

Investigation of Water Cluster ((H₂O)_n , n = 2-6) in Aspect of Structures, Energies and Thermodynamic Properties by Ab Initio methods

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ABSTRACT

The intermolecular forces between water molecules are of great importance in many areas of chemistry including solvation, solution chemistry, and biochemistry. As a result of this (H₂O)_n systems have received a great significant of attention, both experimental and theoretical. All calculation of this study are carried out by Gaussian 98 soft ware. Geometry optimization for each cluster were be performed at HF/6-311++G(2df,2p), single point vibration energy B3LYP/6-311++G (2df,2p) and MP2/6-31+G(2df,p). IR frequencies and intensity were calculated at B3LYP/6-311++G (2df,2p) level of theory.

All calculation was accomplished at 298 k and 0 k. The structures, energies and thermodynamic properties will be discussed.

Keywords: Structure; Energy; Thermodynamic; Ab initio; Water cluster

INTRODUCTION

One of the most amount chemical studies is about water because of it's importance in life. In addition to these "natural" reasons, because it has unique physical properties (structures, energies, thermodynamic quantities and spectra) and a model of hydrogen-bonding in liquids [1,2]. Water clusters have been studied for a long time in order to analyze the interaction between water molecules, and for developing a deeper understanding of liquid and solid phase of bulk water [3]. In the limit $n \rightarrow \infty$, the energies and thermodynamic properties of clusters approach the energies and properties of the liquid phase. In recent years there has been considerable interest in the structures, energies and thermodynamics of small water clusters and it is the subject of

many experimental and theoretical studies because of its fundamental importance in chemical and biological process [4]. Computer simulations of liquid water have been performed for more than three decades, since the pioneering work of Rahman and Stillinger in 1971. Since then simulations have provided a great deal of insight in to the physical properties of water, however; there are still very fundamental open questions regarding the microscopic dynamics of the individual molecules in the liquid [2]. Theoretical calculations on the clusters are largely based upon ab initio calculations.

The present study is one of a series of calculations which investigates the properties of small water clusters. The main focus of this

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work was on a comparison of structures, energies, and thermodynamic properties of different clusters. The optimal structures, energies and thermodynamic properties of these cluster, $(\text{H}_2\text{O})_n$, have been determined at the Hartree-Fock(HF), density functional theory(DFT) and at the correlated Moller-Plesset (MP2) level. In predicting structures and energies from ab initio calculations, the size of basis sets and theoretical methods employed are important issues. Using proper and large Basis sets with considering electron correlation are recommended to describe weakly interacting molecular systems such as hydrogen bonded water clusters. Intra and intermolecular harmonic vibrational frequencies were calculated for $n=2-6$, and infrared bond intensities were determined for these clusters based on the B3LYP/6-311+G(2df,2p). For each value of n , we have considered the conformations corresponding to the lowest-energy minimum and those in nearby relative minima. Thus we report on two dimers, two trimers, two tetramers, two pentamers and two hexamers. Hexamer has diverse isoenergies structures. These diverse isoenergies hexamer conformers would play an important role in entropy, and so be responsible for various phase transitions of water [4]. Most of the above data have been compared to the available experimental data.

COMPUTATIONAL METHOD

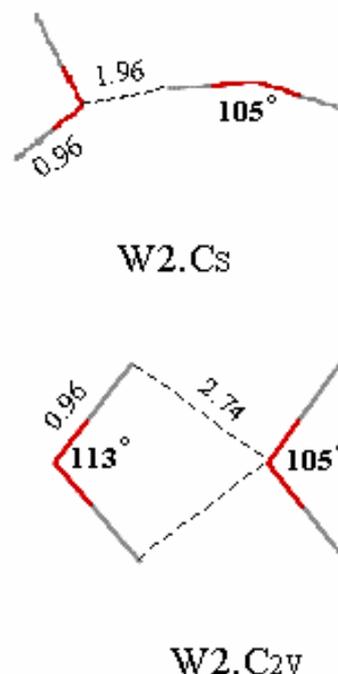
The optimized structures, energies and vibrational frequencies of water clusters dimer to hexamer were obtained at various levels of theory using different basis sets. The theoretical methods include density functional method with Beck's three parameter's employing Lee-Yang-Parr correlation functional (B3LYP/6-311++G(2df, 2p)), and (B3LYP/6-311++G(2df, p)), the Hartree-Fock method (HF/6-311++G(2DF, 2P)), and (HF/6-311+G(2df,p)), Moller-Plesset second order perturbation method (MP2/6-31+G(2df, p)). Density functional method gives the best result for IR vibrational spectra and IR intensities. The MP2 level was used to optimize the structures and energies of the water dimer to hexamer. Zero point vibrational energies were scaled by a factor of

0.9135. All these calculations were carried out with a GAUSSIAN 98 soft ware [5].

RESULTS AND DISCUSSION

A. Structures

In clusters containing dangling hydrogen (Hd) atoms, two different orientations for each Hd atom are possible along the H-bond orientation of the proton donor-proton acceptor ("da")-type water molecules [4]. The numbers of dangling H atoms for cyclic clusters from dimer to hexamer are 2, 3, 4, 5 and 6 and for linear dimer and tetramer are 3 and 5 respectively. There exist various conformers with different hydrogen orientations which have topologically equivalent. The structures with a 2,3,4,5 and 6 membered ring can be easily interconvertible by simple manipulation of one or two hydrogen bonds. Different plane of symmetry for each kinds of cluster from dimer to Hexamer was kept throughout their optimization. The (H-O-H) min for the tetramer is 101° , which is much closed to the most optimal H-bonding angle of water (104.5°). Thus, hydrogen bonding between adjacent water in the tetramer is possible without much strain and it is found to be a stable structure. The features of water clusters are shown in Fig.1.



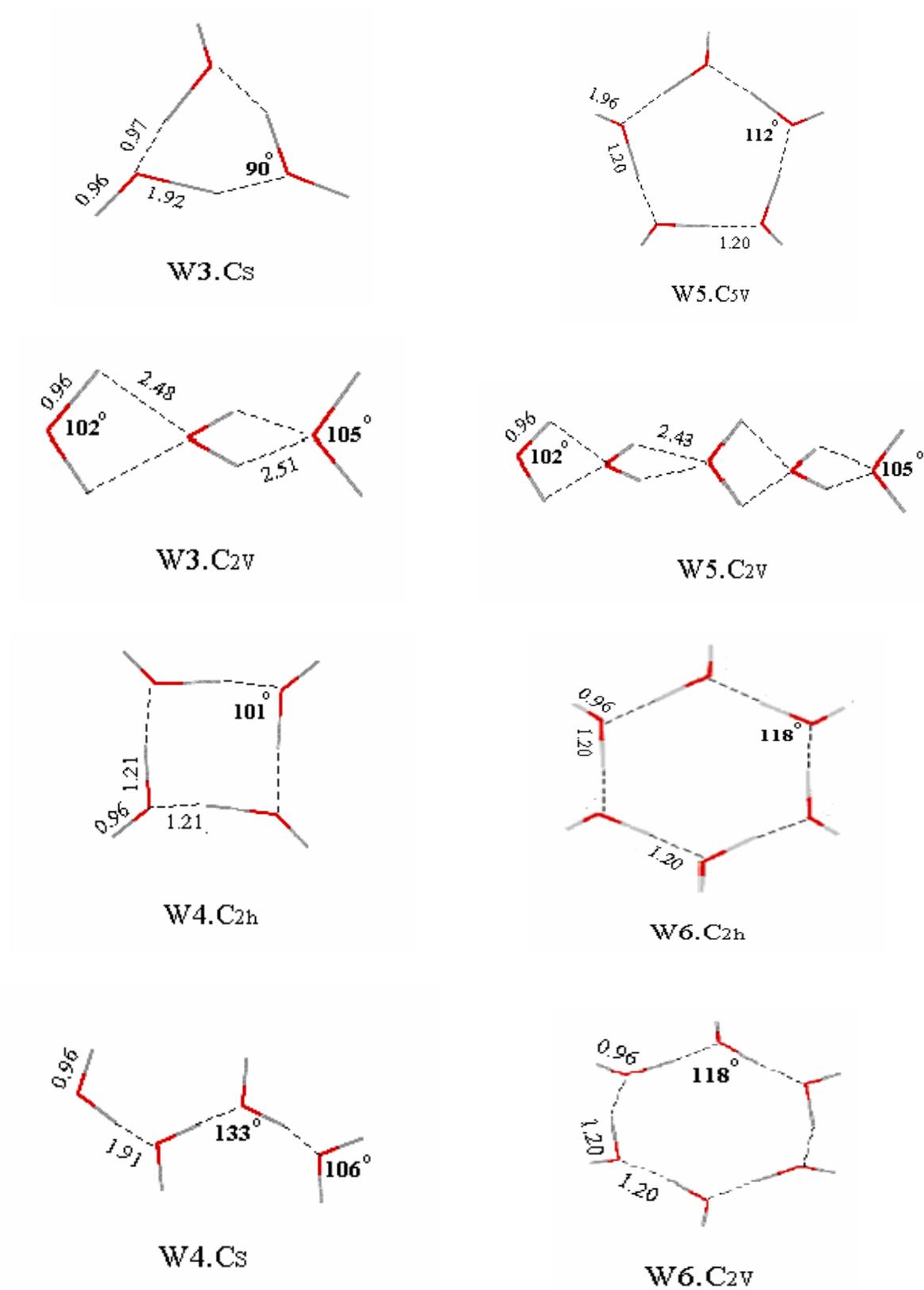


Fig.1. Low-energy structures of water clusters $(\text{H}_2\text{O})_n$, $n=2-6$, distances are in \AA ; angles in degrees.

Energies and thermodynamic quantities

We have investigated the changes in energies with increasing cluster size. The energies of these configurations are given in Table 1 and 2. They correspond to the structures shown in figure 1. The lowest energy conformers from dimer to hexamer are cyclic structures. Water clusters favor chainlike H-bond network (as H bonds are most strengthened with the addition of

a chainlike H bond), while they tend to be more stable with cyclic structures that have one more H bond compared to the linear chain structure[21]. On the basis of Gibbs free energies using B3LYP/6-311++G(2df,2p) basis set we understood that the most stable conformer for dimer is W2.C2V, for trimer is W3.C2V, for tetramer is W4.C2h, for the pentamer is W5.C2V and for the hexamer is W6.C2h.

Table 1. Total energy and ΔG° , ΔH° (Hartree) S° (cal/mol K) and relative energy (kcal/mol)

Feature	W2.Cs	W2.C2v	W3.Cs	W3.C2v	W4.Cs	W4.C2h
HF/6-311++G(2df,2P)	-152.121627	-152.118246	-228.111691	-228.182472	-304.251145	-304.182847
E_{rel}	(0.0)	(1.13)	(41.27)	(0.0)	(0.0)	(37.38)
ZPVE	31.02739	29.94305	42.73722	46.16308	62.69146	56.69338
$G^\circ_{298}-G^\circ_0$	-0.174124	-0.522147	-0.364561	-0.944767	-0.429185	-0.431999
E_{rel}	(0.35)	(0.0)	(0.58)	(0.0)	(0.002)	(0.0)
$H^\circ_{298}-H^\circ_0$	-0.140558	-0.489961	-0.332045	-0.9011	-0.382602	-0.39605
E_{rel}	(0.35)	(0.0)	(0.569)	(0.0)	(0.013)	(0.0)
S°_{298}	70.647	68.480	68.420	91.907	98.042	75.660
HF/6-311+G(2df,P)	-152.121148	-152.114249	-228.111691	-228.177073	-304.243919	-304.177702
E_{rel}	(0.0)	(3.53)	(40.67)	(0.0)	(0.0)	(36.11)
ZPVE	31.02937	29.92520	42.99719	46.17368	62.70460	56.74933
$G^\circ_{298}-G^\circ_0$	-0.178272	-0.523114	-0.366467	-0.947367	-0.433256	-0.449001
E_{rel}	(0.34)	(0.0)	(0.58)	(0.0)	(0.015)	(0.0)
$H^\circ_{298}-H^\circ_0$	-0.144679	-0.490968	-0.334217	-0.904265	-0.382039	-0.472978
E_{rel}	(0.35)	(0.0)	(0.57)	(0.0)	(0.09)	(0.0)
S°_{298}	70.702	67.658	67.875	90.716	107.796	75.816
B3LYP/6-311++G(2df,2P)	-152.933118	-152.9284	-229.412135	-229.398565	-305.875368	-305.855106
E_{rel}	(0.0)	(1.80)	(0.0)	(5.94)	(0.0)	(10.317)
ZPVE	28.96233	27.61112	45.72143	42.89691	58.36078	55.73631
$G^\circ_{298}-G^\circ_0$	-0.164407	-0.480442	-0.411446	-0.853982	-0.401552	-0.443332
E_{rel}	(0.32)	(0.0)	(0.44)	(0.0)	(0.041)	(0.0)
$H^\circ_{298}-H^\circ_0$	-0.131386	-0.449803	-0.373659	-0.81049	-0.358215	-0.406677
E_{rel}	(0.32)	(0.0)	(0.44)	(0.0)	(0.048)	(0.0)
S°_{298}	69.497	64.486	79.53	91.542	91.210	77.146
B3LYP/6-311++G(2df,P)	-152.929361	-152.924614	-229.365397	-229.393751	-305.868665	-305.850396
E_{rel}	(0.0)	(1.83)	(16.63)	(0.0)	(0.0)	(9.205)
ZPVE	28.91523	27.63923	41.71636	42.99259	58.33001	55.85800
$G^\circ_{298}-G^\circ_0$	-0.165082	-0.484079	-0.25197	-0.858025	-0.402324	-0.44695
E_{rel}	(0.32)	(0.0)	(0.61)	(0.0)	(0.045)	(0.0)
$H^\circ_{298}-H^\circ_0$	-0.132115	-0.450446	-0.220293	-0.815296	-0.359226	-0.410237
E_{rel}	(0.32)	(0.0)	(0.60)	(0.0)	(0.051)	(0.0)
S°_{298}	69.384	70.787	66.671	89.930	90.708	77.268
MP2/6-31+G(2df,P)FOPT	-152.553753	-152.564783	-228.821309	-228.853449	-305.147581	-305.123868
E_{rel}	(0.01)	(0.0)	(0.03)	(0.0)	(0.0)	(0.02)

Table 2. Total energy and $\Delta^{\circ}G$, $\Delta^{\circ}H$ (Hartree) $^{\circ}S$ (cal/mol K) and relative energy (kcal/mol)

Feature	W5,Csv	W5,Czv	W6, Czv	W6,C2h
HFV6-311++G(2df,2P)	-380.234678	-380.309596	-456.292462	-456.295956
E_{rel}	(40.19)	(0.0)	(1.67)	(0.0)
ZPVE	70.29302	77.76042	85.56897	86.14863
$G_{298}^{\circ}-G_{0}^{\circ}$	-0.030396	-1.737916	-0.642145	-0.6547104
E_{rel}	(1.70)	(0.0)	(0.01)	(0.0)
$H_{298}^{\circ}-H_{0}^{\circ}$	0.0085178	-1.673736	-0.594375	-0.605584
E_{rel}	(1.68)	(0.0)	(0.01)	(0.0)
S_{298}°	81.898	135.079	100.539	102.120
HFV6-311+G(2df,P)	-380.228771	-380.301048	-456.285941	-456.28952
E_{rel}	(38.51)	(0.0)	(1.67)	(0.0)
ZPVE	70.28009	77.76558	85.79198	86.41867
$G_{298}^{\circ}-G_{0}^{\circ}$	-0.030995	-1.74584	-0.648221	-0.660129
E_{rel}	(1.71)	(0.0)	(0.01)	(0.0)
$H_{298}^{\circ}-H_{0}^{\circ}$	0.008474	-1.682429	-0.600339	-0.611758
E_{rel}	(1.69)	(0.0)	(0.01)	(0.0)
S_{298}°	83.071	133.461	100.776	101.750
B3LYP/6-311++G(2df,2P)	-382.322694	-382.337109	-458.796889	-458.800401
E_{rel}	(0.94)	(0.0)	(76.99)	(0.0)
ZPVE	68.46518	77.32952	81.86312	82.55301
$G_{298}^{\circ}-G_{0}^{\circ}$	-0.030033	-1.547273	-0.670734	-0.683919
E_{rel}	(1.51)	(0.0)	(0.01)	(0.0)
$H_{298}^{\circ}-H_{0}^{\circ}$	0.008724	-1.547273	-0.622854	-0.63276
E_{rel}	(1.55)	(0.0)	(0.01)	(0.0)
S_{298}°	81.571	136.072	100.722	107.673
B3LYP/6-311++G(2df,P)	-382.316734	-382.329296	-458.790426	-458.794122
E_{rel}	(4.37)	(0.0)	(1.66)	(0.0)
ZPVE	68.62422	72.46879	82.38086	83.10653
$G_{298}^{\circ}-G_{0}^{\circ}$	-0.563525	-1.597025	-0.67569	-0.689486
E_{rel}	(1.03)	(0.0)	(0.01)	(0.0)
$H_{298}^{\circ}-H_{0}^{\circ}$	-0.524485	-1.533329	-0.628747	-0.639103
E_{rel}	(1.00)	(0.0)	(0.01)	(0.0)
S_{298}°	82.167	134.060	98.798	106.038
MP2/6-31+G(2df,P)/FOPT	-381.407591	-381.42998	-457.317428	-457.308251
E_{rel}	(0.02)	(0.0)	(0.0)	(0.01)

Vibrational spectra

In water clusters, the individual water monomers are linked by different kinds of H bonds. Water clusters from dimer to hexamer have only "da"-type of water molecules and the numbers of "da" type of water molecules in these clusters are 2, 3, 4, 5 and 6 respectively. Therefore frequency and IR intensity of water cluster are calculated with B3LYP/6-311++G (2df, 2p) basis sets Since this basis set results gives much more reliable results than the other ones reported here so our discussion will be based on this large basis set results. In this paper, we report theoretical frequencies and IR intensities of water clusters with different plane of symmetry from dimer to hexamer which are shown in tables from 3 to 12.

Table 3. OH frequency shifts (cm⁻¹) and IR intensity (km/mol)

W2.CS	B3LYP/6-311++G(2df, 2p)	
Vibrational modes	Frequency	IR intensity
A''	135.7	167.4
A'	158.7	88.7
A''	160.5	12.1
A'	190.5	192.9
A'	366.8	69.7
A''	638.9	125.9
A'	1631.9	91.8
A'	1652.3	37.5
A'	3707	325.1
A'	3811.9	13.6
A'	3893.1	87.2
A''	3912.2	84.7

Table 4. OH frequency shifts (cm⁻¹) and IR intensity (km/mol)

W2.C2V	B3LYP/6-311++G(2df, 2p)	
Vibrational modes	Frequency	IR intensity
A1	86.4	0.2
B2	155.2	42.4
B1	318.4	284.7
A1	1631.2	0
A1	1647.6	192.6
A1	3817	12.6
A1	3828.3	11.1
B2	3912.4	55.7
B2	3917.8	72

Table 5. OH frequency shifts (cm⁻¹) and IR intensity (km/mol)

W3.CS	B3LYP/6-311++G(2df, 2p)	
Vibrational modes	Frequency	IR intensity
-	174.3	33.9
-	183.3	7.4
-	193.1	105.2
-	218.5	134.6
-	219.5	15
-	259.5	46.1
-	351	80.3
-	365.2	37.7
-	450.9	130.8
-	575.9	194.4
-	680.6	319.5
-	871.1	8.9
-	1640.9	100
-	1644.8	60.4
-	1668.1	19.3
-	3565.8	12.5
-	3623.8	558.7
-	3634.3	522.6
-	3884.1	92
-	3887.7	83.4
-	3890.3	69.3

Table 6. OH frequency shifts (cm⁻¹) and IR intensity (km/mol)

W3.C2V	B3LYP/6-311++G(2df, 2p)	
Vibrational modes	Frequency	IR intensity
B2	18.5	2.0
B1	24.7	0.1
A1	90.2	0.7
B2	114.7	11.6
B1	177.9	254
B1	462.9	264.3
B2	465.4	276.2
A1	1625.5	8.1
A1	1643.3	4.4
A1	1659.8	360.6
A1	3813.0	35.6
A1	3818.6	24.7
A1	3823.8	5.2
B2	3893.8	54.2
B1	3895.0	68.8
B2	3915.0	82.4

Table 7. OH frequency shifts (cm⁻¹) and IR intensity (km/mol)

W4.CS	B3LYP/6-311++G(2df, 2p)	
Vibrational modes	Frequency	IR intensity
A'	23.6	0.8
A'	45.2	1.2
A'	133.1	3.2
A'	182.3	1.1
A'	207.8	84.2
A'	241.4	5.7
A'	330.6	99.6
A'	434.1	2.4
A''	492.5	150.9
A'	532.1	124.2
A''	542.4	184.6
A''	570.5	0
A'	1632.2	76.1
A''	1662.8	68.8
A''	1667.2	27.1
A'	1672.4	45.4
A'	3634.6	970.2
A'	3678.7	141.4
A'	3698.1	310.1
A'	3821.4	14.2
A'	3895.6	67.5
A'	3900.3	77.1
A'	3900.7	125
A'	3924.3	99.1

Table 8. OH frequency shifts (cm⁻¹) and IR intensity (km/mol)

W4.C2h	B3LYP/6-311++G(2df, 2p)	
Vibrational modes	Frequency	IR intensity
AU	64.6	6.6
BU	395.8	111.7
AU	502.5	17.5
BU	570.5	40.3
BU	624.8	17.2
AU	625.4	3.9
AU	750.2	884.2
BU	1067.4	6376.9
AU	1076.9	5413.7
BU	1348.5	97.6
BU	1580.3	162.3
AU	1600.7	546.1
BU	1778.8	371.5
AU	3870.6	55
BU	3872.4	118

Table 9. OH frequency shifts (cm⁻¹) and IR intensity (km/mol)

W5.C5v	B3LYP/6-311++G(2df, 2p)	
Vibrational modes	Frequency	IR intensity
E1	311.2	0.1
E1	311.3	0.1
A1	359.4	140.4
E1	570.2	4126.4
E1	570.2	4126.1
E1	584.0	19.1
E1	584.0	19.4
E1	973.2	4567.3
E1	973.2	4567.4
E1	1308.4	111.6
E1	1308.4	111.7
A1	1362.9	259.9
A1	1863.7	39.1
E1	3883.9	65.4
E1	3883.9	65.4
A1	3885.9	58.1

Table 10. OH frequency shifts (cm⁻¹) and IR intensity (km/mol)

W5.C2V	B3LYP/6-311++G(2df, 2p)	
Vibrational modes	Frequency	IR intensity
B2	5.3	0.254
B2	5.9	0.5976
B2	20.0	3.5693
B1	28.1	2.9
B2	48.2	0.8
B1	52.5	0.1
A1	60.8	0.9
B2	131.7	13.0
A1	161.2	0.1
B1	195.7	255.6
B1	474.1	182.3
B2	486.5	177.1
B2	516.7	336.8
B1	516.9	320.9
A1	1625.8	5.7
A1	1635.9	1.1
A1	1646.9	42.5
A1	1658.4	2.1
A1	1666.5	688.1
A1	3810.6	127.7
A1	3812.7	19.9
A1	3816.3	2.6
A1	3819.3	4.8
A1	3822.3	8
B2	3880.9	67.7
B1	3881.6	64.6
B1	3888.7	74.5
B2	3890.3	56.3
B2	3913.8	84.7

Table 11. OH frequency shifts (cm⁻¹) and IR intensity (km/mol)

W6.C2V	B3LYP/6-311++G(2df, 2p)	
Vibrational modes	Frequency	IR intensity
A1	46.6	0.2
A1	84.9	2.6
B2	97.3	3436.8
B2	130.6	2.7
B1	197.7	3414.0
B2	287.4	126.1
A1	299.2	80.1
B1	386.4	3831.4
A1	438.4	4.9
A1	449.6	1.3
B2	459.9	1938.3
B2	535.5	88.7
B1	537.7	12
B1	702.4	1342.1
A1	712	0.2
B1	737.1	1660.6
B1	781.5	688.2
B2	909.7	2199.0
A1	1206.8	231.4
B1	1224.4	131.9
A1	1355.3	110.3
B2	1480.9	9.9
B1	1496.1	405.6
A1	1569.9	389.8
B2	1582.1	2.6
B2	1621.4	1176.8
A1	1646.1	50.0
B1	1646.6	61.7
B1	1807.8	566.8
A1	1818.4	85.3
B2	3873.3	24.7
A1	3873.6	75.0
B2	3879.5	37.4
B1	3881.3	49.4
A1	3881.8	67.9

Table 12. OH frequency shifts (cm⁻¹) and IR intensity (km/mol)

	W6.C2h	B3LYP/6-311++G(2df, 2p)
Vibrational modes	Frequency	IR intensity
AU	38.5	16.4
AG	42.4	11.6
BU	143.5	11.8
AU	205.3	4650.3
BU	208.1	4607.1
BG	305.4	67.9
BU	466.5	3140.4
AG	467.3	3014.4
BU	539.2	198.6
BG	539.8	243.3
AU	724.1	0.3
AG	761.4	2885.2
AU	763.9	2902.4
AG	785.9	2.5
BU	1415.2	0.1
AG	1464	1.2
BU	1577.1	669
AU	1601.4	450.3
AU	1604	453.8
BU	1664.2	751.9
AG	1664.9	750.6
BG	3874.1	96.1
AU	3875.1	113.1
AG	3875.2	56.4

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