Supporting Information

Formation of protonated water-hydrogen clusters in an ion trap mass spectrometer at room temperature

Dongbo Mi, Junqiang Xu, Yunpeng Zhang, Tenggao Zhu, Jiewen Ouyang, Xiaofeng Dong, and Konstantin Chingin*

Jiangxi Key Laboratory for Mass Spectrometry and Instrumentation, East China University of Technology,
Nanchang 330013, China

*Corresponding author
Chingin.k@gmail.com

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Reagents and solvents

All reagents were obtained from commercial suppliers and were used without further purification. Ultrapure water was obtained using a Millipore water purification system (Milli-Q, Millipore; Bedford, MA, USA). Deuterated water (99.9 atom%) purchased from sun Chemical Technology (Shanghai) Co., Ltd.

Theoretical calculations

The quantum chemistry calculations have been performed using semi-experiential MP2 and density function theory by the Gaussian 09 program.[1] The spin-restricted MP2 or B3LYP in conjunction with the 6-311 G++(d, p) basis set was adopted including BSSE calculations. The coordinates, geometries, and energies of the most stable protonated water-hydrogen clusters detected in this work are provided in Table S3. $H^+(H_2O)_n$ (n = 1-3), simulated in our work are consistent with the reported literatures. [2-3]

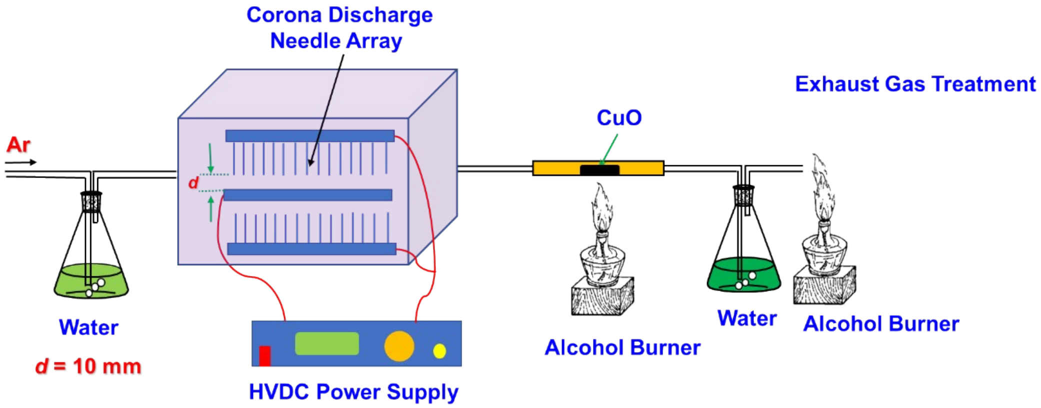


Figure S1. Schematic diagram of the device used for the large-scale reaction.

A corona discharge array was constructed in the laboratory using hundreds of stainless steel needles. Through a single inlet, the carrier argon gas bubbled through liquid water at a flow rate of 20 ml min^{-1} was continuously transferred into the device array. Reaction product was exhausted through a single outlet to a tube filled with black copper oxide powder. When a high voltage (~5.5 kV) was applied to the array, a large volume of corona discharge was lit up.

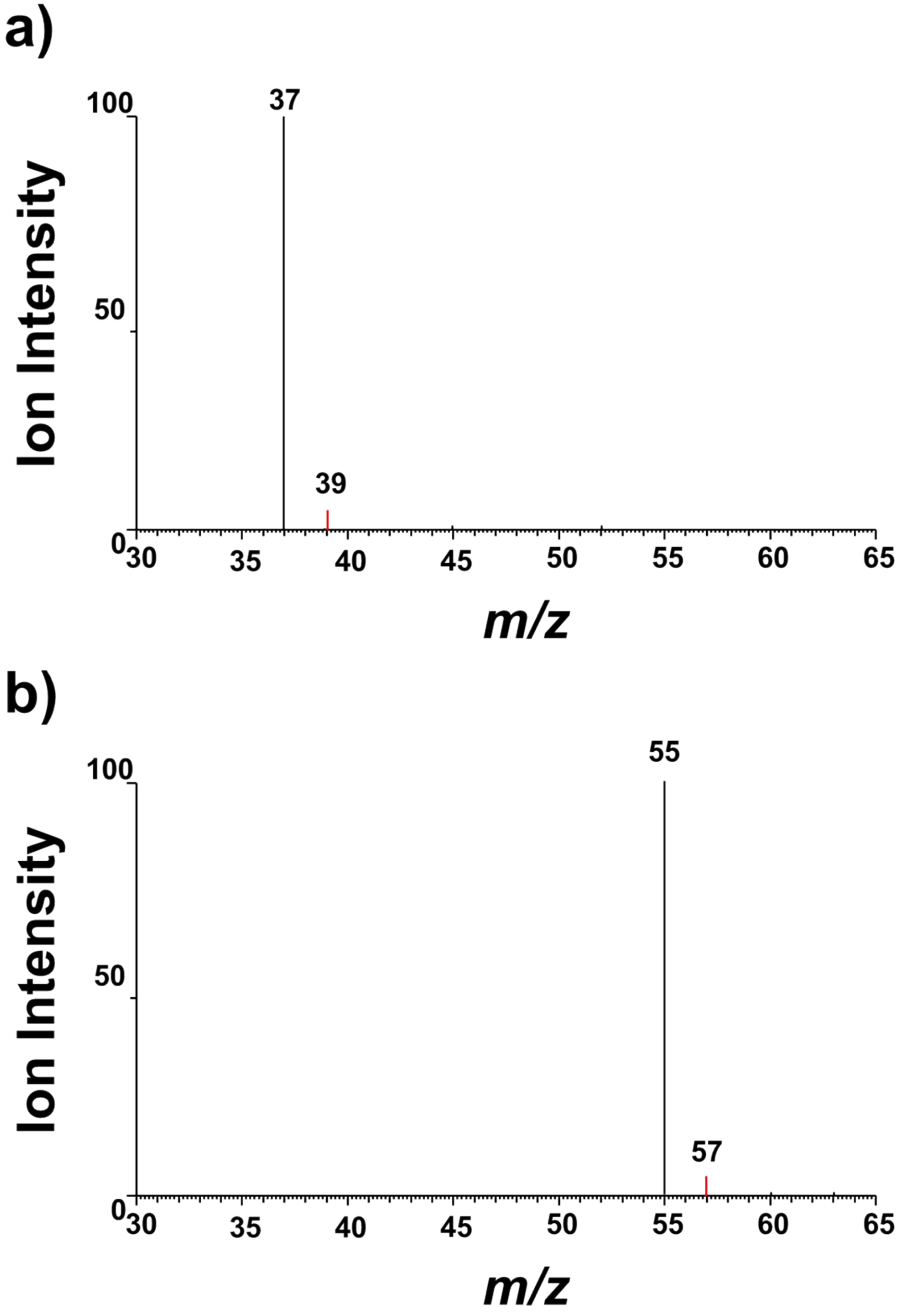


Figure S2. Typical mass spectra obtained upon isolation and trapping of protonated water clusters produced by ambient corona discharge ionization of water vapor. (a) $H^+(H_2O)_2$ (*m/z* 37), and (b) $H^+(H_2O)_3$ (*m/z* 55).

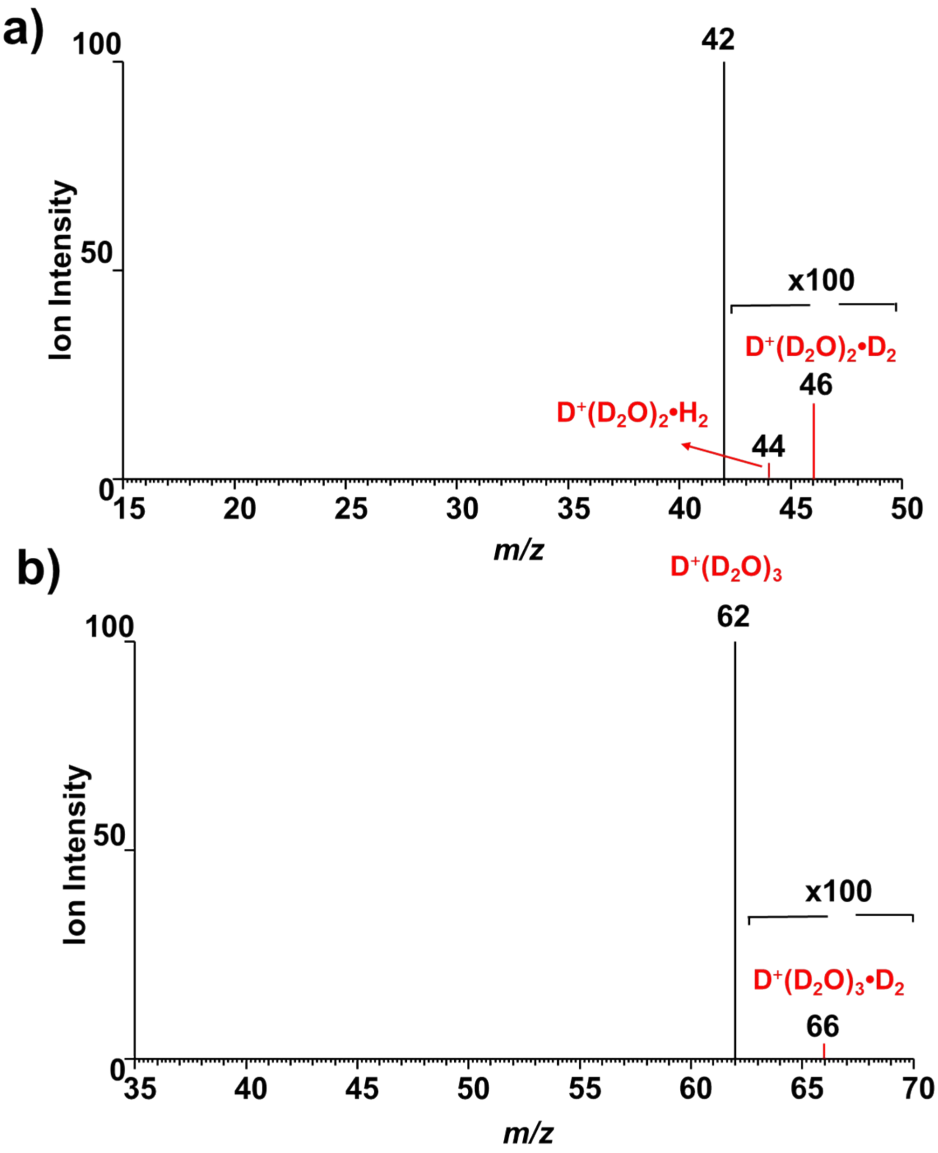


Figure S3. Typical mass spectra obtained upon isolation and trapping of deuterated water clusters produced by ambient corona discharge ionization of deuterated water vapor. (a) $D^+(D_2O)_2$ (*m*/*z* 42), and (b) $D^+(D_2O)_3$ (*m*/*z* 62).

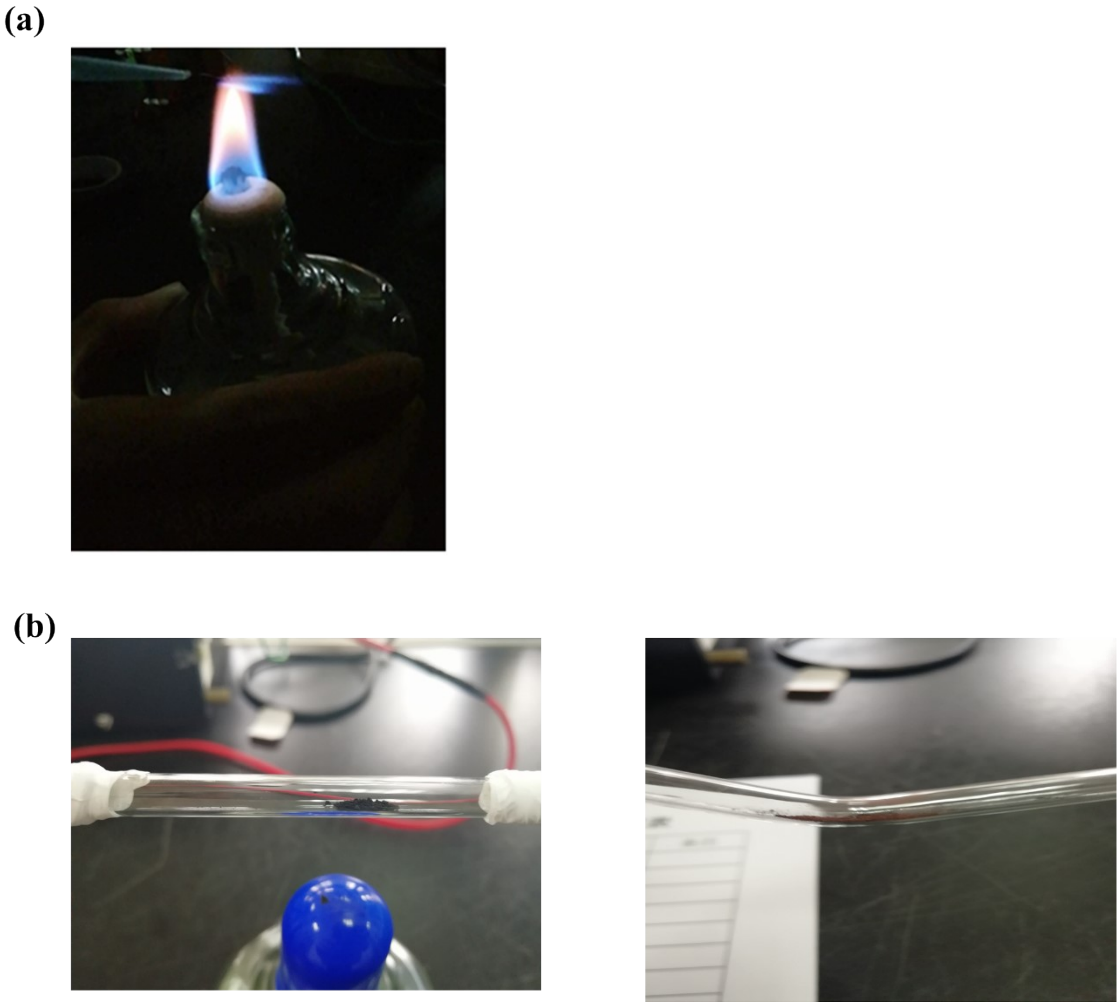


Figure S4. Confirmation of the generation of hydrogen during corona discharge of water vapor. (a) Photograph of a flame test for exhaust, and (b) Reduction of CuO (black, left) to Cu (red, right) following application of +5.5 kV voltage and heating for 30 min.

As shown in Figure S4a, the exhaust gas from the device as illustrated in Figure S1 could be ignited and a light blue flame could clearly be recognized in the dark room. Moreover, after heating this system for several minutes, the black copper oxide powder was transformed into a dark red copper powder (Figure S4b), indicating abundant hydrogen gas could be formed during the corona discharge ionization of water vapor in the ion source.

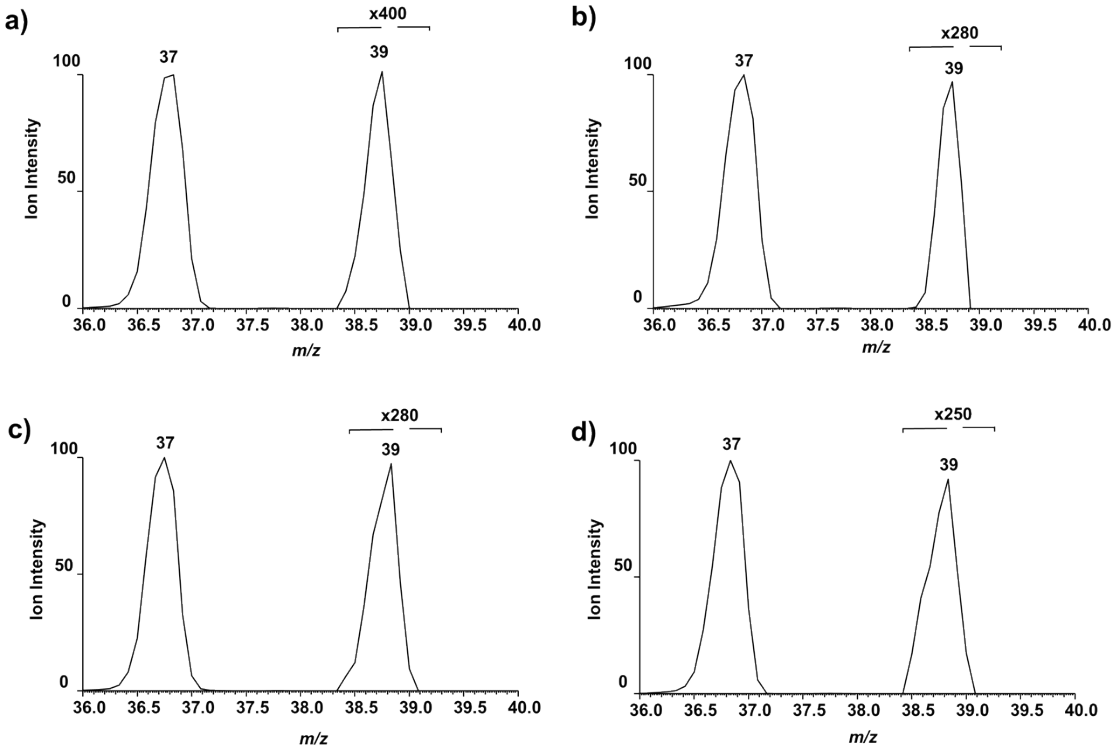


Figure S5. The peak profiles for the mass spectra measured under different trapping time. (a) 0.03 ms, (b) 5.03 ms, (c) 20.03 ms and (d) 200 ms.

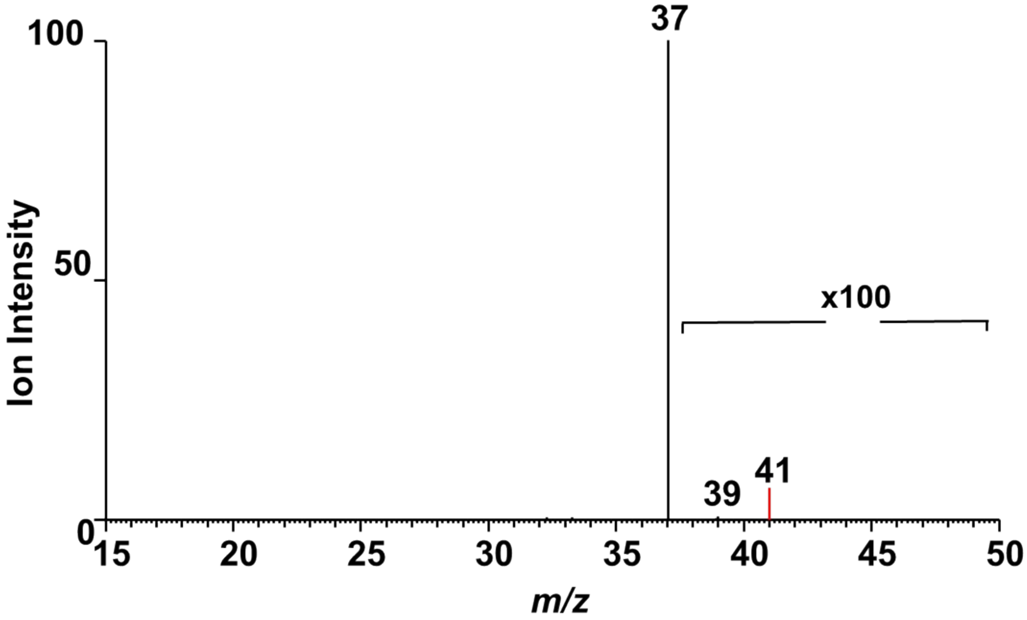


Figure S6. **Detection of $H^+(H_2O)_2 \bullet D_2$ upon the exposure of isolated $H^+(H_2O)_2$ (*m/z* 37) to the mixture of deuterium/helium gas (20%, v/v).**

As illustrated in Figure S6, $H^+(H_2O)_2 \bullet H_2$ (*m/z* 39) as well as $H^+(H_2O)_2 \bullet D_2$ (*m/z* 41) could also be detected.

Table S1. Quantum Chemical calculation results based on the B3LYP/6-311++G(d, p) level of theory.

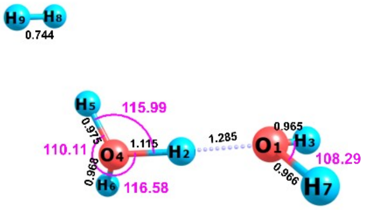
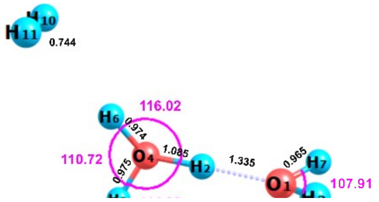
Complex Formula	**Possible Reaction Formula**	**BSSE (kJ/mol)**	**Reaction enthalpy (kJ/mol)**
$\mathbf{H+(H_2O)_2{\bullet}H_2}$	$H^+(H_2O)_2+H_2\rightleftharpoons H^+(H_2O)_2{\bullet}H_2$	0.16	ΔH= -4.61
$\mathbf{H^+(H_2O)_2{\bullet}(H_2)_2}$	$H^+(H_2O)_2+2H_2\rightleftharpoons H^+(H_2O)_2{\bullet}(H_2)_2$	0.31	ΔH=-9.11
	$H^+(H_2O)_2{\bullet}H_2+H_2\rightleftharpoons H^+(H_2O)_2{\bullet}(H_2)_2$	0.14	ΔH=-4.49
$\mathbf{H^+(H_2O)_3{\bullet}H_2}$	$H^+(H_2O)_3+H_2\rightleftharpoons H^+(H_2O)_3{\bullet}H_2$	0.11	ΔH= -1.36

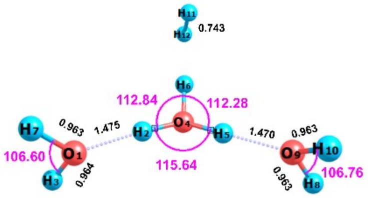
Table S2. Quantum Chemical calculation results based on the MP2/6-311++G(d, p) level of theory.

Complex Formula	Possible Reaction Formula	BSSE (kJ/mol)	Reaction enthalpy (kJ/mol)
$H^+(H_2O)_2\bullet H_2$	$H^+(H_2O)_2+H_2\rightleftharpoons H^+(H_2O)_2\bullet H_2$	1.40	$\Delta H= -1.18$
$H^+(H_2O)_2\bullet (H_2)_2$	$H^+(H_2O)_2+2H_2\rightleftharpoons H^+(H_2O)_2\bullet (H_2)_2$	2.76	$\Delta H=-3.08$
	$H^+(H_2O)_2\bullet H_2+H_2\rightleftharpoons H^+(H_2O)_2\bullet (H_2)_2$	1.35	$\Delta H=-1.90$
$H^+(H_2O)_3\bullet H_2$	$H^+(H_2O)_3 +H_2\rightleftharpoons H^+(H_2O)_3\bullet H_2$	1.33	$\Delta H= -1.06$

In general, the increase of the basis set could effectively reduce the BSSE energy (Tables S1 and S2). As the B3LYP basis set with higher calculation accuracy is much larger than the semi-experiential MP2 basis set, the calculation results based on the B3LYP basis set were adopted (Table S1)

Table S3. The coordinates, geometries, and energies of the most stable $H^{+}(H_2O)_2$•H_2, $H^{+}(H_2O)_2$•$(H_2)_2$ and $H^{+}(H_2O)_3$•H_2.

	Bond angle (°) and bond length (Å)	Coordinates (Å)				Energy (Hartree)
		Center Number	X	Y	Z	
$H^{+}(H_2O)_2$•H_2		1	-1.397782	0.252855	-0.002471	-153.96648
		2	-0.187887	-0.180461	0.014724	
		3	-1.937523	0.334572	0.793718	
		4	0.874895	-0.50831	-0.066846	
		5	1.545947	0.19565	0.004403	
		6	1.134979	-1.271467	0.468595	
		7	-1.979188	0.032206	-0.741525	
		8	2.707396	1.564351	0.353256	
		9	2.899364	1.368789	-0.338636	
$H^{+}(H_2O)_2$•$(H_2)_2$		1	-1.608012	0.02043	0.07909	-155.11445
		2	-0.283354	-0.03003	-0.07833	
		3	-2.074424	-0.24937	0.879156	
		4	0.781961	-0.00220	-0.280175	
		5	1.230629	0.81740	-0.001745	
		6	1.290371	-0.78525	-0.001544	
		7	-2.205593	-0.10268	-0.668677	

		8	1.984489	2.31644	0.736185	
		9	2.143557	2.40128	0.014232	
		10	2.316167	-2.30790	0.000290	
		11	2.206559	-2.20576	0.729117	
$H^+(H_2O)_3$•H_2		1	-2.133228	-0.621823	0.088901	-230.25099
		2	-0.878986	0.125524	-0.122939	
		3	-2.755651	-0.801422	-0.624394	
		4	0.000405	0.605360	-0.343505	
		5	0.858204	0.083682	-0.125722	
		6	0.027659	1.514997	-0.007283	
		7	-2.624777	-0.711654	0.912195	
		8	2.725566	-0.863541	-0.621749	
		9	2.142907	-0.595254	0.097096	
		10	2.40998	-1.098461	0.873435	
		11	0.135538	3.226599	0.842678	
		12	0.021804	3.418015	0.133841	

In our theoretical simulations, the results indicated the most stable structure motifs of $H^+(H_2O)_2$•H_2 and $H^+(H_2O)_2$•$(H_2)_2$ having the H_2 bond roughly perpendicular to the OH…H_2 bond, and the three H atoms forming an elongated isosceles triangle. In the same way in $H^+(H_2O)_3$, water molecules hydrogen bonded to two of the OH bonds of H_3O^+. The third OH group on the hydronium ion was thus indicated to be “free,” and to be the site at which the H_2 molecule would bind.

References

（1） Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. C. J. V., Fox, D. J. Gaussian 09, Revision B.01. Gaussian, Inc., Wallingford CT, 2010.

（2）Mizuse, K., Kuo, J.-L., Fujii, A.: Structural trends of ionized water networks: intrared spectroscopy of watercluster radical cations $(H_2O)_n^+$ (n = 3-11). Chem. Sci. **2**, 868-876 (2011)

（3）Mi, D.; Chingin, K.: Water radical cations in the gas phase: methods and mechanisms of formation, structure and chemical properties. Molecules. **25**, 3490 (2020)