

# Quasiclassical Trajectory Simulation of the Chemical Reaction $\text{Ba} + \text{HF}(v, J) \rightarrow \text{BaF}(v', J') + \text{H}^*$

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**Abstract:** Ba + HF reaction is an interesting example whether for the experiment or theoretical research. But no potential energy surface for this reaction emerges for a long time because of the difficulty of the exact *ab initio* caused by the large mass number of the Ba atom. The first quasiclassical trajectory calculation for the exothermic reaction  $\text{Ba} + \text{HF}(v, J) \rightarrow \text{BaF}(v', J') + \text{H}$  is carried out based on a constructed extended-LEPS PES. The calculated BaF product state distributions agree closely with experiment for both  $\text{Ba} + \text{HF}(v = 0)$  and  $\text{Ba} + \text{HF}(v = 1)$ . The reaction mechanism is described as following two pathways, abstraction and insertion, and the small increment of the barrier height along with the attacking deviation from the linear direction (Ba - F - H) is the main cause of this competition. Low collision energy favors abstraction whereas high vibration excitation leads to insertion.

**Key words** Quasiclassical trajectory method, LEPS potential energy surface, Abstraction reaction, Insertion reaction

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## 1 Introduction

Over several decades, laser induced fluorescence (LIF) has become an important method for the detailed study of the reactions of alkaline earth metal atoms M with hydrogen halide molecules  $\text{HX}$ ,  $\text{M} + \text{HX} \rightarrow \text{MX} + \text{H}$  (M = Be, Mg, Ca, Sr, Ba, X = F, Cl, Br, I). Sr + HF<sup>[1]</sup>, Ca + HF<sup>[1]</sup>, Ba + HF<sup>[2; Ba]</sup> + HCF<sup>[3, 9, 10]</sup>, Ba + HF<sup>[1, 3, 11-13]</sup>, Sr + HF<sup>[2, 14-17]</sup>, Ca + HF<sup>[14, 18, 19]</sup>. Zare and his co-workers have done much experimental work<sup>[3-7, 9, 11-21]</sup>, which employed crossed molecular beams, LIF, and some theoretical simulations in the investigation of the very high detailed dynamical features of these reactions. Recently our group and Stolte and his co-workers comprehensively investigated the reactions between the alkaline earth atoms and halocarbon halide  $\text{RX}$ ,  $\text{M} + \text{RX} \rightarrow \text{MX} + \text{R}$  (M = Be, Mg, Ca, Sr, Ba) theoretically and

experimentally. Many different properties and experimentally observable phenomena to describe the dynamics of this reaction family have been found.<sup>[8, 22-30]</sup>

The reaction  $\text{M} + \text{HX}$  shows interesting dynamical features. There are two processes probably involved in the reactions, which are called direct abstraction and insertion, respectively, and they play different roles in different initial situations and different reactions. In addition, an important feature caused by the HHL mass system is the kinematic limit, which makes the product rotation be strongly aligned about the direction of the reagent's relative velocity. What is the most effective factor that can control the detail dynamics of this reaction will be discussed in what follows. Whether the reagent energy employed to overcome the potential barrier is in translation or vibration is quite important for the descrip-

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tion of the final state distribution.

## 2 Theory

### 2.1 LEPS potential energy surface

The extended LEPS potential energy surface (PES) is employed on the excited state and the ground state in this calculation.

$$V(r_1, r_2, r_3) = Q_1 + Q_2 + Q_3 - (J_{12}^2 J_{23}^2 J_{31}^2 - J_1 J_2 - J_2 J_3 - J_1 J_3)^{1/2} \quad (1)$$

where

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

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

${}^1E_i$  is defined as the diatomic Morse potential, and  ${}^3E_i$  stands for the anti-Morse function

$${}^1E_i = D_i \{1 - \exp[-\beta_i(r - r_{0i})]\}^2 - 1 \quad (4)$$

$${}^3E_i = {}^3D_i \{1 + \exp[-\beta_i(r - r_{0i})]\}^2 - 1 \quad (5)$$

where

$${}^3D_i = \frac{D_i(1 - S_i)}{2(1 + S_i)} \quad (6)$$

$S_i$  is an adjustable parameter (so-called Sato parameter),  $D_i$ ,  $\beta_i$  and  $r_{0i}$  represent the Morse parameters of the diatom, subscript  $i = 1, 2, 3$ , indicates HF, BaF and BaH, respectively. The parameters of  $D_i$ ,  $r_{0i}$  and  $\beta_i$  for potential energy surface are taken from Reference [31] for the reaction Ba + HF. The potential energy surface by adjusting  $S_i$  ( $i = 1, 2, 3$ ) is constructed, and all the parameters are presented in Table 1.

Table 1 Parameters for the LEPS PES for the Ba + HF reaction

	BaF	HF	BaH
$D_i/eV$	6.050	5.869	1.950
$\beta_i/\text{\AA}^{-1}$	1.058	2.269	1.136
$R_{0i}^0/\text{\AA}$	2.162	0.917	2.232
$S_i$	0.178	0.160	0.300

### 2.2 Quasiclassical trajectory (QCT) calculations

The quasiclassical trajectory calculations are standard. The classical Hamilton's equations were integrated numerically for motion in three dimensions. In our calculations,  $2 \times 10^4$  trajectories were sampled and the trajectories were initiated with a Ba-HF inter-nu-

clear separation of 5  $\text{\AA}$ . The integration step size in the trajectories was chosen to be 0.1 fs. And the statistical uncertainty is less than 1.5%.

## 3 Results and discussions

### 3.1 Potential energy surface

The LEPS potential energy surface is constructed according to the experimental data acquired by Zare<sup>[5]</sup>. The reaction profile along the minimum energy path from reactants to products on our chosen PES are shown in Fig. 1, respectively. Almost no potential well is involved and a barrier whose height is about 16.7 kJ/mol appears on the exit valley of the PES. Generally, the PES is repulsive, and the barrier is late for the exothermic reaction. It shows that the barrier change a little when the Ba deviates from the H - F linear direction in a medium degree (less than  $30^\circ$ ). This suggests the small deviation from the linear direction still favors the reactive collision.

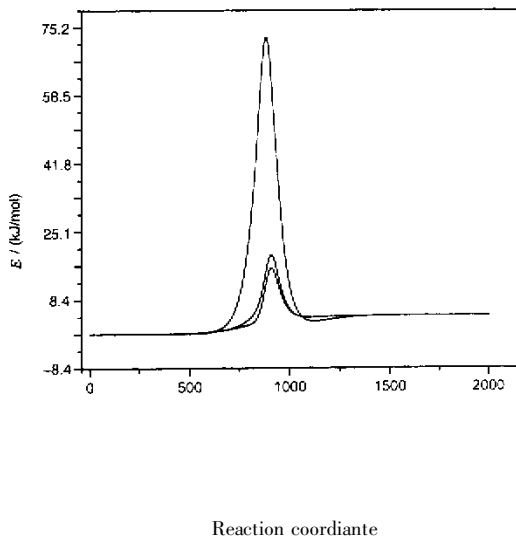


Fig. 1 The reaction profile along the minimum energy path from reactants to products on our chosen LEPS PES of the Ba + HF

### 3.2 Dependence of the internal state disposal

For this reaction, trajectories are initiated with  $v = 0$  and  $v = 1$  levels of the HF molecule. In order to compare with experimental results<sup>[3-5]</sup>, when the initial vibration state of the HF is  $v = 0$ , the collision energies are chosen as 6.7, 21.2 and 55.2 kJ/mol successively; when the initial vibration state of HF is  $v = 1$ , the collision energy is chosen as 6.7 kJ/mol.

The calculated and experimental product vibra-

tional distributions for the HF ( $v = 0$ ) are shown in Fig.2 a , b , c<sup>[5]</sup>. It is easy to figure out the vibrational excitation of product is quite weak , with the most probable population appearing at a low vibration number ( $v' = 1$ ). The shape of the distribution changes in a medium measure while the translational energy of the reactant increases. When the reagent is vibrationally excited , the result does not exhibit the same character as the situation of the HF ( $v = 0$ ) , as shown in Fig. 2d. Most products are highly vibrational excited. In reference [ 7 ] , 57% energy of the BaF product appears as the product vibration , which is lower than what we have calculated as 76% . It is expected that this unconformity be mainly caused by the fault of the LEPS PES. Fig. 3 illustrates the rotational and vibrational energy appearing in the product for different collision energies. Note that  $E_{rot}'$  is lower than  $E_{vib}'$  at first , then exceeds it when the collision energy is about 29.3 kJ/mol , and both  $E_{rot}'$  and  $E_{vib}'$  increase with the collision energy. It agrees well with the experimental results<sup>[5]</sup>.

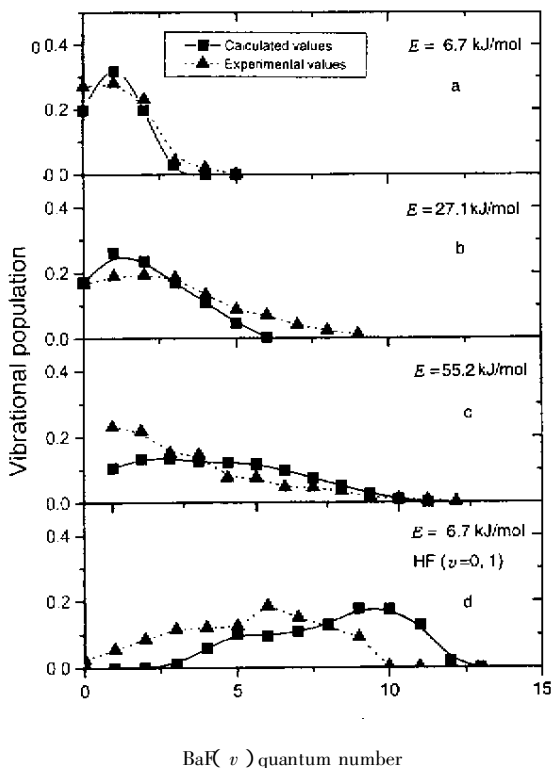


Fig.2 Relative cross-section ( $v$ ) for the product BaF ( $v'$ ) under various initial conditions  
a , b , c : the ground state condition ,  
d : the condition of HF ( $v = 1$ ) with  $E_{col} = 6.7$  kJ/mol.

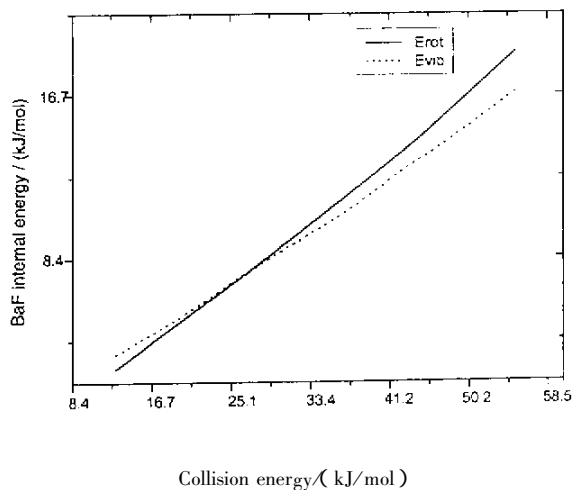


Fig.3 Distribution of the internal energy of the product BaF

### 3.3 Product rotational alignments of Ba + HF reaction

During the reactive collision , the fact that the distribution of the angular momentum  $J'$  of the product is mainly determined by  $L$  can be described by a function  $f(\theta)$  , where  $\theta$  is the angle between  $J'$  and the relative velocity vector  $\mathbf{K}$ .  $f(\theta)$  can be expanded in a set of Legendre polynomials

$$f(\theta) = \sum a_l P_l(\cos\theta) \quad (7)$$

$l = 2$  indicates the product rotational alignment

$$\begin{aligned} a_2 &= 5 P_2(\cos\theta) \\ &= 5 P_2(J' \cdot K) \end{aligned} \quad (8)$$

Because the H atom will take off little orbital angular momentum , the mass combination of H + HL will make the product rotation strongly be aligned about the reagents relative velocity and  $P_2(J' \cdot K)$  should be equal to  $-0.5$ . Fig. 4 shows the calculated results. The calculated  $P_2(J' \cdot K)$  values deviate slightly from  $-0.5$  and the deviation decreases with increasing collision energies. At low collision energies , the significant disposal of angular momentum into product orbital motion makes the product alignment decrease , and the rotation alignment of the product enhances with increasing collision energy. As we know now that the excessive translation energy will channel into rotational and translational excitation , the distinct increment of the alignment shows the collision energy is allocated in the rotation momentum in a great measure. We reported that the product rota-

tion alignment of the HHL mass combination reaction as a function of collision energies is independent of the characterization of the potential energy surface, and suggested that the product rotational alignment increases with increasing collision energy for the H + HL system. Our calculated result has agreed with the previous opinion [32, 33]

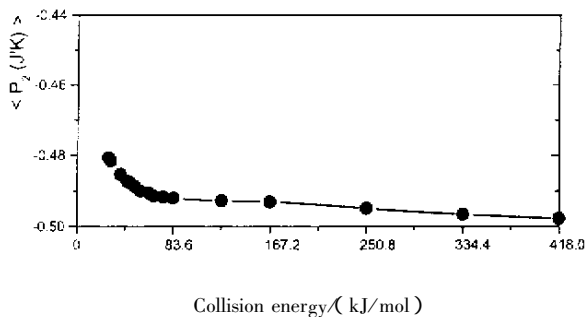


Fig. 4 The product rotational alignment of the HHL mass combination reaction on the LEPS PES as a function of the collision energy

### 3.4 Competition of the abstraction and insertion pathways

The reaction between an alkaline earth atom (M) and a hydrogen halide (HX) to yield  $\text{MX} + \text{H}$  constitutes a family of related results. In this kind of reactions, two pathways are discussed, one is the abstraction, and the other is the insertion. In the former, the metal atom attacks the hydrogen halide molecule directly, and the dissociation of HX happens contemporarily with the forming of the MX. For example, the abstraction pathway will almost be the vital pathway in the reaction  $\text{Ba} + \text{HCl}$ ,  $\text{Ba} + \text{HBr}$  [3, 11] the latter, the covalence of H - X can be broken by the attack of the alkaline earth atom to form an H - M - X intermediate complex, which is expected to be stable enough that the reaction can go through a deep potential well. As

we know now, the insertion pathway dominates in the  $\text{Ca} + \text{HF}$  [14, 18, 49] reaction. As to the  $\text{Ba} + \text{HF}$  reaction, barium has a strong effect on the hydrogen fluoride to dissociate the HF molecule when the distance between the Ba and H is reasonable long; so the H - M - H complex has little chance to exist. On the other hand, the covalence of H - F is hard to be dissociated  $D_0^0 = 564.7$  kJ/mol, and the collisions can be effective in different directions as Fig. 1 shows. It is reasonable that a stable complex may form during the reaction. These suggest that the collision between Ba and HF can go through different pathways at different conditions. Actually, although no potential well appears on the PES that always has the responsibility for the produce of relative stable complex during a reaction, the small increment of the barrier height along with the increasing attacking deviation from the linear direction (Ba - F - H) can predict the chance of the insertion reaction. So this property is the main cause of the competitive mechanism of this reaction.

The trajectories at six initial states are calculated; and in each state 100 reactive trajectories with different initial random number were presented. In each state, no one pathway can occur exclusively, and they are just equal competition relationship (Table 2). When the collision energy and vibrational energy of reagent is low, the abstraction pathway dominates the reaction and the increment of translational energy does not significantly improve the chance of the insertion. But the vibrational excitement of the reagent can considerably

raise the possibility of the insertion pathway. Two extreme conditions can approve this, one is  $E_c = 6.7$  kJ/mol,  $v = 0$ , for the abstraction sample (Fig. 5a) and the other one is  $E_c = 55.2$  kJ/mol,  $v = 2$ , for the latter insertion sample (Fig. 5b) respectively.

Table 2 Percentages of the two pathways under different initial reagent states

	HF (6.7 kJ/mol)	HF (6.7 kJ/mol)	HF (27.2 kJ/mol)	HF (27.2 kJ/mol)	HF (55.2 kJ/mol)	HF (55.2 kJ/mol)
	(0, 0)	(2, 0)	(0, 0)	(2, 0)	(0, 0)	(2, 0)
Abstraction	82	26	78	20	42	8
Insertion	18	74	22	80	58	92

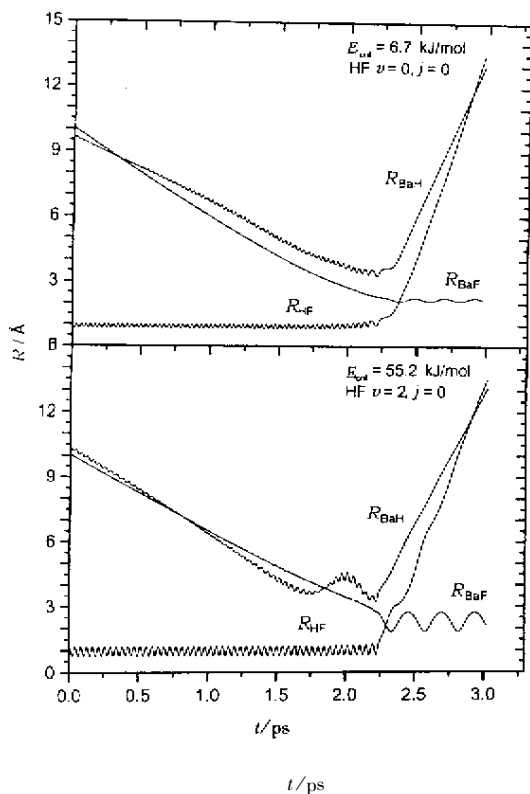


Fig.5 Curves of inter-nuclear distance  $R$  with the variation of the reaction time for  $Ba + HF$

- (a) The typical condition of the direct abstraction mechanism ;  
 (b) The typical condition of the insertion mechanism.

In the process of the abstraction pathway,  $BaF$  has a weak vibrational excitation. And insertion takes place when  $Ba$  moves from the repulsive area to the attractive area, which will lead to a strong vibrational excitation of  $BaF$ . Based on the dynamical calculation of this reaction, the abstraction is favored by low collision energy and the insertion reaction is more likely to occur when the reagent is at vibrationally excited state. The result coincides well with the suggestion that Zhang *et al.* raised several years ago<sup>[20]</sup>.

## 4 Conclusion

In summary, it is shown that the QCT calculations agree well with the experimental data for the exothermic reaction of  $Ba + HF$ . The calculation shows that the  $BaF$  vibrational excitation is weak when the reagent is in vibrational ground state, and it is strong when the reagent is in vibrational excitation. The rotational alignment strongly depends on the mass combination, and it is enhanced by the collision ener-

gy. Moreover, the analysis of each trajectory shows a competition between the direct abstraction and insertion in this reaction, and the small increment of the barrier height along with the attacking deviation from the linear direction ( $Ba - F - H$ ) is the main cause of this competition. In addition, abstraction is much more favored by low collision energy and insertion is more probable to occur when the reagent is at high vibrational level.

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## Ba + HF( $v, J$ ) → BaF( $v', J'$ ) + H 反应的准经典轨线研究\*

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**摘要:** 首次构造了放热反应 Ba + HF( $v, J$ ) → BaF( $v', J'$ ) + H 的 LEPS 势能面, 并且进行了准经典轨线研究. 对于初始基态和初始第一激发态的反应物 HF, 计算得到的 BaF 产物态分布与实验吻合得比较好. 对产物取向的研究表明, 反应体系的质量组合是产物取向的决定因素. 反应过程中, 直接的提取反应和间接的插入反应是两种竞争的微观反应通道, 这种竞争是由于在 Ba 原子进攻 HF 分子的时候, 即使进攻方向偏离了 HF 共线的方向也不会引起能垒高度的明显增加. 而且低的反应物平动能倾向于提取反应而高的 HF 振动激发会导致插入反应.

**关键词:** 准经典轨线; LEPS 势能面; 提取反应; 插入反应

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