Supplementary material for:

Isotope exchange and structural rearrangements in reactions between D_2O and the size-selected ionic water clusters, $H_3O^+(H_2O)_n$ and $NH_4^+(H_2O)_n$

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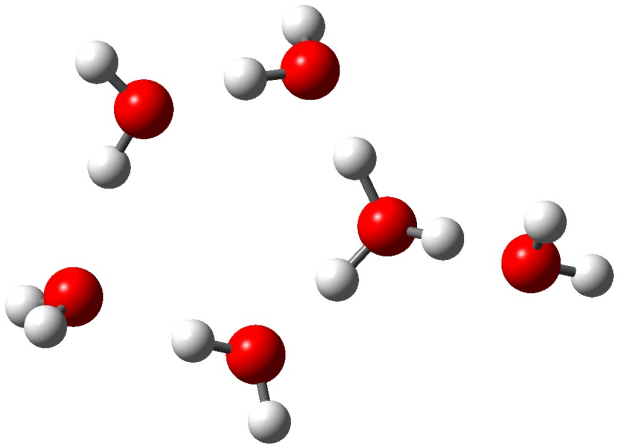
Computational (Quantum chemical calculations, RRKM)

B3LYP/6-31G(d) geometry optimized structure of $H_3O^+(H_2O)_5$



Cartesian co-ordinates (Å)

H	1.005412	0.818841	-0.704668
H	0.808641	-0.879684	-0.628551
H	2.253335	-0.202111	-0.116365

O	1.483394	-0.128853	-0.762177
H	-0.084320	-2.851428	-0.262962
O	-0.298242	-1.943699	-0.509375
H	-1.179950	-1.732224	-0.143302
H	4.336920	-0.591262	0.480061
O	3.478803	-0.394041	0.879721
H	3.648864	0.269907	1.561403
H	-0.556862	1.958667	-0.150714
O	0.345411	2.052743	-0.565139
H	0.247063	2.566277	-1.377172
H	-3.254670	-1.439252	1.112399
O	-2.870564	-1.110446	0.286429
H	-3.505040	-1.346330	-0.406368
H	-2.426137	0.735137	0.435811
O	-1.969985	1.580675	0.596631
H	-2.643793	2.242423	0.791714

Sets of harmonic vibrational frequencies for n = 10, 15, 20 and 25 were constructed based on the quantum chemically derived frequencies for n = 5. In going from n = 5 to n = 10, all frequencies of the set were first taken twice. This gives 102 frequencies. Thereupon, 6 of the frequencies, identified to "belong" to one water molecules were removed, giving a final set of 96 frequencies. During this process, some manual down-adjustment of low frequencies was done to account for the larger number of soft modes with size. To avoid artificial degeneracy of modes of vibration resulting from the doubling of the data set, manual up- and down-sizing was done at this stage. For each n, the TS freqencies were constructed from the ground state set by removing one frequency at around 60 cm^{-1}, and making the following adjustments (approximate values): $30cm^{-1} \rightarrow 20cm^{-1}$, $70cm^{-1} \rightarrow 35cm^{-1}$, $100cm^{-1} \rightarrow 70cm^{-1}$, $200cm^{-1} \rightarrow 150cm^{-1}$, $500cm^{-1} \rightarrow 300cm^{-1}$.

The following water binding energies (E_{ad}; critical energies of dissociation for the corresponding cluster size), in eV, were used — in agreement with binding energies reported at the NIST web page (http://webbook.nist.gov/chemistry/):

n	E_{ad}
5	0.50
10	0.48
15	0.46
20	0.44
25	0.42

Rate/energy relationships, E in eV, rate in s-1.

n	m/z	Ecoll (eV)	Etherm (eV)	Eads	Etot	Etot-Eads	k(tot-Eads)
5,00	109	0,09	0,35	0,50	0.94	0,446023256	2,71E+07
10,00	199	0,05	0,61	0,48	1.14	0,662794521	1,30E+06
15,00	289	0,04	0,86	0,46	1.36	0,901834951	7,24E+05
20,00	379	0,03	1,12	0,44	1.59	1,148075188	7,06E+05
25,00	469	0,02	1,37	0,42	1.82	1,397539877	9,42E+05

The input files to the RRKM program are given below.

Water evaporation from $H_3O^+(H_2O)_5$,
4180, 24180, 300, 4180, 1.D10, 0
10
0
1
51
16.7482 30.8164 60.0273
63.4176 71.6405 101.4642
110.8059 156.9787 167.4944
190.1774 200.1270 208.8569
276.5930 282.9725 288.2642
337.8825 339.9364 354.9565
389.2846 422.7807 439.1516
496.2658 530.9049 558.5186
653.4386 700.9806 754.1550
908.6487 958.2060 1066.3822
1349.2315 1627.5355 1637.7567
1647.2356 1664.1165 1685.0935
1713.3795 1790.2332 2223.8320
2903.1525 3096.2684 3273.1049
3614.0888 3682.2543 3782.0964
3801.4931 3865.7402 3880.8839
3887.5935 3893.9358 3904.2772
16.7482 20.0
35.0 63.4176 70.0
110.8059 150.0 156.9787 167.4944
190.1774 208.8569
276.5930 282.9725 288.2642 300.0
337.8825 339.9364 354.9565
389.2846 422.7807 439.1516
530.9049 558.5186
653.4386 700.9806 754.1550
908.6487 958.2060 1066.3822
1349.2315 1627.5355 1637.7567
1647.2356 1664.1165 1685.0935
1713.3795 1790.2332 2223.8320

2903.1525 3096.2684 3273.1049
3614.0888 3682.2543 3782.0964
3801.4931 3865.7402 3880.8839
3887.5935 3893.9358 3904.2772

Water evaporation from $H_3O^+(H_2O)_{10}$

4010, 24010, 300, 4010, 1.D10, 0
10
0
1
96
14.7 16.7 28.8 32.8 58.0 61.0 63.4 66.4 69.6 72.6 99.5 101.5 110.8
155.0 157.0 166.5 169.5 188.2 190.2 200.1 206.9 210.9 274.6 276.6
281.0 284.0 286.3 290.3 335.9 337.9 339.9 341.9 355.0 357.0 386.3
389.3 422.8 439.2 441.2 494.3 496.3 530.9 532.9 557.5 558.5 651.4
653.4 699.0 703.0 754.2 756.2 906.6 910.6 958.2 959.2 1064.4 1067.4
1348.2 1349.2 1625.5 1629.5 1633.8 1639.8 1647.2 1662.1 1664.1
1683.1 1685.1 1710.4 1716.4 1788.2 1790.2 1900.0 2226.8 2900.2
2907.2 3093.3 3097.3 3273.1 3613.1 3617.1 3681.3 3683.3 3781.1
3782.1 3798.5 3805.5 3863.7 3868.7 3877.9 3885.6 3887.6 3890.9
3893.9 3900.3 3905.3
14.7 16.7 18.8 32.8 34.6 58.0 63.4 66.4 71.5 72.6 99.5 110.8 150.1
155.0 157.0 166.5 169.5 188.2 190.2 206.9 210.9 274.6 276.6 281.0
284.0 286.3 290.3 296.3 335.9 337.9 339.9 341.9 355.0 357.0 386.3
389.3 422.8 439.2 441.2 494.3 530.9 532.9 557.5 558.5 651.4 653.4
699.0 703.0 754.2 756.2 906.6 910.6 958.2 959.2 1064.4 1067.4 1348.2
1349.2 1625.5 1629.5 1633.8 1639.8 1647.2 1662.1 1664.1 1683.1
1685.1 1710.4 1716.4 1788.2 1790.2 1900.0 2226.8 2900.2 2907.2
3093.3 3097.3 3273.1 3613.1 3617.1 3681.3 3683.3 3781.1 3782.1
3798.5 3805.5 3863.7 3868.7 3877.9 3885.6 3887.6 3890.9 3893.9
3900.3 3905.3

Water evaporation from $H_3O^+(H_2O)_{15}$

3850, 23850, 300, 3850, 1.D10, 0
10
0
1
141
12.1 14.7 16.7 28.8 29.3 32.8 58.0 58.5 61.0 61.9 63.4 66.4 69.6
72.6 99.5 100.0 101.5 110.8 155.0 155.5 157.0 166.0 166.5 169.5
188.2 188.7 190.2 200.1 206.9 207.4 210.9 274.6 275.1 276.6 281.0
284.0 286.3 286.8 290.3 335.9 336.4 337.9 338.4 339.9 341.9 353.5
355.0 357.0 386.3 387.8 389.3 422.8 437.7 439.2 441.2 494.3 494.8
496.3 530.9 532.9 557.0 557.5 558.5 651.4 651.9 653.4 699.0 699.5
703.0 752.7 754.2 756.2 900.2 906.6 907.1 910.6 956.7 958.2 959.2
1064.4 1064.9 1067.4 1347.7 1348.2 1349.2 1625.5 1626.0 1629.5
1633.8 1636.3 1639.8 1645.7 1647.2 1662.1 1662.6 1664.1 1683.1
1683.6 1685.1 1710.4 1711.9 1716.4 1788.2 1788.7 1790.2 1901.7 1910.8
1912.0 2226.8 2907.2 3093.3 3094.8 3097.3 3271.6 3273.1 3612.6
3613.1 3617.1 3680.8 3681.3 3683.3 3780.6 3781.1 3782.1 3798.5

3800.0 3805.5 3863.7 3864.2 3868.7 3877.9 3879.4 3885.6 3886.1
3887.6 3890.9 3892.4 3893.9 3900.3 3902.8 3905.3
12.1 14.7 16.7 19.3 28.8 32.8 35.6 58.0 58.5 61.9 63.4 66.4 69.6
70.0 99.5 100.0 110.8 150.1 155.0 155.5 157.0 166.0 166.5 169.5
188.2 188.7 190.2 206.9 207.4 210.9 274.6 275.1 276.6 281.0 284.0
286.3 286.8 290.3 296.3 335.9 336.4 337.9 338.4 339.9 341.9 353.5
355.0 357.0 386.3 387.8 389.3 422.8 437.7 439.2 441.2 494.3 494.8
530.9 532.9 557.0 557.5 558.5 651.4 651.9 653.4 699.0 699.5 703.0
752.7 754.2 756.2 900.2 906.6 907.1 910.6 956.7 958.2 959.2 1064.4
1064.9 1067.4 1347.7 1348.2 1349.2 1625.5 1626.0 1629.5 1633.8
1636.3 1639.8 1645.7 1647.2 1662.1 1662.6 1664.1 1683.1 1683.6
1685.1 1710.4 1711.9 1716.4 1788.2 1788.7 1790.2 1901.7 1910.8 1912.0
2226.8 2907.2 3093.3 3094.8 3097.3 3271.6 3273.1 3612.6 3613.1
3617.1 3680.8 3681.3 3683.3 3780.6 3781.1 3782.1 3798.5 3800.0
3805.5 3863.7 3864.2 3868.7 3877.9 3879.4 3885.6 3886.1 3887.6
3890.9 3892.4 3893.9 3900.3 3902.8 3905.3

Water evaporation from $H_3O^+(H_2O)_{20}$
3680, 23680, 300, 3680, 1.D10, 0
10
0
1
186
10.7 12.1 14.7 16.7 28.2 28.8 29.3 32.8 58.0 58.5 60.0 61.0 61.9
63.4 63.4 66.4 69.6 72.6 99.5 100.0 101.4 101.5 110.8 155.0 155.5
156.8 157.0 166.0 166.5 167.3 169.5 188.2 188.7 190.0 190.2 200.1
206.9 207.4 208.6 210.9 274.6 275.1 276.3 276.6 281.0 284.0 286.3
286.8 288.0 290.3 335.9 336.4 337.5 337.9 338.4 339.6 339.9 341.9
353.5 354.6 355.0 357.0 386.3 387.8 388.9 389.3 422.8 437.7 438.7
439.2 441.2 494.3 494.8 495.8 496.3 530.9 532.9 557.0 557.5 558.0
558.5 651.4 651.9 652.8 653.4 699.0 699.5 700.3 703.0 752.7 753.4
754.2 756.2 900.2 901.7 906.6 907.1 907.7 910.6 956.7 957.2 958.2
959.2 1064.4 1064.9 1065.3 1067.4 1347.7 1347.9 1348.2 1349.2 1625.5
1625.9 1626.0 1629.5 1633.8 1636.1 1636.3 1639.8 1645.6 1645.7
1647.2 1662.1 1662.5 1662.6 1664.1 1683.1 1683.4 1683.6 1685.1
1710.4 1711.7 1711.9 1716.4 1788.2 1788.4 1788.7 1790.2 1821.6
1821.8 1822.3 1826.8 1900.2 2207.2 3093.2 3093.3 3094.8 3097.3
3269.8 3271.6 3273.1 3610.5 3612.6 3613.1 3617.1 3678.6 3680.8
3681.3 3683.3 3778.3 3780.6 3781.1 3782.1 3797.7 3798.5 3800.0
3805.5 3861.9 3863.7 3864.2 3868.7 3877.0 3877.9 3879.4 3883.7
3885.6 3886.1 3887.6 3890.0 3890.9 3892.4 3893.9 3900.3 3900.4
3902.8 3905.3
10.7 12.1 14.7 16.7 19.3 28.2 28.8 32.8 35.6 58.0 58.5 60.0 61.9
63.4 63.4 66.4 70.5 72.6 99.5 100.0 101.4 110.8 150.1 155.0 155.5
156.8 157.0 166.0 166.5 167.3 169.5 188.2 188.7 190.0 190.2 206.9
207.4 208.6 210.9 274.6 275.1 276.3 276.6 281.0 284.0 286.3 286.8
288.0 290.3 295.8 335.9 336.4 337.5 337.9 338.4 339.6 339.9 341.9
353.5 354.6 355.0 357.0 386.3 387.8 388.9 389.3 422.8 437.7 438.7
439.2 441.2 494.3 494.8 496.3 530.9 532.9 557.0 557.5 558.0 558.5
651.4 651.9 652.8 653.4 699.0 699.5 700.3 703.0 752.7 753.4 754.2

756.2 900.2 901.7 906.6 907.1 907.7 910.6 956.7 957.2 958.2 959.2
1064.4 1064.9 1065.3 1067.4 1347.7 1347.9 1348.2 1349.2 1625.5
1625.9 1626.0 1629.5 1633.8 1636.1 1636.3 1639.8 1645.6 1645.7
1647.2 1662.1 1662.5 1662.6 1664.1 1683.1 1683.4 1683.6 1685.1
1710.4 1711.7 1711.9 1716.4 1788.2 1788.4 1788.7 1790.2 1821.6
1821.8 1822.3 1826.8 1900.2 2207.2 3093.2 3093.3 3094.8 3097.3
3269.8 3271.6 3273.1 3610.5 3612.6 3613.1 3617.1 3678.6 3680.8
3681.3 3683.3 3778.3 3780.6 3781.1 3782.1 3797.7 3798.5 3800.0
3805.5 3861.9 3863.7 3864.2 3868.7 3877.0 3877.9 3879.4 3883.7
3885.6 3886.1 3887.6 3890.0 3890.9 3892.4 3893.9 3900.3 3900.4
3902.8 3905.3

Water evaporation from $H_3O^+(H_2O)_{25}$
3510, 23510, 300, 3510, 1.D10, 0
10
0
1
231
9.0 10.7 12.1 14.7 16.7 29.3 25.5 28.2 28.8 32.8 69.6 58.0 58.4 58.5
60.0 61.0 61.8 61.9 63.4 63.4 66.4 99.8 72.6 99.5 100.0 101.4 101.5
190.2 110.8 155.0 155.2 155.5 156.8 157.0 165.7 166.0 166.5 167.3
169.5 188.2 188.3 188.7 190.0 200.1 206.9 206.9 207.4 208.6 210.9
274.5 274.6 275.1 276.3 276.6 281.0 284.0 286.2 286.3 286.8 288.0
495.8 290.3 335.7 335.9 336.4 337.5 337.8 337.9 338.4 339.6 339.9
341.9 352.7 353.5 354.6 355.0 357.0 386.3 387.0 387.8 388.9 389.3
422.8 436.8 437.7 438.7 439.2 441.2 493.8 494.3 494.8 496.3 530.9
532.9 555.9 557.0 557.5 558.0 558.5 650.6 651.4 651.9 652.8 653.4
698.1 699.0 699.5 700.3 703.0 751.1 752.7 753.4 754.2 756.2 895.8
900.2 900.2 901.7 905.3 906.6 907.1 907.2 907.7 910.6 954.8 956.7
957.2 958.2 959.2 1062.8 1064.4 1064.9 1065.3 1067.4 1088.6 1345.0
1347.7 1347.9 1348.2 1349.2 1622.8 1625.5 1625.9 1626.0 1629.5
1633.0 1633.8 1636.1 1636.3 1639.8 1642.4 1645.6 1645.7 1647.2
1659.3 1662.1 1662.5 1662.6 1664.1 1680.2 1683.1 1683.4 1683.6
1685.1 1708.5 1710.4 1711.7 1711.9 1716.4 1785.2 1788.2 1788.4
1788.7 1790.2 2217.9 1821.6 1821.8 1822.3 1826.8 3093.2 3093.3
3094.8 3097.3 3265.1 3269.8 3271.6 3273.1 3605.4 3610.5 3612.6
3613.1 3617.1 3673.4 3678.6 3680.8 3681.3 3683.3 3773.0 3778.3
3780.6 3781.1 3782.1 3792.4 3797.7 3798.5 3800.0 3805.5 3856.5
3861.9 3863.7 3864.2 3868.7 3871.6 3877.0 3877.9 3878.3 3879.4
3883.7 3884.7 3885.6 3886.1 3887.6 3890.0 3890.9 3892.4 3893.9
3895.0 3900.3 3900.4 3902.8 3905.3
9.0 10.7 12.1 14.7 16.7 19.3 25.5 28.2 28.8 32.8 35.6 58.0 58.4 58.5
61.0 61.8 61.9 63.4 63.4 66.4 69.6 70.0 99.5 99.8 101.4 101.5 110.8
150.0 155.0 155.2 155.5 156.8 157.0 165.7 166.0 166.5 167.3 169.5
188.2 188.3 188.7 190.0 190.2 206.9 206.9 207.4 208.6 210.9 274.5
274.6 275.1 276.3 276.6 281.0 284.0 286.2 286.3 286.8 288.0 290.3
296.3 335.7 335.9 336.4 337.5 337.8 337.9 338.4 339.6 339.9 341.9
352.7 353.5 354.6 355.0 357.0 386.3 387.0 387.8 388.9 389.3 422.8
436.8 437.7 438.7 439.2 441.2 493.8 494.3 494.8 495.8 530.9 532.9
555.9 557.0 557.5 558.0 558.5 650.6 651.4 651.9 652.8 653.4 698.1

699.0 699.5 700.3 703.0 751.1 752.7 753.4 754.2 756.2 895.8 900.2
900.2 901.7 905.3 906.6 907.1 907.2 907.7 910.6 954.8 956.7 957.2
958.2 959.2 1062.8 1064.4 1064.9 1065.3 1067.4 1088.6 1345.0 1347.7
1347.9 1348.2 1349.2 1622.8 1625.5 1625.9 1626.0 1629.5 1633.0
1633.8 1636.1 1636.3 1639.8 1642.4 1645.6 1645.7 1647.2 1659.3
1662.1 1662.5 1662.6 1664.1 1680.2 1683.1 1683.4 1683.6 1685.1
1708.5 1710.4 1711.7 1711.9 1716.4 1785.2 1788.2 1788.4 1788.7
1790.2 2217.9 1821.6 1821.8 1822.3 1826.8 3093.2 3093.3 3094.8
3097.3 3265.1 3269.8 3271.6 3273.1 3605.4 3610.5 3612.6 3613.1
3617.1 3673.4 3678.6 3680.8 3681.3 3683.3 3773.0 3778.3 3780.6
3781.1 3782.1 3792.4 3797.7 3798.5 3800.0 3805.5 3856.5 3861.9
3863.7 3864.2 3868.7 3871.6 3877.0 3877.9 3878.3 3879.4 3883.7
3884.7 3885.6 3886.1 3887.6 3890.0 3890.9 3892.4 3893.9 3895.0
3900.3 3900.4 3902.8 3905.3

$(H_3O)^+(H_2O)_n + D_2O \rightarrow H_2O$ or HDO

Zero point vib. energy (a.u.)

$(H_3O)^+(H_2O)_n$	D_2O	$(H_3O)^+(H_2O)_{n-1}(HDO)$	HDO	ΔEzpv, kJmol-1
0.175424	0.018395	0.172456[a]	0.021335	-0.073514
0.175424	0.018395	0.172235[b]	0.021335	-0.6537495
		$(H_3O)^+(H_2O)_{n-1}(D_2O)$	H_2O	
0.175424	0.018395	0.169266	0.0242	-0.9268015

Entropy ($JK^{-1}mol^{-1}$)

$(H_3O)^+(H_2O)_n$	D_2O	$(H_3O)^+(H_2O)_{n-1}(HDO)$	HDO	TΔS, kJmol-1
127.689	47.388	128.749[a]	46.293	-0.04365998
127.689	47.388	128.452[b]	46.293	-0.414146096
h+(h2o)6 + D20 -> +H2O		$(H_3O)^+(H_2O)_{n-1}(D_2O)$	H_2O	
127.689	47.388	129.513	45.117	-0.557600316

a) and b) are two isotopomers, in the latter the hydroxonium ion unit is deuterated