

Supplementary Information

Gas Phase Vibrational Spectroscopy of the Protonated Water Pentamer: The Role of Isomers and Nuclear Quantum Effects

Matias R. Fagiani,^{a,b} Harald Knorke,^a Tim Esser,^a Nadja Heine,^{b,†} Conrad T. Wolke,^c Sandy Gewinner,^b Wieland Schöllkopf,^b Marie-Pierre Gaigeot,^{d,e} Riccardo Spezia,^{d,e} Mark A. Johnson,^c and Knut R. Asmis^a

^a Wilhelm-Ostwald-Institut für Physicalische und Theoretische Chemie, Universität Leipzig, Linnéstrasse 2, D-04103 Leipzig, Germany

^b Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faraday 4-6, D-14195 Berlin, Germany

^c Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States

^d Université d'Evry Val d'Essonne, UMR 8587 LAMBE, Boulevard F. Mitterrand, 91025 Evry Cedex, France

^e CNRS, Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement, UMR 8587, F-91025 Evry Cedex, France

Present Address:

[†]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, U.S.A.

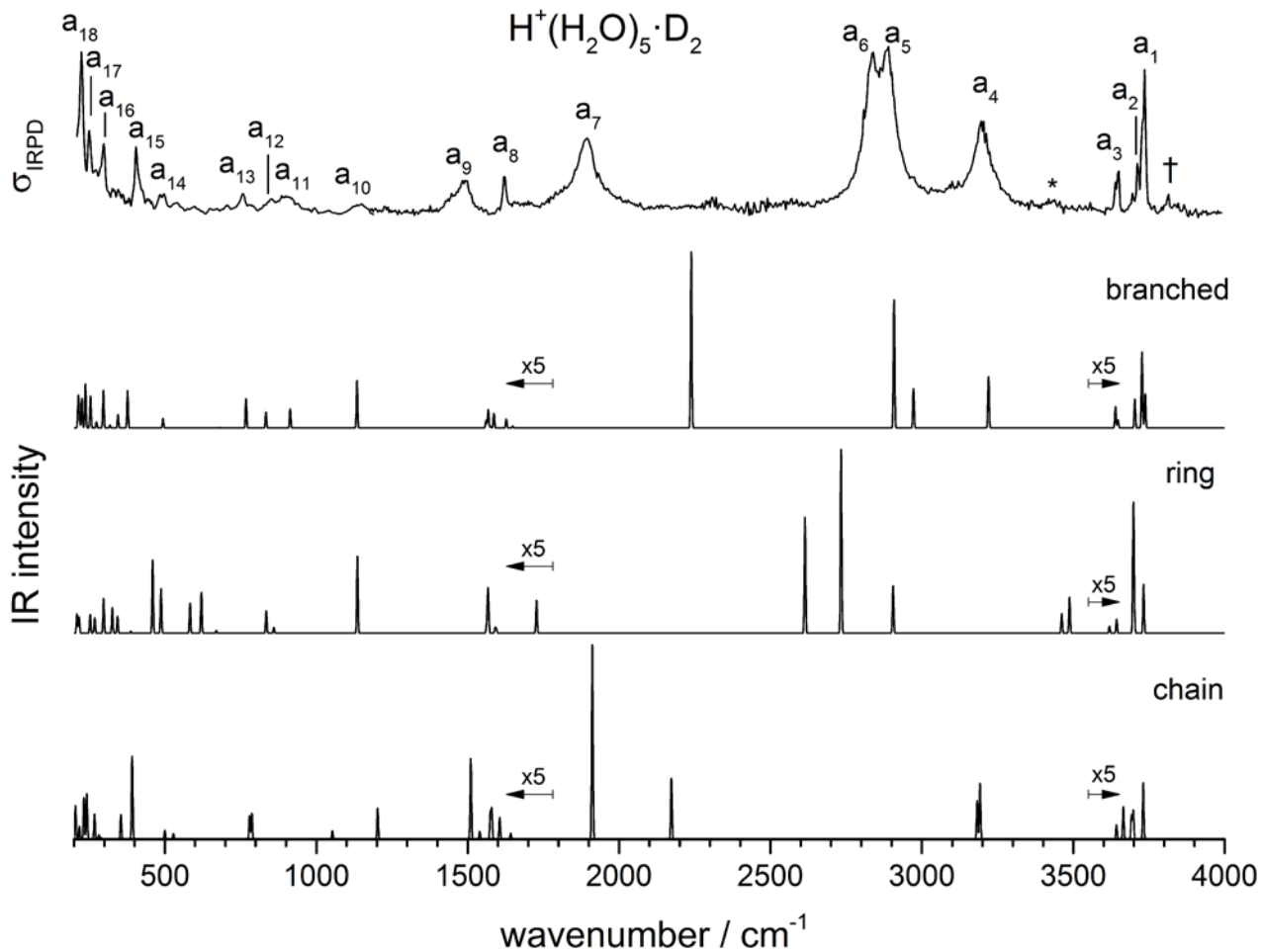


Figure S1 D_2 -predissociation spectra of $\text{H}^+(\text{H}_2\text{O})_5$ in the region 210 to 4000 cm^{-1} compared to scaled (0.908 below 1500 cm^{-1} and 0.962 above) B3LYP-D3/aug-cc-pVTZ harmonic spectra for the three isomers discussed in this work. Traces below 1800 cm^{-1} and above 3550 cm^{-1} are shown with a vertical magnification of x5 for better visibility.

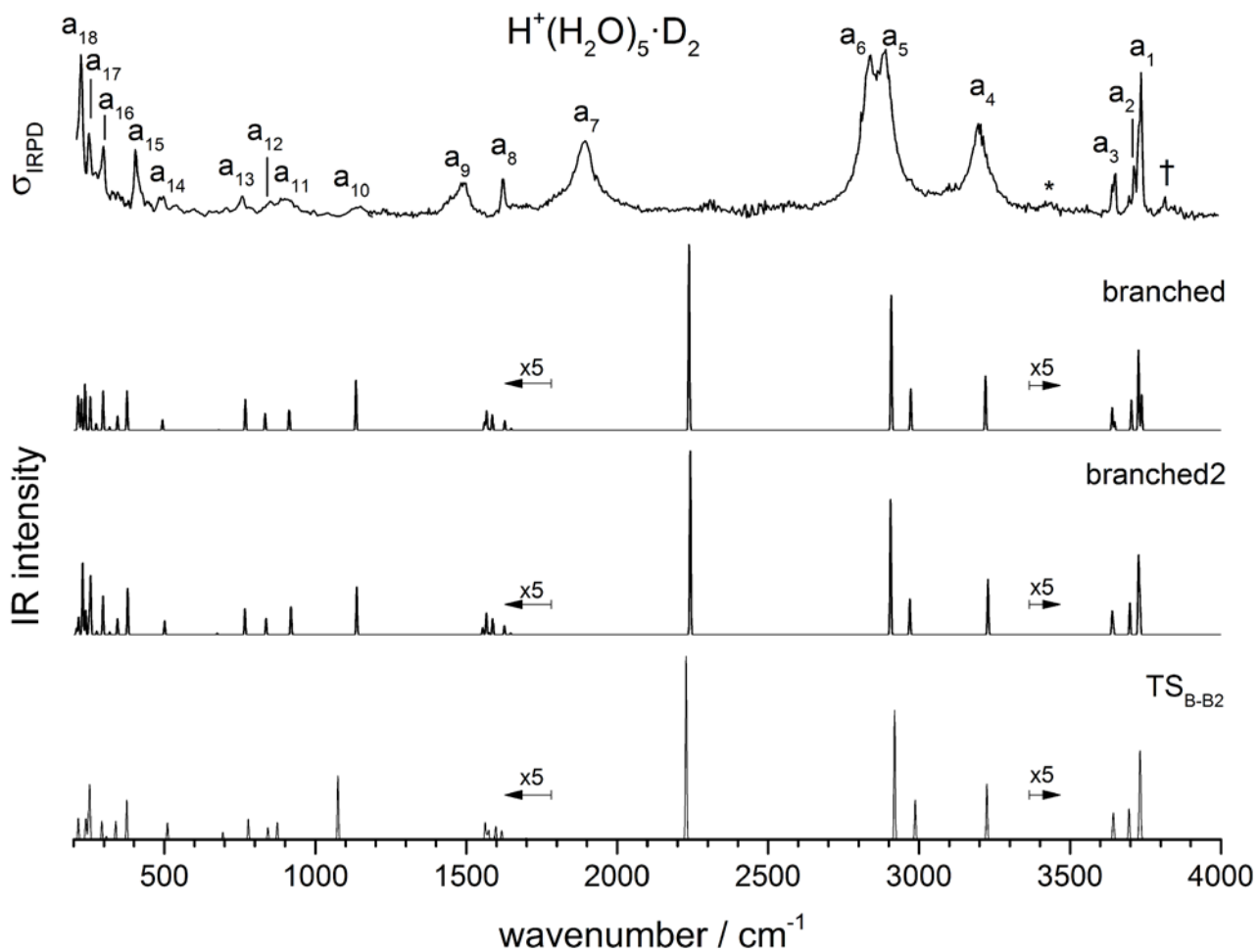


Figure S2 D_2 -predissociation spectra of $\text{H}^+(\text{H}_2\text{O})_5$ in the region 200 to 4000 cm^{-1} compared to scaled (0.908/0.962) B3LYP-D3/aug-cc-pVTZ harmonic spectra for the two conformers of the branched isomer, **B** and **B2**, and the TS between them $\text{TS}_{\text{B-B2}}$. Traces below 1800 cm^{-1} and above 3400 cm^{-1} are shown with a vertical magnification of x5 for better visibility.

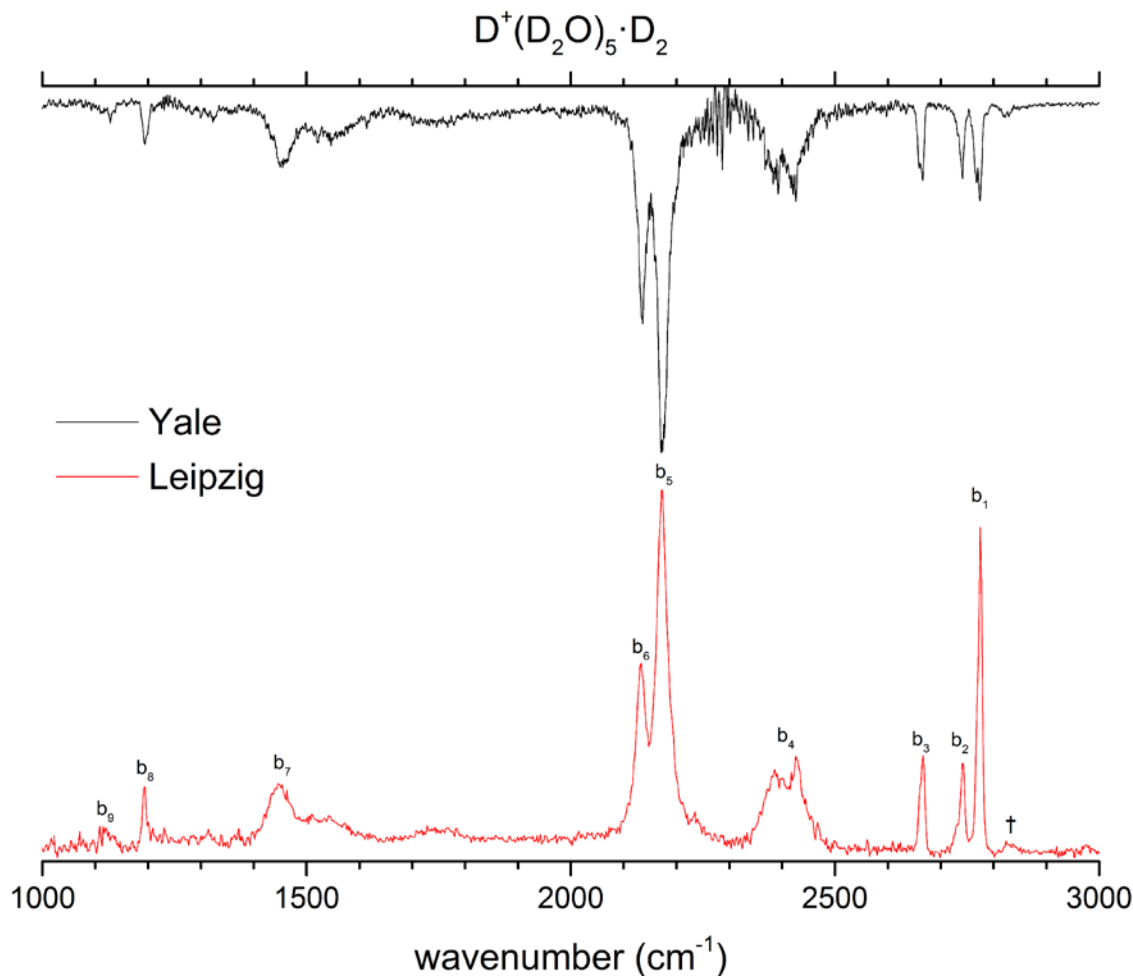


Figure S3 Comparison of the D_2 -tagged IRPD spectra of $D^+(D_2O)_5$ obtained from the experiment performed in Yale (top) and in Leipzig (bottom). The experiments show excellent agreement with the exception of the intensity of band b_1 .

Table S1 Relative electronic energies (in kJ/mol), without (ΔE) and with ZPE (ΔE_0), of the minimum energy structures (isomers R, B, B2 and C) and transition states (TS) for $H^+(H_2O)_5$. The energies obtained from CCSD(T) single point calculations at the corresponding geometries are reported in parenthesis.

	B3LYP 6-311++G(3df,3pd)		B3LYP aug-cc-pVTZ		B3LYP-D3 aug-cc-pVTZ	
	ΔE	ΔE_0	ΔE	ΔE_0	ΔE	ΔE_0
B	0.4 (4.1)	0.0 (0.0)	0.0 (4.5)	0.0 (0.00)	4.6 (4.5)	0.0 (0.0)
B2	0.4 (4.0)	0.6 (0.6)	0.0 (4.5)	0.6 (0.5)	4.5 (4.4)	0.6 (0.5)
R	0.0 (0.0)	5.0 (1.4)	0.4 (0.0)	5.7 (0.8)	0.0 (0.00)	0.7 (0.8)
C	13.2 (19.5)	11.1 (13.7)	12.9 (19.9)	11.2 (13.7)	18.0 (19.9)	11.6 (13.6)
TS_{R-B}	4.3 (6.1)	6.3 (4.4)	4.2 (6.1)	6.7 (4.0)	7.0 (6.5)	4.0 (3.5)
TS_{B-B2}	2.0 (5.6)	1.4 (1.4)	1.5 (5.9)	1.2 (1.0)	6.0 (5.9)	1.0 (1.0)
TS_{B2-C}	20.1 (23.1)	20.1 (19.5)	20.0 (22.8)	20.5 (18.8)	22.4 (23.3)	17.9 (18.8)

Table S2 Relative Gibbs free energies (ΔG_0 , in kJ/mol) of the minimum energy structures (isomers R, B, B2 and C) and transition states (TS) for $\text{H}^+(\text{H}_2\text{O})_5$ computed at 50, 150 and 250 K from CCSD(T) electronic energies and B3LYP-D3/aug-cc-pVTZ thermal correction to Gibbs Free Energies. Boltzmann weighted populations (P_0 , in percent) are obtained from the reported relative Gibbs free energies. The equilibrium populations obtained from the classical (P_{RRKM}) and quantum ($P_{0,\text{RRKM}}$) RRKM kinetic model at 50 K are also reported.

	ΔG_0 50 K	P_0 50 K	P_{RRKM} 50 K	$P_{0,\text{RRKM}}$ 50 K	ΔG_0 150 K	P_0 150 K	ΔG_0 250 K	P_0 250 K
B	0.0	78.7	0.2	72.4	0.0	65.6	0.0	64.7
B2	0.6	19.7	0.2	21.2	0.9	32.5	1.3	34.0
R	1.6	1.6	99.6	6.4	4.5	1.9	8.2	1.2
C	13.6	0.0	0.0	0.0	13.7	0.0	14.5	0.1
TS_{R-B}	4.0				6.2		9.2	
TS_{B-B2}	1.3				3.0		5.2	
TS_{B2-C}	19.2				21.4		25.1	

Table S3 The equilibrium constants (K_0) of the three reactions considered in the kinetic model (see Fig. 2) are calculated from the relative Gibbs free energies at 50, 150 and 250 K.

	K_0 50 K	K_0 150 K	K_0 250 K
R \rightleftharpoons B	47.8	35.4	51.8
B \rightleftharpoons B2	0.250	0.495	0.526
B2 \rightleftharpoons C	2.5E-14	3.4E-5	0.002

Table S4 Scaling factors for $\text{H}^+(\text{H}_2\text{O})_5$ and $\text{D}^+(\text{D}_2\text{O})_5$ calculated with the least-squares procedure on the basis of the comparison of the IRPD spectra with the simulated spectra of the B isomer. Two scaling factors for each method have been computed, one for the spectral region below 1500 (1100) cm^{-1} and one for the higher energy region.

B3LYP 6-311++G(3df,3pd)		B3LYP aug-cc-pVTZ		B3LYP-D3 aug-cc-pVTZ	
H⁺(H₂O)₅	D⁺(D₂O)₅	H⁺(H₂O)₅	D⁺(D₂O)₅	H⁺(H₂O)₅	D⁺(D₂O)₅
0.894/0.958	0.920/0.970	0.905/0.962	0.928/0.973	0.908/0.962	0.927/0.973

Table S5 Comparison of harmonic and anharmonic frequencies (in cm^{-1}) and intensities (in kJ/mol) of $\text{D}^+(\text{D}_2\text{O})_5$ calculated using different basis sets.

B3LYP/6-311++(3df,3pd)				B3LYP/aug-cc-pVTZ			
harmonic		anharmonic VPT2		harmonic		anharmonic VPT2	
cm^{-1}	km/mol	cm^{-1}	km/mol	cm^{-1}	km/mol	cm^{-1}	km/mol
2858	72	2764	58	2848	74	2742	163
2851	147	2759	137	2842	137	2807	160
2851	13	2759	13	2842	26	2780	42
2815	78	2720	71	2806	80	2761	116
2743	22	2657	19	2732	22	2628	19
2738	16	2654	13	2727	18	2730	115
2737	40	2653	36	2726	38	2685	36
2443	498	2350	190	2434	500	2385	53
2245	1250	2115	922	2239	1259	2249	2326
2224	541	2097	476	2216	542	2217	6382
1733	1580	1328	737	1728	1581	1518	731
1237	14	1173	17	1237	14	1170	31
1218	50	1160	56	1219	49	1166	62
1206	52	1165	19	1207	50	1185	45
1200	7	1171	181	1201	10	1192	618
1189	38	1158	1	1191	38	1170	60
1182	2	1131	279	1183	3	1136	213
906	89	821	21	901	88	930	28
736	36	686	28	727	33	802	32
673	28	627	1	663	27	741	19
618	67	567	36	608	66	698	30
539	1	503	2	540	1	610	43
410	52	406	29	410	53	514	1238
378	84	365	74	377	85	459	1545
306	99	258	27	308	100	336	645
288	28	257	5	287	28	489	6638
262	38	230	16	262	45	341	7286
250	22	223	30	249	14	456	26458
229	37	193	25	227	46	272	7287
217	40	185	48	214	30	282	29848
189	91	77	247318	192	100	914	*****
184	75	55	218073	185	60	488	717486
173	72	15	21	176	66	666	*****
137	113	-9	12	134	115	-784	23478
88	15	72	12	89	16	613	42133
80	2	54	12	82	0	672	965553
73	3	50	5	74	1	466	631471
66	7	48	44	69	7	417	160297
61	4	56	32	61	4	205	*****
57	2	46	14	56	3	392	*****
40	1	3	0	41	1	418	3799
16	0	-60	10	15	0	1271	65549

Table S6 Comparison of harmonic and anharmonic frequencies (in cm^{-1}) and intensities (in kJ/mol) of $\text{H}^+(\text{H}_2\text{O})_5$ calculated using different basis sets.

B3LYP/6-311++(3df,3pd)				B3LYP/aug-cc-pVTZ			
harmonic		anharmonic VPT2		harmonic		anharmonic VPT2	
cm^{-1}	km/mol	cm^{-1}	km/mol	cm^{-1}	km/mol	cm^{-1}	km/mol
3898	129	3694	127	3884	133	3691	764
3888	269	3722	230	3875	240	3774	331
3887	22	3723	14	3874	58	3740	191
3864	110	3748	101	3851	113	3730	338
3807	32	3629	25	3791	32	3603	38
3799	24	3640	22	3784	28	3716	87
3798	62	3639	48	3784	59	3671	64
3360	995	3263	269	3348	1000	3198	1047
3094	757	2862	486	3084	764	3015	2641
3027	2524	2826	1386	3019	2536	2968	2290
2334	3466	1548	758	2328	3472	1799	615
1710	9	1598	3	1712	8	1508	36
1689	38	1537	160	1690	37	1523	5
1648	59	1574	231	1648	58	1560	293
1636	6	1583	356	1638	8	1598	398
1627	72	1581	213	1629	71	1592	54
1620	26	1564	412	1622	25	1557	409
1245	185	1126	56	1237	183	1264	58
1020	90	910	77	1008	84	1088	302
939	62	856	6	924	59	1009	56
857	116	743	49	843	114	844	292
755	1	671	8	756	2	744	119
552	33	457	70	552	35	684	327
415	150	397	29	415	149	463	280
381	50	326	34	379	52	634	2915
354	8	306	73	351	9	624	19118
323	156	261	189	325	155	366	8874
304	27	304	21	297	28	207	339
276	123	183	791	277	120	265	1819
255	186	-83	11193	257	204	702	972313
242	115	-107	310100	245	87	498	*****
233	61	135	*****	235	105	538	*****
229	96	-64	*****	231	41	284	*****
183	215	172	263	179	219	-1268	29569
111	43	29	43228	117	29	1102	*****
108	2	101	*****	111	10	201	894933
99	11	156	14652	96	13	-990	170224
79	3	34	54	81	3	473	25659
70	3	74	16	70	4	266	35759
62	1	76	7	62	1	606	4229
43	1	-12	20	43	1	517	4882
18	1	-105	76	17	0	1788	199897

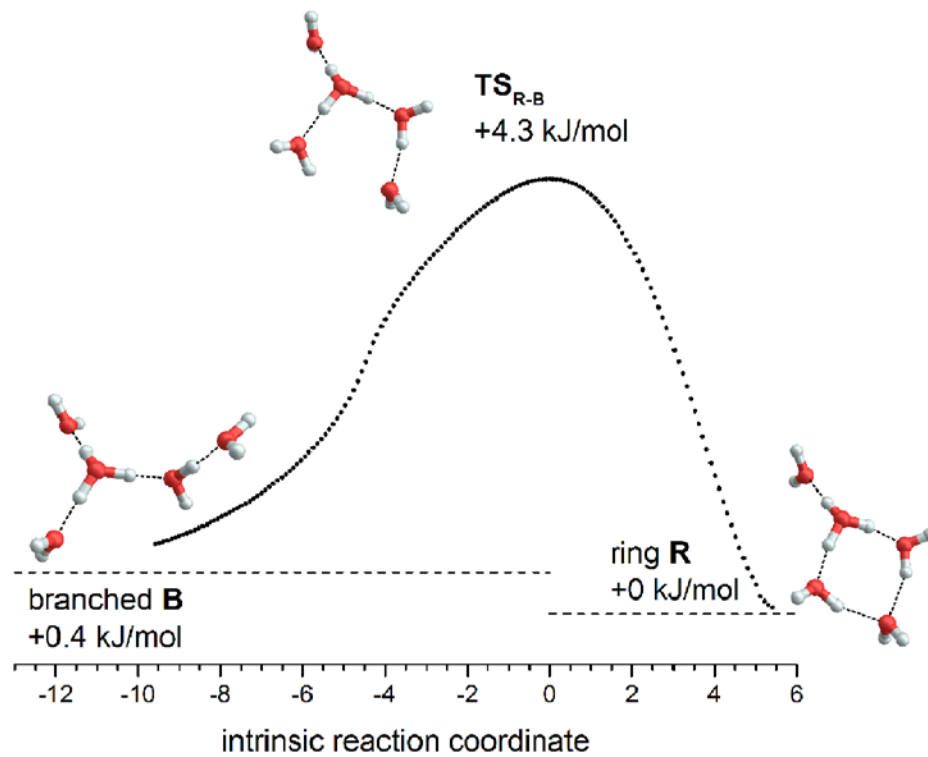


Figure S4 B3LYP/6-311++G(3df,3pd) IRC path from the branched isomer **B** through the TS_{R-B} to the ring isomer **R**.

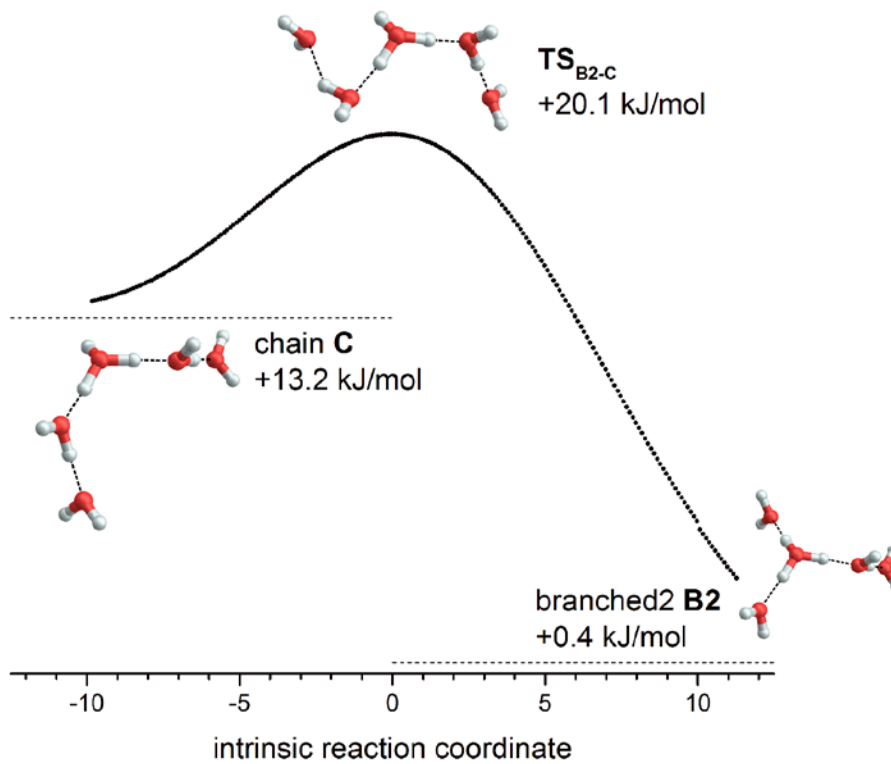


Figure S5 B3LYP/6-311++G(3df,3pd) IRC path from the **C** isomer through the TS_{B2-C} to the **B2** isomer.

Table S7 B3LYP-D3/aug-cc-pVTZ Cartesian coordinates of the **R** isomer of $\text{H}^+(\text{H}_2\text{O})_5$.

h	3.598565	-0.025241	-0.190361
h	-0.414531	0.831648	-0.502433
h	-0.429745	-0.802689	-0.506054
o	0.645112	-1.816885	-0.083617
h	-1.872724	0.024746	-0.224540
h	-4.115377	0.026667	-0.025504
o	-3.286250	-0.025225	0.462365
h	-3.488080	0.138218	1.389674
h	1.522987	-1.416238	0.043587
o	2.815909	-0.020120	0.374701
h	3.151420	-0.027524	1.280193
o	-0.994286	0.020745	-0.720557
h	0.825692	2.680942	-0.488870
o	0.683327	1.823173	-0.075460
h	0.761587	-2.682306	-0.489016
h	1.549704	1.398278	0.053881

Table S8 B3LYP-D3/aug-cc-pVTZ Cartesian coordinates of the **B** isomer of $\text{H}^+(\text{H}_2\text{O})_5$.

h	-4.346707	0.652428	-0.308054
h	1.381790	-0.780703	-0.226267
h	-0.136420	-0.097944	0.199299
o	-1.383053	-0.138783	0.907346
h	1.217011	0.877935	-0.197730
h	2.190689	2.817482	-0.794573
o	2.010826	2.247976	-0.038213
h	1.972184	2.817604	0.737787
h	-2.237017	-0.126855	0.410698
o	-3.673970	-0.017241	-0.469951
h	-4.103578	-0.723602	-0.963211
o	0.756770	-0.003465	-0.343622
h	2.470046	-2.657699	-0.835506
o	2.295631	-2.079565	-0.084437
h	-1.501415	-0.681569	1.692595
h	3.043783	-2.168461	0.515985

Table S9 B3LYP-D3/aug-cc-pVTZ Cartesian coordinates of the **B2** isomer of $\text{H}^+(\text{H}_2\text{O})_5$.

h	3.869698	-0.643780	-1.232805
h	-1.593618	-0.612053	0.136440
h	0.007788	-0.357144	0.698561
o	1.316129	-0.934148	0.812168
h	-1.039860	0.952244	0.313479
h	-1.463622	3.153926	0.501555
o	-1.101355	2.490341	-0.096137
h	-1.235760	2.817815	-0.992087
h	2.092020	-0.601217	0.300405
o	3.366115	-0.043749	-0.672132
h	3.967187	0.669386	-0.431981
o	-0.975593	0.003158	0.636026
h	-3.429401	-1.875298	-0.163786
o	-2.651216	-1.531487	-0.616668
h	1.626433	-1.217080	1.677994
h	-2.433497	-2.159723	-1.313826

Table S10 B3LYP-D3/aug-cc-pVTZ Cartesian coordinates of the **C** isomer of $\text{H}^+(\text{H}_2\text{O})_5$.

h	-3.594616	2.059038	-0.264049
h	0.981168	-1.271589	-0.246276
h	-0.781320	-1.104088	0.145282
o	-1.749664	-0.401882	0.873478
h	-0.230284	-1.811319	-1.281832
h	3.576757	2.095482	-0.605791
o	3.009853	1.690659	0.059755
h	3.168609	2.169969	0.879883
h	-2.433006	0.147633	0.415057
o	-3.509504	1.115870	-0.440616
h	-4.361142	0.826900	-0.785562
o	-0.014521	-1.646604	-0.355889
h	2.935215	-1.438750	0.299060
o	2.304503	-0.870057	-0.153507
h	-2.169240	-0.849786	1.615248
h	2.582514	0.072624	-0.036796

Table S11 B3LYP-D3/aug-cc-pVTZ Cartesian coordinates of the transition state **TS_{R-B}** of $\text{H}^+(\text{H}_2\text{O})_5$.

h	3.821564	0.029979	-0.094766
h	-0.613737	0.912083	-0.455616
h	-0.180384	-0.709226	-0.565375
o	0.932485	-1.620944	-0.321251
h	-1.778182	-0.247423	-0.181256
h	-3.959317	-0.770394	0.065852
o	-3.146369	-0.569710	0.542353
h	-3.255150	-0.896891	1.441573
h	1.779856	-1.185519	-0.074931
o	3.061562	-0.137476	0.474376
h	3.427084	-0.324184	1.347066
o	-0.942756	-0.009641	-0.690745
h	-0.259188	3.149220	-0.499581
o	-0.026504	2.330346	-0.048094
h	1.123945	-2.338658	-0.933400
h	0.866172	2.440418	0.297318

Table S12 B3LYP-D3/aug-cc-pVTZ Cartesian coordinates of the transition state **TS_{B-B2}** of $\text{H}^+(\text{H}_2\text{O})_5$.

h	-4.160844	-0.104438	0.815707
h	1.710084	-0.448855	-0.212966
h	0.003224	-0.513088	-0.267959
o	-1.168565	-1.259486	0.110478
h	0.855720	0.977182	-0.242011
h	0.967419	3.230434	-0.528891
o	0.888681	2.528647	0.126233
h	0.633187	2.942143	0.957400
h	-2.063167	-0.843304	0.066558
o	-3.561724	-0.045156	0.063649
h	-4.116830	0.068347	-0.715225
o	0.874441	0.014590	-0.523916
h	3.710348	-1.482263	-0.441596
o	3.008485	-1.275661	0.185307
h	-1.253111	-2.168848	-0.193385
h	3.383425	-1.360782	1.068357

Table S13 B3LYP-D3/aug-cc-pVTZ Cartesian coordinates of the transition state $\text{TS}_{\text{B2-C}}$ of $\text{H}^+(\text{H}_2\text{O})_5$.

h	3.723012	-1.688901	0.319699
h	-0.907415	0.334265	0.711089
h	0.618648	1.104631	0.142622
o	1.977715	1.118788	-0.028222
h	-0.891085	1.322322	-0.594387
h	-4.053150	0.196153	-0.952747
o	-3.204159	-0.260216	-0.982439
h	-3.274656	-0.884568	-1.714083
h	2.514699	0.290955	-0.119293
o	3.360572	-1.123610	-0.370662
h	3.917069	-1.249453	-1.146914
o	-0.452661	1.159317	0.252094
h	-2.420833	-0.847420	0.559532
o	-1.651181	-0.825039	1.164453
h	2.497321	1.778629	0.441922
h	-1.965897	-0.910547	2.070769

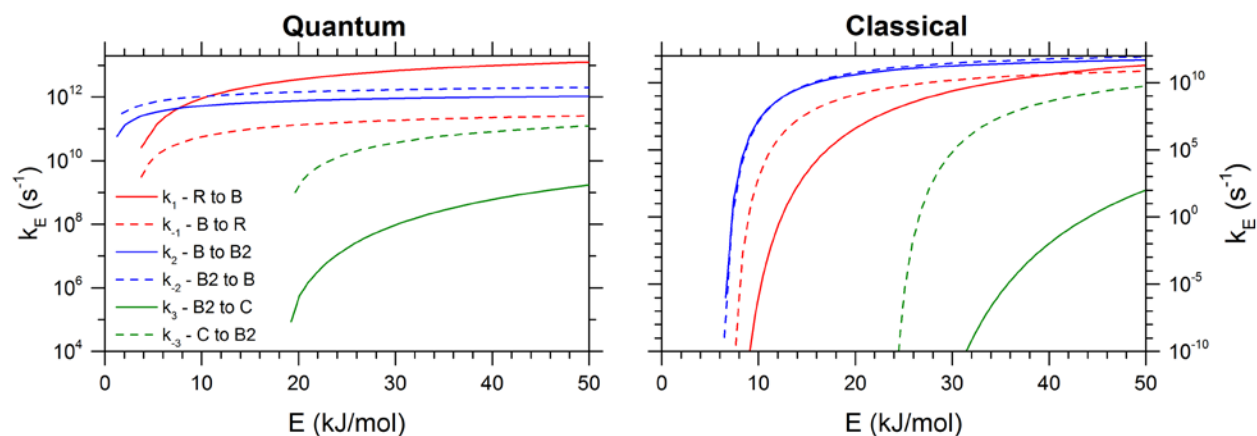


Figure S6 Quantum and classical microcanonical rate constants obtained from RRKM calculations for the forward and backward elementary reactions of the three isomerization pathways considered.