

Quantum Signature of Anisotropic Singularities in Hydrogen Bond Breaking of Water Dimer

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Article

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Abstract

Molecular simulations from small molecules to large bio-macromolecules and polymer systems are routinely used to simulate thermodynamics properties of interests by molecular mechanics-based potentials. In a recent paper, via three different semi-empirical methods, we reported quantum singularities in molecular mechanics torsion potentials as signature of chemical bond break-up process revealed under experimental X-ray as broken chemical moieties. In this present work, applying first principle methods of Hartree-Fock, Density Functional as well as Moller-Plesset techniques we have reconfirmed the previous general predictions of singularities in the torsion potential for the case of water dimer that connects two water monomers by weak hydrogen bond. Due to quantum nature of chemical bond breaking process leading to break-point conditions in otherwise connected molecular topology aided by molecular mechanics based potentials, the singularities are also suggestive of large forces as onset in the bond-breaking process. We have presented the details of these novel interesting findings in this paper. These results of quantum singularities can have significant impacts to improve current force fields and can open up new areas we define as “Fracture Molecular Mechanics” or “Fracture Force Field” in overlap regions of molecular and quantum mechanics based approaches to explore and account for chemical bond-breaking mechanisms in molecular simulation techniques.

Introduction

In our recent paper we have reported for the first time quantum singularities in molecular mechanics torsion potential as signature of chemical bond break-up process revealed in the X-ray structure^{1, 2}. In this present work, via several different ab initio techniques like Hartree-Fock³, Density Functional⁴ as well as Moller-Plesset⁵ methods and with higher basis set we have computed the torsion potential of dissociative water dimer and have consistently observed our previous general predictions of singularities in breaking chemical bonds. Due to the quantum nature of chemical bond break-up process leading to break-point conditions in connected molecular topology or in other expression the singularities in molecular mechanics based potential energy are simultaneously also indicative of large classical force at onset of bond-breaking by torsion of a molecule. Therefore, the effect can be used to enhance current molecular simulation techniques. Although purely quantum mechanical phenomenon, due to weak spectroscopic feature, tracking individual chemical bond break-up experimentally in dissociative or other chemical reaction mechanisms can be challenging both in gas or solution phase by traditional spectroscopies⁶. Spectroscopic detection of such torsion singularities will require advanced state-of-art single molecule based force or torque spectroscopy experiments^{7, 8, 9, 10}.

Development of physics-based force field potentials for molecular modeling of bio-macromolecules and large polymer systems have their origin in the first successful molecular dynamics (MD) simulation of liquid argon carried out by implementing the Lennard Jones potential^{11, 12}. Based on the Born-Oppenheimer theory via assigning an atomic charge at nuclear co-ordinates with van der Waals radii as soft excluded volume, the MD scheme uses Boltzmann equilibrium assembly properties in correlating

ensemble averages with macroscopic properties¹³. In MD simulation force field categories of both BONDED and NON- BONDED terms do connect the atoms by a topology of network and in practice NON- BONDED terms practically link the atoms at longer geometrical distance. In molecular simulations the terms are usually truncated to 10–12 Å in order to save processor time. However, all the force field terms including traditional non- bonded terms are basically a representation of connectivity of atoms in a bonded network with smooth potential as MD inherently does not simulate any phenomena that is based on electronic orbital structure both for nearest or long distance atomic neighbors. However, as routine methods via using high- performance computing, MD simulations have significant successes in prediction of X-ray, Cryo-EM structure within reasonable atomic accuracy^{14,15,16}. The connectivity of atoms by molecular mechanics potential reduces accessible phase space particularly to capture critical phenomena when molecular potential might be redefined in critical transition process; in recent years efforts have been applied in enhanced sampling methods with adaptive polarization and energetics in the assembly^{17,18}. Another simulation field used the Monte Carlo (MC) technique mainly based on the pioneering work of Metropolis et al.¹⁹ so far has reported and reproduced some feature following MD trait^{20,21}. However, all reported classical MD/MC methods in bio-molecular simulation fields so far have been based on connected molecular topology with distinctive phase space sampling technique with no categorical difference in molecular mechanics atomic connectivity based on bond breaking or making information by wave mechanics techniques. As also with the case with *ab initio* MD where refined forces are computed quantum mechanically rather than using molecular mechanics for enhanced phase space sampling but does fall short to capture actual quantized singularity effects in bond- breaking or bond- making²². Due to above inherent limitations, it is not surprising that normal-mode analysis in MD trajectory analysis does not have the expected success in correlating experimental spectroscopy compared to the *ab initio* methods^{23,24}.

Since its discovery water dimer²⁵ has been an extensively studied chemical system by various experimental and theoretical techniques over the last few decades^{26,27,28,29}. It is the simplest form in water cluster formation as has been confirmed by subsequent numerous theoretical and experimental investigations^{30,31,32}. Since its first reporting more than 60 years ago the *ab initio* based studies have been carried out to study and correlate water dimer geometry, dynamics and spectroscopic feature by several methods^{33,34}. In this current report we have repeated and reproduced some of the standard *ab initio* water dimer results previously reported related to optimized geometry and vibrational spectra correlated with experimental methods^{35,36}. Finally results of H-bond breaking as quantum signature in torsion potential have been presented as further conclusive evidence previously reported with semi-empirical techniques. In the following sections we have discussed the methods for computational techniques, discussion, results analysis and conclusions as well as some quantum computational results with scopes for new experiment design based on reported singularity feature as logical sequence of the theoretical observations reported in this work.

Computational Methodologies

- Ground State Geometry of Water Dimer

Ground state geometry of water dimer has been computed by several first principle techniques as implemented in Gaussian 16³⁷ and SPARTAN 18 platform (URL: <https://www.wavefun.com>; Wavefunction, INC., Irvine, CA). Geometry optimization, bond length, bond angle, HOMO-LUMO orbital, energy gap difference, electrostatic potential map of water dimer have been computed by Moller-Plesset (MP2) with aug-ccPVDz basis, Hartree-Fock (HF) with 6-31G* basis, Density Functional Theory (DFT) at theory level wB97X and B3LYP with 6-31G* basis in gas phase, water and polar medium. DFT with wB97X is a relatively new functional form compared to B3LYP³⁸ that uses a long-range corrected hybrid density functional with atom-atom damped dispersion correction³⁹. Besides DFT, post Hartree-Fock ab initio technique with two types of basis set HF/6-31G*^{40,41} and HF/3-21G have been applied for comparison of optimized geometry in gas phase, water and polar medium^{42,43}.

- Water Dimer Binding Energy and Vibrational Spectra

Hydrogen bonds are represented by the well-known 12-10 potential⁴⁴ for bond length range between 1.65 to 3.00 Å and acceptor-donor angle $90^\circ < \theta < 180^\circ$.

$$V(r) = \left(\frac{A}{r^{12}} - \frac{B}{r^{10}} \right) \cos \theta \dots\dots\dots [1]$$

Theoretical binding energy of water dimer formation was estimated from the hydrogen bond well depth between O4 and H2 (Fig.1) atoms linking water monomers. Likewise for geometry optimization several first principle methods have been applied to estimate the binding energy that has reported a value of about 5.2 kcal/mol without zero point energy correction^{45, 46, 47}. As shown in Table 4, the binding energy value obtained by the MP2 technique is in good consistency with reported values after basis-set superposition corrections⁴⁸. Each energy scan for a specific method has been carried out with the structure initially obtained from geometry optimization. The spectral calculation procedure as mentioned in above section and discussed below used the same first principle technique. The scan was performed with O4-H2 distance as variable at 0.1 Å resolution ranging from 1.5 Å to 10 Å as shown in Figs 3 and 4. The dissociation energy has been estimated from the well depth from global minima and the asymptotic unbounded energy threshold computed from the potential plot for each technique. The above method was repeated with O1-O4^{49,50} interaction co-ordinates as well to compare dimer binding energy results from H-bonded O4-H2 separation distance method. The results have been shown in Table. 4.

For vibrational spectral studies several methods with different basis sets have been used for benchmarking and best reproducibility of reported theoretical and experimental spectra^{51, 52, 53}. Infrared vibration peaks were assigned to corresponding different vibrational modes of water dimer atomic vibration groups⁵⁴. Computational vibrational spectra computed by Gaussian 16 have also been reported in the supplementary section. For Spartan 18 based calculations, the systematic error primarily due to the

harmonic approximation is corrected by uniformly scaling the amplitude and spectra lines are broadened to account for finite temperature due primarily to rotational structure.

- Torsion-Dependent H-bond Energy by MM and QM

Torsion potential energy for dissociative water dimer molecule around O4-H2 bond (Figs 9) has been calculated by three separate ab initio methods. A set of three representative ab initio techniques of Hartree-Fock (basis set HF/6-31G*), Moller Plesset (basis MP2/aug-ccPDVZ) and Density Functional Theory (basis set B3YLP/6-31G*) have been applied to map out the torsional energy in the entire conformation span for O4-H2 hydrogen bonded atoms as well as O4-O1 interaction atoms forming reaction co-ordinates also shown in Figs 1 and 8. Torsion potential energy is given by following equation (symbols have their standard meanings).

$$V(f) = V_N[1 + \cos(N * f - f_o)].....[2]$$

Prior to the energy scan each structure was geometry optimized via the corresponding technique for ground state parameters and vibrational spectra as reported below. Dihedral energy scans with two different torsion planes of H5O4H2O1 (O4-H2 hydrogen bonded co-ordinates) and H5O4O1H3 (O4-O1 interaction co-ordinates) have been carried out for entire conformational span of 0o to 360o with 1o resolution. For comparison of the torsion potential with molecular mechanics potential, the process for both cases were repeated with the Merck Force Field popularly known as MMFF ⁵⁵.

- Anisotropic Singularities in Torsion Dependent H-bond Energy Surface

Anisotropic torsion energy of water dimer has been explored both in gas phase and in water medium by semi-empirical AM1 and PM3 techniques which previously we reported can record quantum chemical signature of bond break-up mechanisms. As seen in Fig 9, with fixed O4-H2 or O4-O1 lengths and varied torsion angle for the entire torsional space 0o to 360o, nature of energetics of water dimer can be explored in the critical range where H-bond interaction should be weak to hold two water monomers as integral chemical entity. Since both O1 and O4 atoms are heavier compared to the four hydrogen atoms (H2, H3, H5 and H6), although not bonded by Lewis definition the interaction distance parameters O1- O4 can serve in good approximation as center-of-mass distance between two water monomers as has been pointed out in respect to assessing water dimer binding energy. Any singularities in energetics of such reaction co-ordinates in (*r*, *f*) does imply break-up of molecular mechanics based connected topology of atoms in otherwise chemically stable molecules. For a fixed *r*, that is either O4-H2 or O1- O4 atomic distance; torsion angle *f* has been scanned for entire conformational space from 0o to 360o at 1o resolution. For O1-O4 the calculations have been extended to water medium both by AM1 and PM3 methods ^{56, 57, 58}. We have explored the energy surface in the critical bond distance range of 2.4 to 2.8 Å. Surface energy plots were generated by converting cylindrical symmetry data (bond length *r*, torsion angle *f* and energy) to Cartesian format as per GNUpot 3D graphing routine (URL link: <http://www.gnuplot.info/>). The results are shown in Figs. 14 and 15 and also in Supplementary Figs 4 and 5.

Results & Discussions

1. Optimized Water Dimer Geometry in Gas Phase, Water and Polar Medium

As presented in Tables 1,2, 3 and Supplementary Table 1, prior to vibrational spectra calculations, water dimer geometry was optimized by several ab initio methods in gas phase, water and polar medium. The results for geometric parameters of bond length, bond angle in gas phase are shown in Table 1. For each method subsequent vibrational spectra computations have been performed with the optimized geometry as the starting structure as discussed in next section. As observed below for optimized geometry parameters, all three applied techniques of DFT, MP2 and HF with basis set of 6–31G*, 6–311+G** and 6–311+G(2df, 2p) are in general in good consistency as carried out under Spartan 18 software tools with earlier reported works^{59,60}. Also in the Supplementary Table 1, some of the calculations presented have been repeated and reproduced by Gaussian 16 with similar theory level and basis set and all are in good agreement. The optimized geometry has been also assessed in water and polar medium shown in Table 2 and 3, Conductor-like Polarizable Continuum Model (CPCM)^{61, 62} with discretized boundary⁶³ as implemented in Spartan 18 package have been applied for water and polar medium computations. Compared to gas phase, bond distances show slight reduction in liquid phase which is consistent for higher packing density in liquid⁶⁴.

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
wB97X-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/	2.921	1.960	105.58	105.66	171.29

6-311+G(2df,2p)					
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
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

Optimized geometry of water dimer in gas phase

(Gaussian 16 calculations) (Atoms are defined in Fig.1) [supplementary table]

	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)
Method	ce (Å)	H-bond distance (Å)	angle (degree)	angle (degree)	(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/wB97X- 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

- ○ H-bond Dissociative Energy and Vibrational Spectra

A number of reported works have estimated the binding energy of water dimer taking molecular interaction energy as function of O1-O4 distance instead of O4-H2 shown in Figs 5 and 6. For water dimer structure as centers of mass of both water monomers are localized to heavier O1 and O4 atoms; dissociation energy of the structure is associated with O1-O4 distance and hence corresponding estimation of the binding energy. As seen in Table 4, both methods give similar range of binding energies for water dimer and are within consistent ranges of reported values⁶⁵. Particularly the MP2 technique showed high consistency with previous reported work using similar method^{66,67}. Due to zero point energy fluctuation the water dimer experimental binding energy is lower than above values of around 5.2 kcal/mol as reported in few recent works^{68, 69}. Also from the table DFT techniques, both by B3YLP and wB97X-D, show higher estimates for binding energy as discussed above. In summary, both O1-O4 and O4-H2 methods yield energy values close to reported water dimer binding energy. In a later section, we also have discussed the role of O1-O4 as independent reaction co-ordinates to identify quantum singularities of breaking up in chemically bonded molecules as has been observed for direct H-bond link between O4-H2 atoms.

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
wB97X-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
wB97X-D/6-31G*	651	1620,1652	3511,3598	3688,3711
B3LYP/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

The above Table 5. shows results for vibrational spectra mode calculations of water dimer. The OH-vibration mode is split into symmetric and asymmetric stretch which has distinctively also split to donor and acceptor mode as observed in Figs 7 & 8. Several first principle techniques with different basis set levels have been applied to compute infra-red (IR) spectra. The OH vibration region has donor and acceptor modes for both symmetric [3545 cm^{-1} and 3600 cm^{-1}] and asymmetric [3715 cm^{-1} and 3730 cm^{-1}] modes 70. Bending motion has a mode 71 around 600 cm^{-1} due to out of plane vibration 72. The computational results show consistency with reported experimental work 73. In supplementary section additional data with similar methods for vibrational spectra calculations have been presented with Gaussian 16 software.

- Break-up Signature of Weak H-Bond of Water Dimer
- Energy and Force Estimates for Water Dimer Break-up from Torsion Potential Singularities

The hydrogen bond linking two water molecules as reported and computed above has weak binding energy of around 5.2 kcal/mol without zero point energy corrections. The range of energy makes water dimer structure very unstable under any bond torsion motion. That dissociative bond-breaking tendency makes the water dimer an ideal system to explore for the quantum signature in torsion potential that we reported earlier with semi-empirical techniques. For the dihedral H5O4H2O1 plane in Fig 1 and Fig 9, dihedral rotation does strain the weak O4H2 hydrogen bond and reaches critical conformation that breaks the water dimer structure eventually. As observed in each case of HF/6-31G*, B3LYP/wB97X-D/6-31G*, MP2/aug-cc/PVDZ based calculations in Figs 11, 12 and 13, except for narrow isolated angle ranges of discontinuities, water dimer H bond has mostly isotropic flat energy feature as revealed under with varied torsion angle scans. This common feature in first principle calculations is quite in contrast to molecular mechanics based torsion potentials computed by MMFF method shown in Fig. 10. In contrast to QM potential as reconstructed from the orbital basis set, MM potential curve does not show any singularities in torsion energy curve as also continuous first derivative has been observed in entire the

conformation space in contrast to each of the *ab initio* case for exploring weak H bond in water dimer. The amount of energy transition of around ~ 5.5 eV is well above H-bond binding energy of 0.22 eV or 5.2 Kcal/mol. The values are clear indicative of bond-breaking phenomena under torsion for weak H bonds in water dimer as the jumps have large energetic feature for its dissociation. Based on that observations, *ab initio* based torsion potential can be applied as good exploratory probe to theoretically check molecular stability and estimate of bond incision at different locations of large molecules provided potential profile is reconstructed from quantum functional basis. Reproducibility results by Gaussian 16 also by first principle techniques as seen in Fig. 17 and 18 also have shown instability of water dimer for torsional motion around O4-O1 reaction co-ordinates. The estimates of torsion energy slopes in bond-breaking region by B3YLP/6-31G+ and wBxd4/6-31G+ methods are respectively 2×10^{-3} and 8.5×10^{-3} Hartree/Bohr which are equivalent to 0.16 and 0.69 nN. As per experimental data from single molecule force spectroscopy both force values are several order of magnitude higher than usual required hydrogen bond or co-valent bond breaking force that are order in pN^{74, 75} (<http://www.picotwist.com/index.php?content=smb&option=odg>). The above results can provide a sound theoretical premises to implement single molecule laser based force or torque spectroscopy in context to molecular break-point topology and correlation of experimental bond-breaking force values reported here.

- Anisotropic Singularities in Torsion-dependent Energy Surface

Figs 14 and 15 show interesting critical phenomena suggestive of H-bond breaking in 3D energy surface plots as function of bond length, r and torsion angle, ϕ plotted in range of 2.4 to 2.8 Å for entire conformational space of 360° using AM1 and PM3 techniques in gas phase. Due to weak H-bond linking two water monomer by around 0.22 eV, water dimer undergoes predicted chemical cleavages under torsion for O4-H2 distance ranges of 2.4 to 2.8 Å. Likewise, estimating water dimer binding energy from O1-O4 interaction co-ordinates even in absence of Lewis definition of chemical bonding as explained in the earlier section. Interaction distance of O1-O4 and their torsion angle has been explored by H5O4O1H3 dihedral plane. But as has been pointed out earlier both O4 and O1 nuclear co-ordinates in reality connects the two water monomers, H2-O1-H3 and H5-O4-H6 by the centers of mass point feature of O1-O4 separation co-ordinates. As results, any singularities in rupture of that topology is also in general an indicative of water dimer break-up firstly carried out for H5O4H2O1 dihedral plane with O4-H2 atoms being H-bonded. As a generalized case, we have extended the model to polar medium contrast to H-bonded case of O4-H2 in gas phase as just described in this section. Supplementary Figs 4 and 5 show energy surface as function of O4-O1 interaction length and torsion angle of dihedral plane applying AM1 and PM3 techniques. As observed in Supplementary Figs 4 and 5, water dimer energy in general is isotropic and has large range of stable torsion angle range of stability with distinctive feature of sharp changes of energies near the break-point topology as also observed in case for the gas phase. From characteristics of singularities of energy curves, bond length and torsion angle dependent energy surfaces via applying several different first principle methods and semi-empirical techniques, it can be inferred that jumps in energetics by about 5.5 eV, several order higher than water dimer H-bond of strength 0.22 eV as well as impulse force of nN order due to singularities in torsion potential are related to

chemical bond break-up mechanism. Also hysteresis feature of torsion potential curves as shown in Supplementary Figs 2 and 3 are indicative of the conclusion that large energy jumps not related to transition state geometry. In general, for fragile weak bond that has the tendency to break down under torsion; ab initio based reconstructed MM potential cannot have finite slope over the entire conformation space. For weak H-bonded water dimer system, torsion potential has shown anticipated discontinuities by all ab initio methods applied in torsion energy scan. Results from two different ab initio packages Spartan 18 and Gaussian 16 are supportive of the conclusions.

Conclusions

The scheme of connected topology of atoms by molecular mechanics potentials, although has inherent limitations to underpin bond-breaking feature via quantum mechanics, still has advantages to define a collection of atoms to define molecular entity from small organic molecules to large macro-molecules, like protein, DNA/RNA, carbohydrates, lipids, polymers etc. Although classical force field theory allows explicit bonding between neighboring atoms and by a networks of those linkages; quantum mechanics does not eliminate any long distance instantaneous interaction between atoms not bonded via Lewis definition of proximity^{76, 77}. Given the quantum nature of non-localization of electrons it will not be surprising if distant electrons in a large macro-molecule are effectively coupled as Born-Oppenheimer centers affecting observable macro-molecular properties in rather detectable ways. In addressing such problems, the bottlenecks are how big a system in number of atoms current state-of-art quantum tools can handle so that some new types of reaction co-ordinates can be defined over traditional methods. Towards that goal we have defined a new area of molecular simulation studies by “FRACTURE MOLECULAR MECHANICS” or “FRACTURE FORCE FIELD” that can be an interesting overlap of molecular mechanics and quantum mechanics incorporating chemical bond making and breaking processes in time scale based on electronic orbital properties rather than the current practices of so called hybrid applications of MM and QM in partitioned regions in molecules. Such quantum assembly of atoms and molecules in different physics conditions can capture many spontaneous reaction processes compared to current available state-of-art molecular simulation tools mostly evolved from the paradigm of classical molecular dynamics. Obviously, such simulation results will needed to be rigorously bench-marked against reaction-based fast dynamic laser spectroscopy. While the above should be the enhancement of current state-of-art force fields that can potentially mimic the quantum dynamic nature of bond breaking and making events with time scale with collection of large number of molecules, bio-macromolecules or polymers in the scheme of Fracture Molecular Mechanics/Fracture Force Field, in this paper we have underlined the expected outcomes for single molecules torsion or torque spectroscopy experiments with the water dimer. In above section, we have reported the expected values for bond rupture force in H-bond breaking of water dimer that in fact exceeds the current reported experimental values to actuate bond breaking process. In future publications we expect to report further generalized experimental aspects of the results.

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Figures

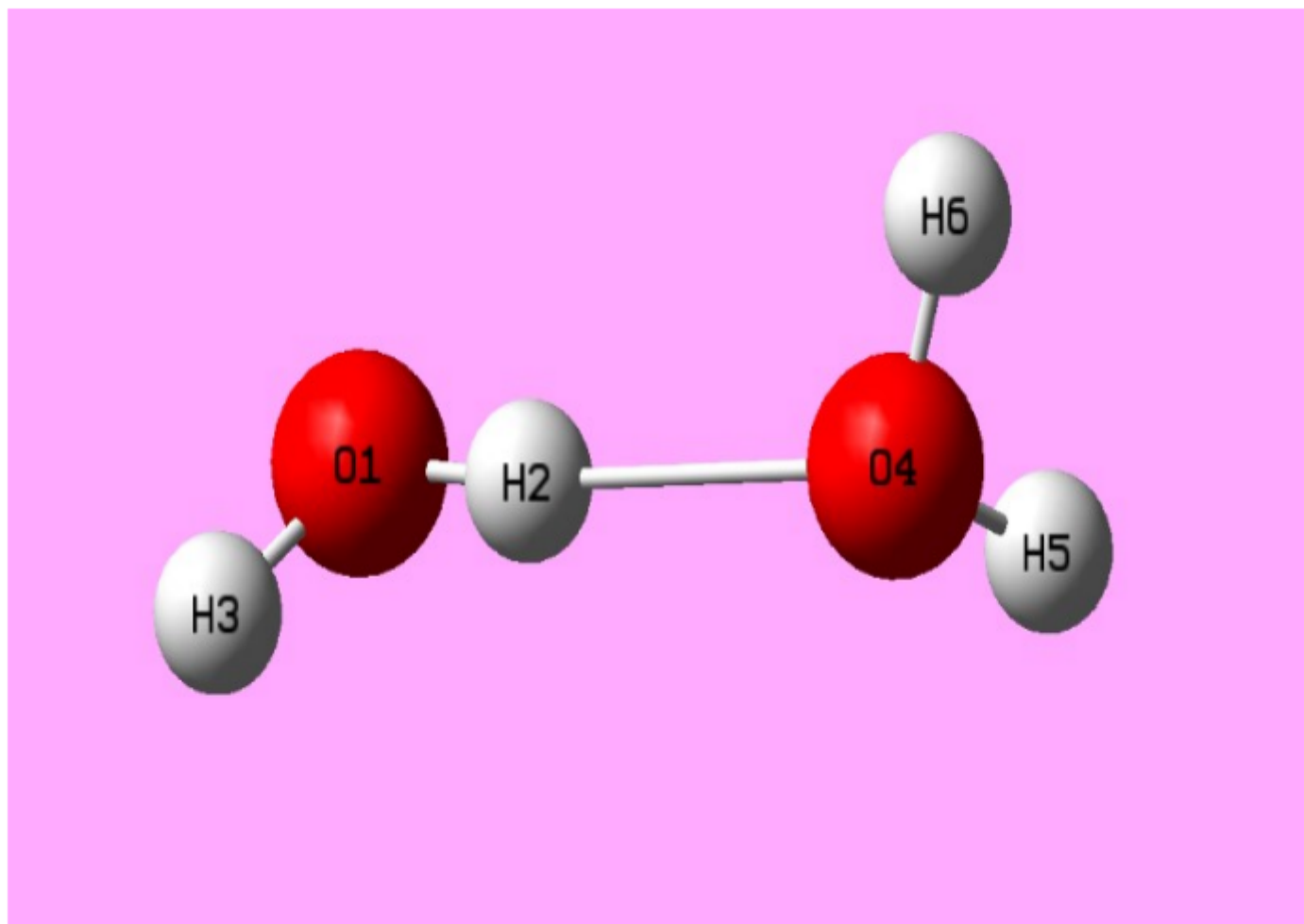


Figure 1

Atomic Labelling of Water Dimer. The Hydrogen Bond is Formed between O4 and H2 atoms; O1 and O4 Atoms are not Under Chemical Bonding Interaction.

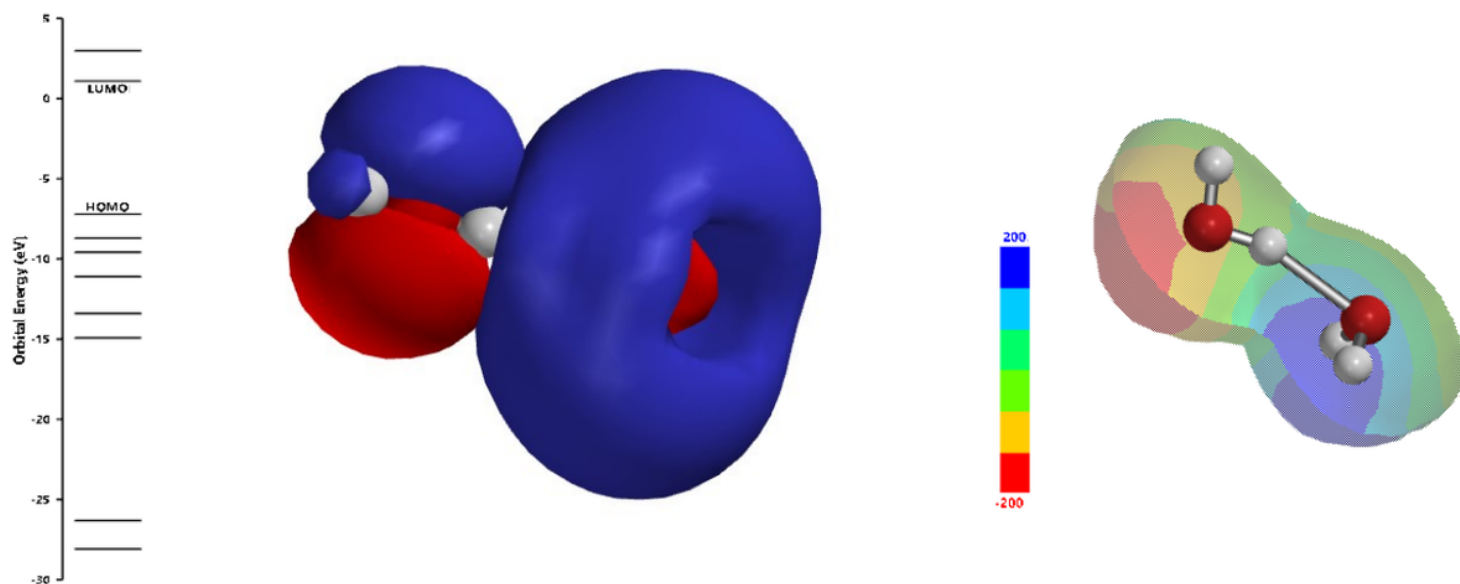


Figure 2

HOMO-LUMO Energy gap and Orbitals of Water Dimer and Electrostatics Potential Map of Water Dimer as computed by B3YLP/6-31G* basis are show below.

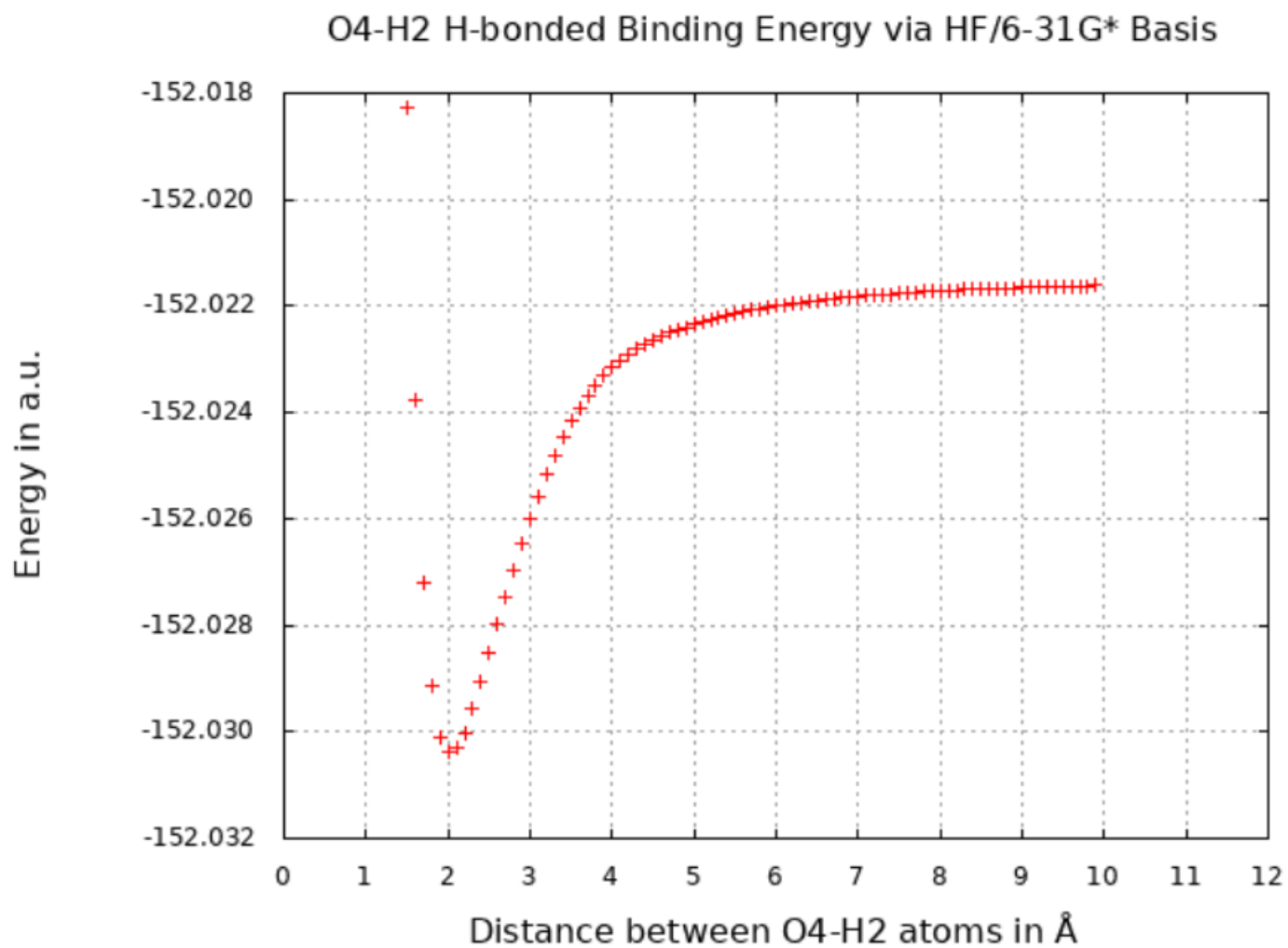


Figure 3

Estimation of Water Dimer Binding Energy from O4-H2 Bond via HF/6-31G* Basis

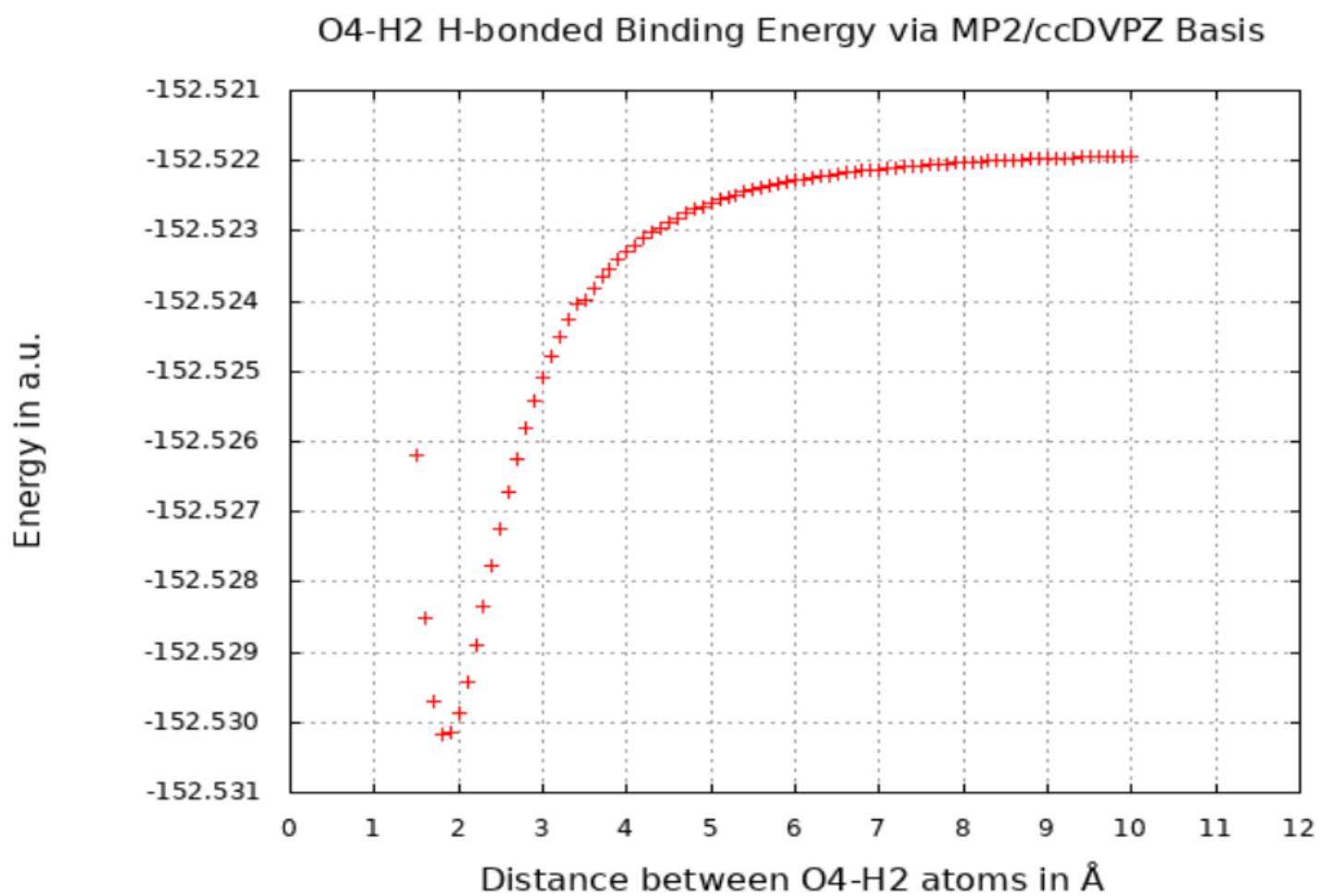


Figure 4

Estimation of Water Dimer Binding Energy from O4-H2 Bond via MP2/ccDVPZ Basis

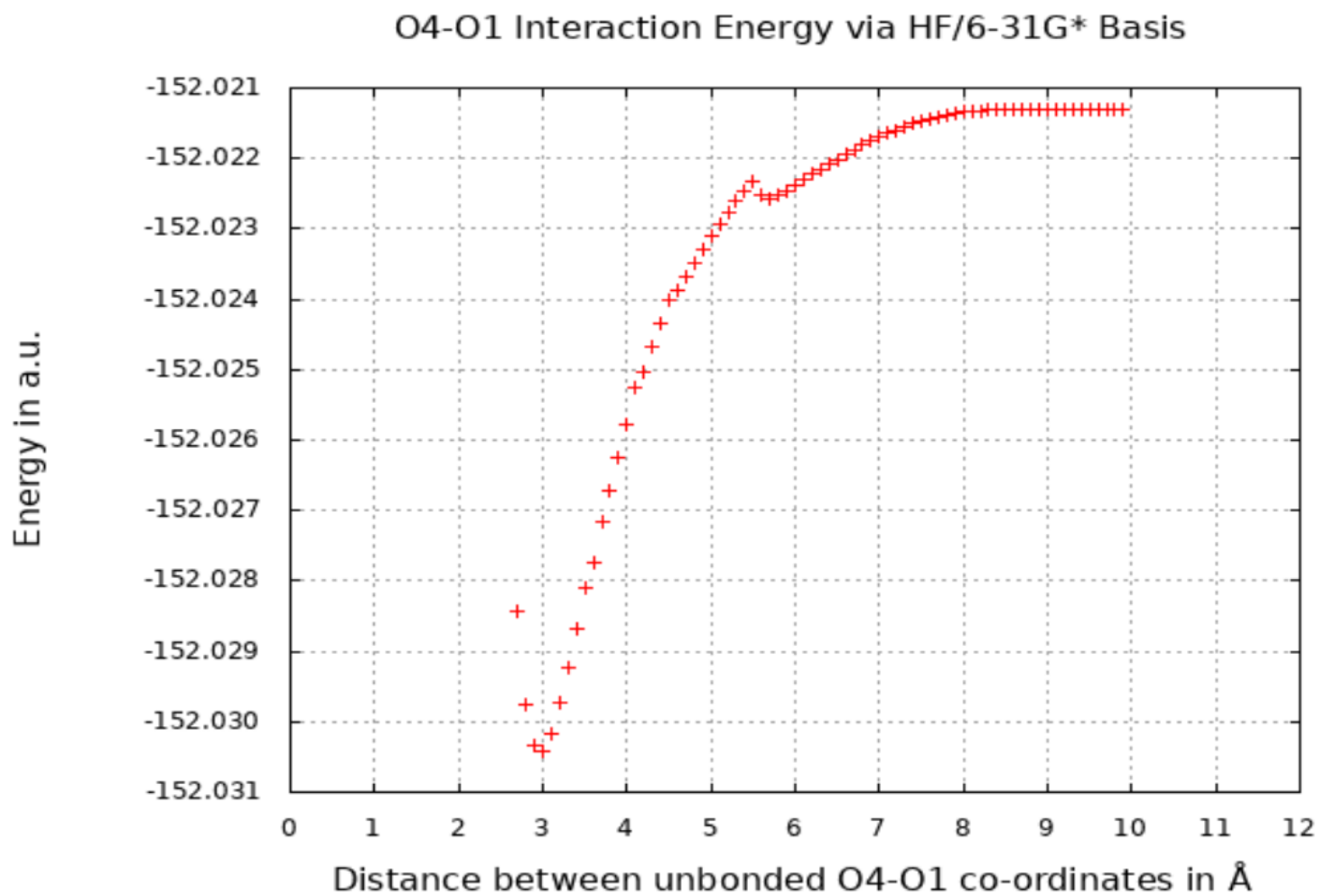


Figure 5

Estimation of Water Dimer Binding Energy from O1-O4 Interaction Distance via HF/6-31G* Basis

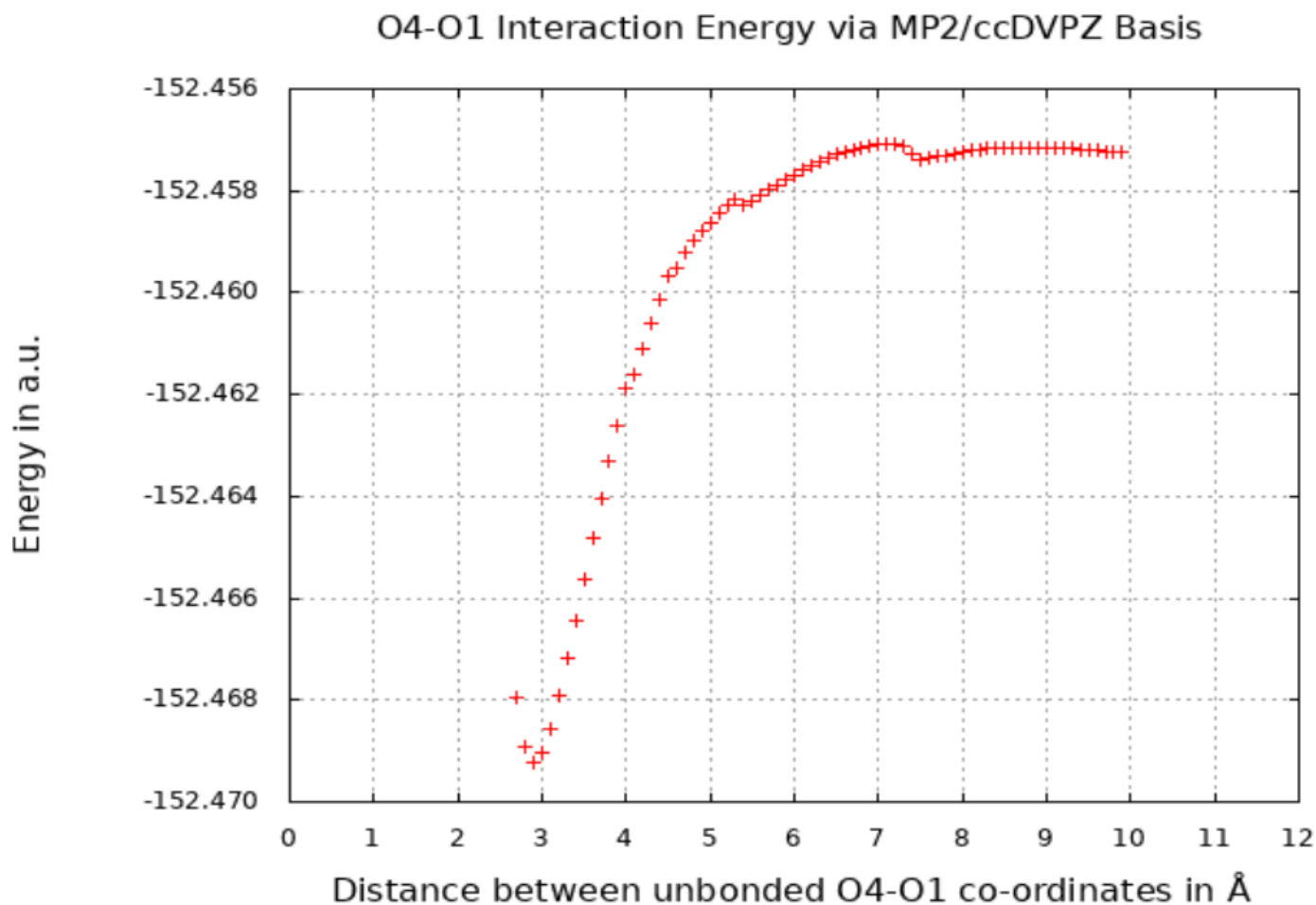


Figure 6

Estimation of Water Dimer Binding Energy from O1-O4 Interaction Distance via MP2/ccDVPZ Basis

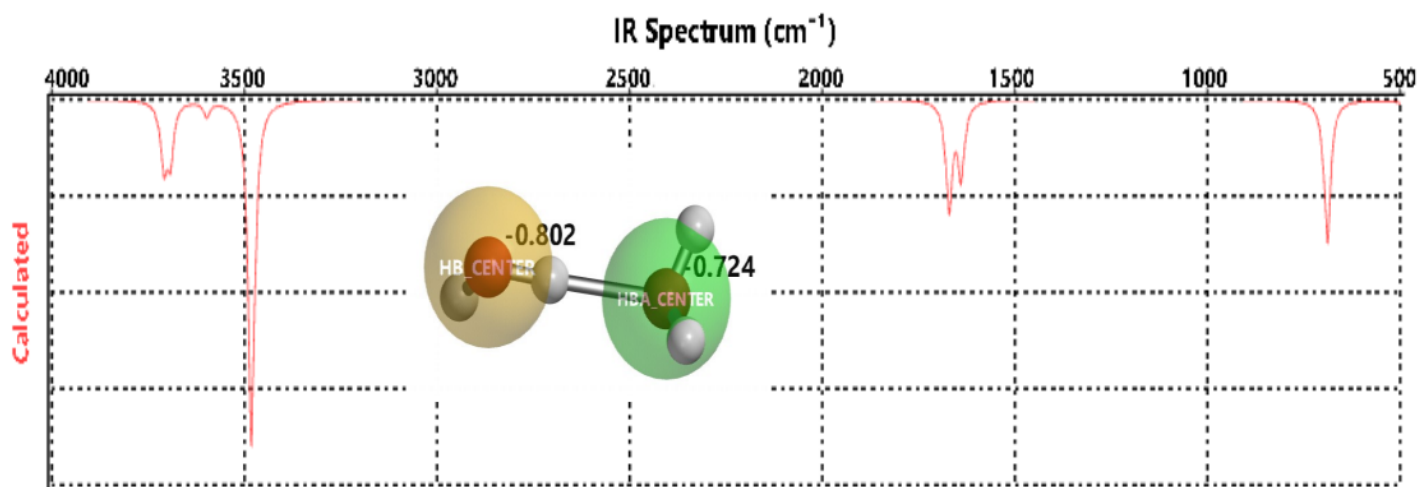


Figure 7

Water Dimer Donor (O4) and Acceptor (H2) Atoms Give Two Separate Split in O-H Vibration Mode of IR as Computed via EDF2/6-31G* in Spartan 18.

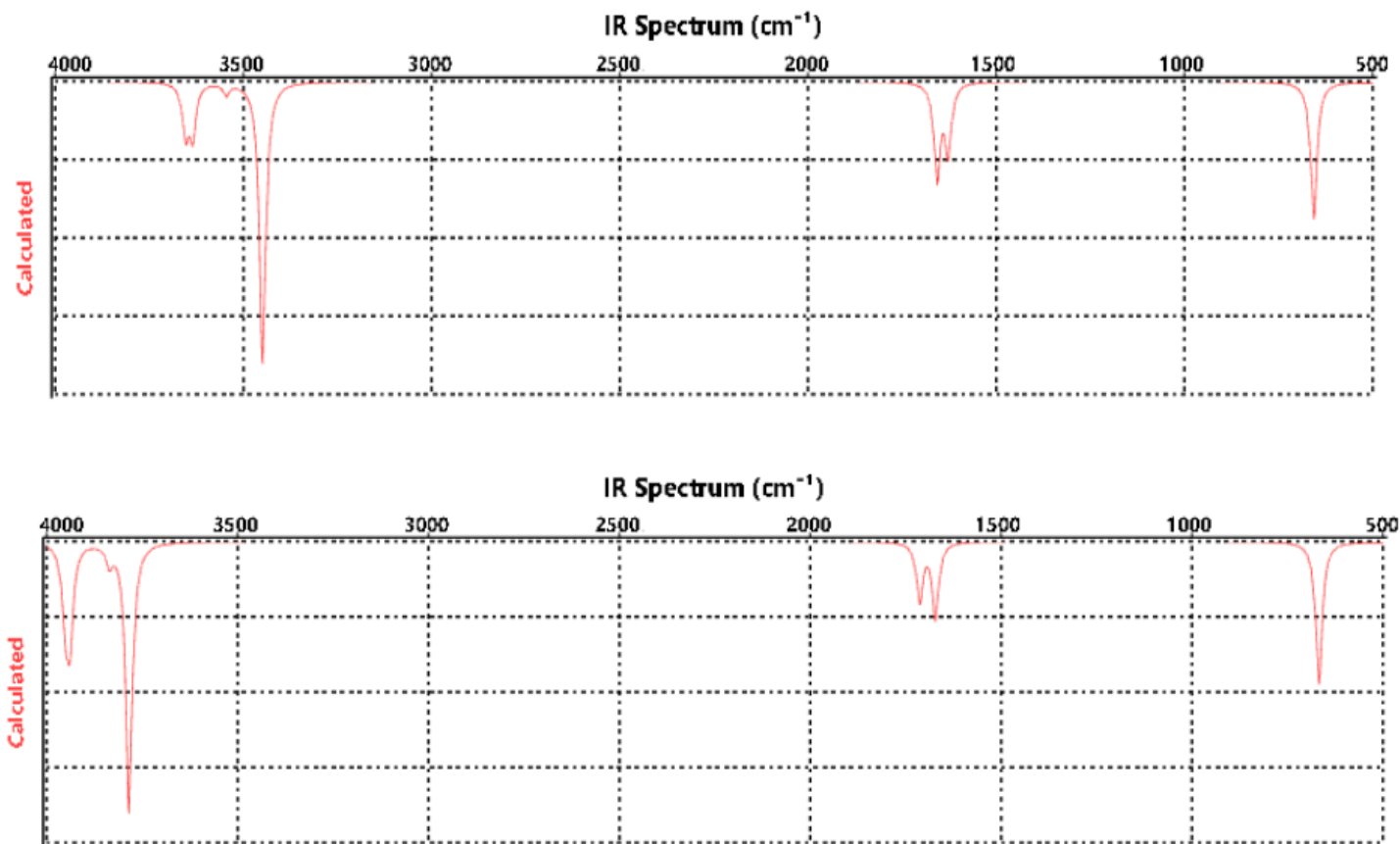


Figure 8

IR Spectra Computed via DFT/wB97/6-31G* (Top) and MP2/ccPVDZ (bottom) as Implemented in Spartan 18.

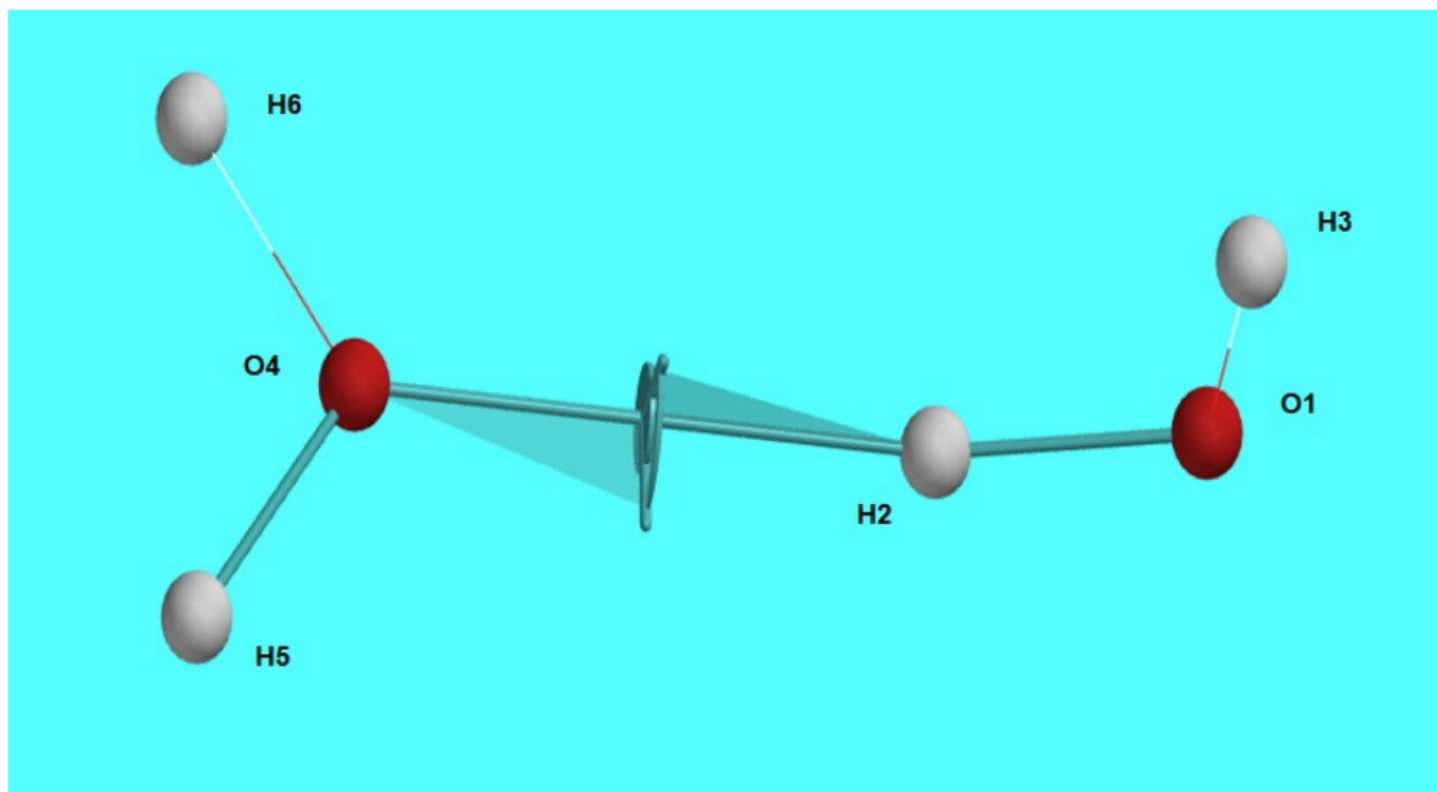


Figure 9

Water Dimer Dihedral Plane H5O4H2O1 of Rotation for MM and QM based Torsion around H-bond Linking Water Monomers.

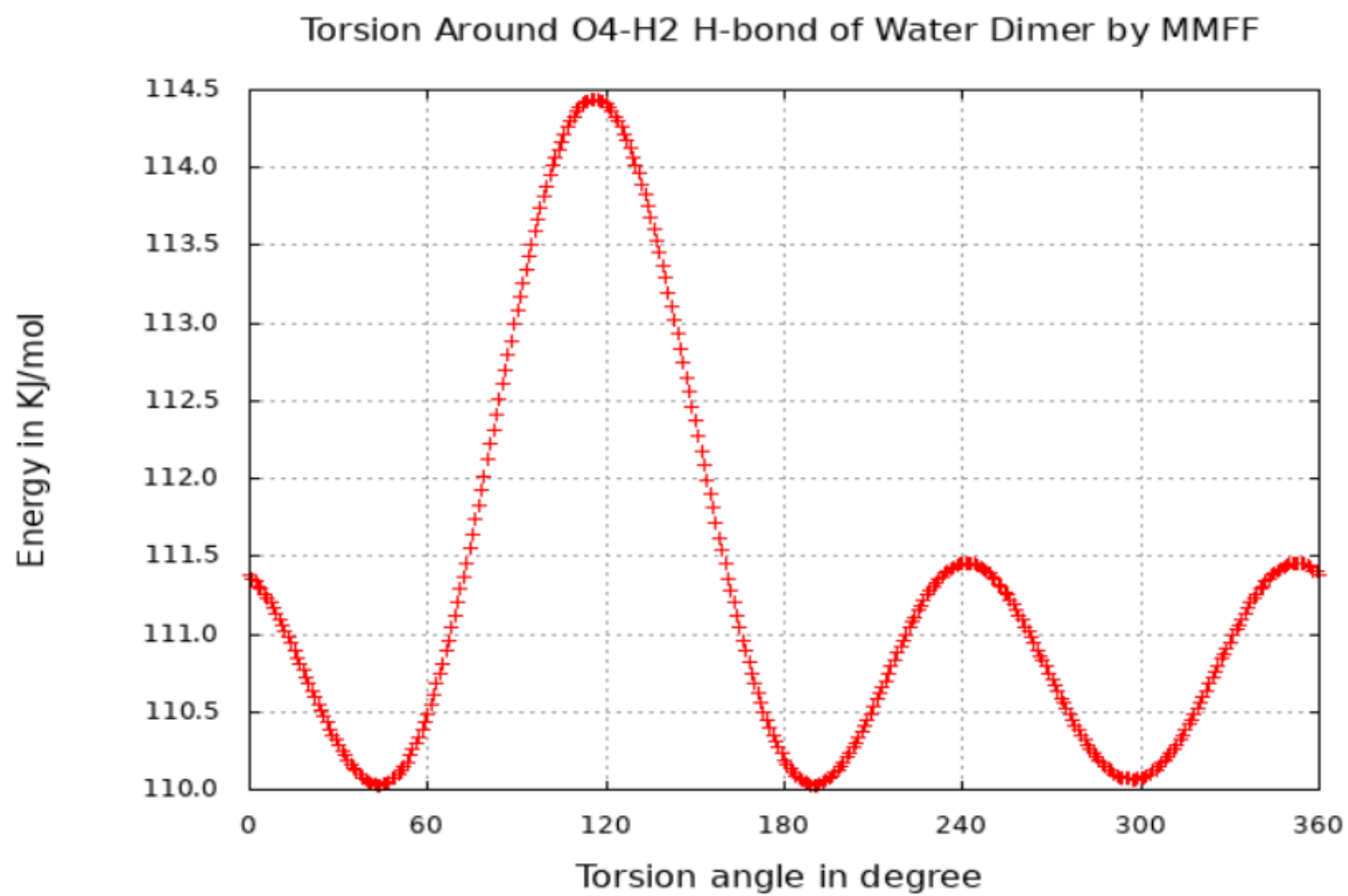


Figure 10

Molecular mechanics based torsion potential scan of water dimer around O4H2 H-bond by MMFF method.

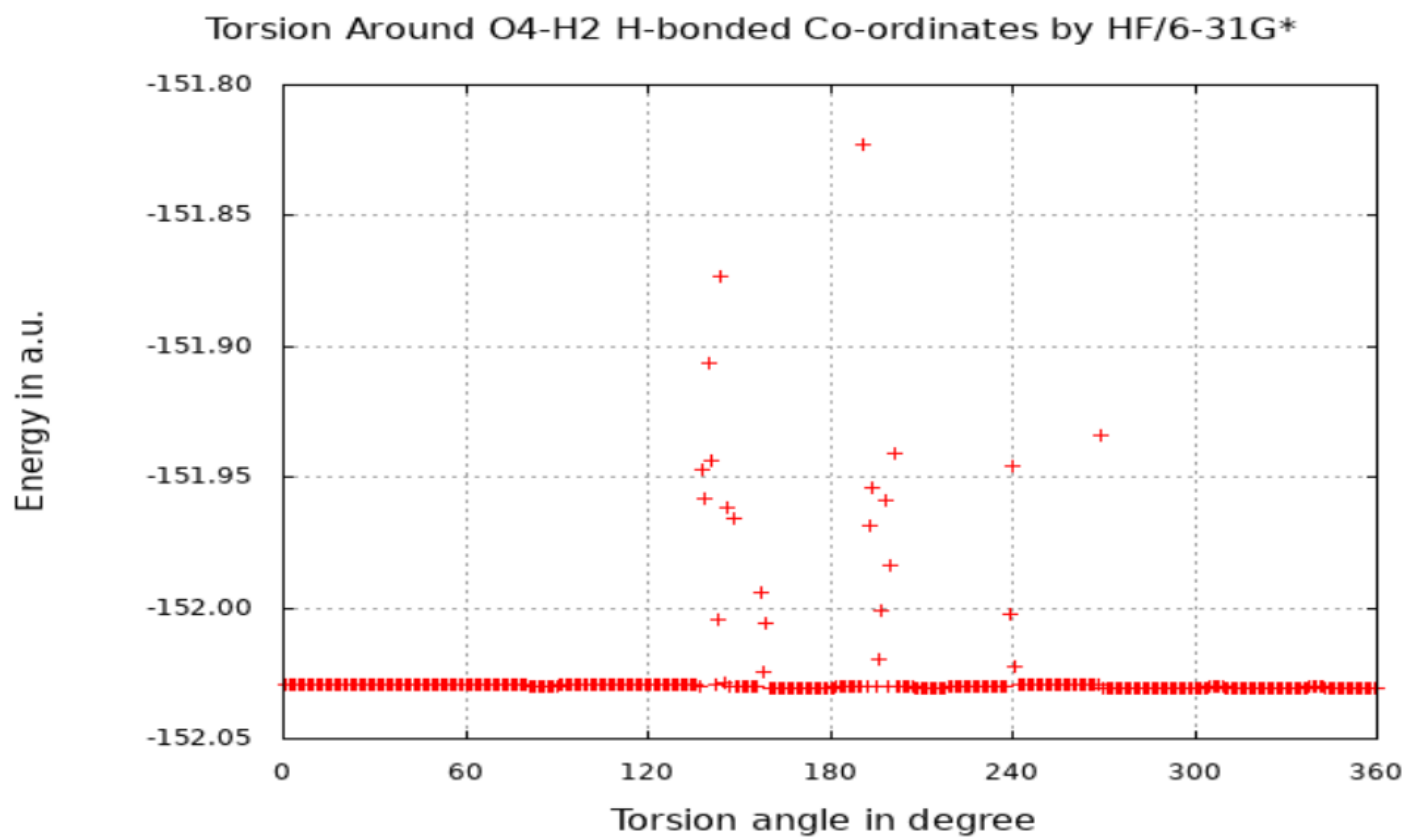


Figure 11

First principle based torsion potential scan of water dimer around O4H2 H-bond by HF/6-31G* method.

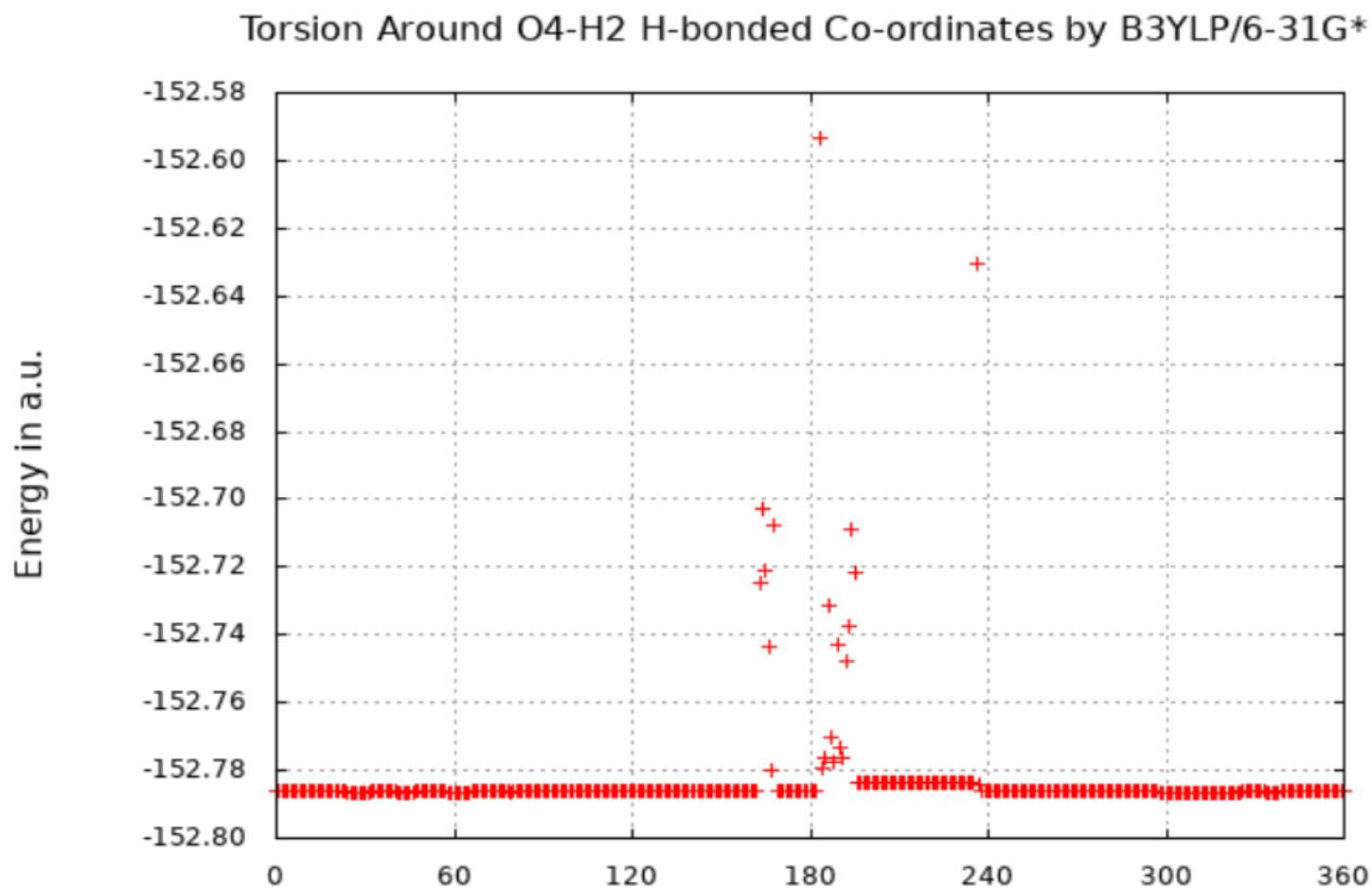


Figure 12

First principle based torsion potential scan of water dimer around O4H2 H-bond by B3YLP/6-31G* method.

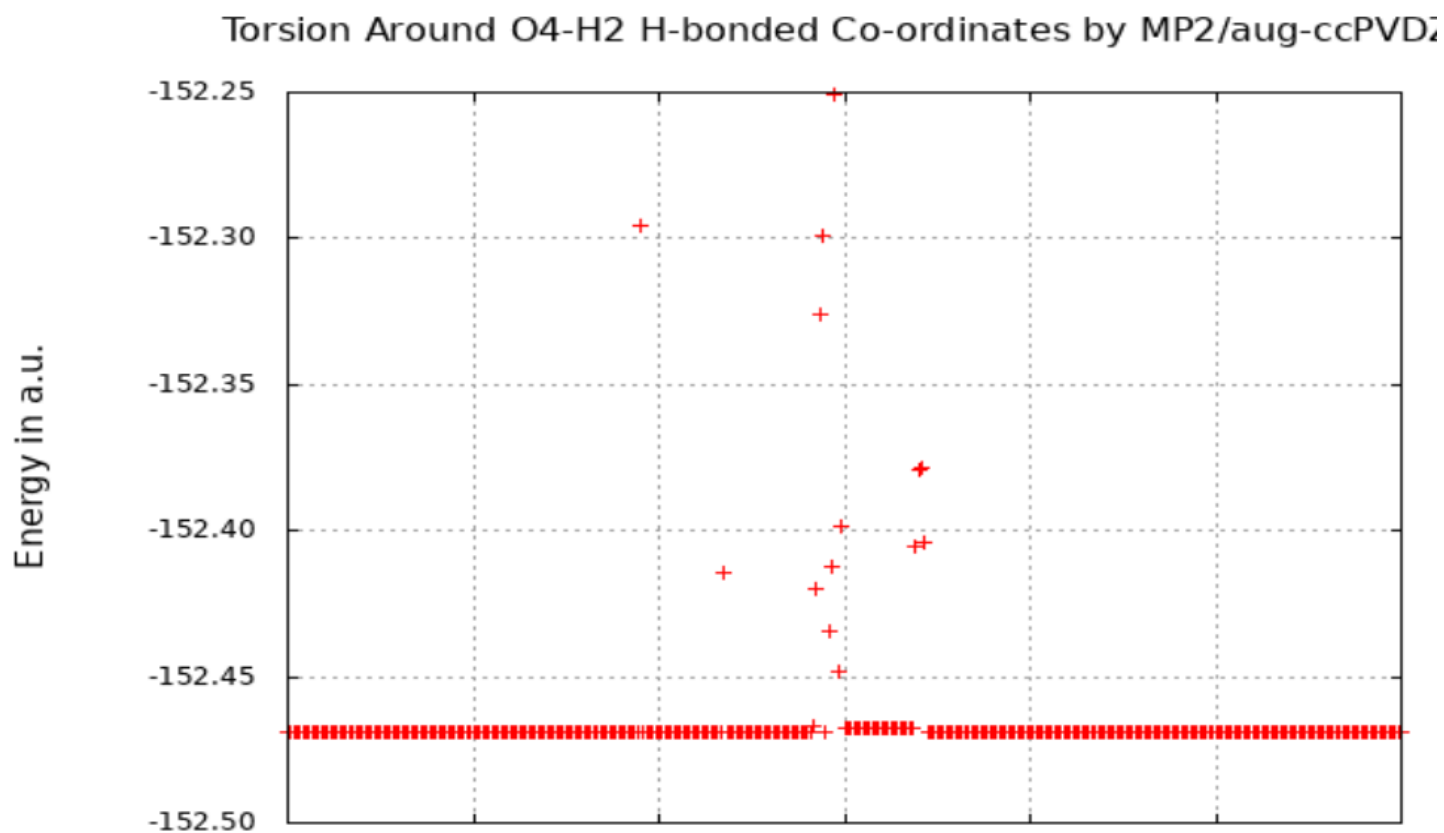


Figure 13

First principle based torsion potential scan of water dimer around O4H2 H-bond by MP2/aug-ccPVDZ method.

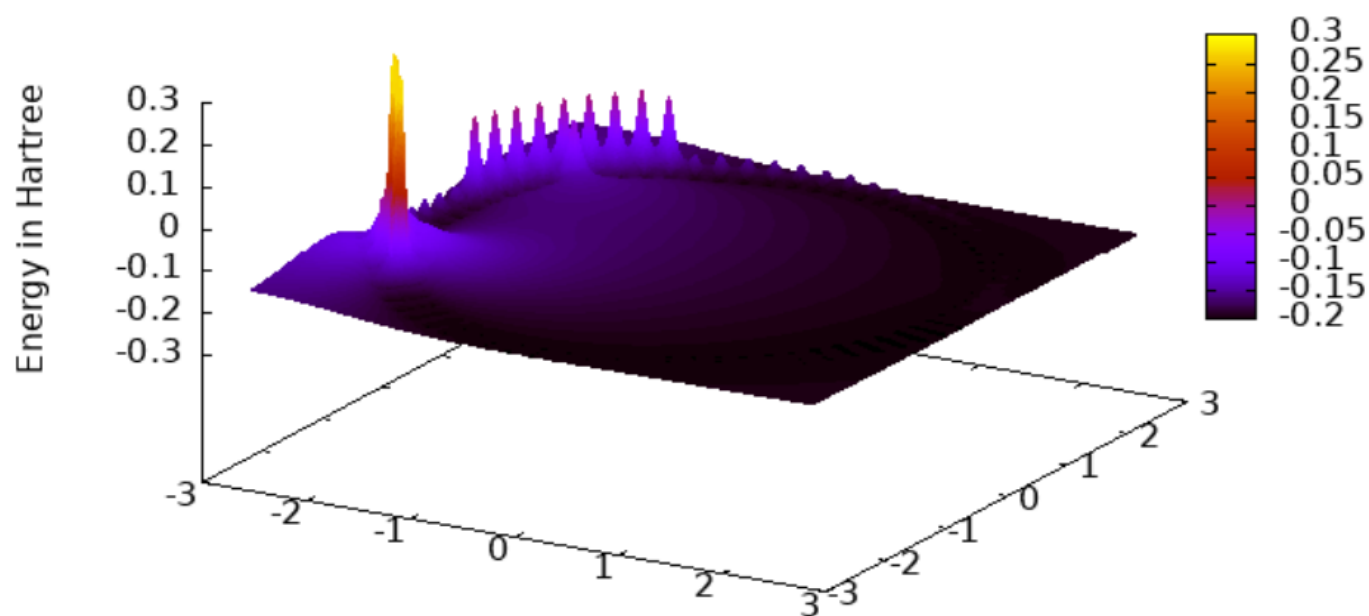


Figure 14

Anisotropic Singularities in H-bond Potential in Torsion Space Computed in Bond-Breaking Critical Range in Gas Phase by AM1 Method.

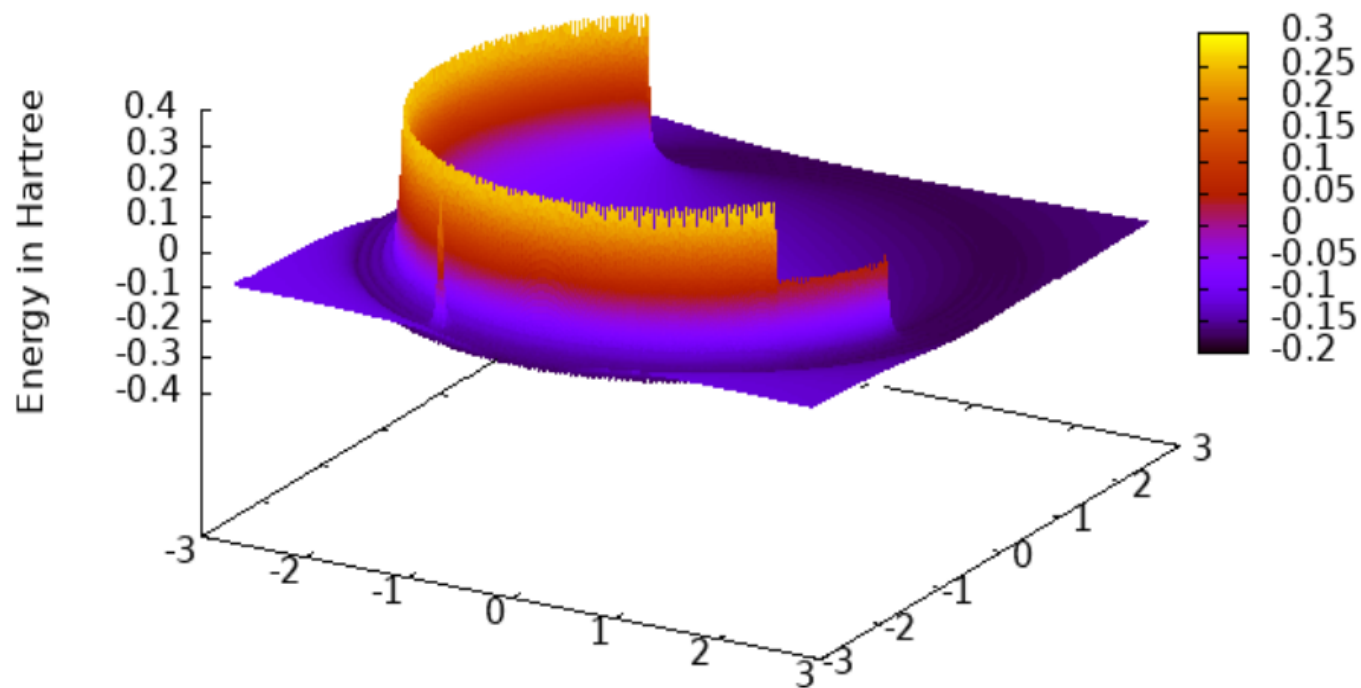


Figure 15

Anisotropic Singularities in H-bond Potential in Torsion Space Computed in Bond-Breaking Critical Range in Gas Phase by PM3 Method.

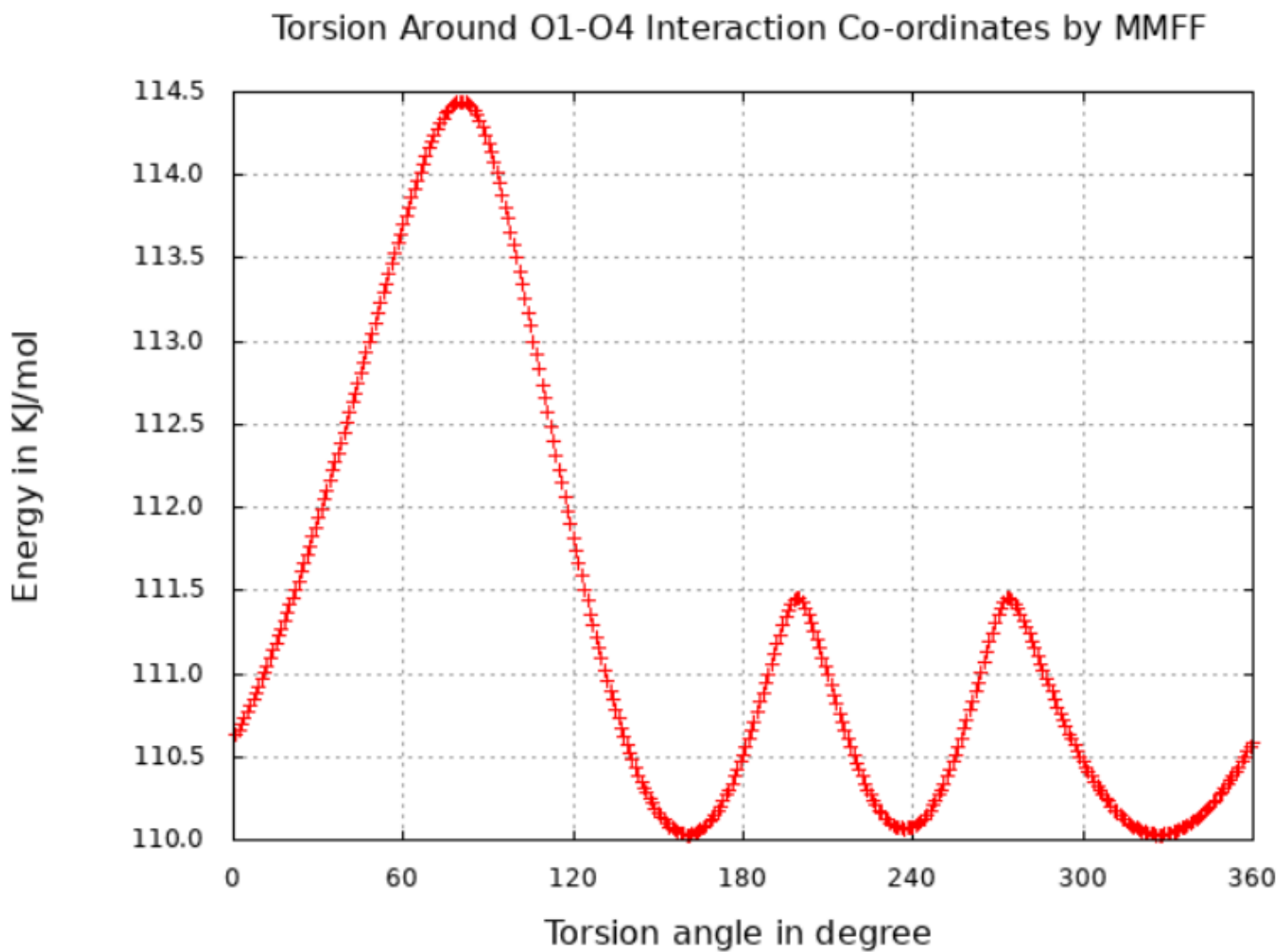


Figure 16

Molecular mechanics based torsion potential scan of water dimer around O1-O4 interaction co-ordinates by MMFF method.

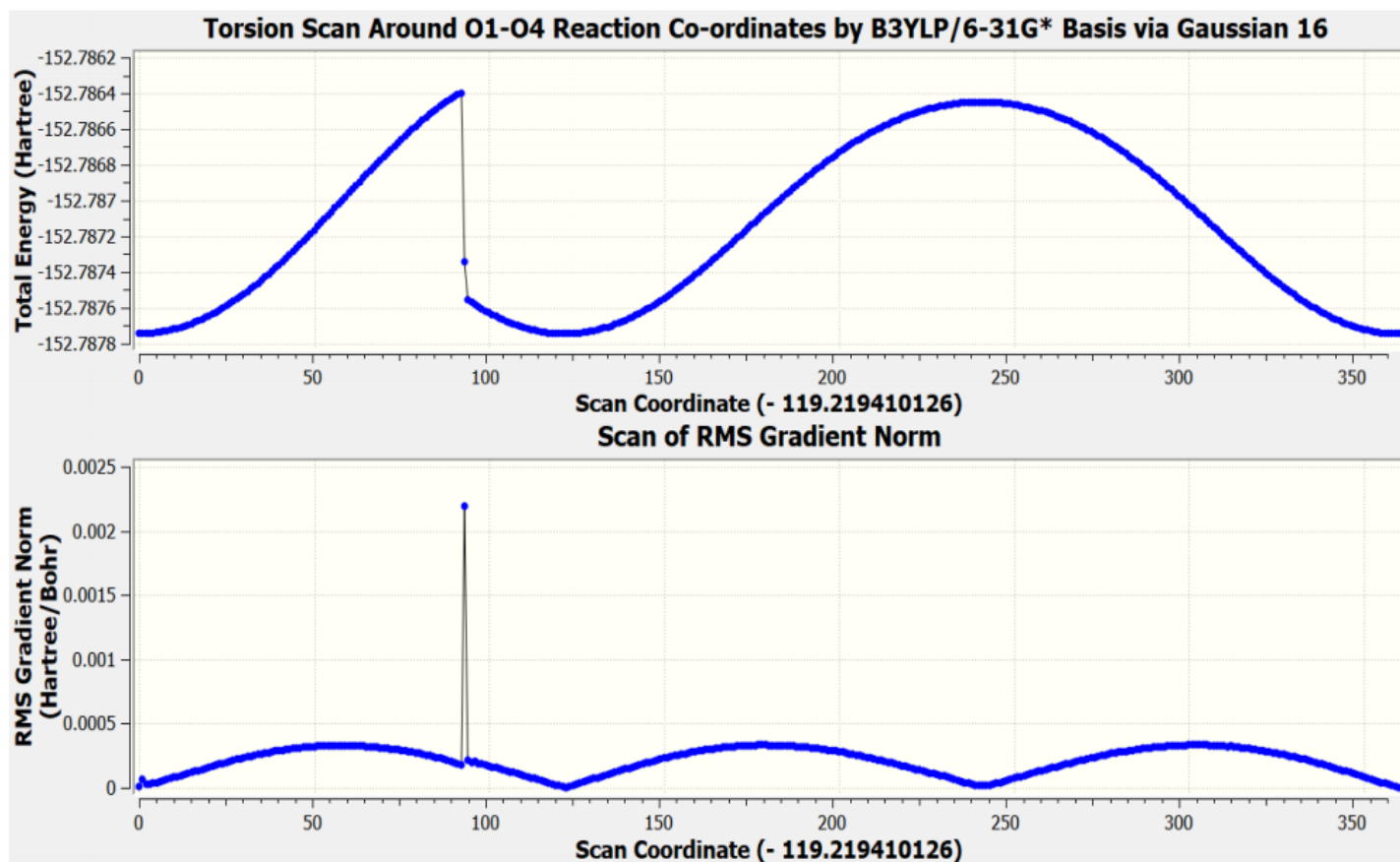


Figure 17

Torsion Scan Around O1-O4 by DFT B3YLP/6-31G* Basis as Applied in Gaussian 16.

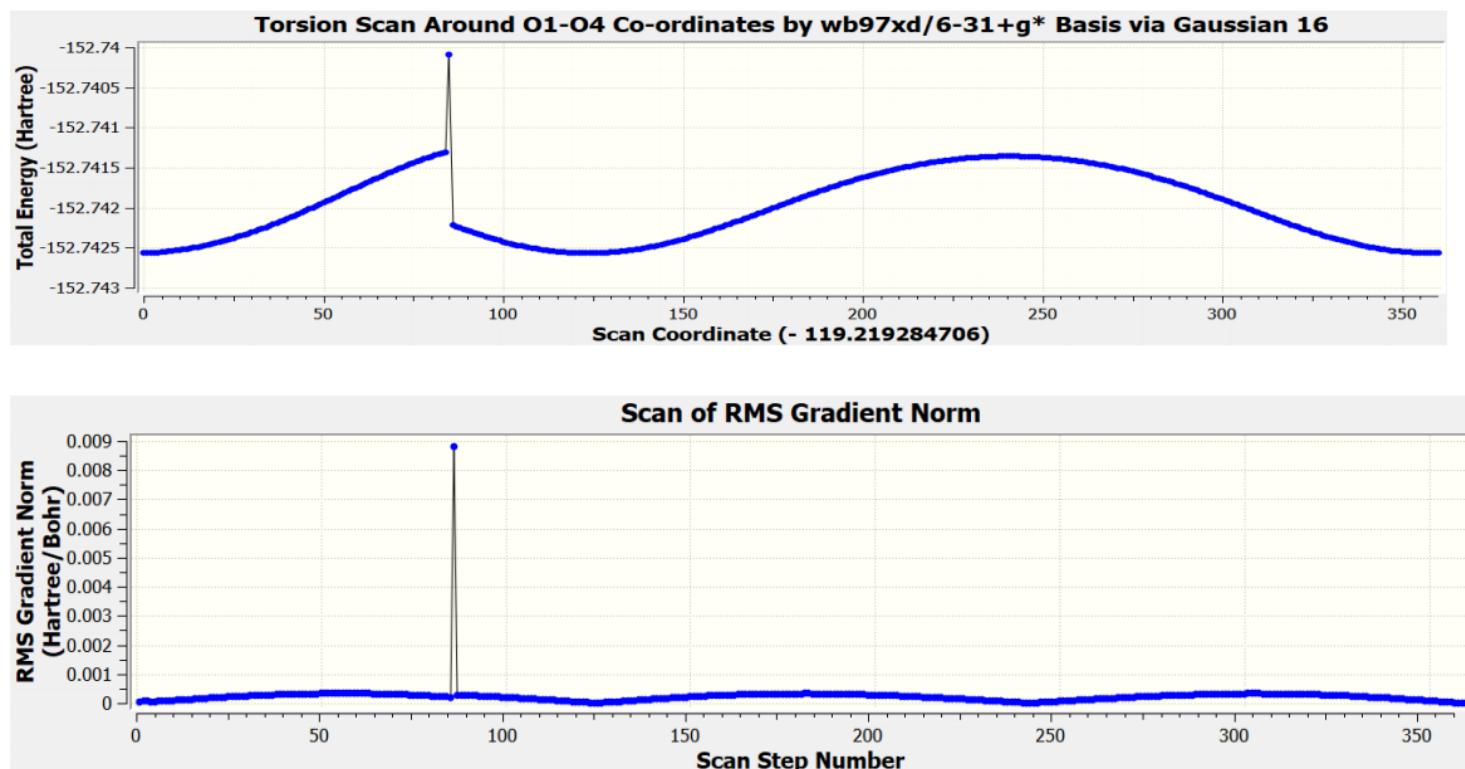


Figure 18

Torsion Scan Around O1-O4 by DFT wB97xd/6-31G* Basis as Applied in Gaussian 16.

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