Investigation of isotope effects of dynamic properties for H(D) + OF reactions by the quasi-classical trajectory method*

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Quasi-classical trajectory (QCT) calculations are employed to study the dynamic properties for H(D)+OF reactions on the adiabatic potential energy surface (PES) of the $1^3A''$ triplet state. Obvious differences between the reaction probabilities for $J = 0$, integral cross sections for $J \neq 0$, branch ratios of the product and internuclear distances as well as product rotational alignments between the title reactions are found. These differences are attributed mainly to the different reduced masses of the reactants and the different zero-point energies (ZPEs) of the transition state.

Keywords: isotope effects, H(D) + OF reactions, quasi-classical trajectory

PACC: 3450L, 8220R

1. Introduction

Over several decades, the reactions of hydrogen halides with oxygen atoms have received much attention due to their contribution to the catalytic destruction cycle;[1−17] among them, the HOF system is considered to be one of the model systems for open shell reactions on account of its relatively simple electronic structure and has been widely studied.[6−14] Since high-level multiconfiguration-reference configuration interaction (MRCI) electronic structure calculations for the adiabatic $1^3A''$ triplet electronic state were performed by Gómez-Carrasco *et al.*,[6] quasi-classical trajectory (QCT) and wave packet studies[6−8] and a quantum state-to-state calculation[9] of the reaction $F(^2P) + OH(^2\Pi) \rightarrow O(^3P) + HF(^1\Sigma^+)$ have been performed; photodetachment spectrum simulations of OHF^- have also been given.[10] Later, they extended the previous dynamic study of the $F(^2P) + OH(^2\Pi) \rightarrow O(^3P) + HF(^1\Sigma^+)$ reaction to the new PESs for the excited $2^3A''$ and $1^3A'$ triplet states of the OHF system,[11] and found that the OHF system could offer an opportunity to perform a nonadiabatic study with coupled electronic states involved as well as many other reaction systems.[15,16] The only set of coupled adiabatic PESs of $1^3A''$, $2^3A''$, and $1^3A'$ was developed and used to calculate the angle resolved photodetachment cross sections of OHF^-.[12] Additionally, the potential energy surfaces (PESs) for the first five singlet states of the OHF system were constructed.[13] Of these, the ground adiabatic $1^1A'$ singlet PES was further employed in the subsequent quasi-classical trajectory and wave packet calculations of $O(^1D) + HF(^1\Sigma^+) \rightarrow F(^2P) + OH(^2\Pi)$.[14]

Our previous work relevant to the HOF system focused on the influence of the rotational excitation of the reagent on product polarization for the reaction H + FO → OH + F, and the results indicated that both the orientation and the alignment of the rotational angular moment were affected by collision energies.[18] Recently, we have also investigated the axial polarization of the product molecule for the reaction F + HO → HF + O[19] and the effect of the reagent vibration on stereo-dynamics of the reaction $O(^1D) + HF \rightarrow F + OH$.[20] The $H(^2S) + FO(^2\Pi) \rightarrow OH(^2\Pi) + F(^2P)$ reaction based on the $1^3A''$ PES has also been studied by using the QCT method[21] and the quantum mechanics (QM) method,[17] and the QCT results presented quite different reaction probabilities for $J = 0$ (the initial total quantum number) from the previous quantum scattering calculations by using the real wave packet method. In order to judge the correctness of these two investigations, a subsequent QM study of H+FO was carried out by Chu *et al.*[22] and gave a fairly good agreement

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with the QCT result, which also shows that there is a convergence problem in the previous QM calculation. Another example could be the disagreement between the QCT and the full-dimensional multiconfiguration time-dependent Hartree (MCTDH) calculations on reactions H+CH_4 and O+CH_4,[23] and the correctness of the QCT results was also tested by the QM calculation,[24−26] which implies that these MCTDH calculations of the two six-atomic systems[27,28] are not quite converged yet. In other words, when the reaction of an atom-polyatomic system is dealt with, if other methods have encountered computational difficulties, the QCT method still can give reasonable results, which is the reason why this method has been widely used to study the dynamics of the chemical reactions.

As is known, the isotopic effect plays an important role in chemical reactions, especially in reactive scatterings, and much work related to isotopic variations has been done.[29−40] For the reactions F + H(D)O, although their isotope effects of the stereo-dynamics were studied,[29] little attention was paid to their reverse reaction H(D) + OF in either the QCT or QM method. In the present paper, we report on the calculation results by using the QCT method to study the reaction probability for $J = 0$, the integral cross-section for $J \neq 0$, the branching ratios and the product rotational alignments of H + OF and its isotopic variations.

2. Computational method

The $1^3A''$ PES used in the calculation is a relatively accurate adiabatic state. It was given by Gómez-Carrasco *et al.*,[6] who fitted 8069 *ab initio* points to two- and three-body polynomial expansions[41] in modified Rydberg coordinates. The detailed function form and deduction process of the PES can be found in Ref. [6].

Although the stable intermediate HOF existing on the $1^1A'$ PES is of central importance for the dynamics of the H+OF reaction, as a minor channel, the reaction H+OF based on $1^3A''$ PES is also significant at high collision energies, and it is an abstraction reaction different from the one on $1^1A'$ PES which is an insertion reaction.

The calculation method of QCT is the same as the one used in Refs. [18]–[38] and [42]–[47]. The classical Hamilton's equations are numerically integrated in three dimensions. In the present work, we carry out calculations of the product rotational polarization with initial vibrational quantum number $v = 0$ and initial rotational quantum number $j = 0$. The collision energies range from 0.2 eV to 0.3 eV with the energy grid being 0.02 eV and from 0.3 eV to 1.0 eV with the energy grid being 0.1 eV. A batch of 10000 trajectories is run for each energy value of the title reactions and the integration step size in the trajectories is chosen to be 0.1 fs, which can guarantee conservation of the total energy and the total angular momentum. For the head-on collision ($J = 0$), the reaction probability is defined as $P = N_r/N$, which is the ratio of the number of reactive trajectories to the total number of trajectories. For the side collision ($J \neq 0$), the maximum value of the impact parameter, $b_{\max}$, is computed by calculating 10000 trajectories at a fixed value of the impact parameter b and systematically increasing the value of b until no reactive trajectories are obtained. The reaction cross section is defined as $\sigma_r = \pi b_{\max}^2 (N_r/N)$. The sampling error is defined as $\varepsilon = \sqrt{(N - N_r)/NN_r} \times 100\%$, and the reaction cross section error in our calculation is defined as $\sigma_{r\varepsilon} = \varepsilon\sigma_r$.

The product rotational alignment calculations have been well-rounded by Han and coworkers.[42] The most common vector correlation is the $\boldsymbol{k}$–$\boldsymbol{j}'$ correlation ($\boldsymbol{k}$ is the reagent relative velocity vector, $\boldsymbol{j}'$ is the final product molecular rotation angular momentum, and θ_r is the angle between these two vectors), and the polar angle distribution function $P(\theta_r)$ can be expanded in a series of Legendre polynomials[42]

$$P(\theta_r) = \frac{1}{2}\sum_k (2k+1) a_0^{(k)} \mathrm{P}_k(\cos\theta_r), \qquad (1)$$

where

$$a_0^{(k)} = \int_0^{\pi} P(\theta_r)\mathrm{P}_k(\cos\theta_r)\sin\theta_r \mathrm{d}\theta_r = \langle \mathrm{P}_k(\cos\theta_r)\rangle \qquad (2)$$

with expanding coefficients $a_0^{(k)}$ called the orientation (k is odd) and alignment (k is even) parameter. In this calculation, $P(\theta_r)$ is expanded up to $k = 18$, which shows good convergence. Because the rotational alignment of the product has been measured in most experiments, in our work, we calculate the average rotational alignment factor $a_0^{(2)}$, i.e. $\langle P_2(\boldsymbol{j}' \cdot \boldsymbol{k})\rangle$.

3. Results and discussion

Figure 1 shows a comparison between the energy-dependent reaction probability for $J = 0$ of the H + FO → OH + F reaction reported by Zhao *et al.*[22] and the counterpart of the D + OF → DO + F reaction calculated in this paper. From this figure, it can

be found that both energy-dependent reaction probabilities display a similar trend in the whole collision energy range, i.e., each of them shows a threshold at a low collision energy and it increases as the collision energy increases.

However, the differences between the two reactions are also obvious, as shown in Fig. 1. For the lower collision energies near the threshold, the reaction probability of D + OF is zero, while the counterpart of H + OF is not. This difference may be ascribed to the different reduced masses of two kinds of reactants H–OF and D–OF which are respectively about 0.97 and 1.90. Therefore, the reagent H–OF relative velocity is larger than that of D–OF for the same collision energy. Furthermore, since there is a barrier in the entrance channel,[22] it is understandable that the lighter H atom more easily leaps over the barrier and reacts with OF molecules near the threshold energy. For the higher collision energies, the reaction probability value of the D + OF → DO + F reaction is larger than that of H + OF → HO + F at the same collision energy. Lin *et al.* have ascribed these dynamical differences between the reactions $O(^1D)+H(D)Cl$ to the vibrational motion of the light atom between the two heavy atoms in their study.[39] In view of the reactions H(D)+OF studied in the present paper, the differences between reaction probability results can also be explained in the zero-point energy (ZPE) effect. That is to say, between the two systems under discussion, the ZPEs of the reactants are the same; however, on the saddle point (transition state), the time scales of the vibrational motions of H···OF and D···DF are quite different, which results from the different masses of D and H atoms. In the same force field, D is heavier than H, therefore, the vibrational frequency and ZPE of D··· OF are smaller than those of H···OF. As a result, compared with the H+OF reactive system, the D+OF system has a low effective energy barrier, and it is natural that the reaction probability value of the D + OF → DO + F reaction is larger than that of H + OF → HO + F at the same collision energy.

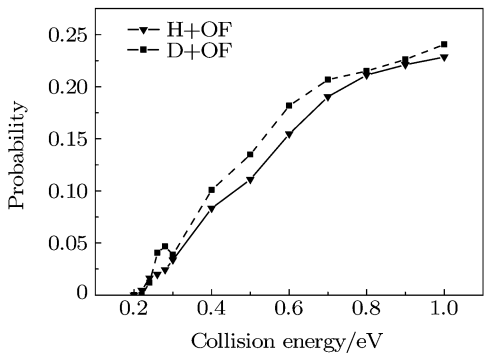


Fig. 1. Comparisons of the reaction probabilities of the H(D)+OF→H(D)O+F reactions, where the solid line indicates the reaction H+OF→ HO+F and the dash line represents the reaction D+OF→DO+F.

Figure 2 shows a comparison between the integral reaction cross section results for $J \neq 0$. As can be seen, the two integral cross sections also present a similar trend, i.e., each of them increases with increasing relative translational energy and has a threshold at a low collision energy. There are also differences between the two reactions in Fig. 2. The reaction section value of the H + OF reaction[22] is smaller than that of the D + OF reaction at the same collision energy. From the definitions of reaction cross section and probability, it is easy to understand that the possible reason for the differences between the reaction cross sections can also be ascribed to the ZPE effect.

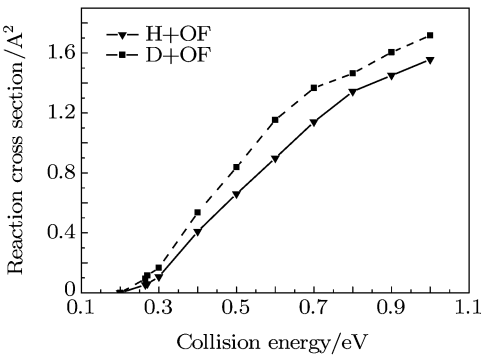


Fig. 2. Comparisons between the reaction cross-sections of the H(D)+OF→H(D)O+F reactions, where the solid line indicates the reaction H+OF→ HO+F and the dash line denotes the reaction D+OF→DO+F.

On the other hand the isotopic variant directly leads the reagent H–OF relative velocity to be larger than that of D–OF at the same collision energy. To analyse this problem clearly, the variations of internuclear distances H(D)–O, O–F and H(D)–F are presented each as a function of propagation time in Fig. 3. Figure 3(a) shows the variations of internuclear distance in the H + OF → HO + F reaction progress on the condition of scattering angle $\theta = 78.463°$ and $E_C = 0.5$ eV and figure 3(b) displays the variations of internuclear distance for the D + OF → DO + F reaction. In this figure, it can be noticed that the H + OF → HO + F reaction occurs at about $t = 0.118$ ps and the D + OF → DO + F reaction appears at $t = 0.135$ ps, although the initial distance between

H and OF is larger than that between D and OF.

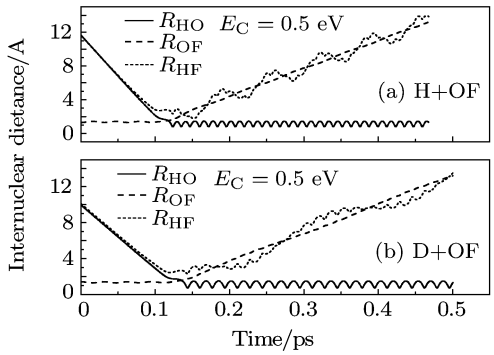


Fig. 3. Internuclear distances of H(D)O, OF, and H(D)F as a function of propagation time, with a scattering angle of $\theta_t = 78.463°$ and $E_C = 0.5$ eV in the reactions H+OF→HO+F (a) and D+OF →DO+F (b), where solid lines indicate the internuclear distances of H(D)O, dash lines denote internuclear distances of OF and short dash lines refer to internuclear distances of H(D)F.

The difference in relative velocity between regents can also be used for analysing the product ratio between branch reactions, i.e., between reactions H(D)O+F (the first channel) and H(D)F+O (the second channel), and a comparison between them is shown in Fig. 4. From this figure one can find that although the values of branch reaction product ratio decrease as the collision energy increases, the reaction in the first channel is principal for both reactions and the product of the D + OF reaction is larger than that of the H + OF reaction at the same collision energy. These results can be attributed to the property of the $1^3A''$ triplet state PES which has a minimal barrier in the entrance channel at a configuration $r_{OH} = 1.70$ Å, $r_{FO} = 1.432$ Å (1 Å=0.1 nm), and $\theta = 123.3°$, H(D) is closer to the O atom, and the reaction in the first channel happens more easily. When the D atom is substituted for the H atom, the reagent relative velocity becomes smaller, and the heavier attacking D atom slowly approaches the OF molecule and falls together with the O atom before it migrates round to meet the F atom; as a result, the product of D + OF is larger than that of the H + OF reaction at the same collision energy

In order to shed more light on the isotopic effect on the title reactions, the isotopic effect was also analysed by taking into account the vector properties. A comparison between the product rotational alignments of the H(D) + OF → H(D)O + F reactions as a function of collision energy is shown in Fig. 5. It can be seen from the figure that the $\langle P_2(\boldsymbol{j}' \cdot \boldsymbol{k})\rangle$ values for the H + OF reaction are almost invariant with collision energy, but with excruciating attention to detail, the $\langle P_2(\boldsymbol{j}' \cdot \boldsymbol{k})\rangle$ value becomes slightly smaller as collision energy increases, indicating that there are weak product rotational alignments and the alignment becomes strong to some extent when the collision energy increases. In this case, we can deduce that the reaction belongs to light-heavy-heavy (LHH) mass combination, the product orbital angular momentum is large, and the reactant orbital angular momentum has less influence on the molecular product rotational alignment, which is consistent with the previous calculations.[45] However, the $\langle P_2(\boldsymbol{j}' \cdot \boldsymbol{k})\rangle$ values for the D + OF reaction present a similar trend to the ones for the H + OF reaction at collision energies larger than 0.3 eV. The difference between these two reactions is that all the values of $\langle P_2(\boldsymbol{j}' \cdot \boldsymbol{k})\rangle$ for the H + OF reaction are larger than the ones for the D + OF reaction, especially at lower collision energies. In our calculation, the maximal rotational quantum number of the DO molecule is larger than that of the HO molecule for the same collision energy (for example, $E_C = 0.27$ eV, $j_{max(DO)} = 43$, $j_{max(HO)} = 32$; $E_C = 0.5$ eV, $j_{max(DO)} = 48$,

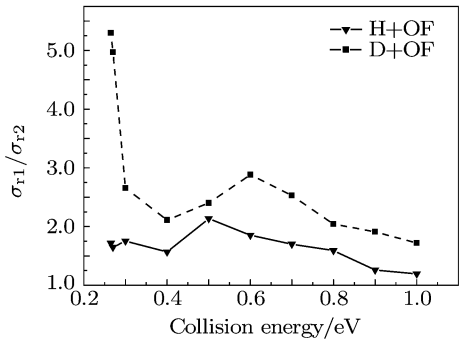


Fig. 4. Comparisons of product ratio between branch reactions H(D)+OF→H(D)O+F, where the solid line indicates the reaction H+OF→ HO+F, the dash line denotes the reaction D+OF→DO+F.

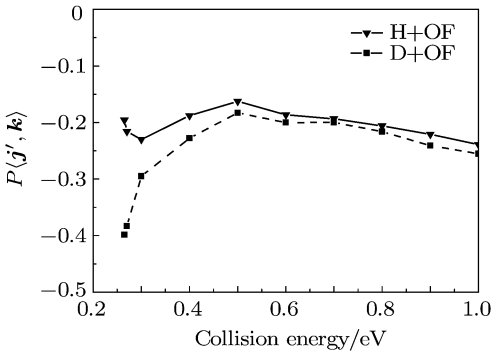


Fig. 5. Comparison between the product rotational alignments of the H(D)+OF→H(D)O+F reactions as a function of collision energy, where the solid line indicates the reaction H+OF→HO+F, and the dash line denotes the reaction D+OF→DO+F.

$j_{\max(HO)} = 36$, etc.), and the rotational alignment of product DO is stronger than that of HO. This difference may be attributed to the difference in mass between the incident atoms. The H atom is much lighter than the D atom, so the reaction H + FO → OH + F is a more typical LHH mass combination than the D + OF → DO + F reaction, and this mass effect is more evident at low collision energy.

4. Conclusions

In this paper we have performed a QCT calculation for the reaction H(D) + OF → H(D)O + F based on the $1^3A''$ state PES and several scalar properties, and the product rotational alignments of the two reactions are compared. Remarkable differences are found though there are many similarities in the two systems. The results imply that both the scalar and the vector properties are affected by the isotopic substitution, which can be ascribed to the kinematic effect and the difference in relative velocity between the reactants. In order to understand a reaction completely, the isotope effect is also an important aspect to be considered. We are looking forward to the experimental studies on the H(D)+OF reaction systems so that a comparison between theory and experiment can be made.

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