

H atom transfer of collinear OH...O system

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A quantum mechanical calculation was performed to study the hydrogen atom transfer of collinear OH...O/OD...O system, for which Delves' coordinates and R-matrix propagation method were applied in a Melius-Blint potential energy surface. The calculation result showed that the state-state H atom transfer probability comported strong oscillation phenomena and collision delay time of the title system was in the fs-ps time scale. The kinetic isotope effect was calculated in this work too.

Keywords OH + O, H atom transfer, state to state probability, lifetime, isotope effect

Introduction

The hydrogen atom transfer of the intramolecular/intermolecular hydrogen bond has been studied extensively over the last twenty years because of its potential importance for the materials science, biochemistry and condense sciences.¹⁻³ Recently, the OH + O fragment model has been used successfully^{4,6} to study a number of important distinctive characters of these systems. In this model, the "real" H bonded system can be regarded as a collinear OH + O fragment whose PES is modified by other atoms. Then a calculation on the collinear "free" OH + O system will provide a good comparison with the "real" H bonded system and a good start point to study the influence of other atoms. The result of state-to-state probability will provide a view of the influence of OH stretching vibration in the system too, which is an very interesting problem in the research of H atom transfer process in H bonded system. So, we performed a state

to state quantum mechanism treatment of the H atom transfer process of OH...O free three-atom-fragment in this work. What is more, in consideration of the fact that the mass of deuterium atom is twice as heavy as that of hydrogen atom, the quantum effect of OD...O system may be less than that of OH...O system. Thus we calculated the D atom transfer probability of OD...O system and compared the result with that of OH...O system to study the influence of mass on the state to state H atom transfer probability. The kinetic isotope effect from 200—600 K was also calculated to know the effect of temperature on this process. The collision delay time of a dynamics process is very interesting and there have been some work in this field.⁷⁻⁸ From the discussion of Smith, we could know that for the delay time Δt when $2E\Delta t > \hbar$, it became meaningful to discuss the event in terms of collision complex,⁷ which is an important question in theory.^{7,10} Recently, Flynn also pointed out in his experiments that the magnitude of the ratio of collision delay time to particle free fly time would decide if the classic gas molecule collision model could be used to discuss the result of the experiments.⁹ So, the study of the collision delay time may be helpful for a clearer understanding of H atom transfer process from both theoretical and experimental view. Thus, we studied the collision delay time of this system in this work too.

PES and computation method

In lots of theory works about HO₂ system (see Ref. 11 and references therein), the analysis formation of the

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Melius and Blint's PES was used and was regarded as a classic PES of this system. So, in this work we use this PES too. Its analytic form was obtained from Ref. 12.

As we have discussed in the introduction, the main purpose of this work is strictly focused on the study of the hydrogen atom exchange of the title system. Since the quantum chemistry studies of many H-bonded systems indicated that the H-bonded triatomic fragment could be regarded as linear system in transition state (Ref. 16 and references therein), it is rational to treat the problem by collinear quantum scattering theory. In this case, the Schrödinger equation for this system can be expressed as:¹⁷

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial R_\lambda^2} + \frac{\partial^2}{\partial r_\lambda^2} \right) + V(R_\lambda, r_\lambda) - E \right] \Psi = 0 \quad (1)$$

where the Delves' coordinates¹⁸ are applied and $\lambda = \alpha, \beta$, which means the reactant channel and the product channel, respectively; E is the total energy; $V(R_\lambda, r_\lambda)$ is the total potential energy for the system. In order to solve this equation the interactive region is divided into sufficiently small wings that in each wing the V can be regarded as a constant. Then we can use the R matrix propagation method^{17,19} that was developed by Light to

solve this equation and calculate the S matrix and hydrogen atom transfer probability. Six symmetric and six anti-symmetric wave functions were used in our calculation in order to expand the state space of this system. More details about the program used here can be found in Ref. 21.

For a given energy E , a collision delay time which is independent of the distance R of them can be defined from the energy derivation with respect to the phase-shift η :

$$\Delta t = \hbar (d\eta/dE) \quad (2)$$

Then, the state to state collision delay time can be calculated from the S matrix by the following formula⁷

$$\Delta t_{ij} = \text{Re}[-i\hbar (S_{ij})^{-1} dS_{ij}/dE] \quad (3)$$

where Δt_{ij} is the collision delay time in the appearance of the peak outgoing signal in the j th channel after the injection of a pulse in the i th, where scattering matrix S was calculated by R matrix propagation method as we had described above. The collision delay time was calculated for OH \cdots O and OD \cdots O system in different energies, initial states and final states.

Since the state to state rate constants can be given by²⁰

$$k_{v\nu'}(T) = (2\pi\mu kT)^{-1/2} \int_{\epsilon\nu}^{\infty} P_{v\nu'}(E) \exp[-(E - \epsilon\nu)kT] dE \quad (4)$$

where μ is the reduce mass. $P_{v\nu'}(E)$ is the reaction probability from initial state v to final state v' . $\epsilon\nu$ means the energy of vibration state v . The kinetic iso-

tope effects of H atom transfer of this system can be calculated by

$$k_H/k_D = \left[\mu_{OD} \int_{\epsilon\nu}^{\infty} P_{Hv\nu'}(E) \exp[-(E - \epsilon\nu)kT] dE \right] / \left[\mu_{OH} \int_{\epsilon\nu}^{\infty} P_{Dv\nu'}(E) \exp[-(E - \epsilon\nu)kT] dE \right] \quad (5)$$

$P_{Hv\nu'}(E)$, $P_{Dv\nu'}(E)$ is the H atom transfer probability from initial state v to final state v' of OH \cdots O system and OD \cdots O system, respectively.

Results and discussion

H atom transfer probability

We have calculated dynamic results of the $v \leq 2$ H/D atom transfer process of the title system in this work. Fig. 1 shows the curves of state to state H atom

transfer probabilities P_{00} and P_{01} of OH \cdots O system versus total energy E , in which $P_{v'}$ was defined as the H atom transfer probabilities from the initial OH vibrational state v to OH final vibration state v' . In our calculation the $P_{v'}$ is equal to $P_{v'v}$ because of the symmetry of the Melius-Blint PES. For the channel i , from the results of the calculation we could find

$$\sum_i (P_{NRij} + P_{Rij}) = 1 \quad (6)$$

where P_{NRij} and P_{Rij} mean the state to state probabilities of non-reaction process and reaction process, respectively. For all the v and v' , the oscillation behavior of the probability is observed. For example, for the case of OH \cdots O, the thresholds E_t of the opening of channel $v = 0, 1, 2$ are 0.23 eV, 0.67 eV and 1.08 eV, respectively, which are consistent with the vibrational energies (E_v) of OH that were calculated from the solving of three-parameter Morse function and were provided in Table 1. For the vibrational adiabatic channels P_{00} , its probability P rises from zero at the thresholds of the opening of channel (0.23 eV), but its value is low now. At 0.65 eV it rises from 2.57×10^{-7} to 0.82 and shows an oscillation behavior at higher energy ($E > E_v(i+1)$). Just as showed by Eq. (6), this oscillation behavior may be a result of the interfering between different reaction and non-reaction channels: when the E is between 0.23 eV and 0.64 eV, the energy is so small that only $v = 0$ channel is open, and the reaction possibility is very small now; when the E reaches 0.65 eV, the reaction probability becomes large and we observed a great decline of the non-reaction probability of the system at this energy; at higher energy, other channels are open, which make the oscillation more complex. The result also shows that the probability of non-adiabatic (P_{01} , P_{02} and P_{12}) process is less than that of adiabatic one (P_{00} , P_{11} and P_{22}). For example, the highest peak of P_{01} is 0.357 at 1.23 eV, while that of P_{00} is 0.992 at 1.37 eV and that of P_{11} is 0.851 at 1.20 eV, which are all higher than that of P_{01} . This result is consistent with the common view that the adiabatic process is predominant for Heavy-Light-Heavy system. We also find that the highest peak of P_{02} is lower than that of P_{12} .

Fig. 1 provided the D atom transfer probabilities

Table 1 Calculation values of OH/OD vibrational energy E_v in different energy level i

Energy level i	E_v (eV)	
	OH	OD
0	0.2283	0.1668
1	0.6661	0.4904
2	1.0786	0.8005
3	1.4658	1.0973
4	1.8277	1.3808

P_{00} and P_{01} of OD \cdots O too. The E_t of channel $v = 0, 1, 2$ are 0.17 eV, 0.50 eV, 0.81 eV, respectively, which are lower than that of OH \cdots O case. This result is consistent with the vibrational energy E_v of OD given in Table 1 too. Since OD \cdots O is still a Heavy-Light-Heavy system and the Melius-Blint PES was still used here, Fig. 1(c) and 1(d) are similar with Fig. 1(a) and 1(b) in many aspects, respectively. For example, for the P_{00} , P_{11} and P_{22} , P rises from zero directly at the thresholds of the opening of channel; it is very small at low energy and shows a oscillation behavior at higher energy; the P of vibrational non-adiabatic ones are smaller than those of the adiabatic ones; the P_{02} is smaller than P_{12} , and so on. However, the D atom transfer probability of OD \cdots O is smaller than the H atom one of OH \cdots O system in adiabatic cases (We do not compared that of non-adiabatic ones here because the interference of different channel will make the result become very complex and be hard to be discussed). For example, the highest peaks of P_{11} and P_{22} of OH \cdots O are 0.851 at 1.20 eV and 0.796 at 1.75 eV, respectively, while that for OD \cdots O is 0.701 at 0.90 eV and 0.372 at 1.69 eV, respectively. This result is consistent with the common idea that the stronger quantum effect of OH \cdots O system may cause greater tunneling probability than that of OD \cdots O. The oscillation peaks of OD \cdots O also show larger peak width and larger distance between peaks than those of OH \cdots O. In summary, the calculation result of H atom transfer confirmed the view that the oscillation is the result of the interfering of different channels. What is more, comparing the dynamics detail of OD \cdots O with that of OH \cdots O, we could find from the calculation that the less tunneling effect of OD \cdots O system may cause larger peak width, larger distance between peaks and lower peak height for adiabatic case.

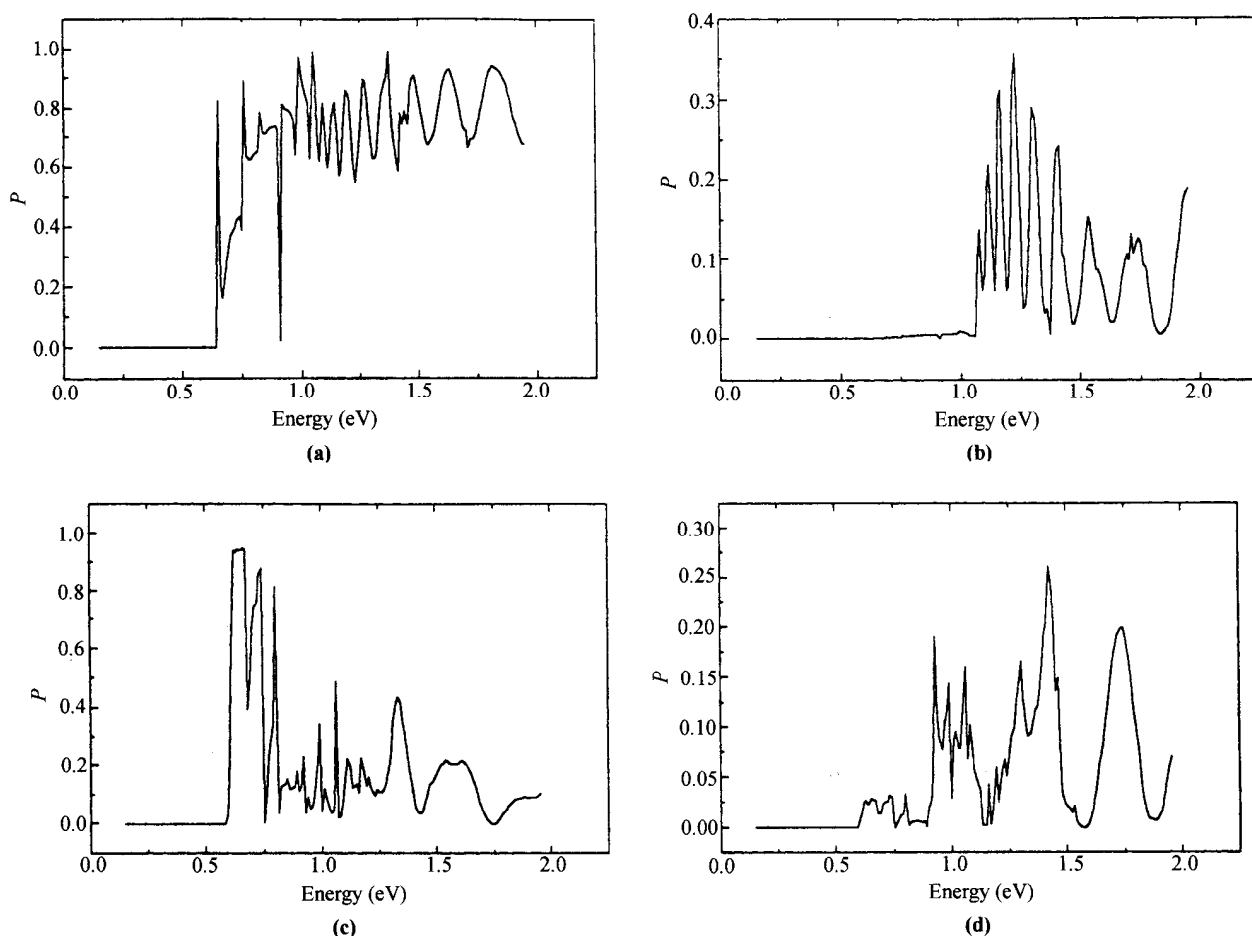


Fig. 1 H atom transfer probability P versus energy E : (a) P_{00} of $\text{OH}\cdots\text{O}$ system; (b) P_{01} of $\text{OH}\cdots\text{O}$ system; (c) P_{00} of $\text{OD}\cdots\text{O}$ system; (d) P_{01} of $\text{OD}\cdots\text{O}$ system.

Delay time

The calculation results of collision delay time Δt_{01} of $\text{OH}\cdots\text{O}/\text{OD}\cdots\text{O}$ are shown in Fig 2. It is well known from experiments that the H atom transfer is very fast so that it is often called "PH jump".² The fs time-resolved studies show that a typical H atom transfer may be on the ps-fs time scale.^{2,3} Our calculation results show that the collision delay time of the H atom transfer of $\text{OH}\cdots\text{O}$ system is in this time scale too. For example, for Δt_{00} of $\text{OH}\cdots\text{O}$ system (see Fig. 2(a)), the main peak occurs at 0.60 eV, the peak height is 480.4 ps. For Δt_{00} of $\text{OD}\cdots\text{O}$ system the main peak is local at 0.53 eV, the peak height is 133.7 ps. For both $\text{OH}\cdots\text{O}$ and $\text{OD}\cdots\text{O}$ systems, the main peak of Δt_{00} is far higher than that of other initial state and final state, which shows that the collision complex formed in $v = 0$ to $v' = 0$ will have the

longest life time. For $\text{OH}\cdots\text{O}$ system, we also found that the main peaks of adiabatic cases are higher than those of non-adiabatic ones, which shows that the collision complexes formed in adiabatic cases have the longer life time for this system.

From the Fig. 2, one may find that for both $\text{OH}\cdots\text{O}$ and $\text{OD}\cdots\text{O}$ systems, there are many peaks for a certain initial state and a final state. For example, the other three main peaks of Δt_{00} of $\text{OH}\cdots\text{O}$ are 33.2 ps at 0.64 eV, 10.3 ps at 0.30 eV and 8.07 ps at 0.56 eV. For Δt_{00} of $\text{OD}\cdots\text{O}$, the other three main peaks are 5.97 ps at 0.58 eV, 4.52 ps at 0.47 eV and 4.09 ps at 0.75 eV. For Δt_{01} of $\text{OH}\cdots\text{O}$, the four main peaks are 837.9 fs at 0.80 eV, 779.3 fs at 0.83 eV, 526.0 fs at 0.87 eV and 408.3 fs at 0.70 eV. For Δt_{01} of $\text{OD}\cdots\text{O}$, the four main peaks are 1851.5 fs at 0.53 eV, 168.6 fs at 0.75 eV, 1161.2 fs at 0.50 eV and 778.8

fs at 0.92 eV. From the discussion of Smith we could know that there may be different collision complexes formed at different energies, different initial states and

final states. The relation of collision time to the energy and the potential energy surface will be discussed in later work.

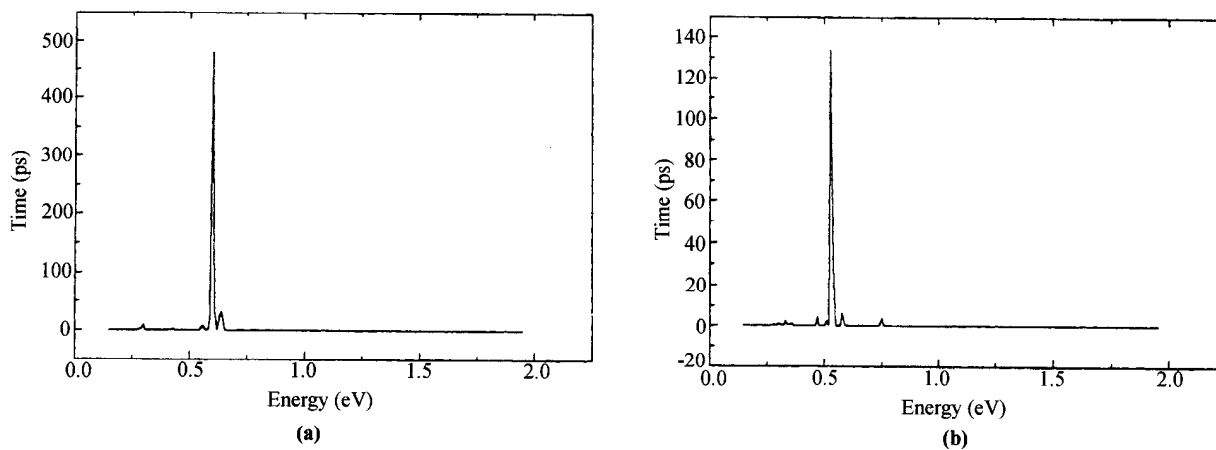


Fig. 2 Life time Δt versus energy E : (a) Δt_{00} of OH \cdots O system; (b) Δt_{00} of OD \cdots O system.

Kinetic isotope effects

The kinetic isotope effect is described by the calculation value of the $\ln(k_H/k_D)$ of the process $v = 0$ to $v' = 0$ and that of $v = 0$ to $v' = 1$ versus reciprocal of temperature in Fig. 3, where k_H and k_D are the H atom transfer rate constants of OH \cdots O and OD \cdots O system, respectively. The data are available from 200 K to 600 K. In this temperature range, for the adiabatic collision case $v = 0$ to $v' = 0$ (Fig. 3(a)) and the non-adiabatic

case $v = 0$ to $v' = 1$ (Fig. 3(b)), the curve is almost linear. The linearity of the curves in low temperatures is better than that in high temperatures, which indicated in low temperature the difference of the active energies of OH \cdots O and OD \cdots O was a constant. From Fig. 3 one can see that the value of $\ln(k_H/k_D)$ increases when the temperature decreases, which means that the isotope effect will be stronger in lower temperature. The increasing of temperature will decrease the influence of isotope effect.

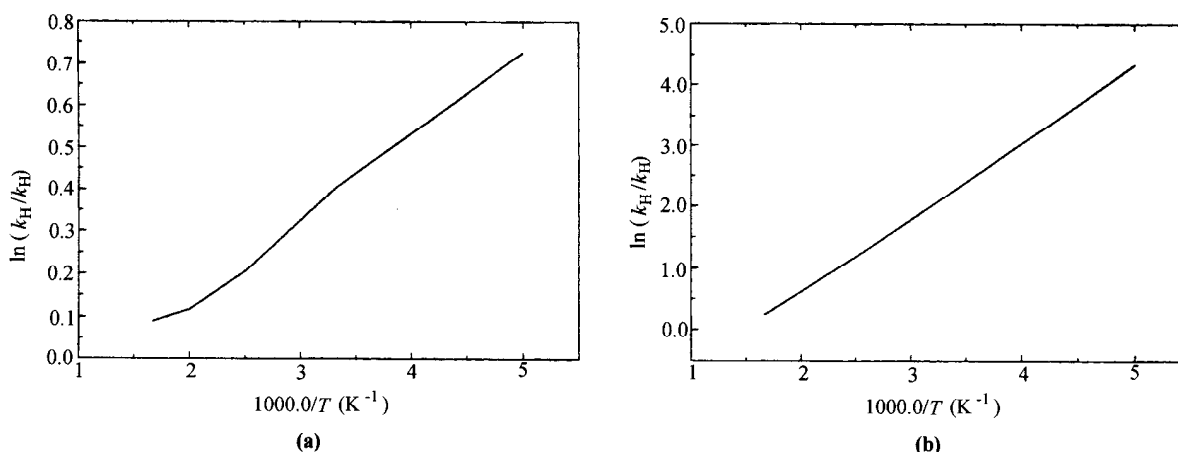


Fig. 3 State to state kinetic isotope effect of collinear OH \cdots O/OD \cdots O system: (a) $v = 0$ to $v' = 0$; (b) $v = 0$ to $v' = 1$.

Conclusion

The first, the calculation result of H atom transfer

probabilities of OH \cdots O and OD \cdots O systems show strong oscillation phenomena, which is a result of the interfering of different channels. What is more, comparing the dynamics detail of OD \cdots O with that of OH \cdots O, we find

from the calculation that the less quantum effect of OD \cdots O system causes less H atom transfer probability for adiabatic case, larger peak width and larger distance between peaks. The calculation results are also consistent with the common view that the adiabatic H/D atom transfer is predominant. The second, the calculation values of collision delay time are in the fs-ps time scale. For both OH \cdots O and OD \cdots O systems, there are many peaks at different energies. This means that there are different collision complexes formed at different energies. The third, in the temperature range of 200–600 K, the curves of $\ln(k_H/k_D)$ are almost linear. Above all, we hope our study may be helpful for a clearer understanding of H atom transfer in free OH \cdots O fragment.

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