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Experimental confirmation of the Badger-Bauer rule in the protonated methanol clusters: Weak hydrogen bond formation as a measure of terminal OH acidity in hydrogen bond networks

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Experimental confirmation of the Badger-Bauer rule in the protonated methanol clusters: Weak hydrogen bond formation as a measure of terminal OH acidity in hydrogen bond networks†

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Abstract We report a linear correlation between the OH stretch frequency shift of the protonated methanol cluster, $\text{H}^+(\text{MeOH})_n$, upon the π -hydrogen bond formation with benzene and the enthalpy change in clustering of $\text{H}^+(\text{MeOH})_n$ to $\text{H}^+(\text{MeOH})_{n+1}$. This result suggests a new method to explore hydrogen bond strength in hydrogen bond networks.

When an OH group forms a hydrogen bond (H-bond), its stretching vibration band shows a characteristic red-shift. Such a red-shift is well known as a marker of H-bond formation.¹ In 1937, Badger and Bauer proposed that the OH stretch frequency shift, $\Delta\nu_{\text{OH}}$, on the H-bond formation linearly correlates with its enthalpy change, ΔH .² This correlation is called Badger-Bauer rule.¹⁻³ Studies on the Badger-Bauer rule have been mainly focused on 1:1 (*i.e.*, singly H-bonded) complexes in both the solution and gas phases.⁴⁻²⁵ On the other hand, for H-bond network systems, such as clusters of protic molecules, in which multiple H-bonds cooperatively work, experimental confirmation of the Badger-Bauer rule has been very scarce. There are several difficulties in experimental confirmation of the Badger-Bauer rule in H-bond networks. Addition of one molecule to the network with new H-bond formation is frequently followed by rearrangement of the whole (or part of) network structure and the measured ΔH does not necessarily correspond to the enthalpy change only for the formation of the new H-bond. In the solution phase, the enthalpy change due to rearrangement of solvents is also involved. Moreover, the stretch band of the newly H-bonded OH oscillator is overlapped/coupled with other H-bonded OH bands, and it is hard to clearly identify the OH stretch band of interest.^{26, 27} Even in the case of gas phase clusters, in which solvent effects are totally removed and H-bond network size and structure are controllable, confirmation of the Badger-Bauer rule has been practically limited to

1:1 systems, to our best knowledge.²²⁻²⁵ In such studies, theoretical computations are also frequently employed to evaluate frequency shifts and/or enthalpy changes.

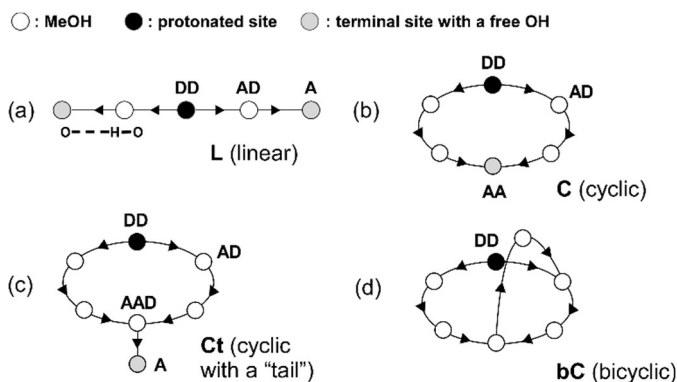


Fig. 1 Schematic representations of possible four hydrogen bond network structure types of protonated methanol clusters, $\text{H}^+(\text{MeOH})_n$. A circle represents a methanol molecule, and an arrow indicates direction of a hydrogen bond from a donor site to an acceptor site. DD: double donor (protonated) site. AD: single acceptor–single donor site. A: single acceptor site. AA: double acceptor site. AAD: double acceptor–single donor site.

Protonated methanol clusters, $\text{H}^+(\text{MeOH})_n$, are a simple model system of proton solvation and are also an attractive model to understand the nature of H-bond networks.²⁸⁻⁴⁴ The cluster size (n) and temperature dependence of the H-bond structures of $\text{H}^+(\text{MeOH})_n$ has been studied by infrared (IR) spectroscopy combined with theoretical computations.^{32, 34-44} Fig. 1 briefly summarizes the H-bond network types of $\text{H}^+(\text{MeOH})_n$.^{38, 40} Possible H-bond structures of $\text{H}^+(\text{MeOH})_n$ can be categorized into only four topological types: linear (L), cyclic (C), cyclic with a "tail" (Ct), and bicyclic (bC), as schematically shown in the figure. In all the types, the protonated site is always a double donor (DD) site. The L type has a one-dimensional chain structure. Each of the terminal sites of the chain is a single acceptor (A) and has a free OH. Sites between the

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protonated site and terminal site are single acceptor – single donor (AD) sites. When the two ends of an **L** structure are bound to each other, a **C** structure is formed. The **C** structure has a double acceptor (AA) site, which has a free OH. **Ct** is a structural type, in which a side chain (“tail”) is extended from the free OH of a **C** structure. This side chain is terminated by an A site. When the A site of a **Ct** structure is bound to the ring moiety, a **bC** structure is formed. The **bC** structure is the most complicated H-bond network type. For $n = 2$ and 3, possible structures are practically limited to the **L** type. In $n \geq 4$, multiple different H-bond network types can compete with each other. The **L**, **C**, **Ct**, and **bC** type structures are the lowest energy ones for $n = 4 - 7$, respectively.³⁸ Clusters in enough low temperature hold their lowest energy form, however more flexible (vibrationally denser) isomers are preferentially populated with a rise in temperature because of the entropy factor in the free energy.^{37-39, 44} The **L** type isomer is the most flexible one and is preferred at high temperature in all the sizes.³⁸

The clustering enthalpy change of $\text{H}^+(\text{MeOH})_n$,



has been extensively studied by ion equilibrium measurements with mass spectrometry.²⁸⁻³² The magnitude of ΔH_c rapidly decreases with increasing n , and becomes almost constant in $n \geq 7 \sim 8$. This size dependence indicates the weakening of the H-bond strength at the terminal site of the H-bond network along with the elongation of the distance between the terminal site and the protonated site. Under the condition of the ΔH_c measurements reported so far (the temperature range for the van't Hoff plots is higher than ~ 200 K),²⁸⁻³² $\text{H}^+(\text{MeOH})_n$ preferentially forms **L** type structures.³⁸ Therefore, in this clustering process of $\text{H}^+(\text{MeOH})_n$, a new single H-bond is formed at one of the terminal A sites, and rearrangement of the whole H-bond network would be minimum. This suggests that the measured ΔH_c would correspond well to Δv_{OH} of the newly H-bonded OH at the clustering and this system can be a prototype to test the Badger-Bauer rule in H-bond networks. However, the H-bonded OH stretch bands of $\text{H}^+(\text{MeOH})_n$ of the **L** structures (measured at ~ 200 K) are heavily broadened because of the overlap and mode mixing among multiple H-bonded OH bands, and Δv_{OH} corresponding to ΔH_c cannot be identified.³⁸

Recently we reported the IR spectra of the $\text{H}^+(\text{MeOH})_n$ -benzene clusters ($n = 2 - 7$) in the gas phase.⁴⁵ This study was performed on the basis of the same concept as the previous study by Stoyanov *et al.* on $\text{H}^+(\text{MeOH})_n$ produced in benzene solutions.⁴⁶ In both the studies, the OH stretch frequency of the terminal site of the $\text{H}^+(\text{MeOH})_n$ moiety, which is weakly π -hydrogen (π -H) bonded to benzene, is of the main interest. The magnitude of the frequency shift of this band ($\Delta v_{\text{OH}\pi}$) can be regarded as a measure of the H-bond ability of the terminal site in the H-bond network of $\text{H}^+(\text{MeOH})_n$. Because the strength of the π -H-bond is much weaker than that of the σ -hydrogen bond between MeOH molecules, the π -H-bonded OH stretch band is well isolated from other H-bonded OH bands and can be clearly identified (see the IR spectra of $\text{H}^+(\text{MeOH})_n$ -benzene

reproduced in Fig. S1 in the Electronic Supplementary Information, ESI). The cluster size dependence of $\Delta v_{\text{OH}\pi}$ of $\text{H}^+(\text{MeOH})_n$ -benzene in the gas phase shows similar behavior to that of $\text{H}^+(\text{MeOH})_n$ in the benzene solution; the rapid decrease with increasing n and convergence to the constant value at $n = \sim 7$.^{45,46} After we published this result of the gas phase clusters, we found that the cluster size dependence of $\Delta v_{\text{OH}\pi}$ is quite similar to that of the previously reported ΔH_c for the clustering of $\text{H}^+(\text{MeOH})_n$.²⁸⁻³² Therefore, here we demonstrate the correlation between them.

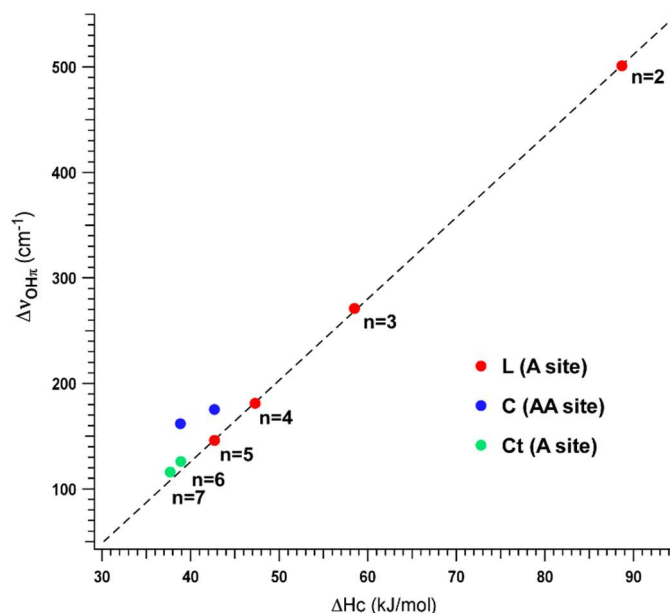


Fig.2 Plot of OH stretch frequency shifts of $\text{H}^+(\text{MeOH})_n$ upon π -hydrogen bond formation with benzene ($\Delta v_{\text{OH}\pi}$) versus clustering enthalpy changes (ΔH_c) in $\text{H}^+(\text{MeOH})_n + \text{MeOH} \rightarrow \text{H}^+(\text{MeOH})_{n+1}$. The $\Delta v_{\text{OH}\pi}$ values are evaluated by the infrared spectra reported in ref.45. The ΔH_c values are taken from ref. 31. The colour codes show the isomer types of the $\Delta v_{\text{OH}\pi}$ data, while all the ΔH_c data are attributed to the **L** isomers. The dashed line is a linear fit line for the points of the **L** isomers (red circles).

Figure 2 shows a plot of $\Delta v_{\text{OH}\pi}$ of $\text{H}^+(\text{MeOH})_n$ -benzene versus ΔH_c of $\text{H}^+(\text{MeOH})_n$ in the size range of $n = 2 - 7$. The $\Delta v_{\text{OH}\pi}$ data are taken from the gas phase spectra reported in our previous paper and are calculated with the free OH frequency (3681 cm^{-1}) of neutral MeOH monomer.^{45, 47} The structure type of the $\text{H}^+(\text{MeOH})_n$ moiety in these clusters depends on the cluster size. This is because of the cooling effect upon the weak π -H-bond formation (so-called “tagging”) and temperature dependence of the isomer distribution.³⁹ In the observed clusters, $n = 2 - 5$ are attributed to the **L** type structures. For $n = 5$ and 6, the **C** type isomers are also found, and for $n = 6 - 7$, the **Ct** type appears. Details on the structure assignments are described in our previous paper.⁴⁵ There have been several reports on ΔH_c of $\text{H}^+(\text{MeOH})_n$,²⁸⁻³¹ and the data in the plot are taken from the latest one by El-Shall *et al.*³¹ We should note that these ΔH_c measurements were performed at temperature higher than 200 K,³¹ and the clusters are considered to form the **L** type structures in all the sizes.³⁸

For the plots for the L isomers of $n = 2-5$ (red circles), a linear correlation is clearly seen. The linearity seems very high, and the dashed line plotted in the figure is a result of the linear fitting for these data points.⁴⁸ This demonstrates that the Badger-Bauer rule is held very well between $\Delta\nu_{\text{OH}\pi}$ and ΔH_c when both of them are measured for the same (L) type H-bond network. Obvious deviation from the linear fit line based on the L isomers is seen for the $\Delta\nu_{\text{OH}\pi}$ data points of the C isomers of $n = 5$ and 6 (blue circles). While the terminal site in the C isomer is an AA site, that in the L isomer is an A site. The acidity of the AA site is expected to be higher than the A site. Therefore, the $\Delta\nu_{\text{OH}\pi}$ values of the C isomers are shifted to the upper (larger shift) side from the fit line for the L isomers. On the other hand, the deviation from the fit line is much smaller for the points of the Ct isomers in $n = 6$ and 7 (green circles). This is because the terminal site of the Ct isomer is an A site, and its acidity would be similar to that of the L isomer of the same size.

The highly linear correlation between $\Delta\nu_{\text{OH}\pi}$ and ΔH_c is found for the L isomers. For these two values, while the proton donor is common (the L type isomer of $\text{H}^+(\text{MeOH})_n$), the proton acceptor is different; $\Delta\nu_{\text{OH}\pi}$ is a result of the π -H-bond formation with benzene and ΔH_c is on the σ -H-bond formation with MeOH. In spite of the difference of the proton acceptor, the Badger-Bauer rule is well held between them. This means that the two linear correlation relations should be held; one is between $\Delta\nu_{\text{OH}}$ and ΔH_c in π -H-bond formation of $\text{H}^+(\text{MeOH})_n$ with benzene. The other is between ΔH_c of $\text{H}^+(\text{MeOH})_n$ with MeOH (σ -H-bond formation) and ΔH_c of $\text{H}^+(\text{MeOH})_n$ with benzene, when the H-bond network of $\text{H}^+(\text{MeOH})_n$ is common and rearrangement of the H-bond network upon the new H-bond formation is negligible. A weakly π -H-bonded OH stretch band can be easily isolated from other σ -H-bonded OH bands, as shown in the present example. Therefore, the general utility of weak π -H-bond formation is expected to measure H-bond ability (acidity) of a terminal or surface (*i.e.*, free OH) site in H-bond networks, once we obtain the slope of the $\Delta\nu_{\text{OH}\pi} - \Delta H_c$ correlation even in a narrow size range. Of course, the slope depends on the structure type of the H-bond network, as indicated by the deviation of the points of the C and Ct isomers from the fit line for the L isomers. We should be also careful in the case that new H-bond formation (clustering) causes large rearrangements of the H-bond network (*e.g.*, switching of the network type).

In conclusion, we demonstrated a highly linear correlation between the red-shift of the OH stretch band of $\text{H}^+(\text{MeOH})_n$ upon the π -H-bond formation with benzene and the enthalpy change in the clustering of $\text{H}^+(\text{MeOH})_n$ with one more MeOH to form $\text{H}^+(\text{MeOH})_{n+1}$. This is a rare example of the Badger-Bauer rule in H-bonded networks, in which multiple H-bonds cooperatively work. The present result suggests that the H-bond ability (acidity) of an OH group at a terminal/surface site in H-bonded networks can be probed by using a weak proton acceptor, which causes a H-bonded OH stretch band well-isolated from other OH bands in the network. For further confirmation of the Badger-Bauer rule in H-bonded networks, a study

on protonated water clusters using a weak proton acceptor is in progress.

Author Contributions

T. K.: investigation, data analysis, and writing. A.F: conceptualization, data analysis, funding acquisition, and writing.

Conflicts of interest

There are no conflicts to declare.

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48. The coefficient of determination R² of the linear fit is calculated to 0.9999 based on the values reported in Refs. 31 and 45. However, error of ΔH_c was estimated to be ~4 kJ/mol (Ref. 31), and ΔV_{OH₂} is also estimated to have uncertainty of 10 and 50 cm⁻¹ in *n* = 5 and *n* = 2, respectively, for the peak position. Therefore, error cancellations may make some contribution to this very high R² value.