Infrared plus vacuum ultraviolet spectroscopy of neutral and ionic methanol monomers and clusters: New experimental results

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We present new observations of the infrared (IR) spectrum of neutral methanol and neutral and protonated methanol clusters employing IR plus vacuum ultraviolet (vuv) spectroscopic techniques. The tunable IR light covers the energy ranges of $2500-4500$ cm^{-1} and $5000-7500$ cm^{-1}. The CH and OH fundamental stretch modes, the OH overtone mode, and combination bands are identified in the vibrational spectrum of supersonic expansion cooled methanol ($2500-7500$ cm^{-1}). Cluster size selected IR plus vuv nonresonant infrared ion-dip infrared spectra of neutral methanol clusters, $(CH_3OH)_n$ ($n=2,\ldots,8$), demonstrate that the methanol dimer has free and bonded OH stretch features, while clusters larger than the dimer display only hydrogen bonded OH stretch features. CH stretch mode spectra do not change with cluster size. These results suggest that all clusters larger than the dimer have a cyclic structure with OH groups involved in hydrogen bonding. CH groups are apparently not part of this cyclic binding network. Studies of protonated methanol cluster ions $(CH_3OH)_nH^+$ $n=1,\ldots,7$ are performed by size selected vuv plus IR photodissociation spectroscopy in the OH and CH stretch regions. Energies of the free and hydrogen bonded OH stretches exhibit blueshifts with increasing n, and these two modes converge to approximately 3670 and 3400 cm^{-1} at cluster size $n=7$, respectively. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357953]

I. INTRODUCTION

Investigation of the structural and dynamical properties of hydrogen bonded clusters can yield information related to solution and solid phase behavior of many different systems.[1,2] These include species such as proteins, DNA, neurotransmitters, as well as organic solute/solvent systems. Alcohols and water are two general types of hydrogen bonding species that are important to such solution chemistry. The advantage of employing clusters as models for such systems is twofold: (1) clusters are of finite size and are thereby more amenable to *ab initio* theoretical studies than are solutions, solids or surfaces and (2) cluster size can be varied and thus "solution" or solvation properties of condensed phases can be investigated in a stepwise fashion, which would otherwise be difficult to accomplish. For molecules containing an OH chromophor group, observation of the OH stretch vibration by infrared (IR) spectroscopy has proven to be a very sensitive indicator of hydrogen bond strength and dynamics.[2–6]

In contrast to studies of water clusters, studies of hydrogen bonded methanol clusters have been much less extensive,[7–13] even though methanol is a prototype molecule for hydrogen bonding alcohols. An x-ray diffraction study of liquid methanol suggests that methanol forms chainlike structures in the liquid phase.[14] IR spectroscopy of neutral methanol clusters $(MeOH)_n$, $n=2-9$, in the gas phase suggests that the clusters $n=3-9$ have cyclic structures.[7–11] A mixed cluster system, benzene-$(MeOH)_n$, $n=1-6$, has also been investigated and spectra of these clusters show that the methanol moiety still holds to a cyclic structure, although the

hydrogen bonded ring is distorted for $n>3$.[12,13] The CH fundamental region of neutral methanol clusters does not appear to have been investigated.

Information on the hydrogen bond structure of protonated methanol cluster ions $(MeOH)_nH^+$ is much more limited. IR spectroscopy of such ions for $n=4,5$ has been reported and a linear chain conformation is suggested to be the predominant structure for $n=4$, and the coexistence of linear chain and cyclic structures is suggested for $n=5$ clusters.[15,16] For larger $(MeOH)_nH^+$, $n=4-15$, IR spectroscopy of the OH stretch region has shown that the free OH stretch feature decreases in intensity with increasing n and finally disappears at $n=7$.[17] This report suggests that a bicyclic hydrogen bonded structure is appropriate for $(MeOH)_nH^+$, $n>7$.

Primary alcohols are apparently difficult to ionize without fragmentation.[18] Typically, instead of producing an intense parent ion (M^+), conventional ionization approaches (e.g., electron impact ionization, multiphoton ionization, chemical ionization, and fast atom bombardment) tend to yield intense fragment features that can be attributed to ion molecule reactions. On the other hand, recent studies have demonstrated that vacuum ultraviolet (vuv) single photon ionization is an excellent "soft" ionization technique that will ionize molecules and clusters with minimal fragmentation.[18–21]

Previously, we have studied the IR spectra of methanol and its neutral clusters.[21] Both experimental results and Born-Haber cycle calculational suggest that protonated cluster ions $(MeOH)_{n-1}H^+$ ($n=2-8$) originate from neutral clusters $(MeOH)_n$. Size-specific IR spectra for $(MeOH)_n$ ($n=4-8$) in the OH stretch fundamental region are measured by IR plus vuv (118 nm) nonresonant ion-dip infrared

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(NRIDip-IR) spectroscopy through the detection chain of IR multiphoton dissociation and subsequent vuv single photon ionization. The lowest energy peak for each cluster spectrum in this region is redshifted with increasing cluster size from $n=4$ to $n=8$, and has a limiting value of 3220 cm^{-1} for $n=7,8$. In addition, IR plus vuv nonresonant ionization detected spectroscopy was employed to study the OH stretch first overtone band of the neutral methanol monomer; rotational temperature was estimated to be ~50 K.

In this report we present new observations of the IR spectrum of neutral methanol and neutral and protonated methanol clusters employing the same spectroscopic techniques. Tunable IR light has been extended to a larger wavelength region (4.0–2.22 μm and 2.0–1.33 μm—2500–4500 cm^{-1} and 5000–7500 cm^{-1}). CH, OH, and OH overtone modes are characterized. Both free and bonded OH features can be identified in cluster spectra. The OH vibration can be employed to estimate structural features of the clusters.

II. EXPERIMENTAL PROCEDURES

A. Generation and detection of methanol clusters

The experimental apparatus used to record the vuv/time of flight mass spectrometry (TOFMS) and IR spectra of methanol clusters has been previously described in detail,[21–24] and only a brief description of this setup is given below. Methanol vapor is seeded into a Ne/He mixture ("first run" Ne total pressure of 3 atm) and the gaseous mixture is expanded by a pulsed nozzle (Parker General Valve Series 9) into a vacuum system. A molecular beam containing both methanol monomers and clusters is generated in the supersonic expansion. The beam is collimated by a 1.5 mm diameter aperture skimmer, located at ~3 cm downstream from the nozzle. This resultant beam is crossed perpendicularly by a 118 nm (vuv) laser beam in the ionization region of a TOFMS. The counterpropagating IR laser beam is focused a few centimeters upstream from the vuv beam by a 40 cm focal length lens.

Generation of vuv 118 nm radiation is similar to that recently employed for the study of metal oxide clusters.[25] Tunable IR radiation is obtained from an optical parametric oscillator (OPO) (Laser Vision) pumped by an injection seeded Nd^{+3}:YAG (yttrium aluminum garnet) laser (Spectra Physics GCR-3). A type II KDP (KH$_2$PO$_4$) doubling crystal is integrated into the OPO to convert the Nd^{+3}:YAG laser fundamental output to 532 nm. Two interchangeable sets of nonlinear crystals in the system are used to produce the outputs that provide coverage from 712 nm to 2.13 μm. For both oscillator configurations, the output beam consists of both signal and idler wavelengths from the down conversion of the 532 nm pump. With simple modification of the optical layout, crystals [KTiOAsO$_4$ (KTA)] of the second oscillator can be employed to generate a difference frequency between the output of the first oscillator and a portion of the 1064 nm pump beam to provide additional wavelength coverage from 2.5 to 4.0 μm. The OPO output energy between 2500 and 4200 cm^{-1} is ~3.5 mJ/pulse with a bandwidth of 2–3 cm^{-1} (broad band mode) or 0.4 cm^{-1} (narrow band mode).
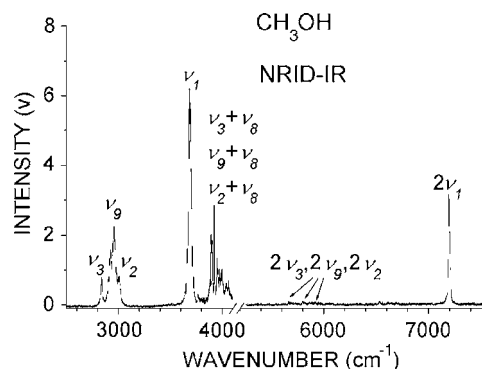

FIG. 1. Mid-IR (2500–7200 cm^{-1}) vibrational spectrum of the jet-cooled methanol monomer recorded by NRID-IR spectroscopy using 5% methanol vapor seeded in 3 atm of He/Ne mixture.

B. IR plus vuv spectroscopic detection of methanol species

The vuv, 10.5 eV single photon is not of sufficient energy to ionize the methanol molecule whose ionization energy (IE) is reported at 10.84 eV.[30] As the IR laser is scanned to excite the jet cooled methanol monomer to vibrationally excited levels of the ground electronic state, the total energy ($h\nu_{IR}+h\nu_{vuv}$) is higher than the IE of methanol, and hence vibrationally excited methanol can be ionized by absorption of 10.5 eV photon. By this technique, the methanol molecule OH and CH stretches and their overtones are recorded as an increase of the CH$_3$OH$^+$ ion signal in the time of flight mass spectrum.

IR spectroscopy of neutral and ionic methanol clusters can be developed along similar lines but based on vibrational photodissociation spectroscopy of weakly bound clusters.[26–29] Previous studies[27] show neutral methanol clusters formed in a supersonic jet can be single photon ionized by vuv 118 nm light. One can also demonstrate that (CH$_3$OH)$_{n-1}$H$^+$ clusters originate from the (CH$_3$OH)$_n$ neutral (parent) clusters. If a tunable IR light pulse is introduced in the molecular beam of approximately 50 ns prior to the vuv laser pulse, the IR absorption will induce photodissociation of the neutral clusters (CH$_3$OH)$_n$, leading to a reduction of the (CH$_3$OH)$_{n-1}$H$^+$ ion signal representing the neutral parent. Thus, by scanning the IR wavelength while monitoring the (CH$_3$OH)$_{n-1}$H$^+$ mass channel signal intensity, a mass selective IR spectrum for the neutral methanol cluster (CH$_3$OH)$_n$ is obtained as an IR ion-dip spectrum.

Similarly, if the IR light pulse is introduced into the beam of approximately 30 ns after the vuv laser pulse, the mass selected IR spectrum of the cluster cations is obtained as an ion-dip spectrum of the (CH$_3$OH)$_{n-1}$H$^+$ or the (CH$_3$OH)$_n^+$ ion by scanning the IR wavelength.

III. RESULTS AND DISCUSSION

A. IR plus vuv (118 nm) nonresonant ionization detected infrared (NRID-IR) spectroscopy of monomer methanol in mid-IR region

The methanol IR spectrum measured by NRID-IR spectroscopy is presented in Fig. 1. Features at approximately 3684 and 7196 cm^{-1} are assigned as the fundamental and
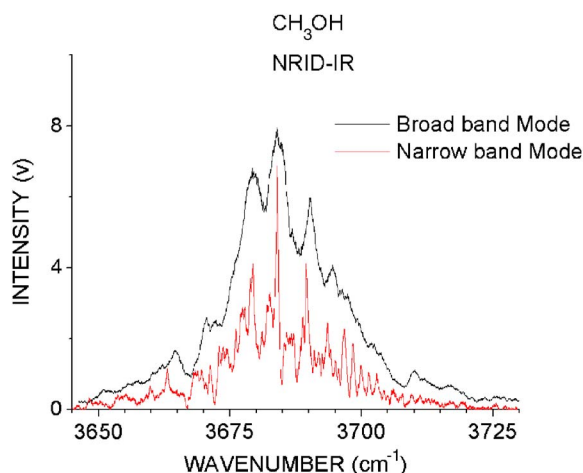
FIG. 2. The OH stretch fundamental vibration of jet-cooled methanol monomer recorded by NRID-IR spectroscopy using 5% methanol vapor seeded in 3 atm of He/Ne mixture. (Broad band mode: 3.0 cm^{-1}; narrowband mode: 0.2 cm^{-1}.)

FIG. 3. The CH, OH stretch fundamental vibrations of methanol clusters, $(CH_3OH)_n$, for $n=1$ (top) to 8 (bottom), recorded by NRIDip-IR spectroscopy through monitoring CH_3OH^+ and $(CH_3OH)_{n-1}H^+$ signals generated by vuv laser ionization.

first overtone of the OH stretch ν_1, respectively.[31,32] The four features at approximately $2800-3100$ cm^{-1} are identified as the symmetric CH fundamental stretch (ν_3), low frequency vibrational combination bands, and the torsional tunneling asymmetric CH stretches (ν_2 and ν_9).[33] The features at approximately 3900 cm^{-1} are combination bands of the CH stretches and the CO stretch fundamental (ν_8).[31]

Figure 2 shows the OH stretch fundamental under higher resolution. Rotational simulation of the envelope employing the rotational constants determined by Rueda et al.[34] yield a rotational temperature for monomeric methanol in the expansion of $T_{rot} \sim 50$ K.

B. IR plus vuv (118 nm) nonresonant ion-dip infrared (NRIDip-IR) spectroscopy of methanol clusters in the CH and OH fundamental stretch region

NRIDip-IR spectroscopy has been employed to detect the spectra of methanol clusters. vuv single photon ionization is an excellent gentle, nonfragmenting method for generating CH_3OH^+.

Shi et al.[19] have discussed in detail the dynamics of vuv (118 nm) single photon ionizaton of methanol in a supersonic expansion. Our previous results confirm the conclusion that sequences of protonated cluster ions $(CH_3OH)_{n-1}H^+$ observed in the TOFMS originate from their neutral parents $(CH_3OH)_n$. Thus, mid-IR spectra obtained by employing IR plus vuv (118 nm) nonresonant photodissociation spectroscopy and by detecting the ion signal in the $(CH_3OH)_{n-1}H^+$ mass channel should reveal information of the neutral parent $(CH_3OH)_n$ cluster. In addition, the dimer ion can be observed with 118 nm vuv ionization along with $(CH_3OH)H^+$ probably because the dimer IE is very close to 10.5 eV.[19,35] The $(CH_3OH)_2$ neutral spectrum can thus be observed in both the $(CH_3OH)_2^+$ and $(CH_3OH)H^+$ mass channels.

Figure 3 presents the mid-IR spectra of methanol clusters $(CH_3OH)_n$ in the CH and OH stretch fundamental regions by monitoring the $(CH_3OH)_{n-1}H^+$ mass channel for $n=2,\ldots,8$. The top spectrum in this figure is of the methanol molecule obtained by employing IR plus vuv photons for
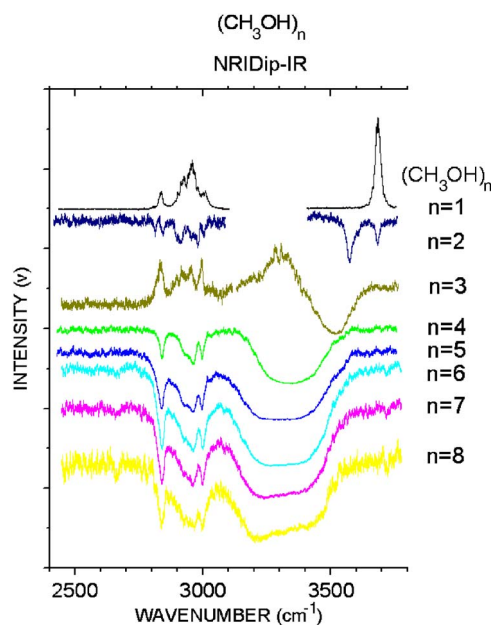
enhancement of the ion signal. The neutral dimer spectrum, detected in the $(CH_3OH)H^+$ mass channel, displays two main negative "dip" features located at approximately 3676 and 3572 cm^{-1}. Based on the position of the higher energy feature, the structure of the dimer is assumed to be not cyclic with the proton acceptor possessing the nonhydrogen bonded OH hydrogen. The feature at 3572 cm^{-1} is assigned as the mode associated with the hydrogen bonded donor hydrogen stretch.[7]

The IR spectra of larger clusters $n>3$ show only the broad hydrogen bonded OH stretch mode, and thus these larger clusters have a cyclic structure. This broad feature shifts to the red with increasing cluster size. Based on previous studies of methanol clusters, we suggest that the switch from positive to negative changes in the methanol trimer IR spectrum of Fig. 4 is due to larger cluster fragmentation, under IR irradiation, into the trimer mass channel. Recall that the IR absorption is most likely multiphoton. Note that the trimer spectrum is enhanced by the IR radiation in this region. We previously suggested that large ($n=5-8$) clusters fragment into this mass channel by loss of $(n-3)$ monomers induced by multiphoton IR absorption. The neutral trimer is energetically stable under these conditions.[22] A summary of the vibrational energies for $(CH_3OH)_n$ $n=1,\ldots,8$ can be found in Table I. Our results are consistent with closed, cyclic structures for clusters with $n \geq 3$ and also with the idea that more isomers of this form exist for larger clusters.[36–43] The CH modes of these species are not significantly influenced by cluster formation. The features between 2800 and 3050 cm^{-1} are not shifted as cluster size increases and thus the CH_3 group is not involved in the hydrogen bonding interaction network.
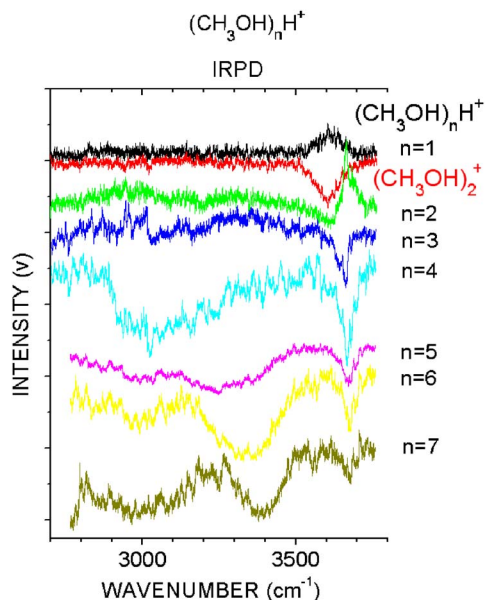
$(CH_3OH)_nH^+$

IRPD

FIG. 4. The CH, OH stretch fundamental vibrations of methanol cluster cations, $(CH_3OH)_2^+$ and $(CH_3OH)_nH^+$, for $n=1$ (top) to 7 (bottom), recorded by IRPD spectroscopy through monitoring $(CH_3OH)_2^+$ and $(CH_3OH)_nH^+$ signals generated by vuv laser ionization.

C. vuv plus IR photodissociation (IRPD) spectroscopy of protonated methanol cluster ions

Mass selected IR photodissociation spectra of $(CH_3OH)_2^+$ ions and the sequence of protonated methanol cluster ions $(CH_3OH)_nH^+$, $n=1,\ldots,7$ in the CH and OH stretch region are shown in Fig. 4. These spectra are monitored in the parent ion mass channel, as indicated by the $n=1,\ldots,7$ label on the right hand side of the figure. The OH features are located at 3604 and 3605 cm^{-1} in the observed IR spectra detected in the $(CH_3OH)_2^+$ and $(CH_3OH)H^+$ mass channels, respectively. The OH stretch features are a signal enhancement for $(CH_3OH)H^+$ and a signal decrease for $(CH_3OH)_2^+$. This implies that $(CH_3OH)_2^+$ will mainly dissociate to $(CH_3OH)H^+$ under IR irradiation at the OH stretch mode.

In the spectrum of the protonated dimer $(CH_3OH)_2H^+$, a decrease in signal at approximately 3625 cm^{-1}, assigned as due to the free OH stretch mode, is distorted by a sharp peak at approximately 3664 cm^{-1}. This sharp feature probably arises from larger clusters fragmenting into this mass channel. The protonated dimer should have a cyclic, symmetric structure; that is, the two molecules of $(CH_3OH)_2H^+$ probably share one proton equally.[18] These two observations suggest that the protonated dimer has an especially stable structure.

For larger protonated cluster cations $(CH_3OH)_nH^+$, $n=3,\ldots,7$, the relatively sharp features of approximately 3670 cm^{-1} are assigned as due to free OH stretch vibrations. The broad bands of these clusters between 3000 and 3500 cm^{-1} are assigned to the hydrogen bonded OH stretch vibrations. The free OH stretch features become less intense as cluster size increases and their energy converges to 3670 cm^{-1}. The broad bands of the hydrogen bonded OH stretch mode blueshift with increasing cluster size and finally at $n=7$ converge to approximately 3400 cm^{-1}. The CH bands (approximately 3000 cm^{-1}) are broad and show no remarkable changes with cluster size.

IV. CONCLUSIONS

The vibrational spectrum of supersonic expansion cooled methanol (2500–7500 cm^{-1}) is measured by IR plus vuv nonresonant ionization spectroscopy. The CH and OH fundamental stretch modes, the OH overtone mode, and combination bands are identified. Rotational resolution for the OH mode and its first overtone yield an estimate for $T_{rot} \sim 50$ K for the methanol monomer in the beam.

Size selected IR plus vuv NRIDip-IR spectroscopy of neutral methanol clusters, $(CH_3OH)_n$ $(n=2,\ldots,8)$ can be employed to characterize cluster structure. These spectra demonstrate that the methanol dimer has free and bonded OH stretch features. All clusters larger than the dimer display only hydrogen bonded OH stretch features. The CH stretch modes do not change with cluster size. These results suggest

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

| $(CH_3OH)_n$ | CH stretch | | | | OH stretch (ν_1) | | |
	ν_3	Combination or overtone	ν_9	ν_2	Resolved[a]	Band center (FWHW)[b]	Calculation[c]
1	2837	2925	2956	3010	3684		3683.9
2					3576,[d] 3679[e]		3612.9, 3758.6
3	2832	2914	2953	2995		3515 (142)	3465.2, 3521.4, 3534.9
4	2839	2932	2962	2996		3339 (260)	3301.1, 3392.0, 3392.3, 3429.3
5	2838	2928	2961	2995		3302 (307)	3259.0, 3338.0, 3348.8, 3392.5, 3405.2
6	2839	2925	2960	2998		3317 (312)	
7	2840	2925	2960	2997		3326 (340)	
8	2837	2925	2966	2995		3322 (345)	

[a]For $n=1,2$, features are resolved.
[b]For $n=3-8$, unresolved features of bonded OH stretches; FWHW: full width at half maximum.
[c]See Ref. 36.
[d]Free OH stretch in the dimer.
[e]Bonded OH stretch in the dimer.

that all clusters larger than the dimer have a cyclic structure with OH groups involved in hydrogen bonding. The CH groups are apparently not part of this cyclic network.

Studies of protonated methanol cluster ions $(CH_3OH)_nH^+$, $n = 1, \ldots, 7$ are performed by size selected vuv plus IRPD spectroscopy for the OH and CH stretch regions. The spectrum of the protonated dimer suggests that it has a particularly stable structure. IR spectra show that the energies of the free and hydrogen bonded OH stretches exhibit blueshifts with increasing n, and that these two modes converge to approximately 3670 and 3400 cm^{-1} at cluster size $n = 7$, respectively.

ACKNOWLEDGMENTS

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