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Toluene–ammonia clusters: Ion fragmentation and chemistry

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The toluene/ammonia cluster system is studied by mass resolved excitation spectroscopy: like the toluene/water system, an extensive ion chemistry is found to exist generating ammonia solvated protons and (solvated) benzyl radicals. Extensive cluster fragmentation (dissociation) is observed even at "threshold ionization energies." Nozzle delay and deuteration studies are applied to elucidate the ion chemistry and dissociation of this cluster system. Proton transfer/cluster fragmentation reactions in this system are driven by the stability of the benzyl radical and $(NH_3)_mH^+$ and solvation stabilization of the toluene ion. Cluster fragmentation by loss of a single ammonia molecule is not observed. Fragmentation is so extensive for this system that spectral features could not be identified with parent clusters.

I. INTRODUCTION

Available evidence[1,2] suggests that clusters between an aromatic species and various small polar solvent molecules (e.g., NH_3, H_2O, ROH) can undergo extensive chemistry upon cluster ionization even at near threshold energies. Recent studies of the toluene/water cluster system[3] show this quite clearly. Our studies of this system demonstrate: (1) nearly complete fragmentation of $C_6H_5CH_3^+(H_2O)_n$ to $C_6H_5CH_3^+(H_2O)_{n-1}$ ($n = 1,...,5$) and $C_6H_5\dot{C}H_2$ and $(H_2O)_mH^+$ ($3 \leqslant m \leqslant n$); (2) apparently single cluster conformations for toluene$(H_2O)_n$, $n = 1,...,4$; and (3) toluene $(H_2O)_n$, $n = 2,...,6$, clusters all appear to have the water molecules clustered together.

The above behavior is not typical for clusters containing organic species and nonpolar solvents. Little if any fragmentation is observed upon threshold or even higher ionization[4] and no ion chemistry is reported for these systems. These differences between cluster ion behavior for polar and nonpolar solvents arise from the binding energies for the various cluster electronic states and the Franck–Condon factors for the $I \leftarrow S_1$ photoinduced transitions. The polar solvent cluster ion in its equilibrium configuration is much more tightly bound than its comparable parent neutral cluster and the Franck–Condon factors for the $I \leftarrow S_1$ transition even at threshold for the transition favor $\Delta v \neq 0$. The equilibrium geometry for the polar solvent cluster ion is much different than that for the neutral polar solvent cluster: this is unlike the situation for the typical nonpolar solvent–organic molecule cluster. Thus, polar solvent–organic molecule cluster ions are created (by absorption of a photon) in a very highly excited vibrational state, far from their equilibrium configuration, in a region of their potential surface with a very high density of chromophore and van der Waals vibrational states: cluster ion fragmentation, chemical reaction, and intracluster vibrational redistribution are to be expected under such circumstances.

The structure of the toluene$(NH_3)_1$ cluster has not been determined experimentally nor can we find a calculated configuration for this cluster in the literature. In this report, we present calculations based on a number of different potential parameters which suggest a reasonable structure for toluene$(NH_3)_1$. In principle, structural calculations for toluene$(NH_3)_n$ clusters would be quite valuable but since cluster structure calculations in these instances are governed to a considerable extent by NH_3–NH_3 interactions depending on lone pair-hydrogen bonding interactions which are difficult to model well, we do not report such calculated structures.

One-color mass resolved excitation spectra (one-color MRES) have been obtained for toluene/ammonia clusters.[1] Spectra are observed in the $(NH_3)_1H$ mass channel which are also identified with the toluene$(NH_3)_1$ mass channel. These features were assigned to the parent cluster toluene $(NH_3)_1$. The reaction

$$C_6H_5CH_3^+(NH_3)_1 \rightarrow C_6H_5\dot{C}H_2 + (NH_3)_1H^+$$

was proposed because it is energetically consistent with the known benzyl radical and NH_3 proton affinities, 839 ± 8 kJ/mol and $854 + 10$ kJ/mol, respectively. In the present studies this dissociation reaction cannot be confirmed.

The studies presented in this report parallel those for the toluene/water system discussed in the preceding paper.[3] The effort reported herein deals with (1) identification of the parent cluster for each transition observed in a given mass channel for mass resolved excitation spectroscopy, and (2) any cluster structural information which can be extracted from these experiments.

II. EXPERIMENTAL PROCEDURES

The experiments performed on this system are identical to those discussed in the preceding paper for toluene/H_2O clusters.[3] The concentration of ammonia employed is typically about 0.1% in the helium carrier gas. The expansion gas is dried by passing it through a NaOH filter.

III. RESULTS

In order to elucidate the ion chemistry and fragmentation reactions for the toluene/ammonia cluster ion system, the cluster parentage for each spectroscopic $S_1 \leftarrow S_0$ transition feature must be determined. As demonstrated in the preceding paper concerning the toluene/water cluster system this can be done in two different ways: following the same spectroscopic features through a series of mass channels and determining the highest mass channel in which they

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can be identified; and employing the nozzle/laser time delay technique discussed in the preceding paper. The details of these two procedures are enumerated below and in the process complete fragmentation of the clusters independent of ionization energy is demonstrated and some of the fragmentation and reaction patterns are revealed. Because the cluster spectra of toluene$(NH_3)_m$, $m \geqslant 3$ are all broad and only two sets of features (**a–d**, **e–j**) belonging to different clusters are identified in the nozzle/laser delay experiment, we are unable to identify uniquely spectral features with clusters of given size.

A. One-color mass resolved excitation spectra

One-color mass resolved excitation spectra (one-color MRES) observed in the $(NH_3)_{1,2}H$ and toluene$(NH_3)_{1,2}$ mass channels are presented in Fig. 1(a)–1(d) and one-color MRES observed in the $(NH_3)_3H$ and toluene$(NH_3)_3$ mass channels are presented in Fig. 2. Surprisingly no tunable transitions can be identified in the latter two mass channels. Even two-color MRES detected in the latter two mass channels do not evidence any tunable features. The features not labeled in Fig. 1 are shown to be due to mixed toluene/NH_3/H_2O clusters as indicated below.

These spectra are superficially similar to those found for the lower mass channels in the toluene/H_2O cluster system, but some significant differences between the spectra of the two cluster systems should be noted: (1) $(NH_3)H^+$ and $(NH_3)_2H^+$ fragments are observed; (2) the spectral overlap between channels does not lead to a readily defined set of parent clusters for the toluene/NH_3 system since toluene $(NH_3)_1$, $(NH_3)_2H$, and toluene$(NH_3)_2$ mass channels share common features with no obvious parent clusters; (3) spectra for toluene$(NH_3)_m$ $m \geqslant 3$ are broad and featureless; and (4) in general, total fragmentation for toluene/NH_3 clusters appears to be the rule and rather than the exception. At this point, one can only question if the features **a** through **d** in Fig. 1(a) and 1(b) are due to the toluene $(NH_3)_1$ parent species; these transitions all have the same concentration dependence for ammonia varied been 0.02 and 10% in the expansion mixture.

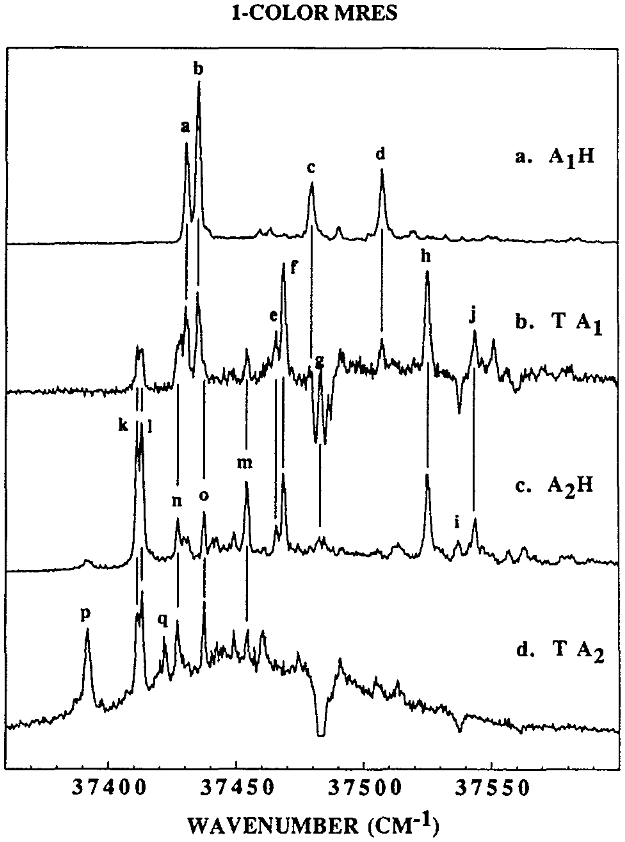

FIG. 1. One-color mass resolved excitation spectra of toluene/ammonia clusters observed in the following mass channels: (a) $(NH_3)_1H^+$, (b) toluene$(NH_3)_1$, (c) $(NH_3)_2H^+$, and (d) toluene$(NH_3)_2$. Features labeled are discussed in the text. The mass channel designations in the figure (A_iH or TA_j) refer to the detection channels not the parent cluster channels.

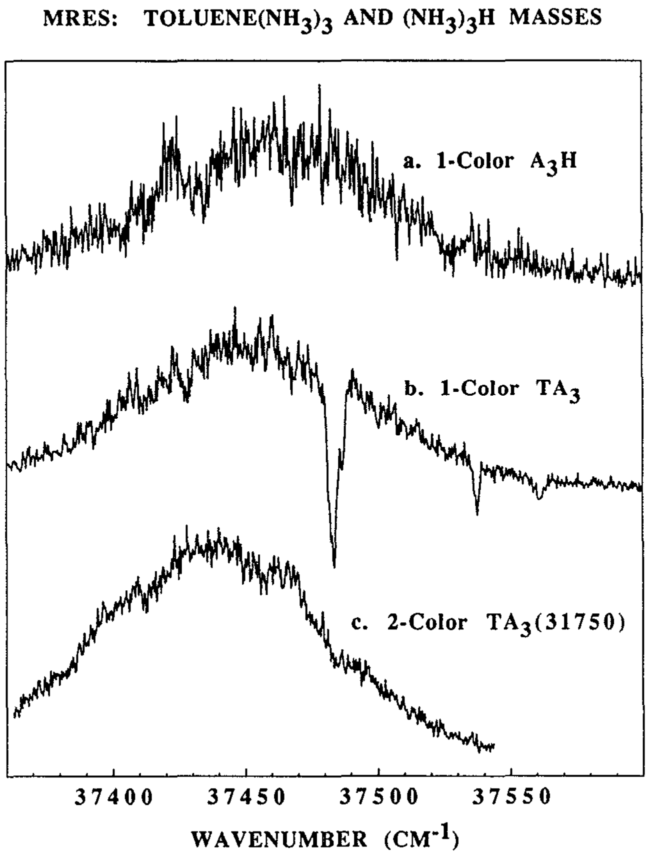

FIG. 2. One/two-color mass resolved excitation spectra of toluene/ammonia clusters observed in the following mass channels: (a) $(NH_3)_3H^+$, (b) toluene$(NH_3)_3$, and (c) toluene$(NH_3)_3$. Traces **c** and **b** differ in ionization energy by nearly 6000 cm^{-1}.

The one-color MRES observed in the $(NH_3)(H_2O)H$ mass channel is presented in Fig. 3(a). It can be compared with those found in the toluene $(NH_3)_1$ mass channel with and without a NaOH filter to trap water contamination presented in Fig. 3(b) and 3(c). The features at 37 551, 37 570, 37 605, and 37 617 cm^{-1} can be identified with toluene $(NH_3)_n(H_2O)_1$, $n \geqslant 1$ clusters. A NaOH filter in the expansion gas mixture line eliminates any possible features due to toluene/water contamination and toluene/water/ammonia contamination.

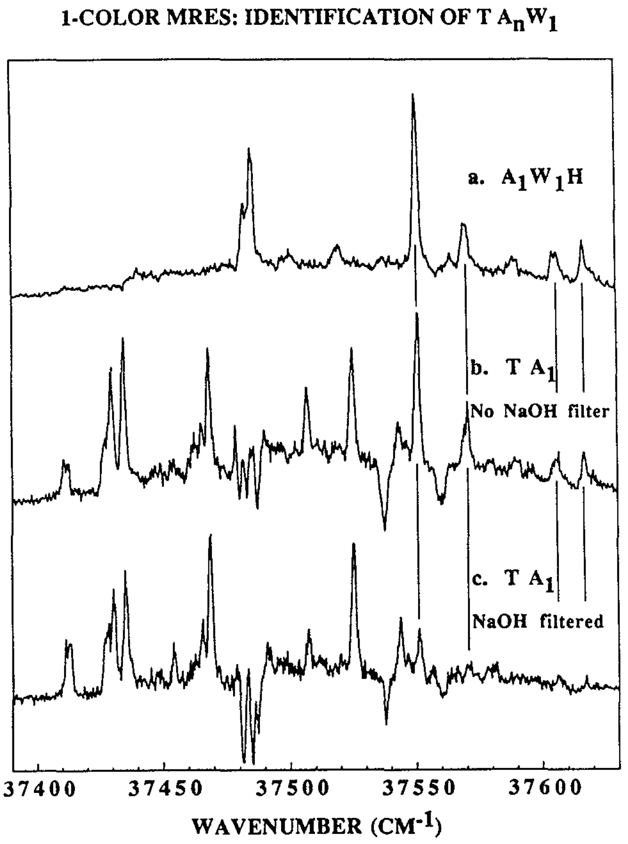

FIG. 3. One-color mass resolved excitation spectra of toluene/ammonia/water clusters observed in the following mass channels: (a) $(NH_3)_1(H_2O)_1H^+$, (b) toluene$(NH_3)_1$, (c) toluene$(NH_3)_1$. The important difference between c and b is that a dry NaOH filter has been installed before the nozzle to absorb residual water from the system.

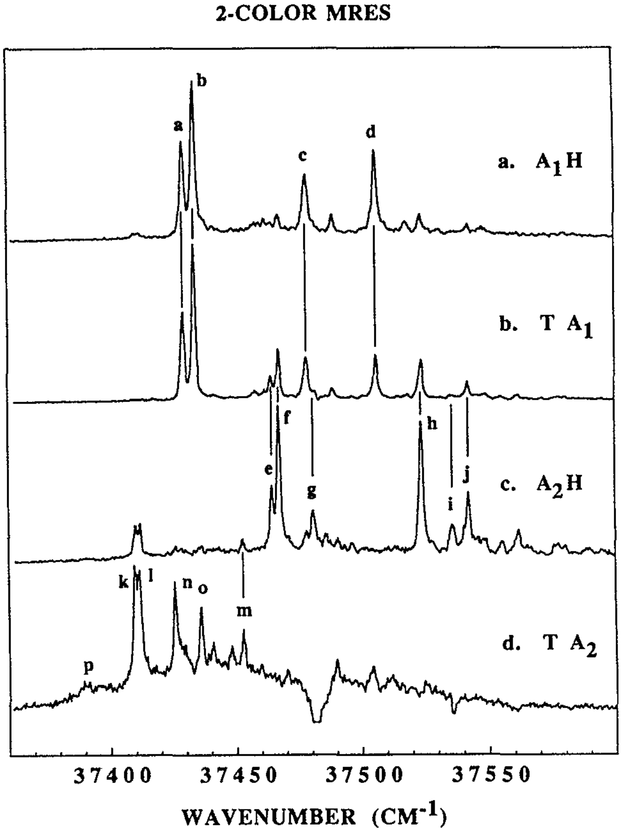

FIG. 4. Two-color mass resolved excitation spectra of toluene/ammonia clusters, with a second photon energy of 33 670 cm^{-1}, observed in the following mass channels: (a) $(NH_3)_1H^+$, (b) toluene$(NH_3)_1$, (c) $(NH_3)_2H^+$, and (d) toluene$(NH_3)_2$. Features are labeled as in Fig. 1. The mass channel designations in the figure (A_iH or TA_j) refer to the detection channels not the parent cluster channels.

B. Two-color mass resolved excitation spectra

Two-color mass resolved excitation spectra with ionization laser energy ($I \leftarrow S_1$) at 33 670 cm^{-1} (about 60 cm^{-1} above the toluene threshold) detected in mass channels $(NH_3)_{1,2}H$ and toluene$(NH_3)_{1,2}$ are presented in Fig. 4(a)–4(d). Transitions **k** through **o** [see Fig. 1(b) and 1(c)] are no longer found in the toluene $(NH_3)_1$ mass channel due to the reduced ionization energy. The spectral pattern in the $(NH_3)_1H$ mass channel is, however, not changed by this nearly 4000 cm^{-1} reduction in ionization energy. Transitions **e** through **j** [Fig. 1(b)] are still quite intense in both the $(NH_3)_2H$ and toluene $(NH_3)_1$ mass channels but do not appear in other channels. Thus, complete fragmentation exists in these toluene/ammonia clusters systems even at this low ionization energy. The intensities of transitions **p** and **q** are highly sensitive to toluene concentration.

Figure 5 presents toluene/ammonia cluster spectra detected in different mass channels and with different (lower) ionization energies ($I \leftarrow S_1$). These spectra should be compared with those of Figs. 1 and 4. Figure 5(a) shows the toluene mass channel with a new feature to the red of the toluene origin. Since the ionization energy is roughly 800 cm^{-1} below that required to ionize toluene the extra features observed in the toluene mass channel must arise from toluene/ammonia cluster fragmentation. The toluene 0_0^0 signal is due to residual one-color intensity for the strong toluene 0_0^0 resonance.

Transitions **e–j** which should appear in the $(NH_3)_2H$ [Figs. 1(c) and 4(c)] and toluene$(NH_3)_1$ [Fig. 1(b) and 1(c)] mass channels are missing in Fig. 5(b) and 5(c) due to the reduced ionization energy. These signals do not appear in other mass channels at lower ionization energies (even at threshold) and therefore total fragmentation occurs for their parent cluster following ionization.

Considering the above results, the observed transitions for the toluene/ammonia cluster system can be organized into several categories: (1) transitions **a–d** which only appear in $(NH_3)_1H$ and toluene$(NH_3)_1$ mass channels; (2) transitions **e–j** which only appear in toluene$(NH_3)_1$ and $(NH_3)_2H$ mass channels and disappear completely at low ionization energy; (3) transitions **k–m** which appear in the $(NH_3)_2H$ and toluene$(NH_3)_2$ mass channels; (4) transitions **n** and **o** which appear in the $(NH_3)_2H$ and toluene$(NH_3)_2$ mass channels at high ionization energy and only in the toluene$(NH_3)_2$ mass channel at low ionization energy; and (5) **p** and **q** which depend dramatically on the toluene concentration and appear in the $(NH_3)_2H$ and toluene$(NH_3)_{1,2}$ mass channels. Additionally, we note that

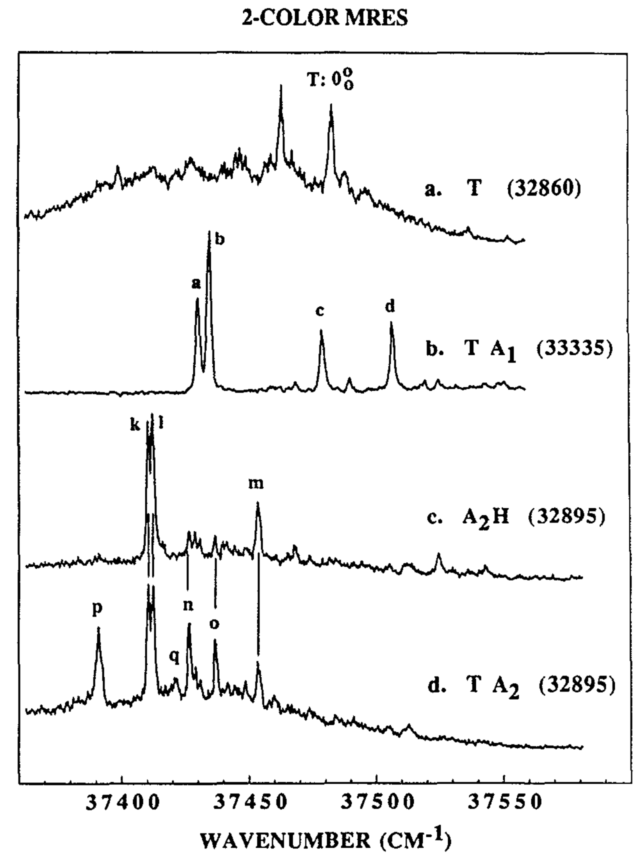

FIG. 5. Two-color mass resolved excitation spectra of toluene/ammonia clusters, with much reduced second photon energy (in parentheses), observed in the following mass channels: (a) toluene, (b), toluene$(NH_3)_1$, (c) $(NH_3)_2H^+$, and (d) toluene$(NH_3)_2$. Features are labeled as in Fig. 1.

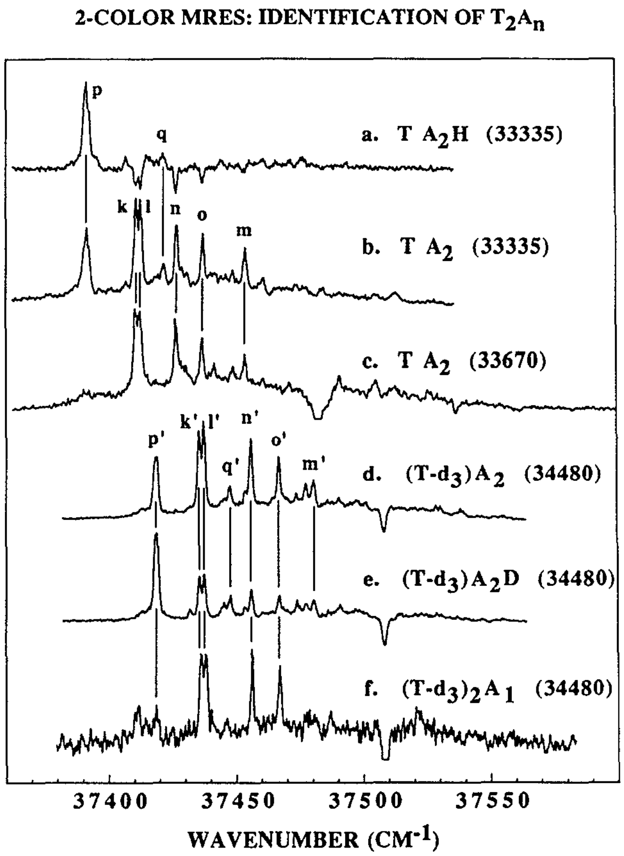

FIG. 6. Identification of parent clusters as $(\text{toluene})_m(NH_3)_n$ for features **k** through **q**. Toluene–h_3/ammonia is used for traces (a)–(c) and toluene–d_3/ammonia is used for trace (d)–(f): (a) toluene$(NH_3)_2H^+$, (b) toluene$(NH_3)_2$, (c) toluene$(NH_3)_2$, (d) toluene–$d_3(NH_3)_2$, (e) toluene–$d_3(NH_3)_2D^+$, and (f) $(\text{toluene–}d_3)_2(NH_3)_1$. The important difference between **c** and **b** is reduced toluene concentration. Features for toluene$(NH_3)_n$ are labeled by unprimed letters as in Fig. 1, and features for toluene–$d_3(NH_3)_n$ are labeled with corresponding primed letters.

transitions **k–q** also appear in the toluene$(NH_3)_2$H mass channel under various ionization conditions as will be discussed below.

C. Toluene–d$_3$/ammonia clusters

To help determine the cluster parentage of some of the observed signals in the various mass channels, toluene–d_3 clusters can be studied. These systems can help eliminate the possibility of toluene/H_2O/NH_3 cluster contributions, to determine if reactions of the form

$$\text{toluene}^+\text{–}d_3(NH_3)_n \rightarrow \text{benzyl radical–}d_2(DNH_2) + (NH_3)_{n-1}H^+ \quad (1)$$

can occur, and to determine if toluene dimer/ammonia clusters contribute to these observations.

Figure 6 presents features **k–q** and **k′–q′** (the toluene–d_3 analogue of **k–q**) as a function of ionization energy and toluene methyl rotor deuteration. Figure 6(a)–6(c) contain spectra for the protonated sample and Fig. 6(d)–6(F) contain spectra for the deuterated sample. These spectra suggest that the benzyl radical is generated and that the parent cluster(s) associated with the features **k–q** and **k′–q′** is(are) $(\text{toluene})_m(NH_3)_n$, $m,n \geqslant 2$.

As pointed out above, spectra of toluene/ammonia clusters can also be observed in the $(NH_3)_m$H mass channels. For toluene–d_3 $(NH_3)_n$ one might expect that the internal proton exchange reaction Eq. (1) might occur as it is identified for the toluene/water system.[3] Transitions **a′–d′** [Fig. 7(a) and 7(b)] are clearly identified in the $(NH_3)_1$D mass channel but not in the $(NH_3)_1$H mass channel when toluene–d_3/ammonia is studied. In like manner, features **e′–j′** [in Fig. 7(c) and 7(d)] can be observed in the $(NH_3)_2$D but not the $(NH_3)_2$H mass channel. Note that features **k′–q′** also appear in the spectra reported in Fig. 7 and must arise from $(\text{toluene–}d_3)_m$ $(NH_3)_n$ clusters [$(NH_3)_2$D] and from reactions involving ammonia/ammonia proton transfer generating the NH_2 radical[2] [$(NH_3)_1$H].

D. Time resolved studies

Two types of time resolved or delay studies have been carried out for the toluene/ammonia cluster system: time delay pump/probe experiments in which the lifetime of the clusters at the intermediate step in the ionization process (i.e., involving S_1 or even perhaps other neighboring states) is monitored; and nozzle-laser firing delay measurements which distinguish neutral clusters of various masses due to their creation and flight times.

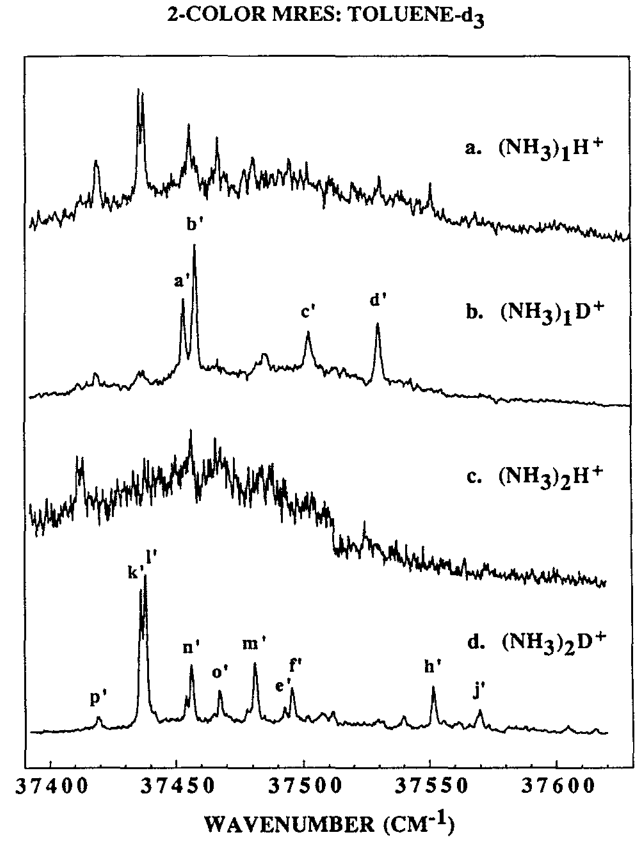

FIG. 7. Two-color mass resolved excitation spectra of toluene–d_3/ammonia clusters, with the second photon energy of 34 480 cm^{-1}, observed in the following mass channels: (a) $(NH_3)_1H^+$, (b) $(NH_3)_1D^+$, (c) $(NH_3)_2H^+$, and (d) $(NH_3)_2D^+$. Primed and unprimed features correspond to deuterated and nondeuterated samples, respectively. No H/D exchange can be identified for features **a'** through **j'**. The observation of features **k'** through **q'** in the $(NH_3)_1H^+$ mass channel indicates H/D exchange involving $(toluene)_2$.

The latter nozzle delay experiment proved to be important for unraveling the parentage of the toluene/water cluster fragments. Here, for the toluene/ammonia cluster system, an even more complex and puzzling pattern of fragmentation behavior is observed. For toluene/water clusters the delay between toluene and toluene$(H_2O)_2$ signal is roughly 5 μs, the delay between toluene$(H_2O)_3$ and $(H_2O)_4$ signals is about 2 μs, and the delay between toluene$(H_2O)_5$ and $(H_2O)_6$ signals is about 1.5 μs. Thereby, spectral features can be identified with their parent clusters through the delay time between the signal appearance and the nozzle opening. Figure 8 presents the delay curves for the toluene–d_3/ammonia cluster signals detected with two-color MRES. The first signal to appear is, of course, toluene–d_3. Features **b'** and **d'** appear at a 7.5 μs delay, **f'** and **h'** are delayed 3 μs more, and **k'**, **n'**, **p'** are 1 μs delayed from **f'** and **h'**. One can conclude from these data that transitions **b'** and **d'** are due to toluene–$d_3(NH_3)_3$ or $(NH_3)_4$ and that the parent cluster for transitions **f'** and **h'** is probably toluene–$d_3(NH_3)_5$ to toluene–$d_3(NH_3)_7$. Such an assignment is consistent with the toluene/water system determination.[3]

The two-color delay measurement on these signals shows that the intermediate state lifetime is ca. 70 ns. This

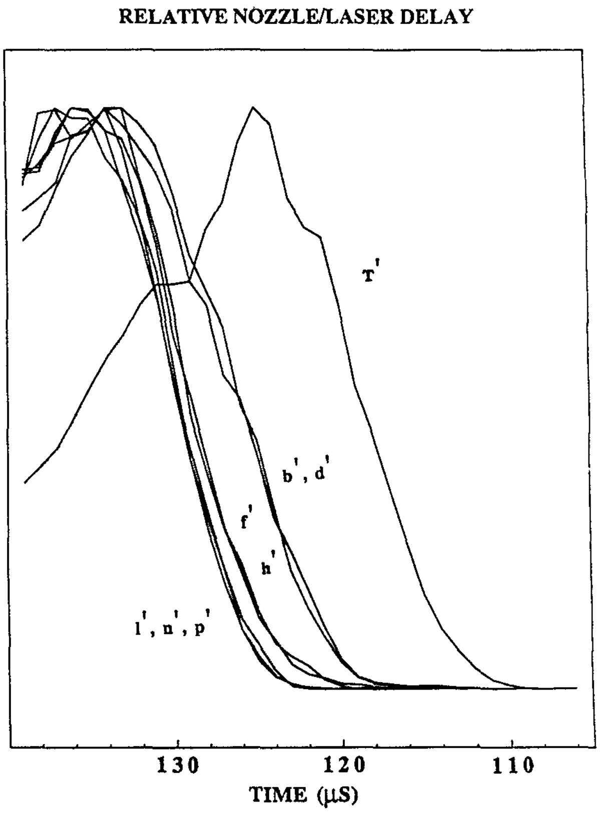

FIG. 8. Pulsed-nozzle/excitation-laser timing effect on signal intensities. Unlike the toluene/water system, parent cluster mass cannot be uniquely determined from the observed curves due to the absence of features between the curves for *T* and **b'**, **d'**. Most likely **b'**, **d'** are due to toluene–$d_3(NH_3)_3$ or $(NH_3)_4$ and **f'**, **h'** are due to toluene–$d_3(NH_3)_5$ to $(NH_3)_7$.

lifetime shows that only the S_1 state is involved as an intermediate.

E. Threshold ionization or appearance energies

Typical ionization action spectra are presented in Fig. 9 for the toluene$(NH_3)_{1,2}$ mass channels. All other action

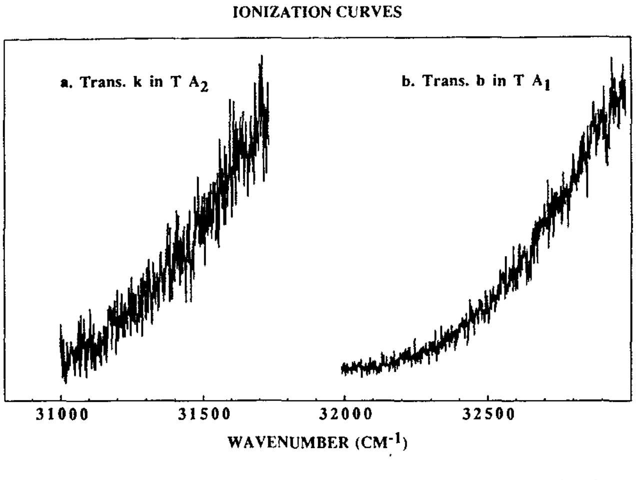

FIG. 9. Ionization action curves. (a) Transition **k** observed in the toluene$(NH_3)_2$ mass channel, and (b) transition **b** observed in the toluene$(NH_3)_1$ mass channel.

TABLE I. Apparent ionization energy of toluene$(NH_3)_n$ in cm^{-1} as detected by the appearance of observed different fragment signals. The numbers in parentheses are the excess energies associated with the one-color ionization for each parent species and fragment.

Transition	Toluene	37 463 cm^{-1}[a]	a–d	e–j	k—m
Observed in mass channel:					
Parent $T(NH_3)_n$	71 090 (3,870)				
Fragment $T(NH_3)_k$		68 550 (6,380)	69 685 (5,185)		68 540 (6,280)
Fragment $(NH_3)_mH^+$			70 735 (4,135)	70 365 (4,575)	68 540 (6,280)

[a] See Fig. 5(a)—fragment feature in toluene mass channel.

spectra taken in this manner are similar. Toluene$(H_2O)_n$ clusters have similar behavior.[3] Such spectra arise from large changes in the equilibrium geometry of the cluster between the neutral states (S_0,S_1) and the ionic state. The Franck–Condon factor for the $I \leftarrow S_1$ transition is such that $\Delta v \gg 0$. This transition is then responsible for the nearly total fragmentation observed in the toluene/ammonia cluster system.

The resulting apparent ionization thresholds and reaction appearance energies are listed in Table I. The appearance energies are considerably lower in general than those found for the toluene/water system.

F. Calculations

Employing standard Lennard-Jones potential parameters and *ab initio* (GAUSSIAN-88, 3-21G*) and semiempirical (MOPAC 6 AM1 Hamiltonian) partial atomic charges, cluster energy minimization calculation yields a single toluene $(NH_3)_1$ cluster structure as depicted in Fig. 10. In this structure the hydrogen atoms of ammonia are coordinated to the π system of the aromatic ring. The general structure is quite similar to that found for toluene$(H_2O)_1$.[3] The S_0 geometry is similar to the S_1 geometry based on the Franck–Condon factors observed for the $S_1 \leftarrow S_0$ cluster transition. In the I state the equilibrium geometry is very different, probably the lone pair electrons on the nitrogen atom are toward the π system and the hydrogens point away from the ring.

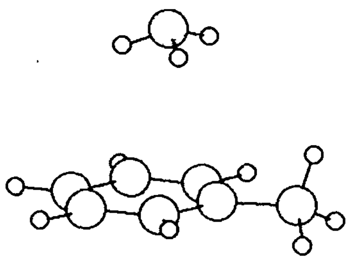

FIG. 10. Calculated cluster geometry of toluene$(NH_3)_1$.

IV. DISCUSSION: FRAGMENTATION AND PARENT CLUSTERS

The only mass channels in which sharp toluene/ammonia signals have been observed are toluene (one feature at 37 463 cm^{-1}), $(NH_3)_1H$, $(NH_3)_2H$, toluene$(NH_3)_1$, and toluene$(NH_3)_2$. For the toluene/water cluster system, sets of mass channels containing the same transitions could be identified which correspond to unique nozzle delay times: these results then led to a clear identification of sets of $S_1 \leftarrow S_0$ cluster transitions with unique parent clusters toluene$(H_2O)_n$ ($n = 1,...,6$). The only set of transitions that might be identified as such are **a** through **d** for toluene $(NH_3)_1$. Unfortunately, the nozzle delay results suggests that these features are best associated with toluene$(NH_3)_3$ or $(NH_3)_4$ clusters, as a regular progress of transition delay times cannot be identified with certainty (see Ref. 3). The other transitions are not even spectroscopically uniquely related to a single observed mass channel. Thus in these clusters, fragmentation of larger clusters [(toluene)$_m(NH_3)_n$ and toluene$(NH_3)_n$] is virtually complete to the $(NH_3)_{1,2}H$ and toluene$(NH_3)_{1,2}$ mass channels. For dissociative fragmentation [toluene$^+(NH_3)_n \rightarrow$ toluene$^+(NH_3)_k + (n-k)NH_3$] $n,k > 1$ and for reactive fragmentation [toluene$^+(NH_3)_n \rightarrow (NH_3)_jH^+ +$ benzyl radical $+ (n-j)NH_3$] $n \geqslant 1, j \geqslant 1$; that is, many possible final product channels are available.

The enhanced fragmentation for the toluene/ammonia system with respect to the toluene/water system probably occurs because of the more highly stabilized products generated by the former cluster system. We have argued[5] that ammonia is a better cluster solvent than water in these instances for two reasons. First, ammonia clusters have a higher basicity than do water clusters. Second, ammonia is also more apt to solvate both the benzyl radical and the proton in a fragmentation reaction because the ammonia solvent molecules are more distributed over the aromatic system than are the water molecules due to the strong hydrogen bonding of water molecules to one another. The ammonia/ammonia interaction (ca. 1000 cm^{-1}) is comparable to the ammonia/aromatic interaction (ca. 800 cm^{-1}), while in the case of water as a solvent, the water/water and water/aromatic interactions are much more disparate (2000 vs 600 cm^{-1}).

Additionally, kinetics can play a role in the enhanced fragmentation found for the toluene/ammonia system compared to the toluene/water system. The $I \leftarrow S_1$ transition in toluene/ammonia clusters generates highly vibrationally excited clusters ions ($\Delta v \neq 0$) for which any barrier to proton transfer/fragmentation can be readily surmounted. Almost certainly both reaction barriers and product stabilities contribute to the overall observed differences in behavior for toluene/ammonia and toluene/water clusters.

V. CONCLUSIONS

A number of general conclusions can be reached from this study even if the detailed fragmentation patterns and parent clusters cannot be enumerated for toluene/ammonia clusters. First, fragmentation is extensive and complete in this system even for "threshold ionization" energies. Second, fragmentation is aided by solvation of both the benzyl radical and the proton because the ammonia molecules do not bond exclusively to one another. Third, fragmentation by loss of a single solvent molecule without the transfer of a proton does not seem to be a possible channel for this cluster system. Fourth, nozzle delay studies, laser delay studies, two-color MRES, deuteration of the solute are all important components of the overall technique by which such ion chemistry can be elucidated.

ACKNOWLEDGMENTS

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