Electronic Supplementary Information

Hydrogen-bonded ring closing and opening of protonated methanol clusters $H^+(CH_3OH)_n$ (n = 4 - 8) with the inert gas tagging

Ying-Cheng Li,[1‡] Toru Hamashima,[2‡] Ryoko Yamazaki,[2] Tomohiro Kobayashi,[2]

Yuta Suzuki,[2] Kenta Mizuse,[2†]Asuka Fujii,[2]* Jer-Lai Kuo[1]*

[1]Academia Sinica, [2]Tohoku University

‡ Ying-Chen Li and Toru Hamashima contributed equally to this study.

† Present address Tokyo Institute of Technology, Tokyo, 152-8551 Japan

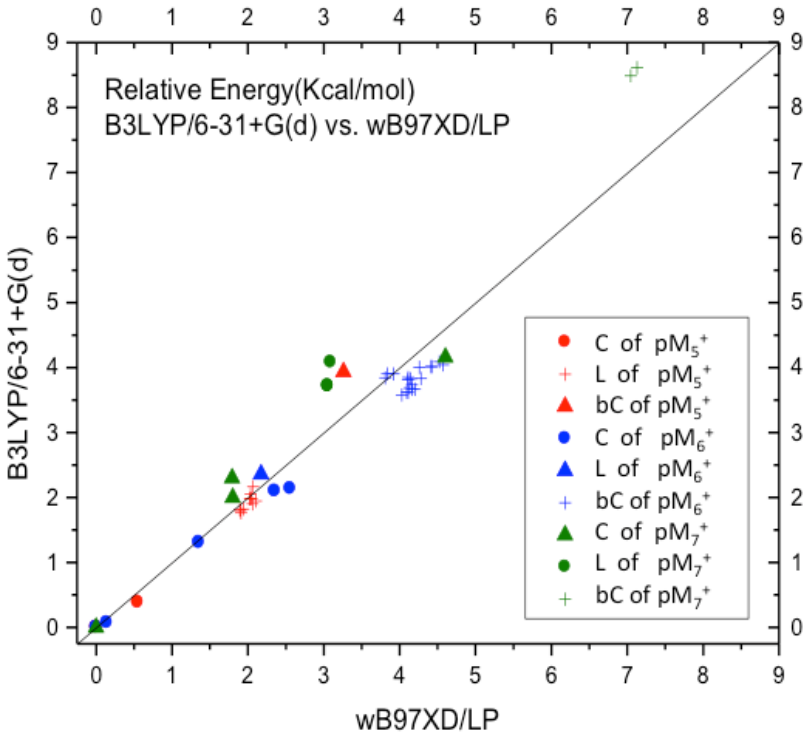
* To whom corresponding should be addressed.

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

Contents

Supplementary Information (I)

Comparisons on the relative energetics between B3LYP/6-31+G(d) with ωB97X-D/ 6-311++G(3df,3pd) for some selected isomers of $H^+(MeOH)_n$ (*n* = 5-7). In each size and calculationn level, the energy of the global minimum isomer is taken as zero.



A clear linear correlation is seen between the relative energies by the two levels of theory. This plot indicates that the relative energy evaluation by B3LYP/6-31+G(d) has the reasonable accuracy in comparison with the dispersion-corrected calculation. More detailed confirmation for *n* = 7 is seen in Ref. 7 of the main text.

Supplementary Information (II)

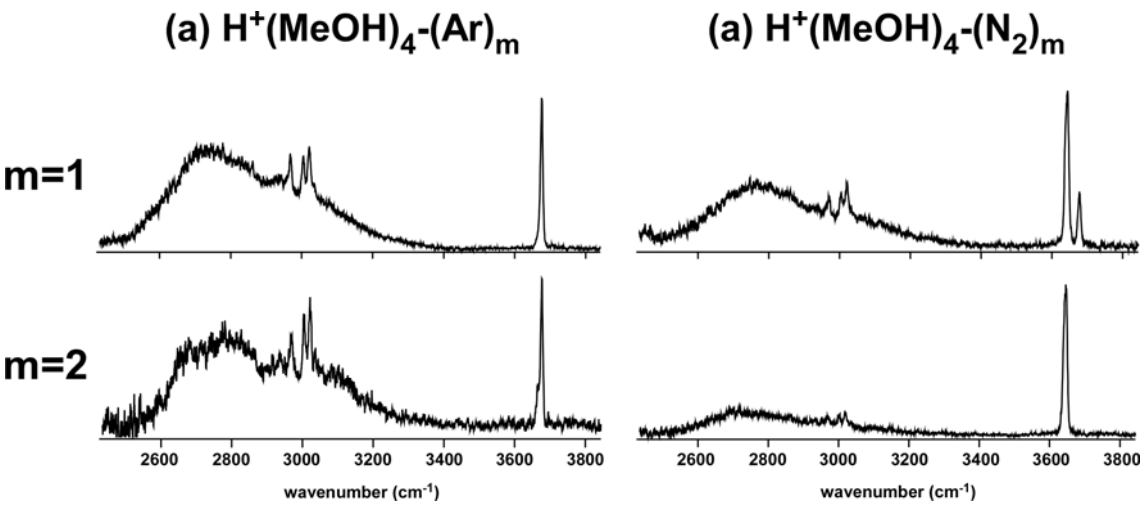
Table SI: Number of stable isomers of $H^+(MeOH)_n$ (n = 4 – 8) optimized with B3LYP/6-31+G(d).

B3LYP/6-31+G(d)	Linear (L)	Cyclic (C & Ct)	bi-Cylic (bC)	all
n=4	1	1	0	2
n=5	10	2	1	13
n=6	16	5	1	22
n=7	35	16	5	56
n=8	47	38	8	93

Geometry of all these isomers is available upon request.

Supplementary Information (III)

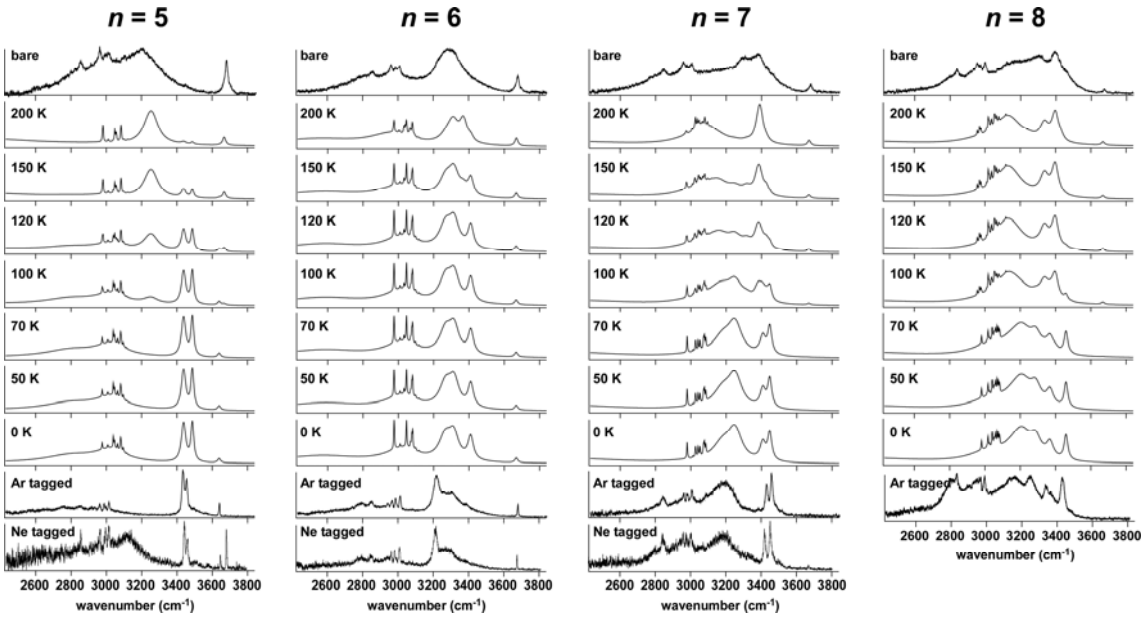
IR Spectra of $H^+(MeOH)_4$ with one and two Ar and N_2 tags.



Two free OH strech bands appear in $H^+(MeOH)_4$-$(N_2)_1$, but only one free OH band is seen in $H^+(MeOH)_4$-$(N_2)_2$. H-bond to the N_2 tag causes the small shift of the "free" OH bond in the terminal methanol moiety. In $H^+(MeOH)_4$-$(N_2)_2$, both the terminal OH bonds are H-bonded to the N_2 tags, and the two "free" OH bands overlap with each other. The spectra of $H^+(MeOH)_4$-$(Ar)_m$, in which the perturbation by the tag is much less, are shown for comparison.

Supplementary Information (IV)

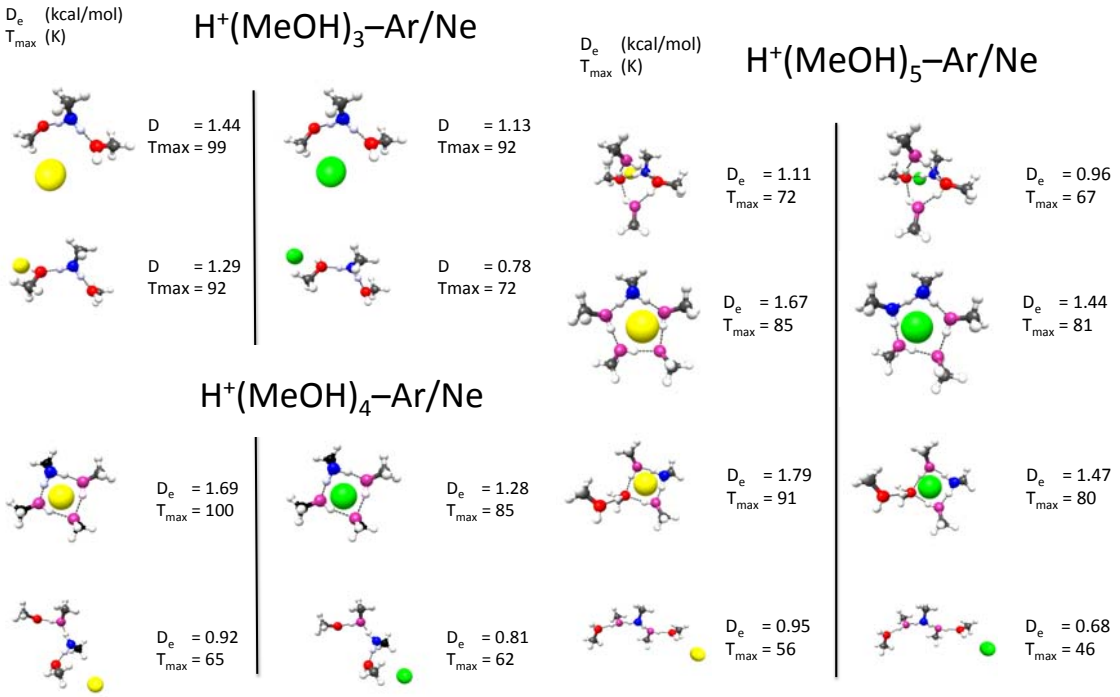
Temperature dependence of simulated spectra of $H^+(MeOH)_n$ (n = 5 – 8) and their comparison with bare and Ne/Ar-tagged spectra. All the simulations were performed at B3LYP/6-31+G(d).



We can see that the experimentally observed spectra of the bare species are comparable with the simulated spectra at 150 ~ 200 K. The Ne/Ar-tagged spectra compare well with the simulated spectra at 0 ~ 70 K.

Supplementary Information (V)

Binding energies (D_e in kcal/mol) of Ar and Ne to $H^+(MeOH)_n$ (n = 3 – 5) at ωB97X-D/6-311++G(3df,3pd). Maximum vibrational temperature (T_{max}) is also shown.



Binding energies of Ar and Ne to $H^+(MeOH)_n$ (n = 3 – 5) are shown above. Ar atoms are shown in yellow and Ne atoms in green. We should note here that binding of Ar and Ne to $H^+(MeOH)_7$ can be found in Figure 5 in one of our previous works (Ref. 7 of the main text)