



Quantum chemical calculation of intramolecular vibrational redistribution and vibrational energy transfer of water clusters



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ABSTRACT

In present letter the adiabatic approximation is applied to the intramolecular vibrational redistribution (IVR) of water clusters. The isotope, blocking and cluster-size effects are investigated. This letter also examines the assumption associated with the transition state theory applied to unimolecular reactions; that is, IVR is assumed to be completed before the reaction takes place. For this purpose, we choose to study $(\text{H}_2\text{O})_2\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{H}_3\text{O}^+$, and $(\text{H}_2\text{O})_2 \rightarrow 2\text{H}_2\text{O}$ processes. In molecular clusters, the vibrational excitation energy transfer between different normal modes has been observed. This will also be investigated for the deuterated species of $(\text{HOD})_2\text{H}^+$.

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1. Introduction

Recently experimental [1–7] and theoretical [8–16] investigations of the vibrational redistribution dynamics of water and other molecules in condensed phases have attracted a considerable attention. Hynes and co-workers studied the vibrational redistribution of OH stretch excitations to bending to librational degrees of freedom in water liquid in linear coupling model [15]. Skinner and co-workers discussed the validity of Förster theory model for the vibrational energy transfer in water liquid [13]. Bowman and co-workers simulated the predissociation of water dimers and discuss the process of energy flow from bond stretching to the bond bending [17]. In comparison the first principle calculation of the vibrational redistribution dynamics of isolated molecules has received much less attention [18–20]. A theoretical approach based on the adiabatic approximation model of vibrational redistribution has been developed [8,12]. In this Letter, we shall present its application to the vibrational dynamics of water clusters $(\text{H}_2\text{O})_n$ and $(\text{H}_2\text{O})_n\text{H}^+$, where $n = 2, 3, 4$, and their isotope species. The RRKM (Rice–Ramsperger–Kassel–Marcus) theory is a very popular and well received theory applied to treat the unimolecular reactions of isolated (i.e., collision-free) molecules and clusters [21–24]. Lin and et al. have recently applied Morse potential model to develop

the anharmonic RRKM theory [25–28]. Fundamentally it is based on the transition state theory which assumes that intramolecular vibrational redistribution (IVR) is much faster than unimolecular reactions so that the vibrational equilibrium is established before the reaction takes place. IVR plays an important role not only in unimolecular reactions but also in photochemistry and photophysics. Due to the fact that in the harmonic oscillator approximation when a vibrational mode is excited the excitation energy will be localized in that mode and will not flow into other modes, for IVR to take place, the anharmonic potential energy function which describes the coupling among different modes is needed. This information has become available only recently in the quantum chemistry programs and will be employed to perform the calculation of IVR in this Letter [29,30].

In treating the unimolecular decomposition of molecular clusters by using the RRKM theory the anharmonic effect is very important and it has been recently included in the conventional RRKM theory. This has been applied to study the decomposition of $(\text{H}_2\text{O})_2$, $((\text{H}_2\text{O})_2 \rightarrow 2\text{H}_2\text{O})$ [27] and $(\text{H}_2\text{O})_2\text{H}^+$, $((\text{H}_2\text{O})_2\text{H}^+ \rightarrow (\text{H}_2\text{O})\text{H}^+ + \text{H}_2\text{O})$ [25]. For the purpose of the investigation of the effect of IVR on the RRKM theory, we shall calculate the IVR of $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_2\text{H}^+$ and compare these IVR rates with the anharmonic decomposition rates of these clusters. This can then be used to examine the validity of the RRKM theory applied to these clusters.

In molecular clusters, the vibrational excitation energy transfer from one mode to another has been observed. This will also be investigated in the deuterated species of $(\text{HOD})_2\text{H}^+$.

The present letter is organized as follows. Following the introduction, a brief theory of IVR will be presented in Section 2, which

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will be followed by the presentation of the calculated results of IVR of $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O})_2\text{H}^+$ and the deuterated species of $(\text{H}_2\text{O})_2\text{H}^+$ in Section 3. The discussion of vibrational energy transfer within $(\text{HOD})_2$, H^+ , and the validity of RRKM method on $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_2\text{H}^+$ will be given in Section 4. Then a brief summary will be given in Section 5.

2. Theory of IVR

We consider the adiabatic approximation model for isolated molecules or clusters, which is similar to the Born–Oppenheimer approximation model for molecules; that is, electronic coordinates corresponds to high frequency normal coordinates $\{Q_i\}$, nuclear coordinates corresponds to low frequency normal coordinates $\{q_i\}$, UV–visible spectra corresponds to IR vibrational spectra and internal conversion corresponds to IVR. It follows that to solve

$$H\Psi_{av}(\mathbf{Q}, \mathbf{q}) = E_{av}\Psi_{av}(\mathbf{Q}, \mathbf{q}) \quad (1)$$

where

$$H = T_L + T_H + V = T_L + H_H \quad (2)$$

is the total vibrational Hamiltonian, and

$$H_H \equiv T_H + V \quad (3)$$

is the high frequency oscillator Hamiltonian including the interaction between high frequency modes and low frequency modes. The subscript ‘H’ and ‘L’ represent ‘high frequency modes’ and ‘low frequency modes’ respectively. We first solve

$$H_H\Phi_a(\mathbf{Q}; \mathbf{q}) = U_a(\mathbf{q})\Phi_a(\mathbf{Q}; \mathbf{q}) \quad (4)$$

to get the ‘potential energy surface (PES)’ of low frequency modes. Then we solve

$$[T_L + U_a(\mathbf{q})]\Theta_{av}(\mathbf{q}) = E_{av}\Theta_{av}(\mathbf{q}) \quad (5)$$

to obtain the total wavefunction

$$\Psi_{av}(\mathbf{Q}, \mathbf{q}) = \Phi_a(\mathbf{Q}; \mathbf{q})\Theta_{av}(\mathbf{q}) \quad (6)$$

Here semicolon means that \mathbf{q} is regarded as a parameter in $\Phi_a(\mathbf{Q}; \mathbf{q})$. The performance for the adiabatic approximation has been tested and is shown to be acceptable [31]. In Eqs. (4)–(6), a denotes the quantum state of the high frequency modes \mathbf{Q} , while ν represents the quantum states of the low frequency modes \mathbf{q} .

Notice that

$$V(\mathbf{Q}, \mathbf{q}) = V_H(\mathbf{Q}) + V_L(\mathbf{q}) + V_{\text{int}}(\mathbf{Q}, \mathbf{q}) \quad (7)$$

$$V_H(\mathbf{Q}) = \sum_I \frac{1}{2} \omega_I^2 Q_I^2 + \frac{1}{6} \sum_{IJK} V_{IJK} Q_I Q_J Q_K + \dots \quad (8)$$

$$V_L(\mathbf{q}) = \sum_i \frac{1}{2} \omega_i^2 q_i^2 + \frac{1}{6} \sum_{ijk} V_{ijk} q_i q_j q_k + \dots \quad (9)$$

$$V_{\text{int}}(\mathbf{Q}, \mathbf{q}) = \frac{1}{2} \sum_{Iji} V_{Iji} Q_I Q_j q_i + \frac{1}{2} \sum_{Iij} V_{Iij} Q_I q_i q_j + \dots \quad (10)$$

V_{ijk} is the anharmonic expansion coefficients of the PES; for example,

$$V_{Iji} \equiv \left(\frac{\partial^3 V}{\partial Q_I \partial Q_j \partial q_i} \right)_0 \quad (11)$$

Using the same treatment in the internal conversion process [32], in the adiabatic approximation the IVR rate for $a \rightarrow b$ can be expressed as [8,31]

$$W_{b \rightarrow av}^{(l)} = \frac{2\pi}{\hbar} \sum_u \left| \left\langle \Theta_{bu} \left| -\hbar\omega_l \left\langle \Phi_b \left| \frac{\partial}{\partial q_l} \right| \Phi_a \right\rangle \right| \frac{\partial \Theta_{av}}{\partial q_l} \right|^2 D(E_{av} - E_{bu}) \quad (12)$$

$$W_{b \rightarrow av} = \sum_l W_{b \rightarrow av}^{(l)} \quad (13)$$

where

$$\left\langle \Phi_b \left| \frac{\partial}{\partial q_l} \right| \Phi_a \right\rangle = \frac{\left\langle \Phi_b \left| \frac{\partial V}{\partial q_l} \right| \Phi_a \right\rangle}{U_a(\mathbf{Q}) - U_b(\mathbf{Q})} \approx \frac{\left\langle \Phi_b^0 \left| \frac{\partial V}{\partial q_l} \right| \Phi_a^0 \right\rangle}{U_a^0 - U_b^0} \quad (14)$$

and $D(E_{av} - E_{bu})$ denotes the line-shape function. This IVR theory has recently been applied to compare with the experimental data of IVR for the two N–H vibrational modes of isolated aniline reported by Ebata et al. [19,20]. The agreement is acceptable in [33].

3. Calculated results- $(\text{H}_2\text{O})_2\text{H}^+$ and $(\text{H}_2\text{O})_2$

3.1. The isotope effect in IVR of $(\text{H}_2\text{O})_2\text{H}^+$

We now consider the application of the adiabatic approximation model of IVR to calculate the IVR rates of the hydrogen-bonded water dimer $(\text{H}_2\text{O})_2\text{H}^+$ and its deuterated and tritiated species. We select the MP2 method and 6-311++G(d, p) basis set to optimize the geometry of all the water clusters using GAUSSIAN 09 program [34], and then calculate the anharmonic coupling parameters. The optimized structure of $(\text{H}_2\text{O})_2\text{H}^+$ is shown in Figure 1.

The vibrational modes of $(\text{H}_2\text{O})_2\text{H}^+$ are shown in Figure S1 in supplementary material and the rates of IVR for the O–H related modes that play the important role for the dissociation of $(\text{H}_2\text{O})_2\text{H}^+$ to H_2O and H_3O^+ will be presented.

The frequencies of normal modes in $(\text{H}_2\text{O})_2\text{H}^+$, $(\text{H}_2\text{O})_2\text{D}^+$, and $(\text{H}_2\text{O})_2\text{T}^+$, which are related to the motions of the bridged hydrogen, deuterium and tritium atoms, obviously decrease due to mass increase. Overall vibrational redistribution rates for high frequency modes 12–15 of $(\text{H}_2\text{O})_2\text{H}^+$, $(\text{H}_2\text{O})_2\text{D}^+$ and $(\text{H}_2\text{O})_2\text{T}^+$ are calculated according to Eq. (13) and listed in Table 1. From this table, we find that the IVR rates slow down with the increase of the atomic weight of the bridged atom, that is, the IVR rates of the O–H modes in the $(\text{H}_2\text{O})_2\text{H}^+$ are faster than those in the $(\text{H}_2\text{O})_2\text{D}^+$ and $(\text{H}_2\text{O})_2\text{T}^+$ species. This phenomenon is often referred to as ‘blocking effect’, for which the bridge hydrogen atom is replaced by deuterium and tritium atom. The decrease of frequency means there must be more quanta of vibrational modes to accept energy, which lowers the vibrational transition rate. For example, for vibrational mode 13, the IVR rate for the H-species is 1.96 ps, while for the D-species and T-species, the rates are 5.20 and 7.46 ps, respectively.

Next we consider other deuterated species of $(\text{H}_2\text{O})_2\text{H}^+$ which are listed in Table 2. Let us first consider $(\text{H}_2\text{O} \cdot \text{H} \cdot \text{HOD})^+$ and $(\text{H}_2\text{O} \cdot \text{O} \cdot \text{D} \cdot \text{HOD})^+$. We can see that the IVR rates of any O–H mode in the H bridged species are faster than those in the D bridged species. On the contrary the IVR rate of the O–D mode is faster in the D bridged species. Similarly we compare the IVR rates in $(\text{D}_2\text{O} \cdot \text{H} \cdot \text{D}_2\text{O})^+$ and $(\text{D}_2\text{O} \cdot \text{D} \cdot \text{D}_2\text{O})^+$; the IVR rates of the four O–D modes in the H-species are faster than those in the D-species except mode 12. Finally we compare the IVR rates in $(\text{HOD} \cdot \text{H} \cdot \text{HOD})^+$ and $(\text{HOD} \cdot \text{D} \cdot \text{HOD})^+$ except mode 12. In conclusion, the IVR rates of the O–H modes in the H-species almost remain to be faster than those in the D-species.

3.2. The vibrational redistribution of water clusters $(\text{H}_2\text{O})_n$

The optimized structure of water dimer is shown in Figure 2. The point group of water dimer is C_s . There are 8 symmetric

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