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Isomeric Transitions between Linear and Cyclic $H^+(CH_3OH)_{4,5}$: Implications for Proton Migration in Liquid Methanol

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Vibrational predissociation spectroscopy of protonated methanol clusters (tetramers and pentamers) reveals linear and cyclic structural isomers in a supersonic expansion. The cyclic pentamer, containing a five-membered ring, is identified by its characteristic free-OH stretch at 3647 cm^{-1} and hydrogen-bonded OH stretches at 3448 and 3461 cm^{-1}. Ab initio calculations indicate that the excess proton in these clusters can be either localized on one methanol unit in cyclic $CH_3OH_2^+(CH_3OH)_3$ and linear $CH_3OH_2^+(CH_3OH)_4$ or delocalized between two methanol molecules in linear $C_2H_9O_2^+(CH_3OH)_2$ and cyclic $C_2H_9O_2^+(CH_3OH)_3$. Dynamic intracluster proton transfer can occur upon repeated ring opening and closing. The association of this process with the anomalously high proton mobility in liquid methanol is discussed.

The study of proton solvation and proton mobility in liquids has recently become an active area of research.[1,2] Theoretical simulations using ab initio molecular dynamics,[3] quantum dynamics,[4] and Born−Oppenheimer molecular dynamics plus density function theory[5] have examined in detail the nature of proton migration in liquid water. The generally accepted interpretation for the exceptionally high proton mobility in liquid water is the Grötthuss mechanism which involves an assumption of proton hopping between, in addition to diffusing through, water molecules. Recent calculations[3,4] on protonated water clusters concluded that the Grötthuss behavior depends critically on the dynamics of water molecules in the second (2°) solvation shell, as well as the inward fluctuations of the O−O distance of the water molecules hydrogen bonded to the $H^+(H_2O)_2$ complex. Specifically, the excess proton can migrate along a “special bond” which links H_3O^+ with an undercoordinated H_2O molecule.[3] The motion, consisting of interconversion between the H_3O^+-centered and the $H_5O_2^+$-centered $H^+(H_2O)_2$ complexes, ultimately drives the proton transfer process. Unfortunately, from a spectroscopic point of view, the reliability of these calculations is difficult to verify because of complex structural isomerism associated with the protonated water clusters.[6]

Protonated methanol clusters offer the merits of simplicity for this study since CH_3OH contains a methyl group which is hydrophobic in nature and does not involve itself in hydrogen bonding. In liquid states, pure methanol forms one-dimensional hydrogen-bonded chains with occasionally occurring branches.[7] Gas-phase methanol clusters [$(CH_3OH)_{3-6}$], however, exist as energetically favored cyclic isomers owing to additional hydrogen bonding.[8,9] In comparison with its neutral counterparts, little information is presently available concerning the structures and dynamics of protonated methanol clusters,[10,11] despite their general importance in chemistry. Our group has recently identified the structures of isomeric $NH_4^+(H_2O)_{2-7}$ using vibrational predissociation spectroscopy (VPS) in combination with ab initio calculations.[12] Further extension of VPS to the study of methanol cluster ions is presented in this article with a special focus on protonated pentamers which exhibit an intriguing property of intracluster proton transfer.

The experiment was conducted using a vibrational predissociation ion trap spectrometer coupled with a pulsed infrared laser system.[12] We synthesized protonated clusters (H^+M_n) by corona-discharging methanol (M) vapor in a pure H_2 supersonic jet. Such synthesized clusters have a typical internal temperature of 200 K which could be varied (±20 K) by properly adjusting the beam expansion conditions.[12] The jet-cooled clusters, after size selection by a sector magnet mass spectrometer, were stored in an octopole ion trap for laser excitation. Upon absorption of resonant infrared photons, the size-selected methanol clusters dissociated as $H^+M_n \rightarrow H^+M_{n-1} + M$. A quadrupole mass spectrometer monitored the concentration increase of the photofragments (H^+M_{n-1}) to obtain the vibrational predissociation spectra.

The ab initio calculations were performed using the Gaussian 94 program package.[13,14] The selected DFT method, employing the Becke3LYP functional with the 6-31+G* basis set, is an effective approach of describing intermolecular hydrogen bonding in water polymers.[15] We optimized the geometries using analytical gradients and obtained the frequencies using analytical second derivatives. The calculations predicted binding energies, harmonic vibrational frequencies and infrared absorption intensities of various structural isomers. The factor used to scale the calculated frequencies was 0.973.[12] Table 1 lists the calculated stepwise and total energies of the clustering and their comparison with experimental measurements. The agreement is good, supporting the use of the B3LYP/6-31+G* method in the calculations.

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TABLE 1: Ab initio Calculated Energies (kcal/mol) of the Clustering (1) $H^+(CH_3OH) + (n - 1)\ CH_3OH \rightarrow H^+(CH_3OH)_n$ and (2) $H^+(CH_3OH)_{n-1} + CH_3OH \rightarrow H^+(CH_3OH)_n$, using B3LYP/6-31$^+$G*, and Their Comparison with Experimental Values at 298.15 K[a]

isomers[b]		calcd				exptl[c]	
$H^+(CH_3OH)_{n-1}$	$H^+(CH_3OH)_n$	ΔE_n	$\Delta E_{n-1,n}$	$\Delta H_{n-1,n}$	$\Delta G_{n-1,n}$	$\Delta H^\circ_{n-1,n}$	$\Delta G^\circ_{n-1,n}$
1I	2I	−32.63	−32.63	−32.82	−23.62	−33.1	−24.0
2I	3I	−52.31	−19.53	−19.23	−11.06	−21.3	−12.9
3I	4I	−66.60	−14.34	−14.17	−5.89	−16.1	−7.5
	4II	−64.79	−12.61	−13.15	−0.08		
4I	5I	−77.42	−11.12	−10.90	−2.68	−13.5	−4.9
	5II	−78.11	−11.71	−12.10	0.09		

[a] ΔE_n and $\Delta E_{n-1,n}$ represent the calculated energies of the clustering via channels 1 and 2, respectively, with basis set superposition errors and zero-point vibrational energies corrected. [b] Both isomers 2I and 3I are linear in geometry (refs 10, 11, and 14), similar to that of 4I and 5I. [c] Meot-Ner, M. *J. Am. Chem. Soc.* **1984**, *106*, 1265.

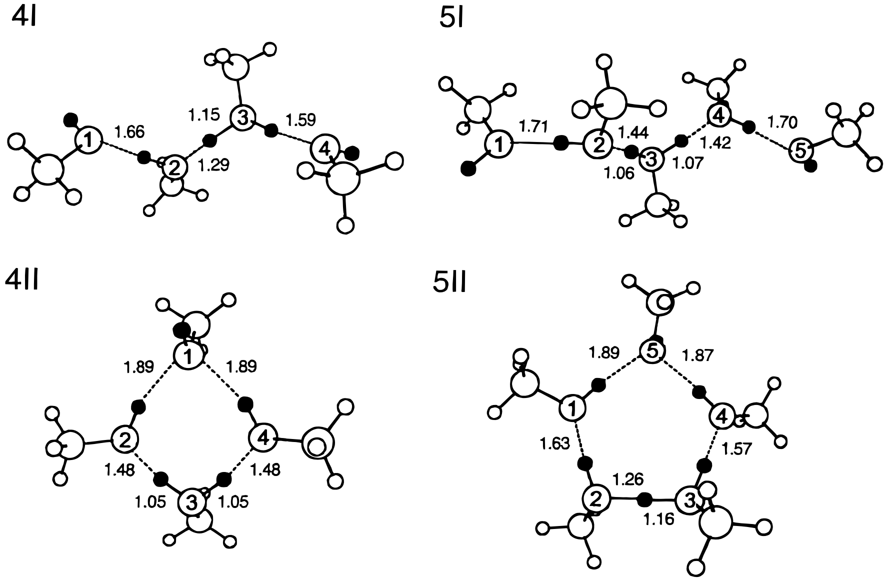

Figure 1. *Ab initio* optimized structures of protonated methanol tetramers and pentamers. The C and H atoms in methyl groups are denoted by empty ○ and ○, and the O and H atoms in hydroxyl groups are denoted by numbered ○ and ●, respectively. The given bond lengths are all in units of angstroms.

Figure 1 illustrates the ab initio optimized structures of protonated methanol tetramers and pentamers. As in protonated water clusters,[16] the proton in these polymers can be either localized at one site or delocalized between two methanol units, depending on the structure of the clusters. In Figure 1, we also indicate the individual bond length (r_{OH^+}) of $O-H^+$ involving the excess proton. The lengths are $r_{OH^+} = 1.15$ and 1.29 Å for isomer **4I** and are $r_{OH^+} = 1.16$ and 1.26 Å for isomer **5II** at their potential minima. A close examination of the potential energy surface along the $O-H^+$ coordinate, however, reveals that the potential wells of these two isomers are nearly flat with an energy variation of less than 0.5 kcal/mol over the range of $r_{OH^+} = 1.10-1.35$ Å.[14] In these wells, the excess proton can move back and forth between two CH_3OH molecules (M2 and M3), and the dynamics is essentially barrierless. As for isomers **4II** and **5I**, a single relatively deep potential well exists and the excess proton is highly localized on the middle CH_3OH molecule (M3).[14] In analogy to $H_5O_2{}^+(H_2O)_{n-2}$, isomers **4I** and **5II** are designated as $C_2H_9O_2{}^+(CH_3OH)_2$ and $C_2H_9O_2{}^+(CH_3OH)_3$, respectively.

Figure 2a and b present the vibrational predissociation spectra of protonated methanol tetramers and their comparison with the ab initio calculated stick diagrams of isomers **4I** and **4II** in the OH stretching region of 3350−3750 cm^{-1}.[17] Only one single feature was recorded at 3676 cm^{-1}, and it can be ascribed to the free-OH stretching of neutral CH_3OH molecules (M1 and M4) in isomer **4I**.[18] No additional absorptions were found as the beam temperature was lowered by ~30 K in Figure 2b. The spectral invariance (except broadening) is consistent with the calculations which predict that isomer **4I** is lower in energy (ΔE_n) than **4II** by 1.8 kcal/mol (Table 1). The ring-shaped isomer (**4II**), if present, should display (i) an intense absorption doublet at ~3430 cm^{-1}, which arises from the stretching of the two hydrogen-bonded-OH groups (M2 and M4) perturbed by the CH_3OH (M1) acting as a double proton acceptor (AA), and (ii) the free-OH stretching absorption of AA−CH_3OH (M1) at ~3640 cm^{-1}. Such absorptions, however, cannot be found in the spectra.[17]

Two groups of transitions were recorded in Figure 2c and d for protonated methanol pentamers: free-OH stretches at 3647 and 3678 cm^{-1} and bonded-OH stretches at 3448 and 3461 cm^{-1}, obtained after spectral deconvolution. The emergence of the new features due to temperature changes in Figure 2d is indicative of structural isomerization for this cluster. Compared with the calculated spectra, the observations of the distinct free-OH stretch at 3647 cm^{-1} and the bonded-OH stretching doublet at 3448 and 3461 cm^{-1} unambiguously identify the ring isomer **5II** in the beam. The identification is further supported by the observed relative absorption intensity of the two bonded-OH stretches (M1 and M4), which agrees quantitatively well with the calculated values. The appearance of the ring isomer in a colder beam suggests that this isomer is lower in energy than

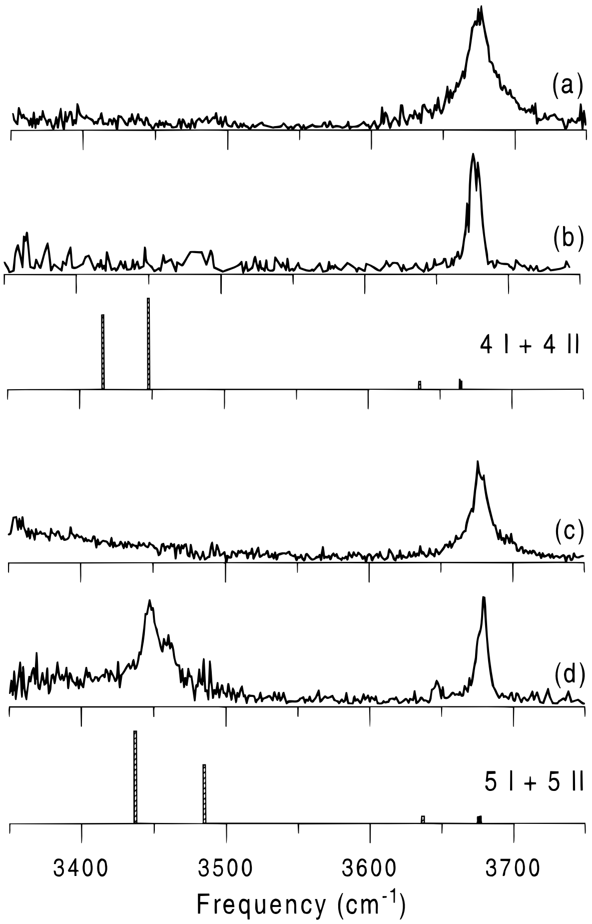

Figure 2. Vibrational predissociation spectra of protonated methanol clusters synthesized by supersonic expansion at (nozzle temperature, backing pressure) of (a) (300 K, 60 Torr) and (b) (250 K, 150 Torr) for tetramers and of (c) (300 K, 60 Torr) and (d) (250 K, 150 Torr) for pentamers. The *ab initio* calculated stick spectra of isomers **4I** (■), **4II** (▨), **5I** (■), and **5II** (▨) were obtained using B3LYP/6-31+G*.

its linear counterpart. The result, in good agreement with the ab initio prediction that isomer **5II** is 0.7 kcal/mol more stable than **5I** (Table 1), is exactly opposite to that of **4I** and **4II**.

An additional information conveyed by Figure 2c and d is the isomeric transition of **5I** → **5II**, which occurred when the clusters were cooled off from 220 to 190 K. The transition reflects an intriguing ring closing process by jet cooling. Notably, the structural transition temperature of ~200 K is comparable to 243 K predicted by Monte Carlo and molecular dynamics simulations for the neutral methanol pentamer.[19] Table 1 lists the ab initio calculated Gibbs energy of each clustering at room temperature. At 298 K, the ring-opened isomer **5I** is predicted to be lower in energy than **5II** owing to entropy effects. The latter is energetically favored, namely, $\Delta G_{n-1,n}(\mathbf{5II}) \leq \Delta G_{n-1,n}(\mathbf{5I})$, only when the cluster temperature reaches below 100 K.

The ring-shaped pentamer has a structure different from that of cyclic neutral $(CH_3OH)_5$.[8,9] It consists of a dangling OH group and a distorted pentagon with an interoxygen distance of 2.42 Å for the shortest side containing the excess proton (Figure 1). Also, owing to the presence of the excess proton, the protonated pentamer contains an AA$-$$CH_3OH$ and four CH_3OH molecules acting like a single proton acceptor and a single proton donor (AD), whereas in $(CH_3OH)_5$, all the molecules are in the form of AD$-$$CH_3OH$. Interestingly, because of the proton intrusion and symmetry breaking, distinct and well-separated vibrational features arise. These distinct features, particularly the hydrogen-bonded-OH stretching doublet, are the fingerprints of a *symmetric*, ring-shaped isomer in protonated water and methanol clusters.[12,14]

The excess protons in isomers **4I** and **5II** are equally shared by two methanol units. It is in marked contrast to that in isomers **4II** and **5I** where the proton is highly localized on the central CH_3OH molecule. This unique feature of proton localization and delocalization, which depends on structures, suggests that the excess proton can make a swift transfer during the course of hydrogen bond rearrangement in these protonated clusters. It leads to the suggestion of a new mechanism of proton transfer, *intracluster proton transfer mediated by ring formation*, as illustrated in Figure 3a for protonated methanol pentamers. Such a transfer involves forming and breaking adjacent hydrogen bonds between molecules in the second (2°) solvation shells of the $CH_3OH_2^+$ ion core, allowing the excess proton to migrate from one methanol unit to another via repeated ring opening and closing processes.

A similar proton transfer mechanism immediately arises as one applies the same concept to the linear forms of the clusters. The mechanism, depicted in Figure 3b, involving both linear tetramers and pentamers, is directly related to that in liquid methanol. In the liquid phase, nuclear magnetic resonance studies[20] determined an activation enthalpy of ~2 kcal/mol for the proton to migrate from $CH_3OH_2^+$ to CH_3OH. Molecular dynamics simulation[21,22] predicted that the average lifetime of hydrogen bond breaking between methanol molecules is less than 10 ps at room temperature. Grunwald et al.[20] have proposed

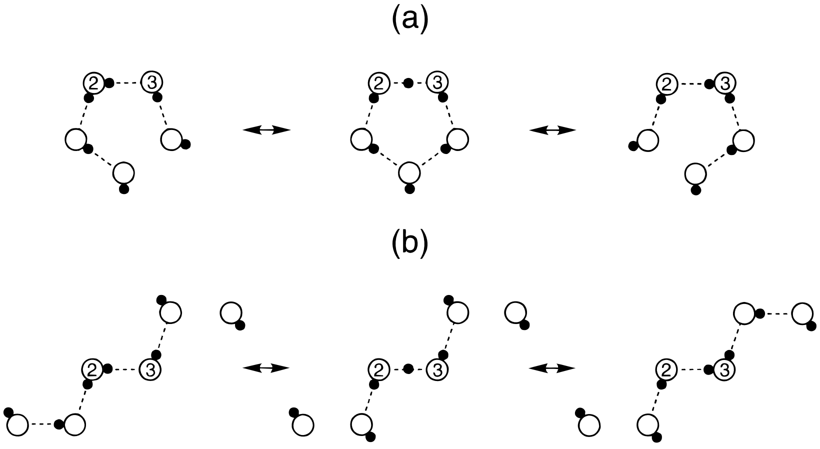

Figure 3. (a) Intracluster proton transfer via repeated ring opening and closing in protonated methanol pentamers. (b) Proposed mechanism of proton migration in liquid methanol. The symbols ○ and ● denote CH_3O and H, respectively.

a structural diffusion model based on a polymolecular transfer to account for the anomalously large conductance (88 Ω^{-1} cm^2) of protons in liquid methanol. The present observations and calculations provide a mechanistic picture for the proton transfer process [Figure 3b]: protons make a transfer when concerted fluctuation in liquid methanol occurs in a way that hydrogen bonds are momentarily ruptured behind, and then reformed ahead of the transferring protons. According to Agmon,[2] the experimentally determined activation enthalpy of ∼2 kcal/mol should be considered as the energy associated with the hydrogen bond cleavage involving the 2°-CH_3OH molecules.

In summary, we have employed both vibrational predissociation spectroscopy and ab initio calculations to investigate the motion of the excess protons in protonated methanol tetramers and pentamers. From VPS, both linear and cyclic isomers were identified according to their characteristic non-hydrogen-bonded- and hydrogen-bonded-OH stretching vibrations. Ab initio calculations indicate that the excess proton can be either localized on one methanol unit or shared by two methanol molecules, depending on the structure and solvation number of the clusters. The findings lead to an alternative interpretation for the exceptionally high proton mobility in liquid methanol. The interpretation, based upon a mechanism of proton transfer mediated by periodic interconversion between $C_2H_9O_2^+(CH_3OH)_{n-2}$ and $CH_3OH_2^+(CH_3OH)_{n-1}$, closely resembles that proposed for liquid water.[2] It is hoped that the present structural identification of cluster isomers can help clarify the nature of proton migration in liquid methanol.

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