



Theoretical study of the O(¹D) reaction with methane

Ang-Yang Yu*

Chinese Academy of Sciences, Shenyang, Liaoning province, 110016, (CHINA)

E-mail: wisdomyay@163.com

ABSTRACT

The quasi-classical trajectory(QCT) calculation for the reaction O(¹D)+CH₄ is carried out based on a constructed London-Eyring-Polanyi-Sato(LEPS) potential energy surface(PES). Importance in this work has been attached to calculating the OH+CH₃ channel. Product angular distribution has been studied so as to make comparison with experiments. The calculated results are in excellent agreement with available experimental results. It indicates strongly that there are a forward scattered peak and a backward scattered peak for the OH product relative to the O(¹D) beam direction at the collision energy of 6.8Kcal/mol. © 2015 Trade Science Inc. - INDIA

INTRODUCTION

Over the past twenty years, There have been tremendous developments in the state-of-art of the crossed molecular beam experiments^[1,2]. The universal crossed molecular beam apparatus^[3] provides us with many useful experimental results about the multiple channel dynamics in the O(¹D) reaction with alkane molecules^[4].

The reactivity of the singlet O atom is very important in many research areas. This is largely due to its high reactivity with other molecules, owing to its ability to insert into other chemical bonds with small or no reactive barriers. The reaction of O(¹D) with CH₄ has been studied previously using various experimental^[5-23] and theoretical methods^[24,25]. It is now well established that the dominant reaction channel of the O(¹D) reaction with CH₄ is the CH₃+OH channel. In spite of the abundant experimental information available for the O(¹D)+CH₄ reaction, theoretical studies on these types of reactions are very scarce. In this article, the QCT cal-

ulation of the O(¹D)+CH₄→CH₃+OH is investigated in order to compare with previous experimental results. Such study allows the theoretical dynamical calculations to compare with experimental results. The comparison is of great importance to the understanding of these complicated reaction systems.

This paper is outlined as follows. In Sec II, the theory and the calculation details are introduced. In Sec III, the calculated results of the potential energy surface and product angular distribution are discussed. We end with a summary in Sec IV

THEORY

LEPS potential energy surface

The extended LEPS potential energy surface(PES) is employed to study the O(¹D)+CH₄→OH+CH₃ reaction using the quasi-classical trajectory (QCT) method. The methyl group was treated as an atom of 16.0amu for the LEPS potential energy surface of the O(¹D)+CH₄→OH+CH₃ system.

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$$V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = Q_1 + Q_2 + Q_3 - (J_1^2 + J_2^2 + J_3^2 - J_1 J_2 - J_2 J_3 - J_1 J_3)^{1/2}$$

Where

$$Q_i = \frac{1}{2}({}^1E_i + {}^3E_i)$$

$$J_i = \frac{1}{2}({}^1E_i - {}^3E_i)$$

1E_i is defined as the diatomic Morse potential,

and 3E_i stands for the anti-Morse function

$${}^1E_i = D_i \{ (1 - \exp[-\beta_i(r - r_0)])^2 - 1 \}$$

$${}^3E_i = {}^3D_i \{ (1 + \exp[-\beta_i(r - r_0)])^2 - 1 \}$$

Where

$${}^3D_i = \frac{D_i(1 - S_i)}{2(1 + S_i)}$$

S_i is an adjustable parameter (The so-called Sato

parameter), D_i , β_i and r_i represent the Morse parameters of the diatom, subscript $i=1,2,3$ indicates OH, H-CH₃ and O-CH₃, respectively. The parameters of , and for potential energy surface are taken from Reference 26 for the reaction O(¹D)+CH₄→OH+CH₃. The potential energy surface

by adjusting ($i=1,2,3$) is constructed, and all the parameters are presented in TABLE 1.

Quasi-classical trajectory(QCT)calculations

The well-known CLASTR program^[27] was used to perform the quasi-classical trajectory calculations. Since this program is only applied to the A+BC system, the methyl group was treated as a single atom of 16.0amu. The classical Hamilton's equations for motion were integrated numerically in three dimensions. In the calculations, 2×10^4 trajectories were sampled and the trajectories were initiated with O-CH₄ inter-nuclear separation of 13U. The integration step size in the trajectories was chosen to be 40fs.

RESULTS AND DISCUSSIONS

Potential energy surface

The LEPS potential energy surface is constructed according to the experimental data^[28]. The reaction profile along the minimum energy path from reac-

TABLE 1 : Morse parameters for the LEPS PES for the O(¹D)+ CH₄ → OH+ CH₃ reaction

	OH	H- CH ₃	O- CH ₃
D_i /eV	6.587	4.8202	6.03
β_i /U ⁻¹	0.6413	0.6230	0.5797
r_{0i} /U	0.9697	1.1562	1.4407
S_i	1.910	0.5	-0.151

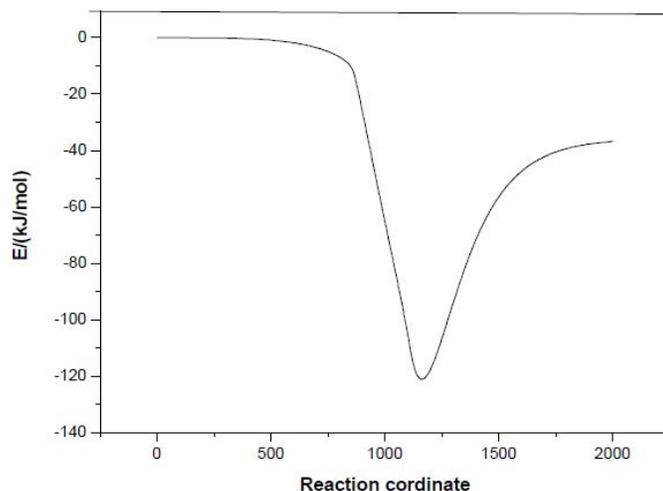


Figure 1 : The reaction profile along the minimum energy path from reactants to products on the LEPS PES of the ¹⁸O(¹D)+CH₄.

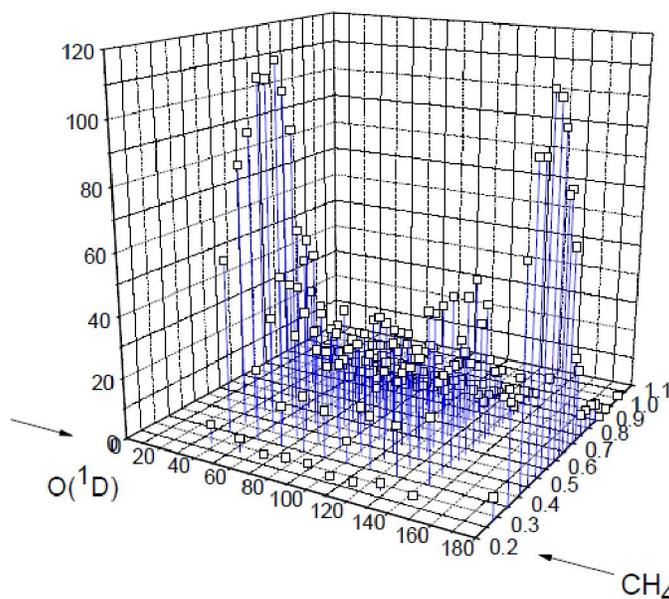


Figure 2 : The 3D product contour plot for the OH product from the OH + CH₃ channel. The high peak scattering direction is the CM forward scattering direction. The arrows in the figure stand for the incoming directions of the reactants

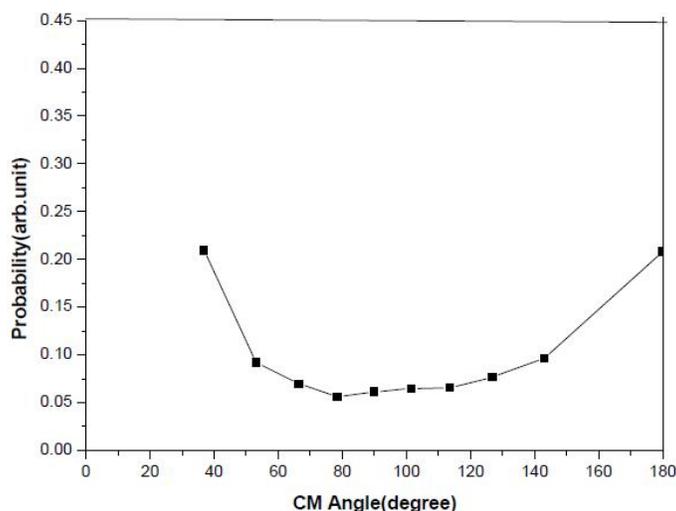


Figure 3 : Theoretical product angular distribution for the ¹⁸OH formation channel from the ¹⁸O(¹D)+CH₄ reaction in the CM frame(The scattered dots are the calculated results)

tants to products on our chosen PES is demonstrated in Figure 1. Almost no potential barrier is involved and a potential well whose depth is about 121.1 kJ/mol appears on the exit valley of the PES.

Product angular distribution

A three-dimension center of mass product flux diagram is constructed. As is shown in the Figure 2 above, the overall OH product is clearly forward scattered relative to the O(¹D) beam direction. In addition to the forward scattered OH product, there is also a backward scattered peak for the OH prod-

uct relative to the O(¹D) beam direction.

In the QCT simulations using the CLASTR program, the O(¹D)+CH₄→OH+CH₃ channel was investigated at the collision energy of 6.8Kcal/mol. Based on the theoretical results, the product angular distribution is plotted in Figure 3.

In comparison with the experiment product angular distribution, the theoretical diagram also illustrates the backward scattered OH peak and the forward scattered OH product. The scattered dots in the figure are calculated from the output file of

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the program. Although there isn't the result in the CM 0° direction, the trend is clear. That is to say, there is a clear forward scattered OH product peak relative to the O(¹D) beam direction. The theoretical product angular distribution is in good agreement with the experimental result.

From the product angular distribution of the O(¹D)+CH₄→OH+CH₃ channel, a long-lived complex pathway is likely to be very important because of the deep well in the MEP path in the LEPS potential energy surface. There could also be a direct pick-up or a short-lived complex mechanism because of the more obvious forward scattered product.

CONCLUSION

In summary, the QCT calculations were performed in order to compare with the experimental results for the O(¹D)+CH₄→OH+CH₃ reaction. The calculated results demonstrate that there is also the forward scattered OH product and a backward scattered peak for the OH product relative to the O(¹D) beam direction at the collision energy of 6.8Kcal/mol. This theoretical product angular distribution is quite consistent with available experimental result. Theoretical studies of other reaction channels O(¹D)+CH₄→H₂COH/H₃CO+H and O(¹D)+CH₄→H₂CO/HCOH+H₂ are underway in order to compare with previous experimental results.

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