SUPPORTING INFORMATION:

Accurate water properties from an efficient ab-initio method

Subrata Jana,*,† Lucian A. Constantin,*,‡ and Prasanjit Samal*,†

†*School of Physical Sciences, National Institute of Science Education and Research, HBNI, Bhubaneswar 752050, India*

‡*Center for Biomolecular Nanotechnologies @UNILE, Istituto Italiano di Tecnologia, Via Barsanti, I-73010 Arnesano, Italy*

E-mail: subrata.jana@niser.ac.in; lucian.constantin@iit.it; psamal@niser.ac.in

List of Tables

Table S1: Binding energies per monomer (in meV/H_2O) of four water hexamer obtained from different functionals. The reference MP2, CCSD(T) and DMC reference values are taken from Refs.[1] The MP2 optimized geometries[1] are considered for single-point energy calculations. The jun-cc-pV(T+d)Z basis of Papajak/Truhlar[2] are used. The most stable structure is in bold style. Only TM and revTM functionals are considered.

Methods	Prism	Cage	Book	Cycle
MP2	**332.3**	331.9	330.2	324.1
DMC	**331.9**	329.5	327.8	320.1
CCSD(T)	**347.6**	345.5	338.9	332.5
TM	**355.8**	337.1	324.6	310.8
E_{TM}-E_{MP2}	23.5	5.2	-5.6	-13.3
E_{TM}-E_{DMC}	23.9	7.6	-3.2	-9.3
E_{TM}-$E_{CCSD(T)}$	8.2	-8.4	-14.3	-21.7
revTM	**334.8**	326.3	322.5	314.4
E_{revTM}-E_{MP2}	2.5	-5.6	-7.7	-9.7
E_{revTM}-E_{DMC}	2.9	-3.2	-5.3	-5.7
E_{revTM}-$E_{CCSD(T)}$	-12.8	-19.2	-16.4	-18.1

Table S2: Relative binding energies (with respect to the prism structure) for different low-lying energy isomer of the water hexamer. The reference values are from high-level wave-function calculations (CCSD(T)/CBS of Ref.[3]). The MP2/aug-cc-pVTZ level geometries,[4] and the jun-cc-pV(T+d)Z basis of Papajak/Truhlar[2] are used. All results are in kcal/mol. Best calculated values are in bold style. Only TM and revTM functionals are considered.

Methods	Cage	Book1	Book2	Bag	Chair	Boat1	Boat2	ME	MAE
Ref.	0.25	0.72	1.02	1.62	1.80	2.79	2.85	–	–
TM	0.67	2.39	2.66	3.15	4.30	5.28	5.37	1.82	1.82
revTM	**0.27**	**0.79**	**1.06**	**1.76**	**1.91**	**2.92**	**3.04**	0.10	**0.10**

Table S3: Details of the harmonic vibrational frequencies of the water monomer using different methods. All values are in cm^{-1} and calculated with an aug-cc-pVTZ basis set. The CCSD(T)/ha5Z reference values are taken from.[5]

	CCSD(T)	PBE	SCAN	TM	revTM
ν_1	1650	1592	1641	1628	1626
ν_2	3835	3697	3805	3704	3707
ν_1	3945	3802	3911	3804	3808

Table S4: Details of the harmonic vibrational frequencies of the water dimer using different methods. All values are in cm^{-1} and calculated with an aug-cc-pVTZ basis set. The CCSD(T)/ha5Z reference values are taken from.[5]

	CCSD(T)	PBE	SCAN	TM	revTM
ν_1	125	128	73	111	120
ν_2	142	161	135	131	139
ν_3	148	1637	146	135	146
ν_4	185	195	198	187	188
ν_5	351	387	380	353	363
ν_6	614	646	670	599	615
ν_7	1650	1592	1645	1627	1625
ν_8	1670	1609	1655	1640	1639
ν_9	3754	3527	3649	3585	3575
ν_{10}	3830	3690	3782	3700	3703
ν_{11}	3917	3770	3870	3775	3778
ν_{12}	3936	3791	3886	3797	3801

Table S5: Details of the harmonic vibrational frequencies of the water trimer using different methods. All values are in cm^{-1} and calculated with an aug-cc-pVTZ basis set. The CCSD(T)/haTZ reference values are taken from.[6]

	CCSD(T)	PBE	SCAN	TM	revTM
ν_1	125	128	73	111	120
ν_2	142	161	135	131	139
ν_3	148	1637	146	135	146
ν_4	185	195	198	187	188
ν_5	351	387	380	353	363
ν_6	614	646	670	599	615
ν_7	1650	1592	1645	1627	1625
ν_8	1670	1609	1655	1640	1639
ν_9	3754	3527	3649	3585	3575
ν_{10}	3830	3690	3782	3700	3703
ν_{11}	3917	3770	3870	3775	3778
ν_{12}	3936	3791	3886	3797	3801

Table S6: Details of the harmonic vibrational frequencies of the water tetramer using different methods. All values are in cm^{-1} and calculated with an aug-cc-pVTZ basis set. The CCSD(T)/haTZ reference values are taken from.[6]

	CCSD(T)	PBE	SCAN	TM	revTM
ν_1	49	55	63	46	48
ν_2	79	96	85	72	81
ν_3	208	218	217	206	218
ν_4	211	248	261	215	218
ν_5	237	263	261	241	249
ν_6	237	263	272	241	249
ν_7	253	283	289	258	264
ν_8	253	289	295	258	264
ν_9	256	289	305	262	267
ν_{10}	288	326	305	282	296
ν_{11}	400	445	472	389	404
ν_{12}	428	485	474	420	439
ν_{13}	443	494	491	432	449
ν_{14}	443	494	491	432	449
ν_{15}	736	803	798	712	735
ν_{16}	802	896	888	795	819
ν_{17}	802	896	888	795	819
ν_{18}	967	1069	1065	968	991
ν_{19}	1666	1599	1646	1629	1630
ν_{20}	1678	1617	1663	1643	1644
ν_{21}	1678	1617	1663	1643	1644
ν_{22}	1703	1649	1696	1669	1671
ν_{23}	3456	3035	3143	3243	3215
ν_{24}	3541	3177	3285	3342	3319
ν_{25}	3541	3177	3285	3342	3319
ν_{26}	3576	3230	3340	3381	3360
ν_{27}	3882	3757	3851	3765	3767
ν_{28}	3882	3758	3852	3765	3768
ν_{29}	3882	3758	3852	3765	3768
ν_{30}	3882	3758	3852	3765	3768

Table S7: Details of the harmonic vibrational frequencies of the water pentamer using different methods. All values are in cm^{-1} and calculated with an aug-cc-pVTZ basis set. The CCSD(T):MP2/haQZ values are taken from ref.[6]

	CCSD(T)	PBE	SCAN	TM	revTM
ν_1	18	26	45	21	23
ν_2	40	45	50	39	41
ν_3	61	76	69	59	66
ν_4	64	79	72	62	68
ν_5	178	189	193	183	186
ν_6	179	231	243	191	202
ν_7	190	239	260	201	212
ν_8	218	256	266	230	238
ν_9	231	259	279	240	244
ν_{10}	235	271	304	243	248
ν_{11}	255	304	328	265	275
ν_{12}	284	328	335	292	303
ν_{13}	293	331	339	301	307
ν_{14}	296	334	366	304	310
ν_{15}	400	456	449	389	408
ν_{16}	417	472	487	409	426
ν_{17}	438	500	507	431	450
ν_{18}	452	511	520	442	461
ν_{19}	509	567	551	495	515
ν_{20}	695	778	771	681	705
ν_{21}	764	849	842	747	772
ν_{22}	833	938	933	832	855
ν_{23}	852	957	956	846	871
ν_{24}	950	1062	1058	950	975
ν_{25}	1669	1599	1647	1630	1630
ν_{26}	1678	1613	1661	1642	1642
ν_{27}	1688	1625	1669	1650	1651
ν_{28}	1704	1649	1694	1671	1673
ν_{29}	1711	1659	1704	1677	1680
ν_{30}	3441	2967	3083	3211	3180
ν_{31}	3514	3099	3214	3298	3272
ν_{32}	3522	3108	3222	3305	3279
ν_{33}	3562	3174	3288	3353	3329
ν_{34}	3569	3184	3306	3358	3336
ν_{35}	3898	3758	3857	3764	3767
ν_{36}	3900	3759	3857	3766	3768
ν_{37}	3902	3760	3862	3767	3770
ν_{38}	3903	3762	3865	3767	3770
ν_{39}	3904	3764	3868	3769	3772

Table S8: Details of the harmonic vibrational frequencies of the water hexamer (book) using different methods. All values are in cm^{-1} and calculated with an aug-cc-pVTZ basis set. The CCSD(T):MP2/haQZ values are taken from ref.[6]

	CCSD(T)	PBE	SCAN	TM	revTM
		$(H_2O)_6$-book			
ν_1	27	32	17	25	27
ν_2	37	45	38	37	40
ν_3	53	62	59	51	55
ν_4	67	81	73	62	69
ν_5	85	103	93	79	88
ν_6	156	143	163	163	159
ν_7	179	189	193	185	188
ν_8	189	212	198	194	203
ν_9	195	227	216	202	208
ν_{10}	225	250	244	230	237
ν_{11}	233	275	255	240	249
ν_{12}	245	279	279	255	263
ν_{13}	250	289	287	260	265
ν_{14}	271	302	300	266	279
ν_{15}	282	319	328	293	299
ν_{16}	291	329	336	298	304
ν_{17}	302	345	370	310	317
ν_{18}	377	422	405	363	381
ν_{19}	393	444	434	384	404
ν_{20}	432	482	472	416	434
ν_{21}	443	505	499	435	455
ν_{22}	467	528	524	460	478
ν_{23}	533	585	573	519	541
ν_{24}	601	649	651	594	610
ν_{25}	708	778	765	692	715
ν_{26}	735	818	812	726	755
ν_{27}	811	904	893	807	833
ν_{28}	829	927	925	822	849
ν_{29}	874	982	987	869	895
ν_{30}	989	1106	1117	997	1020
ν_{31}	1661	1592	1634	1623	1624
ν_{32}	1673	1607	1651	1636	1637
ν_{33}	1675	1613	1655	1640	1642
ν_{34}	1691	1631	1672	1656	1657
ν_{35}	1702	1644	1687	1664	1667
ν_{36}	1730	1676	1717	1692	1696
ν_{37}	3386	2873	2954	3133	3102
ν_{38}	3455	3003	3091	3221	3193
ν_{39}	3503	3067	3159	3270	3246
ν_{40}	3587	3228	3359	3381	3356
ν_{41}	3637	3314	3441	3444	3424
ν_{42}	3651	3332	3462	3458	3438
ν_{43}	3768	3544	3670	3592	3583
ν_{44}	3893	3758	3848	3763	3767
ν_{45}	3898	3759	3851	3764	3767
ν_{46}	3900	3759	3853	3765	3767
ν_{47}	3900	3759	3855	3765	3768
ν_{48}	3903	3763	3859	3768	3772

Table S9: Details of the harmonic vibrational frequencies of the water hexamer (cage) using different methods. All values are in cm^{-1} and calculated with an aug-cc-pVTZ basis set. The CCSD(T):MP2/haQZ values are taken from ref.[6]

	CCSD(T)	PBE	SCAN	TM	revTM
		$(H_2O)_6$-cage			
ν_1	42	51	40	31	42
ν_2	56	66	58	50	58
ν_3	74	85	79	68	76
ν_4	100	101	107	94	102
ν_5	127	115	123	135	128
ν_6	153	135	154	164	157
ν_7	185	184	201	197	195
ν_8	194	218	210	208	218
ν_9	210	239	225	210	225
ν_{10}	223	241	240	218	229
ν_{11}	231	252	250	232	236
ν_{12}	234	259	254	240	245
ν_{13}	242	264	270	249	253
ν_{14}	253	303	291	263	279
ν_{15}	281	311	303	286	296
ν_{16}	293	324	322	293	300
ν_{17}	383	419	380	361	384
ν_{18}	395	441	406	381	401
ν_{19}	437	472	474	424	445
ν_{20}	453	496	486	439	457
ν_{21}	467	517	511	448	474
ν_{22}	534	567	575	523	536
ν_{23}	553	614	610	544	572
ν_{24}	620	667	660	614	634
ν_{25}	682	735	743	678	699
ν_{26}	717	784	778	706	727
ν_{27}	774	858	871	775	798
ν_{28}	790	868	878	786	808
ν_{29}	852	929	941	856	874
ν_{30}	975	1079	1090	977	1000
ν_{31}	1666	1602	1641	1625	1629
ν_{32}	1673	1617	1654	1640	1643
ν_{33}	1684	1626	1671	1644	1648
ν_{34}	1698	1639	1679	1660	1663
ν_{35}	1707	1651	1691	1671	1675
ν_{36}	1722	1666	1711	1685	1688
ν_{37}	3324	2829	2912	3057	3032
ν_{38}	3517	3128	3229	3284	3264
ν_{39}	3556	3197	3307	3347	3318
ν_{40}	3604	3256	3378	3404	3381
ν_{41}	3650	3314	3452	3446	3422
ν_{42}	3718	3499	3625	3552	3542
ν_{43}	3757	3538	3654	3579	3571
ν_{44}	3792	3574	3685	3611	3603
ν_{45}	3895	3755	3838	3759	3763
ν_{46}	3896	3758	3848	3767	3767
ν_{47}	3899	3763	3850	3769	3770
ν_{48}	3908	3765	3870	3772	3774

Table S10: Details of the harmonic vibrational frequencies of the water hexamer (prism) using different methods. All values are in cm^{-1} and calculated with an aug-cc-pVTZ basis set. The CCSD(T):MP2/haQZ values are taken from ref.[6]

	CCSD(T)	PBE	SCAN	TM	revTM
		$(H_2O)_6$-prism			
ν_1	61	44	61	57	64
ν_2	70	66	69	65	72
ν_3	74	75	77	67	77
ν_4	98	83	83	113	98
ν_5	112	92	130	128	112
ν_6	149	140	156	157	152
ν_7	173	171	186	183	180
ν_8	178	178	195	187	182
ν_9	212	220	231	198	211
ν_{10}	217	235	248	223	223
ν_{11}	238	253	262	246	249
ν_{12}	246	255	266	252	252
ν_{13}	275	279	277	267	269
ν_{14}	284	298	296	278	285
ν_{15}	287	317	325	292	297
ν_{16}	357	386	393	356	369
ν_{17}	367	406	408	364	378
ν_{18}	420	460	457	408	426
ν_{19}	427	463	466	417	433
ν_{20}	462	500	493	453	469
ν_{21}	491	522	523	483	501
ν_{22}	530	562	570	516	531
ν_{23}	547	590	592	542	558
ν_{24}	612	660	650	599	621
ν_{25}	638	691	703	639	654
ν_{26}	675	730	724	664	687
ν_{27}	711	775	784	700	723
ν_{28}	823	890	894	812	831
ν_{29}	868	923	940	859	878
ν_{30}	1001	1095	1110	992	1014
ν_{31}	1663	1599	1642	1625	1626
ν_{32}	1674	1611	1654	1634	1637
ν_{33}	1683	1614	1657	1636	1639
ν_{34}	1699	1641	1681	1661	1666
ν_{35}	1716	1655	1709	1684	1683
ν_{36}	1733	1679	1723	1698	1699
ν_{37}	3301	2804	2872	3049	3019
ν_{38}	3509	3175	3263	3292	3271
ν_{39}	3601	3222	3369	3387	3372
ν_{40}	3620	3315	3434	3423	3405
ν_{41}	3717	3490	3601	3554	3545
ν_{42}	3735	3499	3641	3571	3561
ν_{43}	3784	3561	3676	3613	3602
ν_{44}	3799	3615	3728	3630	3622
ν_{45}	3821	3648	3769	3653	3648
ν_{46}	3898	3761	3858	3766	3769
ν_{47}	3899	3762	3859	3768	3770
ν_{48}	3901	3764	3861	3769	3772

Table S11: Details of the harmonic vibrational frequencies of the water hexamer (ring) using different methods. All values are in cm^{-1} and calculated with an aug-cc-pVTZ basis set. The CCSD(T):MP2/haQZ values are taken from ref.[6]

	CCSD(T)	PBE	SCAN	TM	revTM
		$(H_2O)_6$-ring			
ν_1	28	31	23	28	29
ν_2	28	34	32	30	29
ν_3	45	55	50	45	49
ν_4	45	55	52	45	49
ν_5	50	56	53	50	50
ν_6	82	98	93	83	88
ν_7	156	165	166	158	162
ν_8	172	213	227	178	187
ν_9	195	233	236	201	215
ν_{10}	195	235	238	210	215
ν_{11}	211	235	239	216	221
ν_{12}	211	241	270	216	221
ν_{13}	254	293	302	263	274
ν_{14}	254	299	332	268	275
ν_{15}	282	326	334	291	302
ν_{16}	292	331	334	299	306
ν_{17}	292	331	346	299	306
ν_{18}	323	367	369	331	340
ν_{19}	407	461	441	395	414
ν_{20}	426	484	456	414	434
ν_{21}	426	485	466	414	435
ν_{22}	441	507	488	432	450
ν_{23}	450	514	494	442	461
ν_{24}	450	514	504	442	461
ν_{25}	757	838	836	736	763
ν_{26}	776	865	861	758	786
ν_{27}	776	867	866	760	787
ν_{28}	867	972	969	859	888
ν_{29}	867	974	974	861	888
ν_{30}	941	1053	1053	938	966
ν_{31}	1665	1589	1635	1625	1625
ν_{32}	1676	1605	1649	1638	1638
ν_{33}	1676	1605	1652	1638	1638
ν_{34}	1701	1642	1686	1669	1670
ν_{35}	1701	1643	1689	1669	1670
ν_{36}	1716	1664	1709	1686	1688
ν_{37}	3440	2956	3073	3214	3178
ν_{38}	3505	3074	3179	3290	3260
ν_{39}	3505	3074	3200	3290	3260
ν_{40}	3554	3156	3265	3347	3321
ν_{41}	3554	3157	3284	3348	3321
ν_{42}	3570	3182	3302	3366	3340
ν_{43}	3901	3761	3864	3767	3770
ν_{44}	3901	3761	3864	3767	3770
ν_{45}	3901	3761	3864	3767	3770
ν_{46}	3901	3762	3865	3767	3770
ν_{47}	3901	3762	3870	3767	3770
ν_{48}	3901	3762	3870	3767	3770

Table S12: Gas phase dipole moments (in Debye) of the water clusters as calculated by different methods. The available experimental references and MP2 values are also given. The dipole moment of the tetramer is zero by symmetry.

Basis	Methods	Monomer	Dimer	Trimer	Tetramer	Pentamer
	Expt.[7]	1.855	2.643	–	0.000	–
	MP2[8]	1.859	2.638	1.080	0.000	0.989
aug-cc-pVTZ	PBE	1.8044	2.5107	1.1662	0.0001	1.0486
	SCAN	1.8431	2.4751	1.1463	0.0001	1.0535
	TM	1.7940	2.4083	1.1121	0.0001	1.0221
	revTM	1.7985	2.4536	1.1424	0.0001	1.0319
6-311++G(3df,3pd)	PBE	1.8515	2.5167	1.2013	0.0001	1.0803
	SCAN	1.8866	2.4397	1.1848	0.0001	1.0858
	TM	1.8380	2.4236	1.1524	0.0001	1.0581
	revTM	1.8461	2.4536	1.1781	0.0001	1.0592

References

(1) Santra, B.; Michaelides, A.; Fuchs, M.; Tkatchenko, A.; Filippi, C.; Scheffler, M. On the accuracy of density-functional theory exchange-correlation functionals for H bonds in small water clusters. II. The water hexamer and van der Waals interactions. *J. Chem. Phys.* **2008**, *129*, 194111.

(2) Papajak, E.; Truhlar, D. G. Convergent Partially Augmented Basis Sets for Post-Hartree-Fock Calculations of Molecular Properties and Reaction Barrier Heights. *J. Chem. Theory Comput.* **2011**, *7*, 10–18, PMID: 26606214.

(3) Bates, D. M.; Tschumper, G. S. CCSD(T) Complete Basis Set Limit Relative Energies for Low-Lying Water Hexamer Structures. *J. Phys. Chem. A* **2009**, *113*, 3555–3559.

(4) Chen, Y.; Li, H. Intermolecular Interaction in Water Hexamer. *J. Phys. Chem. A* **2010**, *114*, 11719–11724.

(5) Howard, J. C.; Gray, J. L.; Hardwick, A. J.; Nguyen, L. T.; Tschumper, G. S. Getting down to the Fundamentals of Hydrogen Bonding: Anharmonic Vibrational Frequencies of $(HF)_2$ and $(H_2O)_2$ from Ab Initio Electronic Structure Computations. *J. Chem. Theory Comput.* **2014**, *10*, 5426–5435.

(6) Howard, J. C.; Tschumper, G. S. Benchmark Structures and Harmonic Vibrational Frequencies Near the CCSD(T) Complete Basis Set Limit for Small Water Clusters: $(H_2O)_n$ = 2, 3, 4, 5, 6. *J. Chem. Theory Comput.* **2015**, *11*, 2126–2136.

(7) Gregory, J. K.; Clary, D. C.; Liu, K.; Brown, M. G.; Saykally, R. J. The Water Dipole Moment in Water Clusters. *Science* **1997**, *275*, 814–817.

(8) Kolb, B.; Thonhauser, T. van der Waals density functional study of energetic, structural, and vibrational properties of small water clusters and ice I_h. *Phys. Rev. B* **2011**, *84*, 045116.