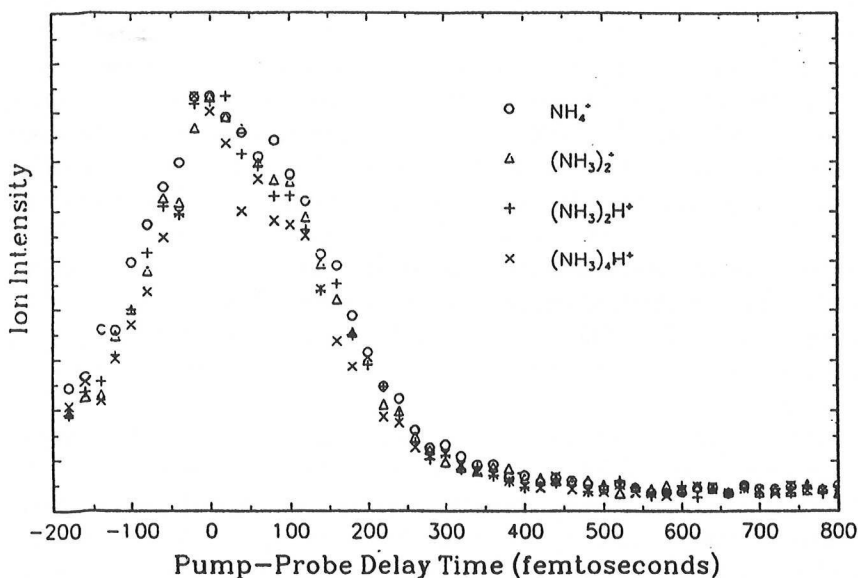


Figure 30. Pump-probe transient of ammonia clusters with both pump and probe pulses at 624 nm through the C' states of ammonia molecules (ref. 88).

the transients in Figure 30, which show the same time dependence for unprotonated and protonated ammonia clusters. Since the former must occur by direct ionization, the implication is that the latter are also formed by direct ionization, followed by dissociation. If ADI was occurring, then the latter group of signals would show a long time dependence resulting from the long predissociation lifetime of the C' state. The situation is much different when exciting through the short-lived A state. AID and ADI mechanisms occurred simultaneously. They measured these relative ratios as a function of vibrational excitation in the A state by varying the pump excitation wavelength. Further details can be found in their contribution in this book.

A different problem using NH_3 as a solvent involves the excitation of $\text{Na}(\text{NH}_3)_n$ through the NaNH_3 complex excited state absorption at 800 nm by the Hertel group.⁹² The excited-state lifetime for the 1:1 complex ($n = 1$) is at least a nanosecond. However, the lifetime for $n = 2$ decreases to about 30 ps. These investigators observe a similar time constant for the rise of Na^+ , indicating that the dynamics involve a dissociation. Interestingly, the lifetimes lengthen by a factor of 30 to 60 upon deuteration, suggesting that the dissociation occurs by an internal rearrangement involving the NH_3 tunneling motion.⁹²

5. ALIGNED BIMOLECULAR REACTIONS

Soep, Jouvet, and coworkers⁹³ and Wittig and coworkers^{94,95} have pioneered spectroscopic studies of reaction products from van der Waals molecules (we distinguish this chemistry from the more extensive studies of van der Waals dissociation). The former group studied a series of excited-state dimer reactions of the type $\text{HgX}_2^* \rightarrow \text{HgX}^* + \text{X}$ ($\text{X} = \text{Cl}, \text{H}$) and measured product rovibrational distributions from dispersed fluorescence spectra of electronically excited HgX^* . Wittig's group measured OH and CO product internal energy distributions for $\text{CO}_2\text{-HX}$ complexes ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) by laser induced fluorescence.^{94,95} These complexes assume specific equilibrium geometries, that vary with X , providing the means to explore chemical dynamics for prealigned collision parameters. The complex reaction $\text{H} + \text{CO}_2$ forms $\text{OH} + \text{CO}$ with a reaction efficiency and partitioning of energy into rotation and vibration that depends strongly on the bimolecular alignment.

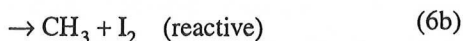
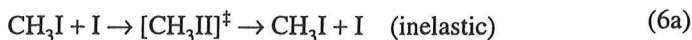
Scherer et al. used aligned complexes to study dynamics of bimolecular reactions in real time.⁹⁶ On ground-state surfaces, the group reported studies of the reaction $\text{H} + \text{CO}_2$ and $\text{Br} + \text{I}_2$. Wittig's group made studies of $\text{H} + \text{CO}_2$ system at different energies and reported rates that were explainable by statistical theories of unimolecular decay.⁹⁵ The Bz-I_2 system was discussed in Section 3.1. Other systems studied by this approach are $(\text{CH}_3\text{I})_2$ ⁹⁷ and $(\text{ICN})_n$, among others.⁹⁸ The theme of measuring reactive and unreactive (inelastic) scattering

in bimolecular collisions initiated in aligned vdW complexes is also being applied to the study of $\text{O}_3\text{--H}_2\text{O}$ complexes.⁹⁹

The Syage lab has been studying reaction dynamics in aligned complexes by monitoring product internal state, translational energy, and recoil angle. Whereas ultrafast techniques probe right in the transition state region of the potential energy surface, the product state-resolved probe looks at total energy partitioning resulting from the rapidly changing potential forces in transition state region. In the following, we review angle-velocity resolved measurements from aligned vdW complexes with time and state resolution on the popular system $(\text{CH}_3\text{I})_n$.

One of the more interesting problems regarding photodissociation of $(\text{CH}_3\text{I})_n$ is the bimolecular reaction $\text{I} + \text{CH}_3\text{I} \rightarrow \text{I}_2 + \text{CH}_3$. Vaida and coworkers first observed I_2^+ in a molecular beam mass spectrometer, but were not able to confirm whether the signal occurred by ionization of neutral product I_2 or by dissociation of cluster ions.¹⁰⁰ The Syage group performed mass-selected photodissociation experiments on $(\text{CH}_3\text{I})_n^+$ cluster ions and picosecond pump-probe experiments on the neutrals to show that the neutral I_2 channel occurred.¹⁰¹ The groups of Ziegler and of Donaldson subsequently directly measured the vibrational energy distribution in the neutral I_2 , further substantiating the neutral pathway.^{102,103} The early picosecond measurements indicated that I_2 was formed within the 10 ps time resolution of the experiment. However, it was not known whether the reaction approached that for CH_3I bond breaking in the repulsive A state, which was measured by the Caltech group to be about 150 fs.⁹⁷

A second interesting question is the partitioning between reactive and inelastic (unreactive) scattering. Recently, the Caltech group reported femtosecond measurements of the bimolecular reaction:



These experiments were conducted using KETOF probing which allowed them to monitor the time evolution of fast vs. slow I atoms.⁹⁷ The I_2 product is relatively cold by comparison (discussed below). Reaction 6 was initiated in an aligned vdW complex $(\text{CH}_3\text{I})_2$. The generally accepted geometry for the dimer involves an $\text{I}\cdots\text{I}$ bond, with evidence for a bent $\text{C}\cdots\text{I}\cdots\text{I}\cdots\text{C}$ structure. The photodissociation of CH_3I initiates the reaction whereby I is launched into the partner CH_3I with a limited impact parameter. The inelastic scattering is measured in time and velocity by probe ionization of I atom. The experiment essentially measures the direct outcome of the $\text{CH}_3\text{II}^\ddagger$ transition state prepared with the $\text{C}\cdots\text{I}$ and $\text{I}\cdots\text{I}$ coordinates of the vdW complex.

The transition state comes late in the potential energy surface as seen in Figure 31. The barrier to forming $\text{CH}_3 + \text{I}_2$ is about 19 kcal/mol. Figure 31 shows an inelastic trajectory whereby an I atom can become trapped in the vdW potential well near the transition state. Without sufficient energy to surmount the reaction barrier, the transition state complex decomposes to $\text{CH}_3\text{I} + \text{I}$. A series of femtosec-

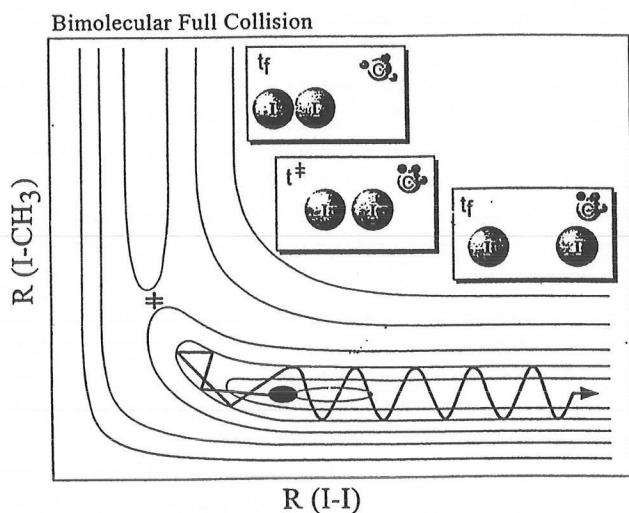


Figure 31. Potential energy map for the bimolecular reaction $CH_3I + I$ reaction showing an inelastic scattering trajectory from an initial wavepacket (black oval). The three panels show the complex in the transition state ($t^\ddagger$), as final products of the inelastic channel $CH_3I + I$ (t_f), or final products of the reactive channel $CH_3 + I_2$ (t_f) (ref. 97).

ond measurements of the appearance of low-velocity I atoms are presented in Figure 32. The traces under monomer and monomer + dimer conditions are given in Figures 32A and B. The difference gives the transient for inelastic I atom scattering for the $CH_3I_2^\ddagger$ complex. Two distinct collisional times were observed for a collision energy of 1.29 kcal/mol; a delay of about 1.4 ps and an exponential rise of about 1.7 ps. The first time scale represents a measure of the coherent process in the entrance channel toward the transition state and the second time scale is a measure of the lifetime of the complex.

Detailed chemical dynamics of the inelastic scattering of an I atom were also measured in the long time limit by state-specific angle-velocity resolved measurements in the Syage lab.¹⁰⁴ These measurements provide direct access to the bimolecular differential cross section for differential cross section to Reaction 6a. In these experiments, the $I(^2P_{3/2})$ was resonantly ionized and the translational energy as a function of angle measured for collision energies of 2.16 kcal/mol and 2.87 kcal/mol. In both cases, a bimodal distribution of velocities was observed as shown in Figure 33. The higher energy distribution was also more anisotropic (forward-backward) scattering. These results are consistent with inequivalent I atoms and may result from a presumed bent dimer geometry in which the impact parameter for each potential I atom projectile is different, one being head-on and the other being glancing.

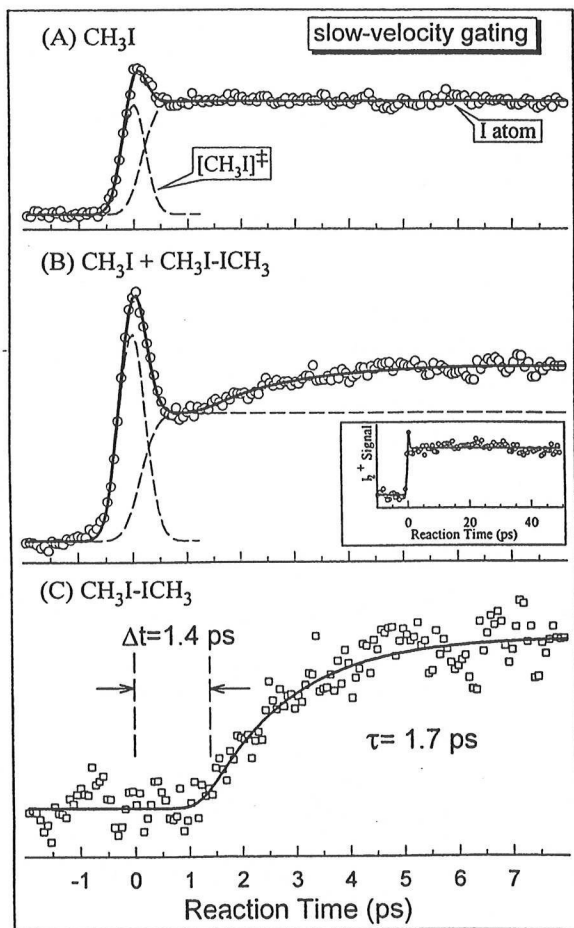


Figure 32. (A) Femtosecond I^+ transient recorded by gating for slow velocity z-component under monomer conditions. (B) Transient obtained under same conditions as (A) except for dimer conditions. (C) Transient response for dimer only obtained by subtracting the first two transients (ref. 97).

The reactive channel (Reaction 6b) leading to I_2 was evident in both the femtosecond KETOF experiments⁹⁷ and the state-resolved angle velocity experiments.¹⁰⁴ This former work (inset to Figure 32B) led to a measured time constant of formation of less than 500 fs, considerably faster than the inelastic dynamics. Interestingly, the reaction occurs even though the collision energy is significantly lower than the reaction barrier above. The reason for the very low collision energy is the kinematics of light-heavy dissociative systems; the methyl radical carries off nearly 90% of the kinetic energy of dissociation. To explain the formation of I_2 requires a

mechanism in which this energy is not lost. One explanation is a concerted mechanism based on a four-center process in which the C–I bonds are simultaneously breaking while the I–I is being formed.¹⁰⁴ Under this scenario, energy is not lost as kinetic energy in the departing CH_3 . It is also possible that the CH_3 groups can bind to form C_2H_6 as it does in larger clusters.^{101,105} The mass spectrum of $(\text{CH}_3\text{I})_n$ following A-state excitation and ionization using picosecond pulses shows an alternating pattern in Figure 34, suggesting loss of CH_3 in pairs. Whether or not C_2H_6 forms in dimers, the formation of I_2 seems to involve a four-center mechanism, analogous to what is observed for hydrogen halide dimers and clusters.^{106–108} Further discussion of the mechanism of I_2 formation from $(\text{CH}_3\text{I})_2$ excitation requires a more exacting determination of the dimer geometry than currently exists. Recent molecular dynamics studies by Shin et al. (private communication) have considered the reverse reaction of $\text{CH}_3 + \text{I}_2$ and the time scales are generally consistent with the observed dynamical picture.⁹⁷

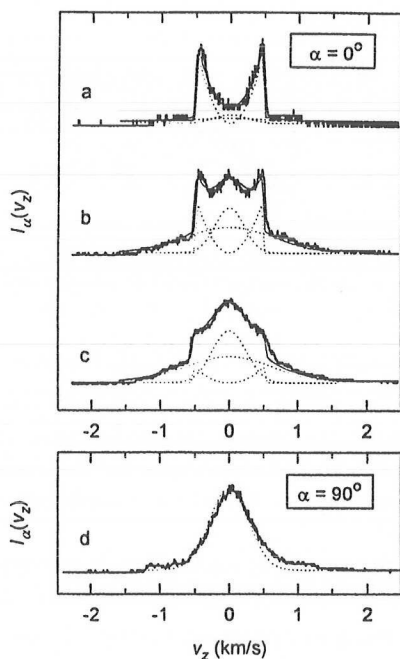


Figure 33. $I(^2\text{P}_{3/2})$ velocity spectrum for 0° scattering following 304 nm excitation of $(\text{CH}_3\text{I})_n$ as a function of increasing clustering conditions from (a) to (c). (d) Velocity spectrum for 90° scattering under clustering conditions (ref. 104).

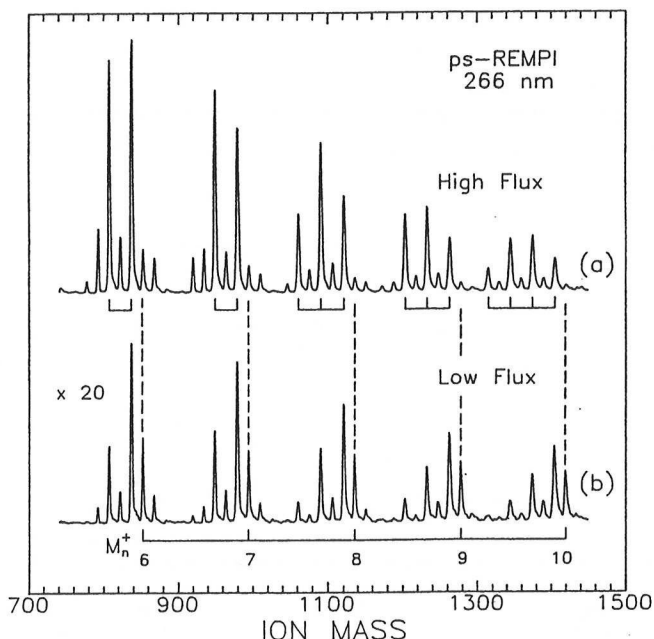


Figure 34. Picosecond REMPI mass spectra at 266 nm for larger $(\text{CH}_3\text{I})_n$ clusters. The alternation pattern represents loss of 2CH_3 , which is presumed to be due to C_2H_6 formation (ref. 101).

6. BARRIER CROSSING: *TRANS*-STILBENE PHOTOISOMERIZATION

The photoisomerization of *trans*-stilbene from its first excited state is a benchmark barrier crossing system that has been extensively studied in the condensed phase and gas phase. Some of the important issues regarding the role of solvation include the influence on the adiabaticity of the reaction and vibrational relaxation, especially, both intramolecular vibrational redistribution (IVR) and intermolecular redistribution through van der Waals interactions.

A particularly interesting problem is an apparent increase in the rate of isomerization in low-viscosity solvents relative to the rates measured at similar energies in molecular beam studies.¹⁰⁹ Two possible explanations have emerged to explain this behavior: a collision-induced reduction in the nonadiabaticity of the barrier, which is presumed to involve a surface crossing,¹⁰⁹ or the influence of solute-solvent cluster formation on the shape and barrier height of the reaction potential.¹¹⁰ A natural test of these premises is to measure isomerization rates as a function of microscopic solvation in clusters.

Heikel et al. at Caltech conducted studies of *trans*-stilbene in hexane clusters ranging from $n = 1$ to 5 solvent molecules.¹¹¹ Measured transients are presented in Figure 35. The general trends in the rate of isomerization as a function of solvent cluster size and how they compare to gas and liquid phase are summarized as follows: First, the barrier height decreases in the presence of solvent molecule.

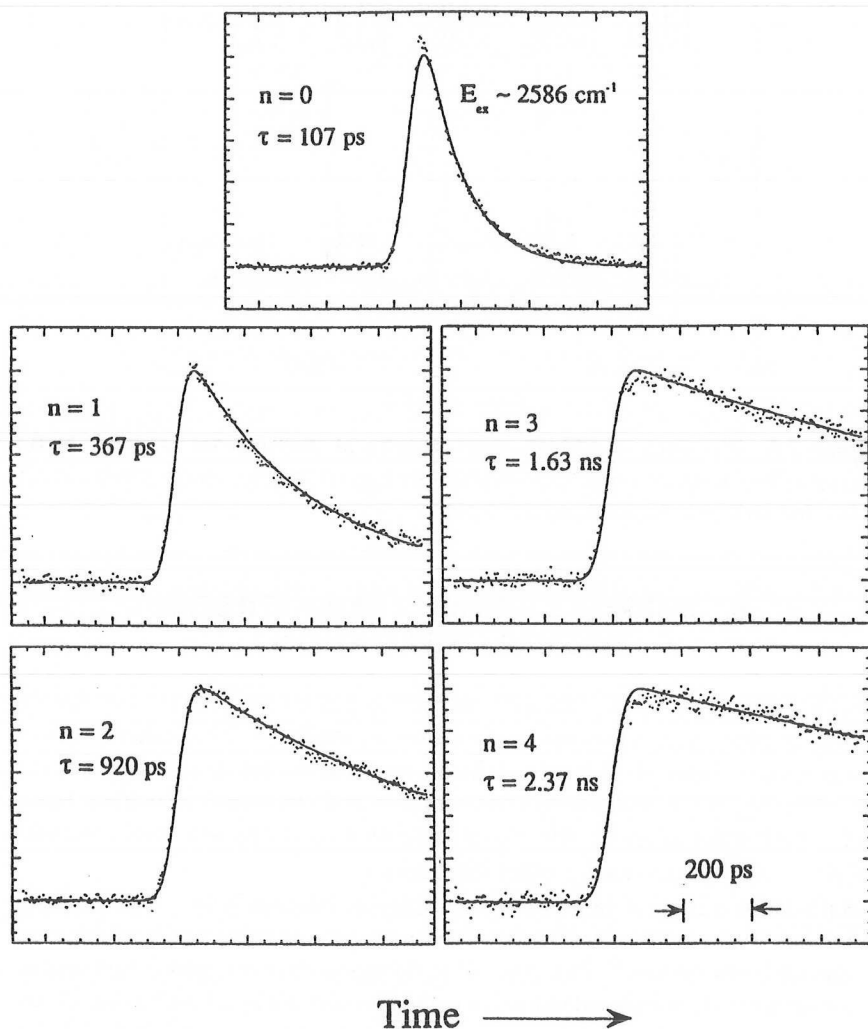


Figure 35. Measured transients of *trans*-stilbene-hexane_n, $n = 0-4$, for $\lambda_{\text{pump}} = 283$ nm, $\lambda_{\text{probe}} = 325$ nm. Fitted single-exponential decay times are shown (ref. 111).

Second, the overall rate and the relative increase with increasing internal energy is lower for the cluster systems than for the isolated *trans*-stilbene case. The results are counter intuitive given the observation that the isomerization rate is greater in the condensed phase than the gas phase at comparable energies. The cluster results are more representative of what is observed in high-density solvents. The decrease in rate with increasing n parallels the trend observed with viscosity. These striking results raised an interesting issue regarding the role of microscopic friction and IVR. Marcus has considered the former with a modified RRKM description¹¹² and further experiments are underway to separate their influences.

7. CONCLUDING REMARKS

This chapter was not designed to survey the field, but instead to illustrate the power of the approach of using clusters as a microscopic media to study bond dynamics and caging, electron and proton transfer reactions, aligned bimolecular reactions, and barrier crossing. Advances in time-, velocity-, state-, and angular-resolution made it possible to examine the elementary steps with unprecedented details of dynamics and mechanisms. Future studies will undoubtedly continue to explore new systems and elucidate new physical and chemical phenomena. Two areas of future research are worth mentioning. On the experimental side, better characterization of cluster structure is needed in order to relate structures to dynamics. The techniques of rotational coherence spectroscopy¹¹³ and ultrafast electron diffraction¹¹⁴ will be of great help; already the former has been successfully used by many groups.¹¹⁵ On the theoretical side, more practical approaches are needed to ascertain structures and dynamics as the system increases in size, reaching the condensed-phase limit. For example, for the Bz_nI_2 system described in the text, we have recently¹¹⁶ obtained an ab initio structure for the 1:1 species, but then used empirical potentials to construct the solvation shell, and subsequently the molecular dynamics to compare with experiments. Can the approach be generalized to test different systems, perhaps based on simple bonding ideas? Much research will continue in this novel area of studying reactions in clusters. In their own right, clusters represent an interesting phase of matter to study and they could become the gateway to condensed-phase chemical dynamics. Besides, they exhibit the influence of weak interactions in a very direct way relevant to all noncovalent chemical structures and syntheses.

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APPENDIX: TUNNELING MODEL FOR PROTON TRANSFER IN CLUSTERS

The details of a proton tunneling model for clusters are given in Refs. 7, 59, and 77. Here we present an overview. A starting point for a tunneling model incorporating the nuclear coordinates outlined in Section 4.1 (and Figure 25) is a Golden Rule-type equation of the form:

$$W = (4\pi^2/h)C^2\rho \quad (7)$$

The coupling term C is obtained from Bell theory for an O–H symmetric double-well potential with an inverted parabolic barrier,¹¹⁷

$$C = \frac{h\nu_H}{2\pi} \exp\left[-\frac{\pi^2 a}{h} (2mU)^{1/2}\right] \quad (8)$$

where C is the tunneling splitting and $2a$ and U are the barrier width and height as depicted in Figure 25. The density of states function ρ represents the set of modes that give rise to a tunneling resonance between reactant and product. We consider two contributions as shown in Figure 25: a Boltzmann term for solvent fluctuations giving the solvent configuration $S^\#$ and a manifold of product vibrational states that are Franck–Condon coupled to the reactant state. The former term follows directly from classical Marcus theory of solvent modes,⁷⁹ usually associated with electron transfer, but applicable to proton transfer. The latter contribution has the embodiment of Jortner–Bixon radiationless transition theory.⁸⁰ The coupling of individual reactant and product states that combines the classical low-frequency Marcus solvent mode expression with the higher frequency Franck–Condon coupled quantum state treatment is given as follows,

$$\rho_{m,n} = \frac{1}{2} \left(\frac{\beta}{\pi\lambda_s} \right)^{1/2} \prod_{i=1}^M \langle m_i | n_i \rangle \exp\{-\beta\Delta G_{m_i, n_i}^\#\} \quad (9)$$

where M is the number of coupled modes, m_i and n_i are the number of quanta of mode i for reactant and product, respectively, β^{-1} is the energy per mode, and:

$$\Delta G_{m_i, n_i}^\# = \frac{1}{4\lambda_s} \left[\Delta G_0 + \lambda_s + \sum_i (n_i - m_i) h\nu_i \right]^2 \quad (10)$$

The reactant and product state m and n are denoted by $|m\rangle = |m_1, \dots, m_M\rangle$ and $|n\rangle = |n_1, \dots, n_M\rangle$, respectively. We note that only two modes are considered important in this analysis, the H oscillator (e.g. O–H and H–N for reactant and product for PhOH–NH₃), and the O···N symmetric stretch mode. The sum over all product states gives an effective density of states:

$$\rho_m = \frac{1}{2} \left(\frac{\beta}{\pi \lambda_s} \right)^{1/2} \sum_{n_1=0}^{\infty} \cdots \sum_{n_{i=M}}^{\infty} \prod_{i=1}^M \langle m_i | n_i \rangle \exp \{ -\beta \Delta G_{m_i n_i}^{\#} \} \quad (11)$$

The term ρ_m effective means a weighted sum of the coupling strengths of all relevant product states.

Proton tunneling rate constants from reactant state m are calculated by averaging the barrier properties over the O...N symmetric stretch vibrational wave function to account for the modulation of barrier height and width as illustrated in Figure 25. This leads to the expression:

$$\begin{aligned} k_m &= \langle \psi_m | W(x) | \psi_m \rangle \\ &= \frac{4\pi^2}{h} \langle \psi_m | C(x)^2 | \psi_m \rangle \rho_m \\ &= \frac{4\pi^2}{h} \rho_m \int_{-\infty}^{\infty} C(x)^2 f_m(x) dx \end{aligned} \quad (12)$$

For low to moderate levels of reactant excitation (less than the O-H vibrational frequency), only the O...N symmetric stretch mode needs to be considered for reactant states, hence, m refers to number of quanta of the O...N stretch. The rate constant as a function of internal energy is then given by some statistical function, $k(E) = \sum_m P_m(E) k_m$, where $P_m(E)$ is the population probability of m quanta of the O...N stretch at energy E . $P_m(E)$ can be a classical expression such as the Marcus-Rice approximation.

Figure 36 presents calculated tunneling rates as a function of ΔG_0 from specific reactant states m . The stick figures show the Franck-Condon term. The envelopes represent the rate constant k_m for 0 K (i.e. $\beta^{-1} = 0$) and 300 K. An interesting outcome of the state-to-state treatment of tunneling is the prediction of a structured dependence of k with ΔG_0 for clusters in the inverted region. The effect is strongest for single-vibronic level excitation, particularly for the vibrationless level. For vibrationless excitation of the reactant $\langle m_N, m_H | = \langle 0, 0 |$, the FC distribution in the product is very structured. Convolution over the Marcus classical solvent mode distribution for 300 K smooths out much of the structure, but it still persists in Figure 36c,c'. For a true thermal sample, a distribution of reactant vibrations would be populated and the oscillations in the density of states would average out. In clusters, however, the oscillatory nature of k vs. ΔG_0 should persist. Now there is no convenient way to vary the ΔG_0 without affecting other properties of the clusters; however, a series of well controlled experiments might reveal the effect predicted here.

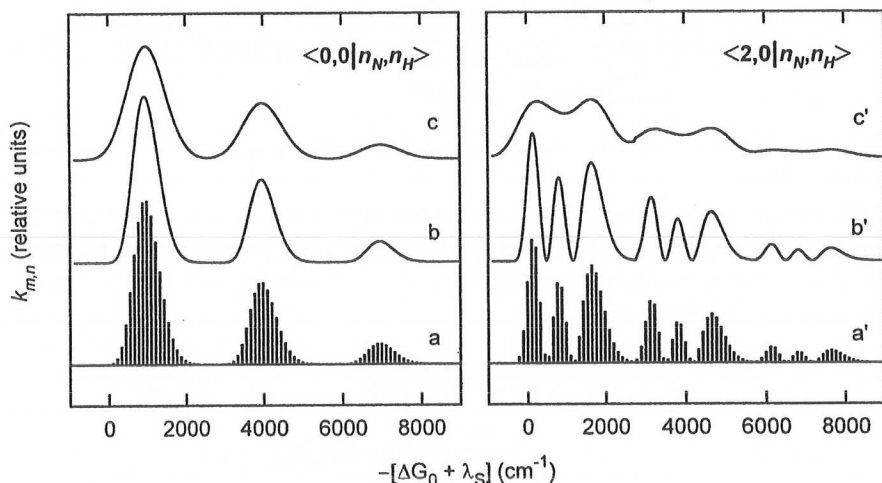


Figure 36. (a,a') Calculated tunneling rates based on Franck-Condon factors for an arbitrary proton transfer system consistent with previous clusters experiments; (b,b') envelope of the stick figure; (c,c') envelope after convolving a classical Marcus-Boltzmann distribution for solvent mode excitation at 300 K. The left and right hand plots correspond to vibrationless and 2 quanta of O---N symmetric stretch excitation. The rate scale on the right hand plot is about a factor of 30 greater than on the left hand plot. (Input details are given ref. 77).

NOTE ADDED IN PROOF

More recently, the Castleman group has trapped the intermediate, using Coulomb explosion, and these elegant experiments¹¹⁸ give time constants similar to those measured by the Caltech group.⁸⁶ Finally, the nonconcerted pathway was also found in our studies of the same system in liquid solutions.¹¹⁹

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