On the calculation of the dissociation rate constant of the water dimer by the *ab initio* anharmonic RRKM theory

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The dissociation rate constant of the water dimer was calculated by using the method proposed by Yao and Lin (YL method). The dividing surface method and RRKM theory are used to calculate the pseudo transition state and the rate constant, respectively. For the canonical case at temperature range of 243–1000 K and for the microcanonical system at total energy 1411–4000 cm^{-1}, the anharmonic rate constant, around 10^9–10^{11} s^{-1}, is close to the experimental prediction. The present results indicate that the anharmonic effect should be included and YL method is suitable for calculating dissociation rate constants of such small flexible water cluster.

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1. Introduction

Due to the ubiquity of water clusters in nature, water cluster kinetics has been a focus of extensive research. The clustering of water molecules is relevant to a variety of physical and chemical processes, which are important in many industrial and environmental processes, including atmospheric aerosol formation, steam erosion of turbines, and atmospheric absorption of solar radiation. Long-lived water clusters composed of up to a few water molecules are known to exist in non-negligible amounts in water vapor and in the atmosphere [1].

Far-infrared vibration–rotation-tunneling spectroscopy techniques have been used to study dimers in experiments. Infrared (IR) spectroscopy has been also used to study larger water clusters. Lee and co-workers [1] predict an upper limit to the excited vibrational state lifetime, 1 μs. The dissociation (evaporation) rate constant of water dimer was predicted to be around 10^9 s^{-1} [1].

The water dimer system has received a great amount of theoretical interest as it provides an important benchmark for further studies of the dynamics of water evaporation. The far-IR spectra of the water dimer, tetramer, and hexamer had been calculated by employing DFT-based MD simulations at two different temperatures corresponding to the experimental measurements by Lee and co-workers [1]. Garrett and co-workers [2] reported the evaporation rate constants for the water dimer to be around 10^{11} s^{-1} of

at *T* = 243 K. They proposed a theoretical method called vapor-phase dynamical nucleation theory (DNT) and applied this approach to evaporation of small water clusters and other systems [3,4]. In particular, Lee et al. considered the rate mechanism [5], whereas Ming et al. [6] used the free energy perturbation method to correct for the errors occurring when some standard models for the bulk water were applied to the water dimer, where the evaporation rate constants around 10^{10} s^{-1} derived from the *ab initio* potential energy surfaces.

Many chemists observed significant anharmonic effects in dissociation of molecular systems, especially of clusters and molecules with highly flexible transition states [7–17]. On the other hand, variational transition state theory (VTST) provides a powerful computational tool for the studies of rates of chemical reactions. VTST has been widely used for the modeling of barrierless radical–radical recombination, dissociation processes and applied successfully to a variety of reactions both in the gaseous and condensed phases [2–4,17,18].

The purpose of the present study is to compute accurate nharmonic rate constants for dissociation (evaporation) of the water dimer at the temperatures where earlier experimental measurements [1] were performed. To calculate the rate constants, we use the systematic method developed recently by Yao et al. [19] (below, the YL method) to examine the anharmonic effect on the molecular dissociation. In the calculations of the anharmonic effect in this Letter, the Morse oscillator has been chosen to fit the potential energy surfaces (PES) and to simulate the bonding. The potential energy curve for the water dimer dissociation has also been calculated, and the variational transition state (VTS) has been

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located to obtain the dissociation rate constants. To our knowledge, this is the first anharmonic study of the temperature dependence of the evaporation rate constant for water clusters.

2. Computational methods

2.1. Ab initio calculations

The geometries of the reactants, products, various intermediates and pseudo transition states have been optimized by using the MP2 method with the 6-311++G** basis set. Vibrational harmonic and anharmonic frequencies, calculated at the same level, are used for characterization of stationary points, zero-point-energy (ZPE) corrections, and for calculations of reaction rate constants using transition state and RRKM theory. All stationary points have been positively identified as local minima or transition states. Single-point energies were recalculated by employing the coupled cluster CCSD(T)/CBS and CCSD(T)/aug-cc-pVTZ methods to achieve higher accuracy and reliability. In order to locate variational transition states, we scanned the PES along the reaction coordinate corresponding to the O–O distance between two water monomers. The GAUSSIAN 03 and MOLPRO 2006 programs were utilized for all *ab initio* calculations.

2.2. RRKM and variational transition state calculations

We used RRKM theory for computation of rate constants for unimolecular dissociation of the water dimer. Rate constant $k(E)$ at an internal energy E for a unimolecular reaction $A^* \rightarrow A^{\neq} \rightarrow P$ (here A^* and P are the reactant and products, respectively, and $A^{\neq}$ denotes the activated complex) can be expressed as:

$$k(E) = \frac{\sigma}{h} \frac{W^{\neq}(E - E^{\neq})}{\rho(E)}, \tag{1}$$

where σ is the symmetry factor (here we set $\sigma = 1$). h is Planck's constant, $\rho(E)$ represents the density of states of the energized reactant molecules, and $W^{\neq}(E - E^{\neq})$ is the total number of states for the transition state (activated complex) $A^{\neq}$ with a barrier $E^{\neq}$. E represents the total internal energy available to the system. We evaluate $\rho(E)$ and $W(E)$ by performing the inverse Laplace transformation of the partition function $Q(\beta)$, where $\beta = \frac{1}{kT}$. The steepest-descent method has been used for carrying out the inverse Laplace transformation up to the second-order approximation [19,20].

For a canonical system, according to the TS theory, the unimolecular rate constant is given by

$$k_f(T) = \frac{kT}{h} \cdot \frac{Q(T)^{\neq}}{Q(T)} e^{-\frac{E^{\neq}}{kT}}. \tag{2}$$

For the case of Morse oscillator we have

$$Q(\beta) = \prod_{i=1}^{N} \sum_{n_i=0}^{n_i(m)} e^{-\beta E_{n_i}} \tag{3}$$

with a similar expression for $Q^{\neq}(\beta)$. Here $n_i(m)$ represents the maximum value of quantum number n_i. To consider the anharmonic effect on a unimolecular reaction, the anharmonic number and density of states for a system of Morse oscillators take a particularly simple form.

Because no distinct transition state exists on the PES for dissociation of water dimer $H_2O \cdots H_2O$ (as for the case of a simple bond-cleavage process), one can consider different positions for the transition state along the reaction path and calculate rate constants corresponding to each of them. In the microcanonical VTST, the minimum in the microcanonical rate constant is found along the reaction path according to the following equation:

$$\frac{dk(E)}{dq^{\neq}} = 0 \tag{4}$$

in which $q^{\neq}$ is the reaction coordinate, such that a different transition state is found for each different energy. The individual microcanonical rate constants are minimized at the point along the reaction path where the total number of states $W^{\neq}(E - E^{\neq})$ has a minimum value. Thus, the reaction bottleneck is located where the minimal $W^{\neq}(E - E^{\neq})$ is found, that is, the sums of states for transition state candidates must be calculated along the reaction path. Each of these calculations requires the optimized structure, single-point energy, zero-point energy, and vibrational frequencies as functions of the reaction coordinate [21–24].

3. Results and discussion

The evaporation process is defined as the removal of a water molecule from a cluster. The reactant is a water dimer, while the product is two water monomers at infinite separation,

$$(H_2O)_2 \xrightarrow{k} 2(H_2O). \tag{5}$$

The optimized structure of the water dimer at the MP2/6-311++G** level is illustrated in Fig. 1, where the numbers show optimized bond lengths and bond angles.

Definitions of the energetic quantities begin with the PES or interaction potential that is a function of all internal coordinates of the water cluster. A series of energies at different distances between two dissociating fragments corresponding to the length of a bond to be broken during dissociation is calculated, which is considered to be the reaction coordinate. To obtain these energies, we performed partial geometry optimization with fixed values of the reaction coordinate and all other geometric parameters being optimized. No intrinsic barrier exists for dissociation of the water dimer because the reverse process, condensation of a water molecule onto the cluster, is barrierless. We have used the following procedure for the VTST calculations. First, we scan the PES considering the dimer separating to two water molecules with varying the bond O–O distances. We calculated 25 optimized geometries corresponding to the O–O distances from 2.9 to 10.0 Å with the step of 0.3 Å. To obtain most accurate position of the variational TS, additionally 40 optimized geometries were calculated at the O–O distances from 7.2 to 7.4 Å. The PES scan along the O–O distance was carried out at the MP2/6-311++G** (Fig. 2a) and B3LYP/6-311++G** (Fig. 2b) levels of theory. As expected, Fig. 2 indicates that no barrier exists for the reaction. The MP2 relative energies at each point along the reaction path in Fig. 2a were scaled by a factor obtained by comparing the water dimer dissociation energies at the CCSD(T)/CBS and MP2/6-311++G** levels and the results were used to fit the Morse potential energy function. The reaction energy calculated at the CCSD(T)/aug-cc-pVTZ and CCSD(T)/CBS levels is 3.19 and 2.33 kcal/mol, respectively, with ZPE, in close agreement with the other theoretical values for the evaporation of water dimer 2.42 ± 0.58 kcal/mol [5] and 3.00 kcal/mol [24]. In
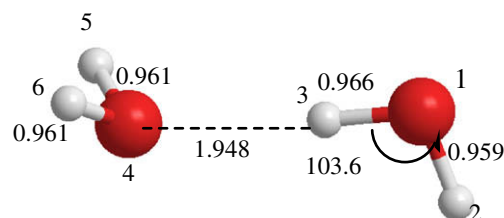

Fig. 1. MP2/6-311++G**-optimized geometries (bond length in Å and angles in degrees) of the reactants water dimer.

this case, the TS, we called it pseudo TS, is located at the O–O distance of 7.365 Å, where the energy barrier is 3.19 kcal/mol. We recomputed the single point energies at the CCSD(T)/CBS and CCSD(T)/aug-cc-pVTZ levels. Finally, the VTS with the minimal values of the number of states were employed to calculate rate constants of the direct dissociation processes by using the above RRKM formalism, and the same minimum point was also taken into the calculation of the rate constant for the canonical and microcanonical case.

The geometric and energetic parameters of the reactant and variational TS are collected in Table 1 including apparent activation energies, relative energies of the VTS with respect to the reactant. It is critical to compute the activation energy as accurate as possible, because evaporation of the water dimer is an activated process and such activated chemical reactions have rates that depend exponentially on the height of an energy barrier. The anharmonic and harmonic evaporation rate constants calculated using VTST are presented in Table 2, at temperatures from 243 to 1000 K for the canonical system. Corresponding to Table 2, the evaporation rate constants for the water dimer are plotted in Fig. 3. In the earlier theoretical works, the rate constants were predicted to be around 10^{11}–10^{12} s^{-1} by Garrett et al. [2–4] and 10^{10}–10^{11} s^{-1} by Ming et al. [6], which is almost 100–1000 times higher than our

anharmonic rate constants (around 10^9 s^{-1} at 243 K). We discuss canonical evaporation rate constant in which the anharmonic effect is included and compare with the DNT results of Garrett et al. [5].

The relationship between the total energy of a microcanonical system and the temperature of a canonical system is the following:

$$E = -\left[\frac{\partial \ln Q}{\partial \beta}\right]. \tag{6}$$

The total energies corresponding to the canonical temperatures of 243, 273, 303, 333, 500, 600, 700, 800, 900, 1000 K are 1.287, 1.571, 1.867, 2.174, 4.035 (1411 cm^{-1}), 5.258 (1839 cm^{-1}), 6.551 (2291 cm^{-1}), 7.909 (2766 cm^{-1}), 9.33 (3263 cm^{-1}), 10.812 (3781 cm^{-1}) kcal/mol, respectively. The first four energies are all lower than the calculated activation energy of 3.017 kcal/mol. Hence, we have to calculate the microcanonical rate constant at higher total energies of 1411–4000 cm^{-1}, corresponding to the vibrational frequencies of the water dimer and high canonical temperatures above 500 K. Table 3 shows the anharmonic and harmonic rate constants of evaporations water dimer at the total energies of 1411–4000 cm^{-1} and the data are also illustrated in Fig. 4. From the results we can see that the rate constant increases with the increasing total energy and the anharmonic result is in the
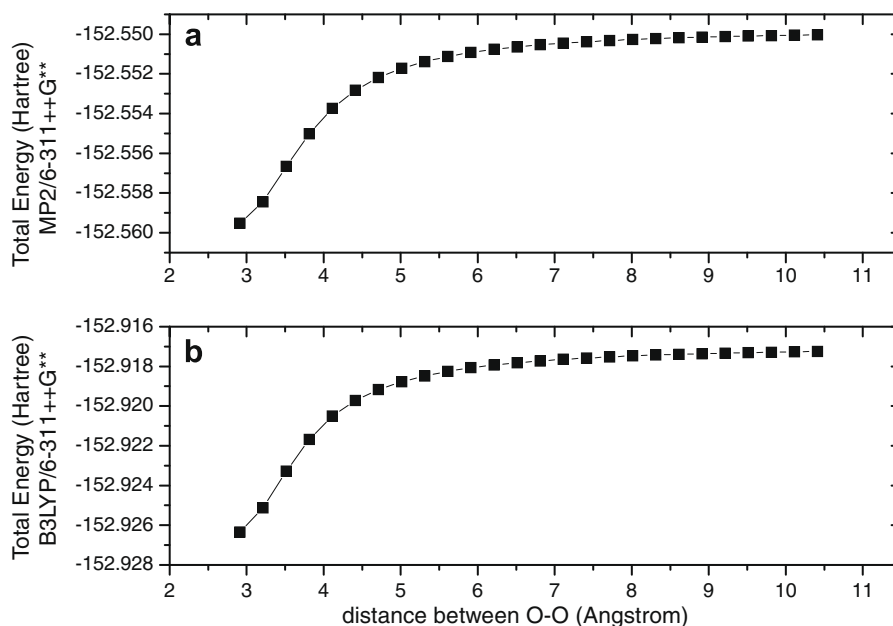

Fig. 2. Changes of the relative MP2/6-311++G** (a) and B3LYP/6-311++G** (b) energies as function of coordinate distance between O1 and O4 in Å.

Table 1
The properties of water dimer and TS, frequencies in cm^{-1}, bond length in Å, and angles in degrees.

E	MP2/6-311++G**		B3LYP/6-311++G**	
	Minimum	TS	Minimum	TS
Zero-point energy (Hartree)	0.047122	0.044165	0.046226	0.043218
Imaginary frequencies	–	10.2873i	–	9.7920i
O1–O4 distance	2.912	7.365	2.902	7.365
O1–H3 distance	0.966	0.960	0.970	0.962
Angle (H2–O1–H3)	103.6	103.2	105.1	104.9
Total energies (Hartree)	−152.559525	−152.550386	−152.926350	−152.917590
Barrier (kcal/mol)	3.19[a]		3.08[b]	

Barrier for MP2/6-311++G** is 3.10 kcal/mol, and for using CCSD(T)/aug-cc-pvtz level the barrier is 3.07 kcal/mol.
[a] The scaling factor is 0.88 of MP2/6-311++G** and CCSD(T)/CBS (energy barrier is 5.27 kcal/mol without zero point energy).
[b] Scaling factor is 0.9044 for B3LYP and CCSD(T)/CBS (energy barrier is 5.27 kcal/mol without zero point energy).

Table 2
Rate constant of evaporation of water dimer for different temperatures for canonical system.

| Temperature (K)	243.0	273.0	303.0	333.0	500.0	600.0	700.0	800.0	900.0	1000.0
Correspond energy (kcal/mol)	1.287	1.571	1.867	2.174	4.035	5.258	6.551	7.909	9.33	10.812
Correspond (cm^{-1})	450	549	653	760	1411	1839	2291	2766	3263	3781
Anharmonic rate constant of canonical case (1/s)	4.75×10^9	8.42×10^9	1.31×10^{10}	1.84×10^{10}	4.65×10^{10}	6.44×10^{10}	8.06×10^{10}	9.52×10^{10}	1.09×10^{11}	1.21×10^{11}
Harmonic rate constant of canonical case (1/s)	2.84×10^{11}	7.66×10^{11}	1.72×10^{12}	3.36×10^{12}	3.42×10^{13}	7.58×10^{13}	1.35×10^{14}	2.08×10^{14}	2.93×10^{14}	3.85×10^{14}
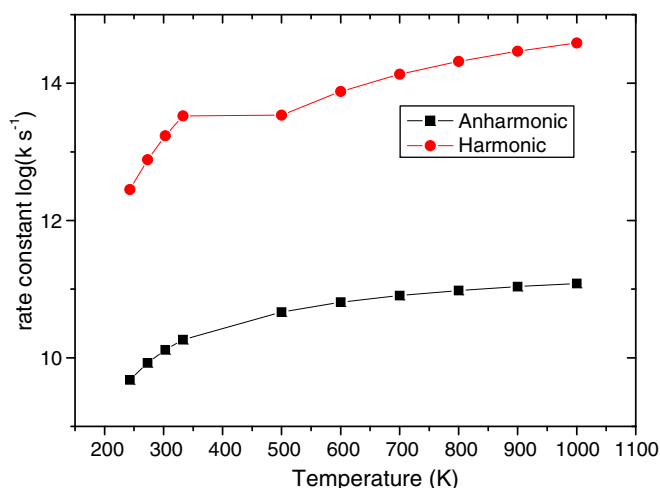
Fig. 3. Canonical rate constant versus temperature for the evaporation of water dimer.

range of 10^{11} cm^{-1} which is closer to the predictions from the literature [6]. The harmonic rate constants increase sharply from 10^{12} s^{-1} at 1411 cm^{-1} to 10^{14} s^{-1} at 4000 cm^{-1}. Moreover, as seen in Table 3, even though the anharmonic VTST evaporation rate constant is nearly insensitive to the available total energy in the given range, the harmonic rate constant is highly sensitive to the total energies. Much difference appears, in the anharmonic case, $W = 169$ at the total energy 4000 cm^{-1}, while $W = 2039698$ in the harmonic case. Table 3 shows the anharmonic and harmonic total number of states, density of states and rate constants of evaporations water dimer at the total energies of 1411–4000 cm^{-1} for microcanonical case (corresponding to 4.035–11.436 kcal/mol for canonical case). The dissociation rate constant with respect to the microcanonical total energies are also illustrated in Fig. 4. From the results in Table 3, much difference appears that total number of states W and density of states ρ in the case is much lower than that of harmonic case. For example, at the total energy 4000 cm^{-1}, W and ρ equal 169 and 20.97 separately for anharmonic case, while

2039698 and 139.72 for harmonic case. The big difference is caused by the different model, harmonic and anharmonic potential, which are used to simulate the vibrational bonds. For the different models and the different vibrational states, we count the total number of states and density of states, which affect the dissociation rate constant. Both of the canonical and microcanonical rate constants increase with the increasing of total energy basically. The harmonic rate constants increase sharply from 2.99×10^{12} s^{-1} at 1411 cm^{-1} to 4.38×10^{14} s^{-1} at 4000 cm^{-1}, while the anharmonic result is in the range of 1.83×10^{11}– 2.42×10^{11} cm^{-1}, which are closer to the calculations from the literature [6]. Our anharmonic results are in reasonable agreement with the experimental predictions. For instance, the calculated value is very close to the result measured by Lee et al. [1] for the hydrogen bond lifetime (reciprocal of the decay rate) of about 10^{-9} s in water clusters.

Within both harmonic and anharmonic approaches, the canonical and microcanonical calculations give very close results. The dividing surface VTST method and RRKM theory within the YL method can be effectively used in the studies of water clusters. In the liquid state, there exist many more ways for energy to be applied to a bond, so one would expect the hydrogen bond lifetime to be shorter than that in clusters but still within two or three orders of magnitude. In contrast to the previous work, we have obtained the total number of states and density of states in order to calculate the microcanonical VTST. VTST evaporation comparison is made between the microcnonical VTST evaporation rate constants and canonical rate constants. The results show the behavior of anharmonic rate constants VST is quite different to that of the harmonic evaporation rate constants. For the flexible system, like water dimer, the Morse potential is more suitable than the harmonic potential to simulate the vibrational bond. The anharmonic effect should be included to obtain the dissociation rate constant of such systems. The method used in this Letter can be extended to treat larger clusters of water or other molecules. The calculations then would become more complex than for the water dimer, not only due to increasing computation costs, but also because there are more contributions to the anharmonic effect from numerous vibra-

Table 3
Rate constant of evaporation of water dimer for different total energies for microcanonical system.

| Total energy (cm^{-1})	1411	1500	1839	2000	2291	2766	3000	3263	3781	4000
Correspond total energy (kcal/mol)	4.035	4.289	5.258	5.718	6.551	7.909	8.577	9.330	10.812	11.436
Anharmonic $W(E)$ of TS	30	33	35	44	46	65	88	94	134	169
Anharmonic $\rho(E)$ of reactant ($1/cm^{-1}$)	4.68	4.79	5.71	6.74	7.20	9.53	12.20	12.77	17.10	20.97
Anharmonic rate constant (1/s)	1.95×10^{11}	2.08×10^{11}	1.83×10^{11}	1.97×10^{11}	1.94×10^{11}	2.07×10^{11}	2.16×10^{11}	2.21×10^{11}	2.35×10^{11}	2.42×10^{11}
Harmonic $W(E)$ of TS	229	517	4944	10918	35282	152991	276825	503386	1393707	2039698
Harmonic $\rho(E)$ of reactant ($1/cm^{-1}$)	2.29	2.81	5.69	7.73	12.96	27.58	38.75	55.68	107.74	139.72
Harmonic rate constant (1/s)	2.99×10^{12}	5.53×10^{12}	2.60×10^{13}	4.23×10^{13}	8.16×10^{13}	1.66×10^{14}	2.14×10^{14}	2.71×10^{14}	3.88×10^{14}	4.38×10^{14}
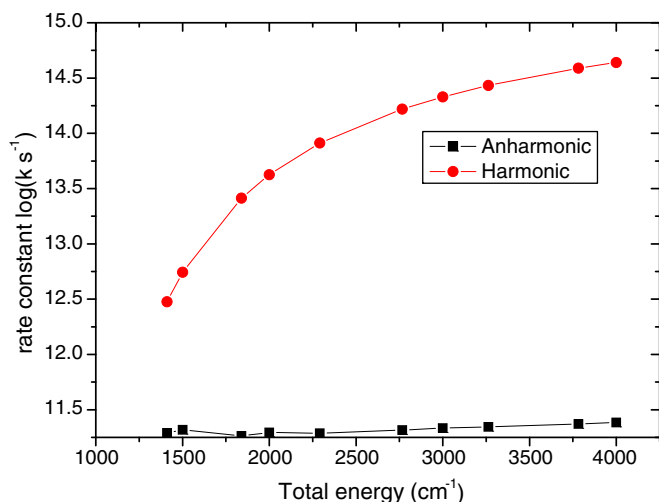
Fig. 4. Microcanonical rate constant versus total energies for the evaporation of water dimer.

tional frequencies. Another complication for bigger clusters is the possibility of existence of a large variety of different isomers and conformations. Nevertheless, the present study clearly demonstrates that the role of anharmonic effects in the kinetics of cluster decomposition is very important and should be taken into account.

Acknowledgments

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