Electronic Supplementary Material (ESI) for Faraday Discussions.

SUPPORTING INFORMATION: Spectral signatures of proton delocalization in $H^+(H_2O)_{n=1-4}$ ions

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Table S1: Frequencies and intensities for OH stretches and HOH bends of $H_5O_2^+$ and its deuterated analogues evaluated in uncoupled and coupled representations.

		Uncoupled[a]			Coupled[b]	
		ω	I(harm)		ω	I(harm)
system	vibration	(cm^{-1})	(km mol^{-1})	vibration	(cm^{-1})	(km mol^{-1})
$H^+(H_2O)_2$	IHB	1016.73	4025.93	IHB	746.78	2657.83
	Bend	1616.27	118.61	Bend	1777.54	1600.89
	OH	3763.86	252.58	OH	3757.85	294.27
$H^+(D_2O)_2$	IHB	1016.73	4036.63	IHB	678.20	1965.64
	Bend	1187.93	51.01	Bend	1432.82	2201.44
	OH	2712.42	118.70	OH	2704.68	181.70
$D^+(H_2O)_2$	IDB	730.09	2023.10	IHB	558.19	1521.06
	Bend	1616.27	119.46	Bend	1705.04	714.41
	OD	3763.86	252.58	OH	3757.57	315.03
$D^+(D_2O)_2$	IDB	730.09	2033.45	IHB	528.42	1321.79
	Bend	1187.93	51.67	Bend	1316.76	827.32
	OD	2712.42	119.35	OH	2704.53	197.08

[a] Frequencies and intensities evaluated based on symmetry adapted linear combinations of equivalent OH bond lengths/HOH angles.
[b] Frequencies and intensities obtained from a full-dimensional normal mode treatment.

Table S2: Frequencies and intensities for OH stretches and HOH bends of $H_7O_3^+$, evaluated in uncoupled and coupled representations.

	Uncoupled[a]			Coupled[b]	
vibration	ω (cm^{-1})	I(harm) (km mol^{-1})	vibration	ω (cm^{-1})	I(harm) (km mol^{-1})
HOH bend	1635.55	56.93	bend	1558.82	7.66
HOH bend	1638.39	60.82	bend	1602.28	18.96
H_3O bend	1641.53	72.88	bend	1647.13	0.00
H_3O bend	1645.27	22.29	bend	1649.97	37.14
IHB	2451.42	4818.86	IHB	2543.60	4542.70
IHB	2617.16	990.18	IHB	2638.04	1003.14
OH sym	3791.89	115.01	OH sym	3785.85	109.09
OH sym	3792.95	28.85	OH sym	3786.75	37.17
free OH	3858.48	219.45	free OH	3858.69	269.09
OH asym	3908.30	0.00	OH asym	3907.12	0.00
OH asym	3908.77	369.42	OH asym	3907.62	405.02

[a] Frequencies and intensities evaluated based on symmetry adapted linear combinations of equivalent OH bond lengths/HOH angles.
[b] Frequencies and intensities obtained from a full-dimensional normal mode treatment.

Table S3: Frequencies and intensities for OH stretches and HOH bends of $H_9O_4^+$, evaluated in uncoupled and coupled representations.

	Uncoupled[a]			Coupled[b]	
vibration	ω (cm^{-1})	I(harm) (km mol^{-1})	vibration	ω (cm^{-1})	I(harm) (km mol^{-1})
HOH bend	1640.63	73.93	bend	1607.49	30.01
HOH bend	1640.63	73.93	bend	1607.49	30.01
HOH bend	1645.19	0.00	bend	1633.64	0.00
H_3O bend	1655.28	45.65	bend	1653.47	26.90
H_3O bend	1655.28	45.65	bend	1653.47	26.90
IHB	2965.63	3359.13	IHB	3007.28	3224.39
IHB	2965.63	3359.13	IHB	3007.28	3224.39
IHB	3022.41	0.00	IHB	3025.48	0.00
OH sym	3799.99	84.31	OH sym	3793.85	76.19
OH sym	3799.99	84.31	OH sym	3793.85	76.19
OH sym	3801.12	0.00	OH sym	3794.88	0.00
OH asym	3917.39	0.00	OH asym	3916.29	0.00
OH asym	3917.39	0.00	OH asym	3916.29	0.00
OH asym	3917.94	468.86	OH asym	3916.89	512.53

[a] Frequencies and intensities evaluated based on symmetry adapted linear combinations of equivalent OH bond lengths/HOH angles.
[b] Frequencies and intensities obtained from a full-dimensional normal mode treatment.

Table S4: Harmonic (ω) and anharmonic (ν) frequencies and intensities evaluated using VPT2 implemented in Gaussian 16 at the MP2/aug-cc-pVTZ level of theory and basis are compared to the quantities obtained from the anharmonically coupled harmonic oscillator (HCAO) model described in the text.

				G16		HCAO	
system	state	ω (cm^{-1})	ν (cm^{-1})	I(harm) (km mol^{-1})	I(anharm) (km mol^{-1})	frequency (cm^{-1})	I(HCAO) (km mol^{-1})
H_3O^+	1	3684.96	3501.65	481.40	483.38	3526.16	490.42
	2	3684.95	3501.69	481.40	483.38	3526.16	490.42
	3	3575.65	3410.41	32.86	25.36	3416.80	34.84
$H_5O_2^+$	1	3837.68	3658.06	336.49	302.36	3682.57	339.79
	2	3837.30	3655.39	240.61	230.48	3682.17	242.92
	3	3741.35	3574.62	8.88	26.03	3586.25	9.35
	4	3733.51	3568.43	240.98	238.15	3578.42	243.87
$H_7O_3^+$	1	3897.355	3721.374	406.88	332.94	3742.26	407.80
	2	3896.857	3719.831	2.27	3.23	3741.76	2.26
	3	3811.823	3680.908	205.21	210.40	3656.64	203.55
	4	3789.753	3572.278	26.84	18.52	3634.62	26.01
	5	3788.976	3621.492	132.60	110.16	3633.62	139.68
	6	2619.978	2293.884	1185.10	208.68	2190.42	1278.88
	7	2463.714	1790.595	4087.41	1799.83	2034.54	4311.99
$H_9O_4^+$	1	3906.38	3710.72	459.33	210.69	3751.73	458.32
	2	3905.84	3730.43	32.61	2.03	3751.19	32.46
	3	3905.84	3750.84	32.60	213.37	3751.18	32.46
	4	3797.78	3651.26	0.06	36.88	3643.10	0.07
	5	3796.76	3631.21	79.61	77.66	3641.94	84.74
	6	3796.76	3613.54	79.61	41.65	3641.94	84.74
	7	3021.19	2852.68	170.00	212.83	2669.18	190.54
	8	2927.37	2674.89	2952.19	1216.55	2575.94	3225.24
	9	2927.37	2573.33	2952.19	691.90	2575.94	3225.25

Table S5: The frequencies and intensities of transitions evaluated using non-degenerate VPT2.

State	Description	Non-deg. PT Frequency (cm^{-1})	Non-deg. PT Intensity (km mol^{-1})
1	H_3O^+ umbrella overtone with OO stretch	1499	4380
2	HOH bend	1504	12
3	HOH bend	1531	20
4	HOH bend	1613	23
5	OOO bend + HOH bend	1639	617
6	out-of-plane H_3O^+ rotation + in-plane H_3O^+ rotation	1768	384
7	H_3O^+ umbrella + out-of-plane H_3O^+ rotation	1930	3796
8	H_3O^+ umbrella overtone	1986	11438
9	out-of-plane H_3O^+ rotation overtone	2016	102
10	out-of-plane HOH rotation + asymmetric IHB	2184	419
11	symmetric IHB	2194	930
12	in-plane H_3O^+ rotation + HOH bend	2211	1004
13	asymmetric IHB	2256	3615
14	out-of-plane HOH rotation + asymmetric IHB	2353	243
15	OO stretch + symmetric IHB	2500	138
16	out-of-plane H_3O^+ umbrella + HOH bend	2638	209
17	OO stretch and asymmetric IHB	2657	237

Table S6: The frequencies and intensities of transitions evaluated using degenerate VPT2.

Frequency (cm^{-1})	Intensity (km mol^{-1})
1427	6
1576	13
1594	20
1603	23
1616	2
1738	3
1864	1996
1962	290
2076	68
2131	175
2182	570
2268	291
2291	493
2370	285
2511	451
2627	84
2643	156

Table S7: The eigenvectors for the excited states in Table S6 with intensities exceeding 250 km/mole.

Basis	1864 cm^{-1} 1996 (km mol^{-1})	2182 cm^{-1} 570 (km mol^{-1})	2291 cm^{-1} 493 (km mol^{-1})	2511 cm^{-1} 451 (km mol^{-1})	2268 cm^{-1} 291 (km mol^{-1})	1962 cm^{-1} 290 (km mol^{-1})	2370 cm^{-1} 285 (km mol^{-1})
H_3O^+ umbrella overtone	-0.0999887	0.0786380	0.0811653	0.0220112	-0.3317440	0.3718431	0.2077090
Asymmetric IHB	-0.7756729	-0.3960983	-0.3693140	-0.3179659	-0.0272219	-0.0482199	-0.0163480
Symmetric IHB	-0.0389290	0.0427128	-0.0499363	-0.0055641	0.5126822	0.5256205	-0.5155341
H_3O^+ umbrella + out-of-plane H_3O^+ rot.	0.5722478	-0.7322176	-0.3099396	-0.1269017	-0.0258428	0.0626847	-0.0098142
in-plane H_3O^+ rot. + HOH bend	0.1784513	0.5108411	-0.8210234	-0.1087296	-0.1436027	0.0148703	-0.0121748
OO stretch + symmetric IHB	0.1636175	0.1764470	0.2659640	-0.9329318	0.0173335	0.0121485	0.0213834
out-of-plane H_3O^+ rot. overtone	-0.0234618	-0.0320670	0.0211757	0.0012558	-0.2395484	0.7155379	0.1659745
out-of-plane H_3O^+ rot. + HOH bend	-0.0009791	0.0018364	-0.0028375	-0.0009023	0.0272687	0.0151659	-0.0382634
out-of-plane HOH rot. + asymmetric IHB	-0.0100928	-0.0721680	0.0235755	0.0010699	-0.2857866	0.2117899	0.1595813
out-of-plane HOH rot. + asymmetric IHB	0.0058616	-0.0210046	0.1103165	-0.0020306	-0.6502292	-0.1007518	-0.7370257
HOH bend + asymmetric IHB	0.0068944	-0.0134888	0.0215635	0.0093126	-0.2053601	-0.1077129	0.3040194