Title: Quantum Signature in Anisotropic Singularities of Dihedral Energy in Hydrogen Bond Breaking of Water Dimer

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Table. 1. Optimized geometry of water dimer in gas phase (Atoms are defined in Fig.1)

Theory level and basis	O1-O4 distance (Å)	Dimeric H-bond distance of O4H2 (Å)	H2-O1-H3 angle (degree)	H5-O4-H6 angle (degree)	O1-H2-O4 angle (degree)
HF/STO-3G	2.771	1.762	100.78	83.84	175.75
HF/3-21G	2.796	1.825	107.87	108.74	175.84
HF/6-31G*	2.991	2.068	104.62	106.24	163.32
HF/6-311G*	2.911	1.969	107.44	108.04	177.32
HF/6-311+G**	3.000	2.054	106.08	106.67	178.03
B3LYP/6-31G*	2.861	1.920	104.06	103.88	161.03
B3LYP/ 6-311+G(2df,2p)	2.921	1.960	105.58	105.66	171.29
ωB97X-D/6-31G*	2.862	1.915	104.13	104.52	163.92
MP2/cc-pVDZ	2.909	1.944	101.78	102.40	172.95
MP2/aug-cc-pVDZ	2.916	1.951	104.28	104.20	171.12

Table. 2. Optimized geometry of water dimer in water medium (Atoms are defined in Fig.1)

Theory level and basis	O1-O4 distance(Å)	O4-H2 dimeric H-bond distance (Å)	H2-O1-H3 angle (degree)	H5-O4-H6 angle (degree)	O1-H2-O4 angle (degree)
HF/STO-3G	2.675	1.685	100.91	100.49	178.00
HF/3-21G	2.728	1.747	107.94	107.20	178.52
HF/6-31G*					
HF/6-311G*	2.873	1.927	107.05	106.77	178.73
HF/6-311+G**	2.947	1.999	105.78	105.79	178.29
B3LYP/6-31G*	2.861	1.920	104.06	103.88	161.03
B3LYP/ 6-311+G(2df,2p)	2.921	1.960	105.58	105.66	171.29

wB97X-D/6-31G*	2.862	1.915	104.13	104.52	163.92
MP2/aug-cc-pVDZ	2.916	1.951	104.28	104.20	171.12

Table. 3. Optimized geometry of water dimer in polar medium (Atoms are defined in Fig.1)

Theory level and basis	O1-O4 distance(Å)	O4-H2 dimeric H-bond distance (Å)	H2-O1-H3 Angle (degree)	H5-O4-H6 angle (degree)	O1-H2-O4 angle (degree)
HF/STO-3G	2.675	1.685	100.78	83.84	175.75
HF/3-21G	2.796	1.825	107.87	108.74	175.84
HF/6-31G*	2.991	2.068	104.62	106.24	163.32
HF/6-311G*	2.911	1.969	107.44	108.04	177.32
HF/6-311+G**	3.000	2.054	106.08	106.67	178.03
B3LYP/6-31G*	2.861	1.920	104.06	103.88	161.03
B3LYP/ 6-311+G(2df,2p)	2.921	1.960	105.58	105.66	171.29
ωB97X-D/6-31G*	2.862	1.915	104.13	104.52	163.92
MP2/aug-cc-pVDZ	2.916	1.951	104.28	104.20	171.12

Table. 4 Estimate of Water Dimer Dissociation Energy Global Minima Depth in Energy Plots

Theory level and basis set	Dimer binding energy from O4-H2 co-ordinates (kcal/mol)	Dimer binding energy from O1-O4 co-ordinates (kcal/mol)
HF/STO-3G	-5.85	-5.89
HF/6-31G*	-5.51	-5.72
HF/6-311G*	-6.33	-6.64
MP2/cc-pVDZ	-5.16	-5.57
MP2/aug-cc-PVDZ	-5.12	-5.23
B3YLP/6-31G*	-7.49	-7.53
ωB97X-D/6-31G*	-7.45	-7.49

Table. 5 IR frequencies and their Assignment to Water Dimer Vibrational Modes

Technique and applied basis set	Out-of-plane vibration mode, cm^(-1)	Bending modes, cm^(-1)	Symmetric stretch modes, cm^(-1)	Asymmetric stretch modes, cm^(-1)
HF/3-21G	832	1793, 1854	3728	3908,3962
ωB97X-D/6-31G*	651	1620,1652	3511,3598	3688,3711
B3YLP/6-31G*	656	1628,1657	3449, 3545	3635,3653
EDF2/6-31G*	689	1640,1671	3482,3598	3692,3709
MP2/cc-PVDz	667	1672,1713	3785,3836	3939
MP2/aug-cc/PVDz	640	1624	3703	3903,3924

Optimized geometry of water dimer in gas phase

(Gaussian 16 calculations) (Atoms are defined in Fig.1) [Supplementary Table 1]

Method	O1-O4 distance (Å)	O4-H2 dimeric H-bond distance (Å)	H2-O1-H3 angle (degree)	H5-O4-H6 angle (degree)	O1-H2-O4 angle (degree)
HF/6-31G	2.842	1.885	111.60	112.18	179.60
HF/6-311+G	2.833	1.870	112.78	112.71	179.12
DFT/B3LP-6-31G	2.777	1.794	108.99	109.61	173.65
DFT/ωB97X-D/6-31G	2.764	1.787	109.82	110.57	174.40
MP2/ cc-pVDZ	2.908	1.943	101.86	105.72	172.67
MP2/aug-cc-pVDZ	2.916	1.951	104.20	104.28	171.12