

Supplementary Information

Structures of Hydrogen Bond Networks Formed by a Few Tens of Methanol Molecules in the Gas Phase: Size-Selective Infrared Spectroscopy of Neutral and Protonated Methanol Clusters

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1. Electronic spectrum of large-sized phenol-(MeOH)_n clusters and mass spectrum obtained by resonant two-photon ionization of phenol-(MeOH)_n

Figure S1(a) shows the 0-0 band region of the S₁-S₀ electronic spectrum of jet-cooled phenol. The origin band of free phenol is seen at 36348 cm⁻¹.¹ By monitoring the [phenol-(MeOH)₁₉]⁺ cluster ion signal produced by the resonant two photon ionization, an electronic spectrum of the phenol chromophore in large-sized methanol clusters is obtained. The spectrum is shown in Figure S1(b). The spectrum is totally broadened and no structure is seen in the 0-0 band region. This situation is same as the spectra of large-sized phenol-(H₂O)_n clusters.² When the ionization laser frequency is fixed at 36220 cm⁻¹, a mass spectrum of produced cluster ions shown in Figure S2 is obtained. Large-sized cluster ions up to *n* = 39 appear in the mass spectrum. These electronic and mass spectra demonstrate that all large-sized phenol-(MeOH)_n clusters are ionized by the excitation of the broadened electronic transition of the phenol chromophore.

Figure S1

(a) Electronic spectrum of free phenol in the S₁-S₀ band origin region. (b) Electronic spectrum of large-sized phenol-(MeOH)_n obtained by monitoring [phenol(MeOH)₁₉]⁺ ion.

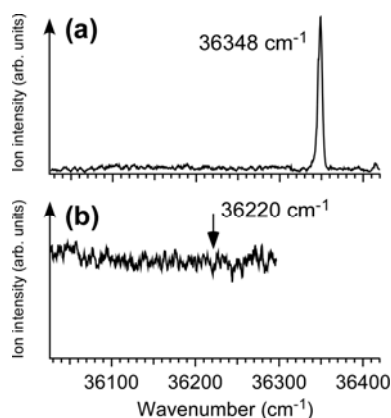
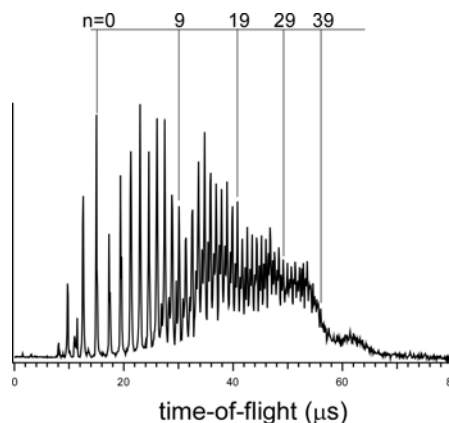


Figure S2

Mass spectrum obtained by the resonant two-photon ionization of phenol-(MeOH)_n



2. Evaluation of the number of evaporated methanol molecules upon the resonant two photon ionization of large-sized phenol-(MeOH)_n

When a phenol-(MeOH)_n cluster is ionized, the excess charge is initially localized in the phenol moiety. In large-sized clusters, however, the proton transfer occurs and the cluster becomes [phenoxy radical-H⁺(MeOH)_n].³⁻⁴ Figure S3 shows the schematic energy diagram on the photoionization and dissociation. When we assume sequential evaporation of single methanol molecules following the resonant two-photon ionization, the maximum number of evaporated molecules upon the ionization (maximum Δn) is given by

$$\text{maximum } \Delta n = E_{\text{excess}}/D(D_0),$$

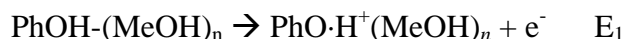
where E_{excess} is the maximum excess energy upon the ionization and $D(D_0)$ is the dissociation energy of the one methanol loss channel in [phenoxy radical-H⁺(MeOH)_n].

In the previous study on large-sized phenol-(H₂O)_n clusters, we evaluate E_{excess} by using DFT calculations.² The phenol containing clusters were constructed on the basis of the minimum energy structures of neutral and protonated water clusters, which have been extensively searched by various theoretical methods. On the other hand, large-sized neutral and protonated methanol clusters lack such theoretical information. Then, in the present study, we roughly estimate E_{excess} from that of the case of water clusters.

The energy scheme shows

$$E_{\text{excess}} = 2E_{\text{UV}} - [E(D_0) - E(S_0)],$$

where E_{UV} is the energy of the UV photon used to ionize the cluster, $E(D_0)$ and $E(S_0)$ are the electronic potential energies of the cationic and neutral ground states, respectively. $[E(D_0) - E(S_0)]$ is equivalent to the enthalpy change of the reaction



This reaction can be decomposed to the following steps



From the thermodynamical cycle,

$$[E(D_0) - E(S_0)] = E_1 = E_2 + E_3 + E_4 + E_5 + E_6$$

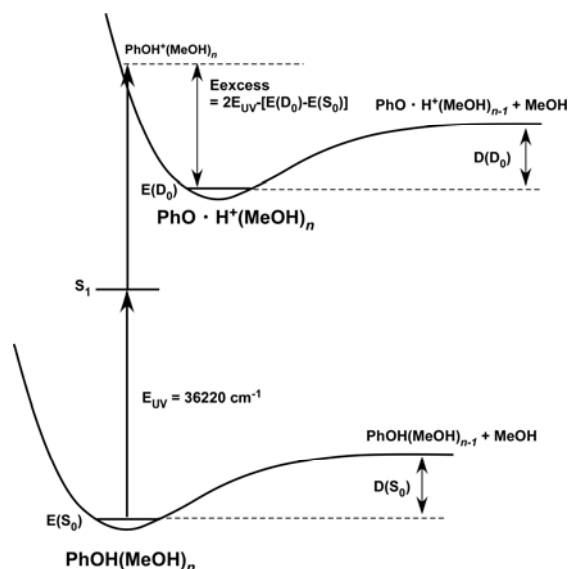
In E_2 - E_6 , E_2 , E_5 , and E_6 should be changed when (MeOH)_n is replaced by (H₂O)_n. E_2

and E_6 are dissociation and solvation energies of one molecule in clusters, respectively, and change of the energy in the replacement of $(\text{MeOH})_n$ by $(\text{H}_2\text{O})_n$ should be within 10 kcal/mol at most. E_5 is proton affinity of a neutral cluster. For $(\text{MeOH})_n$ and $(\text{H}_2\text{O})_n$, those values are available only for $n \leq \sim 6$, and they are 227 and 237 kcal/mol, respectively, at $n = 6$.^{5,6} A clear trend is also seen that the increase of the proton affinity with increasing n of these clusters almost saturates at this size. Therefore, it is reasonable that the change of E_5 in the replacement of $(\text{MeOH})_n$ by $(\text{H}_2\text{O})_n$ is ~ 10 kcal/mol. Thus, the maximum difference of E_1 between $(\text{MeOH})_n$ and $(\text{H}_2\text{O})_n$ is estimated to be ~ 30 kcal/mol (10500 cm^{-1}).

In the previous study,² E_1 of phenol- $(\text{H}_2\text{O})_{19}$ was evaluated to be $\sim 55000 \text{ cm}^{-1}$. Thus, the minimum value of E_1 for large-sized phenol- $(\text{MeOH})_n$ (which results in the maximum excess energy) is $\sim (55000 - 10500) = 44500 \text{ cm}^{-1}$. The maximum excess energy for the UV photon at 36220 cm^{-1} is estimated to be 27640 cm^{-1} . The dissociation energy of one methanol molecule from $\text{H}^+(\text{MeOH})_n$ is $\sim 3000 \text{ cm}^{-1}$.⁷ Therefore, the maximum Δn is ~ 9.2 . With a small margin, we employ the value maximum $\Delta n = \sim 10$ in the present study.

Figure S3

Schematic energy diagram of the resonant two-photon ionization and following dissociation of large-sized phenol- $(\text{MeOH})_n$



References

1. T. Ebata, T. Watanabe, N. Mikami, *J. Phys. Chem.* 1995, **99**, 5761-5764.
2. K. Mizuse, T. Hamashima, A. Fujii, *J. Phys. Chem. A* 2009, **113**, 12134-12141.
3. S. Sato, N. Mikami, *J. Phys. Chem.* 1996, **100**, 4765-4769.
4. T. Sawamura, A. Fujii, S. Sato, T. Ebata, N. Mikami, *J. Phys. Chem.* 1996, **100**,

8131-8138.

5. R. Knochenmuss, O. Cheshnovsky, S. Leutwyler, *Chem. Phys. Lett.* 1988, **144**, 317-323.

6. Y. Kawai, S. Yamaguchi, Y. Okada, K. Takeuchi, Y. Yamaguchi, S. Ozawa, H. Nakai, *Chem. Phys. Lett.* 2003, **377**, 69-73.

7. M. Meot-Ner (Mautner), *J. Am. Chem. Soc.* 1992, **114**, 3312-3322.