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Infrared plus vacuum ultraviolet spectroscopy of neutral and ionic ethanol monomers and clusters

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A high sensitivity spectroscopy is employed to detect vibrational antiitions of ethanol neutrals and ions in a supersonic expansion. The infrared (IR) features located at 3682 and 3667 cm^{-1} can be assigned to the OH stretch for the two neutral C_2H_5OH conformers, *anti* and *gauche*, respectively. Their overtone energies located at 7179 (anti) and 7141 (gauche) cm^{-1} are also identified. The OH fundamental stretch for ethanol ions is redshifted around 210 cm^{-1}, while the CH stretch modes are unchanged for neutral and ionic C_2H_5OH at around 2900–3000 cm^{-1}. The charge on the ethanol ion is apparently localized on the oxygen atom. IR induced photodissociation spectroscopy is applied to the study of neutral and protonated ethanol clusters. Neutral and protonated ethanol cluster vibrations are observed. The CH modes are not perturbed by the clustering process. Neutral clusters display only hydrogen bonded OH features, while the protonated ionic clusters display both hydrogen bonded and non-hydrogen-bonded features. These spectroscopic results are analyzed to obtain qualitative structural information on neutral and ionic ethanol clusters. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2357952]

I. INTRODUCTION

Hydrogen bonding is an important intramolecular and intermolecular interaction that can both affect and effect structural and dynamical behavior of chemical and biological systems. Small to medium size clusters are suggested to be ideal model systems with which to explore such phenomena. Alcohols are often employed solvents and solutes for the study of solution reactions and properties, and their gas phase clusters can be useful models for the understanding of their condensed phase behavior. Ethanol has received much less attention in this regard than methanol,[1–3] even though it serves as a prototypical model system for solute/solvent and solvent/solvent interactions for larger molecules in the condensed phase. This report presents new results for ethanol clusters that should serve to close this gap between methanol and ethanol data and hydrogen bonding analysis.

The ethanol molecule has two stable conformers, anti and gauche: the anti conformer has a torsional angle between the hydroxyl hydrogen and terminal carbon atom about the CO bond (τ_{HOCC}) of 180°, and the gauche conformer has (τ_{HOCC}) of ±60°. Calculations predict that the anti/gauche barrier is around 3.9 kJ/mol and that the anti conformer is slightly more stable. The calculated spectrum for the ethanol monomer is in agreement with the experimental results.[4–6]

More recently, the infrared (IR) spectra of ethanol clusters in the gas phase have been obtained employing molecular beam depletion spectroscopy. These data are limited to the spectral region between 870 and 1100 cm^{-1} in which the symmetric and asymmetric CCO stretches and in-plane and out-of-plane bends absorb.[2] The complicated ethanol dimer spectrum has been interpreted as evidence of multiple linear conformers, while the more simple trimer spectrum has suggested a cyclic structure.

The crystal structure of solid ethanol has also been investigated. The crystal has four molecules/unit cell and exhibits infinite zigzag chains of hydrogen bonds. Liquid ethanol has also been investigated by x-ray diffraction.[7,8] Cavity ringdown absorption spectra have been observed for the OH stretching vibrations of ethanol clusters.[4] Three features around 3500 cm^{-1} are attributed to hydrogen bonded OH modes of the dimer, indicating that more than one conformer exists in the molecular beam for this cluster. An unresolved single feature is observed for both the trimer and tetramer in this region.[4] Laser induced fluorescence has also been used to detect clusters of aromatic alcohols by IR/UV double resonance.[9–12]

Recently, infrared photodissociation (IRPD) spectroscopy has been successfully applied to several protonated solvent clusters, including $(H_2O)_nH^+$,[13–23] $(CH_3OH)_nH^+$,[22–27] and $(H_2O)_n$ $(CH_3OH)_nH^+$.[28–31] Vibrational spectra of isolated, protonated ethanol clusters and mixed clusters with other species (Ar, N_2) have been reported for $(EtOH)_nH^+$ and $(EtOH)_nH^+L_q$ $(n=1-4)$.[32] In contrast to neutral $(EtOH)_n$ clusters, small cyclic protonated clusters $(n \leqslant 4)$ do not appear to be present in the beam: this suggests that the presence of the proton has a substantial effect on the structure of the ethanol hydrogen bond network. In these cluster ions two general structures have been suggested: a proton strongly localized on one ethanol molecule (an "Eigen-type core," $n=1,3$)[33] and a proton shared between two ethanol molecules (a "Zundel-type core," $n=2,4$).[34,35]

In general, primary alcohols are difficult to ionize without fragmentation. Typically, instead of generating high concentrations of parent ion (M^+), conventional ionization

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techniques (electron impact, multiphoton ionization, chemical ionization, fast ion bombardment) tend to yield high concentrations of fragment species attributable to cluster ion-molecule reactions. Nonetheless, recent reports demonstrate that vacuum ultraviolet (VUV) lasers are an excellent "soft" (generally nonfragmenting) ionization source for primary alcohols with minimal fragmentation.[27,36–38]

In the present work, we employ a high sensitivity spectroscopy that can detect vibrational antiitions of ethanol neutrals and ions in a supersonic expansion. Additionally, IR induced photodissociation spectroscopy is applied to the study of neutral and protonated ethanol clusters. The OH stretches and overtones for both neutral and ionic ethanol isomers are identified. Neutral and protonated ethanol cluster vibrations are also observed. The CH modes are not perturbed by the clustering process. The neutral clusters display only hydrogen bonded OH features, while protonated ionic clusters show both hydrogen bonded and non-hydrogen-bonded OH features. Comparisons are drawn between $(\mathrm{EtOH})_n$ and $(\mathrm{MeOH})_n$, and $(\mathrm{EtOH})_n\mathrm{H}^+$ and $(\mathrm{MeOH})_n\mathrm{H}^+$ clusters with regard to these data.

II. EXPERIMENTAL PROCEDURES

A. Generation and detection of ethanol clusters

The experimental apparatus employed to record the VUV/time of flight mass spectrum (TOFMS) and IR spectrum of ethanol clusters has been previously described,[27,39,40] and only a brief description of the experimental design will be presented here. Ethanol vapor is seeded in Ne/He ("first-run" Ne, total pressure 3 atm) and the gaseous mixture is expanded into a vacuum chamber from a pulsed supersonic nozzle (Parker General Valve Series 9). A molecular beam, containing both monomeric and clustered ethanol, is generated in a supersonic jet expansion. The beam is collimated by a 1.5 mm diameter aperture skimmer located around 3.0 cm downstream of the nozzle, and then crossed perpendicularly by the VUV 118 nm laser in the ionization region of the TOFMS. The counterpropagating IR laser beam is focused upstream of the VUV focal point by a 40 cm focal length lens.

Generation of the VUV 118 nm radiation and IR light is the same as reported previously.[27,39] IR light output in the ranges covered is 3–5 mJ/pulse (2500–4000 and 3500–7500 cm^{-1}) with a bandwidth of either 2–3 or 0.4 cm^{-1}.

B. IR plus VUV nonresonant ionization and fragmentation detected (NRIFD-IR) vibrational spectroscopy of the ethanol molecule and ion

The principle of IR plus VUV nonresonant ionization and fragmentation detection of vibrational antiitions is shown in Fig. 1. Note that the VUV (nonresonant) photon energy (~10.49 eV) is only 0.02 eV above the ionization energy (IE) (ethanol=10.47 eV) of the ethanol monomer.[41] This small excess energy is not sufficient for monomer ions to dissociate and generate fragment ions. The two lowest dissociation thresholds of the ethanol ion are 10.8 eV for the reaction $\mathrm{C_2H_5OH} \rightarrow \mathrm{C_2H_5O^+} + \mathrm{H} + e^-$ and 11.25 eV for the reaction $\mathrm{C_2H_5OH} \rightarrow \mathrm{CH_2OH^+} + \mathrm{CH_3} + e^-$.[38,41] If additional energy is absorbed by the molecule (around 0.4 eV or more), one or both of those channels opens for fragmentation.[42] As the IR laser is scanned to excite cooled ethanol molecules to higher vibrational states of their ground electronic state prior to the introduction of VUV light while the $\mathrm{C_2H_5O^+}$ mass channel is monitored, the vibrational spectrum of neutral ethanol is obtained with high sensitivity. On the other hand, if the IR laser pulse follows the VUV pulse in time, the vibrational spectrum observed should be that of ethanol ions. The laser schemes of these two approaches are illustrated in Figs. 1(a) and 1(b). Mass spectra of ethanol molecules under VUV and IR irradiation [under approach (a)] are presented in Fig. 1(c). Comparing the changes in the fragment and parent mass channels makes clear the advantages of monitoring the IR induced dissociation product rather than the parent.

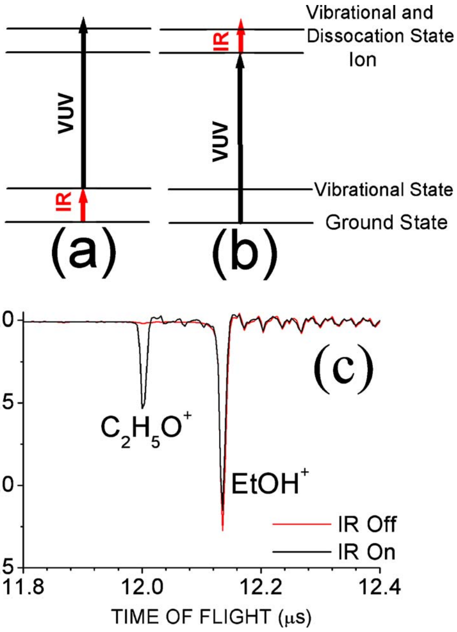

FIG. 1. Schematic diagram showing the principle of NRIFD-IR spectroscopy for (a) neutral ethanol molecules and (b) ethanol cations. (c) Mass spectra in the region of $m/z = 45-46$ in the absence (red) and presence (black) of IR radiation at 3680 cm^{-1}, resonant with the OH stretch fundamental vibration of the ethanol monomer.

C. IR plus VUV vibrational spectroscopy of ethanol neutral [nonresonant ion dip (NRIDip-IR)] and ionic clusters [IR plus VUV photodissociation (IRPD)]

IR spectroscopy of neutral and ionic methanol clusters has been discussed previously.[27] Briefly, if a tunable IR pulse is introduced into the molecular beam at around 50 ns prior to the VUV laser pulse, IR (multiphoton) absorption will induce photodissociation of the neutral clusters. The reduced population of neutral clusters then leads to a reduction of the fragment ion signal representing the neutral parent concentration. Thus, by scanning the IR wavelength while monitoring the ion signal intensity of the appropriate mass channel, mass selective IR spectra for neutral ethanol clusters are obtained as a loss of intensity in appropriate mass channels. On

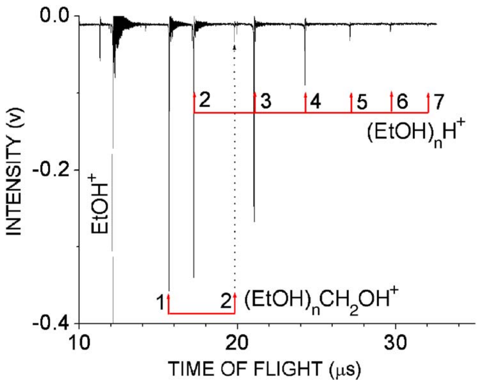

FIG. 2. Mass spectrum of ethanol clusters obtained with VUV (118 nm) radiation as the ionization source, recorded by TOFMS.

the other hand, if a tunable IR light pulse is introduced with a delay of around 30 ns after the VUV laser pulse, mass selective IR spectra of cluster ions are generated by scanning the IR laser wavelength.

III. RESULTS AND DISCUSSION

A. VUV 118 nm single photon ionization of ethanol clusters

The TOFMS of ethanol clusters ionized by VUV photons at 10.49 eV is shown in Fig. 2. In addition to the intense signal for $C_2H_5OH^+$, the main series of cluster ions observed is the protonated ethanol cluster ions $(EtOH)_nH^+$ $(n>1)$. Similar results are reported for methanol clusters.[27] Other intense features in this spectrum are due to the protonated clusters $(EtOH)_n(CH_2OH)^+$ $(n=1,2)$. This series probably arises from a β-carbon-carbon bond fission reaction in the clusters.[42] The additional sequence of mixed ethanol-methanol protonated cluster ions is of low intensity and probably arises because of trace amounts of methanol in the ethanol sample system.

B. IR spectra of ethanol neutral and ion in a supersonic expansion

Figure 3(a) presents the IR spectrum of the neutral ethanol monomer in a supersonic expansion. This spectrum is generated employing IR plus VUV nonresonant ionization/fragmentation spectroscopy for which the mass channel $C_2H_5O^+$ is monitored while the IR laser wavelength is scanned from 4.0 to 1.3 μm (2500–7500 cm^{-1}). Intense features at arount 3000, 3670, and 7160 cm^{-1} in the spectrum can be assigned as the CH fundamental, the OH fundamental, and the OH first overtone vibrations, respectively. The weak features at around 5800 cm^{-1} are due to the CH overtone.[43]

Ethanol is known to exist in two conformers in the gas phase: the anti and gauche structures.[4–6] The conformers can interconvert by internal rotation of the OH hydrogen about the CO bond: the higher frequency mode is assigned as due to the anti conformer. These features are clearly displayed in Fig. 3(a) at ν_1 and 2 ν_1. The OH stretch features at 3667 and 7141 cm^{-1} can be assigned as the fundamental and overtone modes of the gauche conformer, and those at 3682 and 7179 cm^{-1} are associated with the anti conformer.[44,45] From the intensities of the OH overtones, the percentage of the anti isomer in the beam can be estimated at 70%.

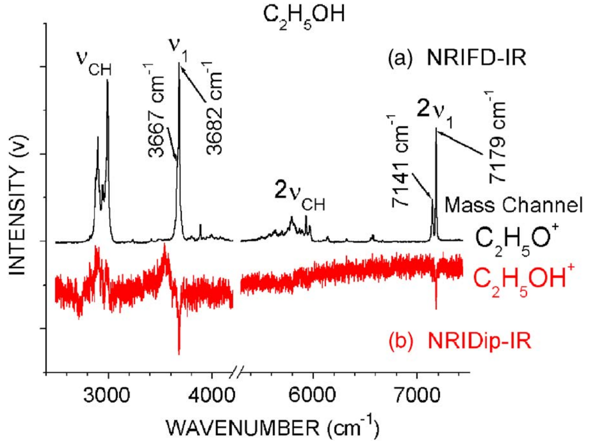

FIG. 3. Mid-IR (2500–7200 cm^{-1}) vibrational spectrum of the jet-cooled ethanol monomer recorded by NRIFD-IR spectroscopy using 3% ethanol vapor seeded in 3 atm of a He/Ne mixture. The upper trace is monitored in the $C_2H_5O^+$ mass channel, while the bottom one is monitored in the $C_2H_5OH^+$ mass channel.

Figure 3(b) shows the NRIDip-IR spectrum of ethanol obtained by monitoring the parent ion mass channel. This spectrum is measured in the same conditions as that of Fig. 3(a) for the NRIFD-IR spectroscopy. The OH modes can be observed in this mass channel but they are apparently distorted by cluster fragmentation. Isomer features cannot be easily distinguished in this spectrum.

In like manner, the IR spectrum of the ethanol ion can be obtained by delaying the IR light pulse to follow the VUV pulse by around 30 ns. The spectrum of $C_2H_5OH^+$ is shown in Fig. 4 as detected in the $C_2H_5O^+$ and $C_2H_5OH^+$ mass channels. The $C_2H_5OH^+$ spectrum as detected in the fragment $C_2H_5O^+$ mass channel is more detailed and intense than that in the parent mass channel. The features at 2900, 3470, 5800, and 6700 cm^{-1} can be assigned to CH stretch, OH stretch fundamental, CH stretch overtones, and OH stretch overtone vibrations, respectively. The fact that the bandwidth

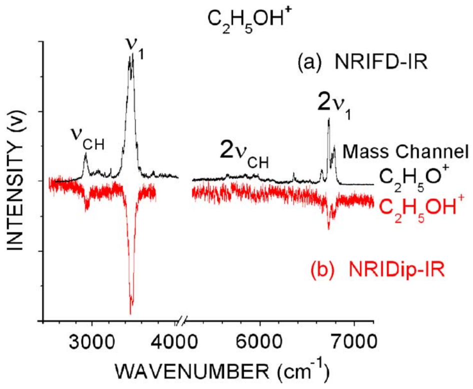

FIG. 4. Mid-IR (2500–7200 cm^{-1}) vibrational spectrum of the ethanol cation recorded by NRIFD-IR spectroscopy using 3% ethanol vapor seeded in 3 atm of a He/Ne mixture. The upper trace is monitored the $C_2H_5O^+$ mass channel while the bottom one is monitored the $C_2H_5OH^+$ mass channel.

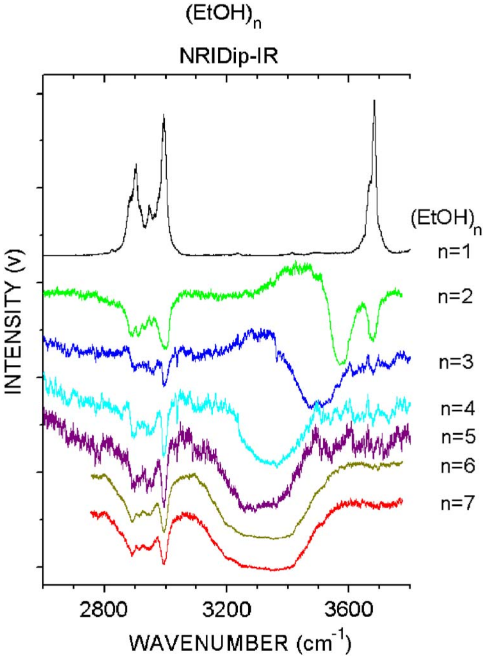

FIG. 5. The CH, OH stretch fundamental vibrations of ethanol clusters, $(EtOH)_n$, for $n=1$ (top) to 7 (bottom), recorded by NRIDip-IR spectroscopy through monitoring $EtOH^+$ and $(EtOH)_{n-1}H^+$ signals generated by VUV laser ionization. n labels refer to the neutral cluster spectra not the observed mass channel n value.

for this ion spectrum is broader than that for the neutral spectrum suggests that the ion may be hotter than the neutral due to excess energy acquired in the ionization process. Some of this excess energy and the IR absorbed energy goes toward generation of $C_2H_5O^+$.

A comparison of the neutral and ion ethanol spectra shows that the CH modes are not changed by the electron loss but the OH modes are shifted to the red by around 210 cm^{-1} in the ion. This can be understood based on the fact that the electron lost in the ionization process is removed from an oxygen atom lone pair orbital. O^+ is thereby chemically similar to N and the OH stretch is reduced in energy, close to the NH stretch energy.[41,46]

C. IR plus VUV 118 nm NRIDip-IR spectroscopy of ethanol clusters in the CH and OH fundament stretch regions

NRIDip-IR spectroscopy has been employed in the detection of neutral methanol clusters. Previous studies demonstrate that the fragment species $(EtOH)(CH_2OH)^+$ (from the dimer) and sequences of protonated cluster ions $(EtOH)_{n-1}H^+$ observed in TOFMS originate from the neutral parent $(EtOH)_n$ under VUV 118 nm single photon photoionization. Thus, the IR spectra of neutral ethanol clusters $(EtOH)_n$ are obtained by monitoring mass channels $(EtOH)\times(CH_2OH)^+$ and $(EtOH)_{n-1}H^+$ (see Fig. 5). Note that the spectra parented in Fig. 5 are labeled with the parent neutral value of n.

Figure 5 presents the mid-IR spectra of neutral ethanol clusters $(EtOH)_n$ in the CH and OH stretching region. The top trace in this figure is for monomer ethanol, $n=1$, obtained by IR plus VUV (118 nm) nonresonant ionization (see Fig. 3). The other traces pertain to neutral ethanol clusters $n=2,\ldots,7$ and arise from IR plus VUV nonresonant ionization and fragmentation spectroscopy. For $n=2$, two main features [decreases or "dips" in the $(EtOH)(CH_2OH)^+$ mass channel] in the OH stretch region (3500–3700 cm^{-1}) are observed at 3573 and 3678 cm^{-1}. The free OH stretch energy in ethanol is at around 3682 cm^{-1}, and thus we assign the higher of these two energy modes to the free OH stretch of the proton acceptor moiety of the dimer and the lower energy OH mode to the proton donor OH stretch species. Similar results are obtained for methanol clusters. These results demonstrate that $(C_2H_5OH)_2$ has a chainlike structure—one molecule as a hydrogen bond donor and the other as a hydrogen bond acceptor with a nonbonded OH hydrogen atom. For $n>3$, the "free" or nonbonded OH features are apparently missing from the spectra; only one broad, unresolved dip feature of bonded OH stretches is observed for all clusters larger than the dimer. The spectra labeled $n=3,\ldots,7$ in Fig. 5 are detected in the $(C_2H_5OH)_{n-1}H^+$ mass channels (see Fig. 2). These broad OH stretch bands are redshifted (around 80 cm^{-1}) and broadened (around 130–300 cm^{-1}) with increasing cluster size. A summary of these results is listed in Table I. The results suggest that ethanol clusters

TABLE I. Vibrational energies for neutral ethanol clusters (cm^{-1}).

		OH stretch (ν_1)	
$(C_2H_5OH)_n$	CH stretch	Resolved[a]	Band center (FWHW)[b]
1	2902, 2946, 2994	3682(*T*), 3667(*G*)[c]	
2	2890, 2952, 3000	3573,[d] 3678[e]	
3	2896, 2955, 2996		3500 (148)
4	2891, 2952, 2994		3346 (179)
5	2890, 2953, 2994		3320 (222)
6	2889, 2950, 2994		3322 (297)
7	2889, 2946, 2994		3316 (306)

[a] For $n=1,2$, features are resolved.

[b] For $n=3-7$, unresolved features of bonded OH stretches; FWHW: full width at half maximum.

[c] T=anti, G=*gauche*.

[d] Bonded OH stretch.

[e] Free OH stretch.

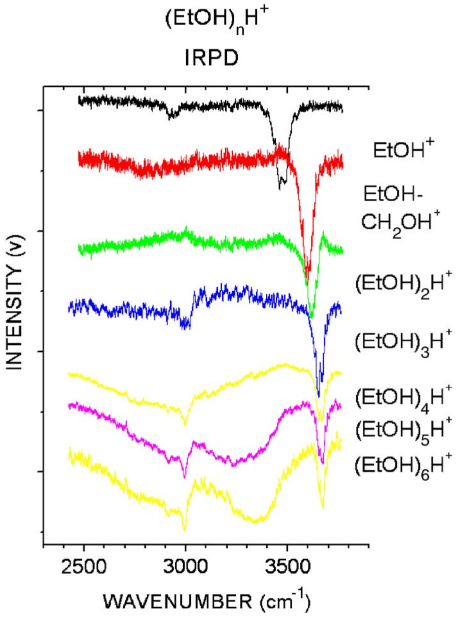

FIG. 6. The CH, OH stretch fundamental vibrations of ethanol cluster cations, $EtOH^+$ $(EtOH)CH_2OH^+$ and $(EtOH)_nH^+$, for $n=2$ (top) to 6 (bottom), recorded by IRPD spectroscopy through monitoring the parent cation signals generated by VUV ionization. These ions arise from the neutral cluster containing one more ethanol molecule.

larger than the dimer have only a cyclic structure with no free OH hydrogen, and that larger clusters may have more cyclic conformers. This interpretation is consistent with those of previous ethanol cluster studies.[3,4,47]

For CH stretch modes, cluster formation and size seem to have little effect on the observed spectra (see Fig. 5; 2800–3100 cm^{-1}). One can conclude from this fact that the CH moieties do not become involved in the hydrogen bonding network of the clusters.

D. IRPD spectroscopy of ethanol cluster ions in the CH and OH fundament stretch regions

Mass selected spectra of $(C_2H_5OH)(CH_2OH)^+$ and $(C_2H_5OH)_nH^+$ $n=1,\ldots,6$ clusters in the CH and OH stretch regions are illustrated in Fig. 6. The spectra are obtained by monitoring the indicated ion mass channels. The CH and OH stretch features of the $C_2H_5OH^+$ ion (top trace in figure) lie at 2919 and 3470 cm^{-1}, respectively. The free OH feature for $(C_2H_5OH)(CH_2OH)^+$ is located at 3598 cm^{-1}, and a broad, weak feature at around 2900 cm^{-1} can be assigned as due to the CH stretch modes.

In the spectra for larger clusters $(C_2H_5OH)_nH^+$ $n>2$, the relatively sharp features at around 3619 cm^{-1} for $n=2$, 3659 cm^{-1} for $n=3$, 3663 cm^{-1} for $n=4$, 3668 cm^{-1} for $n=5$, and 3671 cm^{-1} for $n=6$ can be assigned as the free OH vibrations of those protonated cluster ions. For $n>3$, the relatively broad features in the range from 3000 to 3500 cm^{-1} are assigned to the H bonded OH stretch modes. Energies of the free OH stretch modes blueshift with increasing cluster size and converge to around 3670 cm^{-1} for $n\sim 7$. The broad, hydrogen bonded OH stretch features blueshift with increasing cluster size and finally converge to around 3370 cm^{-1}. The CH modes around 3000 cm^{-1} show no remarkable changes with increasing cluster size. The results suggest that the CH group modes and at least one OH group in each cluster are not involved in the hydrogen bonding network of protonated ethanol cluster ions.

E. Comparison of ethanol and methanol clusters

Both similarities and differences can be found in a comparison of methanol and ethanol clusters and monomer results. Methanol does not display different isomers (gauche and eclipsed) while ethanol displays both anti and gauche isomers in the cooled sample. Both systems display a large redshift with increasing cluster size for the OH hydrogen bond stretches. The hydrogen bonded OH mode bandwidths are greater for ethanol clusters than for methanol clusters, suggesting that more isomers may exist for a given cluster size for ethanol. In both cluster systems the CH stretch modes are not much perturbed and one can conclude that the CH moieties are not involved in the hydrogen bonding network of the clusters.

IV. CONCLUSIONS

High sensitivity mass selective IR spectroscopy is detected for neutral and ionic ethanol monomers on the basis of the following photodissociation reaction:

$$C_2H_5OH \xrightarrow{h\nu\ (10.8\ \mathrm{eV})} C_2H_5O^+ + H + e^-.$$

The IR features located at 3682 and 3667 cm^{-1} can be assigned to the OH stretch for the two neutral C_2H_5OH conformers, anti and gauche, respectively. Their overtone energies located at 7179 (anti) and 7141 (gauche) cm^{-1} are also identified. The OH fundamental stretch for their ions are redshifted around 210 cm^{-1}, while the CH stretch modes are unchanged for both neutral and ionic C_2H_5OH at around 2900–3000 cm^{-1}. The electron removed from the molecule in the above reaction thus comes from the lone pair on the oxygen atom.

IR vibrational spectroscopy is applied to the study of neutral clusters (NRIDip-IR) and protonated cluster ions (IRPD). Results show that all neutral ethanol clusters larger than the dimer have only hydrogen bonded OH stretch features that converge around 3200 cm^{-1} with increasing cluster size. The energies of the free and hydrogen bonded OH stretches in protonated ethanol clusters exhibit blueshifts with increasing cluster size n and these two stretches converge to around 3670 and 3370 cm^{-1}, respectively. These results confirm the conclusions that neutral $(C_2H_5OH)_n$ clusters $(n>2)$ formed in a supersonic expansion have cyclic hydrogen bonded structures, and at least one OH group is not hydrogen bonded in protonated ethanol cluster ions.

ACKNOWLEDGMENTS

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