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Ab initio studies of the water dimer using large basis sets: The structure and thermodynamic energies

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Ab initio calculations with various large basis sets have been performed on the water dimer in order to study the structure, energetics, spectra, and electrical properties. As a reference system, the calculations of the water monomer were also performed. The second order Møller-Plesset perturbation theory (MP2) using a large basis set (O:13s,8p,4d,2f/H:8s,4p,2d) well reproduces various water monomer experimental data except for the somewhat underestimated absolute energy and hyperpolarizability. The monomer energy calculated with the fourth-order Møller-Plesset perturbation theory (MP4) with the above basis set is -76.407 hartrees, which is only 0.073 hartree above the experimental energy. To compare the theoretical and experimental dimer structures and thermal energies accurately, we summarized the quantum statistical thermodynamic quantities with corrections for anharmonic vibration, rotation, rotation-vibration coupling, and internal rotation. With the correction for the anharmonic binding potential and rotation, the predicted interoxygen distance of the dimer is 2.958 Å, which is so far the closest to the experimental value ~ 2.976 Å. The predicted dimer dipole moment is 2.612 D, which is the first agreement with experiment (2.60–2.64 D). The predicted frequency shift of the dimer with respect to the monomer is in good agreement with experiment. With the MP2 calculation using the large basis set, the basis set superposition error correction (BSSEC) of the dimer is only 0.33 kcal/mol, which is by far the smallest among the MP2 results reported. Without BSSEC, the predicted binding energy, enthalpy, free energy, and entropy are all in good agreement with experiment within the error bounds, whereas with BSSEC, some of them seem to be slightly off the experimental error bounds. Nevertheless, the results with BSSEC can be more reliable than those without BSSEC.

I. INTRODUCTION

Since the original matrix isolation for the water dimer by Pimentel and collaborators,¹ experimental methods to determine the structure, binding energy, dipole moment, and spectra of the water dimer have progressed considerably.^{2–13} Along with the experimental progress, a number of theoretical studies of the water dimer have been performed.^{14–21} The information of the accurate structure and energetics of the dimer is very useful to test and refine water-water interaction potential parameters, which are essential for studies of systems in the condensed phase.

As for the dimer structure, there have been some discrepancies between calculations and experiments. Most serious is the discrepancy for the interoxygen distance [$R(\text{O}-\text{O})$], followed by the discrepancy for the angle (ψ) between the interoxygen distance vector and the molecular plane of the proton-accepting monomer. The experimental values for $R(\text{O}-\text{O})$ and ψ are 2.976 Å and $57^\circ \pm 10^\circ$, respectively.³ As an early study, Clementi *et al.*¹⁴ reported extensive Hartree-Fock (HF) results that the interoxygen distance is 3.02 Å and $\psi = 38^\circ$. In general, the interoxygen distance predicted by HF calculations is slightly long, whereas that predicted by post-HF calculations is slightly short. The angle of ψ is in most cases predicted to be somewhat

smaller than the experimental value. With extensive MP2 calculations, Schaefer *et al.*¹⁵ first predicted the ψ in excellent agreement with experiment, but the predicted interoxygen distance (2.91 Å) is rather short.

In addition, as for the binding energy (BE) for the association of two water monomers, there are some controversies over the basis set superposition error correction (BSSEC). The binding energies calculated without BSSEC are in good agreement with the experimental value of -5.44 ± 0.7 kcal/mol, while those calculated with BSSEC are too underestimated, or at best near the upper bound of the experimental value. Nevertheless, Bartlett *et al.*¹⁶ reported that the uncorrected binding energy varies widely with the basis set, while the corrected energy converges smoothly. Thus, they favored the corrected energy which was estimated to be -4.7 ± 0.35 kcal/mol. The most recent extensive work was given by Clementi *et al.*¹⁷ reporting the corrected and uncorrected energies of -5.09 and -5.79 kcal/mol, respectively.

Therefore, one may doubt if the results from extensive calculations using very large basis sets can show excellent agreement with the experiments. For this reason, we study the structure, energetics, and electrical properties of the water dimer with high levels of *ab initio* calculations using very large basis sets with varieties. The calculations of the

water monomer have also been performed as the reference system of the dimer.

II. CALCULATION METHOD

For *ab initio* calculations of the water dimer, we used very large Gaussian basis sets with varieties [6,3,3/3,3], [7,4,2,1/4,2,1], [6,4,3,1/4,3,1], and (13,8,4,2/8,4,2). Here, we use the conventional notations with the primitive and contracted basis sets in parenthesis and brackets, respectively. The numbers in each parentheses (or brackets) denote the numbers of basis functions from the lowest (i.e., *s* function) to the highest (i.e., *p*, *d*, or *f* function) angular momentum quantum number for O/H.

For comparison, we also used the double zeta plus polarization (DZ+P) basis set.²² For the polarization basis set, each O atom has a set of *d* functions with five components (to be denoted by 5*D*), and each H atom has a set of *p* functions with three components. Then, the DZ+P has 50 basis functions for the dimer. Our results are also compared with the results of the 6-311++G(2*d*,2*p*) basis set by Schaefer *et al.*,¹⁵ while some values not reported in their work have been calculated in this work for our discussion. This basis set using 5*D* has 94 basis functions for the dimer. All *ab initio* calculations in this work have been performed with GAUSSIAN90.²³ The levels of the calculations include HF, MP2, MP4(FC), and MP4. Here, "(FC)" denotes the calculation with frozen cores, while others denote full calculations without frozen cores.

For the basis set [6,3,3/3,3], we chose the geometrical basis set.²⁴ Stressing the polarization effects, each oxygen atom used 6*s*, 3*p*, and 3*d* functions (contracted from 13*s*, 8*p*, and 3*d*), while each hydrogen atom used 3*s* and 3*p* functions (contracted from 8*s* and 3*p*). With six-component *d* functions (6*D*), the total number of basis functions for the dimer is 114. The orbital exponents of the *j*th primitives of the geometrical basis set are defined by KC^{j-1} . The reference set (*j*=1) was chosen with $K=0.02$ and $C=2.75$.

The basis set [7,4,2,1/4,2,1] was contracted from van Duijneveldt's primitive basis sets²⁵ (511111,3111,11,1/4111,11,1). The exponents of two *d* and one *f* functions for O are 1.7, 0.425, and 1.4, respectively, while those for H are 1.5, 0.375, and 1.0, respectively. The *d* and *f* basis sets comprised five components (5*D*) and seven components (7*F*), respectively. Then, the total number of basis functions for the dimer is 132.

The basis set [6,4,3,1/4,3,1] was specially devised to reproduce the experimental electrical properties of the water monomer by Maroulis.²⁶ Consequently, the calculated dipole moment (μ), polarizability (α), and hyperpolarizability (β) of the water monomer were in excellent agreement with experiment in comparison with other extensive basis sets. With 5*D* and 7*F*, the total number of basis functions for the dimer is 152.

The largest basis set we used is (13,8,4,2/8,4,2), which comprises van Duijneveldt's primitive basis sets²⁵ (13,8/8) and polarization functions (4*d*+2*f*/4*p*+2*d*). For O, the 4*d* exponents are 4.0, 1.0, 0.25, and 0.0625 while the 2*f* exponents are 1.6 and 0.2, respectively. For H, the 4*p* ex-

ponents are 2.88, 0.72, 0.18, and 0.045, while the 2*d* exponents are 1.0 and 0.15, respectively. The *d* and *f* basis sets comprised five components (5*D*) and seven components (7*F*), respectively. Then, the total number of basis functions for the dimer is 262.

In this paper, the polarizability and the hyperpolarizability are given as the mean polarizability (α) and the vector component of the hyperpolarizability (β_μ) along the dipole moment direction (μ), respectively. Namely,

$$\alpha = \frac{1}{3} \sum_i \alpha_{ii},$$

$$\beta_\mu = \sum_i \beta_{i\mu} / |\mu|,$$

where

$$\beta_i = \sum_j \beta_{ij}.$$

Here, the dummy indices *i* (and *j*) denote *x*, *y*, and *z*.

III. THERMAL ENERGIES AND BOND STRETCHING

In order to accurately compare the theoretical and experimental thermal energies and bond lengths of the water dimer, we need to take into account the contribution from not only harmonic vibration, but also anharmonic vibration, rotation, rotation-vibration coupling, and internal rotation. This section summarizes such quantum mechanical contributions from a potential with weak anharmonicity (in Sec. III A), a Morse potential with vibration-rotation coupling (in Sec. III B), and the bond stretching due to coupling of harmonic vibration with rotation (in Sec. III C). The internal rotation correction is referred to in Pitzer's work.²⁷ To facilitate our discussion, we use the following conventional notations:

x is the coordinate of an oscillation which is the distance vector from the minimum position of a potential to an oscillating particle;

p is the generalized momentum corresponding to *x*;

m is the (reduced) mass of the particle;

k is the Boltzmann's constant;

T is the temperature of the system;

h is the Planck's constant;

\hbar is $h/2\pi$;

ω is the vibrational angular frequency corresponding to the harmonic component of the potential. We also use the following additional notations:

$$a = \frac{1}{2} m \omega^2;$$

$$v = \hbar \omega / kT.$$

A. A weak anharmonic potential

Let us consider a potential of

$$U(x) = U^{(0)}(x) + U^{(a)}(x),$$

where

$$U^{(o)}(x) = ax^2,$$

$$U^{(a)}(x) = bx^3 + cx^4.$$

Here, we assume that $bx^3 \ll ax^2$ and $cx^4 \ll ax^2$.

Hereafter, we use the superscripts “ (o) ” and “ (a) ” to denote the terms related to the harmonic and anharmonic potentials, respectively. The Hamiltonian of an oscillating particle in the weak anharmonic potential is

$$H(p, x) = H^{(o)}(p, x) + U^{(a)}(x),$$

where

$$H^{(o)}(p, x) = \frac{p^2}{2m} + U^{(o)}(x).$$

The n th excited energy in the harmonic potential $U^{(o)}(x)$ is

$$E_n^{(o)} = (n + \frac{1}{2})\hbar\omega,$$

while that in the potential $U(x)$ is

$$E_n = E_n^{(o)} + E_n^{(a)},$$

where, within the second-order perturbation,

$$E_n^{(a)} \approx E_n^{(1)} + E_n^{(2)} + \dots,$$

$$E_n^{(1)} = \langle n | U^{(a)} | n \rangle,$$

$$E_n^{(2)} = \sum_i' \frac{|\langle n | U^{(a)} | i \rangle|^2}{E_n^{(o)} - E_i^{(o)}}.$$

Here, the bra and ket vectors ($\langle n |$ and $| n \rangle$) are the eigenvectors corresponding to the eigenvalue $E_n^{(o)}$. The prime to the sum signifies that the term with $n=i$ must be omitted. Within the orders of $(b/a)^2$ and c/a , we have

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega - \frac{1}{64} \frac{b^2}{a^3} (11 + 30n + 30n^2) - \frac{1}{16} \frac{c}{a^2} (3 + 6n + 6n^2) + \dots$$

Then, the canonical partition function Q is

$$Q = \sum_n e^{-E_n/kT} = \sum_n \exp[-(E_n^{(o)} + E_n^{(a)})/kT] = Q^{(o)} Q^{(a)},$$

where

$$Q^{(o)} = \sum_n e^{-E_n^{(o)}/kT} = \sum_n e^{-(n+1/2)v} = 1 / \left(2 \sinh \frac{v}{2}\right),$$

$$Q^{(a)} = 1 - (E_n^{(1)} + E_n^{(2)})/kT + \frac{1}{2} (E_n^{(1)})^2/(kT)^2 + \dots$$

Thus, the Helmholtz free energy (A), entropy (S), and internal energy (E) are as follows:

$$A = A^{(o)} + A^{(a)},$$

$$S = S^{(o)} + S^{(a)},$$

$$E = E^{(o)} + E^{(a)},$$

where

$$A^{(o)} = kT \ln \left(2 \sinh \frac{v}{2}\right),$$

$$TS^{(o)} = kT \left[-\ln \left(2 \sinh \frac{v}{2}\right) + \frac{v}{2} \coth \frac{v}{2} \right],$$

$$E^{(o)} = kT \frac{v}{2} \coth \frac{v}{2},$$

$$A^{(a)} \approx \left(-\frac{11}{64} \frac{b^2}{a^3} + \frac{12}{64} \frac{c}{a^2} \right) (\hbar\omega)^2 + \left(-\frac{15}{16} \frac{b^2}{a^3} + \frac{12}{16} \frac{c}{a^2} \right) \times (kT)^2 \left(\frac{v}{2} \operatorname{csch} \frac{v}{2} \right)^2,$$

$$TS^{(a)} \approx \left(\frac{15}{8} \frac{b^2}{a^3} - \frac{12}{8} \frac{c}{a^2} \right) (kT)^2 \left(\frac{v}{2} \operatorname{csch} \frac{v}{2} \right)^2 \left(\frac{v}{2} \coth \frac{v}{2} \right),$$

$$E^{(a)} \approx \left(-\frac{11}{64} \frac{b^2}{a^3} + \frac{12}{64} \frac{c}{a^2} \right) (\hbar\omega)^2 + \left(\frac{15}{16} \frac{b^2}{a^3} - \frac{12}{16} \frac{c}{a^2} \right) \times (kT)^2 \left(\frac{v}{2} \operatorname{csch} \frac{v}{2} \right)^2 \left(2 \frac{v}{2} \coth \frac{v}{2} - 1 \right).$$

It should be noted that the zero-point vibrational energy is

$$E_{T=0}^{(o)} = \hbar\omega/2,$$

$$E_{T=0}^{(a)} = \left(-\frac{11}{64} \frac{b^2}{a^3} + \frac{12}{64} \frac{c}{a^2} \right) (\hbar\omega)^2.$$

The average position of the oscillating particle is given by

$$\langle x \rangle = \operatorname{Tr}(xe^{-H/kT}) / \operatorname{Tr}(e^{-H/kT}) \approx -\frac{3}{4} \frac{b}{a^2} kT \left(\frac{v}{2} \coth \frac{v}{2} \right).$$

B. A Morse potential with rotation-vibration coupling

When a body of two particles (with the reduced mass m) rotates in a Morse potential

$$U(r) = D_e(1 - e^{-s(r-r_e)})^2,$$

Pekeris²⁸ showed that the energy levels are

$$E_{n,J} \approx \hbar\omega(n + \frac{1}{2}) - \chi_e \hbar\omega(n + \frac{1}{2})^2 + BJ(J+1) - DJ^2(J+1)^2 - F(n + \frac{1}{2})J(J+1).$$

Here, r is the interparticle distance of the body in motion, while r_e is that in the minimum potential without rotation; and n and J are the principal and angular momentum quantum numbers, respectively. The other notations denote

$$I_e = mr_e^2, \quad \chi_e = \frac{\hbar\omega}{4D_e},$$

$$B_e = \frac{\hbar^2}{2I_e}, \quad D = \frac{4B_e^3}{(\hbar\omega)^2},$$

$$F = \frac{6B_e^2}{\hbar\omega} (sr_e - 1), \quad B = B_e - \frac{F}{2}.$$

Then, the canonical partition function is

$$Q = \frac{1}{\sigma} \sum_n \sum_J (2J+1) e^{-E_{n,J}/kT}.$$

Here, σ is the symmetry number, which is set to 1 for a heterodiatom system. Using the perturbation technique along with the Euler–Maclaurin summation formula for the sum over J , we have

$$Q = Q^{(*)} Q^{(c)} \approx \frac{kT}{\sigma B} \frac{1}{2 \sinh(v/2)} e^{(\chi_e/4)v} \left[1 + \frac{2D}{B^2} kT + 2\chi_e v \frac{e^{-v}}{(1-e^{-v})^2} + \frac{F}{B} \frac{e^{-v}}{1-e^{-v}} + \frac{1}{3} \frac{B}{kT} + \dots \right],$$

where

$$Q^{(*)} = \frac{kT}{\sigma B} \frac{1}{2 \sinh(v/2)}.$$

Hereafter, we use the superscript “(*)” to denote the case for the sum of the rotation and harmonic vibration motions without their coupling. The superscript “(c)” will be used to denote the correction for the anharmonic vibration and rotation–vibration coupling. Then, we have

$$A = A^{(*)} + A^{(c)},$$

$$S = S^{(*)} + S^{(c)},$$

$$E = E^{(*)} + E^{(c)},$$

where

$$A^{(*)} = kT \{ \ln[2 \sinh(v/2)] + \ln(\sigma B/kT) \},$$

$$TS^{(*)} = kT \left\{ -\ln[2 \sinh(v/2)] + \frac{v}{2} \coth \frac{v}{2} \right\}$$

$$-kT \ln(\sigma B/kT) + kT,$$

$$E^{(*)} = kT \left(\frac{v}{2} \coth \frac{v}{2} + 1 \right),$$

$$A^{(c)} \approx -\frac{\chi_e}{4} \hbar\omega - \frac{2D}{B^2} (kT)^2 - 2\chi_e \hbar\omega \frac{e^{-v}}{(1-e^{-v})^2}$$

$$- \frac{1}{2} \frac{F}{B} kT \coth \frac{v}{2} - \frac{1}{3} B,$$

$$TS^{(c)} \approx \frac{4D}{B^2} (kT)^2 + 2\chi_e \hbar\omega \frac{ve^{-v}(1+e^{-v})}{(1-e^{-v})^3}$$

$$+ \frac{F}{B} kT \left[\frac{1}{2} \coth \frac{v}{2} + \frac{ve^{-v}}{(1-e^{-v})^2} \right],$$

$$E^{(c)} \approx -\frac{\chi_e}{4} \hbar\omega + \frac{2D}{B^2} (kT)^2$$

$$+ 2\chi_e \hbar\omega \frac{e^{-v}}{(1-e^{-v})^2} \left[\frac{v(1+e^{-v})}{1-e^{-v}} - 1 \right]$$

$$+ \frac{F}{B} \hbar\omega \frac{e^{-v}}{(1-e^{-v})^2} - \frac{1}{3} B.$$

C. Bond length change due to coupling of harmonic vibration with rotation

The Schrödinger equation of a rotating diatomic molecule with the harmonic interatomic potential is

$$\frac{d^2 R}{dr^2} + \left[-\frac{J(J+1)}{r^2} + \frac{2m}{\hbar^2} \left(E - \frac{m}{2} \omega^2 (r-r_e)^2 \right) \right] R = 0,$$

where R is the radial wavefunction of r , and E is the energy. Putting

$$x = r - r_e,$$

we have

$$r^{-2} \approx r_e^{-2} \left(1 - \frac{2x}{r_e} + \frac{3x^2}{r_e^2} \right).$$

Thus, the Schrödinger equation becomes

$$\frac{d^2 R}{dr^2} + \left\{ \left[\frac{2mE}{\hbar^2} - J(J+1)r^{-2} \right] + 2J(J+1)r_e^{-3}x - \left[\frac{m\omega}{\hbar^2} + 3J(J+1)r_e^{-4} \right] x^2 \right\} R = 0.$$

Putting

$$x = y + \delta,$$

the above Schrödinger equation can be reduced to a simple harmonic oscillator by eliminating the first-order term of y with

$$\delta = \frac{J(J+1)r_e^{-3}}{m\omega/\hbar^2 + 3J(J+1)r_e^{-4}}.$$

Since for the new harmonic oscillator the expectation value of $\langle y \rangle$ is 0, we have

$$\langle x \rangle = \langle y \rangle + \langle \delta \rangle = \langle \delta \rangle \simeq \left\langle r_e \frac{J(J+1)\hbar^2}{m\omega^2 r_e^4} \right\rangle.$$

Since

$$E_{n,J}^{(*)} = (n + \frac{1}{2})\hbar\omega + BJ(J+1)$$

and

$$Q^{(*)} = \sum_n \sum_J \frac{(2J+1)}{\sigma} e^{-E_{n,J}^{(*)}/kT} = \frac{kT}{\sigma B} \frac{1}{2 \sinh(v/2)},$$

the expectation value of $\langle x \rangle$ is

$$\langle x \rangle = \frac{2kT}{mr_e\omega^2} \frac{v}{2} \coth \frac{v}{2} = \frac{kT}{ar_e} \frac{v}{2} \coth \frac{v}{2}.$$

When the anharmonic vibration is included while neglecting the coupling of rotation with the anharmonic vibration, the total increment of the interatomic distance is

$$\Delta r \simeq \left(-\frac{3}{4} \frac{b}{a^2} + \frac{1}{ar_e} \right) kT \frac{v}{2} \coth \frac{v}{2}.$$

IV. THE WATER MONOMER

A large number of high levels of *ab initio* results are available for the water monomer.^{26,29} Nevertheless, to study the water dimer, the water monomer still needs to be studied as the reference system. Table I lists only the results of the monomer which are necessary for our discussion of the dimer. As to the structure, energetics, and electrical properties of the water monomer, the comparison of the calculation with experiments^{30–38} shows clearly the importance of large basis sets and electron correlation. The lowest monomer energy was obtained with the MP4 calculation using the basis set of (13,8,4,2/8,4,2). The energy of -76.407 hartrees is only 0.073 hartree above the experimental energy. This value is slightly lower than the most up-to-date value of -76.404 hartrees obtained from the MP2/(28,18,8,3/18,8,3) calculation by Clementi *et al.*,¹⁷ but the lowest energy among different calculational methods should be referred to the density functional calculation by Clementi *et al.*^{17,18}

For the structure of the water monomer, MP2/MP4 calculations with extended basis sets agree very well with experiment, whereas HF results are consistently somewhat off the experimental values. HF calculations with extended basis sets give slightly short bond distances for $R(\text{O-H})$ and slightly wide bond angles for $\angle\text{HOH}$. As to electrical properties, HF results are rather off experimental values. Even MP2 results give slightly large dipole moments and somewhat small polarizabilities. Only MP2 results with very large basis sets are in good agreement with experiment. The agreement of the MP2/(13,8,4,2/8,4,2) calculation with experiment is remarkable, in particular, for the dipole moment and polarizability, but the hyperpolarizability is still somewhat underestimated because the higher level of electron correlation needs to be taken into account.

Among the basis sets used here, the DZ+P basis set gives very poor electrical properties even with MP2 calculations. The 6-311G++(2d,2p) basis set gives somewhat better electrical properties, while the predicted dipole moment is still large. The [6,3,3/3,3] basis set gives very small atomic charges compared with other basis sets. Although this basis set seems to have many *d* functions in an unbalanced manner, the results of the monomer are rather in reasonable agreement with experiment except for a rather large value for β_μ . Excluding the largest basis set (13,8,4,2/8,4,2) used here, the MP2/[7,4,2,1/4,2,1] results are overall in the best agreement with experiment except for the somewhat underestimated polarizability.

In order to reproduce the experimental electrical properties of the water monomer, the exponents and coefficients for the basis set [6,4,3,1/4,3,1] were optimized by Marouli,²⁶ while the total energy lowering was sacrificed. Therefore, even though the basis set is very large, it gives much higher energy than other smaller basis sets, but the electrical properties are very close to the experimental values. Thus, it would be interesting to calculate the dimer structure with [6,4,3,1/4,3,1].

In Table II, the IR and Raman spectra for the monomer are listed along with their intensities. The vibrational frequencies from the MP4/[DZ+P] calculation are in reasonable agreement with experiment,^{7–13} but the MP2/[7,4,2,1/4,2,1] calculation gives a better agreement. Thus, it is more important to use a more extended basis set than a higher level of electron correlation calculation. The MP2/(13,8,4,2/8,4,2) harmonic vibrational frequencies are within 0.7% of (or 28 cm^{-1} from) the experimental frequencies. The IR intensities are in reasonable agreement with the experimental values of the monomer in the Ar matrix. Some deviations are naturally expected due to the difference between the IR intensities with and without the Ar matrix.

V. THE WATER DIMER

Various experimental data are available for the water dimer, as shown in Table III. Dyke and Muentzer first reported the linear structure of the water dimer based on molecular beam electron resonance spectroscopy and microwave spectroscopy.² The experimental value of the interoxygen distance^{2,3} is 2.97–2.98 Å and that of the dipole moment^{3–5} is 2.60–2.64D. Measuring thermal conductivity, Curtiss *et al.*⁶ reported that the enthalpy change (ΔH) and entropy change (ΔS) for the association of two monomers at 373.15 K are -3.59 ± 0.5 kcal/mol and -18.59 ± 1.3 cal/mol/K, respectively. From their equilibrium constant (0.0111 atm^{-1}), the Gibbs free energy change (ΔG) is 3.34 kcal/mol. Using the zero point vibrational energy (ZPVE) and thermal energy based on a somewhat simple *ab initio* calculation of the dimer, they estimated the binding energy as -5.44 ± 0.7 kcal/mol. The IR spectra of the dimer are also available,^{8–13} as shown in Table II(A).

A number of theoretical studies for the water dimer have been done by using *ab initio* calculations^{14–21} and pair potential methods.^{39–42} For the dimer, several conformations such as linear, bifurcated, cyclic, and closed shapes

TABLE I. Energetics, structure, and electrical properties of the water monomer.^a

	Energy (hartree)	ZPVE ^b (kcal/mol)	E_{therm}^c (kcal/mol)	S^0 (cal/mol/K)	$R(\text{O-H})$ (Å)	$\angle\text{HOH}$ (Å)	$q(\text{O})$ (e^+)	$q(\text{H})$ (e^+)	μ (D)	α (a.u.)	β_{d} (10^{-30} esu)
Exp.	-76.480 2 ^d	13.18 ^c	1.775 ^f	45.10 ^g	0.957 ^h 0.957 ⁱ 0.959 ^j	104.5 ^h 105.0 ⁱ 103.9 ^j			1.855 ^k	9.64 ^l 9.82 ^m	-0.188 ⁿ
DZP											
HF	-76.046 80	14.59	1.778	44.96	0.944	106.7	-0.666	0.333	2.177	5.00	-0.131
MP2	-76.254 84	13.76	1.779	45.09	0.963	104.7	-0.646	0.323	2.161	5.32	-0.147
MP4(FC)	-76.252 75	13.73			0.963	104.7					
MP4	-76.267 12	13.75	1.779	45.09	0.963	104.7					
6-311++G(2d,2p)											
HF	-76.056 83	14.52	1.778	44.93	0.940	106.3	-0.472	0.236	2.015	7.18	-0.096
MP2	-76.317 35	13.61	1.779	45.06	0.957	104.3	-0.464	0.232	1.977	8.13	-0.130
[6,3,3/3,3]											
HF	-76.063 28	14.45	1.779	44.94	0.941	106.0	-0.272	0.136	1.919	7.42	-0.186
MP2	-76.336 40	13.57	1.778	45.07	0.958	104.5	-0.210	0.105	1.785	8.36	-0.270
MP4(FC)	-76.324 42				0.960	104.4					
[7,4,2,1/4,2,1]											
HF	-76.064 39	14.46	1.779	44.93	0.940	106.2	-0.521	0.260	1.981	6.86	-0.112
MP2	-76.356 96	13.59	1.779	45.07	0.958	104.1	-0.504	0.252	1.936	7.54	-0.147
(13,8,4,2/8,4,2)											
HF	-76.067 56	14.44	1.778	44.94	0.940	106.3	-0.517	0.259	1.937	8.32	-0.090
MP2	-76.391 18	13.50	1.779	45.07	0.959	104.2	-0.476	0.238	1.850	9.72	-0.152
MP4	-76.407 06 ^e										
[6,4,3,1/4,3,1]											
HF	-76.052 07	14.43	1.779	44.98	0.947	106.2	-0.831	0.415	1.966	8.40	-0.091
MP2	-76.275 75	13.35	1.779	45.15	0.970	103.9	-0.703	0.351	1.875	10.04	-0.151
[8,6,5,2/4,4,2]^p											
SDQ-MP4									1.854	9.50	-0.145
Energy(hartree)											
6-311++G(3df, 3pd)^q											
HF	-76.058 69				[9,6,3,2/6,3,2] ^r					(13,8,2,1/6,2,1) ^l	
MP2(FC)	-76.324 28				HF	-76.065 77	MP2			HF	-76.065 87
MP4(FC)	-76.338 68				[12,10,4,2/10,4,2] ^s					(28,18,8,3/18,8,3) ^u	
					HF	-76.067 34				HF	-76.067 42
					MRSD-CI	-76.3963				MP2	-76.404 04

^aThis table reports only the results of the water monomer which are necessary for our discussion of HF and post-HF results of the water dimer. Density functional results are given in Refs. 17 and 18; e.g., the lowest energy reported is -76.421 a.u. for the Clementi-Chakravorty model.

^bZero-point vibrational energy.

^cVibrational thermal energy at 25 °C.

^dReference 30.

^eReference 30(c).

^fWhen the temperature changes from 0 to 298.15 K, the enthalpy change is 2.367 kcal/mol (Ref. 31). E_{therm} was obtained by subtracting 0.592 kcal/mol from the enthalpy change.

^gReference 31.

^hReference 32.

ⁱReference 33.

^jReference 34.

^kReference 35.

^lStatic value obtained from dipole oscillator strength distribution (Ref. 36).

^mReference 37.

ⁿMeasured with d.c.-electric-induced second harmonic generation (Ref. 38).

^oCalculated at the MP2-optimized geometry.

^pReference 26.

^qReference 15.

^rReference 16.

^sReference 20.

^tReference 14.

^uReference 17.

TABLE II. IR and Raman spectra of the water monomer and dimer.^a (A) Experimental IR spectra ω_h (ω) (IR). (B1) Calculated IR and Raman spectra ω_h (IR, Raman) of the monomer and (B2) calculated IR and Raman spectra ω_h (IR, Raman) of the dimer. (C) Vibrational frequency shift of the dimer with respect to the monomer $\Delta\omega_h(\Delta\omega)$.

(A)	Monomer				Dimer		
	...	N ₂	Ar	...	N ₂	Ar	He
Matrix	$\omega_h(\omega)$	$\omega_h(\omega)$	(ω) (IR)	(ω)	$\omega_h(\omega)$	(ω)	(ω)
ν_3	3942(3756)	3913(3727)	(3733)(45)	(3730)	3899(3715)	(3726)	(3730)
ν_3				(3714)	3881(3699)	(3709)	(3722)
ν_1	3832(3657)	3808(3635)	(3638)(2)	(3600)	3797(3627)	(3634)	(3600)
ν_1				(3545)	3718(3550)	(3574)	(3532)
ν_2	1648(1595)	1649(1598)	(1590)(64)		1669(1619)	(1611)	
ν_2					1653(1601)	(1593)	
Ref. #	7	8	9,10	11	8	9	12

(B1)	DZP			6-311++G(2d,2p)		(6,3,3/3,3)		[7,4,2,1/4,2,1]		(13,8,4,2/8,4,2)	
	HF	MP2	MP4	HF	MP2	HF	MP2	HF	MP2	HF	MP2
	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h
	(IR,Raman)	(IR)		(IR,Raman)	(IR)	(IR,Raman)	(IR)	(IR,Raman)	(IR)	(IR,Raman)	(IR)
$\nu_3 b_2$	4290(73,37)	4056(86)	4038	4248(93,27)	3989(74)	4227(94,26)	3989(80)	4233(82,28)	3983(63)	4229(93,24)	3970(76)
$\nu_1 a_1$	4165(20,73)	3906(7)	3903	4148(20,73)	3869(10)	4129(11,76)	3868(1)	4133(16,71)	3859(7)	4128(15,86)	3843(6)
$\nu_2 a_1$	1753(112,6)	1663(45)	1675	1762(91,3)	1660(66)	1750(98,2)	1633(73)	1749(97,2)	1640(72)	1745(96,1)	1631(71)

(B2)	DZP			6-311++G(2d,2p)		(6,3,3/3,3)		[7,4,2,1/4,2,1]		[6,4,3,1/4,3,1]
	HF	MP2	MP4	HF	MP2 ^b	HF	MP2	HF	MP2	HF
	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h	ω_h
	(IR,Raman)	(IR)		(IR,Raman)		(IR,Raman)	(IR)	(IR,Raman)	(IR)	(IR,Raman)
$\nu_3 a''$ acceptor	4297(107,38)	4039(74)	4026	4238(114,25)	3975	4221(113,25)	3970(99)	4225(105,28)	3967(89)	4226(112,25)
$\nu_3 a'$ donor	4262(123,45)	4021(94)	4009	4227(136,36)	3958	4205(140,36)	3959(122)	4209(124,37)	3950(102)	4209(142,36)
$\nu_1 a'$ acceptor	4160(28,59)	3897(14)	3899	4141(25,56)	3858	4123(17,58)	3850(5)	4127(22,57)	3846(13)	4114(21,71)
$\nu_1 a'$ donor	4116(197,105)	3826(246)	3847	4102(195,107)	3774	4082(193,108)	3772(282)	4085(187,101)	3765(277)	4067(195,118)
$\nu_2 a'$ donor	1784(111,4)	1700(76)	1710	1783(68,2)	1687	1773(81,1)	1659(42)	1772(81,1)	1667(47)	1759(77,0)
$\nu_2 a'$ acceptor	1757(122,5)	1665(99)	1677	1765(108,2)	1661	1750(105,1)	1637(83)	1751(104,2)	1639(85)	1743(105,1)
a'' o.p. bend ^c	618(233,1)	679(185)	661	578(173,0)	661	573(145,0)	649(87)	568(167,0)	637(112)	569(13,0)
a' i.p. bend ^d	351(142,3)	396(102)	389	327(101,1)	377	322(93,1)	357(59)	317(103,1)	362(60)	307(98,0)
a' o-o stretch	170(116,0)	194(110)	189	162(195,0)	198	166(142,0)	192(143)	153(160,0)	182(59)	153(131,0)
a' i.p. bend ^e	146(210,1)	167(216)	166	134(102,0)	164	138(127,0)	167(104)	134(121,0)	146(229)	129(148,0)
a'' o.p. bend ^f	147(22,5)	156(3)	153	143(60,1)	162	124(0,1)	163(23)	121(27,2)	130(8)	111(58,1)
a'' torsion ^g	136(177,8)	142(203)	140	124(126,0)	135	134(167,2)	133(132)	136(146,1)	137(170)	142(113,0)

(C)	Experiment		DZP			6-311++G(2d,2p)		[6,3,3/3,3]		[7,4,2,1/4,2,1]		[6,4,3,1/4,3,1]
	N ₂ matrix	Ar matrix	HF	MP2	MP4	HF	MP2	HF	MP2	HF	MP2	HF
	$\Delta\omega_h(\Delta\omega)$	$(\Delta\omega)$	$\Delta\omega_h$									
ν_3	-14(-12)	(-7)	7	-17	-12	-10	-14	-6	-19	-8	-16	-9
ν_3	-32(-28)	(-24)	-28	-35	-29	-21	-31	-22	-30	-24	-33	-26
ν_1	-11(-8)	(-4)	-5	-9	-4	-7	-11	-6	-18	-6	-13	-5
ν_1	-90(-85)	(-64)	-49	-80	-56	-46	-95	-47	-96	-48	-94	-52
ν_2	20(21)	(21)	31	37	35	21	27	23	26	23	27	21
ν_2	4(3)	(3)	4	2	2	3	1	0	4	2	-1	5

^a" ω_h " " ω ," "IR," and "Raman" denote ω_{harmonic} (cm⁻¹), $\omega_{\text{experiment}}$ (cm⁻¹), IR intensities (km/mol), and Raman activities (Å⁴/amu), respectively.

^bReference 15.

^cOut-of-plane bending mode which tends to break the hydrogen bonding.

^dIn-plane bending mode which tends to break the hydrogen bonding (rocking motion of molecule 1 with partial wagging motion of molecule 2).

^eIn-plane bending mode which tends to break the hydrogen bonding (wagging motion of molecule 2 with partial rocking motion of molecule 1).

^fOut-of-plane bending mode which tends to break the hydrogen bonding.

^gTwisting of H_{1n} and H_{2n} along the principal axis (or along the two oxygen atoms).

TABLE III. Energetics, structure, and electrical properties of the water dimer.^a (A) Energetics; (B) structure; and (C) electronic properties.

(A)	Energy (hartrees)	BE(BSSEC) (kcal/mol)	$\Delta ZPVE$ (kcal/mol)	ΔE_T (kcal/mol)	ΔH_T (kcal/mol)	ΔA_T (kcal/mol)	ΔG_T (kcal/mol)	ΔS_T (cal/mol/K)
Exp		-5.44 ± 0.7^b -5.5 ± 0.5^c			$[-3.59 \pm 0.5]^b$ $[-3.63 \pm 0.5]^c$		$[3.34]^b$	$[-18.59 \pm 1.3]^b$ $[-18.61 \pm 1.3]^c$
DZP								
HF	-152.101 61	-5.03(-4.73)	2.16	-2.71(-2.41)	-3.30(-3.00)	3.18(3.48)	2.59(2.89)	-19.8
MP2	-152.519 82	-6.36(-5.03)	2.33	-3.98(-2.65)	-4.57(-3.24)	2.30(3.63)	1.71(3.04)	-21.0
MP4(FC)	-152.515 29	-6.14(-4.81)						
MP4	-152.544 08	-6.17(-4.80)	2.33	-3.77(-2.40)	-4.36(-2.99)	2.45(3.82)	1.86(3.23)	-20.9
6-311 + +G(2d,2p)^d								
HF	-152.120 16	-4.08(-3.7)	2.01	-1.84(-1.46)	-2.43(-2.05)	3.82(4.20)	3.23(3.61)	-19.0
MP2	-152.643 39	-5.45(-4.45)	2.25	-3.14(-2.14)	-3.73(-2.73)	3.18(4.18)	2.59(3.59)	-21.1
[6,3,3/3,3]								
HF	-152.132 51	-3.73(-3.64)	1.99	-1.49(-1.40)	-2.08(-1.99)	4.14(4.23)	3.55(3.64)	-18.9
MP2	-152.681 36	-5.37(-4.49)	2.18	-3.10(-2.22)	-3.69(-2.81)	3.09(3.97)	2.50(3.38)	-20.8
MP4(FC)	-152.657 18	-5.24(-4.30)						
[7,4,2,1/4,2,1]								
HF	-152.135 27	-4.08(-3.73)	1.96	-1.85(-1.50)	-2.44(-2.09)	3.72(4.07)	3.13(3.48)	-18.7
MP2	-152.722 80	-5.58(-4.55)	2.09	-3.34(-2.31)	-3.93(-2.90)	2.64(3.67)	2.05(3.08)	-20.0
(Values at 373.15 K)				$[-3.00(-1.97)]$	$[-3.74(-2.71)]$	$[4.26(5.29)]$	$[3.52(4.55)]$	$[-19.5]$
(Internal free rotation) ^e				$[-3.20(-2.17)]$	$[-3.94(-2.91)]$	$[3.73(4.76)]$	$[2.99(4.02)]$	$[-18.6]$
(Internal hindered rotation) ^f				$[-3.07(-2.05)]$	$[-3.81(-2.79)]$	$[3.88(4.91)]$	$[3.14(4.17)]$	$[-18.7]$
(The best estimation) ^g			$[2.08]$	$[-3.04(-2.01)]$	$[-3.78(-2.75)]$	$[3.54(4.57)]$	$[2.80(3.83)]$	$[-17.7]$
(13,8,4,2/8,4,2)								
HF ^h	-152.141 03	-3.71(-3.69)						
MP2 ⁱ	-152.790 31	-4.99(-4.66)	$[2.09]$	$[-2.41(-2.08)]$	$[-3.15(-2.82)]$	$[4.85(5.18)]$	$[4.11(4.44)]$	$[-19.5]$
(Internal free rotation) ^e				$[-2.61(-2.28)]$	$[-3.35(-3.02)]$	$[4.32(4.65)]$	$[3.58(3.91)]$	$[-18.6]$
(Internal hindered rotation) ^f				$[-2.49(-2.16)]$	$[-3.23(-2.90)]$	$[4.47(4.80)]$	$[3.73(4.06)]$	$[-18.7]$
(The best estimation) ^g			$[2.08]$	$[-2.45(-2.12)]$	$[-3.19(-2.86)]$	$[4.13(4.46)]$	$[3.39(3.72)]$	$[-17.7]$
[6,4,3,1/4,3,1]^j								
HF	-152.110 50	-3.95	1.92	-1.75	-2.34	3.79	3.20	-18.6
Frish <i>et al.</i>^k								
HF		-3.79(-3.43)						
MP2(FC)		-5.30(-4.57)						
MP4(FC)		-5.34(-4.56)						
Niesar <i>et al.</i>^l								
MP4		-5.62						
Popkie <i>et al.</i>^m								
HF		-3.67						
Szalewicz <i>et al.</i>ⁿ								
HF		-3.78(-3.73)						
MBPT		(-4.7 \pm 0.35)						
Corongiu <i>et al.</i>^o								
HF		-3.75(-3.73)						
MP2		-5.79(-5.09)						
Carraveta <i>et al.</i>^p								
HF		-3.67(-3.42)						
Density functional		-6.01(-5.76)						
(B)								
	$R(O-O)$ (Å)	Ψ (°)	Φ (°)	$\Delta R(O1-H1a)$ (Å)	$\Delta R(O1-H1n)$ (Å)	$\Delta R(O2-H2)$ (Å)	$\Delta\theta 1$ (°)	$\Delta\theta 2$ (°)
Exp	2.976-0.03 ^q 2.98 \pm 0.01 ^r	57 \pm 10 ^q 58 \pm 6 ^r	1 \pm 10 ^q 1 \pm 6 ^r					

TABLE III. (Continued.)

	$R(\text{O}-\text{O})$ (Å)	Ψ (°)	Φ (°)	$\Delta R(\text{O1}-\text{H1}h)$ (Å)	$\Delta R(\text{O1}-\text{H1}n)$ (Å)	$\Delta R(\text{O2}-\text{H2})$ (Å)	$\Delta\theta_1$ (°)	$\Delta\theta_2$ (°)
DZP								
HF	2.9851	45.5	1.6	0.0046	-0.0006	0.0008	-0.15	0.25
MP2	2.9009	54.6	3.1	0.0065	-0.0010	0.0014	0.10	0.28
MP4(FC)	2.9177	54.8	3.2	0.0059	-0.0010	0.0012	0.25	0.27
MP4	2.9161	55.3	3.1	0.0052	-0.0009	0.0011	0.15	0.39
6-311 + G(2d,2p) ^d								
HF	3.0352	49.2	3.3	0.0039	-0.0009	0.0006	0.02	0.26
MP2	2.9104	56.7	4.5	0.0072	-0.0006	0.0013	0.31	0.49
[6,3,3/3,3]								
HF	3.0155	48.5	0.6	0.0038	-0.0007	0.0005	-0.01	0.37
MP2	2.9012	50.2	3.6	0.0069	-0.0011	0.0013	0.30	0.37
MP4(FC)	2.9189	48.0	1.7	0.0057	-0.0012	0.0010	0.18	0.40
[7,4,2,1/4,2,1]								
HF	3.0288	44.9	1.8	0.0004	-0.0010	0.0006	0.11	0.25
MP2	2.9048	57.7	4.1	0.0068	-0.0009	0.0013	0.17	0.46
(13,8,4,2/8,4,2)								
MP2 ^e	2.925	{57.7}	{4.1}	{0.0068}	{-0.0009}	{0.0013}	{0.17}	{0.46}
[6,4,3,1/4,3,1]								
HF	3.0214	41.1	3.0	0.0042	-0.0008	0.0003	0.03	0.28

(C)	Proton donor			Proton acceptor		$q(\text{transfer})$ (e^+)	μ (D)	α (a.u.)	$\beta_{\text{H}}^{\text{H}}$ (10^{-30} esu)
	$\Delta q(\text{O1})$ (e^+)	$\Delta q(\text{H1}h)$ (e^+)	$\Delta q(\text{H1}n)$ (e^+)	$\Delta q(\text{O2})$ (e^+)	$\Delta q(\text{H2})$ (e^+)				
Exp.							2.60-2.64 ⁸		
DZP									
HF	-0.039	0.036	-0.011	-0.018	0.016	0.013	3.232	10.52	-0.001
MP2	-0.071	0.053	-0.000	-0.043	0.030	0.017	3.092		
6-311 + G(2d,2p)									
HF	-0.063	0.000	0.060	-0.036	0.019	0.002	2.841	14.87	-0.049
MP2	-0.076	-0.001	0.076	-0.046	0.024	0.001	2.701		
[6,3,3/3,3]									
HF	-0.007	-0.005	-0.008	-0.011	0.015	0.020	2.891		
[7,4,2,1/4,2,1]									
HF	-0.040	0.031	-0.060	0.000	0.007	0.015	2.994	14.19	-0.037
MP2	-0.046	0.021	-0.005	0.008	0.010	0.030	2.696		
(13,8,4,2/8,4,2)									
HF ^b	0.017	-0.007	-0.017	0.015	-0.004	0.008	2.951		
MP2 ⁱ	0.011	0.005	-0.035	0.003	0.009	0.020	2.612		
[6,4,3,1/4,3,1]									
HF	-0.039	-0.282	0.368	0.143	-0.094	0.046	3.068	16.80	-0.047

^a"BE" denotes the binding energy at 0 K. The thermodynamic quantities (ΔE_T , ΔH_T , ΔA_T , ΔG_T , and ΔS_T) for the association of two water monomers are given with the values at STP, while the values at $T=373.15$ K are in brackets.

^bCalculated from the equilibrium constant of $K=0.0111$ atm⁻¹ in Ref. 6(a).

^cReference 6(b).

^dSome values were taken from Ref. 15, while some (such as thermodynamic quantities and electrical properties) were calculated in this work.

^eThe torsional vibrational mode was replaced by the internal free rotation (373.15 K).

^fThe torsional vibrational mode was replaced by the internal hindered rotation (373.15 K).

^gSee the text for the best estimation (373.15 K).

^hThe binding energy was calculated at the HF/[7,4,2,1/4,2,1]-optimized geometry.

ⁱBased on the MP2/[7,4,2,1/4,2,1] structure, the interoxygen distance was optimized. The nonoptimized structural values are in braces.

^jThe partial geometry optimization with MP2/[6,4,3,1/4,3,1] gave $R(\text{O}-\text{O})=2.85$ Å and $\Psi=49^\circ$.

^kReference 15 with the basis set 6-311 + G(3df,3pd).

^lReference 19 with the basis set [4,3,1/2,1].

^mReference 14 with the basis set [13,8,2,1/6,2,1].

ⁿReference 16 HF and MP2 energies with various basis sets up to [9,6,3,2,/6,3,2] and [9,6,2,1/6,2,1], respectively.

^oReference 17.

^pReference 18(b) with the basis set [4,3,2/2,1].

^qReference 3.

^rReference 2.

^sReferences 3-5 were studied theoretically. All elaborate calculations conclude that the linear structure is the global minimum energy conformation except for the following. Using some unusual basis sets with many diffuse functions, Robinson *et al.*⁴³ reported recently that the bifurcated structure

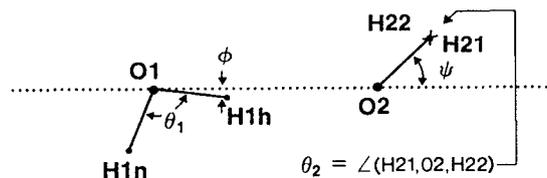


FIG. 1. Geometrical variables for the water dimer structure.

is a local minimum. However, very recently a more elaborate calculation by Marsden *et al.*⁴⁴ showed that the structure is a transition state.

In Table III, we list calculational and experimental results of the most stable water dimer, i.e., the linear structure. The dimer geometry was fully optimized in our calculations regardless of the levels of theory and basis sets except for the HF and MP2 calculations using the very large basis set (13,8,4,2/8,4,2). The latter calculations were performed at the dimer geometries optimized with the HF and MP2 calculations using [7,4,2,1/4,2,1], respectively, but particularly the interoxygen distance was optimized for the MP2 calculation with the very large basis set. The thermal vibrational correction for the MP2/(13,8,4,2/8,4,2) thermodynamic quantities was done with the MP2/[7,4,2,1/4,2,1] results in that the MP2/[7,4,2,1/4,2,1] dimer structure and spectra are found to be in good agreement with experiment.

Notations of atoms and geometrical parameters for the C_s structure of the dimer are shown in Fig. 1. Here, suffixes “h” and “n” (which are added to H1) denote a hydrogen atom participating in hydrogen bonding and that not participating in hydrogen bonding, respectively. In the figure, ψ is the angle between the interoxygen distance vector and the molecular plane of the proton acceptor (molecule 2); ϕ is the angle $\angle O2-O1-H1h$; θ_1 and θ_2 are the bond angles of molecules 1 and 2, respectively.

A. Thermal energies and spectra

In Table III, the MP2 binding energies without BSSEC agree mostly with experiment within the error bound, but the values vary widely (from -5.0 to -6.4 kcal/mol) with the basis sets used. On the other hand, the MP2 binding energies with BSSEC seem to be underestimated, but the values are rather consistent (from -4.5 to -5.1 kcal/mol) with basis sets. The binding energies with BSSEC are in agreement with the values of -4.7 ± 0.35 kcal/mol predicted with BSSEC by Bartlett *et al.*¹⁶ Therefore, in spite of the fact that the binding energies with BSSEC seem to be underestimated, such consistency makes us be in favor of BSSEC.

For most post-HF results reported at the levels of the MP2 theory [or the configuration interaction with single and double excitations (CI/SD)] the BSSEC is ~ 1 kcal/mol. Using the very large basis set (13,8,4,2/8,4,2), the BSSECs from the HF and MP2 calculations are only 0.02 and 0.33 kcal/mol, respectively. The latter value is by far the smallest among the post-HF results reported. Owing to this very small BSSEC, the predicted binding energies with

and without BSSEC (which are -4.66 and -4.99 kcal/mol, respectively) may be considered near the upper and lower bounds of the true binding energy, respectively. Therefore, one may expect that the lower bound of the binding energy would not be far from -5.0 kcal/mol, i.e., it would not be near -5.5 kcal/mol (which is the most probable experimental value). Then, although some small basis sets predict the binding energies without BSSEC that are near the most probable value of the experiment, such agreements seem to be rather fortuitous. Thus, we again refer to BSSEC, favoring the upper bound of the experimental value. This will be further supported as will be discussed below.

The experimental binding energy was estimated from the enthalpy change for the association of the two monomers.⁶ This enthalpy change along with the entropy change was obtained from the Gibbs free energy change for the association. Thus, the most critical comparison between experiment and calculation should be based on the Gibbs free energy change rather than the binding energy. For this reason, in Sec. III we summarized the quantum statistical thermodynamic quantities with correction for anharmonic vibration, rotation, rotation–vibration coupling, and internal rotation.

To obtain the thermodynamic quantities in Table III, even the low frequency modes were treated to be thermally vibrationally excited, unless otherwise specified. Such an assumption is correct only at low temperature. Figure 2 shows the six low frequency modes predicted by the MP2/[7,4,2,1/4,2,1] calculation (a) a' O–O stretching mode; (b) a' in-plane bending mode without hydrogen bond breaking; (c) a' in-plane bending mode involved in hydrogen bond breaking; (d) a'' torsion mode; (e) a'' out-of-plane bending mode without hydrogen bond breaking; (f) a'' out-of-plane bending mode involved in hydrogen bond breaking. At very high temperature, the dissociation of the dimer changes the six low vibrational modes to three translational and three rotational modes. If the temperature is neither high nor low, three of the six low vibrational modes can be changed to three rotational modes. In fact, as shown in Table II(B) and Fig. 2, there are three such vibrational modes of (d), (b), and (c).

Torsional mode (d) can be considered as the almost-free internal rotation of molecule 2 because the rotation barrier was predicted to be 0.59 kcal/mol with the MP4(FC)/6-311+(2df,2p) calculation at the MP2/6-31+G(d,p)-optimized geometries by Schaefer *et al.*⁴⁴ In-plane modes of (b) and (c) can be considered as hindered internal rotations because the potential barriers for the inversion symmetries were predicted to be ~ 1.8 kcal/mol by Schaefer *et al.* These two modes are somewhat strongly hindered rotations, which can be approximated as the vibrational excitations at 373.15 K. Thus, only the torsional vibration mode can be approximated as the free internal rotation at 373.15 K. Namely, the corresponding enthalpy is only 0.5 kT instead of 1.0 kT .

Here, the thermal energy changes for the association of two water monomers at 373.15 K are discussed with the MP2/(13,8,4,2/8,4,2) results with BSSEC, unless otherwise specified. Without any correction for anharmonic vi-

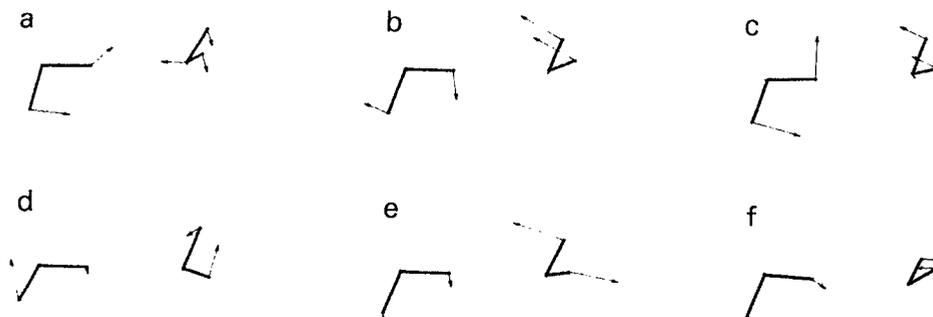


FIG. 2. The six low vibrational frequency modes of the water dimer predicted by the MP2/[7,4,2,1/4,2,1] calculation: (a) O–O stretching mode; (b) in-plane bending mode which tends to keep the hydrogen bonding; (c) in-plane bending mode which tends to break the hydrogen bonding; (d) torsional mode; (e) out-of-plane bending mode which tends to keep the hydrogen bonding; (f) out-of-plane bending mode which tends to break the hydrogen bonding. Modes (a), (b), and (c) have the symmetry a' , while modes (d), (e), and (f) have the symmetry a'' .

bration, rotation–vibration coupling, and hindered internal rotation, the simple thermal energies including rotation and harmonic vibration at 373.15 K are -2.82 and 4.44 kcal/mol, and -19.5 cal/mol/K for ΔH , ΔG , and ΔS , respectively. Including the almost-free internal rotational motion of the mode (d), ΔH , ΔG , and ΔS are -3.02 and 3.91 kcal/mol and -18.6 cal/mol/K, respectively. With approximate correction for the partially hindered rotational motion of the mode (d) with Pitzer's work,²⁷ the above three thermal quantities become -2.90 and 4.06 kcal/mol and -18.7 cal/mol/K. Although the two in-plane vibrational modes of (b) and (c) are strongly hindered rotational motions, these motions can partially correct the thermal energies with respect to the pure vibrational excitations. Then, this correction partially tends to be canceled with the correction for the hindered rotation of the mode (d) with respect to the free rotational motion. Owing to the above tendency and somewhat approximated hindered rotational thermal energies, our best estimation for the thermal energies will be given with the correction for the system which comprises the free internal rotation of the mode (d), the rotor of the O–O stretching mode (a) in a Morse potential, and the anharmonic vibration motions for the two in-plane modes (b) and (c). The correction for the two remaining out-of-plane modes (e) and (f) was neglected because these modes do not have cubical potential terms except for small quartic potential terms. Further, the frequency of mode (f) is reasonably high, so that the correction would not be significant.

The potential functions for the three a' modes (a), (b), and (c) were obtained with the MP2/[7,4,2,1/4,2,1] calculations. The potential function for mode (a) with respect to the interoxygen distance change ($\Delta r = r - r_e$ in Å) is given as $U(\Delta r) \approx 12.1\Delta r^2 - 24.2\Delta r^3 + 19.8\Delta r^4$, or a more reduced form of $U(\Delta r) \approx 3.8(1 - e^{-1.8\Delta r})^2$ with the potential energy in kcal/mol (Fig. 3). For the two in-plane modes (b) and (c), the potential functions with respect to a certain deviation (x) along each normal coordinate vector are given as $U(x) \approx 0.205x^2 - 0.020x^3 - 0.223x^4$ and $U(x) \approx 0.488x^2 - 0.428x^3 - 1.86x^4$, respectively. Therefore, excluding the free internal rotational correction, the total thermal energy correction for the three a' modes with the

anharmonic vibration and rotation–vibration coupling is given as 0.16 and -0.19 kcal/mol and 0.9 cal/mol/K for the internal energy, free energy, and entropy, respectively. In addition, the zero-vibrational correction is -0.01 kcal/mol.

Without BSSEC, the MP2/(13,8,4,2/8,4,2) binding energy, enthalpy, free energy, and entropy are all in good agreement with experiment within the error bounds. With BSSEC, the binding energy and enthalpy are slightly off the experimental error bounds. Nevertheless, as discussed earlier, we find that the energies with BSSEC can be more reliable than those without BSSEC. Consider the thermal energies predicted by MP2 calculations with other basis sets, e.g., [7,4,2,1/4,2,1]. Apparently, the calculated binding energy without BSSEC (-5.58 kcal/mol) is in good agreement with experiment, whereas that with BSSEC (-4.55 kcal/mol) seems to be too underestimated, but we recall that the Gibbs free energy change for the association of two monomers is the most important and critical test for comparison between experiment and calculation. The best

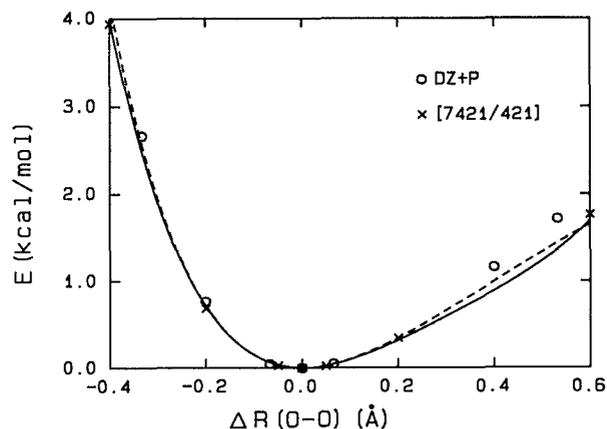


FIG. 3. The energy profile with respect to the interoxygen distance predicted by the MP2 calculations using the basis sets of [7,4,2,1/4,2,1] and DZ+P. A Morse potential of $U(\Delta r) = 3.8(1 - e^{-1.8\Delta r})^2$ is drawn in the dotted curve, while a more accurate expression with the potential of $U(\Delta r) = 12.1\Delta r^2 - 24.2\Delta r^3 + 19.8\Delta r^4$ is drawn in the solid curve.

estimated Gibbs free energy change without BSSEC is 0.54 kcal/mol lower than experiment, whereas that with BSSEC is 0.49 kcal/mol higher. Similarly, almost all basis sets having large BSSEC give too low free energy without BSSEC, resulting in an overestimation of the binding energy. These overestimated binding energies happen to agree with the most probable experimental binding energy. Consequently, this supports that the apparent agreement of the uncorrected binding energy with experiment seems to be rather fortuitous. Furthermore, various thermal energies with BSSEC have somewhat consistent values for many different basis sets, while those without BSSEC are widely varied. For example, the ΔG 's predicted by the MP2 calculations using (13,8,4,2/8,4,2) and [7,4,2,1/4,2,1] are 3.83 and 3.72 kcal/mol with BSSEC, respectively, and are 2.80 and 3.39 kcal/mol without BSSEC, respectively. Thus, the thermal energies with BSSEC can be more favored.

With BSSEC, the best estimated ΔH , ΔG , and ΔS predicted by the MP2/(13,8,4,2/8,4,2) calculation are -2.86 and 3.72 kcal/mol and -17.7 cal/mol/K at 373.15 K, respectively. This ΔS is in agreement with experiment (-18.59 ± 1.3 cal/mol/K) within the error bound.

The IR and Raman frequencies of the dimer and these intensities are compared with those of the monomer in Table II. It is interesting to compare experimental spectra (in a Ne or Ar matrix) with the results from the MP4/[DZ+P] and MP2/[7,4,2,1/4,2,1] calculations. To predict correct vibrational frequencies of the dimer, a larger basis set is more important than a higher level of electron correlation calculation, just as in the monomer case. Spectral shifts of the asymmetric stretching, symmetric stretching, and bending modes of the dimer with respect to those of the monomer show reasonable consistency with experiment. It is worth noting good consistency between the experimental harmonic frequency shifts ($\Delta\omega_h$) for the dimer in the N_2 matrix⁷ and the calculated harmonic frequency shifts ($\Delta\omega_h$) for the free dimer predicted by the MP2 calculation using [7,4,2,1/4,2,1] or 6-311++G(2d,2p). The ν_1 mode related to the proton donor of the dimer has very strong IR and Raman intensities. This is in agreement with the work of Lee *et al.*¹¹ showing that the mode has a strong broad band in the IR spectra.

B. Structure and electrical properties

The MP2 interoxygen bond lengths predicted with various basis sets are 2.90–2.92 Å, which are somewhat shorter than the experimental values^{2,3} (2.97–2.98 Å). The calculated angle ψ is 57° for 6-311++G(2d,2p) (Ref. 15) and 58° for [7,4,2,1/4,2,1], in excellent agreement with experiment^{2,3} (57° ± 10°), but the angle predicted with [6,3,3/3,3] is somewhat off the experimental value. Since the polarizability is poorly predicted by most basis sets, we performed a calculation using [6,4,3,1/4,3,1] (which was specially optimized to reproduce the experimental electrical properties of the monomer) to test if the interoxygen distance can increase. The HF calculation gave 3.02 Å for $R(O-O)$ and 41° for ψ . These two geometrical variables were partially optimized with the MP2 calculation using

the MP2/[7,4,2,1/4,2,1]-predicted geometry. Then, $R(O-O)$ decreased down to 2.85 Å against the experimental value, while ψ was only $\sim 49^\circ$. Thus, this basis set was not useful for geometrical prediction, so that we did not pursue further elaborate calculation.

Instead, using the MP2/(13,8,4,2/8,4,2) calculation, the interoxygen distance of the MP2/[7,4,2,1/4,2,1]-optimized structure was reoptimized. The optimized interoxygen distance is 2.925 Å, which is slightly longer compared with the distances predicted by other basis sets. Such a distance increment seems to arise from the particularly small BSSEC due to the very large basis set. It should be noted that when the binding energy of two rigid water monomers is maximized, the interoxygen distance is increased compared with the case when the total energy for two flexible water molecules is maximized. Using the formula derived in Sec. III C, the anharmonic potential for mode (a) and the rotational motion of two water molecules increase the interoxygen distance by 0.032 and 0.001 Å, respectively, at 20 K (which is the experimental temperature that the dimer structure was obtained). Thus, the MP2/(13,8,4,2/8,4,2)-predicted interoxygen distance becomes 2.958 Å, which is the closest to the experimental value (~ 2.976 Å) among the *ab initio* calculations reported so far.

Among the basis sets studied here (excluding the very large basis set with which the full geometry optimization was not performed), the dimer structure is the most well predicted by the MP2 calculation with [7,4,2,1/4,2,1], followed by that with 6-311++G(2d,2p). For the MP2/[7,4,2,1/4,2,1] calculation, the angle ϕ is predicted to be about 4°, in agreement with experiment^{2,3} (1° ± 10°). The increment of the O1–H1*h* bond length with respect to the monomer is predicted to be 0.007 Å. The increments of the bond angles θ_1 and θ_2 are 0.17° and 0.46°, respectively. The angle θ_2 is widened mainly due to the fact that the electron charge (0.03e⁻) is transferred from molecule 2 (proton acceptor; electron donor) to molecule 1 (proton donor; electron acceptor). For the MP2/(13,8,4,2/8,4,2) calculation, the transferred charge is 0.02e⁻. In molecule 2, the repulsion between the enhanced positive charges in H2's widens the bond angle. The bond angle θ_1 widens very slightly. The bond lengths of $R(O1-H1n)$ and $R(O2-H2)$ hardly change.

The flexibility effect of each monomer in the dimer can be understood by decomposing the binding energy into (intramolecular) deformation energy, intermolecular energy, and the very small coupling terms. For MP2/[7,4,2,1/4,2,1], the deformation energy is only 0.036 kcal/mol; the main portion (0.029 kcal/mol) comes from the elongation of the bond length $R(O1-H1h)$ and the remainder comes mostly from the widened bond angles. Therefore, for the water dimer, the deformation energy due to the water flexibility is very small compared with many-body intermolecular interaction energies.

It is interesting to see Slanina's report⁴⁰ that for the Matsuoka, Clementi, and Yoshimine (MCY) potential,⁴¹ the binding energy, $R(O-O)$, ψ , and ϕ are -5.72 kcal/mol, 2.99 Å, 32.4°, and 2.9°, respectively, while for another

modified MCY potential,⁴² those values are -5.87 kcal/mol, 2.87 Å, 37.6° , and 4.1° , respectively. All these sophisticated interaction potentials cannot reproduce correctly the water dimer structure (in particular, for ψ). Furthermore, such interaction potentials fail in predicting somewhat simple systems, such as the hexamer structure.⁴⁵ In order to make the potentials as effective pairwise additive potentials for condensed phase systems, the MCY potentials need to be further modified, including the correction for ψ .

As to the electrical properties, the MP2/[7,4,2,1/4,2,1] calculation gives the dipole moment of 2.70 D, in reasonable agreement with experiment (2.60 – 2.64 D).^{3–5} The MP2/(13,8,4,2/8,4,2) dipole moment is 2.612 D, which is the first agreement with experiment. If we conjecture that the increment of the interoxygen distance due to anharmonic vibration and rotation increases the dipole moment in proportion to the distance change, the predicted dipole moment may increase up to 2.64 D ($2.612 \times 2.958/2.925$). For the predicted dimer structure, the vector sum of the two monomer dipole moments gives 2.23 D; thus, the enhancement of the dipole moment (0.38 D) arose mainly from the charge transfer. Indeed, the enhancement of the dipole is 0.30 D (or 0.40 D) for the case when $0.02e^-$ is transferred from molecule 2 to molecule 1 which is at the distance of 3 Å (or 4 Å) from molecule 2. Although the interoxygen distance is ~ 3 Å, the distance between hydrogen atoms at both ends of the dimer is ~ 4 Å.

The dimer polarizability (α) predicted by the HF/[7,4,2,1/4,2,1] calculation is 14.2 a.u. We recall that for the water monomer, the [7,4,2,1/4,2,1] basis set slightly overestimates the dipole moment and somewhat underestimates the polarizability. With the HF/[7,4,2,1/4,2,1], the predicted dimer hyperpolarizability component along the dipole vector (β_μ) is 0.04×10^{-30} esu. In spite of the charge transfer effect, this value is much smaller than the HF/[7,4,2,1/4,2,1] monomer value (-0.11×10^{-30} esu) because the vector direction of the hyperpolarizability is almost perpendicular to the dipole direction.

VI. CONCLUSION

The structure, energetics, spectra, and electrical properties of the water dimer as well as the monomer have been studied with *ab initio* calculations using various large basis sets. In order to compare accurately the theoretical and experimental thermal energies, we summarized the quantum statistical thermodynamic quantities with the correction for the anharmonic vibration, rotation, rotation–vibration coupling, and internal rotation.

The MP2/(13,8,4,2/8,4,2) results of the monomer are in excellent agreement with various experimental data except for the somewhat underestimated hyperpolarizability. The MP4 energy for the monomer with the same basis set is -76.407 hartrees, which is 0.073 hartree above the experimental energy.

The largest basis set used for the full geometry optimization and frequency analysis of the dimer is [7,4,2,1/4,2,1]. For this basis set the MP2 calculation gives an excellent agreement with experiment except for the slightly

short interoxygen distance. For this geometry, the interoxygen distance was reoptimized with the MP2/(13,8,4,2/8,4,2) calculation, which predicts 2.925 Å for the interoxygen distance. With the correction of 0.033 Å for the anharmonic binding potential and molecular rotation at 20 K, the best estimated interoxygen distance is 2.958 Å. This value is the closest to the experimental value ~ 2.976 Å among *ab initio* calculations so far reported. The predicted angle ψ is 58° , in excellent agreement with experiment. The O–H distance participating in the hydrogen bonding lengthens as much as 0.007 Å. The bond angle in the proton-accepting molecule widens as much as 0.5° , due to the enhanced charge repulsion between two hydrogen atoms. Since the geometrical change for each monomer is rather small, the deformation energy is extremely smaller than the intermolecular interaction energy. This indicates that the flexibility effect of each monomer is rather less important than many-body interaction potentials. The best-predicted dipole moment is 2.612 D, which is the first agreement with the experimental values of 2.60 – 2.64 D. The predicted frequency shift of the dimer with respect to the monomer is in good agreement with experiment. The frequency mode related to the symmetric stretching of the proton-donating monomer has very strong IR and Raman intensities.

The MP2 calculation with the very large basis set gave the BSSEC of only 0.33 kcal/mol, which is by far the smallest among post-HF results. Without BSSEC, the predicted binding energy, enthalpy, free energy, and entropy are all in good agreement with experiment within the error bounds, while with BSSEC some of those are slightly off the experimental error bounds. Nevertheless, we support that the results with BSSEC can be more reliable than those without BSSEC with the following reasons: First, for the various basis sets used, the binding energies with BSSEC are rather consistent, whereas those without BSSEC vary widely. Second, the most reliable MP2 calculation with the very large basis set gives the binding energy without BSSEC of -4.99 kcal/mol. Although this value can be considered as the lower bound of the binding energy, it is 0.5 kcal/mol higher than the most probable experimental value. Therefore, although the binding energies without BSSEC predicted by some small basis sets are rather near the most probable value of the experiment (-5.5 kcal/mol), such agreements seem to be rather fortuitous. Third, we recall that the Gibbs free energy change for the association of two monomers is the most important and critical test for comparison between experiment and calculation. The best estimated Gibbs free energy without BSSEC is obtained with various corrections discussed in Sec. III. For the various basis sets used, the free energies with BSSEC are consistent, whereas those without BSSEC are widely varied. Fourth, as an example, the MP2/[7,4,2,1/4,2,1] Gibbs free energy change without BSSEC is 0.5 kcal/mol lower than the experimental value. This in turn overestimates the binding energy that much. Such an overestimation is common with other basis sets which have large BSSEC. Fifth, while the error deviation of the equilibrium constant (i.e., free energy change) was not re-

ported in the experiment, the error deviation of the experimental entropy change was ± 1.3 cal/mol/K, which can change the binding energy and enthalpy by ± 0.5 kcal/mol at 373.15 K.

Then, from the MP2/(13,8,4,2/8,4,2) results, our most reliable binding energy with BSSEC is -4.66 kcal/mol. The best estimated ΔH , ΔG , and ΔS for the association of two monomers are -2.86 and 3.72 kcal/mol and -17.7 cal/mol/K at 373.15 K. This ΔS is in good agreement with experiment within the error bound.

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