Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Accurate quantum-chemical fragmentation calculations for ion–water clusters with the density-based many-body expansion

Stefanie Schürmann[1], Johannes R. Vornweg[2], Mario Wolter[3], Christoph R. Jacob*,[4]

Technische Universität Braunschweig,

Institute of Physical and Theoretical Chemistry,

Gaußstraße 17, 38106 Braunschweig, Germany

Supporting Information

[1]ORCID: 0000-0002-0230-7263

[2]ORCID: 0000-0002-1457-0173

[3]ORCID: 0000-0001-6948-6801

[4]ORCID: 0000-0002-6227-8476, E-Mail: c.jacob@tu-braunschweig.de

S1 $\mathbf{Ca^{2+}(H_2O)}_N$ $(N = 3, \ldots, 20)$

The following tables S1 to S4 contain additional raw data for the calculations presented in Section 3.1 of the main text.

Table S1: Total interaction energy $E_{\mathrm{int}}^{(n)}$, errors in the total interaction energy $\Delta E_{\mathrm{int}}^{(n)}$, and errors in the total interaction energy per water molecule $\Delta E_{\mathrm{int}}^{(n)}/N$ for $Ca^{2+}(H_2O)_N$ clusters of increasing size ($N = 3, \ldots, 20$) for an energy-based two-body [eb-MBE(2)] and three-body expansion [eb-MBE(3)] as well as for a density-based many-body expansion of first [db-MBE(1)], second [db-MBE(2)], and third [db-MBE(3)] order. The MBEs have been performed using calculations of the **isolated** monomers and dimers ("Iso") with **PBE0/TZP**. All values are given in kJ/mol.

		$E_{\mathrm{int,tot}}^{\text{xx-MBE(n)}}$					$\Delta E_{\mathrm{int}}^{\text{xx-MBE(n)}}$					$\Delta E_{\mathrm{int}}^{\text{xx-MBE(n)}}/N$				
N	$E_{\mathrm{int,tot}}^{\mathrm{super}}$	eb(2)	eb(3)	db(1)	db(2)	db(3)	eb(2)	eb(3)	db(1)	db(2)	db(3)	eb(2)	eb(3)	db(1)	db(2)	db(3)
3	−593.37	−651.51	−589.57	−443.97	−569.71	−597.21	−58.14	3.80	149.39	23.66	−3.84	−19.38	1.27	49.80	7.89	−1.28
4	−747.42	−856.95	−732.84	−579.66	−695.51	−761.30	−109.54	14.58	167.76	51.91	−13.88	−27.38	3.64	41.94	12.98	−3.47
5	−872.51	−1053.36	−836.62	−708.11	−773.25	−908.71	−180.85	35.89	164.41	99.26	−36.19	−36.17	7.18	32.88	19.85	−7.24
6	−986.31	−1244.06	−918.33	−826.51	−827.12	−1052.97	−257.75	67.98	159.79	159.18	−66.67	−42.96	11.33	26.63	26.53	−11.11
7	−1057.01	−1398.99	−946.00	−926.43	−840.89	−1166.61	−341.98	111.01	130.58	216.12	−109.60	−48.85	15.86	18.65	30.87	−15.66
8	−1124.88	−1547.70	−960.46	−1018.53	−844.36	−1279.22	−422.81	164.42	106.35	280.53	−154.34	−52.85	20.55	13.29	35.07	−19.29
9	−1226.33	−1561.03	−1130.05	−1047.88	−992.91	−1358.03	−334.71	96.27	178.45	233.41	−131.71	−37.19	10.70	19.83	25.93	−14.63
10	−1299.11	−1638.00	−1208.85	−1102.11	−1051.46	−1445.82	−338.89	90.26	197.00	247.65	−146.71	−33.89	9.03	19.70	24.77	−14.67
11	−1342.71	−1766.65	−1197.81	−1179.61	−1033.47	−1535.19	−423.94	144.90	163.09	309.24	−192.48	−38.54	13.17	14.83	28.11	−17.50
12	−1407.56	−1843.59	−1266.07	−1235.13	−1081.13	−1623.90	−436.04	141.49	172.43	326.42	−216.34	−36.34	11.79	14.37	27.20	−18.03
13	−1469.35	−1913.28	−1335.96	−1285.96	−1128.65	−1695.24	−443.93	133.38	183.39	340.70	−225.89	−34.15	10.26	14.11	26.21	−17.38
14	−1529.78	−1966.77	−1401.66	−1322.39	−1177.24	−1830.35	−436.98	128.12	207.40	352.54	−300.57	−31.21	9.15	14.81	25.18	−21.47
15	−1595.16	−2028.14	−1448.83	−1367.66	−1152.77	−2032.91	−432.98	146.34	227.50	442.40	−437.74	−28.87	9.76	15.17	29.49	−29.18
16	−1648.62	−2099.40	−1508.00	−1425.00	−1190.55	−2103.44	−450.78	140.61	223.62	458.07	−454.82	−28.17	8.79	13.98	28.63	−28.43
17	−1714.16	−2164.23	−1551.06	−1472.53	−1161.17	−2051.20	−450.07	163.10	241.63	552.99	−337.04	−26.47	9.59	14.21	32.53	−19.83
18	−1768.25	−2232.92	−1610.18	−1526.82	−1197.42	−2093.62	−464.67	158.07	241.43	570.82	−325.37	−25.81	8.78	13.41	31.71	−18.08
19	−1829.79	−2270.02	−1683.69	−1544.63	−1267.30	−2379.49	−440.24	146.10	285.15	562.49	−549.71	−23.17	7.69	15.01	29.60	−28.93
20	−1874.01	−2328.13	−1743.44	−1573.43	−1365.80	−2552.91	−454.13	130.57	300.58	508.21	−678.91	−22.71	6.53	15.03	25.41	−33.95

Table S2: Total interaction energy $E_{\text{int}}^{(n)}$, errors in the total interaction energy $\Delta E_{\text{int}}^{(n)}$, and errors in the total interaction energy per water molecule $\Delta E_{\text{int}}^{(n)}/N$ for $Ca^{2+}(H_2O)_N$ clusters of increasing size ($N = 3, \ldots, 20$) for an energy-based two-body [eb-MBE(2)] and three-body expansion [eb-MBE(3)] as well as for a density-based many-body expansion of first [db-MBE(1)], second [db-MBE(2)], and third [db-MBE(3)] order. The MBEs have been performed using electrostatic **point-charge embedding** ("PC") with **PBE0/TZP**. All values are given in kJ/mol.

		$E_{\text{int,tot}}^{\text{xx-MBE(n)}}$					$\Delta E_{\text{int}}^{\text{xx-MBE(n)}}$					$\Delta E_{\text{int}}^{\text{xx-MBE(n)}}/N$				
N	$E_{\text{int,tot}}^{\text{super}}$	eb(2)	eb(3)	db(1)	db(2)	db(3)	eb(2)	eb(3)	db(1)	db(2)	db(3)	eb(2)	eb(3)	db(1)	db(2)	db(3)
3	−593.37	−602.48	−593.37	−631.51	−586.77	−594.16	−9.11	0.00	−38.14	6.60	−0.80	−3.04	0.00	−12.71	2.20	−0.27
4	−747.42	−760.89	−750.48	−796.21	−733.01	−749.81	−13.47	−3.06	−48.79	14.41	−2.39	−3.37	−0.76	−12.20	3.60	−0.60
5	−872.51	−893.17	−881.85	−931.62	−849.05	−879.33	−20.66	−9.34	−59.11	23.46	−6.81	−4.13	−1.87	−11.82	4.69	−1.36
6	−986.31	−1006.36	−999.31	−1051.87	−948.92	−995.56	−20.06	−13.00	−65.56	37.38	−9.26	−3.34	−2.17	−10.93	6.23	−1.54
7	−1057.01	−1074.94	−1074.41	−1132.78	−1020.03	−1074.62	−17.93	−17.40	−75.78	36.97	−17.62	−2.56	−2.49	−10.83	5.28	−2.52
8	−1124.88	−1135.18	−1138.66	−1207.91	−1083.20	−1145.23	−10.29	−13.77	−83.03	41.69	−20.34	−1.29	−1.72	−10.38	5.21	−2.54
9	−1226.33	−1228.94	−1254.72	−1300.73	−1190.01	−1243.51	−2.61	−28.40	−74.41	36.32	−17.18	−0.29	−3.16	−8.27	4.04	−1.91
10	−1299.11	−1298.11	−1334.00	−1373.48	−1260.80	−1314.09	1.00	−34.89	−74.37	38.31	−14.98	0.10	−3.49	−7.44	3.83	−1.50
11	−1342.71	−1338.98	−1371.40	−1428.56	−1302.80	−1361.79	3.73	−28.69	−85.86	39.90	−19.08	0.34	−2.61	−7.81	3.63	−1.73
12	−1407.56	−1400.85	−1440.12	−1496.65	−1368.53	−1427.75	6.71	−32.56	−89.09	39.03	−20.19	0.56	−2.71	−7.42	3.25	−1.68
13	−1469.35	−1463.99	−1506.89	−1559.01	−1428.05	−1484.23	5.35	−37.55	−89.66	41.30	−14.88	0.41	−2.89	−6.90	3.18	−1.14
14	−1529.78	−1517.62	−1568.45	−1620.20	−1491.00	−1546.16	12.16	−38.67	−90.42	38.78	−16.37	0.87	−2.76	−6.46	2.77	−1.17
15	−1595.16	−1580.44	−1637.29	−1686.73	−1554.89	−1610.11	14.73	−42.13	−91.57	40.27	−14.95	0.98	−2.81	−6.10	2.68	−1.00
16	−1648.62	−1637.67	−1695.61	−1749.16	−1611.15	−1665.03	10.95	−46.99	−100.55	37.47	−16.42	0.68	−2.94	−6.28	2.34	−1.03
17	−1714.16	−1699.66	−1762.50	−1814.58	−1673.33	−1727.56	14.50	−48.34	−100.42	40.84	−13.40	0.85	−2.84	−5.91	2.40	−0.79
18	−1768.25	−1757.64	−1820.50	−1874.81	−1729.66	−1782.66	10.61	−52.26	−106.57	38.59	−14.41	0.59	−2.90	−5.92	2.14	−0.80
19	−1829.79	−1811.02	−1883.22	−1933.58	−1786.89	−1843.16	18.77	−53.44	−103.80	42.90	−13.37	0.99	−2.81	−5.46	2.26	−0.70
20	−1874.01	−1849.00	−1924.88	−1979.56	−1834.18	−1883.38	25.00	−50.88	−105.56	39.83	−9.38	1.25	−2.54	−5.28	1.99	−0.47

Table S3: Total interaction energy $E_{\text{int}}^{(n)}$, errors in the total interaction energy $\Delta E_{\text{int}}^{(n)}$, and errors in the total interaction energy per water molecule $\Delta E_{\text{int}}^{(n)}/N$ for $Ca^{2+}(H_2O)_N$ clusters of increasing size ($N = 3, \ldots, 20$) for an energy-based two-body [eb-MBE(2)] and three-body expansion [eb-MBE(3)] as well as for a density-based many-body expansion of first [db-MBE(1)], second [db-MBE(2)], and third [db-MBE(3)] order. The MBEs have been performed using a **frozen-density embedding** potential obtained from isolated molecule electron densities ("**FDE**") with **PBE0/TZP**. All values are given in kJ/mol.

		$E_{\text{int,tot}}^{\text{xx-MBE(n)}}$					$\Delta E_{\text{int}}^{\text{xx-MBE(n)}}$					$\Delta E_{\text{int}}^{\text{xx-MBE(n)}}/N$				
N	$E_{\text{int,tot}}^{\text{super}}$	eb(2)	eb(3)	db(1)	db(2)	db(3)	eb(2)	eb(3)	db(1)	db(2)	db(3)	eb(2)	eb(3)	db(1)	db(2)	db(3)
3	−593.37	−636.92	−591.06	−641.48	−588.38	−594.40	−43.55	2.31	−48.12	4.99	−1.04	−14.52	0.77	−16.04	1.66	−0.35
4	−747.42	−826.27	−738.99	−808.78	−736.72	−749.96	−78.86	8.43	−61.36	10.70	−2.54	−19.71	2.11	−15.34	2.67	−0.64
5	−872.51	−995.38	−852.00	−943.75	−854.86	−878.57	−122.86	20.51	−71.23	17.65	−6.05	−24.57	4.10	−14.25	3.53	−1.21
6	−986.31	−1150.95	−944.89	−1061.51	−958.17	−993.56	−164.64	41.41	−75.20	28.14	−7.26	−27.44	6.90	−12.53	4.69	−1.21
7	−1057.01	−1249.38	−1000.20	−1134.99	−1031.08	−1071.09	−192.37	56.81	−77.98	25.93	−14.09	−27.48	8.12	−11.14	3.70	−2.01
8	−1124.88	−1338.99	−1044.34	−1201.70	−1096.24	−1140.83	−214.10	80.54	−76.82	28.64	−15.95	−26.76	10.07	−9.60	3.58	−1.99
9	−1226.33	−1419.06	−1179.23	−1302.76	−1202.41	−1240.36	−192.73	47.10	−76.44	23.92	−14.04	−21.41	5.23	−8.49	2.66	−1.56
10	−1299.11	−1497.38	−1257.18	−1375.13	−1273.78	−1311.52	−198.27	41.93	−76.03	25.33	−12.41	−19.83	4.19	−7.60	2.53	−1.24
11	−1342.71	−1564.08	−1275.26	−1421.83	−1317.27	−1358.92	−221.38	67.45	−79.12	25.43	−16.21	−20.13	6.13	−7.19	2.31	−1.47
12	−1407.56	−1634.45	−1342.01	−1489.38	−1383.68	−1425.55	−226.89	65.55	−81.82	23.88	−17.99	−18.91	5.46	−6.82	1.99	−1.50
13	−1469.35	−1703.44	−1409.08	−1552.22	−1443.61	−1482.38	−234.09	60.26	−82.88	25.73	−13.04	−18.01	4.64	−6.38	1.98	−1.00
14	−1529.78	−1766.48	−1468.49	−1612.70	−1507.39	−1544.64	−236.69	61.29	−82.92	22.39	−14.86	−16.91	4.38	−5.92	1.60	−1.06
15	−1595.16	−1830.25	−1536.18	−1680.84	−1572.89	−1607.50	−235.09	58.98	−85.67	22.28	−12.33	−15.67	3.93	−5.71	1.49	−0.82
16	−1648.62	−1894.40	−1593.81	−1743.32	−1629.38	−1663.25	−245.78	54.80	−94.70	19.24	−14.64	−15.36	3.43	−5.92	1.20	−0.91
17	−1714.16	−1957.42	−1659.37	−1810.01	−1693.06	−1725.31	−243.26	54.79	−95.84	21.10	−11.15	−14.31	3.22	−5.64	1.24	−0.66
18	−1768.25	−2022.97	−1717.21	−1870.33	−1749.11	−1781.12	−254.72	51.04	−102.08	19.13	−12.88	−14.15	2.84	−5.67	1.06	−0.72
19	−1829.79	−2073.30	−1777.47	−1929.36	−1808.55	−1841.52	−243.51	52.31	−99.57	21.23	−11.73	−12.82	2.75	−5.24	1.12	−0.62
20	−1874.01	−2127.39	−1816.32	−1970.89	−1854.91	−1883.76	−253.38	57.69	−96.88	19.10	−9.76	−12.67	2.88	−4.84	0.96	−0.49

Table S4: Total interaction energy $E_{\text{int}}^{(n)}$, errors in the total interaction energy $\Delta E_{\text{int}}^{(n)}$, and errors in the total interaction energy per water molecule $\Delta E_{\text{int}}^{(n)}/N$ for $Ca^{2+}(H_2O)_N$ clusters of increasing size ($N = 3, \ldots, 20$) for an energy-based two-body [eb-MBE(2)] and three-body expansion [eb-MBE(3)] as well as for a density-based many-body expansion of first [db-MBE(1)], second [db-MBE(2)], and third [db-MBE(3)] order. The MBEs have been performed using a **frozen-density embedding** potential obtained after three freeze-and-thaw cycles ("**FDE-ft**") with **PBE0/TZP**. All values are given in kJ/mol.

		$E_{\text{int,tot}}^{\text{xx-MBE(n)}}$					$\Delta E_{\text{int}}^{\text{xx-MBE(n)}}$					$\Delta E_{\text{int}}^{\text{xx-MBE(n)}}/N$				
N	$E_{\text{int,tot}}^{\text{super}}$	eb(2)	eb(3)	db(1)	db(2)	db(3)	eb(2)	eb(3)	db(1)	db(2)	db(3)	eb(2)	eb(3)	db(1)	db(2)	db(3)
3	−593.37	−600.65	−593.39	−643.29	−591.65	−593.57	−7.28	−0.02	−49.92	1.72	−0.20	−2.43	−0.01	−16.64	0.57	−0.07
4	−747.42	−758.13	−747.26	−812.96	−742.44	−747.17	−10.71	0.16	−65.54	4.98	0.25	−2.68	0.04	−16.39	1.24	0.06
5	−872.51	−886.46	−871.86	−952.80	−862.38	−872.75	−13.95	0.66	−80.28	10.13	−0.23	−2.79	0.13	−16.06	2.03	−0.05
6	−986.31	−1002.93	−980.27	−1076.40	−966.85	−984.10	−16.62	6.04	−90.10	19.45	2.21	−2.77	1.01	−15.02	3.24	0.37
7	−1057.01	−1074.91	−1051.13	−1156.21	−1038.43	−1059.79	−17.90	5.88	−99.20	18.58	−2.78	−2.56	0.84	−14.17	2.65	−0.40
8	−1124.88	−1145.78	−1111.22	−1228.32	−1102.00	−1128.12	−20.90	13.67	−103.43	22.88	−3.24	−2.61	1.71	−12.93	2.86	−0.41
9	−1226.33	−1234.30	−1225.46	−1325.70	−1211.06	−1228.14	−7.97	0.87	−99.37	15.27	−1.81	−0.89	0.10	−11.04	1.70	−0.20
10	−1299.11	−1306.10	−1301.51	−1398.80	−1283.23	−1298.78	−6.99	−2.40	−99.69	15.88	0.32	−0.70	−0.24	−9.97	1.59	0.03
11	−1342.71	−1355.93	−1336.81	−1450.45	−1324.64	−1344.86	−13.22	5.90	−107.75	18.07	−2.16	−1.20	0.54	−9.80	1.64	−0.20
12	−1407.56	−1419.62	−1402.25	−1518.77	−1391.68	−1410.62	−12.06	5.30	−111.21	15.88	−3.06	−1.01	0.44	−9.27	1.32	−0.26
13	−1469.35	−1482.60	−1467.01	−1581.58	−1452.19	−1466.87	−13.26	2.33	−112.24	17.16	2.48	−1.02	0.18	−8.63	1.32	0.19
14	−1529.78	−1540.87	−1526.37	−1643.83	−1516.04	−1528.51	−11.09	3.41	−114.05	13.75	1.27	−0.79	0.24	−8.15	0.98	0.09
15	−1595.16	−1603.85	−1592.77	−1713.12	−1581.80	−1591.90	−8.68	2.39	−117.96	13.36	3.26	−0.58	0.16	−7.86	0.89	0.22
16	−1648.62	−1660.04	−1648.59	−1775.32	−1638.91	−1646.18	−11.42	0.03	−126.70	9.71	2.44	−0.71	0.00	−7.92	0.61	0.15
17	−1714.16	−1722.43	−1713.09	−1843.05	−1702.49	−1708.66	−8.26	1.07	−128.89	11.67	5.50	−0.49	0.06	−7.58	0.69	0.32
18	−1768.25	−1780.59	−1769.30	−1902.79	−1759.30	−1763.70	−12.35	−1.05	−134.54	8.94	4.54	−0.69	−0.06	−7.47	0.50	0.25
19	−1829.79	−1834.95	−1827.63	−1965.83	−1819.45	−1821.96	−5.17	2.16	−136.05	10.33	7.82	−0.27	0.11	−7.16	0.54	0.41
20	−1874.01	−1881.52	−1868.60	−2009.63	−1866.05	−1865.28	−7.51	5.40	−135.63	7.95	8.73	−0.38	0.27	−6.78	0.40	0.44

S2 $F^-(H_2O)_{10}$

The following tables S5 to S8 contain additional raw data for the calculations presented in Section 3.2 of the main text.

Table S5: Total interaction energies $E_{\text{int}}^{\text{xx-MBE}(n)}$(PBE0/TZP, in kJ/mol) of ten isomers of $F^-(H_2O)_{10}$ relative to the lowest-energy isomer as calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The total interaction energies from supermolecular calculations as well as the errors in the total interaction energies compared to the supermolecular calculation $\Delta_{\text{int}}^{\text{xx-MBE}(n)}$, are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

		iso		PC		FDE		FDE-ft	
		E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}
01	eb-MBE(2)	−771.88	−169.62	−672.37	−70.12	−687.42	−85.17	−649.52	−47.27
	eb-MBE(3)	−475.06	+127.20	−554.03	+48.22	−550.07	+52.18	−571.87	+30.38
	db-MBE(1)	−498.35	+103.90	−607.04	−4.79	−608.35	−6.10	−610.31	−8.05
	db-MBE(2)	−435.16	+167.09	−594.25	+8.01	−596.06	+6.20	−601.69	+0.56
	db-MBE(3)	−687.37	−85.12	−606.84	−4.59	−607.41	−5.16	−602.66	−0.41
	supermol.	−602.25		−602.25		−602.25		−602.25	
02	eb-MBE(2)	−765.44	−157.40	−671.90	−63.86	−684.84	−76.80	−652.41	−44.37
	eb-MBE(3)	−480.92	+127.12	−560.16	+47.88	−556.00	+52.03	−577.10	+30.94
	db-MBE(1)	−487.25	+120.79	−610.60	−2.56	−612.33	−4.30	−615.38	−7.34
	db-MBE(2)	−442.44	+165.60	−600.12	+7.91	−602.37	+5.67	−608.03	+0.00
	db-MBE(3)	−691.49	−83.46	−612.40	−4.37	−613.09	−5.06	−608.40	−0.36
	supermol.	−608.04		−608.04		−608.04		−608.04	
03	eb-MBE(2)	−753.83	−135.65	−676.47	−58.28	−690.91	−72.73	−658.31	−40.13
	eb-MBE(3)	−496.40	+121.78	−571.92	+46.26	−568.44	+49.74	−588.14	+30.04
	db-MBE(1)	−486.16	+132.02	−618.25	−0.06	−620.39	−2.21	−624.26	−6.08
	db-MBE(2)	−449.85	+168.33	−609.37	+8.81	−611.77	+6.41	−617.20	+0.98
	db-MBE(3)	−691.35	−73.17	−621.49	−3.31	−622.22	−4.04	−617.68	+0.50
	supermol.	−618.18		−618.18		−618.18		−618.18	
04	eb-MBE(2)	−751.61	−146.57	−673.44	−68.40	−680.89	−75.85	−644.39	−39.35
	eb-MBE(3)	−494.24	+110.80	−560.73	+44.30	−561.40	+43.64	−580.86	+24.17
	db-MBE(1)	−481.29	+123.74	−603.79	+1.25	−604.85	+0.19	−607.17	−2.14
	db-MBE(2)	−448.80	+156.24	−596.54	+8.49	−599.84	+5.20	−605.12	−0.08
	db-MBE(3)	−690.55	−85.51	−608.55	−3.51	−608.05	−3.01	−603.41	+1.63
	supermol.	−605.04		−605.04		−605.04		−605.04	
05	eb-MBE(2)	−734.49	−149.41	−643.24	−58.15	−658.85	−73.76	−627.68	−42.60
	eb-MBE(3)	−463.31	+121.77	−539.76	+45.33	−536.41	+48.67	−554.36	+30.72
	db-MBE(1)	−467.57	+117.52	−581.33	+3.75	−582.85	+2.24	−585.36	−0.27
	db-MBE(2)	−417.84	+167.24	−577.80	+7.29	−579.27	+5.82	−584.70	+0.39
	db-MBE(3)	−661.43	−76.34	−586.38	−1.30	−587.59	−2.50	−583.68	+1.40
	supermol.	−585.08		−585.08		−585.08		−585.08	

Table S6: (Continued) Total interaction energies $E_{\text{int}}^{\text{xx-MBE}(n)}$(PBE0/TZP, in kJ/mol) of ten isomers of $F^-(H_2O)_{10}$ relative to the lowest-energy isomer as calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The total interaction energies from supermolecular calculations as well as the errors in the total interaction energies compared to the supermolecular calculation $\Delta_{\text{int}}^{\text{xx-MBE}(n)}$, are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

		iso		PC		FDE		FDE-ft	
		E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}
06	eb-MBE(2)	−788.48	−174.44	−677.07	−63.02	−696.09	−82.04	−655.94	−41.90
	eb-MBE(3)	−476.79	+137.26	−567.68	+46.36	−559.71	+54.34	−585.62	+28.43
	db-MBE(1)	−474.39	+139.66	−613.39	+0.66	−616.67	−2.62	−620.54	−6.49
	db-MBE(2)	−421.96	+192.09	−605.60	+8.45	−606.07	+7.98	−612.80	+1.25
	db-MBE(3)	−715.00	−100.95	−616.95	−2.91	−619.90	−5.85	−613.78	+0.27
	supermol.	−614.05		−614.05		−614.05		−614.05	
07	eb-MBE(2)	−731.65	−147.12	−649.18	−64.65	−657.25	−72.72	−622.57	−38.04
	eb-MBE(3)	−469.10	+115.44	−541.72	+42.81	−540.38	+44.16	−559.89	+24.65
	db-MBE(1)	−461.18	+123.35	−584.32	+0.21	−584.47	+0.06	−587.35	−2.82
	db-MBE(2)	−426.79	+157.74	−577.26	+7.27	−579.24	+5.30	−584.15	+0.38
	db-MBE(3)	−681.74	−97.21	−586.99	−2.46	−587.70	−3.17	−583.12	+1.42
	supermol.	−584.53		−584.53		−584.53		−584.53	
08	eb-MBE(2)	−737.45	−158.93	−641.04	−62.52	−654.72	−76.19	−618.68	−40.16
	eb-MBE(3)	−446.68	+131.84	−530.62	+47.90	−526.33	+52.19	−549.91	+28.61
	db-MBE(1)	−461.10	+117.42	−585.38	−6.85	−586.24	−7.72	−589.60	−11.07
	db-MBE(2)	−404.65	+173.87	−570.77	+7.75	−571.92	+6.60	−577.45	+1.08
	db-MBE(3)	−662.92	−84.40	−581.42	−2.89	−582.94	−4.42	−577.97	+0.55
	supermol.	−578.52		−578.52		−578.52		−578.52	
09	eb-MBE(2)	−749.27	−173.76	−646.36	−70.85	−658.17	−82.66	−623.06	−47.55
	eb-MBE(3)	−428.12	+147.39	−514.70	+60.80	−513.37	+62.13	−538.04	+37.47
	db-MBE(1)	−461.83	+113.68	−579.25	−3.74	−580.22	−4.72	−583.98	−8.48
	db-MBE(2)	−391.06	+184.44	−564.47	+11.04	−568.80	+6.70	−574.78	+0.72
	db-MBE(3)	−625.28	−49.78	−579.61	−4.10	−578.93	−3.42	−574.31	+1.20
	supermol.	−575.50		−575.50		−575.50		−575.50	
10	eb-MBE(2)	−780.94	−168.72	−686.95	−74.73	−702.19	−89.97	−658.38	−46.16
	eb-MBE(3)	−470.74	+141.48	−562.04	+50.17	−556.65	+55.57	−583.73	+28.48
	db-MBE(1)	−475.02	+137.19	−614.68	−2.47	−614.39	−2.18	−617.70	−5.49
	db-MBE(2)	−424.66	+187.56	−605.39	+6.82	−606.87	+5.34	−612.66	−0.45
	db-MBE(3)	−691.41	−79.20	−616.45	−4.24	−618.86	−6.64	−612.53	−0.32
	supermol.	−612.21		−612.21		−612.21		−612.21	

Table S7: Interaction energies (PBE0/TZP, in kJ/mol) of ten isomers of $F^-(H_2O)_{10}$ relative to the lowest-energy isomer calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The relative interaction energies from supermolecular calculations are given as reference. Included are results from the isolated MBEs ("iso") as well as embedded MBEs using point charges ("PC"). All values are given in kJ/mol.

	isomer	$E_{\text{int,rel}}^{\text{super}}$	$E_{\text{int,rel}}^{\text{eb-MBE}(n)}$		$E_{\text{int,rel}}^{\text{db-MBE}(n)}$		
			$n=2$	$n=3$	$n=1$	$n=2$	$n=3$
iso	**03**	0.00	0.00	0.00	0.00	0.00	0.00
	06	4.13	−34.65	19.62	11.77	27.89	−23.65
	10	5.97	−27.10	25.67	11.14	25.19	−0.07
	02	10.15	−11.61	15.48	−1.09	7.41	−0.15
	04	13.14	2.22	2.16	4.87	1.05	0.80
	01	15.93	−18.04	21.35	−12.19	14.69	3.97
	05	33.10	19.34	33.09	18.59	32.01	29.92
	07	33.65	22.18	27.31	24.98	23.06	9.60
	08	39.66	16.38	49.72	25.06	45.20	28.43
	09	42.68	4.57	68.28	24.33	58.78	66.06
PC	**03**	0.00	0.00	0.00	0.00	0.00	0.00
	06	4.13	−0.60	4.24	4.86	3.77	4.54
	10	5.97	−10.48	9.88	3.56	3.98	5.04
	02	10.15	4.57	11.76	7.65	9.25	9.09
	04	13.14	3.03	11.19	14.46	12.83	12.94
	01	15.93	4.09	17.89	11.20	15.12	14.65
	05	33.10	33.23	32.17	36.92	31.57	35.11
	07	33.65	27.28	30.20	33.93	32.11	34.50
	08	39.66	35.43	41.30	32.87	38.60	40.07
	09	42.68	30.11	57.22	39.00	44.91	41.88

Table S8: Interaction energies (PBE0/TZP, in kJ/mol) of ten isomers of $F^-(H_2O)_{10}$ relative to the lowest-energy isomer calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The relative interaction energies from supermolecular calculations are given as reference. Included are results for the frozen-density embedded MBEs using the unrelaxed frozen densities of the isolated fragments ("FDE") and using a relaxed frozen density obtained using three freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

	isomer	$E_{\text{int,rel}}^{\text{super}}$	$E_{\text{int,rel}}^{\text{eb-MBE}(n)}$		$E_{\text{int,rel}}^{\text{db-MBE}(n)}$		
			$n=2$	$n=3$	$n=1$	$n=2$	$n=3$
FDE	**03**	0.00	0.00	0.00	0.00	0.00	0.00
	06	4.13	−5.18	8.73	3.72	5.70	2.33
	10	5.97	−11.28	11.79	6.00	4.90	3.37
	02	10.15	6.07	12.44	8.06	9.40	9.13
	04	13.14	10.02	7.04	15.54	11.93	14.18
	01	15.93	3.49	18.37	12.04	15.71	14.81
	05	33.10	32.06	32.03	37.54	32.50	34.63
	07	33.65	33.66	28.06	35.92	32.53	34.52
	08	39.66	36.19	42.11	34.15	39.85	39.28
	09	42.68	32.74	55.07	40.17	42.97	43.29
FDE-ft	**03**	0.00	0.00	0.00	0.00	0.00	0.00
	06	4.13	2.37	2.52	3.72	4.40	3.90
	10	5.97	−0.07	4.41	6.56	4.54	5.14
	02	10.15	5.90	11.05	8.88	9.17	9.28
	04	13.14	13.92	7.28	17.09	12.08	14.27
	01	15.93	8.79	16.27	13.96	15.51	15.02
	05	33.10	30.63	33.78	38.91	32.51	33.99
	07	33.65	35.74	28.26	36.91	33.05	34.56
	08	39.66	39.63	38.23	34.67	39.76	39.71
	09	42.68	35.25	50.10	40.28	42.42	43.37

S2.1 $\mathbf{OH^-(H_2O)}_N$ $(N = 3, 4, 5)$

The following tables S9 to S14 contain additional raw data for the calculations presented in Section 3.3 of the main text.

Table S9: Total interaction energies $E_{\text{int}}^{\text{xx-MBE}(n)}$(PBE0/TZP, in kJ/mol) of six isomers of $OH^-(H_2O)_3$ relative to the lowest-energy isomer as calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The total interaction energies from supermolecular calculations as well as the errors in the total interaction energies compared to the supermolecular calculation $\Delta_{\text{int}}^{\text{xx-MBE}(n)}$, are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

		iso		PC		FDE		FDE-ft	
		E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}
1	eb-MBE(2)	−395.78	−37.02	−379.20	−20.44	−383.06	−24.30	−365.20	−6.44
	eb-MBE(3)	−356.72	+2.04	−359.82	−1.05	−360.45	−1.69	−360.66	−1.89
	db-MBE(1)	−177.44	+181.32	−323.20	+35.56	−324.81	+33.95	−330.23	+28.53
	db-MBE(2)	−320.26	+38.50	−355.03	+3.73	−356.26	+2.50	−357.52	+1.24
	db-MBE(3)	−374.89	−16.13	−360.08	−1.32	−359.68	−0.92	−359.14	−0.38
	supermol.	−358.76		−358.76		−358.76		−358.76	
2	eb-MBE(2)	−415.94	−66.98	−386.75	−37.78	−391.07	−42.10	−365.58	−16.62
	eb-MBE(3)	−342.60	+6.36	−345.77	+3.20	−345.18	+3.79	−348.50	+0.47
	db-MBE(1)	−203.46	+145.51	−328.88	+20.08	−329.69	+19.28	−332.58	+16.38
	db-MBE(2)	−325.31	+23.66	−347.50	+1.46	−347.55	+1.41	−348.32	+0.65
	db-MBE(3)	−354.72	−5.76	−349.79	−0.83	−349.98	−1.02	−349.27	−0.30
	supermol.	−348.97		−348.97		−348.97		−348.97	
3	eb-MBE(2)	−417.40	−67.53	−388.92	−39.05	−393.13	−43.27	−368.04	−18.18
	eb-MBE(3)	−343.69	+6.17	−346.60	+3.27	−345.96	+3.91	−349.25	+0.62
	db-MBE(1)	−199.02	+150.85	−327.85	+22.02	−328.78	+21.08	−331.62	+18.25
	db-MBE(2)	−327.48	+22.39	−348.29	+1.57	−348.29	+1.58	−349.00	+0.86
	db-MBE(3)	−354.59	−4.73	−350.31	−0.45	−350.57	−0.70	−349.81	+0.06
	supermol.	−349.87		−349.87		−349.87		−349.87	
4	eb-MBE(2)	−414.69	−67.88	−385.67	−38.85	−389.41	−42.59	−363.30	−16.48
	eb-MBE(3)	−340.14	+6.68	−343.31	+3.51	−342.53	+4.28	−346.01	+0.81
	db-MBE(1)	−203.65	+143.17	−326.98	+19.84	−328.14	+18.68	−331.12	+15.70
	db-MBE(2)	−321.69	+25.13	−344.98	+1.84	−344.43	+2.39	−345.38	+1.44
	db-MBE(3)	−351.76	−4.94	−347.01	−0.20	−347.53	−0.71	−346.80	+0.02
	supermol.	−346.82		−346.82		−346.82		−346.82	
5	eb-MBE(2)	−398.93	−58.96	−370.81	−30.84	−376.04	−36.07	−354.01	−14.04
	eb-MBE(3)	−335.23	+4.75	−337.54	+2.44	−337.36	+2.61	−339.60	+0.37
	db-MBE(1)	−216.31	+123.67	−327.41	+12.56	−327.29	+12.68	−330.53	+9.44
	db-MBE(2)	−316.05	+23.93	−337.63	+2.34	−338.01	+1.97	−338.70	+1.27
	db-MBE(3)	−344.93	−4.96	−340.80	−0.82	−340.86	−0.88	−340.30	−0.33
	supermol.	−339.97		−339.97		−339.97		−339.97	
6	eb-MBE(2)	−412.87	−69.17	−381.73	−38.02	−385.91	−42.21	−360.00	−16.29
	eb-MBE(3)	−336.60	+7.10	−340.43	+3.27	−339.29	+4.41	−342.91	+0.79
	db-MBE(1)	−203.64	+140.07	−323.42	+20.29	−324.85	+18.86	−327.97	+15.74
	db-MBE(2)	−317.89	+25.81	−342.08	+1.62	−341.48	+2.23	−342.48	+1.23
	db-MBE(3)	−349.06	−5.36	−343.69	+0.02	−344.39	−0.68	−343.69	+0.02
	supermol.	−343.71		−343.71		−343.71		−343.71	

Table S10: Total interaction energies $E_{\text{int}}^{\text{xx-MBE}(n)}$(PBE0/TZP, in kJ/mol) of four isomers of $OH^-(H_2O)_4$ relative to the lowest-energy isomer as calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The total interaction energies from supermolecular calculations as well as the errors in the total interaction energies compared to the supermolecular calculation $\Delta_{\text{int}}^{\text{xx-MBE}(n)}$, are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

		iso		PC		FDE		FDE-ft	
		E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}
1	eb-MBE(2)	−497.56	−73.61	−459.64	−35.69	−467.61	−43.66	−438.10	−14.16
	eb-MBE(3)	−413.37	+10.58	−420.90	+3.05	−420.73	+3.22	−424.56	−0.61
	db-MBE(1)	−265.99	+157.95	−405.29	+18.65	−407.02	+16.93	−411.09	+12.86
	db-MBE(2)	−374.25	+49.69	−418.70	+5.24	−420.18	+3.77	−421.85	+2.10
	db-MBE(3)	−448.68	−24.73	−425.99	−2.04	−425.49	−1.54	−424.26	−0.31
	supermol.	−423.95		−423.95		−423.95		−423.95	
2	eb-MBE(2)	−502.54	−79.09	−465.70	−42.25	−472.07	−48.62	−439.45	−16.00
	eb-MBE(3)	−407.19	+16.25	−419.45	+4.00	−419.19	+4.26	−424.77	−1.33
	db-MBE(1)	−251.02	+172.43	−399.88	+23.57	−401.73	+21.72	−405.31	+18.14
	db-MBE(2)	−362.53	+60.92	−419.31	+4.14	−419.98	+3.46	−421.89	+1.55
	db-MBE(3)	−461.78	−38.33	−425.28	−1.83	−425.38	−1.93	−423.66	−0.21
	supermol.	−423.45		−423.45		−423.45		−423.45	
3	eb-MBE(2)	−482.40	−67.04	−447.40	−32.04	−453.24	−37.88	−426.49	−11.13
	eb-MBE(3)	−396.07	+19.29	−410.56	+4.80	−409.72	+5.65	−415.76	−0.40
	db-MBE(1)	−231.33	+184.03	−385.75	+29.62	−386.92	+28.44	−392.24	+23.12
	db-MBE(2)	−351.16	+64.20	−412.26	+3.11	−412.60	+2.76	−414.53	+0.84
	db-MBE(3)	−456.26	−40.90	−416.92	−1.56	−417.28	−1.91	−415.66	−0.30
	supermol.	−415.36		−415.36		−415.36		−415.36	
4	eb-MBE(2)	−444.39	−28.16	−425.00	−8.77	−429.68	−13.45	−413.71	+2.52
	eb-MBE(3)	−397.15	+19.08	−414.03	+2.20	−413.74	+2.49	−418.25	−2.02
	db-MBE(1)	−183.18	+233.05	−364.93	+51.30	−366.97	+49.26	−375.53	+40.70
	db-MBE(2)	−328.92	+87.31	−411.69	+4.54	−412.07	+4.16	−415.06	+1.17
	db-MBE(3)	−470.21	−53.98	−417.69	−1.46	−418.06	−1.83	−416.16	+0.07
	supermol.	−416.23		−416.23		−416.23		−416.23	

Table S11: Total interaction energies $E_{\text{int}}^{\text{xx-MBE}(n)}$(PBE0/TZP, in kJ/mol) of four isomers of $OH^-(H_2O)_5$ relative to the lowest-energy isomer as calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The total interaction energies from supermolecular calculations as well as the errors in the total interaction energies compared to the supermolecular calculation $\Delta_{\text{int}}^{\text{xx-MBE}(n)}$, are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

		iso		PC		FDE		FDE-ft	
		E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}
1	eb-MBE(2)	−574.72	−80.83	−531.25	−37.36	−541.91	−48.02	−508.71	−14.82
	eb-MBE(3)	−476.91	+16.98	−491.34	+2.55	−490.52	+3.37	−495.73	−1.84
	db-MBE(1)	−309.59	+184.30	−472.15	+21.74	−475.14	+18.75	−479.88	+14.02
	db-MBE(2)	−420.50	+73.39	−487.55	+6.34	−490.08	+3.81	−492.54	+1.35
	db-MBE(3)	−546.58	−52.69	−497.61	−3.72	−496.95	−3.05	−494.84	−0.95
	supermol.	−493.89		−493.89		−493.89		−493.89	
2	eb-MBE(2)	−583.72	−94.30	−534.94	−45.52	−544.59	−55.17	−504.30	−14.88
	eb-MBE(3)	−458.15	+31.27	−484.36	+5.06	−484.51	+4.91	−493.24	−3.82
	db-MBE(1)	−300.80	+188.62	−465.61	+23.80	−467.70	+21.72	−471.59	+17.83
	db-MBE(2)	−384.80	+104.62	−483.37	+6.04	−485.24	+4.18	−488.12	+1.30
	db-MBE(3)	−572.26	−82.85	−493.05	−3.63	−492.81	−3.39	−489.98	−0.57
	supermol.	−489.42		−489.42		−489.42		−489.42	
3	eb-MBE(2)	−593.81	−114.89	−531.00	−52.07	−540.70	−61.77	−500.57	−21.65
	eb-MBE(3)	−449.26	+29.67	−469.01	+9.92	−467.42	+11.51	−477.48	+1.45
	db-MBE(1)	−340.07	+138.86	−472.74	+6.19	−474.50	+4.43	−477.92	+1.01
	db-MBE(2)	−405.95	+72.98	−472.46	+6.47	−474.23	+4.70	−476.63	+2.30
	db-MBE(3)	−524.36	−45.43	−481.93	−3.00	−481.58	−2.65	−479.34	−0.41
	supermol.	−478.93		−478.93		−478.93		−478.93	
4	eb-MBE(2)	−526.00	−58.07	−496.46	−28.53	−499.43	−31.50	−474.61	−6.68
	eb-MBE(3)	−438.66	+29.27	−463.01	+4.92	−463.19	+4.74	−469.58	−1.65
	db-MBE(1)	−258.66	+209.27	−437.05	+30.88	−437.63	+30.30	−444.41	+23.52
	db-MBE(2)	−367.89	+100.04	−463.21	+4.72	−464.23	+3.70	−466.48	+1.45
	db-MBE(3)	−555.34	−87.41	−469.89	−1.96	−469.94	−2.01	−467.88	+0.05
	supermol.	−467.93		−467.93		−467.93		−467.93	

Table S12: Interaction energies (PBE0/TZP, in kJ/mol) of six isomers of $OH^-(H_2O)_3$ relative to the lowest-energy isomer calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The relative interaction energies from supermolecular calculations are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

	isomer	$E_{\text{int,rel}}^{\text{super}}$	$E_{\text{int,rel}}^{\text{eb-MBE}(n)}$		$E_{\text{int,rel}}^{\text{db-MBE}(n)}$		
			$n=2$	$n=3$	$n=1$	$n=2$	$n=3$
iso	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	3	8.90	−21.61	13.03	−21.58	−7.22	20.29
	2	9.80	−20.16	14.12	−26.02	−5.05	20.16
	4	11.94	−18.91	16.58	−26.21	−1.43	23.13
	6	15.05	−17.09	20.12	−26.20	2.36	25.82
	5	18.79	−3.15	21.50	−38.87	4.21	29.95
PC	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	3	8.90	−9.72	13.22	−4.65	6.74	9.77
	2	9.80	−7.55	14.05	−5.68	7.53	10.29
	4	11.94	−6.47	16.50	−3.78	10.05	13.07
	6	15.05	−2.53	19.38	−0.22	12.95	16.39
	5	18.79	8.39	22.28	−4.21	17.40	19.29
FDE	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	3	8.90	−10.07	14.49	−3.97	7.97	9.11
	2	9.80	−8.01	15.27	−4.88	8.70	9.69
	4	11.94	−6.34	17.91	−3.33	11.83	12.15
	6	15.05	−2.85	21.16	−0.05	14.77	15.28
	5	18.79	7.02	23.09	−2.48	18.25	18.82
FDE-ft	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	3	8.90	−2.84	11.41	−1.39	8.52	9.33
	2	9.80	−0.38	12.16	−2.36	9.20	9.88
	4	11.94	1.90	14.65	−0.89	12.14	12.34
	6	15.05	5.20	17.74	2.26	15.04	15.45
	5	18.79	11.19	21.05	−0.30	18.82	18.84

Table S13: Interaction energies (PBE0/TZP, in kJ/mol) of four isomers of $OH^-(H_2O)_4$ relative to the lowest-energy isomer calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The relative interaction energies from supermolecular calculations are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

	isomer	$E_{\text{int,rel}}^{\text{super}}$	$E_{\text{int,rel}}^{\text{eb-MBE}(n)}$		$E_{\text{int,rel}}^{\text{db-MBE}(n)}$		
			$n=2$	$n=3$	$n=1$	$n=2$	$n=3$
iso	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	0.50	−4.98	6.18	14.98	11.73	−13.11
	4	7.72	53.17	16.22	82.81	45.33	−21.54
	3	8.58	15.16	17.30	34.67	23.09	−7.59
PC	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	0.50	−6.06	1.45	5.42	−0.60	0.71
	4	7.72	34.64	6.87	40.36	7.01	8.30
	3	8.58	12.23	10.34	19.54	6.45	9.06
FDE	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	0.50	−4.46	1.54	5.29	0.20	0.11
	4	7.72	37.92	6.99	40.05	8.11	7.43
	3	8.58	14.36	11.01	20.10	7.58	8.21
FDE-ft	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	0.50	−1.34	−0.22	5.78	−0.05	0.60
	4	7.72	24.39	6.31	35.56	6.79	8.10
	3	8.58	11.61	8.80	18.85	7.32	8.59

Table S14: Interaction energies (PBE0/TZP, in kJ/mol) of four isomers of $OH^-(H_2O)_5$ relative to the lowest-energy isomer calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The relative interaction energies from supermolecular calculations are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

	isomer	$E_{\text{int,rel}}^{\text{super}}$	$E_{\text{int,rel}}^{\text{eb-MBE}(n)}$		$E_{\text{int,rel}}^{\text{db-MBE}(n)}$		
			$n=2$	$n=3$	$n=1$	$n=2$	$n=3$
iso	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	4.47	−9.00	18.76	8.80	35.70	−25.68
	3	14.96	−19.09	27.65	−30.47	14.55	22.22
	4	25.96	48.72	38.25	50.93	52.61	−8.76
PC	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	4.47	−3.68	6.99	6.53	4.18	4.56
	3	14.96	0.26	22.33	−0.59	15.09	15.68
	4	25.96	34.79	28.33	35.10	24.34	27.72
FDE	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	4.47	−2.68	6.01	7.44	4.84	4.13
	3	14.96	1.21	23.10	0.64	15.85	15.36
	4	25.96	42.48	27.33	37.52	25.85	27.01
FDE-ft	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	4.47	4.41	2.49	8.28	4.42	4.86
	3	14.96	8.13	18.25	1.96	15.91	15.50
	4	25.96	34.10	26.16	35.46	26.06	26.96

S2.2 $\mathbf{H_3O^+(H_2O)}_N$ $(N = 3, 4, 5)$

The following tables S15 to S20 contain additional raw data for the calculations presented in Section 3.4 of the main text.

Table S15: Total interaction energies $E_{\text{int}}^{\text{xx-MBE}(n)}$(PBE0/TZP, in kJ/mol) of four isomers of $H_3O^+(H_2O)_3$ relative to the lowest-energy isomer as calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The total interaction energies from supermolecular calculations as well as the errors in the total interaction energies compared to the supermolecular calculation $\Delta_{\text{int}}^{\text{xx-MBE}(n)}$, are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

		iso		PC		FDE		FDE-ft	
		E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}
1	eb-MBE(2)	−399.39	+4.81	−402.80	+1.40	−402.26	+1.95	−400.94	+3.26
	eb-MBE(3)	−405.91	−1.71	−405.44	−1.24	−405.58	−1.38	−405.11	−0.90
	db-MBE(1)	−126.71	+277.49	−277.20	+127.00	−286.31	+117.89	−298.07	+106.13
	db-MBE(2)	−395.90	+8.30	−401.49	+2.71	−402.42	+1.79	−403.24	+0.96
	db-MBE(3)	−404.20	+0.01	−403.74	+0.46	−403.68	+0.53	−403.72	+0.48
	supermol.	−404.20		−404.20		−404.20		−404.20	
2	eb-MBE(2)	−401.68	+2.61	−403.01	+1.28	−404.03	+0.25	−401.97	+2.31
	eb-MBE(3)	−406.60	−2.31	−406.10	−1.82	−406.18	−1.89	−405.60	−1.31
	db-MBE(1)	−129.47	+274.81	−278.58	+125.71	−288.12	+116.16	−299.55	+104.73
	db-MBE(2)	−395.41	+8.88	−402.27	+2.02	−403.35	+0.93	−404.26	+0.02
	db-MBE(3)	−404.19	+0.10	−404.70	−0.41	−404.69	−0.40	−404.75	−0.46
	supermol.	−404.29		−404.29		−404.29		−404.29	
3	eb-MBE(2)	−400.77	−57.94	−377.76	−34.92	−384.23	−41.39	−367.17	−24.33
	eb-MBE(3)	−340.50	+2.34	−341.27	+1.57	−340.93	+1.91	−341.77	+1.06
	db-MBE(1)	−216.14	+126.70	−298.29	+44.55	−302.28	+40.55	−304.20	+38.64
	db-MBE(2)	−331.38	+11.46	−344.16	−1.32	−344.60	−1.76	−344.71	−1.87
	db-MBE(3)	−344.74	−1.90	−343.04	−0.20	−343.15	−0.32	−342.82	+0.02
	supermol.	−342.84		−342.84		−342.84		−342.84	
4	eb-MBE(2)	−362.08	−20.22	−354.41	−12.55	−359.30	−17.44	−349.47	−7.61
	eb-MBE(3)	−346.80	−4.93	−345.29	−3.43	−345.05	−3.19	−343.76	−1.90
	db-MBE(1)	−187.17	+154.69	−285.42	+56.45	−290.57	+51.29	−294.90	+46.96
	db-MBE(2)	−336.43	+5.43	−341.22	+0.65	−342.27	−0.41	−342.23	−0.37
	db-MBE(3)	−340.40	+1.46	−341.21	+0.65	−340.97	+0.89	−341.13	+0.73
	supermol.	−341.86		−341.86		−341.86		−341.86	

Table S16: Total interaction energies $E_{\text{int}}^{\text{xx-MBE}(n)}$(PBE0/TZP, in kJ/mol) of four isomers of $H_3O^+(H_2O)_4$ relative to the lowest-energy isomer as calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The total interaction energies from supermolecular calculations as well as the errors in the total interaction energies compared to the supermolecular calculation $\Delta_{\text{int}}^{\text{xx-MBE}(n)}$, are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

		iso		PC		FDE		FDE-ft	
		E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}
1	eb-MBE(2)	−405.59	+10.88	−415.38	+1.10	−413.91	+2.57	−413.03	+3.44
	eb-MBE(3)	−422.03	−5.56	−420.24	−3.77	−420.58	−4.10	−418.98	−2.50
	db-MBE(1)	−192.62	+223.85	−333.85	+82.63	−339.35	+77.12	−346.76	+69.72
	db-MBE(2)	−413.40	+3.07	−414.56	+1.91	−415.50	+0.97	−415.84	+0.63
	db-MBE(3)	−414.65	+1.82	−415.66	+0.81	−415.55	+0.93	−415.75	+0.72
	supermol.	−416.47		−416.47		−416.47		−416.47	
2	eb-MBE(2)	−457.05	−47.28	−438.71	−28.93	−444.04	−34.26	−428.55	−18.78
	eb-MBE(3)	−407.55	+2.23	−408.78	+1.00	−408.17	+1.61	−409.02	+0.76
	db-MBE(1)	−237.94	+171.84	−348.52	+61.25	−354.22	+55.56	−359.03	+50.75
	db-MBE(2)	−395.14	+14.63	−410.03	−0.25	−411.27	−1.50	−411.56	−1.79
	db-MBE(3)	−412.96	−3.18	−409.85	−0.08	−409.87	−0.09	−409.50	+0.28
	supermol.	−409.78		−409.78		−409.78		−409.78	
3	eb-MBE(2)	−462.50	−54.91	−439.58	−32.00	−449.16	−41.57	−429.71	−22.13
	eb-MBE(3)	−409.71	−2.12	−409.02	−1.44	−408.28	−0.69	−408.21	−0.62
	db-MBE(1)	−266.01	+141.57	−363.64	+43.94	−368.00	+39.58	−370.66	+36.93
	db-MBE(2)	−395.23	+12.36	−408.47	−0.89	−409.70	−2.12	−409.75	−2.17
	db-MBE(3)	−408.39	−0.80	−408.03	−0.44	−407.93	−0.34	−407.68	−0.09
	supermol.	−407.59		−407.59		−407.59		−407.59	
4	eb-MBE(2)	−451.96	−43.33	−435.69	−27.06	−441.80	−33.18	−427.10	−18.47
	eb-MBE(3)	−409.49	−0.86	−409.26	−0.63	−409.05	−0.43	−409.14	−0.52
	db-MBE(1)	−245.27	+163.36	−353.43	+55.19	−358.16	+50.46	−361.64	+46.99
	db-MBE(2)	−397.27	+11.36	−409.31	−0.68	−410.08	−1.46	−410.47	−1.84
	db-MBE(3)	−409.86	−1.23	−409.13	−0.50	−409.20	−0.57	−408.91	−0.28
	supermol.	−408.63		−408.63		−408.63		−408.63	

Table S17: Total interaction energies $E_{\text{int}}^{\text{xx-MBE}(n)}$(PBE0/TZP, in kJ/mol) of four isomers of $H_3O^+(H_2O)_5$ relative to the lowest-energy isomer as calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The total interaction energies from supermolecular calculations as well as the errors in the total interaction energies compared to the supermolecular calculation $\Delta_{\text{int}}^{\text{xx-MBE}(n)}$, are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

		iso		PC		FDE		FDE-ft	
		E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}	E_{int}	Δ_{int}
1	eb-MBE(2)	−547.88	−24.92	−538.84	−15.89	−542.46	−19.51	−530.54	−7.59
	eb-MBE(3)	−526.39	−3.44	−525.47	−2.52	−525.82	−2.87	−525.15	−2.20
	db-MBE(1)	−233.38	+289.57	−399.49	+123.46	−409.93	+113.02	−421.35	+101.60
	db-MBE(2)	−502.25	+20.70	−520.97	+1.98	−522.52	+0.43	−523.93	−0.98
	db-MBE(3)	−526.57	−3.62	−523.34	−0.39	−523.37	−0.42	−523.09	−0.13
	supermol.	−522.95		−522.95		−522.95		−522.95	
2	eb-MBE(2)	−511.21	−42.73	−496.93	−28.46	−504.10	−35.62	−486.33	−17.85
	eb-MBE(3)	−473.81	−5.34	−471.66	−3.19	−471.38	−2.90	−470.42	−1.95
	db-MBE(1)	−290.74	+177.74	−413.28	+55.20	−418.60	+49.88	−422.99	+45.48
	db-MBE(2)	−455.63	+12.85	−469.42	−0.95	−470.91	−2.43	−471.18	−2.70
	db-MBE(3)	−468.53	−0.06	−469.15	−0.68	−469.01	−0.53	−468.75	−0.27
	supermol.	−468.48		−468.48		−468.48		−468.48	
3	eb-MBE(2)	−504.07	−35.34	−491.60	−22.88	−499.77	−31.04	−484.49	−15.76
	eb-MBE(3)	−471.93	−3.20	−470.71	−1.98	−470.00	−1.27	−469.62	−0.89
	db-MBE(1)	−292.57	+176.16	−417.42	+51.31	−422.23	+46.49	−426.63	+42.10
	db-MBE(2)	−458.85	+9.88	−469.77	−1.04	−471.33	−2.60	−471.46	−2.73
	db-MBE(3)	−468.45	+0.28	−469.70	−0.97	−469.49	−0.76	−469.30	−0.57
	supermol.	−468.73		−468.73		−468.73		−468.73	
4	eb-MBE(2)	−497.15	−33.06	−487.08	−22.99	−492.18	−28.09	−478.66	−14.57
	eb-MBE(3)	−468.28	−4.18	−466.72	−2.63	−466.74	−2.65	−465.99	−1.90
	db-MBE(1)	−278.79	+185.30	−405.39	+58.71	−410.30	+53.79	−414.46	+49.64
	db-MBE(2)	−453.45	+10.65	−464.13	−0.04	−465.11	−1.01	−465.60	−1.51
	db-MBE(3)	−464.17	−0.07	−464.40	−0.30	−464.42	−0.32	−464.19	−0.10
	supermol.	−464.09		−464.09		−464.09		−464.09	

Table S18: Interaction energies (PBE0/TZP, in kJ/mol) of four isomers of $H_3O^+(H_2O)_3$ relative to the lowest-energy isomer calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The relative interaction energies from supermolecular calculations are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

	isomer	$E_{\text{int,rel}}^{\text{super}}$	$E_{\text{int,rel}}^{\text{eb-MBE}(n)}$		$E_{\text{int,rel}}^{\text{db-MBE}(n)}$		
			$n=2$	$n=3$	$n=1$	$n=2$	$n=3$
iso	**2**	−0.08	−2.29	−0.68	−2.76	0.49	0.01
	1	0.00	0.00	0.00	0.00	0.00	0.00
	3	61.36	−1.39	65.41	−89.43	64.52	59.46
	4	62.34	37.31	59.12	−60.46	59.47	63.80
PC	**2**	−0.08	−0.21	−0.67	−1.38	−0.77	−0.95
	1	0.00	0.00	0.00	0.00	0.00	0.00
	3	61.36	25.04	64.17	−21.08	57.33	60.71
	4	62.34	48.39	60.15	−8.21	60.27	62.53
FDE	**2**	−0.08	−1.78	−0.60	−1.81	−0.94	−1.01
	1	0.00	0.00	0.00	0.00	0.00	0.00
	3	61.36	18.03	64.66	−15.97	57.82	60.52
	4	62.34	42.96	60.53	−4.26	60.15	62.71
FDE-ft	**2**	−0.08	−1.03	−0.49	−1.48	−1.02	−1.03
	1	0.00	0.00	0.00	0.00	0.00	0.00
	3	61.36	33.77	63.33	−6.13	58.53	60.90
	4	62.34	51.47	61.34	3.17	61.01	62.59

Table S19: Interaction energies (PBE0/TZP, in kJ/mol) of four isomers of $H_3O^+(H_2O)_4$ relative to the lowest-energy isomer calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The relative interaction energies from supermolecular calculations are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

	isomer	$E_{\text{int,rel}}^{\text{super}}$	$E_{\text{int,rel}}^{\text{eb-MBE}(n)}$		$E_{\text{int,rel}}^{\text{db-MBE}(n)}$		
			$n=2$	$n=3$	$n=1$	$n=2$	$n=3$
iso	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	6.70	−51.46	14.48	−45.31	18.26	1.70
	4	7.85	−46.37	12.55	−52.65	16.13	4.79
	3	8.89	−56.91	12.32	−73.39	18.17	6.26
PC	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	6.70	−23.33	11.47	−14.68	4.53	5.81
	4	7.85	−20.31	10.98	−19.59	5.25	6.53
	3	8.89	−24.21	11.22	−29.80	6.09	7.64
FDE	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	6.70	−30.13	12.41	−14.87	4.23	5.68
	4	7.85	−27.90	11.52	−18.81	5.42	6.35
	3	8.89	−35.25	12.30	−28.65	5.80	7.62
FDE-ft	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	2	6.70	−15.52	9.96	−12.27	4.28	6.25
	4	7.85	−14.07	9.83	−14.88	5.37	6.84
	3	8.89	−16.68	10.77	−23.90	6.09	8.07

Table S20: Interaction energies (PBE0/TZP, in kJ/mol) of four isomers of $H_3O^+(H_2O)_5$ relative to the lowest-energy isomer calculated with the energy-based MBE [eb-MBE(n), $n = 2, 3$] as well as the density-based MBE [db-MBE(n), $n = 1, 2, 3$]. The relative interaction energies from supermolecular calculations are given as reference. Included are results from both the isolated MBEs ("iso") and the embedded MBEs using point-charge embedding ("PC") as well as using frozen-density embedding with the unrelaxed frozen densities of the isolated fragments ("FDE") and a relaxed frozen density obtained using freeze-and-thaw cycles ("FDE-ft"). All values are given in kJ/mol.

	isomer	$E_{\text{int,rel}}^{\text{super}}$	$E_{\text{int,rel}}^{\text{eb-MBE}(n)}$		$E_{\text{int,rel}}^{\text{db-MBE}(n)}$		
			$n=2$	$n=3$	$n=1$	$n=2$	$n=3$
iso	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	3	54.22	43.81	54.46	−59.19	43.41	58.13
	2	54.47	36.66	52.57	−57.36	46.63	58.04
	4	58.86	50.72	58.11	−45.41	48.81	62.41
PC	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	3	54.22	47.24	54.76	−17.92	51.20	53.64
	2	54.47	41.91	53.81	−13.79	51.55	54.19
	4	58.86	51.76	58.75	−5.90	56.84	58.94
FDE	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	3	54.22	42.69	55.82	−12.30	51.19	53.88
	2	54.47	38.36	54.44	−8.66	51.61	54.36
	4	58.86	50.27	59.08	−0.37	57.41	58.96
FDE-ft	**1**	0.00	0.00	0.00	0.00	0.00	0.00
	3	54.22	46.05	55.53	−5.27	52.47	53.79
	2	54.47	44.21	54.73	−1.64	52.75	54.34
	4	58.86	51.88	59.16	6.90	58.32	58.89