SUPPLEMENTARY MATERIAL

for

Exploring the next step in micro-solvation of CO in water: Infrared spectra and structural calculations of $(H_2O)_4$- CO and $(D_2O)_4$- CO

by

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Table A-1. Observed and calculated transitions of $(D_2O)_4$ – CO (in cm^{-1})

Note: when two or more transitions are assigned to the same observed line (equal Obs), then this line was fitted to their intensity weighted blend, indicated by "Blend" in the Obs column.

J′	Ka′	Kc′	J″	Ka″	Kc″	Obs	Calc	Obs – Calc
11	11	0	12	12	1	2142.8741	2142.8747	-0.0005
11	11	1	12	12	0	2142.8741	2142.8747	-0.0005
						Blend	2142.8747	-0.0005
11	9	3	12	10	2	2142.9050	2142.9053	-0.0003
11	9	2	12	10	3	2142.9050	2142.9053	-0.0003
						Blend	2142.9053	-0.0003
11	7	5	12	8	4	2142.9363	2142.9358	0.0004
11	7	4	12	8	5	2142.9363	2142.9358	0.0004
						Blend	2142.9358	0.0004
10	10	1	11	11	0	2142.9793	2142.9790	0.0002
12	1	12	13	0	13	2142.9793	2142.9809	-0.0016
10	10	0	11	11	1	2142.9793	2142.9790	0.0002
12	0	12	13	1	13	2142.9793	2142.9809	-0.0016
						Blend	2142.9796	-0.0003
10	9	2	11	10	1	2142.9947	2142.9944	0.0003
10	9	1	11	10	2	2142.9947	2142.9944	0.0003
						Blend	2142.9944	0.0003
10	8	2	11	9	3	2143.0100	2143.0096	0.0003
10	8	3	11	9	2	2143.0100	2143.0096	0.0003
						Blend	2143.0096	0.0003
10	7	4	11	8	3	2143.0250	2143.0248	0.0002
10	7	3	11	8	4	2143.0250	2143.0248	0.0002
						Blend	2143.0248	0.0002
10	6	4	11	7	5	2143.0406	2143.0400	0.0006
10	6	5	11	7	4	2143.0406	2143.0400	0.0006
11	2	9	12	3	10	2143.0406	2143.0425	-0.0018
						Blend	2143.0405	0.0002
10	5	5	11	6	6	2143.0560	2143.0554	0.0006
10	5	6	11	6	5	2143.0560	2143.0551	0.0009
11	1	10	12	2	11	2143.0560	2143.0577	-0.0016
11	3	9	12	2	10	2143.0560	2143.0555	0.0005
						Blend	2143.0559	0.0001
9	9	1	10	10	0	2143.0833	2143.0835	-0.0002
9	9	0	10	10	1	2143.0833	2143.0835	-0.0002
						Blend	2143.0835	-0.0002
9	8	2	10	9	1	2143.0992	2143.0988	0.0004
9	8	1	10	9	2	2143.0992	2143.0988	0.0004
						Blend	2143.0988	0.0004

9	7	2	10	8	3	2143.1141	2143.1140	0.0001
9	7	3	10	8	2	2143.1141	2143.1140	0.0001
						Blend	2143.1140	0.0001
9	6	3	10	7	4	2143.1289	2143.1292	-0.0003
9	6	4	10	7	3	2143.1289	2143.1292	-0.0003
						Blend	2143.1292	-0.0003
10	2	9	11	1	10	2143.1450	2143.1462	-0.0012
9	5	4	10	6	5	2143.1450	2143.1444	0.0006
9	5	5	10	6	4	2143.1450	2143.1443	0.0007
						Blend	2143.1448	0.0002
8	8	1	9	9	0	2143.1883	2143.1881	0.0002
8	8	0	9	9	1	2143.1883	2143.1881	0.0002
						Blend	2143.1881	0.0002
8	7	1	9	8	2	2143.2035	2143.2033	0.0002
8	7	2	9	8	1	2143.2035	2143.2033	0.0002
						Blend	2143.2033	0.0002
8	6	2	9	7	3	2143.2185	2143.2185	0.0000
8	6	3	9	7	2	2143.2185	2143.2185	0.0000
						Blend	2143.2185	0.0000
8	5	3	9	6	4	2143.2337	2143.2336	0.0001
8	5	4	9	6	3	2143.2337	2143.2336	0.0001
9	2	8	10	1	9	2143.2337	2143.2342	-0.0004
						Blend	2143.2337	0.0000
9	1	9	10	0	10	2143.2408	2143.2411	-0.0003
9	0	9	10	1	10	2143.2408	2143.2409	-0.0002
						Blend	2143.2410	-0.0003
8	4	4	9	5	5	2143.2492	2143.2492	0.0000
8	4	5	9	5	4	2143.2492	2143.2484	0.0008
						Blend	2143.2488	0.0004
7	7	1	8	8	0	2143.2929	2143.2928	0.0001
8	2	6	9	3	7	2143.2929	2143.2946	-0.0017
7	7	0	8	8	1	2143.2929	2143.2928	0.0001
						Blend	2143.2930	-0.0002
7	6	2	8	7	1	2143.3078	2143.3079	-0.0001
7	6	1	8	7	2	2143.3078	2143.3079	-0.0001
						Blend	2143.3079	-0.0001
7	5	2	8	6	3	2143.3229	2143.3230	-0.0001
7	5	3	8	6	2	2143.3229	2143.3230	-0.0001
8	2	7	9	1	8	2143.3229	2143.3229	0.0000
						Blend	2143.3230	-0.0001
8	1	8	9	0	9	2143.3281	2143.3284	-0.0003
8	0	8	9	1	9	2143.3281	2143.3280	0.0000
						Blend	2143.3282	-0.0001
7	4	3	8	5	4	2143.3382	2143.3383	0.0000
7	4	4	8	5	3	2143.3382	2143.3380	0.0002
						Blend	2143.3382	0.0001
6	6	1	7	7	0	2143.3976	2143.3975	0.0001
6	6	0	7	7	1	2143.3976	2143.3975	0.0001
						Blend	2143.3975	0.0001
7	4	4	8	4	5	2143.4021	2143.4038	-0.0017
7	4	3	8	4	4	2143.4021	2143.4032	-0.0011
7	5	3	8	5	4	2143.4021	2143.4039	-0.0017
7	5	2	8	5	3	2143.4021	2143.4038	-0.0017
7	6	2	8	6	3	2143.4021	2143.4038	-0.0017
7	6	1	8	6	2	2143.4021	2143.4038	-0.0017
						Blend	2143.4037	-0.0016
6	5	2	7	6	1	2143.4129	2143.4126	0.0003

7	2	6	8	1	7	2143.4129	2143.4126	0.0003
6	5	1	7	6	2	2143.4129	2143.4126	0.0003
						Blend	2143.4126	0.0003
7	0	7	8	1	8	2143.4152	2143.4153	0.0000
7	1	7	8	0	8	2143.4152	2143.4159	-0.0007
						Blend	2143.4156	-0.0003
6	4	2	7	5	3	2143.4276	2143.4277	-0.0001
6	4	3	7	5	2	2143.4276	2143.4276	0.0000
						Blend	2143.4277	-0.0001
6	3	4	7	4	3	2143.4426	2143.4420	0.0007
6	3	3	7	4	4	2143.4426	2143.4437	-0.0011
						Blend	2143.4428	-0.0002
6	1	5	7	2	6	2143.4880	2143.4876	0.0004
6	3	4	7	3	5	2143.4951	2143.4941	0.0010
6	4	3	7	4	4	2143.4951	2143.4936	0.0015
6	1	5	7	1	6	2143.4951	2143.4938	0.0013
6	5	1	7	5	2	2143.4951	2143.4937	0.0014
6	4	2	7	4	3	2143.4951	2143.4934	0.0017
6	5	2	7	5	3	2143.4951	2143.4937	0.0014
						Blend	2143.4938	0.0014
6	1	6	7	0	7	2143.5026	2143.5038	-0.0012
6	2	5	7	1	6	2143.5026	2143.5033	-0.0007
5	5	0	6	6	1	2143.5026	2143.5022	0.0003
5	5	1	6	6	0	2143.5026	2143.5022	0.0003
6	0	6	7	1	7	2143.5026	2143.5025	0.0001
						Blend	2143.5027	-0.0001
5	4	1	6	5	2	2143.5172	2143.5173	-0.0001
5	4	2	6	5	1	2143.5172	2143.5173	-0.0001
						Blend	2143.5173	-0.0001
5	3	2	6	4	3	2143.5315	2143.5326	-0.0011
5	3	3	6	4	2	2143.5315	2143.5320	-0.0005
						Blend	2143.5323	-0.0008
5	2	4	6	3	3	2143.5430	2143.5434	-0.0004
5	2	3	6	3	4	2143.5514	2143.5512	0.0002
4	4	0	5	5	1	2143.6070	2143.6070	0.0000
4	4	1	5	5	0	2143.6070	2143.6070	0.0000
						Blend	2143.6070	0.0000
4	3	1	5	4	2	2143.6218	2143.6221	-0.0003
4	3	2	5	4	1	2143.6218	2143.6219	-0.0002
						Blend	2143.6220	-0.0002
0	4-		1	5:		2143.6769	2143.6768	0.0001
1	4-		0	5:		2143.6808	2143.6808	0.0000
3	3	0	4	4	1	2143.7118	2143.7118	0.0000
3	3	1	4	4	0	2143.7118	2143.7118	0.0000
						Blend	2143.7118	0.0000
3	2	1	4	3	2	2143.7266	2143.7273	-0.0007
3	2	2	4	3	1	2143.7266	2143.7262	0.0005
						Blend	2143.7268	-0.0001
3	1	3	4	2	2	2143.7347	2143.7344	0.0003
3	1	2	4	3	3	2143.7460	2143.7462	-0.0002
3	0	3	4	1	4	2143.7638	2143.7638	0.0001
3	1	3	4	0	4	2143.7702	2143.7702	0.0000
2	2	0	3	3	1	2143.8165	2143.8167	-0.0002
2	2	1	3	3	0	2143.8165	2143.8164	0.0000

						Blend	2143.8166	-0.0001
2	1	2	3	2	1	2143.8285	2143.8283	0.0002
2	1	1	3	2	2	2143.8340	2143.8337	0.0003
2	1	2	3	0	3	2143.8602	2143.8602	0.0000
1	1	0	2	2	1	2143.9213	2143.9221	-0.0008
1	1	1	2	2	0	2143.9213	2143.9204	0.0009
						Blend	2143.9213	0.0000
1	0	1	2	1	2	2143.9386	2143.9385	0.0001
1	1	1	2	0	2	2143.9506	2143.9506	0.0000
0	0	0	1	1	1	2144.0274	2144.0268	0.0006
7	5	2	7	6	1	2144.0430	2144.0426	0.0004
6	5	2	6	6	1	2144.0430	2144.0421	0.0009
9	5	4	9	6	3	2144.0430	2144.0440	-0.0010
9	5	5	9	6	4	2144.0430	2144.0439	-0.0009
10	5	6	10	6	5	2144.0430	2144.0449	-0.0019
8	5	4	8	6	3	2144.0430	2144.0432	-0.0002
6	5	1	6	6	0	2144.0430	2144.0421	0.0009
7	5	3	7	6	2	2144.0430	2144.0426	0.0004
8	5	3	8	6	2	2144.0430	2144.0432	-0.0002
						Blend	2144.0430	0.0000
5	4	2	5	5	1	2144.0580	2144.0569	0.0011
8	4	4	8	5	3	2144.0580	2144.0591	-0.0011
6	4	2	6	5	1	2144.0580	2144.0574	0.0006
6	4	3	6	5	2	2144.0580	2144.0573	0.0007
7	4	3	7	5	2	2144.0580	2144.0581	-0.0001
7	4	4	7	5	3	2144.0580	2144.0578	0.0002
5	4	1	5	5	0	2144.0580	2144.0570	0.0010
8	4	5	8	5	4	2144.0580	2144.0585	-0.0005
9	4	6	9	5	5	2144.0580	2144.0591	-0.0011
10	4	7	10	5	6	2144.0580	2144.0598	-0.0018
						Blend	2144.0579	0.0001
5	3	2	5	4	1	2144.0722	2144.0725	-0.0003
5	3	3	5	4	2	2144.0722	2144.0720	0.0002
6	3	3	6	4	2	2144.0722	2144.0736	-0.0014
6	3	4	6	4	3	2144.0722	2144.0722	0.0000
7	3	5	7	4	4	2144.0722	2144.0722	-0.0001
4	3	1	4	4	0	2144.0722	2144.0719	0.0003
9	3	7	9	4	6	2144.0722	2144.0714	0.0008
4	3	2	4	4	1	2144.0722	2144.0717	0.0005
8	3	6	8	4	5	2144.0722	2144.0720	0.0002
						Blend	2144.0723	-0.0001
10	2	8	10	3	7	2144.0941	2144.0936	0.0005
9	2	7	9	3	6	2144.0941	2144.0956	-0.0016
7	2	5	7	3	4	2144.0941	2144.0949	-0.0008
6	0	6	6	1	5	2144.0941	2144.0942	-0.0001
8	2	6	8	3	5	2144.0941	2144.0960	-0.0019
8	1	7	8	2	6	2144.0941	2144.0948	-0.0007
4	1	4	4	2	3	2144.0941	2144.0939	0.0002
						Blend	2144.0947	-0.0006
2	1	1	2	2	0	2144.1045	2144.1031	0.0015
5	1	4	5	2	3	2144.1045	2144.1047	-0.0002
3	1	2	3	2	1	2144.1045	2144.1043	0.0002
4	1	3	4	2	2	2144.1045	2144.1050	-0.0005
6	1	5	6	2	4	2144.1045	2144.1030	0.0015
						Blend	2144.1042	0.0003

3	0	3	3	1	2	2144.1106	2144.1108	-0.0002
2	0	2	2	1	1	2144.1140	2144.1136	0.0004
1	0	1	1	1	0	2144.1140	2144.1152	-0.0013
						Blend	2144.1143	-0.0003
1	1	0	1	0	1	2144.1327	2144.1315	0.0011
2	1	1	2	0	2	2144.1327	2144.1333	-0.0006
						Blend	2144.1325	0.0001
3	1	2	3	0	3	2144.1362	2144.1363	0.0000
5	2	3	5	1	4	2144.1422	2144.1423	-0.0001
4	2	2	4	1	3	2144.1422	2144.1418	0.0004
3	2	1	3	1	2	2144.1422	2144.1424	-0.0002
2	2	0	2	1	1	2144.1422	2144.1436	-0.0014
						Blend	2144.1424	-0.0002
6	1	5	6	0	6	2144.1542	2144.1546	-0.0005
4	2	3	4	1	4	2144.1542	2144.1538	0.0004
7	3	4	7	2	5	2144.1542	2144.1524	0.0018
						Blend	2144.1536	0.0006
4	4	1	4	3	2	2144.1752	2144.1749	0.0003
6	4	2	6	3	3	2144.1752	2144.1736	0.0016
6	4	3	6	3	4	2144.1752	2144.1752	0.0000
7	4	4	7	3	5	2144.1752	2144.1757	-0.0005
8	4	5	8	3	6	2144.1752	2144.1767	-0.0015
8	2	7	8	1	8	2144.1752	2144.1759	-0.0007
5	4	2	5	3	3	2144.1752	2144.1750	0.0002
4	4	0	4	3	1	2144.1752	2144.1748	0.0005
5	4	1	5	3	2	2144.1752	2144.1744	0.0008
						Blend	2144.1750	0.0003
6	5	2	6	4	3	2144.1897	2144.1896	0.0001
7	5	2	7	4	3	2144.1897	2144.1894	0.0003
9	5	4	9	4	5	2144.1897	2144.1881	0.0016
5	5	1	5	4	2	2144.1897	2144.1896	0.0001
7	5	3	7	4	4	2144.1897	2144.1897	0.0001
9	5	5	9	4	6	2144.1897	2144.1899	-0.0002
6	5	1	6	4	2	2144.1897	2144.1896	0.0002
5	5	0	5	4	1	2144.1897	2144.1896	0.0002
8	5	3	8	4	4	2144.1897	2144.1890	0.0008
8	5	4	8	4	5	2144.1897	2144.1897	0.0000
						Blend	2144.1895	0.0003
9	6	3	9	5	4	2144.2046	2144.2045	0.0000
9	6	4	9	5	5	2144.2046	2144.2047	-0.0001
6	6	0	6	5	1	2144.2046	2144.2043	0.0003
7	6	2	7	5	3	2144.2046	2144.2044	0.0001
7	6	1	7	5	2	2144.2046	2144.2044	0.0002
10	6	5	10	5	6	2144.2046	2144.2048	-0.0002
10	6	4	10	5	5	2144.2046	2144.2045	0.0001
6	6	1	6	5	2	2144.2046	2144.2043	0.0003
8	6	2	8	5	3	2144.2046	2144.2045	0.0001
8	6	3	8	5	4	2144.2046	2144.2046	0.0000
						Blend	2144.2045	0.0001
1	1	1	0	0	0	2144.2196	2144.2200	-0.0003
8	8	1	8	7	2	2144.2345	2144.2338	0.0007
8	8	0	8	7	1	2144.2345	2144.2338	0.0007
10	8	2	10	7	3	2144.2345	2144.2345	-0.0001
11	8	4	11	7	5	2144.2345	2144.2350	-0.0005

11	8	3	11	7	4	2144.2345	2144.2350	-0.0005
10	8	3	10	7	4	2144.2345	2144.2345	-0.0001
9	8	2	9	7	3	2144.2345	2144.2342	0.0003
9	8	1	9	7	2	2144.2345	2144.2342	0.0003
12	8	5	12	7	6	2144.2345	2144.2355	-0.0010
12	8	4	12	7	5	2144.2345	2144.2355	-0.0010
						Blend	2144.2344	0.0001
2	1	2	2	0	1	2144.3084	2144.3084	-0.0001
2	2	0	1	1	1	2144.3253	2144.3263	-0.0010
2	2	1	1	1	0	2144.3253	2144.3246	0.0007
						Blend	2144.3255	-0.0001
3	1	3	2	0	2	2144.3956	2144.3963	-0.0007
3	2	2	2	1	1	2144.4132	2144.4131	0.0001
3	2	1	2	1	2	2144.4183	2144.4186	-0.0003
3	3	1	2	2	0	2144.4301	2144.4300	0.0002
3	3	0	2	2	1	2144.4301	2144.4302	-0.0001
						Blend	2144.4301	0.0000
4	0	4	3	1	3	2144.4776	2144.4775	0.0001
4	1	4	3	0	3	2144.4838	2144.4840	-0.0001
4	2	3	3	1	2	2144.5007	2144.5008	-0.0001
4	4	0	3	3	1	2144.5349	2144.5347	0.0001
4	4	1	3	3	0	2144.5349	2144.5347	0.0002
						Blend	2144.5347	0.0002
5	0	5	4	1	4	2144.5685	2144.5677	0.0009
5	1	5	4	0	4	2144.5715	2144.5717	-0.0002
5	2	4	4	1	3	2144.5878	2144.5879	-0.0001
5	2	3	4	1	4	2144.6083	2144.6090	-0.0007
5	3	3	4	2	2	2144.6083	2144.6082	0.0001
						Blend	2144.6084	-0.0001
5	3	2	4	2	3	2144.6114	2144.6118	-0.0004
5	4	2	4	3	1	2144.6249	2144.6247	0.0002
5	4	1	4	3	2	2144.6249	2144.6249	0.0001
						Blend	2144.6248	0.0001
5	5	0	4	4	1	2144.6397	2144.6394	0.0003
5	5	1	4	4	0	2144.6397	2144.6394	0.0003
						Blend	2144.6394	0.0003
6	4	3	5	3	2	2144.7148	2144.7145	0.0003
6	4	2	5	3	3	2144.7148	2144.7151	-0.0003
						Blend	2144.7148	0.0000
6	5	1	5	4	2	2144.7293	2144.7295	-0.0002
6	5	2	5	4	1	2144.7293	2144.7295	-0.0002
						Blend	2144.7295	-0.0002
6	6	1	5	5	0	2144.7452	2144.7440	0.0012
7	1	6	6	2	5	2144.7452	2144.7453	-0.0001
6	6	0	5	5	1	2144.7452	2144.7440	0.0012
						Blend	2144.7442	0.0010
8	5	4	7	4	3	2144.9091	2144.9095	-0.0004
8	5	3	7	4	4	2144.9091	2144.9098	-0.0007
						Blend	2144.9097	-0.0005
8	7	1	7	6	2	2144.9386	2144.9388	-0.0002
8	7	2	7	6	1	2144.9386	2144.9388	-0.0002
						Blend	2144.9388	-0.0002

8	8	0	7	7	1	2144.9536	2144.9532	0.0004
8	8	1	7	7	0	2144.9536	2144.9532	0.0004
						Blend	2144.9532	0.0004
9	5	4	8	4	5	2144.9990	2145.0002	-0.0011
9	5	5	8	4	4	2144.9990	2144.9993	-0.0002
						Blend	2144.9997	-0.0007
10	2	9	9	1	8	2145.0238	2145.0227	0.0010
9	7	2	8	6	3	2145.0287	2145.0291	-0.0004
9	7	3	8	6	2	2145.0287	2145.0291	-0.0004
						Blend	2145.0291	-0.0004
9	8	1	8	7	2	2145.0434	2145.0435	-0.0001
9	8	2	8	7	1	2145.0434	2145.0435	-0.0001
						Blend	2145.0435	-0.0001
9	9	0	8	8	1	2145.0577	2145.0578	-0.0001
9	9	1	8	8	0	2145.0577	2145.0578	-0.0001
						Blend	2145.0578	-0.0001
10	7	3	9	6	4	2145.1183	2145.1194	-0.0012
10	7	4	9	6	3	2145.1183	2145.1194	-0.0012
						Blend	2145.1194	-0.0012
10	8	3	9	7	2	2145.1340	2145.1339	0.0001
10	8	2	9	7	3	2145.1340	2145.1339	0.0001
						Blend	2145.1339	0.0001
10	9	1	9	8	2	2145.1485	2145.1482	0.0003
10	9	2	9	8	1	2145.1485	2145.1482	0.0003
						Blend	2145.1482	0.0003
10	10	0	9	9	1	2145.1630	2145.1625	0.0005
10	10	1	9	9	0	2145.1630	2145.1625	0.0005
						Blend	2145.1625	0.0005
4	4	0	4	4	1	2144.1236	2144.1232	0.0004
4	4	1	4	4	0	2144.1236	2144.1232	0.0004
3	3	0	3	3	1	2144.1236	2144.1233	0.0003
3	3	1	3	3	0	2144.1236	2144.1233	0.0003
5	5	0	5	5	1	2144.1236	2144.1231	0.0004
5	5	1	5	5	0	2144.1236	2144.1231	0.0004
2	2	0	2	2	1	2144.1236	2144.1236	0.0000
2	2	1	2	2	0	2144.1236	2144.1231	0.0005
6	6	0	6	6	1	2144.1236	2144.1231	0.0005
6	6	1	6	6	0	2144.1236	2144.1231	0.0005
						Blend	2144.1232	0.0004

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Table A-2. Optimized geometries (in Angstroms) and **corresponding equilibrium rotational constants values (in GHz)** of $(D_2O)_4$-CO at the B2PLYP-D3BJ/m-aug-cc-pVTZ-dH level of theory for the isomers (Geo#1 to Geo#**6**) listed in Table 2 of the paper

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*************************************************************************
Geo #1
O   -1.63818497439361      0.78450170942506      0.18960086176552
D   -1.50077952480934     -0.18487578517861      0.13122586703526
D   -2.31648849249492      0.99277465605407     -0.45717830896441
D   0.03322838716825      1.40736064272081      0.00017222379479
O   1.00038359052084      1.52964301957340     -0.09110263875635
D   1.27839619778856      2.03408087273902      0.68006882573315
O   -0.88640812198796     -1.84020612319305     -0.06049363825853
D   -0.95161454321030     -2.47425762242800      0.65746484270175
D   0.07365595997946     -1.69865532286994     -0.20859623116477
O   1.71649487002351     -1.07604717598203     -0.40014507086530
D   2.18517164319315     -1.19187145009491     -1.23001773032812
D   1.58432898749369     -0.10693959496095     -0.29743052360147
C   2.03096243282128      3.15235233252727      2.57502456749823
O   2.39085357790738      3.67213982166783      3.51140695341023
Ae = 2.4118 Be = 0.6750 Ce = 0.5935

Geo #2
C   2.07920086798628     -0.94066517791645     -0.26824242708418
O   2.39877377685638      0.14401698203279     -0.30344035962624
O   -1.08396258848902     -1.82181426502063      0.01832253867644
D   -0.86181772425673     -1.29736360836817      0.81593053764601
D   -0.34382990676734     -2.42369033907017     -0.09901564707327
D   -1.22761942785676     -0.56472718299936     -1.21187160827771
O   -1.21589624882164      0.25961878691517     -1.74579780050961
D   -2.05233690433454      0.28533147042113     -2.21637033382419
O   -0.34686391635747     -0.04939243200276      1.98397419436813
D   -0.84449681041238      0.12738238280454      2.78575093817275
D   -0.36989747108693      0.78018232607894      1.45938655267184
O   -0.48125068485028      2.02527784514654      0.21268429407082
D   0.32745987423737      2.47162572577517     -0.05036223487114
D   -0.76998283584692      1.51236048620327     -0.57191164433965
Ae = 1.6150 Be = 1.4106 Ce = 1.3495

Geo #3
O   -1.09427793076395     -1.37463264140794     -0.07740767954757
D   -0.11501163024293     -1.34824590145076     -0.00036735790340
D   -1.28873977016773     -2.00276115535048     -0.77694105282506
D   -1.51846878670777      0.33237839659393     -0.22381883500269
O   -1.53961241957901      1.31291340096083     -0.26660025013403
D   -2.16059872807359      1.59401539559541      0.40945903831902
O   1.59136457104923     -0.92319355472328      0.09597511055045
D   2.01781999854355     -1.01206762404931      0.95340428506090
D   1.56404546931568      0.04282998283659     -0.06052903610185
O   1.14970830983481      1.78970783860352     -0.15027637031070
D   1.42704389470911      2.33785599798906     -0.88824548112409
D   0.16957655764241      1.75844167537366     -0.19075560647815
C   2.41920579790614      0.75684318168858      2.80631043584739
O   2.37794467653405      1.73591499734018      3.36979279964977
Ae = 2.1414 Be = 0.9691 Ce = 0.8321
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Geo #4

C	-0.81282455532802	1.08694824817435	-0.10833960170486
O	-0.63470663276061	2.15075454737177	0.22774499851589
D	-3.66980960813687	-3.54214757458237	-2.88366799548683
O	-3.56052647542068	-3.49935316511830	-3.85812468343655
D	-1.10630435692184	-1.10948832444421	-0.84878875457685
D	-3.72038453042464	-4.38948122958478	-4.17983455573924
O	-1.21677848495386	-2.01635972320159	-1.15091583272966
D	-1.08233083985023	-1.99428887992688	-2.12032724905445
D	-2.73306794483583	-2.91018873181538	-0.98865038277053
O	-3.54567977800030	-3.44530682717978	-1.12427414088320
D	-4.23616110242163	-3.01315367859915	-0.61650494727120
D	-0.49667389570461	-2.57494659548701	-4.39727566926432
O	-1.18147035496535	-2.11328012747393	-3.90790425498815
D	-2.00328144027549	-2.62970792813270	-4.04313691061003

Ae = 2.6026 Be = 0.6481 Ce = 0.5608

Geo #5

C	0.61600205723008	0.34648486542185	0.82612381266079
O	0.68504498969410	0.39949845080459	-0.30066948924175
D	3.08023915299415	4.21687048250424	0.56366288720586
O	2.52145339992812	3.56861508494717	0.99810237529945
D	1.72587098605214	3.83260113686250	2.58217212245426
D	3.08346713279005	2.78005234904443	1.15108411706341
O	1.36567802043265	3.72828675104648	3.48638359269082
D	0.50879731695016	4.16050004295871	3.48765800258116
D	1.65631060691908	1.97085046075025	3.81587565051302
O	1.94877440323878	1.03805106580930	3.77440103837564
D	1.22541862337503	0.57321395380927	3.34211563634646
D	3.19224132532807	1.07977453194426	2.53875105019540
O	3.74029249672157	1.22882509451035	1.73491457367197
D	4.65040948834597	1.07637570958656	1.99942460018346

Ae = 1.7945 Be = 1.1852 Ce = 1.1172

Geo #6

C	0.38728651384714	-0.43204772625366	0.36164328614003
O	-0.10567725568781	-1.33599907114627	-0.11012566584850
D	2.83132231123195	-4.99181218409773	-2.13862653580643
O	2.93448124822849	-4.21590966198574	-2.69422139995951
D	3.90609019277404	-2.82643688605698	-2.19368179390267
D	2.03631131529543	-3.83666308237103	-2.80346852168266
O	4.26422750836148	-1.94272243934857	-1.96273614076466
D	5.12446106796964	-1.88651223430990	-2.38485186641943
D	2.90406330373792	-0.84728133700420	-2.30483044329626
O	2.02224074031153	-0.45422270067376	-2.47790097999440
D	2.16079950277413	0.23347617054481	-3.13332510898920
D	1.01506109484251	-1.88330030449210	-2.85436637063242
O	0.61507988349100	-2.76957603554025	-2.97418843876057
D	-0.09574743717750	-2.81099252726457	-2.32932000008328

Ae = 2.0854 Be = 1.0987 Ce = 0.9237

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COMPUTATIONAL METHODOLOGY

For computing the CBS limit of the binding energies, many single point energy calculations were performed on the optimized geometries (obtained at B2PLYP-D3BJ level of theory) in conjunction with the aug-cc-pV*n*Z basis sets with *n* = T, Q and 5 were employed.[1,2] Besides, some calculations were done using the cc-pCVTZ basis set.[3]

We followed this composite scheme, which is based on separate extrapolation of the CBS limit for the Hartree-Fock (HF-SCF) energy, E_{CBS}(HF-SCF) and for the correlation energy computed at MP2 level of theory, $E_{CBS}(corr)$. For computing the E_{CBS}(HF-SCF) we used the expression proposed by Fenner[4], while for $E_{CBS}(corr)$ we employed the following inverse cubic function

$$E_{CBS}(corr) = N^3 E_N^{corr} -.$$

The CBS limit was then obtained as:

$$E_{CBS} = E_{CBS}(HF - SCF) + E_{CBS}(corr)$$

The effects due to higher-order electron correlation past the MP2 level of theory were accounted for as the difference between the CCSD(T) and MP2 single point energies, calculated using the aug-cc-pVTZ basis set.

$$\Delta_{MP2}^{CCSD(T)} = E_{CCSD(T)} - E_{MP2}$$

For computing the core-valence (CV) corrections, we performed two calculations at MP2 level and using the cc-pCVTZ basis set, correlating all the electrons, E_{ae-MP2}, and within the frozen-core approximation,E_{fc-MP2}.

$$\delta_{MP2}^{CV} = E_{ae-MP2} - E_{fc-MP2}$$

The CBS-1 limit was therefore given as

$$E_{CBS-1} = E_{CBS}(HF - SCF) + E_{CBS}(corr) + \Delta_{MP2}^{CCSD(T)} + \delta_{MP2}^{CV}$$

By using the data thus obtained (and with the inclusion of zero-point vibrational correction), the most stable isomer of $(D_2O)_4$-CO among the different structures optimized was therefore identified.

The DFT-D3BJ calculations were carried out using the ORCA suite of programs,[5] single point energy calculations were carried out using the Gaussian suite of quantum chemical programs.[6] For the geometry optimizations the *TightOpt* criteria, as implemented in the Orca software, were employed.

QTAIM analysis was carried out on the most stable structures of each cluster of the series $(D_2O)_n$-CO by using the corresponding B2PLYP-D3BJ wavefunctions in conjunction with the Multiwfn 3.7 code.[7]

SAPT analysis was performed at the SAPT(0)/jun-cc-pVDZ level of theory and using the Psi4 program.[8] As done in other studies,[9] the SAPT calculations on clusters of the series $(D_2O)_n$-CO (n = 2, 3 and 4) considered the water dimer, trimer and tetramer units as one single moiety, so that only the interactions between the water dimer/trimer/tetramer (as a whole) and CO can be taken into account.

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