On the calculation of rate constants of the small cyclic water cluster by anharmonic RRKM theory

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ARTICLE INFO

ABSTRACT

The rate constants for concerted exchange reaction of the small cyclic water clusters $(H_2O)_n(3,4)$ were calculated with the YL method. The anharmonic effect on the concerted hydrogen exchange reaction was examined. For the trimer water, at temperature 300 K, the anharmonic rate constant is $k = 4.70 \times 10^{-4}$ s^{-1}, and for the tetramer water, the value is 0.55 s^{-1}. The tunneling effect is very small for this two concerted hydrogen exchange reactions and can be neglected in the two reactions. The results are in reasonable agreement with the value given by Loerting et al. Besides that, the anharmonic effect is not significant for the concerted hydrogen exchange reaction of $(H_2O)_n(3,4)$.

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1. Introduction

Recent studies indicate that the anharmonic effect becomes very important in molecular and clusters [1]. In molecule reaction, according to the RRKM theory, the total number of states and the density of states play important roles in the calculations of rate constant. In general, to describe the anharmonic effect, the Morse oscillators (MOs) are commonly used. Some vibrational modes in molecules or clusters correspond to relatively weak bonds, in this case, the Morse potential can be used to fit the potential energy surface and to simulate the bonding. The characteristic features of the anharmonic effect include a decrease in vibrational bond-stretching frequencies, and an increase in the bond lengths and distance of bond dissociation. The requirement for anharmonic correction to existing reaction rate theories has been emphasized by several authors [2–5]. Our authors (Yao and Lin) have present a new method (below, YL method) [6], which can carry out the first principle calculations about the rate constants of molecular reactions within the framework of the transition state theory (TST). Yao et al. apply this method to examine the anharmonic effect on the dissociation of molecular reaction [6]. The mentioned results indicated that the YL method is suitable for calculating the rate constants of unimolecular reactions.

Due to the ubiquity of water clusters in nature, the water cluster kinetics has been a focus of extensive researches. The neutral, cyclic water clusters $(H_2O)_n$ are important molecular species for the understanding of condensation process and the nature of hydrogen bonded networks [7–10]. For $(H_2O)_3$, with all three water molecules acting as both hydrogen bond donors and acceptors, it is the global minimum. While, for $(H_2O)_4$, the achiral ring structure with solely donor/acceptor oxygen atoms is also found to be the global minimum. These findings have been confirmed both theoretically and experimentally. The transition states to the concerted exchange of bridging hydrogens have higher symmetry because that the hydrogen atoms are exactly in the middle of the shortened OO distances. On the other hand, many chemists observed significant anharmonic effects in dissociation of clusters and molecular systems [11–21].

In 1991, Garrect and Melius pointed out that the reaction rate constant of trimer water, with small curvature tunneling effect (SCT), is $k(300 \text{ K}) = 10^{-14}$ s^{-1} [22]. However, their result was in disagreement with the one given by Loerting et al. [23]. Loerting et al. found that the rate constant with large curvature tunneling effect (LCT) $k(300 \text{ K}) = 3.4 \times 10^{-4}$ s^{-1} and $k(300 \text{ K}) = 0.44$ s^{-1} for trimer and tetramer water, respectively. The purpose of this letter is to compute rate constant for the concerted hydrogen exchange reaction of the small cyclic water clusters $(H_2O)_n$ ($n = 3, 4$) as a function of energy. Therefore, we will use the YL method to examine the anharmonic effect upon the concerted hydrogen exchange reaction in the present Letter. Whereas the tunneling is very important for the reactants involving the motion of hydrogen atoms [24], then the tunneling effect is also considered in the Letter. The details of computational methods in Section 2. Numerical results and detailed discussions are given in Section 3. Section 4 contains the main conclusion of this work.

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2. Computational methods

2.1. Ab initio calculations

The geometries of the reactant and transition state have been optimized, with 6-311++G** basis set, by the MP2 method and the B3LYP method, respectively. The vibrational harmonic and anharmonic frequencies, calculated at the same level, are used for characterization of stationary points, zero-point-energy corrections, as well as for the calculations of reaction rate constant within the framework of the TST and the RRKM theory, respectively. All stationary points have been positively identified as local minima or transition states. The GAUSSIAN 03 program was utilized for all *ab initio* calculations [25].

2.2. RRKM and anharmonic effect

For a microcanonical system, using the RRKM theory, the unimolecular reaction rate constant for the system with energy E is given by [26]

$$k_u(E) = \frac{1}{h} \frac{W^{\neq}(E - E_a^{\neq})}{\rho(E)},$$ (1)

where h is Planck's constant, $\rho(E)$ is the density of the states of the reactant, and $W^{\neq}(E - E_a^{\neq})$ is the total number of states of the activated complex. Here, E and $E_a^{\neq}$ represent the total energy given to the system and the activation energy, respectively. Thus, in essence, as is expected in a statistical treatment, the RRKM theory simply states that the rate constant is proportional to the fraction of molecules having an internal energy E that are apt to react irrespective of the way that the molecule has been activated to that energy [27,28]. It should be emphasized that conventionally $W^{\neq}(E - E_a^{\neq})$ and $\rho(E)$ have been evaluated in the Morse oscillator potential. Notice that, in general, from the definition of $W(E)$, the total number of states can be expressed as

$$W(E) = \sum_i H(E - E_i),$$ (2)

where $H(E - E_i)$ denotes the Heaviside function. In this case, energy levels E_i are calculated explicitly and $W(E)$ can then be obtained by direct counting of those states, which are below or equal to E. By applying the Laplace transformation to Eq. (2), we obtain

$$\int_0^\infty dE e^{-\beta E} W(E) = \frac{Q(\beta)}{\beta} = L[W(E)],$$ (3)

where $\beta = 1/kT$, k is Boltzmann's constant, T is the temperature of the system and $Q(\beta)$ is the partition function of the system. Similarly, we obtain

$$\int_0^\infty dE e^{-\beta E} \rho(E) = Q(\beta) = L[\rho(E)].$$ (4)

That is, Eqs. (3) and (4) denote the Laplace transformations of $W(E)$ and $\rho(E)$, respectively. In other words, $W(E)$ and $\rho(E)$ can be obtained from Eqs. (3) and (4) by the inverse Laplace transformation. The detail of derivation can be found in Ref. [6].

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

$$k_f(T) = \frac{kT}{h} \frac{Q^{\neq}(T)}{Q(T)} e^{-\frac{E_a^{\neq}}{kT}},$$ (5)

where $Q(T)$ and $Q^{\neq}(T)$ represent the partition functions for the reactant and activated complex, respectively. In this case, we have

$$\begin{cases} Q^{\neq}(T) = \prod_i^{N-1} q_i^{\neq}(T), \\ Q(T) = \prod_i^N q_i(T), \end{cases}$$ (6)

where N is the number of the vibrational modes of the reactant, $q_i^{\neq}(T)$ and $q_i(T)$ are the vibrational partition functions for the activated complex and the reactant for each mode, respectively.

The above discussion notes that the partition function plays a very important role in calculating the total number of states, the density of states and the rate constant. To investigate the anharmonic effect on a unimolecular reaction, the anharmonic number and the density of states for a system of coupled MOs take a simple form. For the MO, we have

$$E_{n_i} = \left(n_i + \frac{1}{2}\right)\hbar\omega_i - x_i\left(n_i + \frac{1}{2}\right)^2 \hbar\omega_i,$$ (7)

where x_i is the Morse parameter, ω_i is the frequency of the ith vibrational mode, and n_i is the vibration quantum number of the vibrational mode. The maximum value of n_i is represented by n_i^{max}. In other words, the anharmonic effect has two features: One is that the energy spacings are not equal, and the other is the existence of a maximum quantum number n_i^{max}. It should be noted the anharmonic constant x_i for various molecules can be determined by *ab initio* calculation. In this Letter, we shall discuss the anharmonic rate constant of the concerted exchange reaction in the cyclic trimer and tetramer water.

3. Discussion of results

For the concerted exchange reaction of trimer and tetramer water, the geometric and the energetic parameters of the reactant and transition state are collected in Tables 1 and 2, respectively, including apparent activation energies (total energy barrier), relative energies of the transition states with respect to the reactant. The information was obtained with the MP2/6-311++G** method, which is based on the much cheaper B3LYP/6-311++G** method. It need to point out that the results given by two methods are close.

Table 1
Water trimer. Energies in kcal/mol, frequencies in cm^{-1}, bond lengths in Å, and angles in degrees. H_b corresponds to a 'bridged', and H_f to a 'free' hydrogen atom.

| E	MP2/6-311++G**		B3LYP/6-311++G**	
	Minimum	TS	Minimum	TS
Zero-point-energy (Hartree)	0.072566	0.063168	0.073143	0.066243
Imaginary frequencies	–	1470.9i	–	1737.8i
Total energies (Hartree)	−228.52638	−228.48349	−229.29827	−229.25526
H_bO distance	0.986	1.229	0.984	1.229
H_fO distance	0.968	0.966	0.968	0.969
Angle (OH$_b$O)	144.5	148.0	148.6	152.0
Angle (H$_b$OH$_f$)	113.2	122.8	106.6	112.7
Barrier (kcal/mol)	21.01		22.66	

Table 2
Water tetramer. Energies in kcal/mol, frequencies in cm^{-1}, bond lengths in Å, and angles in degrees. H_b corresponds to a 'bridged', and H_f to a 'free' hydrogen atom.

E	MP2/6-311++G**		B3LYP/6-311++G**	
	Minimum	TS	Minimum	TS
Zero-point-energy (Hartree)	0.099865	0.089806	0.098940	0.089027
Imaginary frequencies	–	1100.4i	–	1463.9i
Total energies (Hartree)	−305.34326	−305.30615	−305.88314	−305.70746
H_bO distance	0.994	1.214	0.992	1.216
H_fO distance	0.968	0.967	0.969	0.970
Angle (OH$_b$O)	162.1	163.9	167.1	168.1
Angle (H$_b$OH$_f$)	112.8	120.0	106.3	110.7
Barrier (kcal/mol)	16.98		16.80	

Table 3
The rate constant of the trimer at different temperatures for the canonical system.

Temperature (K)	100.0	150.0	200.0	250.0	300.0	400.0	600.0	1000.0	
Total energy (kcal/mol)	0.222	0.632	1.210	1.918	2.727	4.572	8.908	19.325	
Anharmonic rate constant of canonical case (s^{-1})	1.46×10^{-34}	2.90×10^{-19}	1.23×10^{-11}	4.43×10^{-7}	4.70×10^{-4}	2.75	1.64×10^4	1.93×10^7	
Harmonic rate constant of canonical case (s^{-1})	1.83×10^{-34}	3.25×10^{-19}	1.17×10^{-11}	3.61×10^{-7}	3.35×10^{-4}	1.59	7.09×10^3	6.50×10^6	
Temperature (K)	1200.0	1300.0	1400.0	1500.0	1600.0	1700.0	1800.0	1900.0	2000.0
Total energy (kcal/mol)	25.221	28.315	31.494	34.755	38.087	41.485	44.943	48.455	52.015
Anharmonic rate constant of canonical case (s^{-1})	1.16×10^8	2.32×10^8	4.20×10^8	7.04×10^8	1.11×10^9	1.65×10^9	2.35×10^9	3.23×10^9	4.30×10^9
Harmonic rate constant of canonical case (s^{-1})	3.80×10^7	7.59×10^7	1.38×10^8	2.33×10^8	3.71×10^8	5.60×10^8	8.11×10^8	1.13×10^9	1.53×10^9
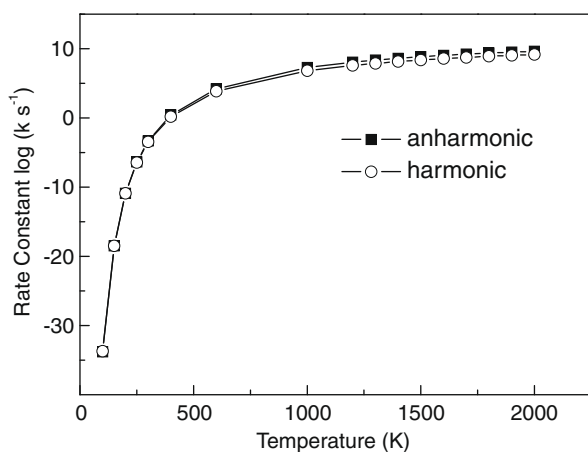
Fig. 1. The canonical rate constant versus temperature for the water trimer.

3.1. Trimer

The anharmonic and the harmonic canonical rate constants calculated are presented in Table 3, at temperatures from 100 to 2000 K for a canonical system. Corresponding to Table 3, the rate constant for the water trimer are plotted in Fig. 1. In the earlier theoretical work [23], the rate constant was predicted to be $k(300\,\text{K}) = 3.4 \times 10^{-4}\,\text{s}^{-1}$, which is reasonable agreement with our results ($k(300\,\text{K}) = 4.70 \times 10^{-4}\,\text{s}^{-1}$ and $k(300\,\text{K}) = 3.35 \times 10^{-4}\,\text{s}^{-1}$ are anharmonic and harmonic rate constant, respectively). Table 3 shows that the energies for 100–1000 K are lower than the calculated activation energy of 21.01 kcal/mol. Hence, we have to calculate the microcanonical rate constant at higher total energies.

The relationship between the total energy of a microcanonical system and the temperature of a canonical system is the following [6]

$$E = -\left[\frac{\partial \ln Q}{\partial \beta}\right]. \tag{8}$$

Table 4
The rate constant of the trimer at different energies for the microcanonical system.

Total energy (kcal/mol)	19.325	21.050	22.222	25.221	28.315	31.494	34.755	38.087	41.485	44.943	48.455	52.015
Anharmonic W(E) of TS	–	1.00	5.19	1.75×10^2	2.33×10^3	1.97×10^4	1.25×10^5	6.48×10^5	2.88×10^6	1.13×10^7	4.04×10^7	1.33×10^8
Anharmonic $\rho(E)$ of reactant (1/cm^{-1})	–	1.16×10^6	1.80×10^6	5.06×10^6	1.33×10^7	3.33×10^7	7.90×10^7	1.79×10^8	3.90×10^8	8.18×10^8	1.66×10^9	3.26×10^9
Anharmonic rate constant of microcanonical case (s^{-1})	–	2.57×10^4	8.66×10^4	1.01×10^6	5.20×10^6	1.78×10^7	0.48×10^8	1.08×10^8	2.21×10^8	4.15×10^8	7.30×10^8	1.22×10^9
Harmonic W(E) of TS	–	1.08	4.49	1.77×10^2	2.73×10^3	2.64×10^4	1.90×10^5	1.11×10^6	5.48×10^6	2.39×10^7	9.38×10^7	3.36×10^8
Harmonic $\rho(E)$ of reactant (1/cm^{-1})	–	8.84×10^5	1.46×10^6	4.90×10^6	1.55×10^7	4.65×10^7	1.33×10^8	3.64×10^8	9.60×10^8	2.43×10^9	5.95×10^9	1.41×10^{10}
Harmonic rate constant of microcanonical case (s^{-1})	–	3.68×10^4	9.20×10^4	1.08×10^6	5.28×10^6	1.70×10^7	4.27×10^7	9.08×10^7	1.71×10^8	2.95×10^8	4.73×10^8	7.16×10^8

Table 4 shows the anharmonic and harmonic rate constants of trimer water for the microcanonical system. The data are also illustrated in Fig. 2.

From Table 3, Fig. 1 and Table 4, Fig. 2, it is concluded that within both the canonical approach and the microcanonical one, the harmonic and the anharmonic calculations give close results. That is, the anharmonic effect is very small for the concerted exchange reaction of the small cyclic water clusters $(H_2O)_3$. Moreover, as seen in Tables 3 and 4, the rate constant is insensitive to the higher energies for the microcanonical case, while it is very sensitive to the lower temperature for the canonical case. The rate constant increases with increasing energy.

3.2. Tetramer

Referring to the trimer water, the anharmonic and the harmonic rate constants are presented in Table 5, at temperatures from 100 to 1500 K for a canonical system. Corresponding to Table 5, the rate
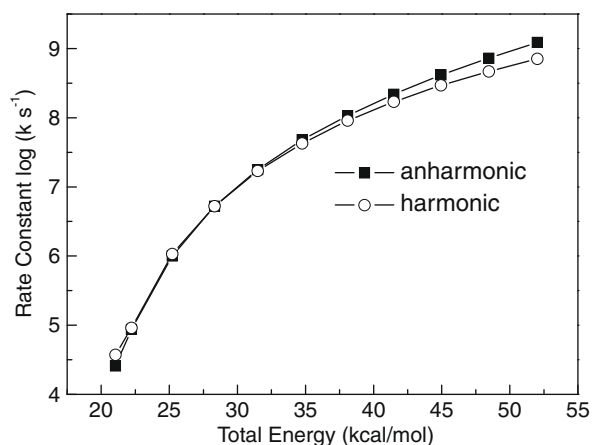

Fig. 3. The same as Fig. 1 but for the water tetramer.
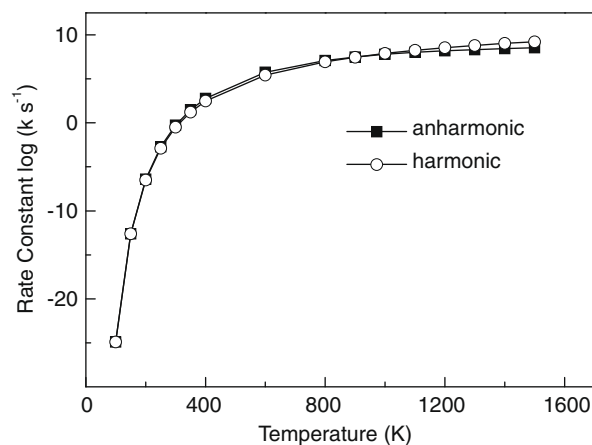

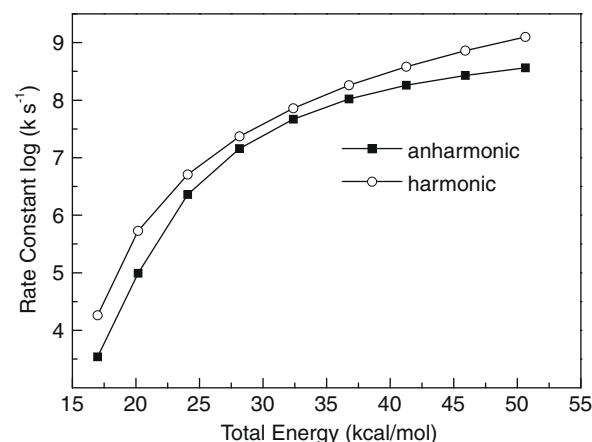**Fig. 2.** The microcanonical rate constant versus total energies for the water trimer.

Fig. 4. The same as Fig. 2 but for the water tetramer.

Table 5
The rate constant of the tetramer at different temperatures for the canonical system.

Temperature (K)	100.0	150.0	200.0	250.0	300.0	350.0	400.0	600.0
Total energy (kcal/mol)	0.347	0.951	1.796	2.820	3.985	5.265	6.645	12.934
Anharmonic rate constant of canonical case (s^{-1})	1.16×10^{-25}	2.71×10^{-13}	3.96×10^{-7}	1.94×10^{-3}	0.55	3.01×10	6.19×10^{2}	5.49×10^{5}
Harmonic rate constant of canonical case (s^{-1})	1.17×10^{-25}	2.52×10^{-13}	3.17×10^{-7}	1.32×10^{-3}	0.33	1.61×10	2.98×10^{2}	2.70×10^{5}
Temperature (K)	800.0	900.0	1000.0	1100.0	1200.0	1300.0	1400.0	1500.0
Total energy (kcal/mol)	20.166	24.070	28.145	32.378	36.756	41.267	45.900	50.642
Anharmonic rate constant of canonical case (s^{-1})	1.21×10^{7}	3.07×10^{7}	6.15×10^{7}	1.04×10^{8}	1.57×10^{8}	2.15×10^{8}	2.77×10^{8}	3.38×10^{8}
Harmonic rate constant of canonical case (s^{-1})	8.77×10^{6}	2.90×10^{7}	7.68×10^{7}	1.73×10^{8}	3.46×10^{8}	6.29×10^{8}	1.06×10^{9}	1.67×10^{9}

Table 6
The rate constant of the tetramer at different energies for the microcanonical system.

Total energy (kcal/mol)	16.448	16.993	20.166	24.070	28.145	32.378	36.756	41.267	45.900	50.642
Anharmonic W(E) of TS	–	1.00	2.25×10^{3}	5.22×10^{5}	2.77×10^{6}	6.65×10^{8}	9.57×10^{9}	9.64×10^{10}	7.49×10^{11}	4.76×10^{12}
Anharmonic $\rho(E)$ of reactant (1/cm^{-1})	–	8.49×10^{7}	6.87×10^{8}	6.81×10^{9}	5.75×10^{10}	4.22×10^{11}	2.73×10^{12}	1.58×10^{13}	8.28×10^{13}	3.95×10^{14}
Anharmonic rate constant of microcanonical case (s^{-1})	–	3.52×10^{3}	9.81×10^{4}	2.30×10^{6}	1.45×10^{7}	4.73×10^{7}	1.05×10^{8}	1.83×10^{8}	2.71×10^{8}	3.61×10^{8}
Harmonic W(E) of TS	–	10.6	2.29×10^{3}	1.88×10^{5}	6.57×10^{6}	1.40×10^{8}	2.14×10^{9}	2.55×10^{10}	2.48×10^{11}	2.04×10^{12}
Harmonic $\rho(E)$ of reactant (1/cm^{-1})	–	1.75×10^{7}	1.26×10^{8}	1.11×10^{9}	8.50×10^{9}	5.78×10^{10}	3.55×10^{11}	1.99×10^{12}	1.03×10^{13}	4.92×10^{13}
Harmonic rate constant of microcanonical case (s^{-1})	–	1.82×10^{4}	5.43×10^{5}	5.07×10^{6}	2.32×10^{7}	7.29×10^{7}	1.81×10^{8}	3.84×10^{8}	7.23×10^{8}	1.25×10^{9}

Table 7
The tunneling probabilities for the trimer and the tetramer, respectively.

Total energies (kcal/mol)	10.0	11.0	12.0	13.0	14.0	15.0	16.0
Probabilities	2.08×10^{-7}	1.12×10^{-6}	5.57×10^{-6}	2.60×10^{-5}	1.15×10^{-4}	4.79×10^{-4}	1.91×10^{-3}
Total energies (kcal/mol)	17.0	18.0	19.0	20.0	21.0	22.0	23.0
Probabilities	7.25×10^{-3}	2.61×10^{-2}	8.69×10^{-2}	2.46×10^{-1}	0.52	0.78	0.92

Total energies (kcal/mol)	5.0	6.0	7.0	8.0	9.0	10.0	11.0	12.0
Probabilities	1.71×10^{-9}	1.70×10^{-8}	1.41×10^{-7}	1.01×10^{-6}	6.41×10^{-6}	3.68×10^{-5}	1.94×10^{-4}	9.51×10^{-4}
Total energies (kcal/mol)	13.0	14.0	15.0	16.0	17.0	18.0	19.0	20.0
Probabilities	4.35×10^{-3}	1.86×10^{-2}	7.23×10^{-2}	2.34×10^{-1}	0.54	0.81	0.94	0.98

constants for the water tetramer are plotted in Fig. 3. The anharmonic and the harmonic rate constants are $k(300\,\mathrm{K}) = 0.55\ \mathrm{s}^{-1}$ and $0.33\ \mathrm{s}^{-1}$, respectively, which are in reasonable agreement with the earlier theoretical work ($k(300\,\mathrm{K}) = 0.44\ \mathrm{s}^{-1}$) [23]. Table 5 suggests that the energies for 100–600 K are lower than the calculated activation energy of 16.98 kcal/mol. Hence, we have to calculate the microcanonical rate constant at higher total energies. Table 6 shows that the anharmonic and the harmonic rate constants of tetramer water for the microcanonical system. The data are also illustrated in Fig. 4.

The results show that within both canonical and microcanonical approaches, the harmonic and the anharmonic calculations give very close results. That is, the anharmonic effect is not very pronounced for the concerted exchange reaction of the small cyclic water clusters $(H_2O)_4$. The rate constant increases with increasing energy. Moreover, as seen from Tables 5 and 6, the rate constant is insensitive to the higher energies for the microcanonical case, but, it is very sensitive to the lower temperature for the canonical case.

Figs. 1–4 and Tables 3–6 show that the difference of the harmonic and the anharmonic rate constants is rather small for the canonical case, while it is quite large for the microcanonical case. The difference increases with increasing molecular numbers and increasing total energy. For a system, the more the molecular numbers, the more vibrational mode. Thus we conclude that the anharmonic effect becomes obvious with increasing molecular numbers.

Furthermore, we use the following formulism to obtain the tunneling probabilities for trimer and tetramer in Table 7 [24],

$$P(E_1) = \frac{\sinh(a)\sinh(b)}{\sinh^2\left(\frac{a+b}{2}\right) + \cosh^2(c)}, \tag{9}$$

where

$$a = \frac{4\pi}{\hbar\omega_b}\sqrt{E_1 + V_0}\left(V_0^{-1/2} + V_1^{-1/2}\right)^{-1},$$

$$b = \frac{4\pi}{\hbar\omega_b}\sqrt{E_1 + V_1}\left(V_0^{-1/2} + V_1^{-1/2}\right)^{-1},$$

$$c = 2\pi\sqrt{\frac{V_0 V_1}{(\hbar\omega_b)^2} - \frac{1}{16}}.$$

Here, ω_b is the magnitude of the imaginary frequency, V_0 is the barrier height relative to reactants, and V_1 is the barrier height relative to products. $V_1 - V_0$ is the exoergicity of the reactions (neglecting the zero-point-energies).

Table 7 shows that the tunneling probabilities increase with increasing of the total energy. The values are about 0.5 for trimer in the barrier of 21.0 kcal/mol, and for tetramer in the barrier of 17.0 kcal/mol, respectively. It notes that the tunneling effect is very small for the concerted hydrogen exchange reaction of $(H_2O)_n$ $(n = 3, 4)$.

4. Conclusions

In this Letter, we have calculated the anharmonic and the harmonic rate constants of the concerted hydrogen exchange reaction in the cyclic trimer and tetramer water with the YL method. For the trimer water, the calculated rate constant is $k(300\,\mathrm{K}) = 4.70 \times 10^{-4}\ \mathrm{s}^{-1}$ for the anharmonic case, and $k(300\,\mathrm{K}) = 3.35 \times 10^{-4}\ \mathrm{s}^{-1}$ for the harmonic case. While, for the tetramer water, the anharmonic and the harmonic rate constants are $k(300\,\mathrm{K}) = 0.55\ \mathrm{s}^{-1}$ and $k(300\,\mathrm{K}) = 0.33\ \mathrm{s}^{-1}$, respectively. Our results are in good agreement with the values ($k(300\,\mathrm{K}) = 3.4 \times 10^{-4}\ \mathrm{s}^{-1}$ and $0.44\ \mathrm{s}^{-1}$) given by Loerting et al. Moreover, we observed that within both canonical and microcanonical approaches, the harmonic and the anharmonic calculations give close results, i.e., the anharmonic effect is not very pronounced for the concerted exchange reaction of the small cyclic water clusters. At the same time, the results show that the difference between the harmonic rate constant and the anharmonic one is rather small for the canonical case, while it is quite significant for the microcanonical case. The difference of rate constant increases with increasing of molecular number and increasing of total energy, i.e., the anharmonic effect becomes obvious with increasing molecular number. Furthermore, the rate constants increase with increasing total energy. The rate constants are very sensitive to the lower energies for the canonical case, while it is insensitive to the higher energies for the microcanonical case. The tunneling effect is very small for the concerted hydrogen exchange reaction of $(H_2O)_n$ $(n = 3, 4)$ and can be neglected in the two reactions. Hence, the present results indicate that the YL method is suitable for studying the rate constant of such small cyclic water clusters.

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