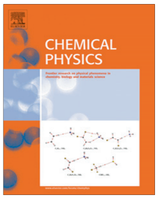
Chemical Physics 421 (2013) 1–9

Contents lists available at SciVerse ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys



Proton location in $(CH_3)_3N\text{-}H^+\text{-}(CH_3OH)_n$: A theoretical and infrared spectroscopic study

Dan Bing [a,1], Toru Hamashima [b], Chen-Wei Tsai [c,d], Asuka Fujii [b,*], Jer-Lai Kuo [a,d,*]

[a] School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore
[b] Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
[c] Department of Physics, National Taiwan University, Taipei 10617, Taiwan
[d] Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan

ARTICLE INFO

Article history:
Received 25 March 2013
In final form 15 May 2013
Available online 23 May 2013

Keywords:
Protonation
Proton affinity
Hydrogen bond network
Density functional theory calculation
Infrared spectroscopy

ABSTRACT

The dependence of the preferential protonated site in $(CH_3)_3N\text{-}H^+\text{-}(CH_3OH)_n$ on the cluster size was investigated using theoretical calculations and infrared spectroscopy measurements. While simple estimation from the magnitude of proton affinity suggested that the excess proton prefers the methanol site in $n \geqslant 4$, density functional theory calculations of the stabilization energy indicated the clear preference as protonation of the trimethylamine site, even for $n = 9$. Infrared spectra of the clusters were observed for $n = 3–7$. Spectral simulations were also performed using the quantum harmonic superposition approximation. The observed $(CH_3)_3N\text{-}H^+\text{-}(CH_3OH)_n$ spectra were well interpreted by simulations of the isomers with the protonated trimethylamine ion core. It was shown that both the proton affinity and the mutual solvation energy govern the preferential location of the excess proton in binary component clusters.

1. Introduction

Proton transfer in hydrogen-bonded (H-bonded) systems is one of the most important reactions for many chemical and biological systems [1–4]. For multiple component systems with an excess proton, the preferential site for protonation has been the subject of extensive studies [5–33]. The proton affinity (PA) in the gas phase is often used as an index to infer the preferential protonation site. For instance, the systematic infrared (IR) spectroscopic study on protonated binary clusters by Roscioli et al. has demonstrated that the vibrational frequency of the shared proton (the magnitude of localization/delocalization of the excess proton) well correlates with the difference of the proton affinities of the two molecules [25]. Some studies on binary component clusters have shown that proton transfer can occur from a site with larger PA to a site with less PA via stepwise solvation, because H-bonds induce a cooperative enhancement of PA [17–19]. Even in such cases, if we suppose the PA of a cluster consisting only of one component, the PA can be useful to predict the protonated site. The dependence of the proton location on the cluster size for $C_6H_5O\text{-}H^+\text{-}(H_2O)_n$ has been well explained by a simple comparison of the PA magnitudes of C_6H_5O and $(H_2O)_n$ clusters [17,18]. However, there have also been many reports on the clear failure of such a simple comparison of the PA magnitudes [8,9,12,13,15,20,23–33]. For example, Fridgen has calculated the preferential proton location in many protonated binary clusters and has predicted that a site of less PA holds the excess proton if the counterpart possesses much larger dipole moment than that of the partner [23]. This has been experimentally confirmed by IR spectroscopy of the $CH_3CN\text{-}H^+\text{-}H_2O$ cluster [24]. In this cluster, water, which has less PA (167 kcal/mol) [34], holds the proton though acetonitrile has larger PA (186 kcal/mol). This result is interpreted that the smaller protonation energy of water is compensated by the larger solvation energy of acetonitrile due to its larger dipole moment (3.9 D) than that of water (1.85 D). The $C_6H_6\text{-}H^+\text{-}H_2O$ cluster is a similar example [31,32]. PA of benzene (180 kcal/mol) is much larger than that of water. However, the formation of H_3O^+ in $C_6H_6\text{-}H^+\text{-}H_2O$ has recently been confirmed by theoretical calculations and infrared (IR) spectroscopy. In this case, the larger polarizability of benzene than that of water causes the larger solvation energy to the protonated partner. An recent IR spectroscopic study on naphthalene-$H^+\text{-}(H_2O)_n$ also concluded a competition between the PA and solvation energy [33]. These results demonstrate that the solvation energy following protonation is also an important factor to determine the preferential protonation site in multicomponent systems. Mass spectrometry has also been utilized to study the proton location in more complicated systems [5–15]. The preferential protonation site is inferred by size

---

[*] Corresponding authors. Address: Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan (J.-L. Kuo).

E-mail addresses: asukafujii@m.tohoku.ac.jp (A. Fujii), jlkuo@pub.iams.sinica.edu.tw (J.-L. Kuo).

[1] Present address: Institute of Theoretical and Computational Chemistry, Nanjing University.

0301-0104/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemphys.2013.05.009

distribution and fragmentation channels, and such studies suggest the preferential site is dependent on the cluster structures and mixing ratio among multiple components.

Many previous studies on the preferential protonation site have been concerned with binary component systems containing water [5–12,14–33]. A major problem in such systems is the large number of possible isomer structures, due to the 3-dimensional nature of the water H-bond network. To examine the physical essence of the preferential site, methanol clusters, $(MeOH)_n$, would be a more suitable system than water clusters. Methanol has similar H-bonding capability as water, but has only one OH group. This difference from water prohibits the formation of complicated 3-dimensional H-bond network structures in methanol [35–40]. This simplification suppresses exceptional geometric factors such as magic number behavior, and it also allows a complete survey of all possible isomer structures. As a counter-component, trimethylamine ($(CH_3)_3N$; TMA) was selected. TMA can act only as a proton acceptor in H-bond networks, and has a high PA of 227 kcal/mol [34]. The PA of methanol (180 kcal/mol) is also higher than that of water (165 kcal/mol) [34]; therefore, competition between the PAs of TMA and methanol clusters is suitable to investigate the preferential protonation site in two component systems. While the structures of protonated TMA-water clusters have been studied using mass spectrometry and IR spectroscopy [6,7,14–16,30], there have been no systematic studies reported for protonated TMA-methanol clusters.

The PAs of $(MeOH)_n$ were evaluated from the thermochemical cycle by Knochenmuss et al. [41], and are shown in Table 1. The PAs increase with increasing n, due to the cooperative stabilization by H-bonds. The PAs of $(MeOH)_n$ for $n \geqslant 4$ are larger than TMA. If we simply use the magnitude of the PA to estimate the preferential location of the excess proton in TMA-H^+-$(MeOH)_n$, then the results suggest that the excess proton would locate at the TMA site for $n \leqslant 3$, but remain in a methanol site for $n \geqslant 4$.

In this work, the excess proton location in TMA-H^+-$(MeOH)_n$ was investigated using theoretical computations and IR spectroscopy. Stable structures are calculated according to density functional theory. The IR spectra of size-selected clusters are observed using predissociation spectroscopy, and the observed spectra are compared with simulations based on the superposition of multiple isomer contributions to examine the excess proton location.

2. Computational methods

The geometries of TMA-H^+-$(MeOH)_n$ were optimized at the B3LYP/6-31+G* level using the Gaussian 09 program package [42]. The harmonic frequencies, zero-point energy, and Gibbs free energy at 190 K were calculated for each energy-optimized structure. Relative energetics were also evaluated using the ωB97X-D functional with the 6–311++G(3df, 3pd) basis set.

Table 1
Proton affinities for TMA and $(MeOH)_n$. The datum of TMA is taken from Ref. [31] and all other data are taken from Ref. [41]. All units are in kcal/mol.

	Proton affinity
TMA	227
MeOH	182
$(MeOH)_2$	211
$(MeOH)_3$	224
$(MeOH)_4$	231
(MeOH)5	234
$(MeOH)_6$	237
$(MeOH)_7$	238
$(MeOH)_8$	240
$(MeOH)_9$	241

The experimental IR spectroscopy adopted for this study has no isomer selectivity; therefore, the quantum harmonic superposition approximation (Q-HSA) was employed to simulate IR spectra; the details of this method have been reported in our recent work [28]. The IR absorption intensity $I_a(\omega)$, of each isomer a, in the selected system A, was obtained from the results of the B3LYP calculations. The averaged intensity $I_A(\omega, T)$ at temperature T was then calculated as the weighted sum of $I_a(\omega)$ with the canonical probability $P_a(T)$ of isomer a derived from the thermodynamic simulations:

$$I_A(\omega, T) = \sum_a I_a(\omega) P_a(T), \tag{1}$$

where

$$P_a(T) = \frac{Z_a(\beta)}{Z(\beta)}. \tag{2}$$

The total partition function $Z(\beta)$ of an N-atom system at T is given by

$$Z(\beta) = \sum_a n_a Z_a(\beta), \tag{3}$$

where $Z_a(\beta)$, under the Q-HSA, is given by

$$Z_a(\beta) = \exp(-\beta E_a) \prod_f \frac{\exp\left(-\beta\hbar\omega_f^a/2\right)}{1 - \exp(-\beta\hbar\omega_f^a)}, \tag{4}$$

where $\beta \equiv \frac{1}{k_B T}$ is the "inverse temperature", E_a is the electronic energy, and ω_f^a is the f-th vibrational frequency of isomer a. Simulated spectra are obtained by superposition of the spectra of the isomers. The relative weight of the spectrum for each isomer is its canonical probability. Calculated stick spectra are converted into continuous spectra by convolution using Lorentzian functions. For the homogeneous width, supposing a Lorentzian spectral function, the power law formula proposed by Takahashi and co-workers is adopted to determine the vibrational decay lifetime of the OH bond stretch [43,44]. The homogeneous width Γ for the intramolecular hydrogen-bonded OH stretch is expressed as:

$$\Gamma = \alpha(\Delta\omega)^\beta = \alpha\left(\omega_{free\ OH} - \omega_{H-bonded\ OH}\right)^\beta, \tag{5}$$

where $\Delta\omega$ is the low-frequency shift of the H-bonded OH band peak with respect to the free OH peak of the experimental spectra. The units selected for Γ and $\Delta\omega$ are wavenumber (cm^{-1}). The parameters α and β are determined using the least square fitting procedure in combination with the experiment results within the H-bonded OH stretch region from 3000 to 3600 cm^{-1}. The α and β values used here are $\alpha = 0.0009$ and $\beta = 1.9$. Note that this power law formula was not applied to CH stretches, which do not have strong mixing with H-bonded OH stretches and are free from line broadening by H-bond formation.

All calculated harmonic frequencies were scaled by a factor 0.973, which has been determined to reproduce the free OH-stretch band in protonated clusters [45].

3. Experimental methods

IR spectra of TMA-H^+-$(MeOH)_n$ ($n = 3$–7) were recorded using IR predissociation spectroscopy with a mass spectrometer equipped with linearly aligned tandem quadrupole mass filters connected by an octopole ion guide [30]. TMA-H^+-$(MeOH)_n$ was produced by pulsed discharge of a TMA/methanol mixed vapor seeded in Ar buffer gas (total stagnation pressure of 7 atm). The gaseous mixture was expanded from a pulsed supersonic jet valve. A pin electrode was installed beside the nozzle and a pulsed voltage of