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Structure-reactivity effects in the picosecond dynamics of isolated clusters

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ABSTRACT

The link between gas-phase and condensed-phase chemical dynamics is being sought by the study of reactivity in small molecular clusters. We present measurements of reaction rates as a function of cluster size and composition to elucidate the role of solvent on a single-molecule basis. In previous work we showed that reactivity in clusters is strongly correlated to the stepwise binding energies of individual solvent molecules. Here, we show that solvent structure also plays a large role in determining chemical reactivity. This paper focuses on the excited state proton transfer reaction of phenol (PhOH) in a cluster of solvent-like molecules (i.e., NH_3 and CH_3OH). Three cases of structure-reactivity effects are reported: (1) rate inhibition by the addition of a CH_3OH molecule to an $(NH_3)_n$ solvent cluster (60 ps vs 500 ps), (2) very different reaction rates for the inequivalent phenol molecules in phenol dimer solvated by $(NH_3)_n$ (50 ps vs 500 ps), and (3) solvent reorganization following proton transfer that occurs on the time scale of 0.3 ns.

1. INTRODUCTION

Molecular clusters are proving to be an important medium for probing the correspondence between gas-phase and condensed-phase properties.[1-3] In recent work we have exploited the cluster environment using picosecond molecular beam spectroscopy to study chemistry under single-molecule solvent interactions.[4-9] The most common method of producing clusters is by supersonic expansion in that it provides molecular cooling and low energy collisions that favor cluster growth.[10] If the internal energy of the clusters is low relative to the photoexcitation energy then the excited-state clusters are nearly isoenergetic and constitute a microcanonical ensemble (i.e., an ensemble of noninteraction subsystems at constant energy). Thermal averaging effects are minimized in photochemical cluster studies.

The focus of this paper is on the correlation of solvent structure and reactivity. In previous work we showed that reactivity is strongly correlated with the stepwise binding energies of individual solvent molecules, but also showed instances where solvent structure played a major role. The results presented here are for the excited state proton transfer (ESPT) reaction of phenol in a cluster of solvent-like molecules (i.e., NH_3 and CH_3OH). We have published a series of papers on phenol/cluster proton transfer covering the subjects of solvent basicity and cluster size effects for excited state proton transfer (paper I),[6] dynamics and energetics of phenol cation (paper II),[7] and solvent structure and ground state ion-pair formation (paper III).[8] In this paper we discuss three examples of structure-reactivity effects. First we show that the addition of a single CH_3OH to an otherwise pure $(NH_3)_n$ solvent core causes a disruption of the hydrogen bonding network resulting in a reduction of reaction rate from $(\sim 60\ \text{ps})^{-1}$ to $(>750\ \text{ps})^{-1}$. Next, we discuss phenol dimer solvated by $(NH_3)_n$ where the inequivalent hydroxy binding sites account for a large difference in reactivity (50 ps vs 500 ps). Finally, we present measurements of solvent reorganization following proton transfer. These geometry changes are measurable because they give rise to time-dependent Franck-Condon factors for ionization.

2. EXPERIMENTAL METHOD AND BACKGROUND

The picosecond molecular beam apparatus has been described before,[4-6,11] hence, we give only the briefest details. The molecular beam employs a temperature-controlled pulsed supersonic nozzle which serves as the cluster source. The free-jet expansion passes through a skimmer to form a 5-mm-diam beam at the ionization region of a time-of-flight mass spectrometer. Phenol (Aldrich, 99+%, used as is) is contained in a sample holder in the pulsed nozzle, which is heated to about 50°C. For ammonia solvation, a 2-liter high-pressure cylinder was filled with a sample contain-

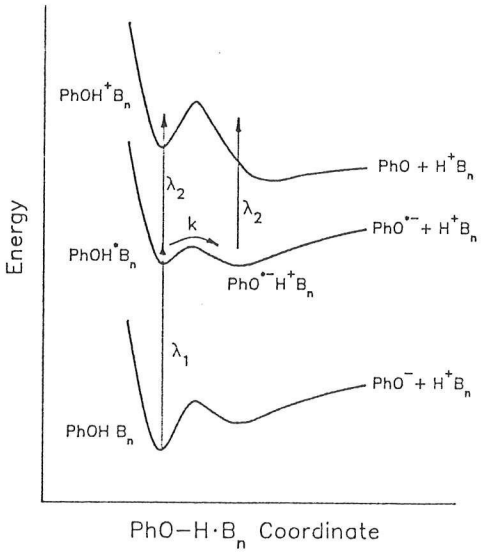

Figure 1. Energy diagram for PhOH·$(NH_3)_n$ consistent with a cluster size of $n \sim 5$. ESPT produces an excited state ion-pair product that is ionized to the weakly-bound outer potential well of the cluster ion.

ing 10% NH_3 in helium. For the NH_3/CH_3OH experiments, the NH_3/He sample was passed through a bubbler containing CH_3OH. Each of these solvent/He samples was flowed over the phenol contained in the pulsed valve. The flow mixture, typically at 35 psi, was expanded through a nozzle with a 750-μm diam aperture and 60° conical throat.

The picosecond laser is based on a pulsed active/passive mode-locked Nd:YAG laser, which produces output at 532 nm, 355 nm, and 266 nm. Time-resolved spectra were recorded by delaying a probe pulse λ_2 relative to a pump pulse λ_1 (266 nm) using a scanning optical delay line.[4–8] Calculated curves were fitted to the data using a convolution that assumed a Gaussian-shaped instrument function (typically 25–30 ps, FWHM).

The picosecond pump-probe excitation/detection scheme is given in Fig. 1 and shows approximate potential curves for the relevant ground, excited, and ionic states of the cluster. The potential curves are strongly dependent on solvent cluster size and basicity and are discussed in detail in paper I.[6] The illustration given in Fig. 1 approximates the case for phenol-$(NH_3)_5$. The phenol (PhOH) excited-state proton transfer (ESPT) reaction

$$PhOH^*{\cdot}B_n \underset{k}{\longrightarrow} PhO^{*-}H^+B_n$$

corresponds to a conversion from the locally excited S_1 state of the acid phenol to an excited ion-pair state (B_n refers to the solvent cluster consisting of n molecules of base B). Reactant and product are distinguishable by mass spectrometry because each species fragments differently upon ionization. The energetics and dynamics of the solvent-clustered phenol cation are reported in paper II.[7] Briefly, a double-well minima with a large barrier exists for the cluster ions. As illustrated in Fig. 1, ionization of the reactant cluster $PhOH^*{\cdot}B_n$ to the inner ion potential well produces strongly bound $PhOH^+{\cdot}B_n$ ions. The product ion-pair $PhO^{*-}H^+B_n$ is ionized to the outer ion well, which is weakly bound and therefore readily dissociates to form H^+B_n ions. It is important to remember that the detected ion signals are probes of the dynamics along the neutral excited S_1/ion-pair reactive surface.

3. STRUCTURE-REACTIVITY EFFECTS OF THE SOLVENT CLUSTER

The sensitivity of chemical reactivity to solvent structure is very pronounced in small clusters. We discuss a few studies illustrating significant structural sensitivity. To begin, we present measurements of ESPT rates in pure solvent clusters representing idealized structures, thus serving as the control case for the structure-reactivity results that follow.

3.1. Reaction dynamics - pure solvent

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).[12] In the present picosecond cluster experiment, the $\lambda_1 = 266$ nm pump pulse excites the $PhOH^+{\cdot}B_n$ clusters to S_1 with excess energy ranging from about 1900 cm^{-1} ($n = 1$) to about 2250–2800 cm^{-1} (estimated for $n = 3 - 7$).[13,14] The S_1 origin of uncomplexed phenol is at 274.7 nm.[14] A set of reactant decay measurements are presented in Fig. 2 ($\lambda_2 = 532$ nm) as a function of solvent cluster size n for the solvents NH_3 and CH_3OH. The NH_3 solvent clusters induce ESPT for solvent sizes $n > 4$. No evidence of reaction was observed for CH_3OH (up to $n = 11$, Fig. 2). Results for other solvents are given in paper I.[6]

The sharp reaction threshold at $n = 4$ for the $(NH_3)_n$ solvent can be explained almost entirely by energetic arguments involving the ion-pair Coulombic potential and stepwise proton affinities for successive NH_3 molecules. This analysis was presented in paper I and assumes a solvent structure based on the well established geometry of ammoniated ammonium ion.[15] The assumed geometry for PhOH·$(NH_3)_4$, representing filling of the first solvation shell, is drawn in Fig. 3.

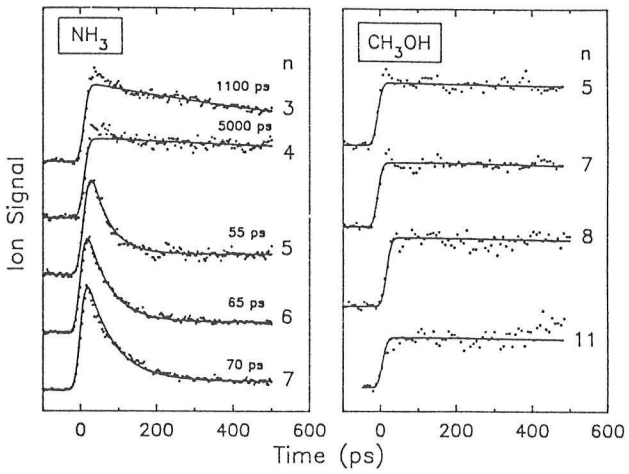

Figure 2. Observed lifetime of the reactant $PhOH^*{\cdot}B_n$ (as measured by $PhOH^+{\cdot}B_n$ detection) in solvent clusters $(NH_3)_n$ and $(CH_3OH)_n$. The calculated curves are described in paper I. Calculated curves for the $(CH_3OH)_n$ data assume a 10 ns lifetime.

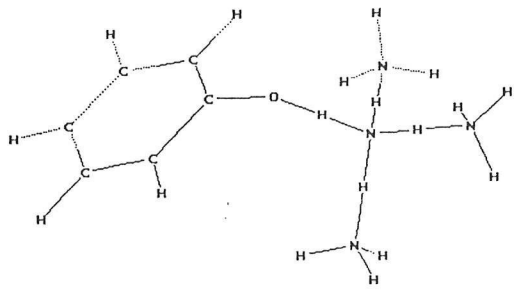

Figure 3. Assumed structure for $PhOH{\cdot}(NH_3)_4$.

3.2. Disruption of the solvent shell - mixed solvents

Reaction rates for mixed solvent distributions $PhOH{\cdot}(NH_3)_n(CH_3OH)_m$ of similar cluster size $(n+m = 6$ or $7)$ were measured and are presented in Fig. 4. The substitution of a single CH_3OH molecule for an NH_3 molecule causes a substantial deceleration 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. Because the (5,0) cluster reacts in 60 ps (Fig. 2), the (5,1) result indicates that the mere *addition* of a CH_3OH molecule effectively "poisons" the reactivity of the (5,0) cluster. This is quite surprising because one would not expect the proton affinity of the solvent to decrease by the adding CH_3OH. One explanation for the slowed reaction is that CH_3OH acts as an intruder that disrupts the hydrogen bonding network of the neat $(NH_3)_n$ solvent structure that is crucial to solvating and stabilizing the dissociated proton.[16,17] Although NH_3 forms the stronger bond to PhOH, CH_3OH forms the stronger bond to $PhOH{\cdot}NH_3$ and may, therefore, displace an NH_3 from the first solvation shell.[8] Also CH_3OH can form a stable hydrogen bond to the phenol oxygen which diminishes excited state acidity, whereas NH_3 avoids that site.[19,20]

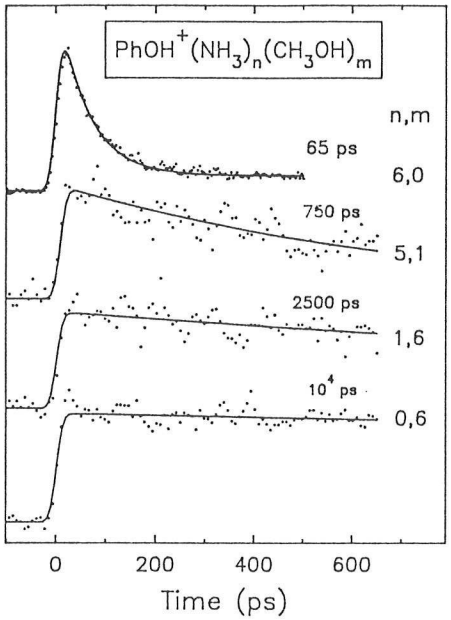

Figure 4. Measured rates of ESPT for the mixed solvent clusters $PhOH^*(NH_3)_n(CH_3OH)_m$ using 266-nm pump and 532-nm probe excitation.

The concept of critical solvent structures in ESPT reactions has been investigated in the solution phase by Robinson and coworkers.[16] Their picosecond measurements and theoretical analyses on aromatic acids (e.g., 1- and 2-naphthol) in H_2O and alcohol (CH_3OH and C_2H_5OH) support the notion that a critical solvent cluster core is necessary to act as an efficient proton acceptor. For naphthol in H_2O, the critical solvent-core size is about four.[16] Regarding the present results, it is known from gas-phase cluster studies that the closed-shell structure $NH_4^+(NH_3)_4$ is very favorable for stabilizing a proton.[15,21] The presence of CH_3OH can disrupt this structure because the NH_3–CH_3OH bond is stronger than the NH_3–NH_3 bond.[22,23] Hence, CH_3OH can displace NH_3 from the first solvation shell and prevent a pure NH_3 closed-shell structure from forming. The structure of the solvent about a reactive solute molecule has never been directly measured. Studies of cluster distributions for mixed solvent systems are beginning to yield information on the bonding structure

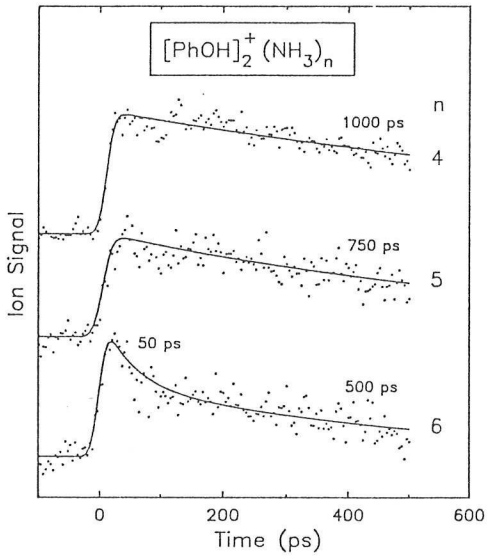

Figure 5. Time dependence for the excited state dimer cluster $[PhOH]_2^*(NH_3)_n$. Single exponential curves are calculated for $n = 4$ and 5. The sum of two exponential curves is calculated for $n = 6$.

of the solvent.[8,24] These investigations should provide new insight into the influence of solvent structure on chemical reactivity.

3.3. Different proton binding sites - phenol dimer

The phenol molecule (like many other aromatic acids and bases, e.g., carboxylic acids and certain amines) forms a stable dimer in solution.[25] The reaction rate of excited state (S_1) phenol dimer in $(NH_3)_n$ solvent clusters was measured by detecting the $[PhOH]_2^+(NH_3)_n$ ion signal (Fig. 5). Whereas phenol monomer undergoes an abrupt change in reaction rate at $n = 5$ (Fig. 2), similar behavior for the dimer acid is not evident. The decay traces in Fig. 5 show progressively faster rates with increasing n; however, it cannot be established that this is due to ESPT. There is some indication of a $\sim$ 50 ps response for $n = 6$, followed by a slower decay of about 500 ps.

The apparent inhibition of proton transfer in phenol dimer relative to phenol monomer in comparable solvent clusters can be explained by the nature of the dimer bond. Spectroscopic evidence[26,27] indicates that the individual phenol molecules in the dimer are inequivalent as shown in Fig. 6. A linear O–H–O hydrogen bond forms in which the hydroxy proton of one phenol (type-I) is bound not to the solvent but to the oxygen of the other phenol. This other phenol (type-II) is similar to monomer phenol in that it has a proton that binds directly to the solvent. Type-I phenol has

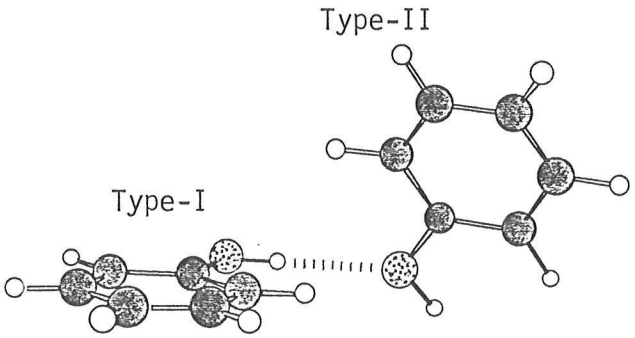

Figure 6. Structure of the phenol dimer deduced spectroscopically (Figure adapted from Ref. 27).

a restricted proton, which should quench ESPT. The fast 50 ps decay component in Fig. 5 for $n = 6$ may be due to ESPT from excitation of type-II phenol and the slow component to excitation of type-I phenol.

3.4. Solvent reorganization in clusters

Product formation kinetics, as measured by the ion-pair dissociative ionization signal $H^+(NH_3)_n$, are given in Fig. 7. This signal arises by ion-pair ionization to the weakly bound outer potential well of the cluster ion followed by cluster ion dissociation (Fig. 1).[6,7] Formation kinetics are observed for values of n less than the reaction threshold of $n = 5$ because the exothermicity of the cluster ion dissociation causes some evaporation (typically one or two molecules depending on the photoionization energy).[9] The formation curves in Fig. 7 have two time dependences; a fast one ($\simeq$ 65 ps) which matches the decay of reactant in Fig. 2, and a slow one (0.3 ns), which we attribute to solvent reorganization following the proton transfer event. Other explanations seem less plausible. The slow component is not due to a structural isomer, because this would also appear in the reactant decay curves. Evaporation can be ruled out for the following reasons: (1) Evaporation in the neutral ion-pair state should show decay, not formation kinetics.[28] (2) Dissociation from the cluster ion outer-well does cause one or two solvent molecules to evaporate;[9] however, this process occurs after the λ_2 pulse and, therefore, the effect on intensity is independent of the pump-probe delay time.

The dual time dependence in Fig. 7 can be explained by fast ESPT followed by a slower reorganization of the solvent hydrogen-bond network in response to the electric-dipole forces imposed by the ion-pair structure. ESPT is expected to be fast because it in-

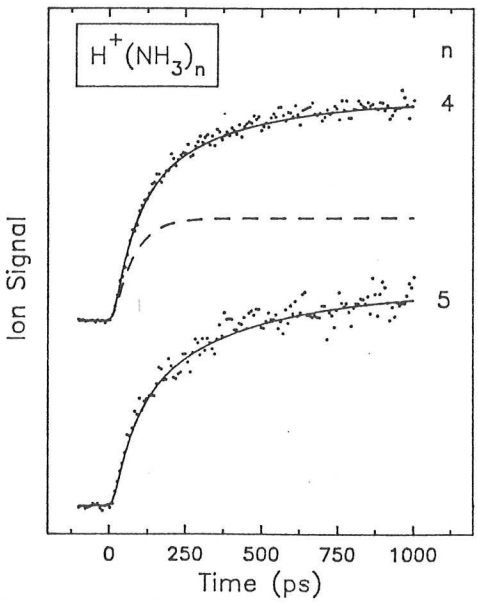

Figure 7. Observed $PhO^{*-}H^+B_n$ ion-pair formation kinetics (as measured by H^+B_n detection) for NH_3 solvation. Traces were recorded using 266-nm pump and 532-nm probe excitation. The data were fitted according to paper I for $k^{-1} = 65$ ps, $k_s^{-1} = 350$ ps, $i_c/i_b = 2.4$ (for $n = 4$); and $k^{-1} = 65$ ps, $k_s^{-1} = 300$ ps, $i_c/i_b = 2.0$ (for $n = 5$)

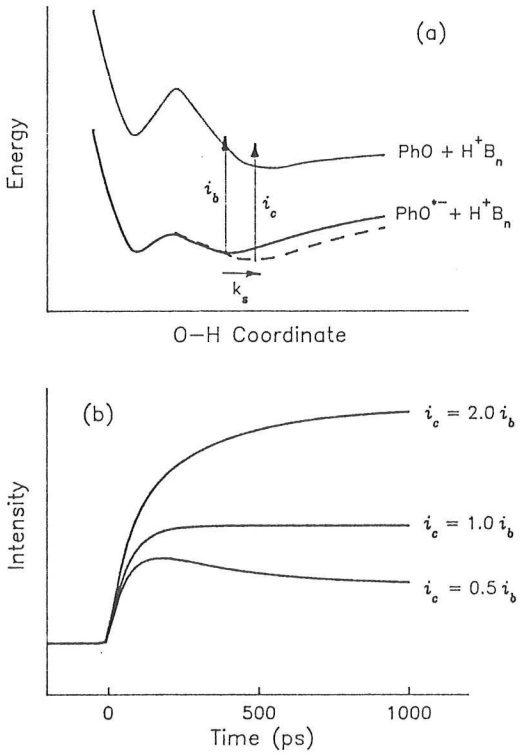

Figure 8. (a) Schematic representation of the evolving solvent-relaxed ion-pair potential. (b) Calculated ion time dependence according to paper I, for $k^{-1} = 65$ ps, $k_s^{-1} = 300$ ps and different relative values of the unrelaxed (i_b) and relaxed (i_c) ionization efficiencies.

volves an electron transfer and a geometry change along a single coordinate O–H. Solvent relaxation, on the other hand, should be slower because it involves many coordinates. Time-dependent ionization efficiencies are analogous to time-dependent Stokes shifts, which are used to measure structural reorganization in solution.[29] Both phenomena are due to changing Franck-Condon factors brought about by molecular motion.

How the potential energy along the O–H coordinate might change with time due to solvent reorganization is illustrated qualitatively in Fig. 8. The equilibrium bond distance for the cluster ion $PhO{\cdot}H^+B_n$ should be greater than for the neutral solvated ion-pair $PhO^{*-}H^+B_n$ because of the loss of Coulombic attraction upon ionization.[6] The equilibrium solvent structure prior to proton transfer is a nonequilibrium structure for the newly formed ion pair. The solvent network must reorganize to achieve a structure that best accomodates the proton. This reorganization or "solvation of the proton" causes delocalization of charge and lengthening of the O–H bond (Fig. 8a). The relaxing ion-pair moves closer to a geometry representing the cluster-ion equilibrium configuration. This improves the Franck-Condon factors for ionization and leads to an increased ionization efficiency with time.

Calculated time dependences are plotted in Fig. 8b for the $H^+(NH_3)_n$ ion signal where we define a solvent relaxation rate constant k_s and vary the relative ionization effiency from the unrelaxed (i_b) and relaxed form (i_c). The details of this simple kinetic model are given in paper I.[6] For simplicity, we assume here that ionization from the reactant excited state does not dissociate to form $H^+(NH_3)_n$ and that ionization from the unrelaxed and relaxed ion pair leads to complete dissociation to form $H^+(NH_3)_n$. The calculations that best fit the data in Fig. 7 are those for which the ionization efficiency increases with time. These results are consistent with Franck-Condon factors for ionization that improve as a result of solvent reorganization.

It is difficult to judge whether 0.3 ns is a reasonable time scale for solvent reorganization in $(NH_3)_n$ solvent clusters because we do not know the cluster temperatures. Most models of solvent reorientation about a dipole include more than one time constant, reflecting many types of molecular motion.[29–31] The fastest motions are due to bond rotations, whereas the slowest reorientations involve breaking and reforming of intermolecular solvent bonds. These would be particularly slow for hydrogen-bonded solvents. Extensive measure-

ments of solvent relaxation for each of the reorientational degrees of freedom have been reported by many groups over a wide range of temperatures.[29–31] For the variety of solvents, molecular motions, and temperatures considered, relaxation times ranged from the experimentally detectable limit of about 100 fs to greater than a nanosecond. The intermolecular motional time constant for ethanol at 253 K, for example, was 112 ps (responding to a dipole excitation in a dye molecule).[30] This is an activated process because of hydrogen-bond energy and, therefore, the rates vary significantly with temperature. We have not found any measurements of NH_3 solvent relaxation rates; however, it is certainly reasonably to expect the reorientation of hydrogen bonds at low temperatures ($\leq$ 100 K) to be on the nanosecond time scale in accord with our experimental results.

4. SUMMARY AND CONCLUSIONS

Studies of reactivity in isolated molecular clusters are providing valuable information on the interactions of individual solvent or lattice molecules on chemical dynamics. In this paper we have focused on the role of structure particularly regarding the surrounding solvent. Though stepwise solvent binding energies are a strong driving force to reactivity, simple additivity arguments are insufficient for describing the role of first- and second-shell solvent molecules. The ability of the solvent to form a optimum hydrogen bonding network for proton stabilization is a cooperative effect. Disruption of energetically favorable solvent structures have been observed to reduce reaction rates by over an order of magnitude.

5. ACKNOWLEDGEMENTS

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