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

Table 1. Calibration of the method. Vibrational frequencies (cm^{-1})

HgClOH

	MP2/ AVTZ	B3PW91/ AVTZ	B3LYP/ AVTZ	M06/ AVTZ	B971/ AVTZ	PBE0/ AVTZ
1	137.9	115.0	110.6	110.6	110.9	118.8
2	141.8	128.7	124.5	135.8	125.1	130.6
3	381.8	369.8	358.7	369.9	365.1	375.8
4	635.5	589.2	572.3	571.1	592.2	600.3
5	907.4	956.5	950.3	947.0	955.5	955.5
6	3823.1	3837.6	3805.5	3880.8	3839.1	3868.7

$HgClOH\text{-}H_2O$

	MP2/ AVTZ	B3PW91/ AVTZ	B3LYP/ AVTZ	M06/ AVTZ	B971/ AVTZ	PBE0/ AVTZ
1	76.1	62.3	34.6	81.8	53.0	65.3
2	109.6	105.8	66.3	87.1	67.3	77.8
3	133.8	115.0	115.8	135.7	120.5	122.1
4	152.0	138.5	134.4	153.8	136.2	134.8
5	198.2	175.6	195.8	178.4	193.2	203.0
6	216.1	241.0	203.3	230.0	203.2	215.7
7	344.8	319.8	313.9	326.2	304.8	317.5
8	377.6	364.4	359.2	368.8	364.8	373.8
9	541.5	560.2	527.0	577.1	543.6	547.0
10	609.5	590.6	577.1	650.1	593.6	594.7
11	871.4	931.7	928.1	912.9	933.9	931.2
12	1614.2	1619.0	1619.1	1609.9	1628.8	1623.8
13	3733.1	3707.3	3719.1	3753.5	3755.5	3762.2
14	3847.6	3852.3	3827.5	3900.6	3859.3	3890.9
15	3911.0	3896.7	3871.6	3939.1	3904.7	3928.3

$HgClOH\text{-}(H_2O)_2$

	MP2/ AVTZ	B3PW91/ AVTZ	B3LYP/ AVTZ	M06/ AVTZ	B971/ AVTZ	PBE0/ AVTZ
1	27.4	39.3	38.6	26.4	37.0	39.2
2	66.2	69.7	68.5	67.0	67.9	69.8
3	106.2	107.6	108.1	106.5	108.0	109.2
4	132.0	139.2	137.9	132.8	138.9	139.6
5	183.8	157.6	158.2	153.4	155.3	166.3
6	205.9	188.1	186.0	167.4	182.6	191.3
7	245.5	245.8	240.8	215.2	236.9	252.5
8	254.8	250.3	246.9	252.9	246.7	256.9
9	263.3	280.6	266.6	269.9	263.2	280.8
10	270.7	316.8	291.4	278.1	291.3	310.7
11	371.8	362.5	352.7	364.5	359.4	367.7
12	431.4	416.4	406.2	378.1	395.9	419.9
13	463.0	495.2	480.9	466.6	471.8	497.9
14	591.0	566.9	556.4	564.8	569.0	573.2
15	746.2	754.8	729.8	709.4	719.2	761.1
16	854.3	899.5	868.8	855.8	862.1	902.5
17	924.3	966.6	954.6	944.5	957.1	969.1
18	1627.5	1633.4	1628.8	1606.3	1636.5	1636.0
19	1662.7	1654.9	1652.1	1635.0	1657.5	1659.7
20	3414.5	3382.6	3406.5	3505.7	3461.3	3400.8
21	3494.7	3469.9	3483.2	3584.7	3533.2	3489.4
22	3850.6	3861.3	3832.6	3904.5	3863.9	3893.1
23	3887.4	3888.6	3857.6	3925.5	3890.2	3915.2
24	3896.8	3890.9	3860.1	3934.2	3892.6	3918.4

Table 2. B3PW91/6-311G(d,p) HgClOH-$(H_2O)_n$ Gibbs water binding free energies at 298K, incremental free binding energies (kcal/mol) and number of direct Hg-O(water) interactions.

N	Direct Hg-O_w interactions[a]	ΔG^o_{298}	Incremental energy
1	1	-0.40	-0.40
2	1	-3.80	-3.40
3	1	-5.75	-1.94
4	2	-6.48	-0.73
5	2	-5.66	+0.81
6	2	-7.78	-2.12
7	3	-9.28	-1.50
8	3	-11.65	-2.37
12	3	-15.08	-3.42
16	3	-20.40	-5.33
20	3	-22.02	-1.62
21	3	-25.34	-3.32
22	3	-28.83	-3.49
23	3	-30.90	-2.07
24	3	-31.42	-0.52

ΔG^o_{298}=[G^o(system with *n* water molecules)-*n*$G^o(H_2O)$-G^o(HgClOH)],
[a]A water molecule is considered to be directly interacting with Hg if its distance to mercury is less than 2.8 Å.

Table 3. B3PW91/6-311G(d,p) optimized geometrical parameters HgClOH-$(H_2O)_n$ (n=1 up 24). O_w label corresponds to the water oxygen atoms directly linked to Hg. Distances in Å, angles in degrees. PCM optimized values in parentheses, see the text.

n	Hg-Cl	Hg-O(H)	Cl-Hg-O(H)	Hg-O_w	Hg-O_w	Hg-O_w
0	2.34 (2.45)	1.99 (2.05)	176.6 (178.2)			
1	2.34 (2.46)	2.02 (2.08)	178.8 (177.0)	2.70 (3.89)		
2	2.35 (2.49)	2.04 (2.10)	173.2 (174.4)	2.53 (3.56)	3.77 (3.62)	
3	2.36 (2.44)	2.04 (2.10)	170.8 (173.0)	2.47 (3.49)	4.18 (4.15)	4.41 (4.73)
4	2.37	2.07	170.1	2.53	2.75	3.70
5	2.40	2.08	165.9	2.50	2.61	3.65
6	2.44 (2.46)	2.07 (2.08)	159.3 (172.8)	2.45 (3.81)	2.61 (3.95)	3.75 (3.96)
7	2.42	2.12	164.4	2.51	2.65	2.79
8	2.42	2.09	161.0	2.49	2.65	3.35
12	2.46 (2.52)	2.10 (2.15)	154.2 (148.8)	2.49 (2.94)	2.51 (3.09)	3.40 (3.61)
16	2.52	2.18	159.51	2.41	2.53	2.62
20	2.50	2.13	171.7	2.47	2.55	2.62
21	2.49	2.13	168.6	2.46	2.50	2.74
22	2.49	2.13	170.2	2.47	2.52	2.71
23	2.52	2.16	169.7	2.41	2.48	2.63
24	2.46	2.10	170.0	2.45	2.61	2.65

Table 4. B3PW91/6-311G** vibrational frequencies (cm^{-1}) for HgClOH-H_2O complex *in vacuo* and with the PCM scheme with water as continuous solvent.

Mode	B3PW91/6-311G**	B3PW91-PCM/6-311G**
1	79	45
2	111	68
3	128	107
4	174	128
5	207	253
6	257	270
7	354	284
8	363	444
9	546	463
10	651	797
11	927	893
12	1627	1668
13	3717	3395
14	3872	3844
15	3907	3888