A/A' and X state recombination is not accurately known.

Given what is expected for the energy relaxation rate in the bulk solvent, it is remarkable that it is even possible to observe a hot solvent cage with a 15 ps pulse. If it is assumed that the energy in the solvent is dissipated at a rate equal to the speed of sound[11] in CCl_4, then a rate of $(0.5\ \text{ps})^{-1}$ would be expected. The fact that the solvent cage is observed to contain a significant fraction of this energy on a picosecond time scale is an important consideration for condensed phase reaction dynamics. This result may also be a relevant consideration for time-dependent fluorescence measurements of solvent relaxation dynamics.

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Picosecond mass-selective measurements of phenol-$(NH_3)_n$ acid–base chemistry in clusters

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Acid–base reactions are among the most fundamental in chemistry. A comparison of gas-phase[1,2] and solution-phase[2,3] studies have revealed extraordinary differences in acid–base properties attesting to the profound influence of the solvent. Recently, investigators have turned to the use of molecular clusters to study chemical reactions as a function of specific solvent cluster size.[4–8] For example, very distinct solvent-size threshold effects were observed for acid–base type reactions for excited states of 1-naphthol[4] and phenol,[5] and for the ground electronic state of aniline cation.[6] These cluster experiments, however, were sensitive only to the equilibria of reactant and product. Time-resolved measurements have been performed only for bulk-phase systems.[3,9–13] In this letter, we report direct picosecond measurements of the rate constants for acid dissociation k_a and geminate recombination k_{-a} as a function of solvent cluster size for the seeded cluster system phenol-$(NH_3)_n$ (henceforth $ROH\cdot M_n$).

The method of picosecond mass-selective measurement of cluster reactions has been described in previous work.[7,8] Briefly, a pulsed molecular beam time-of-flight (TOF) mass spectrometer apparatus was used to prepare the cluster species and to detect photoionized reactants and products.[6–8] A pulsed (10 Hz) active/passive mode-locked and amplified Nd:YAG laser was used to produce frequency doubled (532 nm, 25 ps), tripled (355 nm, 25 ps), and quadrupled (266 nm, 18 ps) output, and to pump a short-cavity tunable dye laser (10 ps). Time-resolved spectra were recorded by delaying a probe pulse λ_2 relative to a pump pulse λ_1 using a scanning optical delay line. The nominal time resolution before deconvolution was about 20 ps. The pulse energy densities (see figure caption) were reduced so that no ion signal was observed with either pulse alone or at negative delays.

Aromatic alcohols in solution are known to be more acidic in their S_1 state than in S_0 (i.e., the so-called pH jump).[3] In the present picosecond cluster experiment, the $\lambda_1 = 266$ nm pump pulse excites the $ROH\cdot M_n$ clusters to S_1 with excess energy ranging from about 1900 cm^{-1} ($n = 1$) to about 2250–2800 cm^{-1} (estimated for $n = 3$–7).[5,14] The S_1 origin of uncomplexed phenol is at 274.7 nm.[14] Figure 1 consists of time-resolved traces for the decay of undissociated acid and the formation of protonated solvent as a function of solvent cluster size $(NH_3)_n$. A reaction mechanism modeled after solution phase behavior (described shortly) is given in Fig. 1, along with the λ_2 detection method. The excited state clusters absorb strongly at $\lambda_2 = 532$ nm (probably by two-photon ionization) to give either parent ion $ROH\cdot M_n^+$ or protonated solvent M_nH^+ (see below), depending on whether a proton transfer has occurred in the excited state acid $ROH^*\cdot M_n$ to form $RO^{*-}\cdot H^+M_n$. The most prominent observation in Fig. 1 is the onset of $ROH^*\cdot M_n$ reactive decay for solvent cluster size $n = 5$ with a decay time of 60 ± 10 ps. Interestingly, in a steady-state dispersed fluorescence experiment on the more acidic (0.3–0.5 eV) reaction

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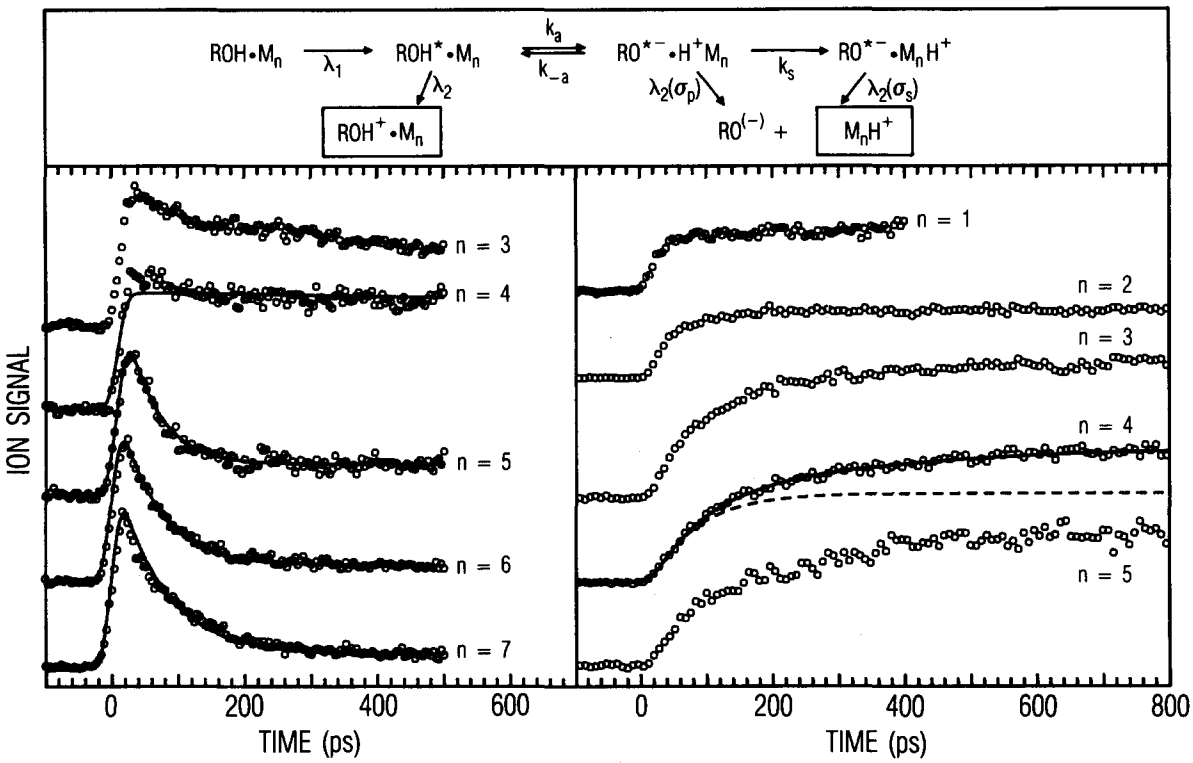

FIG. 1. Picosecond measurements for decay of reactant cluster $ROH^*\cdot M_n$ (as detected by $ROH\cdot M_n^+$) and formation of product $RO^{*-}\cdot H^+M_n$ (as detected by M_nH^+). The reaction mechanism and detection method are described in the text. Pulse characteristics were λ_1 (266 nm, ~20 μJ, 2 mm diam) and λ_2 (532 nm, ~1 mJ, 3 mm diam). The calculated traces for $ROH\cdot M_n^+$ are based on the equilibrium model ($n = 4$ assumes $k_a = 0$). The calculated curve for M_nH^+ $n = 4$ (—) assumes $k_a = (70\ \text{ps})^{-1}$, $k_s = (0.5\ \text{ns})^{-1}$, and $\sigma_s/\sigma_p = 1.6$. A calculation for $k_s = 0$ is also shown (- - -). All traces have been normalized approximately to the same intensity.

in 1-napththol* $(NH_3)_n$, a solvent threshold for proton transfer was observed at $n = 4$.[4] Two other observations support the proton transfer mechanism, for $ROH\cdot M_n$: (1) the formation rate of M_nH^+ matches the decay rate of reactant $ROH^*\cdot M_n$, and (2) no evidence of reaction was observed when phenol was seeded in the less basic solvent clusters $(H_2O)_n$ ($n \leqslant 5$) or $(CH_3OH)_n$ ($n \leqslant 11$).

The detected M_nH^+ signals in Fig. 1 are produced by dissociative ionization of reactant $ROH^*\cdot M_n$ and product $RO^{*-}\cdot H^+M_n$ clusters by the probe pulse λ_2. The former process gave a low yield of M_nH^+ that was recognizable by a step-function response. For larger values of n, the M_nH^+ signal is dominated by a component that grows in at a rate that matches the 60 ± 10 ps decay of the reactant. Apparently M_nH^+ is produced more efficiently by ionization from the ion pair form $RO^{*-}\cdot H^+M_n$ than from the reactant form $ROH^*\cdot M_n$. This is consistent with the much greater energy available for dissociation in the ionized product due to the ~1 eV lower ionization potential for $RO^{*-}\cdot H^+M_n$ relative to $ROH^*\cdot M_n$.[5] An alternative explanation that M_nH^+ is produced by ion pair dissociation is not consistent with the negligible yield of RO^- that we measured by negative ion detection. The excess energy in the product ion also induces NH_3 evaporation. For two-photon ionization at $\lambda_2 = 532$ nm, two NH_3 molecules can dissociate as noted by the M_nH^+ formation threshold at $n = 3$ versus the reactant decay threshold at $n = 5$. For less energetic one-photon ionization at $\lambda_2 = 355$, the formation threshold is at $n = 4$ indicating a loss of only one NH_3.

In addition to the pronounced solvent threshold effect for acid dissociation, a number of other observations in Fig. 1 can be made: (1) the trace for $n = 5$ decays to a distinct plateau; (2) the decay time for $ROH^*\cdot M_n$ does not vary greatly for $n \geqslant 5$; (3) the production of M_nH^+ is not described by a single exponential time constant. These results conform remarkably well to the mechanism for intermolecular proton transfer in solution.[3,10–13] We therefore use his description as a consistent (but not necessarily unique) model for the microsolvation cluster results. The reaction mechanism portrayed in Fig. 1 considers a fast acid-base equilibrium defined by the acid dissociation and geminate recombination rate constants (i.e., equilibrium constant $K = k_a/k_{-a}$) and a slower diffusion-controlled rate constant k_s for solvent reorganization about the proton, which we denote by $RO^{*-}\cdot M_nH^+$.

The picosecond trace for reactant $ROH^*\cdot M_n$ $n = 5$ is suggestive of an acid–base equilibrium. This assumption leads to calculated best fit rate constants of $k_a = (60 \pm 10\ \text{ps})^{-1}$ and $k_{-a} = (350 \pm 100\ \text{ps})^{-1}$. The rate constant for dissociation k_a does not vary much for values of n larger than the critical solvent size [$k_a \sim (65\ \text{ps})^{-1}$ for $n = 6, 7$]. On the other hand, K changes dramatically in the solvent threshold region $n = 4$–6. A strong dependence of K with n was also reported for 1-naphthol*-$(NH_3)_n$ on the basis of steady-state dispersed fluorescence spectra.[4] Finally,we speculate that the slow rise component (2 ns timescale) in the M_nH^+ traces that follows the kinetics of proton transfer

may be due to a solvent reorganization about the newly formed proton causing some amount of charge separation in the ion pair. Similar processes occur in solution on the nanosecond timescale.[3,10] The geometry of the reorganized solvated proton should have a better Franck–Condon overlap with the cluster ion potential and therefore an increased cross-section (σ_s) for detection of M_nH^+ relative to the initially formed bound ion pair (σ_p). Calculated traces indeed show that the formation curves for M_nH^+ fit well to a biexponential function with the aforementioned long-time component of 0.5 ns and a ratio of cross sections of $\sigma_s/\sigma_p = 1.6$ (cf. Fig. 1, $n = 4$, solid line).

In conclusion, a well-defined acid–base reaction was studied as a function of incremental solvation in molecular clusters and has provided new detail regarding the role of solvation on a single-molecule basis.

Note added in proof: Since this paper went to proof, a very relevant picosecond mass-selective study was published by Breen, *et al.*[15] for the system 1-naphthol*-$(NH_3)_n$. Thier results also show a distinct solvent size threshold effect for proton transfer.

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NOTES

The origin of small and large molecule behavior in the vibrational relaxation of highly excited molecules

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The internal energy dependence of the vibrational relaxation of highly excited molecules has been a subject of continuing interest for the last decade. A recent review[1] highlighted the qualitatively different behavior of diatomic and polyatomic molecules. In the former case the average amount of energy transferred per collision, $\ll\Delta E\gg$, has been observed to vary as a power of the average vibrational energy of the excited molecule $\ll E_v\gg$,

$$\ll\Delta E\gg = -C\ll E_v\gg^n, \tag{1}$$

where n is a constant greater than one. In contrast, polyatomic molecules tend to follow an exponential (or possibly slower than exponential) decay law with $n\approx 1$.

The purpose of this note is to inquire into the underlying physical difference between diatomic and polyatomic molecules producing these two types of behavior. An insightful paper published by Nesbitt and Hynes[2] points to a possible answer. Nesbitt and Hynes used classical trajectories to calculate the relaxation rate for collinear collisions between an atom and a Morse oscillator with a repulsive exponential potential. They demonstrated that for adiabatic collisions a modified power law is obeyed, whereas exponential decay ($n\lesssim 1$) results in the impulsive limit. The modification to Eq. (1) is that $\ll\Delta E\gg$ scaled by the local oscillator frequency, $\omega(E_v)$, varies as a power of the vibrational quantum number v. Their findings have been confirmed in a number of theoretical studies with varying degrees of approximation.[3–5] The outcome of these studies is that a linear dependence of $\ll\Delta E\gg$ on $\ll E_v\gg$ is characteristic of hard sphere scattering,[2,3] whereas the adiabatic power law can be derived

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