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Benzyl alcohol–water and benzyl alcohol–ammonia clusters: Ion fragmentation and chemistry

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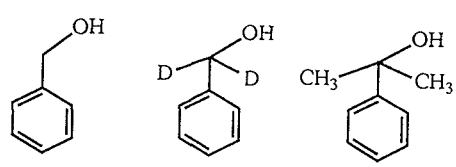
Benzyl alcohol/ammonia, α,α-dimethylbenzyl alcohol/ammonia, and benzyl alcohol/water cluster ion fragmentation and chemistry are studied for isolated cold clusters by means of one and two-color mass resolved excitation spectroscopy, nozzle/laser timing delay, and deuteration experiments. Experiments lead to an identification of parent clusters for all fragment ion clusters observed. Three types of cluster ion fragmentation are observed for these systems: dissociation—$\text{solu}^+(\text{solv})_n \rightarrow \text{solu}^+(\text{solv})_k + m$ solv; acid-base chemistry—$\text{ArCH}_2\text{OH}^+(\text{B})_n \rightarrow \text{ArCH}_2\text{O}(\text{B})_k + \text{B}_m\text{H}^+$; and (benzyl) radical chemistry—$\text{ArCH}_2\text{OH}^+(\text{B})_n \rightarrow \text{ArCHOH}(\text{B})_k + \text{B}_m\text{H}^+$, $\text{ArCD}_2\text{OH}^+(\text{B})_n \rightarrow \text{ArCDHOH}^+(\text{B})_k + \text{B}_m\text{B}-d_2$ and $\text{ArCMe}_2\text{OH}^+(\text{B})_n \rightarrow \text{ArCMeOH}^+(\text{B})_k + \text{B}_m\text{Me}$. Fragmentation reactions depend on cluster size, structure, and (weakly) on the vibrational energy deposited in the ion. Specifically, for benzyl alcohol$^+(\text{NH}_3)_1$ only cluster radical chemistry and dissociation take place, while for higher order clusters, the acid-base reaction rate increases and this reaction becomes a major fragmentation pathway for benzyl alcohol$^+(\text{NH}_3)_4$. For the benzyl alcohol$(\text{H}_2\text{O})_n$ system, cluster radical chemistry is not observed with $n=1$, only a weak α-hydrogen transfer reaction is observed with $n=2$, and acid base chemistry is not observed for clusters of any size. Cluster dissociative fragmentation is also a function of cluster size; large water and ammonia clusters dissociate much more easily than do $n=1$ clusters. The possible mechanisms for these fragmentation patterns are discussed.

I. INTRODUCTION

The study of clusters composed of an aromatic solute molecule and polar solvent molecules reveals that extensive cluster fragmentation (both dissociative and reactive) occurs upon cluster ionization, even at the lowest possible energy. This behavior is suggested to arise from the markedly different equilibrium geometry for the ground and first excited ($\pi\pi^*$) states (S_0,S_1) of the cluster on the one hand, and the ground electronic state of the cluster ion (I) on the other. The equilibrium structure difference leaves the cluster ion (typically accessed through absorption of photons ($I \overset{h\nu_2}{\leftarrow} S_1 \overset{h\nu_1}{\leftarrow} S_0$) initially in a very highly excited vibrational state. Published and to be published examples of this behavior include benzene/water,[1] toluene/water[2] and ammonia,[3] and benzylamine/water[4] clusters and others.[5]

In addition to cluster dissociation, toluene/water and ammonia cluster systems experience an extensive ion chemistry in which the C_α-proton is transferred to the solvent [i.e. $(\text{H}_2\text{O})_m\text{H}^+$, $m \geqslant 3$ and $(\text{NH}_3)_m\text{H}^+$, $m \geqslant 1$], a benzyl radical is formed and the cluster fragments into the radical and solvated proton moieties. This remarkable and surprising chemistry is driven both by the stability of the products (solvated proton and benzyl radical) and reduction of the barrier to reaction as the cluster size and structure change.

In this paper we report results on cluster ion fragmentation and chemistry for benzyl alcohol (**1**), benzyl alcohol-α,α-d_2 (**2**), and benzyl alcohol-α,α-Me_2 (**3**) clustered with water and ammonia. Three types of cluster ion fragmentation are now possible for these systems: cluster dissociation—$\text{solu}^+(\text{solv})_n \rightarrow \text{solu}(\text{solv})_k^+ + m$ solv, etc.; cluster acid-base chemistry—$\text{RCH}_2\text{OH}^+(\text{B})_n \rightarrow \text{RCH}_2\text{O}(\text{B})_k + \text{B}_m\text{H}^+$ etc.; and cluster (benzyl) radical chemistry—$\text{RCH}_2\text{OH}^+(\text{B})_n \rightarrow \text{RCHOH}(\text{B})_k + \text{B}_m\text{H}^+$, and $\text{RCMe}_2\text{OH}^+(\text{B})_n \rightarrow \text{RCMeOH}^+(\text{B})_k + \text{Me}(\text{B})_m$, etc. All three types of reactions are observed for these cluster ions and are discussed in this report. The detailed cluster ion fragmentation and chemistry observed for these systems is summarized in Schemes I, II, and III. The observed reactions depend on the specific solute, the solvent, the cluster size, and the cluster ion energy content.



1 2 3

II. EXPERIMENTAL PROCEDURES

Benzyl alcohol and α,α-dimethyl benzyl alcohol are purchased from Aldrich Co. α,α-Dideuterobenzyl alcohol is provided by Drs. J. I. Seeman and H. V. Secor of Philip Morris Corp. All samples are used without additional purification. The supersonic expansion mixture consists of saturated vapor pressure of water at 300 K, 50 psig of He and saturated vapor pressure of the benzyl alcohol at 310 K. Ammonia gas is added to the expansion gas at 0.1% pressure of the total expansion. Other aspects of the procedure are as described in Ref. 2.

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Three different types of experiments are performed for these studies:[2] one- and two-color mass resolved excitation spectra (MRES) and nozzle/laser timing delay studies. One- and two-color MRES are obtained for the clusters in the usual manner with the exception that individual cluster $S_1 \leftarrow S_0$ excitation spectra can be observed in a number of different mass channels due to cluster ion fragmentation. For this system of clusters the difference in the extent of fragmentation between one- and two-color ionization is small because Franck–Condon factors for the $I \leftarrow S_1$ transition and the reaction exothermicity control the cluster ion fragmentation.[2,3] For one-color MRES a single Nd/YAG pumped dye laser (LDS 698), the fundamental output of which is doubled and mixed with 1.064 μm, is employed. The ionization laser for a two-color MRES experiment is another Nd/YAG pumped dye laser (the output of which is doubled) with R640 or kiton red dye as the active lasing medium. Nozzle/laser timing delay experiments[2] are performed to help identify the parent cluster of the various fragments observed. Due to cluster formation time and cluster mass, clusters of different masses arrive at the excitation point in the ion extraction region of the mass spectrometer at different times. This segregation of clusters by mass can be employed to identify parent clusters of the observed fragment clusters. The timing sequence is scanned and fragment clusters with the same relative arrival time belong to the same parent. Clusters observed in this work are separated by 3–5 μs (depending on cluster mass) per added solvent molecule.

Relative intensities of the same spectral features observed in different mass channels should in principle give information on the relative efficiencies of the various cluster ion fragmentation reactions. In practice, such an intensity comparison is only useful for a very qualitative estimation; nozzle timing, laser intensity, background signals, mass channel overlap, and spectroscopic resolution all contribute to the uncertainly of such a comparison. Nonetheless, by comparing the same spectroscopic features observed in a number of different mass channels one can get a qualitative notion of which fragmentation reactions are the dominant ones for particular ionic clusters.

Cluster temperature can in general be estimated from spectroscopic linewidth and hot bands. The collection of spectroscopic data is too complex to analyze fully so specific temperatures cannot be assigned to individual clusters. Mass resolved spectra taken of expansions with helium, argon, or mixtures of these gases are all identical with regard to the number of features and linewidths. We can thereby only conclude that the observed clusters are all cold (i.e., rotational temperature $\sim$4 K and vibrational temperature $\sim$10 K). Such results are typical for solute/solvent clusters.[1–4]

III. RESULTS

A. Benzyl alcohol/ammonia

1. Mass resolved excitation spectroscopy (MRES)

One-color MRES observed in benzyl alcohol (ammonia)$_m$ [BA$(NH_3)_m$] mass channels are presented in Fig. 1 and these same spectra are observed in $(NH_3)_mH$ mass channels as presented in Fig. 2. Similar fragmentation and spectral patterns are observed for toluene/ammonia and water clusters.[2,3] As before, we reserve the subscript n to imply the number of solvent molecules in the parent cluster and the subscript m to imply the number of solvent molecules remaining in a fragment cluster. Bare solute molecule transitions are labeled B_i (i=1,2,3,...) and cluster transitions are labeled alphabetically **a** through **l**. As shown previously for toluene/water and ammonia clusters a confusing profusion of features appears in many different mass channels, giving evidence that both cluster ion dissociative fragmentation and proton transfer reaction chemistry occur for these clusters.

The featureless appearance of the spectrum in the BA$(NH_3)_4$ mass channel [Fig. 1(e)] is probably due to cluster ion fragmentation from higher mass clusters as can be seen in Figs. 2(d) and 2(e).

Near threshold two-color MRES observed in the various BA$(NH_3)_m$ mass channels generates similar overall results. Only transitions **a** and **b** change such that these features gain intensity in the m=1 mass channel. Thus even at threshold ionization energies complete cluster ion fragmentation occurs. In general, for the cluster systems under consideration in this work, two-color threshold ion-

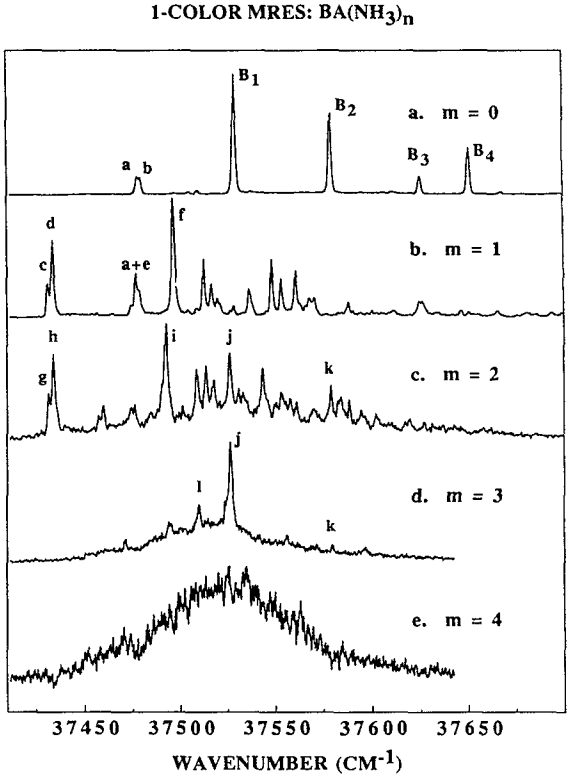

FIG. 1. One-color mass resolved excitation spectra of benzyl alcohol/ammonia clusters observed in the benzyl alcohol$(NH_3)_m$ mass channels. (a) Benzyl alcohol; (b) benzyl alcohol$(NH_3)_1$; (c) benzyl alcohol$(NH_3)_2$; (d) benzyl alcohol$(NH_3)_3$; and (e) benzyl alcohol$(NH_3)_4$. Features labeled are discussed in the text. The mass channel designations in the figure BA$(NH_3)_m$ refer to the detection channels not the parent cluster channels.

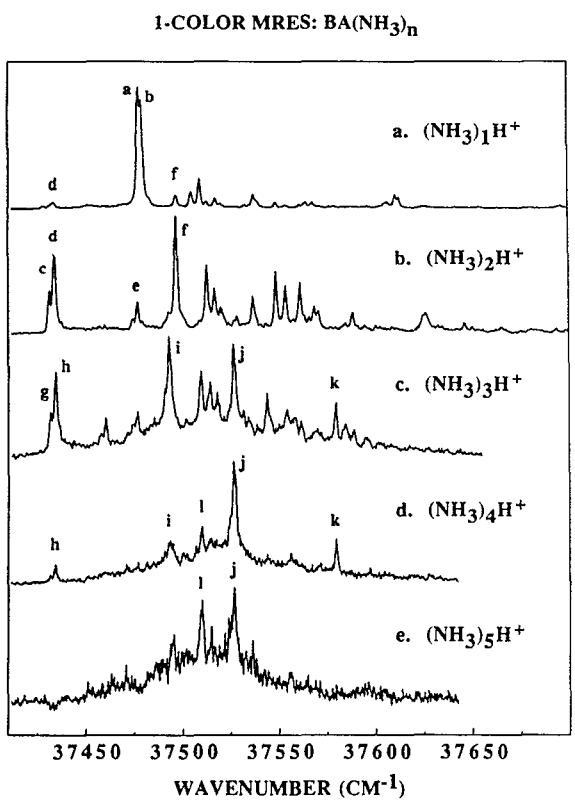

FIG. 2. One-color mass resolved excitation spectra of benzyl alcohol/ammonia clusters observed in $(NH_3)_mH$ mass channels. (a) $(NH_3)_1H$; (b) $(NH_3)_2H$; (c) $(NH_3)_3H$; (d) $(NH_3)_4H$; and (e) $(NH_3)_5H$. Features are labeled as in Fig. 1.

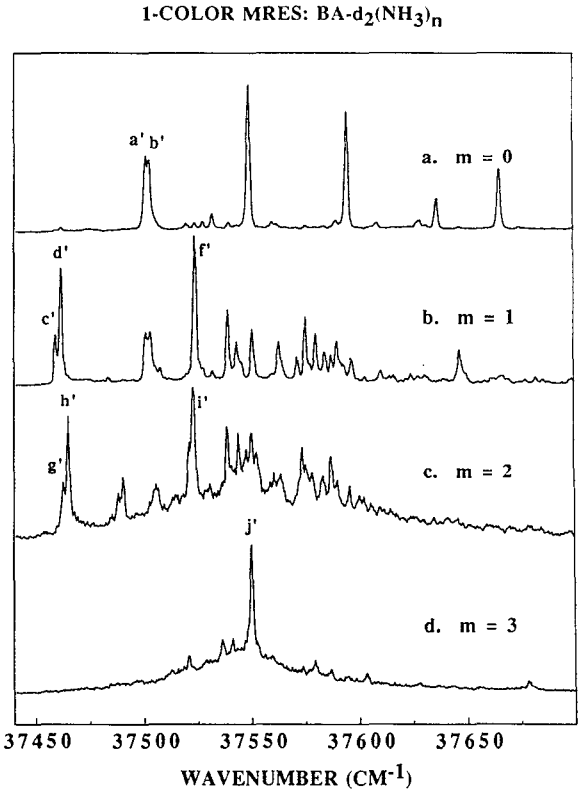

FIG. 3. One-color mass resolved excitation spectra of benzyl alcohol-d_2/ammonia clusters observed in the benzyl alcohol-$d_2(NH_3)_m$ mass channels. (a) Benzyl alcohol-d_2; (b) benzyl alcohol-$d_2(NH_3)_1$; (c) benzyl alcohol-$d_2(NH_3)_2$; and (d) benzyl alcohol-$d_2(NH_3)_3$. Features are labeled with primed letters corresponding to the undeuterated system.

ization has little effect on the cluster ion fragmentation yields. Franck–Condon factors for the $I \leftarrow S_1$, transition and cluster ion reaction exothermicity must control the fragmentation even at the lowest possible ionization energies. Under higher resolution, features with apparently similar excitation energies but different labels in the various mass channels (e.g., **c**, **d**, and **g**, **h**; **a** and **e**) are actually distinct.

2. Nozzle/laser timing delay studies

In general, identification of a cluster $S_1 \leftarrow S_0$ transition with a cluster of a particular mass under conditions of extensive or even complete cluster ion fragmentation involves significant detective work. The first part of this effort entails identification of the $S_1 \leftarrow S_0$ transitions in the various different fragment ion mass channels. This process

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

Transition	BA Origin	$BA(NH_3)_1$	$BA(NH_3)_2$	$BA(NH_3)_4$	$BA(NH_3)_5$
Observed in mass channel					
Parent	72 290	69 980			
$BA(NH_3)_n$	(2770)	(4980)			
Fragment		70 330	69 430		
$BA(NH_3)_{n-1}$		(4630)	(5430)		
Fragment				68 730	68 430
$BA(NH_3)_{n-2}$				(6130)	(6630)
Fragment					68 430
$BA(NH_3)_{n-3}$					(6630)
Fragment		70 330	69 230		
$(NH_3)_nH^+$		(4630)	(5630)		
Fragment				68 730	68 330
$(NH_3)_{n-1}H^+$				(6130)	(6730)

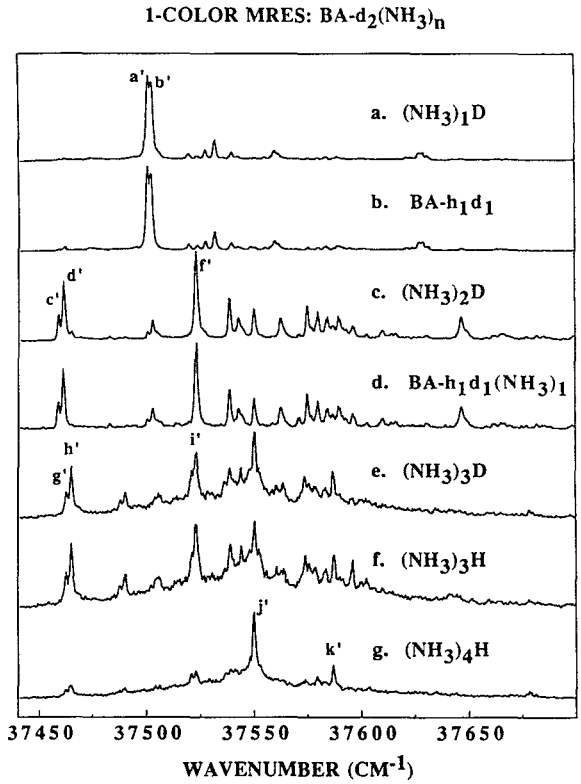

FIG. 4. One-color mass resolved excitation spectra of benzyl alcohol-d_2/ammonia clusters observed in the following mass channels: (a) $(NH_3)_1D$; (b) benzyl alcohol-h_1d_1; (c) $(NH_3)_2D$; (d) benzyl alcohol-$h_1d_1(NH_3)_1$; (e) $(NH_3)_3D$; (f) $(NH_3)_3H$; and (g) $(NH_3)_4H$. Features are labeled with primed letters corresponding to the undeuterated system.

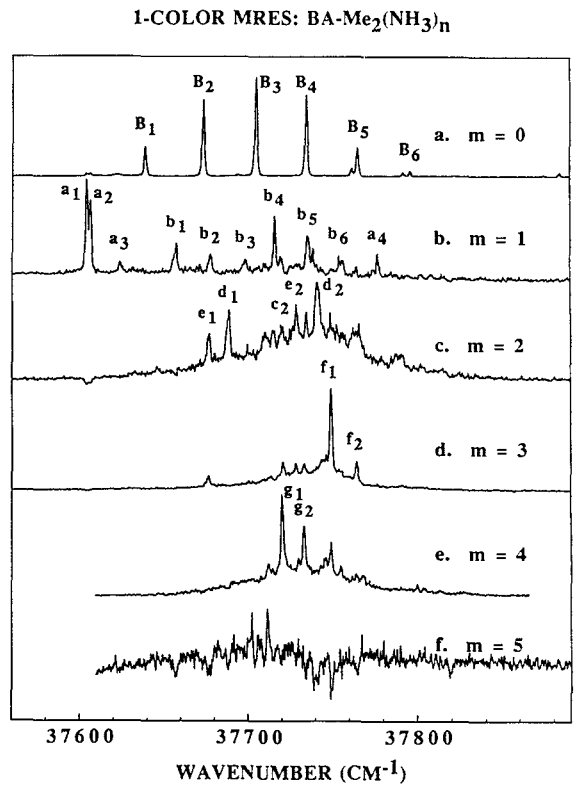

FIG. 5. One-color mass resolved excitation spectra of benzyl alcohol–Me_2/ammonia clusters observed in the benzyl alcohol–$Me_2(NH_3)_m$ mass channels. (a) Benzyl alcohol–Me_2; (b) benzyl alcohol–$Me_2(NH_3)_1$; (c) benzyl alcohol–$Me_2(NH_3)_2$; (d) benzyl alcohol–$Me_2(NH_3)_3$; (e) benzyl alcohol–$Me_2(NH_3)_4$; and (f) benzyl alcohol–$Me_2(NH_3)_5$. Features labeled are discussed in the text.

is discussed above and the peaks are so labeled in the presented figures. Additionally, the nozzle opening/laser firing time interval difference needed to achieve maximum intensity signals, can be used to identify the appropriate parent cluster for a given MRES feature. Following procedures outlined in Ref. 2 and briefly discussed above in Sec. II, transitions can be identified with $BA(NH_3)_n$ parent clusters as follows: **a**, **b**, $n=1$; **d**, **f**, $n=2$; **h**, **i**, $n=4$; and **k**, **j**, $n=5/6$. Transitions for the $BA(NH_3)_3$ clusters overlap with other features (probably of $n=2$ and 4 clusters) and cannot be well resolved or identified. Identifying spectroscopic features with specific parent clusters is, of course, an essential task if cluster ion chemistry and fragmentation is to be established.

3. Apparent ionization thresholds and time-of-flight mass spectroscopy

Table I presents ionization energies for benzyl alcohol and its ammonia clusters ($n\leqslant 5$) as measured at various mass channels. These numbers are actual parent and fragment appearance potentials for the dissociative and reactive fragmentation processes observed. The ionization action curves for all systems (even bare benzyl alcohol) are very broad due to reorganization of both the molecular and cluster structure upon $I\leftarrow S_1$ excitation.

The time-of-flight mass spectrum (TOFMS) signal observed for feature **a** [$BA(NH_3)_1$ parent cluster] has different shapes depending on which mass channel is employed to detect it, $(NH_3)_1H$, BA, or $BA(NH_3)_1$. The feature **a** TOFMS signal is asymmetric to higher masses (longer flight times) in both the $(NH_3)H$ and BA mass channels by ~ 0.1 μs. This spread to longer flight time implies that the fragmentation processes $BA^+(NH_3)_1 \rightarrow BA\cdot + (NH_3)H^+$ and $BA^+ + NH_3$ are slow compared to the extraction of the ions from the acceleration region of the TOFMS. Similar behavior has been characterized for toluene/water clusters.[2]

TOFMS detected signal **e**+**a** [partly due to $BA(NH_3)_2$ parent] in the $BA(NH_3)_1$ mass channel is broadened to lower mass channels (shorter time) by ~ 0.08 μs, suggesting that the fragmentation $BA(NH_3)_2^+ \rightarrow BA(NH_3)_1^+ + NH_3$ occurs with the release of cluster vibrational energy into kinetic energy.

B. Benzyl alcohol-α,α-d_2/ammonia

This isotopically substituted compound is studied to answer a specific question concerning the cluster ion reactive fragmentation discussed, that is, from which site in the benzyl alcohol does the hydrogen ion come in the fragment $(NH_3)_mH^+$. As can be seen in Figs. 3 and 4, the answer to this question depends on cluster size. The features in these figures are labeled according to the designations for $BA(NH_3)_n$ clusters with the addition of a prime for the BA-$d_2(NH_3)_n$ features.

No signal is observed in the $(NH_3)H^+$ mass channel,

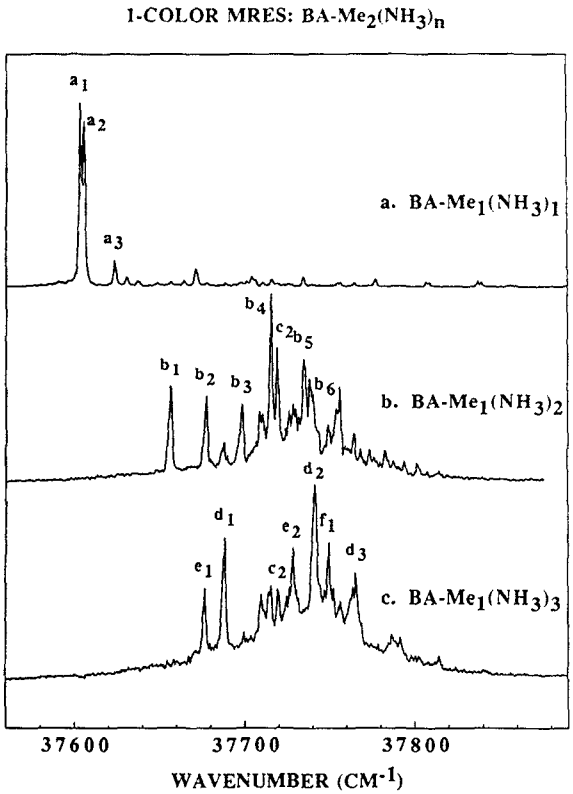

FIG. 6. One-color mass resolved excitation spectra of benzyl alcohol–Me_2/ammonia clusters observed in the benzyl alcohol–$Me_1(NH_3)_m$ mass channels. (a) Benzyl alcohol–$Me_1(NH_3)_1$; (b) benzyl alcohol–$Me_1(NH_3)_2$; and (c) benzyl alcohol–$Me_1(NH_3)_1$. Features are labeled as in Fig. 5.

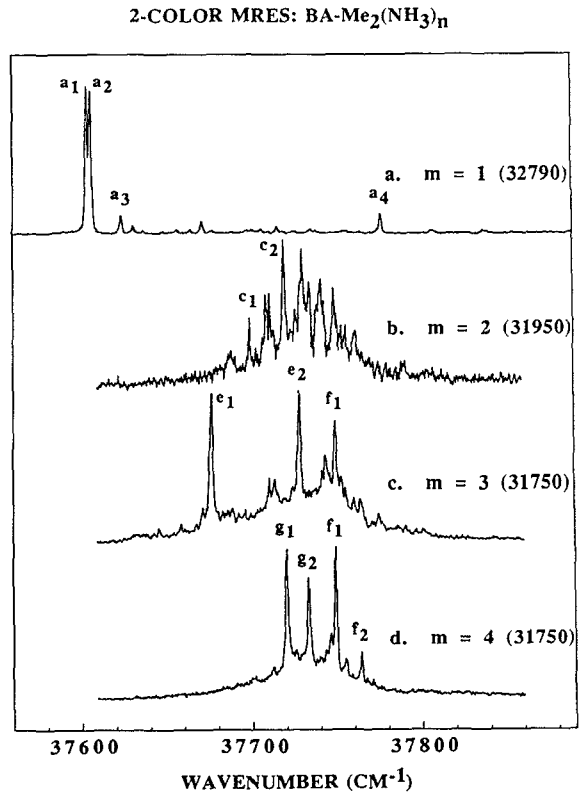

FIG. 7. Two-color mass resolved excitation spectra of benzyl alcohol–Me_2/ammonia clusters observed in the benzyl alcohol–$Me_2(NH_3)_m$ mass channels. The second photon energy is given in parentheses. (a) benzyl alcohol–$Me_2(NH_3)_1$; (b) benzyl alcohol–$Me_2(NH_3)_2$; (c) benzyl alcohol–$Me_2(NH_3)_3$; and (d) benzyl alcohol–$Me_2(NH_3)_4$. Features are labeled as in Fig. 5. The mass channel designations in the figures refer to the detection channels not the parent channels.

thus, BA-$d_2(NH_3)_1$ (features **a'**, **b'**) fragments to BA-d_1·$+(NH_3)D^+$. In this small cluster, benzyl radical chemistry, not acid-base (OH) chemistry, drives the reaction. As cluster size increases [$BA(NH_3)_{2,3,4,...}$], acid-base chemistry begins to occur, and for $BA(NH_3)_{4,5,6}$ only acid-base chemistry is observed. Cluster size can affect both the thermodynamics and kinetics of these processes. In making these assignments we assume that only the minimum rearrangements in the clusters have occurred and that $C_6H_5CD_2O$ does not subsequently rearrange to C_6H_5CDOD. Additionally, an exchange reaction takes place for BA-$d_2(NH_3)_n^+$, $n \leqslant 2$, such that BA-$d_1h_1(NH_3)_k^+$ and NH_2D can be formed (see Fig. 4).

C. α,α-Dimethyl benzyl alcohol/ammonia

One-color MRES observed in the BA–$Me_2(NH_3)_m$ $m=0,...,5$ mass channels are presented in Fig. 5. These cluster spectra are quite different from the benzyl alcohol bare molecule and cluster spectra and therefore we have employed a different labeling scheme for them. Small letters **a**, **b**, **c**, etc. refer to features of the $n=1, 2, 3,...$ *parent* clusters and subscripts 1, 2, 3, etc. refer to the series of transitions for that cluster. Thus, according to this notation, the $\mathbf{f}_1$ and $\mathbf{f}_2$ features would be two transitions belonging to the BA–$Me_2(NH_3)_6$ cluster and $\mathbf{g}_1$ and $\mathbf{g}_2$ would belong to the BA–$Me_2(NH_3)_7$ cluster.

No one-color or two-color MRES signals are observed in the $(NH_3)_mH$ $m=1, 2, 3,...$ mass channels for this system (no acid-base chemistry for this system), but moderate to strong signals are observed in the $C_6H_5\dot{C}(CH_3)OH(NH_3)_m$, $m=1, 2, 3$ mass channels as shown in Fig. 6. Clearly benzyl radical (cation) chemistry and dissociation dominates the cluster ion fragmentation. No tunable signals for the solvated radical cations are observed with $m>3$. Both the (solvated) benzyl-like radical cation and the (solvated?) methyl radical are quite stable.[2]

Two-color spectra taken near ionization threshold (Figs. 7 and 8) show reduced fragmentation. Features previously appearing in a given mass channel under one-color MRES conditions, now appear in higher mass channels.

Nozzle/laser timing delay studies in addition to the above fragmentation data show that $\mathbf{a}_i$, $\mathbf{b}_i$, $\mathbf{c}_i$, $\mathbf{d}_i$, $\mathbf{e}_i$, and $\mathbf{f}_i$ transitions correspond to clusters BA–$Me_2(NH_3)_n$, $n=1, 2, 3, 4, 5$, and 6. Transitions $\mathbf{g}_i$ can be associated with either $n=6$ or 7 clusters.

D. Benzyl alcohol/water

One-color MRES spectra of benzyl alcohol/water clusters are presented in Figs. 9 and 10 detected in the $BA(H_2O)_m$, $m=0$, 1, 2, 3 and $(H_2O_3)_mH^+$, $m=3$, 4, 5 mass channels, respectively. Several representative cluster transitions are labeled **r** through **y** in these figures. Again

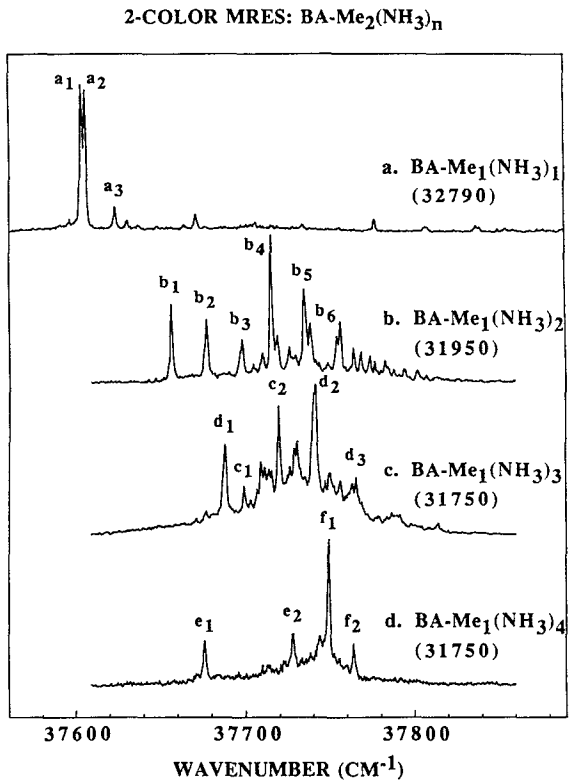

FIG. 8. Two-color mass resolved excitation spectra of benzyl alcohol–Me_2/ammonia clusters observed in the benzyl alcohol–$Me_1(NH_3)_m$ mass channels. The second photon energy is given in parentheses. (a) Benzyl alcohol–$Me_1(NH_3)_1$; (b) benzyl alcohol–$Me_1(NH_3)_2$; (c) benzyl alcohol–$Me_1(NH_3)_3$; and (d) benzyl alcohol–$Me_1(NH_3)_4$. Features are labeled as in Fig. 5.

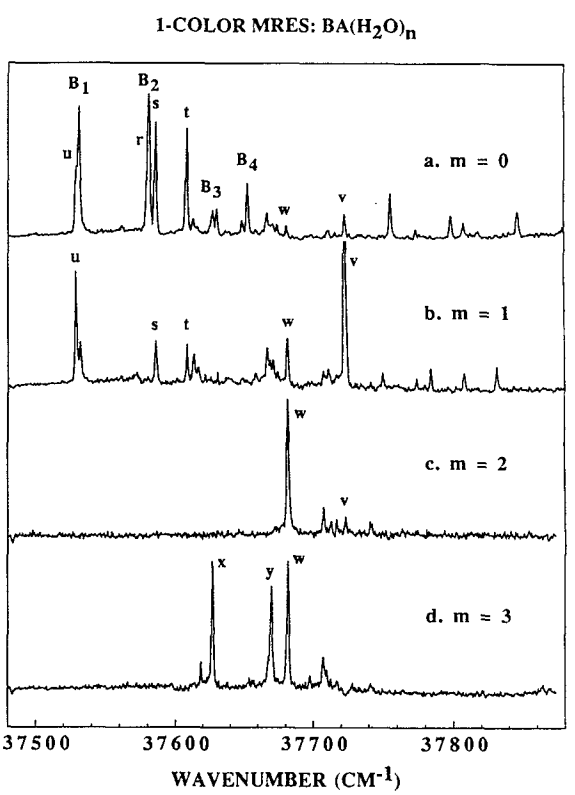

FIG. 9. One-color mass resolved excitation spectra of benzyl alcohol/water clusters observed in the benzyl alcohol$(H_2O)_m$ mass channels. (a) Benzyl alcohol; (b) benzyl alcohol$(H_2O)_1$; (c) benzyl alcohol$(H_2O)_2$; and (d) benzyl alcohol$(H_2O)_3$. Features labeled are discussed in the text.

extensive fragmentation occurs in these clusters and proton transfer to water clusters can occur only for $(H_2O)_m$, $m \geqslant 3$ due to the gas phase basicity of the water cluster system.[2]

Nozzle/laser timing delay studies associate transitions and clusters of specific size as follows: **s**, **t**, $BA(H_2O)_1$; **u**, $BA(H_2O)_2$; **v**, $BA(H_2O)_3$; **w**, $BA(H_2O)_4$, and **x** and **y**, $BA(H_2O)_5$. Transition **r** is shown below for BA-d_2/water clusters to be due to $BA(H_2O)_1$.

Clusters signals of benzyl alcohol and water are very intense, almost as intense as those for the bare benzyl alcohol. Fragmentation of larger clusters is more complete than for smaller clusters probably because the ionization energy of the larger clusters is greatly reduced.

E. Benzyl alcohol-α,α-d_2/water

One-color MRES observed in BA-$d_2(H_2O)_m$, $m = 0,...,3$ and BA-$d_1h_1(H_2O)_m$, $m = 1, 2$ mass channels are presented in Figs. 11 and 12, respectively. The observed transitions are labeled with primed letters **r′** through **w′** in accord with the features for $BA(H_2O)_m$ of Figs. 9 and 10. The assignments presented above for transition and clusters apply here as well. Nozzle/laser timing delay studies show that **r′**, **s′**, **t′** are associated with $BA(NH_3)_1$ clusters, but ionization energy studies suggest that **r′** and **s′**, **t′** arise from two clusters of different geometry. Note that H/D exchange is observed now for $BA(H_2O)_n$, $n = 2, 3, 4$. Again a proton is transferred only to a $(H_2O)_m$, $m \geqslant 3$ cluster. Only radical cation chemistry, not acid-base (OH)

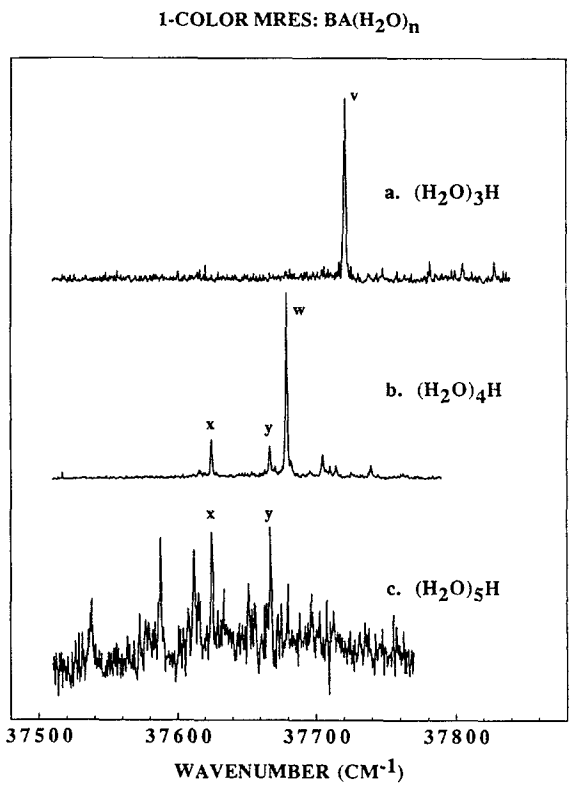

FIG. 10. One-color mass resolved excitation spectra of benzyl alcohol/water clusters observed in $(H_2O)_mH$ mass channels. (a) $(H_2O)_3H$; (b) $(H_2O)_4H$; and (c) $(H_2O)_5H$. Features are labeled as in Fig. 9.

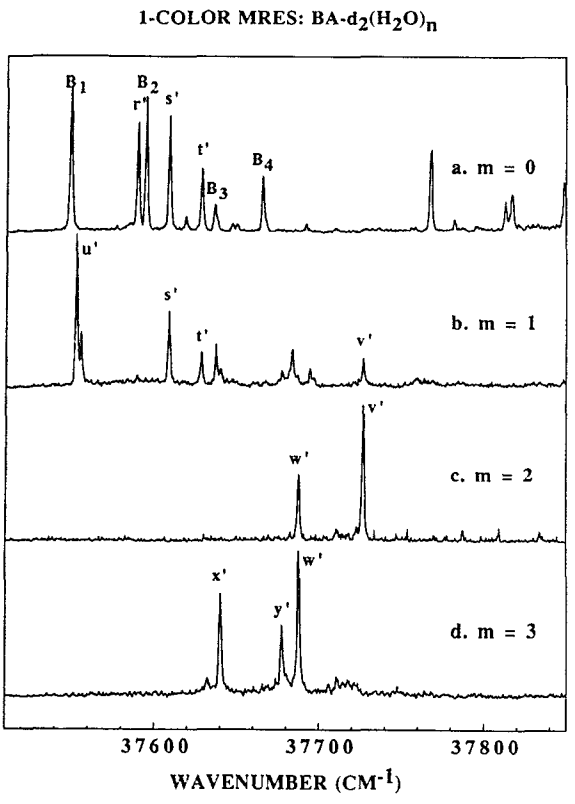

FIG. 11. One-color mass resolved excitation spectra of benzyl alcohol-d_2/water clusters observed in the benzyl alcohol-$d_2(H_2O)_m$ mass channels. (a) Benzyl alcohol-d_2; (b) benzyl alcohol-$d_2(H_2O)_1$; (c) benzyl alcohol-$d_2(H_2O)_2$; and (d) benzyl alcohol-$d_2(H_2O)_3$. Features are labeled with primed letters corresponding to the undeuterated system.

chemistry, is observed for this system as only the D ion/atom is transferred to water or is exchanged with a water proton. No hydrogen exchange is found for the BA-α, α-$d_2(H_2O)_1$ cluster.

IV. DISCUSSION

A. Cluster chemistries, fragmentations, and cluster size effects

A number of reactions are found to occur in these cluster systems following $I \leftarrow S_1 \leftarrow S_0$ ionization. These reactions are presented in schemes I, II, III. We can summarize these reactions as follows:

(1) Benzyl alcohol$(NH_3)_n$ (schemes I, II) (a) dissociation, loss of ammonia molecule(s) or cluster [mNH_3 or $(NH_3)_m$]; (b) hydrogen transfer, NDH_2+mNH_3 fragmentation, etc. with D from C_α-position $m<n<4$; (c) proton transfer from –OH, loss of $(NH_3)_kH^+$, $k=2...,\leqslant n$; (d) proton transfer from C_α-position, loss of $(NH_3)_kD^+$, $k=1...\leqslant n<4$; and (e) formation of two radicals, loss of methyl group for BA–$Me_2(NH_3)_n^+$ $(n<6)$, with and without solvation.

(2) Benzyl alcohol$(H_2O)_n$ (scheme III) (a) dissociation, loss of water molecule(s) or cluster [mH_2O or $(H_2O)_m$]; (b) hydrogen transfer, $HDO+mH_2O$ or $(HDO)(H_2O)_m$ with D from C_α-position; and (c) proton transfer from C_α-position, loss of $(HDO)^+(H_2O)_k$, $k=2,...,<n$.

Scheme I

Observed Fragmentations in Benzyl Alcohol/Ammonia Clusters*

$C_6H_5CD_2OH(NH_3)_1^+$	→ $C_6H_5CD\,OH + NH_3D^+$		
	→ $C_6H_5CDHOH^+ + NH_2D$		
	→ $C_6H_5CD_2OH^+ + NH_3$		
$C_6H_5CD_2OH(NH_3)_2^+$	→ $C_6H_5CD\,OH + (NH_3)_2D^+$		
	→ $C_6H_5CD_2OH(NH_3)_1^+ + NH_3$		
	→ $C_6H_5CD_2O + (NH_3)_2H^+$		
	→ $C_6H_5CDHOH(NH_3)_1^+ + NH_2D$		
$C_6H_5CD_2OH(NH_3)_4^+$	→ $C_6H_5CD_2OH(NH_3)_j^+ + (NH_3)_{4-j}$		j = 1,2
	→ $C_6H_5CD_2O\,(NH_3)_k + (NH_3)_{4-k}H^+$		k= 0,1,2
	→ $C_6H_5CD\,OH(NH_3)_k + (NH_3)_{4-k}D^+$		k= 1,2
$C_6H_5CD_2OH(NH_3)_5^+$	→ $C_6H_5CD_2OH(NH_3)_j^+ + (NH_3)_{5-j}$		j = 1,2,3
	→ $C_6H_5CD_2O\,(NH_3)_k + (NH_3)_{5-k}H^+$		k= 0,1,2,3
	→ $C_6H_5CD\,OH(NH_3)_k + (NH_3)_{5-k}D^+$		k= 1,2,3

*The unobserved neutral fragment species, though written as an aggregate, may be individual molecules.

Scheme II

Observed Fragmentations in α,α-Dimethyl Benzyl Alcohol/Ammonia Clusters*

$C_6H_5CM_2OH(NH_3)_1^+$	→ $C_6H_5CM\,OH(NH_3)_1^+ + M$	
	→ $C_6H_5CM_2OH^+ + NH_3$	
	→ $C_6H_5CM\,OH^+ + (NH_3M \text{ or } NH_3 + M)$	
$C_6H_5CM_2OH(NH_3)_2^+$	→ $C_6H_5CM\,OH(NH_3)_2^+ + M$	
	→ $C_6H_5CM_2OH(NH_3)_1^+ + NH_3$	
$C_6H_5CM_2OH(NH_3)_4^+$	→ $C_6H_5CM_2OH(NH_3)_2^+ + (NH_3)_2$	
	→ $C_6H_5CM\,OH(NH_3)_3^+ + (NH_3M \text{ or } NH_3 + M)$	
$C_6H_5CM_2OH(NH_3)_n^+$, n>=6	→ $C_6H_5CM_2OH(NH_3)_k^+ + (NH_3)_{n-k}$	

*The unobserved neutral fragment species, though written as an aggregate, may be individual molecules.

Scheme III

Observed Fragmentations in Benzyl Alcohol/Water Clusters*

$C_6H_5CD_2OH(H_2O)_1^+$	→ $C_6H_5CD_2OH^+ + H_2O$	
$C_6H_5CD_2OH(H_2O)_2^+$	→ $C_6H_5CD_2OH(H_2O)_1^+ + (H_2O)_1$	
	→ $C_6H_5CDHOH(H_2O)_j^+ + HDO(H_2O)_{1-j}$	j = 0,1
$C_6H_5CD_2OH(H_2O)_3^+$	→ $C_6H_5CD_2OH(H_2O)_j^+ + (H_2O)_{3-j}$	j = 1,2
	→ $C_6H_5CDHOH(H_2O)_j^+ + HDO(H_2O)_{2-j}$	j = 0,1,2
	→ $C_6H_5CD\,OH + (H_2O)_3D^+$	
$C_6H_5CD_2OH(H_2O)_4^+$	→ $C_6H_5CD_2OH(H_2O)_j^+ + (H_2O)_{4-j}$	j = 2,3
	→ $C_6H_5CDHOH(H_2O)_j^+ + HDO(H_2O)_{4-j}$	j = 1,2,3
	→ $C_6H_5CD\,OH + (H_2O)_4D^+$	
$C_6H_5CD_2OH(H_2O)_5^+$	→ $C_6H_5CD_2OH(H_2O)_j^+ + (H_2O)_{5-j}$	j = 3,4
	→ $C_6H_5CDHOH(H_2O)_j^+ + HDO(H_2O)_{5-j}$	j = 3,4
	→ $C_6H_5CD\,OH(H_2O)_k + (H_2O)_{5-k}D^+$	k = 0,1

*The unobserved neutral fragment species, though written as an aggregate, may be individual molecules.

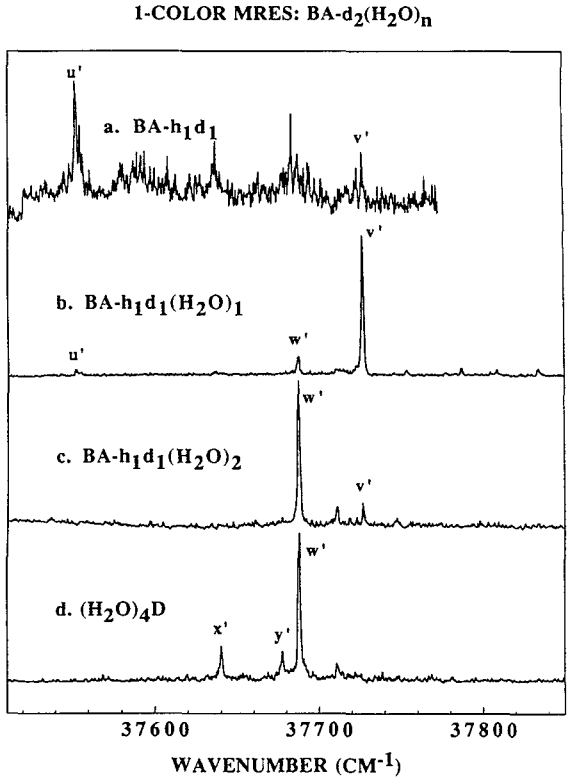

FIG. 12. One-color mass resolved excitation spectra of benzyl alcohol-d_2/water clusters observed in the following mass channels: (a) benzyl alcohol-h_1d_1; (b) benzyl alcohol-$h_1d_1(H_2O)_1$; (c) benzyl alcohol-$h_1d_1(H_2O)_2$; and (d) $(H_2O)_4D$. Features are labeled as in Fig. 11.

The observed fragmentations and cluster chemistries depend on cluster size; they are driven by radical and radical cation stability, solvent cluster basicity, and solvation effects. These effects can be summarized as follows: (1) proton transfer in $BA(NH_3)_n$ cluster system, for $BA^+(NH_3)_1$ only the α-protons transfer, whereas for $BA^+(NH_3)_{2,3,4,5...}$ both C_α and –OH-protons transfer with the acid-base chemistry becoming dominant for the larger clusters: (2) hydrogen transfer/exchange in BA-$d_2(NH_3)_n$ clusters, as cluster size increases C_α-hydrogen transfer to form BA-$h_1d_1^+(NH_3)_m$ and $NDH_2(NH_3)_m$ becomes less favorable, and the reaction is not observed for $n \geqslant 4$; and (3) benzyl alcohol$(H_2O)_n$ clusters, C_α-proton transfer for $n \geqslant 3$ and C_α-hydrogen transfer/exchange is observed for $n \geqslant 2$.

In general, cluster ion fragmentation for solute(solvent)$_1$ clusters is only partial; that is, transitions are observed in the parent mass channel for these clusters. For larger clusters, the cluster ion fragmentation reactions are complete, such that transitions are not observed for the parent clusters directly. Identification of $(S_1 \leftarrow S_0)$ transitions and their parent clusters for the larger clusters is made through nozzle/laser firing delay studies. This behavior is related to the large geometry change for the molecule and cluster upon ionization ($\Delta v > 0$ for the $I \leftarrow S_1$ transition)[2] and enhanced stability of the large cluster ions.

B. Molecular and cluster geometry

Molecular and cluster geometry information can be deduced from both calculational and experimental results. The geometry of benzyl alcohol for S_0 and S_1 is determined to be such that $\tau_1(C_{ortho}-C_{ipso}-C_\alpha-OH)=90°$ and $\tau_2(C_{ipso}-C_\alpha-O-H)=0°$.[6] Ionization threshold studies suggest that unlike molecular toluene, significant geometry changes occur for the benzyl alcohol molecule upon ionization. Most likely both τ_1 and τ_2 change for the ion with $\tau_1 \rightarrow 0°$ and $\tau_2 \rightarrow 180°$.

Since the charge–dipole interaction is much larger than the hydrogen bonding interaction for $BA^+(NH_3)_n$ one can suggest that for the cluster ion the NH_3 molecules interact much more strongly with the ring than with the isolated OH group. This may contribute to the C_α-hydrogen/proton (radical) chemistry rather than acid-base chemistry for small ($3 \leqslant n$) benzyl alcohol/ammonia clusters.

For the benzyl alcohol/water neutral clusters both $ROH\cdots OH_2$ and $RHO\cdots HOH$ hydrogen bonding can occur and for $BA(H_2O)_1$ clusters two origin transitions (**r** and **s**) can be identified. Nonetheless, a single cluster geometry for $BA(H_2O)_{3,4}$ is suggested by the spectroscopic data. Water molecules will tend to cluster together and not solvate the organic moiety as well as ammonia molecules. Such structures, along with the reduced gas phase basicity of water clusters with respect to ammonia clusters, may account for the absence of acid-base (OH) chemistry in $BA(H_2O)_n$ clusters. In ionic $BA(H_2O)_n$ clusters, again the charge–dipole interactions are expected to be dominant and significant geometry changes are expected upon ionization leading to cluster ion chemistry and fragmentation.

V. CONCLUSIONS

(1) Benzyl alcohol, benzyl alcohol-α-α-d_2, and benzyl alcohol-α-α-$(CH_3)_2$ clusters with water and ammonia have been investigated for clusters up to six solvent molecules. Cluster transitions and transition patterns are uniquely associated with clusters of specific size through one and two-color MRES and nozzle/laser delay timing experiments.

(2) Experimental and calculational results lead to some insight into the structure of small clusters.

(3) A number of reactions are found to occur in these clusters following $I \leftarrow S_1$ ionization. These are given in detail for the clusters studied in schemes I, II, III, and summarized in the Discussion.

(4) The possible mechanisms for these reactions are discussed in the text. Cluster size and structure are important for the types of chemistries (acid-base, radical, radical cation, fragmentation, etc.) that occur in these cluster ions.

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