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journal homepage: www.elsevier.com/locate/cplettQuasi-classical trajectory study of the reaction $\text{H} + \text{FO} \rightarrow \text{OH} + \text{F}$

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ABSTRACT

Quasi-classical trajectory (QCT) calculations are carried out for the reaction $\text{H} + \text{FO}(0,0) \rightarrow \text{OH} + \text{F}$ on the adiabatic potential energy surface (PES) of the ground $^3\text{A}''$ triplet state [S. Gómez-Carrasco, L. González-Sánchez, A. Aguado, M. Paniagua, O. Roncero, M.L. Hernández, J.M. Alvarino, Chem. Phys. Lett. 383 (2004) 25]. The reaction probability for total angular momentum $j = 0$ has been calculated, and the integral cross sections as a function of collision energy have been presented. The calculated results with QCT are found to be well consistent with the new quantum mechanical wave packet results calculated by Chu et al. The product rotational alignments have also been calculated and the $\langle P_2(j \cdot k) \rangle$ values are almost invariant with collision energies.

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1. Introduction

Recently, the accurate potential energy surfaces of ground triplet state of the OHF reactive system have been calculated by Gómez-Carrasco et al. [1], and many studies have also been carried out based on these PESs. Furthermore, Gómez-Carrasco et al. have simulated photodetachment spectrum [2] and the existing kinetic and dynamical experiments for the $\text{F}(^2\text{P}) + \text{OH}(^2\Pi) \rightarrow \text{O}(^3\text{P}) + \text{HF}(^1\Sigma^+)$ chemical reaction using quasi-classical trajectory (QCT) method [1]. Later, they carried out wave packet and QCT calculations on the $\text{F} + \text{OH}(\nu = 0, j = 0)$ reactive collision [3], and the reaction $\text{F}(^2\text{P}) + \text{OH}(^2\Pi) \rightarrow \text{O}(^3\text{P}) + \text{HF}(^1\Sigma^+)$ has also been studied on the Global three-dimensional adiabatic potential energy surfaces for the excited $2^3\text{A}''$ and $1^3\text{A}'$ triplet states of OHF system [4]. As mentioned above, most of the studies so far have focused on $\text{F} + \text{OH} \rightarrow \text{O} + \text{HF}$ reaction. However, Gogats has recently performed three-dimensional real wave packet calculations for the reverse $\text{H}(^2\text{S}) + \text{FO}(^2\Pi) \rightarrow \text{OH}(^2\Pi) + \text{F}(^2\text{P})$ reaction based on the ground $^3\text{A}''$ state PES [5]. He found the total reaction probabilities showed a threshold followed by a fast rise and then a level off, and the cross section increased first gradually with relative translational energy and then decreased. More recently, Chu et al. [6] have done the same work using time dependent wavepacket (TDWP) method and obtained the different results with Gogats'.

In order to compare with the results calculated by quantum method, here we perform QCT calculations for $\text{H}(^2\text{S}) + \text{FO}(^2\Pi) \rightarrow \text{OH}(^2\Pi) + \text{F}(^2\text{P})$ based on the ground $^3\text{A}''$ state PES [3]. In this work, the reaction probability and the integral cross sections as a function of collision energy have been calculated. In order to understand this reaction better, the average rotational alignment [7] of the product is calculated as well.

2. Calculating scheme

In the calculations, the ground $^3\text{A}''$ PES [3] fitted by Gómez-Carrasco et al. [1–4] has been employed. In this PES, they fitted 8069 *ab initio* points to a many-body expansion [8] using modified Rydberg coordinates for the analytical representation, and obtained a relatively accurate adiabatic ground potential energy surface.

The general method for the calculation of QCT is the same as the one used in Refs. [7–11], and the classical Hamilton's equations are integrated numerically for motion in three dimensions. In the present work, we have carried out calculations with initial rotational number $j = 0$ and initial vibrational number $\nu = 0$. The collision energies are 0.2 eV, 0.265 eV, 0.27 eV and they are swept from 0.3 to 1.0 eV. The energy grid in our calculation is 0.1 eV. A batch of 50000 trajectories is run for each energy of the title reactions and the integration step size in the trajectories is chosen to be 0.1 fs, which guarantees the conservation of the total energy and total angular momentum.

The product rotational alignment calculations have been well-rounded by Han and coworkers [9]. Therefore, in addition to the scalar properties stated above, the average rotational alignment of the product has also been calculated by using the method in Ref. [9].

3. Results and discussion

A comparison among the time dependent wavepacket (TDWP) result of the reaction probability which has been calculated by Chu et al. [6], the quantum result reported by Gogats in Ref. [5] and our QCT results for the reaction $\text{H} + \text{FO}(0,0) \rightarrow \text{OH} + \text{F}$ is shown in Fig. 1. From this figure, it is clear that the results from TDWP method and QCT method agree with each other very well in the whole collision energy range. In addition, it also can be seen in Fig. 1 that the reaction probability shows a threshold at low

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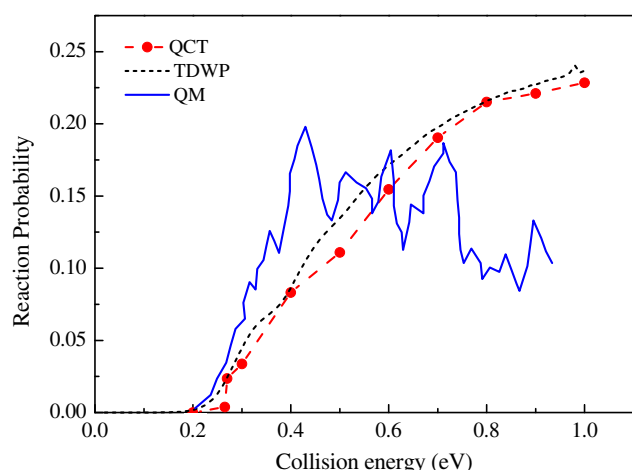


Fig. 1. A comparison among the QCT-computed reaction probability in this work, the new quantum results calculated by Chu et al. [6] and Gogtas' result in Ref. [5] for $\text{H} + \text{FO}(0,0) \rightarrow \text{OH} + \text{F}$. The dash line [QCT] is the QCT-computed result of this work. The dotted line [TDWP] is the result of Chu's work [6]. The solid line [QM] is the result reported by Gogtas in Ref. [5].

collision energy and the value of it increases with the increasing of collision energy. This is ascribed to the property of the ground $^3A''$ PES which has a barrier of 0.265 eV in the entrance channel at a configuration $r_{\text{OH}} = 1.70 \text{ \AA}$, $r_{\text{FO}} = 1.432 \text{ \AA}$, and $\theta = 123.3^\circ$ shown in Fig. 2. The topographic features of the PES will lead to the appearance of threshold behavior and the fact that the reaction probability and the reaction cross section increase with increasing of the collision energy.

Fig. 3 shows the total reaction cross section results from our QCT calculations. Due to the barrier of 0.265 eV appearing in reactant region, it is clear that the integral cross section not only has a threshold at low collision energy, but also increases with relative translational energy.

Our calculation results described above are inconsistent with the corresponding ones in Ref. [5], although same PES is used in both calculations. This inconformity attracts us and we predict that the reason for it may be due to Gogtas' results [5] having lack of convergence since the previous QCT results are in excellent agreement with quantum ones for most other reactions such as $\text{H}^- + \text{D}_2$ [12,13], $\text{H}^+ + \text{D}_2$ [14], $\text{H} + \text{D}_2$ [15–17], $\text{Cl} + \text{H}_2$ [18–21], $\text{O} + \text{H}_2$ [22–24], $\text{He} + \text{H}_2^+$ [13,25], and so on [26].

Certainly, the QCT method has a serious drawback – its inability to properly treat the quantum mechanical zero-point energy

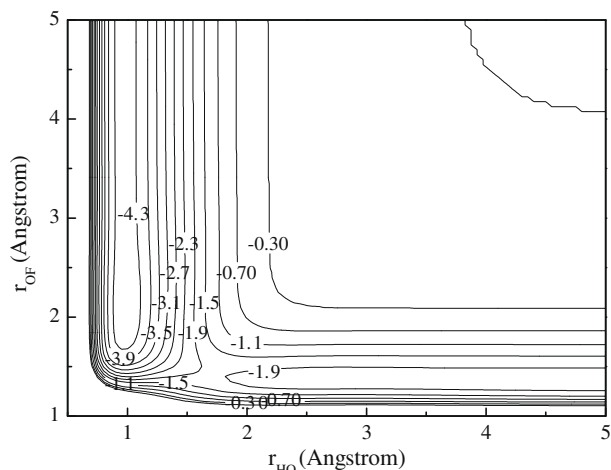


Fig. 2. The contour plots of the three-dimensional $^3A''$ ground state PES for $\theta = 123.3^\circ$.

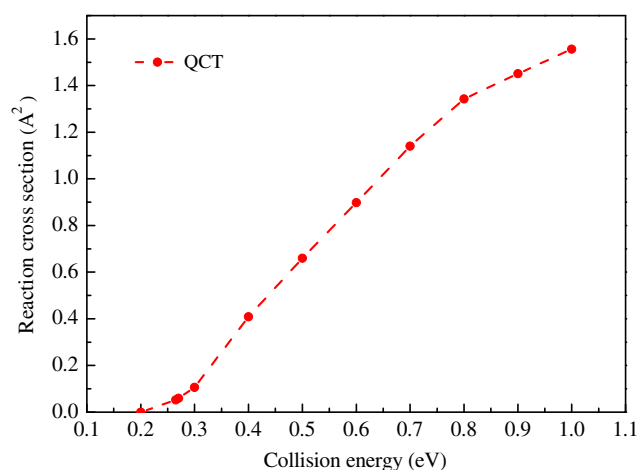


Fig. 3. The QCT-computed reaction cross sections in this work for $\text{H} + \text{FO}(0,0) \rightarrow \text{OH} + \text{F}$.

[12,27–33], and recently, Varandas et al. have suggested a simple scheme to 'quantize' the continuous vibrational–rotational energy distributions obtained from QCT calculations, the so called QCT/MGB method, which has been applied to some reactions with promising results [34]. But the drawback mentioned above is not the reason for the significant disagreement between our results and Gogtas' [5], and the main reason is the later one has lack of convergence. This has been approved from a recent TDWP calculation by Chu et al. [6]. In Fig. 1, it can be seen that the result of the reaction probability calculated by Chu et al. shows a threshold behavior at low collision energy and increases as collision energy increasing, which is in good accord with our QCT result.

Not only can the scalar properties be obtained from QCT calculations, but also the vector properties can be acquired by means of QCT [9]. Because the rotational alignment of the product has solely been measured in most experiments, we only calculated the average rotational alignment factor $\langle P_2(j' \cdot k) \rangle$ (the detailed analysis can be referred to that in Ref. [9]), and the dependence of the product rotational alignment on collision energies is shown in Fig. 4. It can be seen from the figure that the $\langle P_2(j' \cdot k) \rangle$ values are almost invariant with collision energies, but in detail, the $\langle P_2(j' \cdot k) \rangle$ value slightly becomes smaller with the collision energy increase, indicating 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

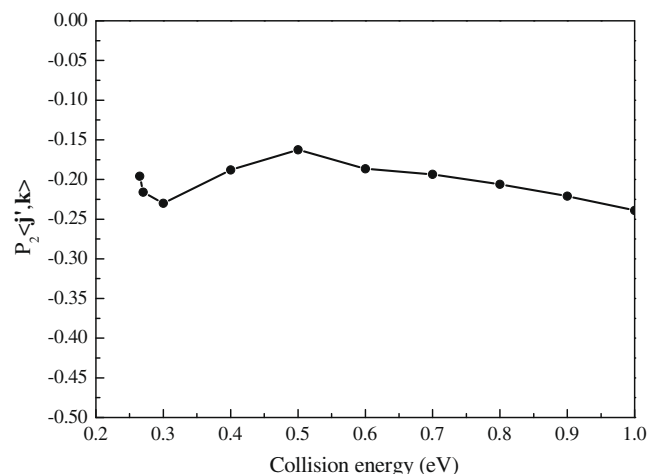


Fig. 4. The product rotational alignment $\text{H} + \text{FO}(0,0) \rightarrow \text{OH} + \text{F}$ as a function of collision energy.

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 calculation [35].

4. Conclusions

The QCT calculation for reaction $\text{H}(^2\text{S}) + \text{FO}(^2\Pi) \rightarrow \text{OH}(^2\Pi) + \text{F}(^2\text{P})$ based on the ground $^3\text{A}''$ state PES has been performed. The result of reaction probability as a function of collision energy has been found to be well consistent with the new quantum mechanical wave packet calculation result which is calculated by Chu et al. In virtue of the barrier, the reaction probability and the integral cross sections increase while collision energy is increasing as plotted in Figs. 1 and 3. In addition, the average rotational alignment of the product is calculated, and the $\langle P_2(j' \cdot k) \rangle$ values are almost invariant with collision energies as the result of LHH mass combination.

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