

## Density Functional Theory for Calculating the OH Stretching Frequency of Water Molecules

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**ABSTRACT.** The anharmonic frequency of a local OH stretching mode of a water monomer and dimer was calculated using various levels of density functional theory. The quantum chemical potential energy curves as a function of the OH bond distance were calculated, and they were fitted with the Morse potential function to analytically obtain the fundamental transition frequency. By comparing those values with the frequencies similarly calculated using an *ab initio* quantum chemical method, the coupled cluster theory including both single and double excitations with the perturbative inclusion of triple excitation in the complete basis limit, the accuracy of various density functional methods in the calculation of anharmonic vibration frequency of water molecules was assessed. For a water monomer, X3LYP and B3LYP methods give the best accuracy, whereas for a water dimer, B972, LCBLYP,  $\omega$ B97X,  $\omega$ B97 methods show the best performance.

**Key words:** Anharmonic frequency, Water molecule, OH bond

### INTRODUCTION

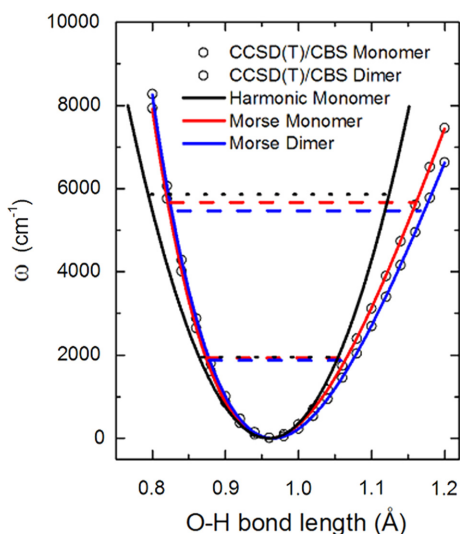
The stretching frequency of hydrogen-bonded OH bond in liquid water is sensitive to its environment, and thus the OH stretching frequency has been obtained experimentally for providing information about molecular structure and dynamics. Theoretical analyses often help one interpret the experimental data.<sup>1</sup> To reproduce the experimental results, quantum chemical calculation on water molecules in many molecular configurations is essential. Therefore, it is necessary to have quantum chemical calculation methods that take minimal time, and a reasonable choice would be the density functional theory (DFT) that satisfies the conditions of high accuracy and low calculation costs. Indeed, in computational and theoretical chemistry, studies on the OH stretching frequency calculation of H<sub>2</sub>O molecules in small water clusters have been actively performed using the DFT methods.

However, water molecules in the liquid phase experience strong hydrogen bonding, and thus the vibrational motions of hydrogen atoms differ according to their hydrogen bond strength. Therefore, the identification of a density functional theory that can reproduce the changes in OH stretching frequency resulting from changes in hydrogen bond strength is an important issue. With such an objective, an *ab initio* quantum chemical method, CCSD(T), which is one of the coupled cluster theories and is regarded as the standard of modern quantum chemistry, was used to calculate the single-point potential energies of an OH oscillator. We con-

sidered a water monomer and dimer where the latter is the smallest unit with hydrogen bonding. The calculation results are shown in *Fig. 1* with the curves fitted by the Morse function, and the analytically calculated frequencies are shown in *Table 1*.

*Fig. 1* shows that, with the increase of OH bond length from the equilibrium value, the increase in potential energy is slower in dimer compared to in monomer. In other words, the restoring force of hydrogen atom is smaller in dimer than in monomer, resulting in decrease of stretching frequency. Because of the interaction with other molecules, the frequency of dimer becomes lower than that of monomer. *Table 1* shows that the frequency difference between monomer and dimer is 130 cm<sup>-1</sup>. In other words, the frequency is sensitive to the strength of interaction of the hydrogen atom with other molecules. However, because of limited information on what DFT method effectively calculates the changes in OH frequency, it is difficult to validate whether the DFTs used in the theoretical calculation of the OH frequency of water such as the examples discussed above are appropriate in predicting the actual frequency of liquid water.

To overcome such uncertainty and effectively predict frequencies, the calculations for water clusters should be performed with many DFT methods and the most accurate one should be selected. However, prior to such calculations, CCSD(T) and various DFT methods were used to calculate the potential energy as a function of the bond lengths of OH (with hydrogen bonding in dimers) for the



**Figure 1.** Potential energy of an OH bond in water monomer and dimer calculated by CCSD(T) (open circles), fitting results using Morse potential function (red and blue curves), and harmonic potential energy of water monomer (black curve). The complete basis limit (CBS) is explained below.

**Table 1.** Harmonic frequency of water monomer and Morse frequencies of water monomer and dimer

	Harmonic	Morse/monomer	Morse/dimer
Frequency (cm <sup>-1</sup> )	3903	3723	3593

experimentally optimum structures of water monomer and dimer. The obtained potential curves were approximated by Morse potential function to calculate the  $1 \leftarrow 0$  transition energy.

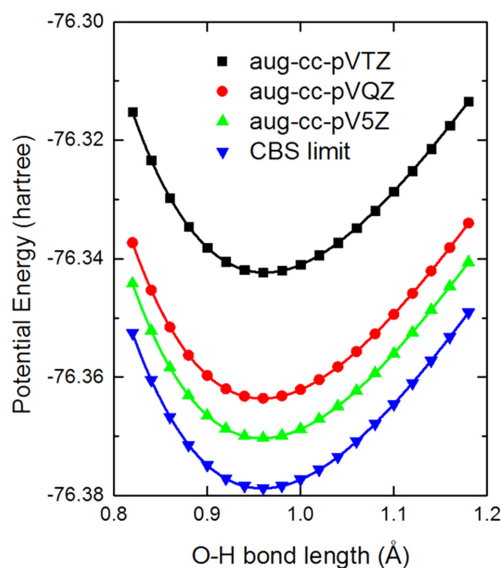
## THEORY AND CALCULATION METHOD

To find the optimal calculation method for the stretching frequency of a water molecule for the experimentally determined structures of water monomer and dimer, the single-point energies of nineteen molecular configurations, which are obtained by varying the OH distance with 0.02 Å interval from 0.82 to 1.18 Å were calculated using Gaussian 09 package and CCSD(T) methods with the basis sets, aug-cc-pVDZ and aug-cc-pVTZ.

Using the CBS limit discussed below, the extrapolated energies were obtained for the energies of monomer and dimer.

$$E_{\infty}^{tot} = \frac{3^{\alpha}}{3^{\alpha}-2^{\alpha}} E_3^{HF} - \frac{2^{\alpha}}{3^{\alpha}-2^{\alpha}} E_2^{HF} + \frac{3^{\beta}}{3^{\beta}-2^{\beta}} E_3^{cor} - \frac{2^{\beta}}{3^{\beta}-2^{\beta}} E_2^{cor} \quad (1)$$

The subscripts 2 and 3 of HF and cor energy symbol refer to the SCF and correlation energies calculated from aug-



**Figure 2.** Single-point energy curves as a function of the OH bond length of water monomer calculated by CCSD(T) using four basis sets.

cc-pVDZ and aug-cc-pVTZ basis sets, respectively. This method was used in all the nineteen configurations of monomer and dimer to obtain the potential energy curves from the extrapolated values with CBS limit.

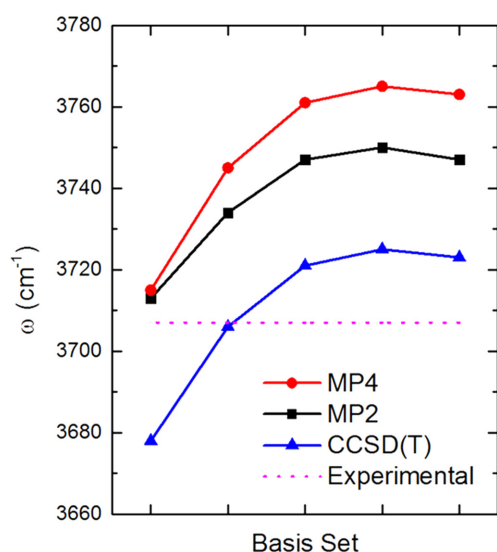
To validate the CBS limit extrapolation, CCSD(T) was used to obtain the potential energy curve of a water monomer. The basis sets were aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z, and the calculation results of CBS limits on these four basis sets are shown in Fig. 2. As the size of the basis set used in the calculation increases, the potential curve converges to the CBS limit. In other words, the results in the graph validate the CBS limit extrapolation determined by equation (1).

However, the objective of this study was not to obtain the potential energy curve, but the OH frequency. Therefore, the OH frequencies in water monomer were obtained by the three theoretical methods, MP2, MP4, and CCSD(T), using the five basis sets, aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, aug-cc-pV5Z, and CBS limit. The results are shown in Fig. 3.

As shown in Fig. 3, as the size of the basis set increases, the frequency converges to the CBS limit. Although aug-cc-pV5Z predicts a slightly higher frequency compared to the CBS limit, the difference is small enough to be negligible. Therefore, the CBS limit extrapolation in equation (1) can be concluded as valid for the frequency calculation.

## RESULTS AND DISCUSSION

The calculations with the *ab initio* methods discussed



**Figure 3.** The fundamental transition frequency of water monomer, calculated by MP2, MP4, and CCSD(T) methods with five basis sets. Basis sets from the left to the right are aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, aug-cc-pV5Z, and CBS limit.

above were repeated by DFT methods for the experimental structures of monomer and dimer. The following nineteen DFT methods were considered in this paper: exchange-correlation functional methods, BLYP, PBE/PBE, and PW91/PW91; hybrid functional methods, B3LYP, X3LYP, B971, B972, B98, APF, B2PLYP, PBE1PBE, BHandHLYP, M052X, and M062X; and long-ranged corrected functional methods, LC- $\omega$ PBE, LC-BLYP, CAM-B3LYP,  $\omega$ B97, and  $\omega$ B97X. The basis sets used in the DFT calculations were 6-311+G(3df, 3pd). The calculated single-point energies were fitted to the Morse potential function:

$$V(r) = D(1 - e^{-a(r-r_e)})^2 + m \quad (2)$$

Here,  $D$  is the bond dissociation energy,  $r_e$  is the OH equilibrium bond length, and  $a$  is a parameter reflecting the gradient of the function.  $m$  is the potential energy when the OH bond length is in equilibrium. From the Morse function expressed by equation 2, the analytic expression of the vibrational energy was obtained as following:

$$\tilde{G}(v) = \left(v + \frac{1}{2}\right) - \chi_e \tilde{v} \left(v + \frac{1}{2}\right)^2, \tilde{v} = \frac{a}{2\pi c} \sqrt{\frac{2D}{\mu}} \quad (3)$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \chi_e = \frac{hc\tilde{v}}{4D} \quad (4)$$

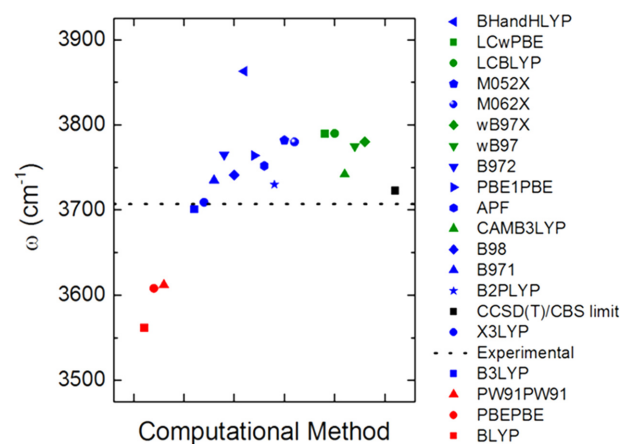
$$\Delta \tilde{G}_{v+\frac{1}{2}} = \tilde{G}(v+1) - \tilde{G}(v) = \tilde{v} - 2(v+1)\chi_e \tilde{v} \quad (5)$$

$$\Delta \tilde{G}_{\frac{1}{2}} = \tilde{v} - 2\chi_e \tilde{v} = \tilde{v} \left(1 - \frac{hc\tilde{v}}{2D}\right) \quad (5)$$

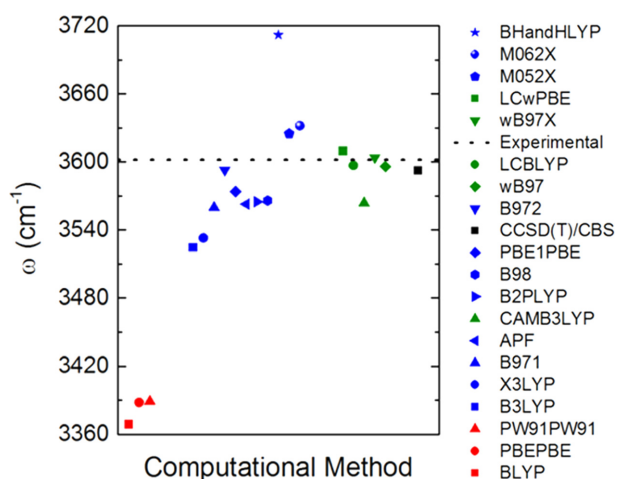
Using the Origin 9.0 Program, the calculated quantum chemical potential energies were fitted to the Morse function to determine  $D$  and  $a$ . To determine the reduced mass of an OH oscillator in equation (3), a diatomic approximation that assumes HOH to be a two-body divided into HO and H was employed, and the reduced mass is 0.9514 amu. The  $R^2$  value obtained for the fit was 0.99998, which is almost identical to that obtained from the fit for the potential energies obtained by the previous ab initio methods. The calculated frequencies for water monomer and dimer are shown in Figs. 4 and 5.

Figs. 4 and 5 show that the frequencies calculated by the CCSD(T)/CBS for the monomer and dimer were 3723  $\text{cm}^{-1}$  and 3593  $\text{cm}^{-1}$ , respectively, which are similar to the respective experimental values, 3707  $\text{cm}^{-1}$  and 3602  $\text{cm}^{-1}$ .<sup>6,7</sup> The calculated results in Figs. 4 and 5 exhibits a tendency that, even though there are a few exceptions, the frequencies of dimers are predicted to be more red-shifted than the experimental value is.

The results show that a few DFT methods give better results, which are closer to the experimental values, compared to the CCSD(T) method. That is, B3LYP and X3LYP methods predict the closest values to the experimental data for the monomer while the methods predict significantly different values from the experimental value for the dimer. However, B972, LC-BLYP,  $\omega$ B97X, and  $\omega$ B97 methods predict very close values to the experimental data for dimer while they are worse in monomer frequency. Therefore, because the accuracy of DFT methods differs according to the OH bond environment, it is difficult to conclude



**Figure 4.** Fundamental transition frequency of a local OH stretching of water monomer calculated by various DFT methods and CCSD(T)/CBS. The experimental value was assumed to be the average (3706.5  $\text{cm}^{-1}$ ) of the symmetrical (3657.1  $\text{cm}^{-1}$ ) and asymmetrical (3755.9  $\text{cm}^{-1}$ ) stretching frequencies of gaseous monomer.<sup>6</sup> This average value is similar to the experimental OH frequency of isotope HDO, 3707.5  $\text{cm}^{-1}$ .<sup>6</sup>



**Figure 5.** Fundamental transition frequency of a local OH stretching of water dimer calculated by various DFT methods and CCSD(T)/CBS. The experimental frequency of the hydrogen-bonded OH bond in a dimer was obtained as  $3601\text{ cm}^{-1}$ .<sup>7</sup>

that the DFT methods provide effective predictions for water clusters and also for a general molecular system. Thus, the validity of the DFT methods does not appear to be concluded from the calculations of water monomer and dimer alone. Therefore, it would be necessary to use the CCSD(T) calculation results as the standard for frequency calculation for a more expanded molecular cluster system.

In this study, the range of OH bond length was varied from 0.82 to 1.18 Å, and the obtained single-point energies were fitted to the Morse function to obtain the stretching frequency. The above range was used to minimize the difference between the frequencies of single-point potential curves for  $1 \leftarrow 0$  and the Morse potential curves obtained from the fitting, thus determining the accurate Morse frequencies.

As a harmonic oscillator function can only be approximated within a limited range of OH distance, the range for the validity of Morse potential function is also limited. We determined the range from the calculations by B3LYP/6-311++G\*\*. When the range is extended, for example, to 0.6572–1.7572 Å, the Morse frequency of water monomer was obtained as  $3817\text{ cm}^{-1}$ , and the  $R^2$  value of the Morse function was 0.99908. However, when the present range was employed, the  $R^2$  value increases up to 0.99998 which implies the fitted Morse function is almost completely overlap with the discrete set of single-point energies and the frequency was calculated to be  $3705\text{ cm}^{-1}$ . A significant difference (of  $\sim 112\text{ cm}^{-1}$ ) is created in the frequency by changing the range of displacement variation. The broader range for dimer gives an  $R^2$  value of 0.99992 and a frequency of  $3587\text{ cm}^{-1}$ , whereas the present range gives an  $R^2$  value of 0.99999 and a frequency of  $3529\text{ cm}^{-1}$ . Hence, the broader

range results in a higher error of  $\sim 58\text{ cm}^{-1}$ . If the range of displacement is narrower than 0.82–1.18 Å, the stretching displacement in the excited vibrational state cannot be sufficiently reflected in the calculation. Therefore, in this study, the stretching displacement range of 0.82–1.18 Å was selected.

Further, the Morse potential function was used to approximate the quantum chemically calculated potential energy because the vibrational motion of water molecules is anharmonic, and thus the approximation with a harmonic oscillator function would result in a significant error. To quantitatively estimate the extent of anharmonic characteristics of water molecules, the single-point values from the CCSD(T)/CBS limit of water monomer were approximated using the harmonic function. To obtain the harmonic frequency, we employed the Taylor expansion for the quantum chemical potential energies:

$$V(x) = \sum_{n=1}^{\infty} \left\{ \frac{x^n}{n!} \cdot \left[ \frac{d^n N}{dx^n} \right]_{x=0} \right\} \quad (6)$$

Here, the potential energy at the equilibrium distance is set to zero. The 1<sup>st</sup> order term is the force at the equilibrium OH distance, it becomes zero. And if the range of OH bond length is limited to near the equilibrium, the higher order terms can be neglected, resulting in the following equation.

$$V(x) = \frac{1}{2!} \cdot \left[ \frac{d^2 V}{dx^2} \right]_{x=0} \cdot x^2 \quad (7)$$

The second-order derivative in Equation 7 is the force constant  $k$ . Thus, if the OH bond length is near the value of equilibrium, the above mentioned harmonic function can be used.

To determine the force constant  $k$ , the quantum chemical energy was fitted to the Morse potential function (Equation 2), and the 2<sup>nd</sup> order with respect to OH bond distance was performed to obtain the following equation.

$$\frac{d^2 V}{dx^2} = 2Da^2(2e^{-ax} - 1) \cdot e^{-ax} \quad (8)$$

Here, a substitution of  $x = 0$  was made to Equation 8, giving the value of  $k$  as  $2Da^2$ . Finally, the harmonic function can be written as follows when the OH bond distance is near the equilibrium.

$$V(r-r_e) = Da^2(r-r_e)^2 \quad (9)$$

The use of this harmonic function to obtain the transition energy of  $1 \leftarrow 0$  yields the following equation.

$$\Delta \tilde{G} = \left( v + \frac{1}{2} \right) \tilde{\nu}, \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c} \sqrt{\frac{2Da^2}{\mu}} = \frac{1}{\pi c} \sqrt{\frac{Da^2}{2\mu}} \quad (10)$$

$$\Delta\tilde{G}_{v+\frac{1}{2}} = \tilde{G}(v+1) - \tilde{G}(v) = \tilde{\nu} \quad (11)$$

The harmonic potential curve and the 0-1 vibrational transition energies of monomer obtained from Equations 10 and 11 are shown in *Fig. 1* and *Table 1*. As shown in *Fig. 1*, the shapes of the Morse potential function curves of water monomer and dimer differ from the harmonic function curves of water molecules; this illustrates that the OH bonds in water molecules are not harmonic oscillators.

Based on the difference in the fundamental transition energies shown in *Fig. 1*, the difference in the vibrational energy in the harmonic and Morse functions and the difference in the Morse vibrational energy between the monomer and dimer are  $\sim 150\text{--}200\text{ cm}^{-1}$ . As shown in *Table 1*, the actual  $1 \leftarrow 0$  frequencies in the Morse curves of harmonic function and monomer and the Morse curves of monomer and dimer show a significant difference of  $130\text{--}188\text{ cm}^{-1}$ , indicating the significant anharmonic characteristics of water molecules in vibrational motion.

Because of the above-mentioned reasons, the frequency calculation of the hydrogen-bonded OH stretching of water molecules, an approximation of potential curves using a harmonic function, results in a significant error, and thus a curve approximation method that can effectively incorporate the anharmonic characteristics of OH vibrational motion should be identified and selected. The present paper shows that the potential curve for each configuration of monomer and dimer was accurately approximated using the Morse function, and thus the use of Morse function on the OH potential curves of water molecules can be concluded as valid.

## CONCLUSION

In this study, a quantum chemical density functional method was identified to quantitatively calculate the OH stretching vibrational energy of water monomer and dimer. An analysis comparing the experimental data and DFT calculation results showed that X3LYP and B3LYP methods for monomer and B972, LCBLYP,  $\omega$ B97X, and  $\omega$ B97 methods for dimer are appropriate methods that provide accurate results.

X3LYP functional method was shown to give accurate predictions of the stable structure and bond energy of molecular systems such as water clusters where the dispersion force interactions including hydrogen bonding are important.<sup>8,9</sup> However, the present study shows that performance of X3LYP in the calculation of anharmonic vibration frequency of dimer becomes worse. To accurately calculate the anharmonic frequency, accurate calculations of the potential energy of the nonequilibrium structures for the extended

or contracted bond length of the oscillator are needed. Therefore, we think that X3LYP functional method has a lower performance in the calculations of the potential energy of the nonequilibrium structure of dimers with hydrogen bonding.

In this study, no DFT theory could accurately predict the OH frequencies of both monomer and dimer. Nevertheless, the ab initio method CCSD(T) provides relatively consistent results for the monomer and dimer, and thus this method could be used as the quantum chemical standard to calculate the frequency in larger molecular clusters.

In many studies that use quantum chemical calculations, the frequency calculations for an anharmonic oscillator are conducted by obtaining the harmonic frequency first, followed by a modification, multiplying the value by a frequency factor. Thus, for oscillators such as liquid water under diverse environmental conditions, the anharmonic characteristics of one oscillator can differ according to the environmental condition, resulting in a large frequency range. Therefore, the method involving the multiplication of harmonic frequency by frequency factor cannot be used in this case. The vibrational perturbation theory should be employed to approximate the anharmonic characteristics,<sup>10</sup> or as in this study, the nonuniform anharmonic potential energy should be directly obtained, followed by frequency calculation.

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