Supporting Information

for

The Unique Nature of H^+ in Water

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(4 pages)

Experimental

Determination of *n* in $H^+(H_2O)_n$.

The molar concentrations of water in the acid solutions ($C_{H2O}{}^{HA}$) and in the salt solutions ($C_{H2O}{}^{NaA}$), which are necessary for *n* determination in $H^+(H_2O)_n$, for $A^- = CHB_{11}Cl_{11}{}^-$ and $CHB_{11}I_{11}{}^-$ were determined via equation $(g_{sol} - g_{CatA})/18$, where g_{sol} is the weight of 1 l of solution, g_{CatA} is the weight of 1 l of HA or NaA solution, 18 is molecular weight of water. To determined g_{sol} and g_{CatA} the specific gravity of solutions where determined by the bottle method.

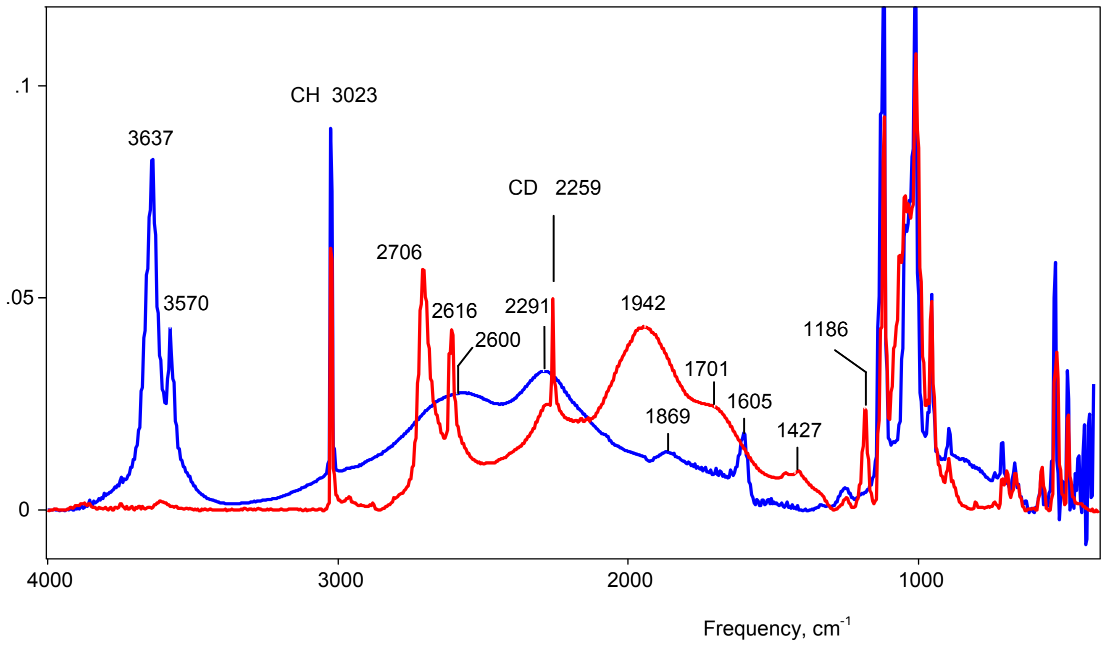

Figure S1. IR spectra of crystalline $[H_3O^+{\cdot}3H_2O]\ CHB_{11}Cl_{11}{}^-$ (blue) and $[D_3O^+{\cdot}3D_2O]\ CHB_{11}Cl_{11}{}^-$ (red).

Table S1. Comparison of deuterated $D_3O^+ \cdot 3D_2O$ and protic $H_3O^+ \cdot 3H_2O$ IR frequencies.

$H_3O^+ \cdot 3H_2O$	$D_3O^+ \cdot 3D_2O$	H/D
3637*	2706*	1.344
3570*	2616*	1.364
2600	1942	1.340
2291	1701	1.346
1869	1427	1.310
1605*	1186*	1.353
νCH 3023**	νCD 2259**	1.338

* Vibrations of three peripheral H_2O molecules;
** CH stretch vibration of $CHB_{11}Cl_{11}^-$ anion

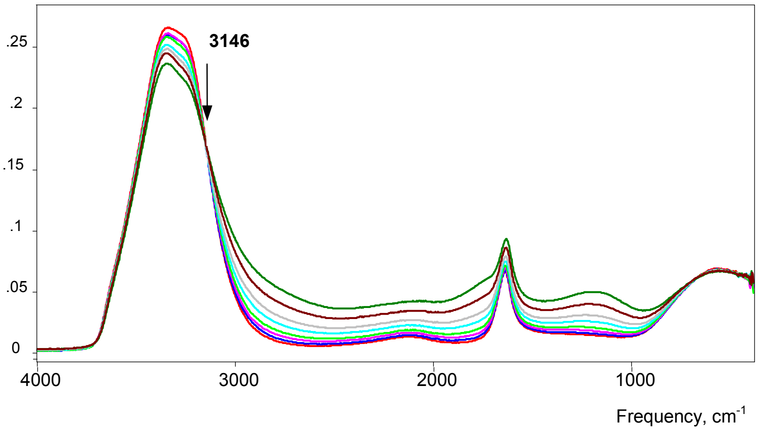

Figure S2a. Normalized IR spectra of 0.25 - 4.0 M HCl solutions (from red to green) with isosbestic point at 3146 cm^{-1}.

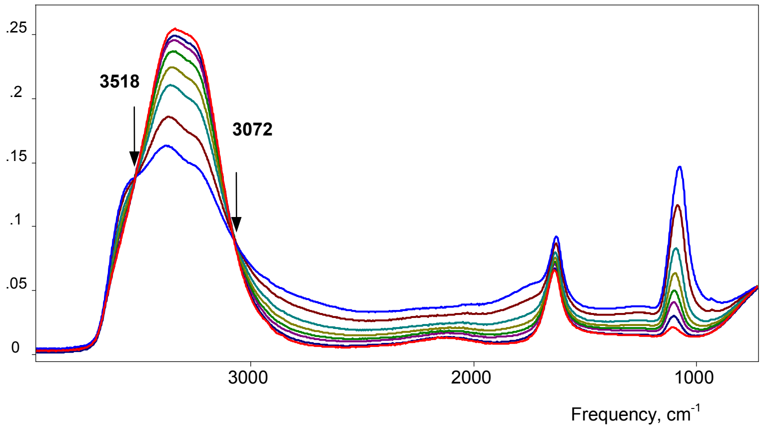

Figure S2b. Normalized IR spectra of 0.25 - 4.0 M $HClO_4$ (from red to blue) with isosbestic points at 3518 and 3072 cm^{-1}.

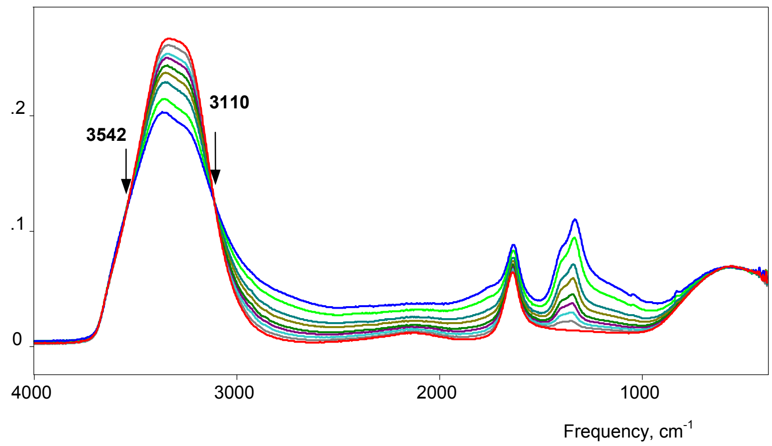

Figure S2c. Normalized IR spectra of 0.25 - 4.0 M HNO_3 (from red to blue) with isosbestic points at 3542 and 3110 cm^{-1}.

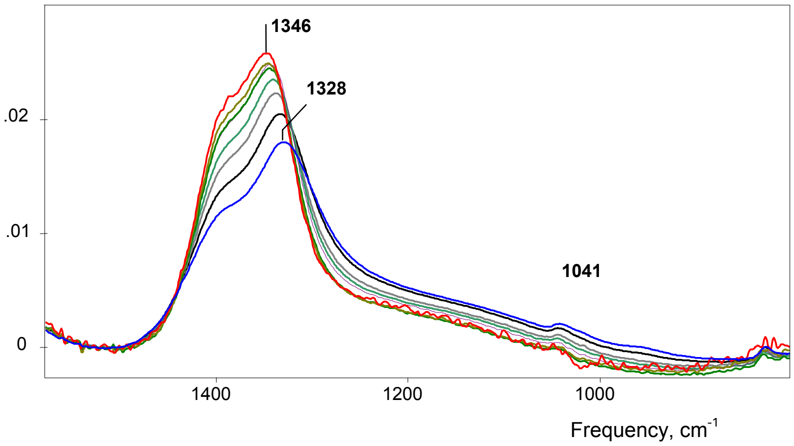

Figure S3. Normalized IR spectra of 0.25 - 4.0 M HNO_3 (from red to blue) in the frequency range of ν_3NO_3 double degenerate band. Its splitting reflects decreasing D_{3h} NO_3^- symmetry with increasing the acid concentration because of increasing electrostatic interaction $H_{aq}^+ - NO_3^-$.

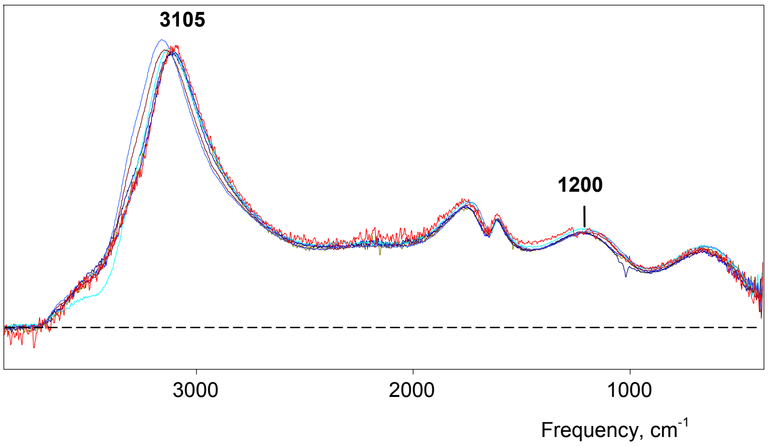

Figure S4. IR spectra of $H(H_2O)_n^+$ clusters normalized to unit concentration for HCl water solutions with concentrations varied from 0.3 (red) to 4.0 M (blue).