

Solvation Ultrafast Dynamics of Reactions. 8. Acid-Base Reactions in Finite-Sized Clusters of Naphthol in Ammonia, Water, and Piperidine

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In this contribution, studies of the dynamics of proton-transfer reactions in solvent cages are presented, building on earlier work [Breen, J. J.; et al. *J. Chem. Phys.* **1990**, 92, 805. Kim, S. K.; et al. *Chem. Phys. Lett.* **1994**, 228, 369]. The acid-base system studied in a molecular beam is 1-naphthol as a solute and ammonia, piperidine, or water as the solvent, with the number of solvent molecules (n) varying. The rates and threshold for proton transfer have been found to be critically dependent on the number and type of solvent molecules: $n = 2$ for piperidine and $n = 3$ for ammonia; no proton transfer was observed for water up to $n = 21$. With subpicosecond time resolution, we observe a biexponential transient for the $n = 3$ cluster with ammonia. From these observations and the high accuracy of the fits, we provide the rate of the proton transfer at short times and the solvent reorganization at longer times. From studies of the effect of the total energy, the isotope substitution, and the number and type of solvent molecules, we discuss the nature of the transfer and the interplay between the local structure of the base solvent and the dynamics. The effective shape of the potential energy surface is discussed by considering the anharmonicity of the reactant states and the Coulombic interaction of ion-pair product states. Tunneling is related to the nature of the potential and to measurements specific to the isotope effect and energy dependence. Finally, we discuss a simple model for the reaction in finite-sized clusters, which takes into account the proton affinity and the dielectric shielding of the solvent introduced by the local structure.

I. Introduction

Proton transfer is ubiquitous in chemistry and biology (for some reviews, see refs 1-3). A key point in the measurements of proton-transfer rates is the ability to induce an acid-base reaction on a relatively short time scale ("pH jump") and to follow the change with time. Since the first report by Weber⁴ in 1931 for the evidence of excited-state proton transfer, Förster⁵ and Weller⁶ showed that with light such instantaneous changes of the pK_a can be induced by excitation to the excited state. By using a four-level description, the Förster cycle, one can deduce the energetics as follows:

$$N_A[h\nu(A^*H \leftrightarrow AH) - h\nu(A^{*-} \leftrightarrow A^-)] = \Delta H_d(AH) - \Delta H_d(A^*H) \quad (1)$$

where AH is the acid and A^- is the conjugate base. The asterisk denotes the excited state, $h\nu$ represents the excitation energy between origins, N_A is the Avogadro number, and ΔH_d is the enthalpy of deprotonation. The enthalpy of deprotonation is related to the pK_a of the acid by the following thermodynamic relation when the change of entropy is neglected:

$$2.303RT[pK_a(AH) - pK_a(A^*H)] = \Delta H_d(AH) - \Delta H_d(A^*H) \quad (2)$$

That is, the enthalpy of deprotonation in the excited state decreases compared to that in the ground state with a significant increase in pK_a introduced by the excitation.

Fundamental to the proton-transfer reaction are the energetics of the initial and final states and the dynamical structure of the solvent. With femtosecond and picosecond time resolution, it is possible to study the elementary processes of structural changes due to solvent organization. Here, the system under study is 1-naphthol (referred to here as AH or 1-NpOH). The pK_a of 1-NpOH in solution is determined to be 9.4 in the ground state and 0.5 ± 0.2 in the excited state.⁷ This large change in pK_a by the excitation makes it possible to induce the acid-base reaction on a very short time scale.

In solutions and in clusters, the naphthol systems have been studied to elucidate the proton-transfer mechanism. Spectroscopically, the broadening of the absorption peaks and the red shift of the emission have been used as indicators of proton transfer. Leutwyler's group^{8,9} carried out thorough spectroscopic studies of 1-NpOH clusters with solvent molecules, such as water, ammonia, methanol, and piperidine, and deduced the energetics and the approximate size dependence for the onset of the process. In solutions, measurement of the rise time of the red-shifted emission can give the time constant for proton transfer, and many groups have been involved in such studies. For naphthols in water (and other solvents), the groups of Robinson and Clark¹⁰ have studied the proton transfer in pure water and in mixed solvents; they reported 32 ps for pure water. Eigen's early studies¹¹ of acid solutions provided the dissociation and recombination rates (hence, equilibrium constants) and proposed a local structure for the proton, $(H_9O_4)^+$, in water. Robinson proposed, based on his studies, that in water the

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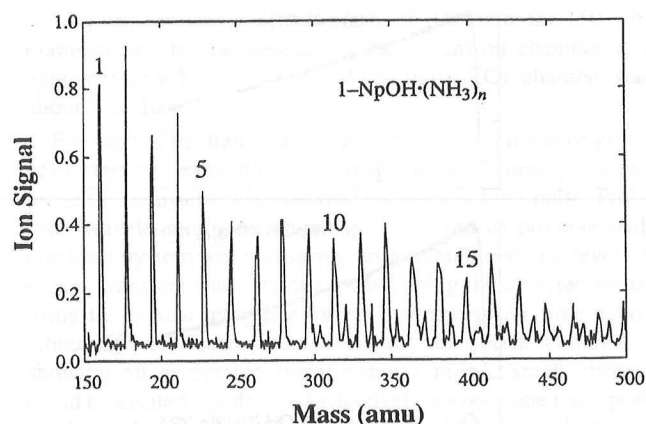


Figure 4. Multiphoton ionization time-of-flight mass spectrum of $1\text{-NpOH}\cdot(\text{NH}_3)_n$ showing a typical cluster distribution obtained using the setup described in section II.B.

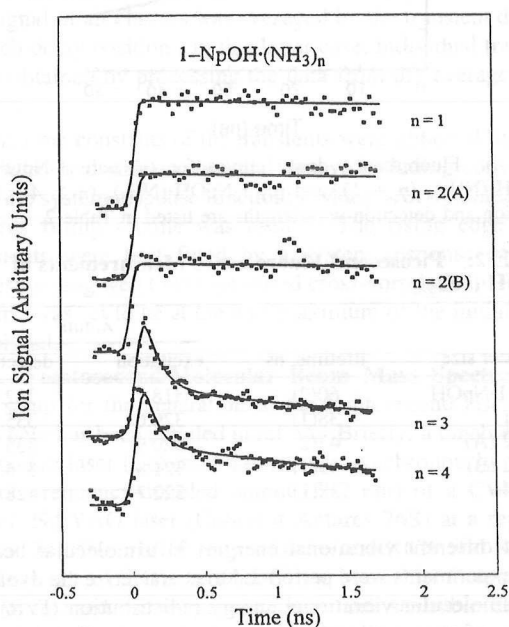


Figure 5. Picosecond (pump-probe) transients recorded for the clusters of $1\text{-NpOH}\cdot(\text{NH}_3)_{n=1-4}$. Excitation conditions are listed in Table 1. The solid lines are calculated fits using a double-exponential function (see text).

dynamics. The slight decay observed in the transients at these relatively short times is related to the excited-state lifetimes which are on the order of tens of nanoseconds, Table 2. As the delay line has a usable range of up to 4 ns, these lifetimes could not be reproduced as accurately with the pump-probe apparatus as with the photon-counting results given in section III.B.

For the clusters $1\text{-NpOH}\cdot(\text{NH}_3)_n$ ($n = 3, 4$), the measured transients reveal dynamics on the picosecond time scale. Each of the transients was fitted to a double-exponential decay. The fitted time constant for the fast decay component was 87 ± 30 ps for $n = 3$ and essentially the same value for $n = 4$ (in ref 14, τ was 100 ± 30 ps). These measurements were first reported in our earlier communication.¹⁴ The slow decay time constants are estimated to be more than a nanosecond, Figure 5. As discussed below, with subpicosecond resolution, these rates can be obtained more accurately and the form of the transient, short and long decay components, becomes certain in the assignment.

(b) Naphthol-Ammonia ($n = 1-6$) Subpicosecond Resolution. The proton-transfer dynamics of the ammonia system were studied again with a subpicosecond resolution. In this

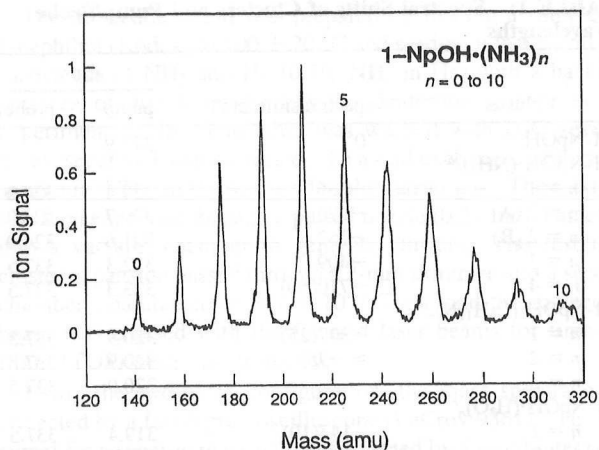


Figure 6. Multiphoton ionization time-of-flight mass spectrum of $1\text{-NpOH}\cdot(\text{NH}_3)_n$ showing a typical cluster distribution obtained using the setup described in section II.C.

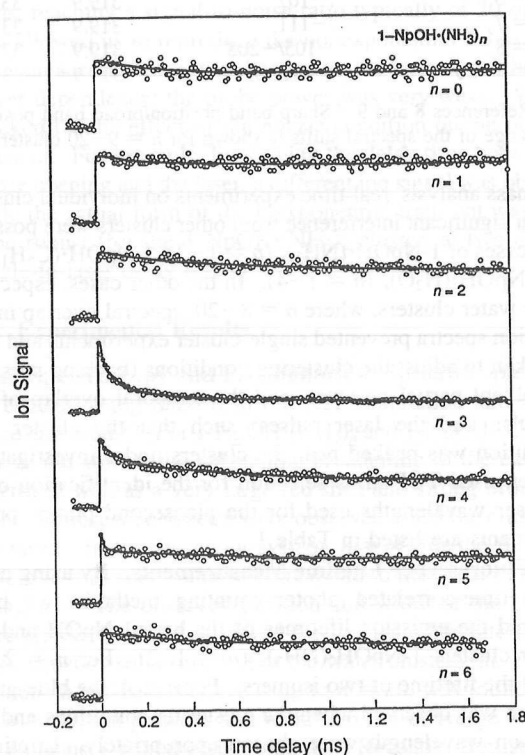


Figure 7. Subpicosecond (pump-probe) transients for $1\text{-NpOH}\cdot(\text{NH}_3)_n$, with n varying from 0 to 6. Pump/probe wavelengths are as follows: 320/340 nm for $n = 0-4$; 320/370 nm for $n = 5$; and 326/370 nm for $n = 6$.

apparatus, the cluster distribution obtained is shown in Figure 6. Transients obtained for $n = 0$ to $n = 6$ are shown in Figure 7. The transients for $n = 0-4$ were taken at 320/340 nm (pump/probe), while those for $n = 5$ and 6 were obtained at 320/370 and 326/370 nm, respectively. With the 320/340-nm arrangement, no time-dependent signal was observed for clusters larger than $n = 4$, possibly due to ion fragmentation.³⁹ The transients for clusters of $n = 3-5$ show an initial fast decay, while the others show relatively slow decay with time constants of tens of nanoseconds, which are comparable to the fluorescence lifetimes of the excited state, Table 2. A very fast initial decay with small amplitude was observed within the first few picoseconds for the $n = 5$ transient.

The transients for $\text{A}^*\text{H}\cdot(\text{NH}_3)_3$ and $\text{A}^*\text{D}\cdot(\text{ND}_3)_3$ taken at two different pump energies are shown in Figure 8. These transients show distinct biexponential decays and were fit with a function

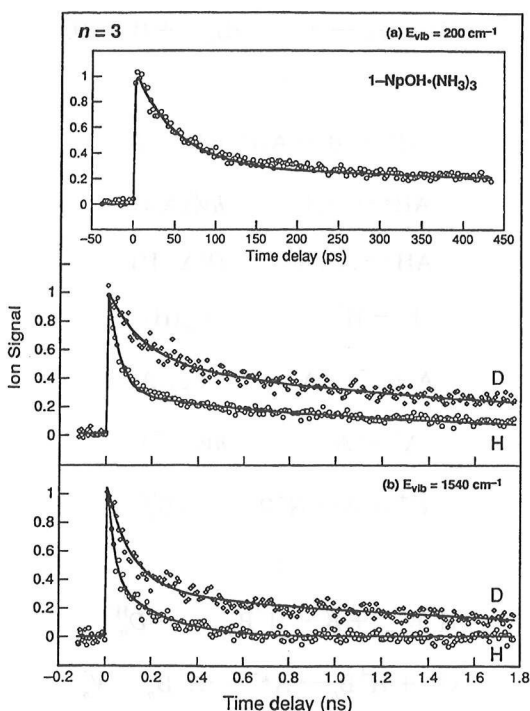


Figure 8. Subpicosecond experimental transients and theoretical fits for 1-NpOH·(NH₃)₃ and 1-NpOD·(ND₃)₃: (a) pump/probe wavelengths of 320/340 nm and (b) 307/340 nm. Excess vibrational energies are given relative to the origin at 31 050 cm⁻¹ for the *n* = 3 cluster.

TABLE 3: Biexponential Fits to Observed Transients of 1-NpOH·(NH₃)_n^a

		H, <i>n</i> = 3	D, <i>n</i> = 3	H, <i>n</i> = 4	D, <i>n</i> = 4
320 nm	τ_1	52(4)	150(20)	93(8)	335(200)
	τ_2	1210(60)	>2100	>2700	>8000
	<i>R</i>	2.5	1.0 ^b	0.6 ^b	0.4 ^b
307 nm	τ_1	25(3)	100(10)	70(6)	152(35)
	τ_2	226(20)	1720(150)	727(25)	>5000
	<i>R</i>	2.2	2.1	0.8	0.4 ^b

^a τ_1 and τ_2 are in picoseconds. The values in parentheses are standard deviations. The uncertainty of *R*, which is defined in the text, is within 20–30%. ^b Less reliable due to large uncertainties of τ_2 .

of the form $S(t) = A_0[R \exp(-t/\tau_1) + \exp(-t/\tau_2)]$, which is convoluted with the instrumental response function. The results of the fits for *n* = 3 and 4 clusters are listed in Table 3. The results for the fast decay component are consistent with those obtained with the picosecond resolution of the previous section but provide more accurate time constants. For the long-decay components, the results obtained here are quantitatively quite different from the values given in ref 15. For example, for the *n* = 3 cluster, our fast decay component is 52 ± 4 ps, while the slow component is 1210 ± 60 ps. The results in ref 15 gave 57 ± 15 and 440 ± 125 ps, respectively.

(c) Naphthol–Piperidine (*n* = 1–3) Picosecond Resolution. Figure 9 shows our picosecond real-time results for the 1-NpOH–piperidine clusters. For all the clusters, the same excitation wavelength (320.9 nm) was used in our experiments. This wavelength corresponds to the *S*₁ origin of the 1-NpOH·(C₅H₁₁N)₁ cluster and is within one of the broad bands reported in the R2PI spectrum for the 1-NpOH·(C₅H₁₁N)₂ cluster.⁸ Again, each transient was recorded individually with the experimental conditions set to maximize the ion signal for the particular cluster under consideration. The probe wavelength was to the red of the excitation wavelength.

Similar to the observations reported for the ammonia clusters, a significant change in the transients can be noticed when

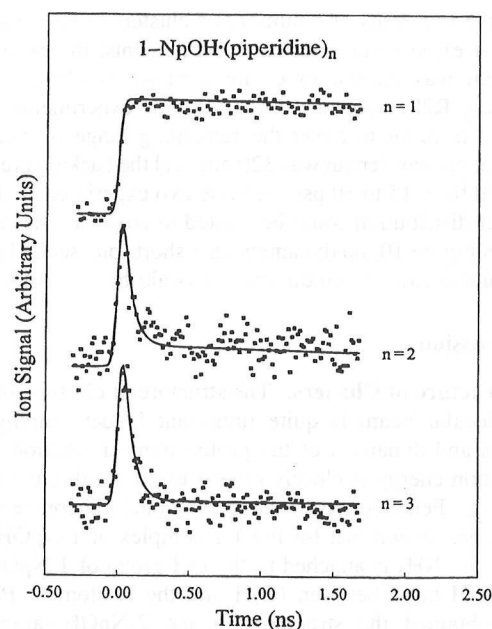


Figure 9. Picosecond (pump–probe) transients obtained for the clusters of 1-NpOH·(C₅H₁₁N)_n, *n* = 1–3. Excitation conditions are listed in Table 1. The solid lines are fits using a single-exponential function (see text).

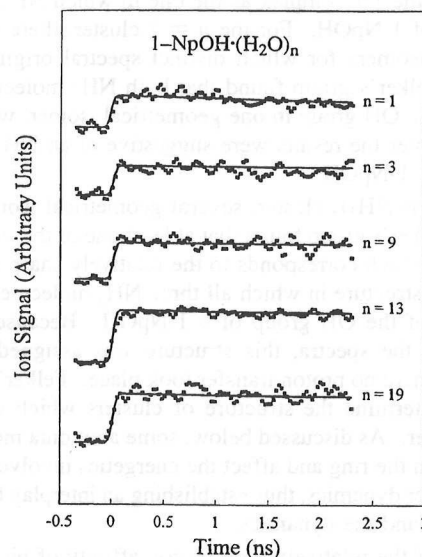


Figure 10. Picosecond (pump–probe) transients obtained for the clusters of 1-NpOH·(H₂O)_n, *n* = 1–19. Excitation conditions are listed in Table 1. The solid lines are fits using a single-exponential function (see text).

increasing the cluster size. For the *n* = 1 cluster, a very slight decay on the nanosecond time scale can be seen which is consistent with being due to the excited-state lifetime. Both the *n* = 2 and *n* = 3 clusters reveal picosecond time-scale dynamics. Each of the transients exhibits a characteristic proton-transfer time of ~65 ps. From the transients shown in Figure 9, it can be seen that only the *n* = 2 transients shows a slight leveling off, whereas the *n* = 3 transient reaches the zero background within less than 500 ps.

(d) Naphthol–Water (*n* = 1–21) Picosecond Resolution. In Figure 10, our real-time results of the 1-NpOH·(H₂O)_n (*n* = 1–21) clusters are summarized showing the transients for *n* = 1, 3, 9, 13, and 19. Individual experiments were performed for the water clusters with *n* = 1–4 using the reported cluster origins.⁹ The remaining transients were recorded using a transient digitizer with signal-averaging capabilities which

allowed the transients of a number of clusters to be measured in a single experiment. For such experiments, the excitation wavelength was chosen to excite a range of clusters with overlapping R2PI spectra. Two different experiments were performed in order to cover the remaining range of clusters. The excitation wavelength was 320 nm, and the backing pressure was varied from 15 to 30 psig in these two experiments. Thus, the cluster distribution could be shifted to larger n . As can be seen from Figure 10, no dynamics on a short (picosecond) time scale characteristic of proton transfer could be observed.

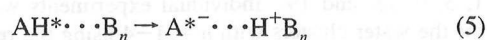
IV. Discussion

A. Structure of Clusters. The structure of clusters formed in a molecular beam is quite important in determining the energetics and dynamics of the proton-transfer reaction since the solvation energy is closely related to the local structure of the solvent. Felker's group, using rotational coherence spectroscopy, has shown that for the 1:1 complex of 1-NpOH and ammonia the NH_3 is attached to the OH group of 1-NpOH by forming a H bond between (O)H and the N atom.⁴⁰ Pratt's group⁴¹ obtained the structure for the 2-NpOH-ammonia complex from the high-resolution spectra; the structure is similar to that of 1-NpOH, with slightly different interatomic distances. Bernstein and co-workers³⁶ have calculated the most probable structure for the 1:1 complex as the one in which NH_3 resides on the ring of 1-NpOH. For the $n = 2$ cluster, there are two geometrical isomers for which distinct spectral origins were observed. Felker's group found that both NH_3 molecules are attached to the OH group in one geometrical isomer, while for the other isomer the results were suggestive of an NH_3 bound to the ring of 1-NpOH.

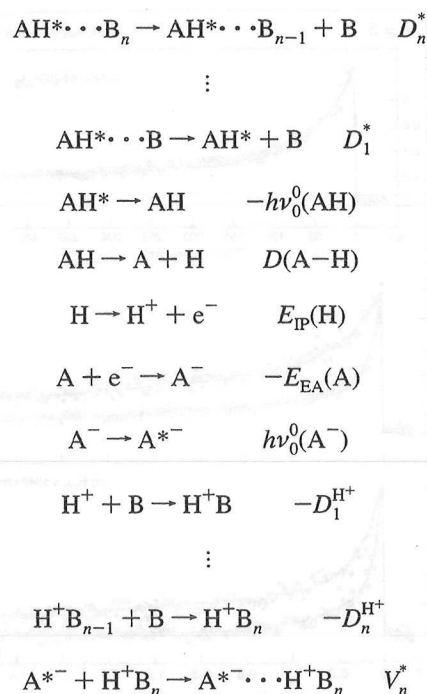
For the $\text{AH}(\text{NH}_3)_3$ cluster, several geometrical isomers are possible. Felker's group found that at least one of the structural conformers, which corresponds to the relatively sharp spectral origin, has a structure in which all three NH_3 molecules reside on the side of the OH group of a 1-NpOH. Because of the sharpness of the spectra, this structure was assigned to the conformer where no proton transfer took place. Felker's group could not determine the structure of clusters which undergo proton transfer. As discussed below, some ammonia molecules may reside on the ring and affect the energetics involved in the proton-transfer dynamics, thus establishing an interplay between the structure and the dynamics.

Because of the relatively high proton affinity of piperidine, a strong hydrogen bonding is expected between the OH group of 1-NpOH and the N atom of piperidine. Felker's result for piperidine is consistent with this structure.⁴⁰ For water clusters, Felker's group found that the water solvent is attached to the OH group of 1-NpOH in both 1:1 and 1:2 (1-NpOH:water) complexes.⁴⁰ This is consistent with the calculation by Bernstein and co-workers, who found that the water molecules have a tendency to bind together and reside as a group in the vicinity of the OH group of 1-NpOH.³⁶ This local structure of the water solvent is not in favor of the solvation of ion-pair states; therefore, it could be one of the factors in preventing the proton-transfer reaction in water clusters.

B. Energetics: The Thermochemical Cycle. We begin by outlining a thermochemical cycle that identifies the energetics of bare 1-NpOH and the stepwise energies of solvation necessary for describing the cluster system. The reaction of interest,



can be broken down to the following sequence:



where AH is shorthand for 1-NpOH and D represents the dissociation energy. The energy terms are known to reasonable accuracy except for the ion-pair bond energy V_n^* . Calculations of Coulombic potentials are presented below. The above description allows us to compare the energetics of gas-phase reactions to cluster reactions and to compare the energetics of proton transfer for different solvents. The enthalpy of the gas-phase deprotonation of AH to form $\text{A}^- + \text{H}^+$ is given by

$$\begin{aligned} \Delta H_d &= D(\text{A-H}) + E_{\text{IP}}(\text{H}) - E_{\text{EA}}(\text{A}) \\ &= 3.60 + 13.60 - 2.51 = 14.69 \text{ eV} \quad (6) \end{aligned}$$

(where the stated values are from refs 42, 43, and 44, respectively). The analogous energy for AH^* is given by

$$\begin{aligned} \Delta H_d^* &= \Delta H_d - hv_0^0(\text{AH}) + hv_0^0(\text{A}^-) \\ &= 14.69 - 3.90 + 3.2 = 14.0 \text{ eV} \quad (7) \end{aligned}$$

(where the spectral energies were obtained from spectra in ref 8).^{7,45} These very endothermic gas-phase reactions undergo significant stabilization under cluster (or condensed-phase) solvation conditions. The excited-state enthalpy for dissociative proton transfer in clusters of solvent size n (i.e., $\text{AH}^* \cdots \text{B}_n \rightarrow \text{A}^{*-} + \text{H}^+ \text{B}_n$) is given by

$$\Delta H_{d,n}^* = \Delta H_d^* + \sum_i^n D_i^* - \sum_i^n D_i^{\text{H}^+} \quad (8)$$

The importance of defining the dissociative proton-transfer enthalpies is that these energies can be determined fairly accurately. A tabulation of stepwise energies and enthalpies for NH_3 solvation is given in Table 4. The proton transfer measured here does not involve a full dissociation; instead, the proton remains bound to the counterion by Coulombic attraction. The enthalpy of proton transfer in clusters is, therefore, given by

$$\Delta H_{\text{PT},n}^* = \Delta H_{d,n}^* - V_n^* - \epsilon_n^* \quad (9)$$

where we have included an additional solvation energy, ϵ_n^* , that describes further stabilization, due to geometry change or

TABLE 4: Coulombic Potential Parameters for 1-NpOH•(NH₃)^a

q_0	V_n^* , eV	r_e , Å
-0.2	3.68	1.85
-0.53	3.76	1.8
-0.82	4.43	1.5

^a Parameters used here are $r_{\text{Ph-O}} = 2.5$ Å, $r_{\text{H-N}} = 1.04$ Å, $r_{\text{N-H}_3} = 0.52$ Å; $q_{\text{ring1}} = q_{\text{ring2}} = -0.235$; $q_{\text{H}} = 0.54$, $q_{\text{N}} = -1.01$, $q_{\text{H}_3} = 1.38$. The repulsive parameters are $A = 100$ eV and $\rho = 0.32$ Å. The potential energy curves for ion-pair states in Figure 11 are calculated using the following parameters: $q_0 = -0.53$ and $q_{\text{H}} = +1.0$ ($n = 0$); for $n = 2-4$, $q_{\text{H}} = 0.52, 0.507, 0.49$; $q_{\text{N}} = -1.06, -1.11, -1.15$; $q_{\text{H}_3} = 1.40, 1.44, 1.47$, respectively.

anion solvation that are not explicitly accounted for in the ion-pair bond (along the OH coordinate) energy, V_n^* , or elsewhere in the above thermochemical cycle.

C. Coulombic Interaction and Potential Energy Curves.

Here, we consider the form of the potential from an approximate charge distribution in the ion-pair configuration. The ion-pair state representing the proton-transfer product can be described by a Coulombic potential $V(r)$, where r is the O-H internuclear separation. We are interested not only in the well depth V_n^* , which is needed for the thermochemical expressions, but in the shape of the potential energy curve, which determines the barrier properties and tunneling rates. The potential $V(r)$ is calculated from the sum of the pairwise attraction and repulsion interactions between specific sites i and j (e.g., atoms within a molecule or cluster),

$$V(r) = \sum_{i < j} V_{ij}(r) = \sum_{i < j} \left[\frac{q_i q_j}{r_{ij}} + A \exp\left(-\frac{r_{ij}}{\rho}\right) \right] \quad (10)$$

where the q 's are charge densities separated by distance r_{ij} and A and ρ are constants.⁴⁶ Such potentials have been introduced by Syage for the phenol system^{17,39} and may now define V_n^* (well depth) and the equilibrium distance of the ion-pair state.

Charge densities for $\text{H}^+(\text{NH}_3)_n$ (up to $n = 4$) were calculated by Deakne.⁴⁷ The only charge density data we could find for naphtholate was a 1968 molecular orbital calculation⁴⁸ and an ESR study;⁴⁹ however, they gave very different results for the charge density of the O atom of naphtholate (q_0) of -0.82 and -0.20 , respectively, although the ESR work was for the T_1 state. We use charge densities for 1-NpO^{•-} based on molecular orbital calculations for PhO⁻ by Taft and co-workers (i.e., $q_0 = -0.53$),⁵⁰ which turns out to be close to the average of the two values mentioned above. We computed potential curves for all three cases, and the results together with the potential parameters are given in Table 4, with the following in mind: (1) to simplify the analysis, we have grouped some charges as outlined in Table 4, (2) we adopt the same repulsive parameters used for $\text{PhOH} \cdot (\text{NH}_3)_n$ ($A = 100$ eV and $\rho = 0.32$ Å), since these values lead to an OH equilibrium bond length of about 1.8 Å for the 1-NpO^{•-}•H⁺NH₃ ion-pair state.^{40,41,51-53} The calculated ion-pair potentials neglect some potentially important contributions, such as (1) interatomic potential terms (although these should be small relative to V), (2) stabilization of the 1-NpO^{•-} anion by the solvent, and (3) charge redistribution or ion-induced dipole effects that might be transmitted through the O-H bond (i.e., polarizability or dielectric screening).⁵⁴ The latter two effects are solvation properties that we relegate to the ϵ_n^* term above in eq 9.

For the bare naphthol ion-pair state, the positive charge resides on the H atom (we assume $q_{\text{H}} = 1.0$) in close proximity to the negatively charged phenoxy. Hence, at the equilibrium position,

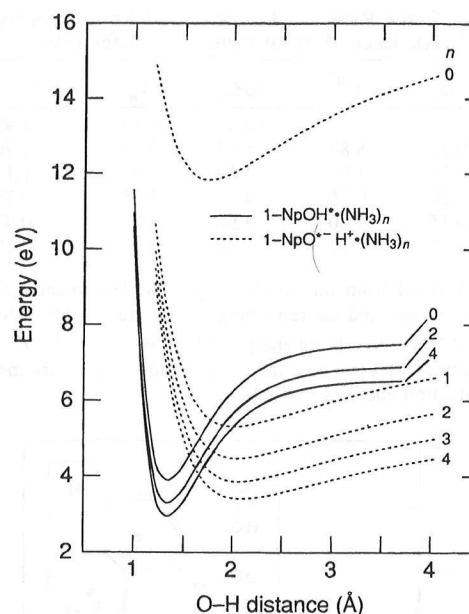


Figure 11. Calculated potential energy curves for 1-NpOH•(NH₃)_n along the O-H coordinate. The ion-pair Coulomb potential parameters are listed in Table 4. The figure gives both the covalent (solid lines) and ionic (dotted lines) potentials and defines the values of V_n^* , the equilibrium distances, and the change of ΔH^* (difference between minima of covalent and ionic potentials).

the Coulombic well depth for bare naphthol is relatively large ($V_0^* = 6.1$ eV) and the O-H bond length is short ($r_e = 1.4$ Å). A single NH₃ molecule delocalizes the positive charge, causing the ion-pair bond energy to decrease to $V_1^* = 3.8$ eV and the bond length to increase to 1.75 Å. Additional solvation further weakens and extends the O-H bond (e.g., $V_5^* = 3.1$ eV and $r_e = 1.9$ Å for $n = 5$).

To complete our picture of the proton-transfer surface crossing, the initially excited S_1 potential curves are fitted to a Morse function of the form

$$V(r) = D\{1 - \exp[-\beta(r - r_e)]\}^2 \quad (11)$$

The bond energy D is reported in eq 6. We take the equilibrium O-H bond length to be $r_e = 0.95$ Å.⁵⁵ The vibrational amplitude is calculated from the classical turning points of a harmonic oscillator. For an O-H ($\nu = 1$) fundamental of frequency 3500 cm⁻¹, one obtains $|r_{\text{max}} - r_e| = 0.16$ Å. Fitting eq 11 to these values gives $\beta = 2.25$ Å⁻¹. The addition of a single NH₃ molecule does not change the shape of the 1-NpO-H potential curves nearly as much as it lowers the energies relative to uncomplexed naphthol.

Figure 11 and Table 5 illustrate how proton transfer is stabilized in the presence of base molecules. $\Delta H_{\text{PT},n}^*$ changes in value from about 8 eV for $n = 0$ to about zero for $n = 5$ (note the difference in energy between minima of the solid and dotted curves, representing the covalent and ionic potentials, respectively). From the observed threshold at $n = 3$, we assume a value of $\Delta H_{\text{PT},3}^* \leq 0$ compared to a calculated value of 0.78 eV. Our proton solvation/Coulomb model, therefore, accounts for >90% of the observed solvent stabilization energy. Better agreement is expected by including the additional interactions outlined above that were lumped together as solvation energy ϵ_n^* . For example, the Coulomb model favors a solvent geometry in which the second level of NH₃ molecules, which carries 0.07–0.15 units of positive charge for $n = 2-4$, respectively, establish close proximity to the negative charge density on the O atom or aromatic ring. This would give an additional

TABLE 5: Some Relevant Energies and Enthalpies for 1-NpOH·(NH₃)_n Excited-State Proton Transfer (eV)

<i>i, n</i>	<i>D_i[*]</i>	<i>D_i^{H⁺}</i>	$\Delta H_{a,n}^*$	<i>V_n[*]</i>	$\Delta H_{PT,n}^* + \epsilon_n^*$
0			14.00	6.07	7.93
1	0.36 ^a	8.84 ^b	5.52	3.76	1.76
2	0.25	1.08	4.69	3.50	1.19
3	0.20	0.76	4.13	3.35	0.78
4	0.15	0.60	3.68	3.21	0.47
5	0.15	0.54	3.29	3.10	0.19

^a *D_i^{*}* is obtained from the spectroscopically determined value for PhOH·NH₃ (ref 58), and the remaining values are chosen to converge to the neutral NH₃–NH₃ bond energy of 0.15 eV (ref 62). ^b *D_i^{H⁺}* is the proton affinity of NH₃ (ref 43), and the remaining values are measured stepwise solvation energies (ref 63).

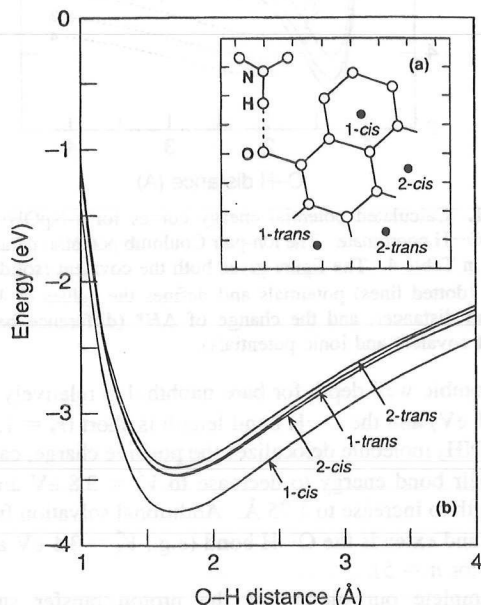


Figure 12. (a) Geometry of NpOH·NH₃ used to calculate Coulomb potentials for different isomers and rotomers of NpOH. The charges *q_{ring1}* and *q_{ring2}* are assigned to the center of mass of the aromatic rings marked by a solid circle. The tic marks on the axes represent 1-Å units. (b) Coulombic potentials calculated for the cis and trans rotomers of 1- and 2-NpOH. The dissociative limit is at zero energy.

stabilization of roughly 0.2 eV for charges of say +0.1 and −0.4 separated by 3 Å. It is also possible that NH₃ binds to the ring, which we have not considered in these calculations.

The Coulomb potential is useful for explaining the relative excited-state acidities for the 1-NpOH and 2-NpOH isomers and their cis and trans rotomers. It is apparent from the molecular structure in Figure 12a that the cis rotomer of 1-NpOH permits the closest approach of oppositely charged sites and, therefore, gives the most stable ion-pair state as calculated in Figure 12b. Indeed, the *pK_a* of 0.5 for 1-NpOH is lower than that of 2.8 for 2-NpOH.⁷ This corresponds to an energy difference of 0.14 eV, which compares favorably to the calculated Coulomb potential difference (averaging over rotomer energies) of about 0.21 eV. It is interesting that this cis and trans rotomers of 1-NpOH differ in energy by the fairly large value of 0.34 eV. This interpretation may have bearing on the conclusions of Bernstein et al. that only a certain isomer of the 1-NpOH·(NH₃)₃ clusters undergoes proton transfer.³⁶ Note that in the molecular beam the trans rotomer of 1-NpOH is predominantly populated.³⁶

We now examine the enthalpy of reaction $\Delta H_{PT,n}^*$ as a function of solvent size using the model for potential energy outlined above. A tabulation of $\Delta H_{PT,n}^* + \epsilon_n^*$ values for NH₃

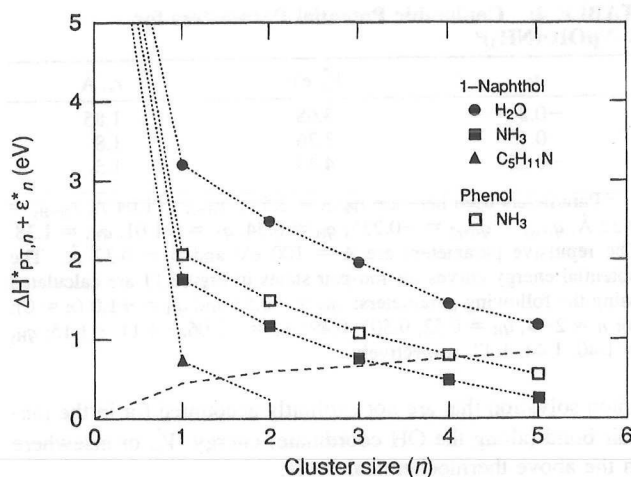
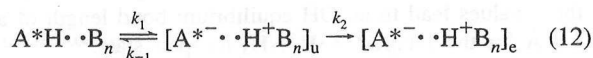


Figure 13. Computed enthalpy of proton transfer as a function of solvent type and size. The dashed line originating from the origin is an estimate of the magnitude of ϵ_n^* and, therefore, represents the line for which $\Delta H_{PT,n}^* = 0$. The proton affinities *D_i^{H⁺}* of piperidine, NH₃, and H₂O are 9.82, 8.84, and 7.36 eV, respectively (ref 43). The curve for piperidine could not be extended because stepwise solvation energies *D_{i>1}^{H⁺}*, to our knowledge, are not known.

solvation is given in Table 5. As defined earlier, ϵ_n^* accounts for a certain amount of solvent stabilization energy, which is closely related to the local solvent structure and not accounted for by the simple terms $\Delta H_{PT,n}^*$ and *V_n^{*}*. If we assume that the observed threshold at *n* = 3 indicates that $\Delta H_{PT,n}^* < 0$, then one might argue from Table 5 that $\epsilon_3^* > 0.78$ eV. A plot of $\Delta H_{PT,n}^* + \epsilon_n^*$ vs *n* is presented in Figure 13 for various solvents with 1-NpOH and for NH₃ with phenol. Stepwise solvation energies for H⁺(C₅H₁₁N)_n are not known other than for the proton affinity, so only a single point at *n* = 1 and an extrapolation to *n* = 2 are given. Nonetheless, it is evident that piperidine is predicted to give the smallest threshold solvent size for proton transfer for the cases shown, which is in agreement with experiments. The relative ordering of enthalpies of reaction for the other cases in Figure 13 also conforms with the ordering of threshold solvent size observed experimentally. Quantitative predictions of threshold solvent sizes are not obtained by Figure 13 but require a more rigorous theory that avoids the need to invoke the correction factor ϵ_n^* . However, it is encouraging that a smooth and reasonable function for ϵ_n^* can be drawn that crosses with the solvation energy curves (indicating $\Delta H_{PT,n}^* = 0$) at points that are in close agreement with the observed threshold solvent sizes for all cases measured.

D. Elementary Steps in Dynamics. Since the observed rates are much slower than those characteristic of coherent wavepacket motion,¹³ we shall use rate processes to describe the system outlined in eq 4:



From the above reaction scheme, it is clear that a biexponential decay would be observed by monitoring the reactant, *A***H*·*B_n*. From the solution of the population equations, it follows that the fast component is determined by $\sim(k_1 + k_{-1})$, while the slow component reflects the effect of the *k₂* process. This is true when the ionization cross section of the optically prepared excited states is dramatically decreased to nearly zero when the proton transfers to the solvent in clusters. It is important to realize that eq 12 in the absence of *k₋₁* process can also give rise to an apparent biexponential decay if both *A***H*·*B_n* and

TABLE 6: 1-NpOH·(NH₃)_n (n = 3) System: k_1 , k_{-1} , and k_2 ^a

$E_{\text{vib}}, \text{cm}^{-1}{}^b$	time, ps	H, $n = 3$	D, $n = 3$
200	$1/k_1$	71(9)	275(40)
(320 nm)	$1/k_{-1}$	200(40)	370 ^c
	$1/k_2$	910(60)	> 1120
1540	$1/k_1$	35(4)	143(10)
(307 nm)	$1/k_{-1}$	106(30)	357(90)
	$1/k_2$	164(25)	1200(170)

^a Rate constants are obtained from time constants and ratios listed in Table 3 using the following relations: $1/\tau_1 + 1/\tau_2 = k_1 + k_{-1} + k_2$, $1/(\tau_1\tau_2) = k_1k_2$, and $R = (\alpha + k_1 - k_{-1} - k_2)/(\alpha - k_1 + k_{-1} + k_2)$, where $\alpha = [(k_1 + k_{-1} + k_2)^2 - 4k_1k_2]^{1/2}$. ^b Vibrational energies were calculated relative to the origin at 31 050 cm⁻¹ for the $n = 3$ cluster (see refs 8 and 36), and they represent the average values at the center of our excitation pulses. ^c Less reliable due to uncertainties of values in Table 3.

[A*⁻·H⁺B_n]_u are assumed to be detectable with different ionization cross sections; a ratio of around 1:0.1–0.3 for A*H··B_n and A*⁻·H⁺B_n can be invoked. In this case, the fast and slow decays represent the proton transfer and solvent reorganization rate, respectively, and the ratio of fast-to-slow decays represents the relative ionization cross sections. The transient for 1-NpOH·(NH₃)₃ at 307 nm (where $k_2^{-1} \sim 150$ ps) decays to zero background (Figure 8), suggesting that the final product, [A*⁻·H⁺B_n]_e, is not detectable since one expects for this species a rise with a plateau.

In Table 6, for AH·(NH₃)_n, we present the fit parameters to the biexponential form given by eq 12. We note, from Table 6, that the fast rate of transfer is very sensitive to the isotopic substitution and to the total energy, consistent with the trends given in ref 15. With the subpicosecond resolution reported here, we observed no faster decay than the picosecond value given for AH·(NH₃)₃. From Table 6, it is apparent that k_1 increases with the total energy and decreases with D substitution. The value of k_{-1} is consistently smaller than that of k_1 , and on the time scale of both k_1 and k_{-1} , IVR may play a role. The IVR rate is expected to become faster as the density of states increases in 1-NpOH itself³⁸ or due to cluster modes.⁵⁶ Hence, increasing the vibrational energy, decreasing the vibrational frequencies by H/D isotopic substitution, or increasing the number of degrees of freedom by increasing the number of solvent molecules should increase the rate constant of IVR. The time constants listed in Table 3 show that neither τ_1 nor τ_2 is consistent with the above trend except for vibrational energy. Moreover, some of our measurements were made near the origin where one expects IVR to be on a very long time scale. Accordingly, our scheme in eq 12 does not include an IVR process, although it is part of the description of the solvent reorganization. In the following sections, we discuss the different elementary steps expressed by k_1 , k_{-1} , and k_2 and consider the interplay between structures and dynamics.

E. Proton Transfer: Tunneling. The mechanism of proton transfer has been extensively modeled and studied (see, e.g., refs 1–3, 15, and 57). There are mainly three coordinates to be considered: the motion of the proton along the reaction coordinate (q), the vibration of O and N atoms of 1-naphthol and ammonia, respectively, along the intermolecular coordinate (Q), and the motion of solvent molecules along the solvent coordinate (S). The crossing of the S_1 Morse-type potential and the ion-pair Coulomb potential suggests the existence of a barrier to proton transfer, Figure 11. In this case, the potential curve is adiabatic and the crossing is avoided. In clusters, at early times the solvent configuration may be fixed. Accordingly, the proton transfer may be described as tunneling along the q coordinate through the barrier, with the height and width being modulated by the O–N van der Waals stretch motion along

the Q coordinate. Experimental evidence for a barrier includes the relatively slow (many picoseconds) rates measured for naphthol, and also for phenol,^{17,39} in relatively strong base solvents such as ammonia. Support for a tunneling mechanism is found in results showing reactivity from the vibrationless level of 1-NpOH and a very large deuterium isotope effect in 1-NpOH and in phenol.^{15,17,39}

Generally, the semiclassical expression for the tunneling rate constant from bound-to-free (inverted) parabolic potential energy surface is given by¹

$$k = \nu \exp\left[-\frac{a_0}{\hbar} \pi (2mU_0)^{1/2}\right] \quad (13)$$

where ν is the OH vibrational frequency, m is the effective mass, a_0 is the half-width of the barrier, and U_0 is the barrier height (see Figure 1). Different potentials are used to account for the parameters. For example, Bernstein and co-workers¹⁵ used a model potential energy surface for which the untransferred proton is bound in a well and the transferred proton is a free particle. Syage, on the other hand, used a bound potential instead of a free particle.¹⁷ U_0 and a_0 are strongly modified by the O–N stretching vibrational motion, and these effects can be considered by calculating an expectation value of tunneling rate constant for each quantum state of the O–N stretch.¹⁵

At the origin, k in eq 13 should be averaged over the zero-point vibrational motion of the O–N stretch;¹⁵ $k(\nu=0) = \langle \phi_0 | k | \phi_0 \rangle$, where ϕ_0 is the harmonic wavefunction for the O–N stretch mode at $\nu = 0$. Then $k(\nu=0)$ is given by

$$k(\nu=0) = \nu \left(\frac{\alpha}{p}\right) \exp\left\{q\left(\frac{q}{p} + 2a_0\right)\right\}$$

$$\alpha = \frac{4\pi^2 \mu \nu_2}{h}$$

$$q = -\frac{\pi^2}{h} (2mU_0)^{1/2}$$

$$p = \alpha - q/2a_0 \quad (14)$$

where ν is the OH vibrational frequency as in eq 13, μ and ν_2 are the reduced mass and frequency of the O–N oscillator, and U_0 and a_0 are the barrier height and width at the equilibrium O–N position as defined above. As the total vibrational energy increases, the probability of being populated in the quantum states of the O–N stretch mode increases and the rate should be averaged over energetically accessible quantum states of the O–N stretch mode. Expressions for tunneling rate constants for vibrationally excited states of the O–N stretch mode are elaborate and are given in ref 15; they have been used to account for the trends of experimental results.

The approximations and limitations of the two-dimensional tunneling model have been discussed before.^{15–17} Our intention here is to give an order of magnitude estimate of the rates and to predict their changes, accounting for the following effect and dependencies: deuterium isotope effect, vibrational energy dependence, dependence on barrier height and width, and variations with cluster size. At the origin, the tunneling rate constant can be calculated using eq 14. However, there are several parameters that we must consider. First, ν of ~ 3500 cm⁻¹ in bare 1-NpOH is expected to be lower in clusters with base solvents due to a strong hydrogen bonding. Bernstein and co-workers have estimated ν to be ~ 3000 cm⁻¹.¹⁵ The frequency of the O–N stretch mode (ν_2) has been estimated to be ~ 110 cm⁻¹ in ref 15, while it has been measured to be ~ 182

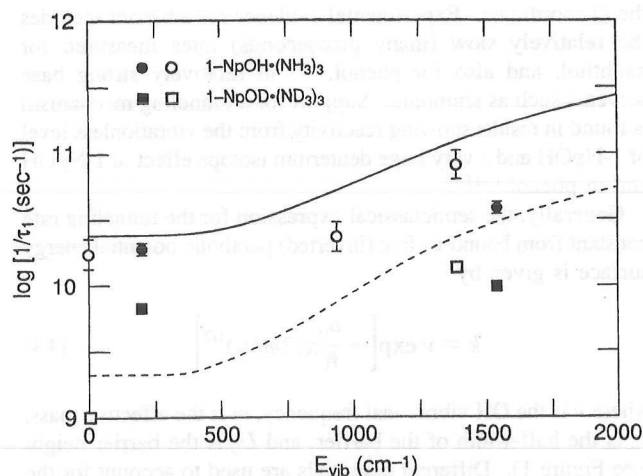


Figure 14. Calculated tunneling rate constants for $\text{AH}\cdot(\text{NH}_3)_3$ (solid line) and $\text{AD}\cdot(\text{ND}_3)_3$ (dashed line) as a function of the vibrational energy. The time constants for the fast decay components are plotted from Table 3 (filled circles and squares) and ref 15 (open circles and squares). Parameters for calculation are $\nu(\text{O}-\text{H}) = 3000 \text{ cm}^{-1}$, $\nu(\text{O}-\text{D}) = 2150 \text{ cm}^{-1}$, $\nu_2(\text{O}-\text{N}) = 110 \text{ cm}^{-1}$, $\mu(\text{H}) = 38 \text{ amu}$, $a_0 = 0.2 \text{ \AA}$, and $U_0 = 7500 \text{ cm}^{-1}$.

cm^{-1} in the $\text{PhOH}\cdot\text{NH}_3$ cluster.⁵⁸ For the barrier width (a_0), this can be estimated from recent spectroscopic studies.^{40,41} According to Pratt's group, the $\text{O}-\text{N}$ distance in the $2\text{-NpOH}\cdot(\text{NH}_3)$ cluster is ~ 2.6 and $\sim 2.8 \text{ \AA}$ in the excited and ground states, respectively.⁴¹ On the other hand, Felker's group determined the $\text{O}-\text{N}$ distance in $1\text{-NpOH}\cdot(\text{NH}_3)_n$ ($n = 1-3$) to be $\sim 3.0 \text{ \AA}$.⁴⁰ Felker's group reported the average of the ground- and excited-state values. Hence, if it is assumed that the $\text{O}-\text{N}$ distance in the excited state is $\sim 0.2 \text{ \AA}$ shorter than that in the ground state, its value will range from 2.8 to $2.9 \text{ \AA}$. For the $\text{O}-\text{N}$ distance of 2.6 and $2.8 \text{ \AA}$, a_0 is estimated to be ~ 0.2 and $\sim 0.3 \text{ \AA}$, respectively, by considering the classical turning points of the zero-point energy levels ($\sim 0.1 \text{ \AA}$) and the $\text{O}-\text{H}$ and $\text{N}-\text{H}$ distances ($\sim 1.0 \text{ \AA}$ each). The absolute value of the rate constant for a cluster at the given energy can be fit by varying the barrier parameters. Since the energetics is strongly dependent on the basicity and the number of the solvent (see section IV.B), the shape of the barrier is expected to be unique for the specific cluster under examination. Therefore, it is less meaningful to compare tunneling rate constants for different clusters using the same reaction barrier. Here, we calculate rate constants for the $\text{AH}\cdot(\text{NH}_3)_3$ and $\text{AD}\cdot(\text{ND}_3)_3$ clusters as a function of the total vibrational energy. As in ref 15, the vibrational states are assumed to be statistically populated, and the rate constant is averaged over all energetically accessible quantum states of the $\text{O}-\text{N}$ stretch mode. However, we pointed out in ref 16 that the distribution need not be complete or statistical.

In Figure 14, the calculated tunneling rate constants are compared with the experimental results for $\text{AH}\cdot(\text{NH}_3)_3$ and $\text{AD}\cdot(\text{ND}_3)_3$ clusters. The parameters used in the calculation of rate constants are listed in the caption for Figure 14. For comparison with experimental results, the time constants for the fast decay component (τ_1) reported here (Table 3) and in ref 15 are plotted together. The effect of the H/D isotopic substitution near the origin is much smaller than that reported in ref 15. As shown in Figure 14, the proton-transfer rate becomes only 3–4 times slower by the H-to-D substitution, while ref 15 gave ~ 20 times slower rate for the deuterium cluster. Because of the subpicosecond time resolution, our energy spread is larger than that reported in ref 15 and this may contribute to some difference. However, at an excess vibrational energy of $\sim 1500 \text{ cm}^{-1}$, the

ratio of the isotope effect here is similar to that reported in ref 15 (see Figure 14). It is fair to say that calculations based on the tunneling model give reasonable estimates of the rate constants and explain their qualitative trends (see Figure 14).

The free particle tunneling model implies the irreversibility of the proton transfer; the model works only when the product states have a much higher density of states than the reactant states. The experimental results using the reaction scheme in eq 12 suggest that the proton transfer may be reversible before it reaches the final equilibrium. Furthermore, there could be other intermolecular modes that can modify the tunneling barrier. For example, the reaction coordinate $\text{O}-\text{H}-\text{N}$ is not linearly oriented; instead, it has been found that it is tilted,^{40,41} which suggests that the bending motion could also modify the barrier parameters. Syage has introduced the activated solvent model to account for the phenol system.¹⁷ The activated solvent model is based on the mechanism that the proton transfer occurs by the nonadiabatic crossing of two adiabatic potential energy surfaces of reactants and products driven by the dynamical solvent effect. This treatment only works in the high-temperature limit and strong-solvation approximation. Most of our experimental results were carried out near the origin; hence, this model has not been tried here.

In the studies of intramolecular proton transfer,^{25,59,60} the reaction coordinate is shown to involve low-frequency modes and not the OH stretch vibration. In the intermolecular proton-transfer case, the reaction coordinate is coupled to the solvent coordinate, as one knows that solvent reorganization must take place. Second, from a molecular dynamics point of view, it is not clear that the proton transfer involves only one step. In fact, the study by Ando and Hynes²⁶ of HCl in water shows a two-step process for the creation of the "contact" and "solvent-separated" ion pairs. Tunneling was shown to be not significant in the first step.²⁶ It would be interesting to follow the proton-transfer dynamics of the system under study here with molecular dynamics simulations in clusters of different sizes. This will allow us to examine the motion of the individual solvent molecules involved, reaching the dielectric continuum limit in the bulk. This work is currently in progress in collaboration with the Hynes group.

F. Structures and Dynamics: Size Dependence. The structure of the cluster has not been considered explicitly in the energetics discussed in section IV.C. The structure has a significant influence, since V_n (or ϵ_n as defined in section IV.B and C) is closely related to the geometrical structures of the cluster, as discussed earlier (see section IV.C). As mentioned earlier, there could be more than one geometrical isomer for the same-sized cluster. For example, let us consider two geometrical isomers I and II for the $\text{AH}\cdot(\text{NH}_3)_n$ ($n = 3$) cluster; I has a structure in which all three NH_3 molecules are on the side of the OH group and II has a structure in which two NH_3 molecules are attached to the OH group and one NH_3 resides on the ring. As pointed out by Felker's group,⁴⁰ V_n of I is expected to be smaller than that of II since the delocalization of the positive charge in the ion-pair state would be more effective for I than II. In addition, for the geometrical isomer II, Coulombic interaction between ammonia and the naphthol ring would contribute to the increase of V_n . Therefore, from eq 9, structure II would be more favorable for proton transfer than I assuming that the proton affinity remains similar; the stability will depend on the net change in the proton affinity and the ion-pair bond energy upon changing the NH_3 position. This indicates that the energetics and dynamics of proton transfer are critically dependent on the structure. This point is significant even in bulk studies, as discussed in the Introduction.

The size dependence of dynamics is quite dramatic in 1-NpOH·(NH₃)_n clusters (Figure 7). The proton-transfer rate constant for the $n = 4$ cluster is smaller than that of $n = 3$. This trend is consistent with the findings of eq 12. The forward reaction is ~ 3 times faster than the reverse reaction for $n = 3$. This means that the reaction is exothermic, giving the negative ΔG° . For $n = 4$, the ratio of k_1 and k_{-1} is nearly 1, giving ΔG° of nearly zero. The sharp initial decay observed for $n = 5$ could be consistent with a continued increase in k_{-1} , giving the small $\sim 20\%$ amplitude. (Note that the excess vibrational energy is larger for the larger clusters and the decay is expected to be faster.)

Based on the energetics without considering the local solvent structure, as shown in Table 5, the experimental results cannot be explained; $n = 4$ is more exothermic than $n = 3$, and we expect a faster rate for $n = 4$. As discussed before, the hydrogen-bonded structure determines the stability of charge separation, and the above trend suggests that the solvent configuration for clusters formed in the molecular beam may become more favorable for reactants, compared to products, as the cluster size increases. But there are other possibilities. For example, for clusters larger than $n = 4$, proton transfer might occur even in the ground state, and the transients for $n = 5$ and 6 clusters in Figure 7 may be due to the significant contribution from ion-pair states in the ground state. The other possibility is the passage through the Marcus inverted region, where the absolute value of ΔG° exceeds the solvent reorganization energy. In other words, as the number of solvent molecules increases, the free-energy difference exceeds the solvent reorganization, resulting in an increase in the activation energy, hence a smaller rate constant.¹⁷ This description is based on the assumption that strong solvation is the driving force of the proton-transfer reaction.

As discussed in the Experimental Results section, we did not observe proton transfer for clusters with (H₂O)_n of $n \leq 21$. This observation is in line with the results of the spectroscopic work by the groups of Leutwyler⁹ and Bernstein.³⁶ The fact that no proton transfer in the water clusters is detectable is common to both 1-naphthol and phenol.^{9,17,36} Although Leutwyler and co-workers observed a moderate red shift of the fluorescence with increasing cluster size, at $n \geq 20$ the emission did not converge, however, to that observed for the naphtholate anion in aqueous solutions. The work of Knochenmuss *et al.*, however, shows that red-shifted naphtholate emission is observed for very large water clusters, 1-naphthol·(H₂O)_n clusters (n up to about 800), that they attribute to proton transfer.⁶¹ The rate constants reported, ranging from 0.5 to 1.5 ns (the rate constant decreases with increasing cluster size), were much slower compared to the time constant of 32 ps measured in liquid water.¹⁰ Knochenmuss *et al.* explained the slow rates measured in clusters as being due to a cold fluxional state of water that impedes proton transfer.⁶¹

Leutwyler and co-workers interpreted the resistance of water to promote proton transfer, even in relatively large clusters, to water molecules being concentrated around the OH group of the naphthol moiety.⁹ The latter interpretation is consistent with the calculations of Bernstein and co-workers,³⁶ who found that the water molecules tend to concentrate near the OH group of 1-NpOH and prefer to bind to each other rather than to the aromatic system (see section IV.A). Thus, there is incomplete solvation of the naphtholate anion, at least for intermediate-sized clusters, and the proton transfer does not take place. It should be noted that the relevant potential hypersurfaces are multidimensional in nature, and even if there exists a low

tunneling barrier along the proton-transfer coordinate, there may be insurmountable barriers along other coordinates which prevent such a favorable situation. These arguments are in line with considerations of the rigidity of the cluster or other geometrical constraints preventing proton transfer.

G. Solvent Reorganization. For the AH·(NH₃)_n clusters, distinct biexponential decays were observed (Figures 7 and 8). According to the model of eq 12, the long-time decay component is related to the irreversible processes of equilibration, as discussed in section IV.D, which could involve fragmentation, IVR, emission, or solvent reorganization. If the fragmentation is one of the processes, then the product would be the H⁺·(NH₃)_n complex. But, in contrast to the case of the phenol·(NH₃)_n complex,^{17,39} no protonated ammonia complex could be detected in this work. Lifetime of emission has been measured to be tens of nanoseconds (Table 2), and therefore, this process is excluded. Accordingly, the slow decay time in transients is associated with solvent reorganization which includes IVR in the product form. The ion-pair complex is formed on the picosecond time scale, and the solvent rearrangement takes place for further stabilization of the acid-base product state. The reorganization requires the dissociation and formation of hydrogen bonds as well as the "rotation" of solvent molecules. In the clusters at low temperatures, the time scale for solvation is therefore expected to be slower compared to that in bulk media. Recent time-resolved photoelectron spectroscopic studies showed that the time constant for solvent reorganization in phenol-ammonia clusters is around 300 ps.¹⁸ Syage found that for the phenol system, the Franck-Condon distribution for ionization is shifted by solvent reorganization to increase the total ion signal. But for the naphthol system, even when it is assumed that the ion-pair state before the solvent rearrangement, [A^{*-}·H⁺B_n]_u, is detectable, the solvent reorganization seems to decrease the ionization cross section. Actually, the ion signal went down to zero background in transients for AH·(NH₃)₃ taken at 307 nm (pump), Figure 8.

The dependence of τ_2 or $1/k_2$ on vibrational energy, cluster size, and H/D isotope substitution is quite noticeable (see Tables 3 and 6). The time constant decreases as the vibrational energy increases. For the $n = 3$ cluster, $1/k_2 \sim 910$ ps at the vibrational energy (E_{vib}) ~ 200 cm⁻¹ decreases to $1/k_2 \sim 164$ ps at $E_{\text{vib}} \sim 1540$ cm⁻¹. This dependence is more dramatic than that for proton transfer. As the total vibrational energy increases, the intermolecular vibrational motions are increasingly excited, thus facilitating the solvent motion, hence, an increase in the rates. The deuterium effect on k_2 is also large. For example, $1/k_2 \sim 1.2$ ns for AD·(ND₃)₃ at $E_{\text{vib}} \sim 1540$ cm⁻¹ is ~ 7 times larger than $1/k_2 \sim 164$ ps for AH·(NH₃)₃ at the same E_{vib} . This suggests the involvement of the intermolecular modes in solvent motion associated with solvent reorganization.

The dependence of τ_2 on the cluster size is shown in Table 3. The time constant $\tau_2 \sim 1.2$ ns for $n = 3$ cluster at $E_{\text{vib}} \sim 200$ cm⁻¹ increases to $\tau_2 > 2.7$ ns for $n = 4$ at an even higher vibrational energy (see the spectral shifts in Table 1). As the cluster size gets larger, the number of intermolecular modes associated with solvent motions increases. The solvent reorganization along a certain coordinate is accordingly expected to be slower as the probability of populating this coordinate decreases with the number of modes increasing. The solvation energies associated with solvent motions are not accurately known, and, therefore, one cannot rule out the possibility of the existence of structural isomers which undergo different (or no) proton-transfer dynamics. As discussed before, the reaction coordinate must involve the solvent motions, and the local structure of the solvent is therefore critical.

Finally, we should mention that the solvation effect on excited dipoles is expected and has been examined by, e.g., the change of fluorescence with time.⁶⁴ Therefore, the excitation of $\text{AH}\cdot\text{B}_n$ could lead to reorganization even in the absence of proton transfer. However, as shown in Figure 8, the proton transfer occurs on a much shorter time scale than the reorganization, and in the "absence" of proton transfer in higher n clusters (Figure 7), we do not observe the characteristic decay of the reorganization observed when, e.g., $n = 3$ and proton transfer is present.

V. Conclusions

In this paper, we reported real-time picosecond and subpicosecond studies of solvation involving proton-transfer reactions in clusters. The solute/solvent systems are 1-naphthol-(ammonia)_{*n*} ($n = 1-6$), 1-naphthol-(piperidine)_{*n*} ($n = 1-3$), and 1-naphthol-(water)_{*n*} ($n = 1-21$), all prepared in a molecular beam. The occurrence of proton transfer on the picosecond time scale was observed for the ammonia clusters at a critical number of solvent molecules where $n = 3$, while for piperidine $n = 2$. The water clusters show no sign of short time scale (picosecond) dynamics for $n = 1-21$, indicating no evidence of proton transfer in these solvent clusters. To understand the nature of the transfer and the role of structural changes, we made the following studies: (1) accurate measurements of the transient decay and its form (biexponential, etc.); (2) the isotope effect; (3) the vibrational energy dependencies; (4) the effect of the number and type of solvent molecules. From these results, we describe a simple model which takes into account deprotonation by tunneling process, protonation, and solvent reorganization.

The distinct cluster size thresholds for proton transfer and the variation among different solvents was explained in the model by considering the thermodynamics of solvation and the Coulombic potential energies for the ion-pair state. Though we use a rather simple approach, important insights were gained. For example, the model is able to explain why 1-naphthol is a stronger acid than 2-naphthol and why a certain isomer of 1-naphthol-(NH₃)_{*n*} can be reactive. The barrier to proton transfer is due to a crossing of a covalent reactant state and a Coulombic ion-pair state. The characteristic proton-transfer times of 50–100 ps were well reproduced in the model by the simple tunneling between two states. The role of tunneling was examined and the origin of the barrier was tested by comparing calculated rates to the measured rates reported here and to other observations made elsewhere.

The importance of the local structure of solvent molecules in determining the proton-transfer dynamics was discussed. It is suggested that the overall dynamics of the transfer is governed by the interplay between the energetics and the solvent effective dielectric screening which determines the strength of the Coulombic interactions of the ion pairs. By considering the rates of deprotonation and protonation and the cluster size dependence, we conclude that the change in free energy with the structural changes shifts the equilibrium toward the acid as the cluster size increases. The critical value found for the number of solvent molecules ($n = 3$ for NH₃; $n = 2$ for piperidine; $n > 21$ for H₂O) for proton transfer elucidates the key role of the local structure on proton transfer, a central point to the argument made in bulk studies by Eigen, Robinson, and others. We are currently involved in further studies of the molecular dynamics under these stepwise solvation conditions in these and other acid-base reactions.

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Note Added in Proof. Very recent publications have reported on studies of the naphthol-water system in clusters (fluorescence) and ice crystals. The findings are relevant to the discussion in this paper. See: Oi, P.; *et al. Chem. Phys. Lett.* **1994**, 230, 322; Knochenmuss, R. D.; Smith, D. E. *J. Chem. Phys.* **1994**, 101, 7327. Also, see the article on complexes of 2-naphthol with cyclodextrins for structural modeling: Park, H.-R.; *et al. J. Phys. Chem.* **1994**, 98, 6158.

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