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Proton transfer dynamics and cluster ion fragmentation in phenol/ammonia clusters

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Excited-state proton transfer dynamics are reported for the phenol$(NH_3)_n$ cluster system. Excited-state proton transfer is shown to occur for this system by isotopic substitution of the hydroxyl proton and ammonia protons. The observed dynamics slow from 80 to 600 ps upon cluster deuteration. The effects of cluster vibrational energy and ammonia concentration in the expansion gas are also studied. The results of these experiments are compared with a previous study [Syage and Steadman, J. Chem. Phys. **95**, 2497 (1991)] which used a single excitation energy and varied ionization energy. Our experiments indicate that a significant amount of cluster ion fragmentation occurs for this system and caution must be exercised in assigning the decays observed in a given ion mass channel to a particular parent cluster. Due to the difficulties of associating a given decay curve with a cluster of particular mass, a previously proposed model of proton transfer in isolated clusters [Hineman *et al.*, J. Chem. Phys. **97**, 3341 (1992)] which details the effect of cluster vibrational energy on the proton transfer rate cannot be applied to the phenol/ammonia system.

I. INTRODUCTION

Proton transfer is an important component of many reactions. Because of this importance, many studies have been performed to determine the effects of pH, solvent, and hydrogen isotope on condensed phase proton transfer reactions.[1,2] One of the best methods for studying proton transfer involves excitation of a molecule which undergoes a substantial change in acidity upon excitation from its ground- to excited-state potential surface; commonly, aromatic alcohols are used. Excited-state proton transfer (ESPT) is employed because the light pulse used to excite the acid is a convenient "on switch" for the proton transfer. The pulse electronically excites the molecule, changes it pK_a ($\Delta pK_a \sim 8$), and serves as a time zero marker. In order to determine the effects of individual solute/solvent interactions on the proton transfer process, matrix isolation[3] and gas phase cluster[4–10] studies have been done. These studies have investigated both the spectroscopy and dynamics of systems which undergo ESPT. Systems which exhibit ESPT show strongly red shifted fluorescence and red shifted ionization potentials.

The gas phase cluster studies center on two proton donors—naphthol[4,5,7,9,10] and phenol[6,8]—and their clusters with various bases, such and ammonia, water, methanol, and various amines. We have previously published a study of proton transfer in naphthol/ammonia clusters which suggests a proton transfer mechanism based on proton tunneling and additionally accounts for the effect of vibrational energy on the cluster transfer dynamics.[10] We are therefore interested in applying this ESPT model to the phenol/ammonia system in order to make comparisons and to substantiate the model further. Syage and Steadman have studied the excited-state dynamics of phenol/ammonia clusters in molecular beams using time-resolved pump–probe photoionization spectroscopy[8] (Ref. 8 will hereafter be referred to as SS). Throughout these studies, the excitation wavelength was constant and the effect of variations in the amount of vibrational energy could not be assessed. The present study was initiated to extend the experiments of SS to encompass the effects of vibrational energy and hydrogen isotope substitution. Overlapping experiments were performed to verify the compatibility of the our data set with that of SS. We find essentially identical results under comparable experimental conditions.

Before we can discuss the present study, we emphasize the differences in the ionization/fragmentation models used in the two previous studies[8,10] to explain the observed kinetics. In our previous study of the naphthol/ammonia clusters, we proposed that a fast decay time observed for clusters which undergo ESPT is due to a change (decrease) in photoionization cross section upon proton transfer. Ionization was performed near threshold and no evidence of cluster ion fragmentation was observed. As such, this was the only probable explanation for the naphthol/ammonia system. In the study of phenol/ammonia clusters, ionization was considerably above threshold, and several ion fragmentation channels were observed. SS proposed a model for the signal decay which includes both the effect of changes in cross section and the effect of differences in cluster ion fragmentation efficiency following proton transfer in the S_1 excited state. This model is quite reasonable given the observation of a rise time in fragment ion $[(NH_3)_nH^+]$ mass channels. The model of SS for phenol/ammonia proton transfer is of course based on the observed fragmentation and includes different ionization cross sections for reactants and products. Nonetheless, SS attribute the decrease in ion signal associated with proton transfer to phenol/ammonia cluster fragmentation rather than a decrease in ionization cross section as is found for the naphthol/ammonia system.

In this report, we present a more extensive data set for the phenol/ammonia cluster system, including H/D substitution and variation of $S_1 \leftarrow S_0$ excitation. From these

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data, we conclude that while proton transfer does indeed occur for this cluster system, under these experimental conditions, one is not able to assign the specific dynamics (decay curves) observed uniquely to clusters of particular masses.

II. EXPERIMENTAL PROCEDURES

The technique employed to study the excited state dynamics of phenol/ammonia clusters is time-resolved, pump–probe photoionization spectroscopy with mass resolved detection. The apparatus for these studies has been described previously.[10] It consists of a mode-locked Nd/YAG laser which synchronously pumps two dye lasers (one containing R590 and the other DCM as the gain media) and seeds a Nd/YAG regenerative amplifier (repetition rate 10 Hz). The output of the regenerative amplifier then pumps two four-cell dye amplifiers which amplify the outputs of the two dye lasers. The result is two frequency tunable picosecond pulses which can be frequency doubled into the ultraviolet giving up to 250 μJ/pulse in each beam and pulse widths $\sim$6–8 ps. The pump beam for these experiments is obtained by summing the output of the R590 dye/amplifier system with $\sim$4 mJ of the 532 nm output of the regenerative amplifier. The ionization laser is the frequency doubled output of the DCM dye/amplifier system. The ionization laser wavelength was 335 nm. Tuning this laser further red (closer to threshold ionization) results in signals which are too weak to be usable. For experiments using 266 nm excitation, the 4 mJ of 532 nm radiation which is used to sum with the R590 laser output is doubled in the same KDP crystal. For the time-resolved pump–probe ionization experiments, the pump beam energy is 20–30 μJ, while the probe laser energy is 120–200 μJ. The instrument response function for the origin excitation experiments was $\sim$10–12 ps and for 266 nm excitation was $\sim$50 ps.

The phenol$(NH_3)_n$ clusters are formed in a jet expansion from a 0.5 mm diameter pulsed nozzle. The nozzle and phenol sample compartment are heated to 50 °C. At this temperature, the vapor pressure of phenol is approximately 2 Torr. The driving gas is 0.15%–1.5% NH_3 in He at 40 psig driving pressure. The resulting ratio (NH_3):(phenol) falls in the range 2:1 to 20:1.

The time of flight mass spectrometer has 1.25 cm grid spacings for both extraction and acceleration regions, followed by a 1.5 m drift tube and a microchannel plate detector. The extraction and acceleration voltages are 300 and 3700 V, respectively. This results in extraction/acceleration times of about 1 μs.

The data are fit to a two component time dependence (t_1,t_2) with an exponential rise, exponential decay, and amplitude (A_1,A_2) for each component. None of the signals appearing in phenol$(NH_3)_n^+$ mass channels evidences a rise time and therefore the experimental time dependencies are fit to a biexponential decay. The observed experimental time dependences found in the $(NH_3)_nH^+$ mass channels are fit to a biexponential rise. The decays are long compared to the time delay scanned in the experiments. The nonlinear fitting routine used to extract parameters from the data is based on the Levenberg–Marquardt algorithm.[11]

TABLE I. Decay parameters from fits of origin region excitation data (1.5% NH_3/He expansion gas at 40 psig). All times are in picoseconds. Ionization laser wavelength is 335 nm.

Ion	t_{rise}	t_{decay1}	t_{decay2}	A_1/A_2
$Ph(NH_3)_1$	0	>2000	···	···
$Ph(NH_3)_2$	0	80	1600	3.3
$Ph(NH_3)_3$	0	73	1300	2.0
$Ph(NH_3)_4$	0	100	>2000	0.23
$Ph(NH_3)_5$	0	>1500	···	···
$Ph(d_1)(ND_3)_2$	0	600	···	···
$Ph(d_1)(ND_3)_3$	0	1400	···	···

For isotopic substitution experiments, the hydroxyl proton on phenol is exchanged with D_2O. The phenol is then extracted from the water into benzene. The benzene is then removed under vacuum and the phenol dryed under vacuum for 2 hs. One and a half percent ND_3 in He is used as the expansion gas and the nozzle is again heated to 50 °C.

III. RESULTS

A. Time integrated spectra

The mass resolved excitation spectra and ionization threshold spectra of phenol/ammonia clusters have been reported previously.[6] Phenol$(NH_3)_1$ has a sharp origin feature at 35 710 cm^{-1} (280.03 nm) which is red shifted 650 cm^{-1} from the bare phenol origin at 36 360 cm^{-1}. The phenol$(NH_3)_2$ cluster has a progression in a low frequency mode at its origin, which is shifted by 820 cm^{-1} from the bare phenol origin. The phenol$(NH_3)_3$ cluster spectrum is broad and peaks 10 cm^{-1} to the red of the phenol$(NH_3)_1$ cluster origin. A continuous background in the excitation spectra of phenol$(NH_3)_n^+$ for $n=1,2$ is observed and is due to fragmentation from higher clusters, even at the lower ammonia concentrations detailed above. Obviously, given the broad spectra of the larger clusters, one cannot determine all the possible fragmentation patterns from the spectra. Fragmentation of phenol/ammonia clusters to yield $(NH_3)_mH^+$, in which m is not equal to the number of ammonia molecules in the parent cluster ion, is also reported in this system.[6] These results are verified in our studies and are in stark contrast to the results for the naphthol/ammonia cluster system.[10]

B. Dynamics

1. Origin excitation

Excited-state dynamics are measured following excitation of the S_1–S_0 origin transition for phenol$(NH_3)_n$ clusters. For $n=1$ and 2, sharp transitions are accessed for excitation, while for $n>3$ clusters, the maximum of the broad $n=3$ cluster spectrum is used for excitation. In all cases, ionization wavelength is 335 nm for these studies. The results of these experiments are collected in Table I. The phenol$(NH_3)_1$ cluster ion shows only a long time de-

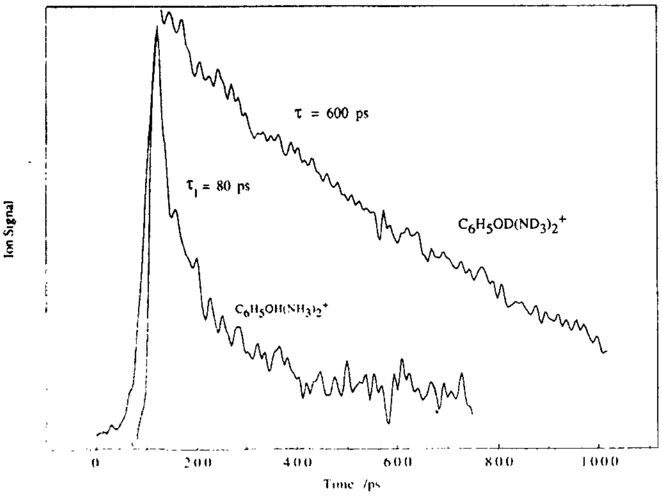

FIG. 1. The kinetic isotope effect for the signal observed in the phenol$(NH_3)_2^+$ mass channel (origin excitation and ionization laser at 335 nm). Expansion gas contains 1.5% ammonia in helium.

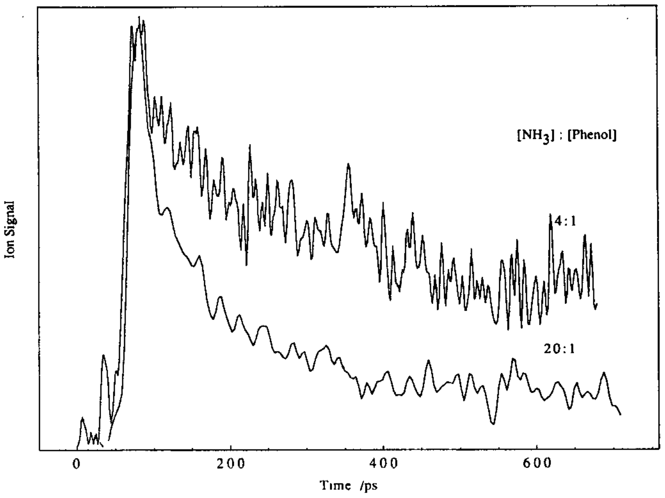

FIG. 2. Concentration dependence of the $Ph(NH_3)_2^+$ signal (origin excitation and ionization wavelength is 335 nm). Expansion gas contains 0.3% ammonia and 1.5% ammonia, respectively.

cay. Phenol$(NH_3)_n$, $n=2,3,4$, cluster signals have biexponential decays for which one of the decay components is fast (< 100 ps). No fast decay components are observed for phenol$(NH_3)_5$ clusters. We find that for origin excitation and 335 nm ionization, the $(NH_3)_mH^+$ mass channel signals are not strong enough to give useful pump–probe signals.

In order to determine the origin of this fast decay in the low mass channels, isotopic substitution experiments are performed. The results for the phenol$(NH_3)_2^+$ ion mass channel are shown in Fig. 1. All time-dependence curves shown in the figures are smoothed using a three point smoothing routine; however, all parameters in the tables are obtained from fits of the raw (unsmoothed) data. The time constant for the decay changes from 80 to 600 ps for the deuterated cluster. The phenol$(d_1)(ND_3)_3$ cluster ion signal is fit with a decay constant of 1400 ps. The substantial decrease in rate upon isotopic substitution is indicative of proton transfer by a tunneling mechanism. Similar results have also been observed by Syage.[12]

The observation of fast decays at low cluster ion mass channels ($n=2$ and 3) is unexpected and not consistent with known thermodynamic information[4,6] or the results of the naphthol/ammonia system.[10] In order to determine if these fast decays arise from the broad background of higher clusters fragmenting into the lower mass channels, the effect of ammonia concentration on the observed decays is studied. The results for the $n=2$ cluster ion mass channel are shown in Fig. 2. The fast component constitutes a much higher fraction of the total amplitude at higher ammonia concentrations. Since higher ammonia concentrations favor the production of larger clusters, this result suggests that the fast decaying part of the signal is indeed due to a larger parent cluster ion fragmenting into the $n=2$ mass channel. At low ammonia concentration $[(NH_3)/(\text{phenol})$ ratio 4:1], the larger cluster ion signals are not intense enough to give good pump–probe ionization signals. Note that the lowest solvent/solute concentration ratios used here (4:1) are still larger than the highest ratios used in the naphthol/ammonia study (3.5:1), even though clusters up to $n=5$ are observed in the naphthol case at this concentration ratio.[10] In order to detect phenol/ammonia cluster ions of the same size as naphthol/ammonia cluster ions, one must use significantly higher concentration ratios (approximately ten times higher for phenol than for naphthol).

2. A 266 nm excitation

Based on the previous naphthol study,[10] one expects that addition of vibrational energy to the cluster should increase the rate of the proton transfer reaction. The results of experiments in which the excitation wavelength is 266 nm and the ionization laser remains 335 nm are collected in Table II. With the extra neutral cluster S_1 energy and the extra cluster ion energy, a fast decay is observed in the phenol$(NH_3)_1^+$ mass channel as well as the phenol$(NH_3)_2^+$ mass channel. The effect of excitation energy on the phenol$(NH_3)_1^+$ signal is shown in Fig. 3. Again,

TABLE II. Decay parameters from fits of 37 580 cm^{-1} (266 nm) excitation data (1.5% NH_3/He expansion gas at 40 psig). All times are picoseconds. For all ammonia cluster–proton ions, the decay time is long (> 2000 ps). Ionization laser wavelength is 335 nm.

Ion	t_{rise}	t_{decay1}	t_{decay2}	A_1/A_2
$Ph(NH_3)_1$	0	150	···	···
$Ph(NH_3)_2$	0	52	1400	12.6
$Ph(NH_3)_3$	0	40	300	0.9
$Ph(NH_3)_4$	0	93	> 2000	0.34
$Ph(NH_3)_5$	0	> 1500	···	···
Ion	t_{rise_1}	t_{rise_2}	A_1/A_2	
$(NH_3)_3H$	50	···	···	
$(NH_3)_4H$	87	280	1.4	

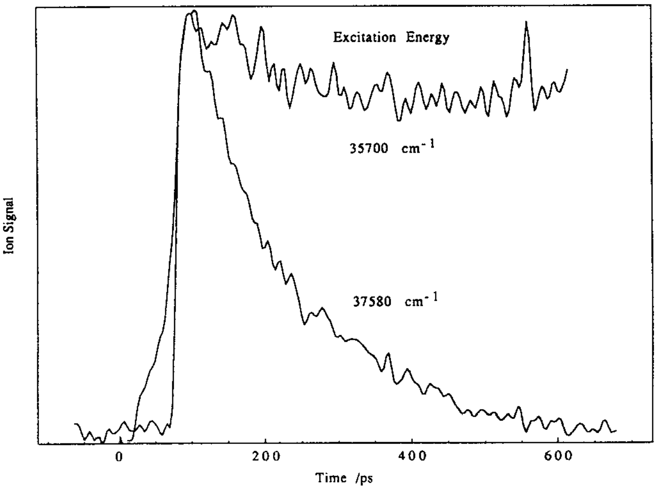

FIG. 3. Excitation energy dependence of the Ph$(NH_3)_1^+$ signal. Expansion gas contains 1.5% ammonia in helium.

isotopic substitution experiments confirm that both the $n=1$ and 2 mass channel fast decay signals arise from proton tunneling events. Note, however, that the time constants for the decays are not significantly different from those of the origin excited clusters which exhibit decays. The observed fast decay is ammonia concentration dependent. No fast decay component is observed in the phenol$(NH_3)_1^+$ mass channel at low ammonia concentrations (4:1). The fast decay component of the phenol$(NH_3)_2^+$ mass channel signal decreases in amplitude relative to the long lived component with decreasing concentrations. The same concentration dependence is observed for this mass channel with origin excitation.

For the larger clusters [phenol$(NH_3)_n$, $n=3$,4, and 5], the present results match those of SS with 266 nm excitation and 355 nm ionization wavelengths. The fast decaying components are very small and most of the signal is due to the long lived component.

At this high excitation energy, the signals in the $(NH_3)_mH^+$ mass channels are intense enough to allow pump–probe experiments to be performed. The results are presented in Table II. These signals rise with a time constant of less than 100 ps and the $(NH_3)_4H^+$ mass channel shows a biexponential rise—the longer rise time is approximately 300 ps. Again, the $n=4$ results match the results of SS for equivalent excitation and ionization energies; however, the concentration dependent results indicate that phenol$(NH_3)_m^+$ and $(NH_3)_mH^+$ ions originate from different parent molecules.

The signal intensity in the $(NH_3)_mH^+$, $m=3$, 4, and 5 mass channels relative to that in the phenol$(NH_3)_m^+$ mass channels increases with increasing ammonia concentration. At low ammonia concentrations, the signals in the $(NH_3)_mH^+$ mass channels are too weak to obtain pump–probe signals.

IV. DISCUSSION

A. Phenol$(NH_3)_2^+$ and phenol$(NH_3)_1^+$ time dependence

The observation of a fast time decay for the $n=2$ mass channel excited at the cluster origin is surprising. Isotopic substitution experiments show that the decay is due to proton tunneling, yet naphthol, which is stronger excited state acid, does not exhibit proton transfer until it is clustered with three ammonia molecules.[10] A simple calculation of the thermodynamics of the proton transfer, using the observation that naphthol transfers at $n=3$ and assuming that binding energies are roughly the same for the two systems, predicts that phenol should have a cluster size threshold for proton transfer at $n=4$ or 5. [This uncertainty in the predicted phenol threshold is due to uncertainty in naphthol/ammonia reaction thermodynamics, i.e., ESPT in naphthol$(NH_3)_n$ may be only slightly favorable at $n=3$ or may be only slightly unfavorable at $n=2$.] Most likely the clusters which give rise to the proton transfer dynamics observed in the phenol$(NH_3)_2^+$ mass channel are larger ($n \geqslant 4$) clusters which fragment to the lower mass channel. These same clusters probably give rise to the broad background observed to be associated with the low mass channels ($n<3$) in the excitation spectra.

The concentration dependence of this signal also suggests that the signal is due to fragmentation of larger clusters. Changing the ammonia concentration changes the distribution of cluster sizes formed in the jet and thereby changes the relative importance of various parent cluster contributions to a given mass channel signal. Thus, if both the fast and slow components of the $n=2$ mass channel signal are from $n=2$ parent clusters, the relative amplitudes would not be expected to vary with ammonia concentration. The decay times of the fast component also vary slightly with concentration, although the low concentration results are relatively noisy. This indicates that more than one parent cluster may fragment into a given mass channel and thus ammonia loss for each cluster is not fixed.

The ionization energy could be lowered in order to minimize the amount of fragmentation in the cluster ion; however, the cross section for ionization drops rapidly below the employed ionization energy making pump–probe experiments difficult. In the experiments reported here, nearly 10 000 cm^{-1} of excess energy is placed in the large cluster ions ($n \geqslant 4$). This extra energy may account for the extensive cluster fragmentation into many different daughter ions.

Attempts to sort out the fragmentation pathways can also be made using the technique of laser/nozzle delay.[13] In this technique, the rising edge of the gas pulse is examined by adjusting the nozzle delay time with respect to the firing of the laser. Larger clusters form later in the expansion than smaller clusters or monomers and therefore each parent cluster size has a different appearance time with respect to nozzle opening. These experiments are more useful, however, for small clusters with sharp spectra than for large clusters with broad spectra. Additionally, the time separation between successively larger clusters decreases reducing the resolution of the technique. The broad spectra of large clusters allow several clusters to be excited simultaneously, and if the cluster fragmentation patterns are complex, several parents may contribute to the signal in a given mass channel. The rise of signal in that mass channel would not be sharp and would not correspond to the rise for any specific cluster. The laser/nozzle delay studies for the phenol/ammonia clusters only confirm that the broad background in the $n=2$ cluster ion excitation spectrum is due to clusters larger than $n=2$. Identification of an exact cluster size is unfortunately not possible. One is thus not able to identify an observed signal rise or decay with a cluster of specific mass. Thus, a detailed quantitative cluster proton transfer model cannot be applied to the kinetics observed in the phenol$(NH_3)_2$ mass channel.

The phenol$(NH_3)_1$ mass channel shows only a slow decay following origin (280 nm) excitation, but shows a fast component following 266 nm excitation. Excitation at 266 nm provides the cluster with an additional ~2200 cm^{-1} of vibrational energy. Isotopic substitution experiments confirm that the fast time decay observed in the $n=1$ mass channel following 266 nm excitation is indeed due to proton transfer. Certainly, this signal is due to larger clusters fragmenting into the $n=1$ mass channel, as the concentration dependence demonstrates. We suggest that 266 nm excitation provides sufficient energy to fragment larger clusters (which undergo proton transfer) into the $n=1$ mass channel. Moreover, the spectrum of phenol$(NH_3)_1$ is sharp and structured, and may have little absorption at 266 nm. This would contribute to the observed dynamics being dominated by fragmentation of larger clusters.

An alternative explanation can also be suggested. Large clusters which undergo proton transfer with 266 nm excitation and fragment into the $n=1$ mass channel may have a large barrier to proton transfer and thus the proton transfer rate following 280 nm excitation is slow. The observed decay following origin excitation would then just be the phenol S_1 lifetime. While this possibility may seem unlikely, it cannot be excluded based on our results.

B. The effect of vibrational energy

The model of proton transfer proposed for the naphthol/ammonia system[10] predicts a substantial cluster vibrational energy effect on proton transfer in the cluster size range $n<6$. Nonetheless, the observed time constants for 266 nm excitation (~2200 cm^{-1} of vibrational energy in the large clusters $n\geqslant 3$) do not decrease significantly. As mentioned above, deuteration studies show that the observed decays are indeed due to proton transfer. One possible explanation for the apparent absence of S_1 vibrational energy dependence of the proton transfer rates is that the cluster distribution which contributes to a given mass channel for origin excitation may not be the same as that which contributes to the same mass channel with 2200 cm^{-1} of additional vibrational energy in S_1. In fact, the increased $(NH_3)_nH^+$ signals at the higher excitation energy suggests that the fragmentation patterns are indeed different at different excitation energies.

Because of the uncertainty in fragmentation pathways and cluster ion parentage, the proton transfer model used to interpret the naphthol/ammonia results quantitatively[10] (or any model which predicts cluster size dependent proton transfer rates) cannot be applied to the present data for phenol/ammonia. Qualitatively, increased vibrational energy is expected to increase the proton transfer rate; however, the cluster distribution giving rise to the proton transfer dynamics observed in any mass channel cannot be sorted out at either of the excitation energies used. Furthermore, no correlation or correspondence between the two fragmentation distributions at the two energies can be achieved. As a result, not even qualitative expectations for the observed rates can be generated.

C. A comparison with previous studies

The experiments in this study can be compared with those reported in Ref. 8. Two different experiments are reported in Ref. 8: (1) 266 nm excitation and 355 nm ionization; and (2) 266 nm excitation and (two photon) 532 nm ionization. In both cases, the ammonia concentration is considerably higher than in our studies, but the apparatuses and expansion conditions are otherwise quite similar. With respect to the first set of experimental conditions, our results are consistent with those of Ref. 8 for the same mass channels, although only the present study reports decays for the $n=1$ mass channel. For the second set of experimental conditions reported in Ref. 8, considerable excess energy is placed into the cluster ions. (The photon energies correspond to an excess energy of almost 19 000 cm^{-1}, but some of this energy may be removed by the photoelectron.) This excess energy results in extensive fragmentation of phenol/ammonia clusters $n=1,...,7$. Under these conditions of excitation and ionization, a dominant 65 ps decay is reported for $n=5$, 6, and 7 clusters. We observe no time dependence at lower energy excitation and ionization and at lower concentration in these mass channels. Our results show both fast and slow signal decay components in mass channels $n=1,...,4$ only.

V. CONCLUSIONS

S_1 dynamics of the phenol/ammonia cluster system are determined by isotopic substitution to be due to a proton tunneling event. By comparison with naphthol/ammonia experimental and theoretical results, we conclude that the observed decay times are due to a proton transfer reaction [i.e., $PhOH(NH_3)_n \rightarrow PhO^-(NH_3)_nH^+$] which takes place in the S_1 excited electronic state of the neutral cluster. Significant fragmentation of the clusters is observed following ionization with ~10 000 cm^{-1} of excess energy. The dynamics observed in a specific mass channel cannot be assigned to a specific parent cluster as the fragmentation pathways are a function of excess energy in the cluster ion. Because of these complications, the phenol/ammonia cluster system cannot be used as a further test of the model for proton transfer proposed in earlier work on the naphthol/ammonia system. The naphthol/ammonia cluster system serves as a test case for the proton transfer model because it does not exhibit significant cluster ion fragmentation at the ion energies probed.

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