Rotational Alignment of the Reaction $\text{Sr} + \text{HF}$ as a Function of Collision Energies

Cai Meng-Qiu Tang Bi-Yu Yang Guo-Wei Yang Yi-Ming Han Ke-Li¹

(Department of Physics, Xiangtan University, Xiangtang 411105; ¹The State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023)

Abstract The trajectory calculations of the reaction $\text{Sr} + \text{HF}$ on the extended London-Eyring-Polanyi-Sato (LEPS) potential energy surface have been carried out to study the dependence of product rotational alignment on the collision energies. The calculated results for the reaction of $\text{Sr} + \text{HF}$ were compared with the predictions from the constrained product orbital angular momentum model. The final rotational angular momentum was found to be perpendicularly polarized with respect to the reagents' relative velocity vector. The higher the collision energies are the more anisotropic is the distribution of the product rotational angular momentum vector.

Keywords: Trajectory calculation, LEPS potential energy surface, Collision energies, Rotational alignment

1 Introduction

Theoretical and experimental interest in vector correlation of the reaction processes

has increased significantly in recent decades^[1]. Vector properties, such as velocities and angular momentum, process not only magnitudes that can be directly related to translational and rotational energies, but also well-defined directions. Only by understanding the scalar and vector properties together, as well as possible correlations among them, can the fullest picture of the scattering dynamics be emerged. Clearly, one of the most important works is the determination of the product rotational alignments and orientation about the reagent relative velocity vector.

Experimentally the product alignments of a large number of reactions have been determined using polarization-resolved chemiluminescence, polarized laser

induced fluorescence, electric deflection methods, *etc.*, under molecular-beam and bulb conditions^[2-18].

To rationalize experimental results, one needs the assistance of computational work. For example, the characterization of a potential energy surface is evaluated by classical trajectory calculations. Angular momentum polarization has been studied by using either quasiclassical trajectory methods, quantum scattering, wave packet propagation techniques, or simple models^[11, 20-28]. Perhaps because of a shortage of experimental data with which to make comparisons and/or limitation of slow computer in the early time, vector correlation effects have been evaluated by updating appropriate statistical quantities after each trajectory integration. To obtain clear indications from these statistical quantities, large batches of trajectories need to be calculated.

Blais and Truhlar reported their Monte Carlo

trajectory calculations of the product HBr rotational alignment as a function of scattering angle for reaction $\text{H} + \text{Br}_2$, and they first introduced the Legendre moment method to classical trajectory calculations^[28]. We have discussed the dynamics of the reaction of $\text{Sr} + \text{HF}$ ^[29, 30] on the extended LEPS potential energy surface. In this paper, we only report the product rotational alignment of the reaction of $\text{Sr} + \text{HF}$ as a function of collision energies on the extended LEPS potential energy surface.

2 Theory

2.1 Potential energy surface (PES)

The extended LEPS potential energy surface is employed in the calculation^[30].

$$V(r_1, r_2, r_3) = Q_1 + Q_2 + Q_3 - (J_1^2 + J_2^2 + J_3^2 - J_1J_2 - J_2J_3 - J_1J_3)^{1/2} \quad (2)$$

Where

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

$$J_i = ({}^1E_i - {}^3E_i) \quad (4)$$

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

$${}^1E_i = D_i(\{1 - \exp[-\beta_i(r_i - r_i^0)] \}^2 - 1) \quad (5)$$

$${}^3E_i = {}^3D_i(\{1 + \exp[-\beta_i(r_i - r_i^0)] \}^2 - 1) \quad (6)$$

where

$${}^3D_i = D_i(1 - S_i/2(1 + S_i)) \quad (7)$$

S is the adjustable parameter. Subscript $i = 1, 2, 3$ indicates HF, SrF, and SrH, respectively. These parameters, taken from Ref. [19], are presented in Table 1.

2.2 Rotational alignment (Refs. [28] and [32])

During reactive encounter, the total angular momentum is conserved

$$J + L = J' + L' \quad (8)$$

where L and L' are the reagent and product orbital momentum, respectively. When the reagent angular momentum J is small (as is commonly the case), the product rotation can only be resulted from L . The distribution of the angular momentum J' of the product molecule is described by a function $f(\theta)$, where θ is the angle between J' and the relative velocity vector k . The $f(\theta)$ can be expanded in a set of Legendre polynomials^[28, 32]

$$f(\theta) = \sum a_i P_i(\cos \theta) \quad (9)$$

$i = 2$ indicates the product rotational alignment

$$a_2 = 5 \langle P_2(\cos \theta) \rangle = 5 \langle P_2(J', k) \rangle \quad (10)$$

Here we only calculate the average rotational alignment of the product since it has solely been measured in most experiments until now.

2.3 Classical trajectory calculations

The classical Hamilton's equations were integrated numerically for motion in three dimensions. Initial conditions for trajectories were: Sr-HF internuclear separation of 1.5×10^{-10} m and HF molecule in the $V = 0$ and $J = 0$ levels. For each collision energy, 100 000 trajectories were sampled. The limited number of trajectories may result in some statistical noise less than 10% in the calculated results.

3 Results and Discussions

The calculated results for the product rotational alignment of the reaction $\text{Sr} + \text{HF}$ on the LEPS potential energy surface are presented in Fig. 1. The reaction $\text{Sr} + \text{HF}$ is of the mass combination of heavy + heavy-light ($\text{H} + \text{H}'\text{L}$) to form heavy-heavy + light ($\text{HH}' + \text{L}$). This indicates that an important feature of this kind of reaction is the kinematic limit, *i. e.*, the

Table 1 The parameters used in the LEPS potential energy surface of the $\text{Sr} + \text{HF}$ reaction

Species	D_e/J	β/nm^{-1}	r_o/pm	S_i
HF	9.40×10^{-19}	12.67	91.68	0.28
SrF	8.95×10^{-19}	26.56	207.53	0.13
SrH	2.66×10^{-19}	11.4	214.56	0.45

Fig.1 The product SrF rotation alignment parameters $\langle P_2(k, J') \rangle$ of the reaction Sr + HF as a function of collision energy (E)

initial orbital angular momentum L completely goes into the product rotational J' angular momentum. This leads to the product rotation being strongly aligned about the reagents relative velocity and $\langle P_2(J', k) \rangle$ should be equal to -0.5 . But the calculated $\langle P_2(J', k) \rangle$ values deviate slightly from -0.5 and decrease with increasing collision energies. The significant disposal of angular momentum in product orbital motion, $L \rightarrow J' + L'$, particularly at lower collision energies, declines product rotational alignments.

An improvement over the simplistic kinematic limit expectation can be obtained by following a

constrained product orbital angular momentum (CPOAM) model approach introduced by Hartree, Simons, and Gonzalez-Urena^[26]. This model is a modification of the constant product recoil (CPR) model^[33]. It assumes first that the disposal of the angular momentum into the orbital angular momentum L' of products is not negligible but has a constant value. As a result, the CPOAM model corrects the kinematic limit expectation^[26].

$$\langle P_2(k, J') \rangle = -0.5 + Z_m^2(-\ln Z_m + 1/3) \quad (11)$$

$Z_m = L' / L_{\max}$, $L_{\max} = \nu b_{\max}$, where ν is the reagent relative velocity and $b_{\max}$ the maximum impact parameter. For trajectory results, we have replaced the single L' value implied by the CPOAM model by the mean value $\langle L' \rangle$. As a consequence, we calculate Z_m as $Z_m = \langle L' \rangle / L_{\max}$. Both $\langle L' \rangle$ and $L_{\max}$ values of the reaction of Sr + HF are given in Table 2. Table 2 also shows $\langle P_2(k, J') \rangle$ values derived from both the CPOAM model and the trajectory calculations for the reaction at different collision energies, respectively.

It can be seen from table 1 that the trajectory and model calculations predict a similar tendency, *i. e.*, the product rotational alignment increases as the collision energy increases. The small difference between trajectory and model calculated results is due to the following reasons. (1) A slight increase of the product

Table 2 The product SrF alignment parameters $\langle P_2(k, J') \rangle$ calculated from the CPOAM model and from trajectory calculations ($L_{\max}$ and $\langle L' \rangle$ in a. u. units)

Collision energies $E/\text{kJ} \cdot \text{mol}^{-1}$	$L_{\max}$	$\langle L' \rangle$	$\langle P_2(k, J') \rangle$	
			CPOAM	Trajectory
25.08	50.9	3.22	-0.4876	-0.4865
33.44	75.39	4.27	-0.4895	-0.4868
41.8	92.44	4.48	-0.4912	-0.4874
50.16	127.79	5.89	-0.4925	-0.4889
62.7	152.76	5.54	-0.4935	-0.4892
75.24	173.08	7.09	-0.4944	-0.4885
83.6	187.81	7.60	-0.4943	-0.4919
167.2	222.70	8.53	-0.4945	-0.4935
200.9	244.05	9.43	-0.4947	-0.4942
334.4	272.86	10.90	-0.4944	-0.4974
418	362.09	12.48	-0.4955	-0.4976

orbital angular momentum L' with increasing collision energies. (2) The LEPS potential energy surface is a type of unrigged PES that may result in large error. (3) The collision energy of the experiment is average energy but the collision energy in our calculation is individual. (4) Because the reaction product SrF is in a specified low rotational state, the quantum effect is significant. In further work, time-dependent-wave-packet method will be used to study this reaction.

These results confirm the validity of the CPOAM 26 model in general and its ability to give quantitative estimates for either attractive or repulsive potential surfaces.

4 Conclusions

An investigation of the product rotational alignments on collision energies for the reaction of Sr + HF on the extended potential energy surface has been carried out. The calculated results show that the product rotational alignments increase with increasing collision energies. We direct our attention to the CPOAM 26 model and confirm that the CPOAM approach is much better in estimating the alignment parameter $\langle P_2(J', k) \rangle$ than the kinematic limit prediction. Finally, we hope that this calculation may provide experimentalists with some help when they interpret their experimental data.

References

- 1 Orr-Ewing A J, Zare R N. *Annu. Rev. Phys.*, **1994**, **45**: 315
- 2 Hsu D S Y, Herschbach D R. *Faraday Discuss. Chem. Soc.*, **1973**, **55**: 116
- 3 Tyndall G W, Vries M S, Cobb C L, *et al.* *Chem. Phys. Lett.*, **1992**, **195**: 279
- 4 Li R J, Li F, Han K L, *et al.* *Proc. Int. Conf. Laser*, **1995**, **92**: 456
- 5 Li R J, Han K L, Li F E, Lu R C, *et al.* *Chem. Phys. Lett.*, **1994**, **220**: 281
- 6 Hsu D S Y, Weinstein N D, Herschbach D R. *Mol. Phys.*, **1975**, **29**: 257
- 7 Hennessy R J, Simons J P. *Chem. Phys. Lett.*, **1980**, **75**: 43
- 8 Hennessy R J, Simons J P. *Mol. Phys.*, **1982**, **43**: 181
- 9 Menezes M, Garay M, Verdasco E. *J. Phys. Chem.*, **1993**, **97**: 5836
- 10 Green F, Hancock G, Orr-Ewing A J. *Faraday Discuss. Chem. Soc.*, **1991**, **91**: 79
- 11 Costen M L, Hancock G A J, *et al.* *Chem. Phys.*, **1994**, **100**: 2754
- 12 Hartree W S, Simons J P. *J. Chem. Soc. Faraday Trans.*, **1990**, **86**: 11
- 13 Sauder D G, Stephenson J C, King D S, *et al.* *J. Chem. Phys.*, **1992**, **97**: 952
- 14 Kleinermanns K, Linnebach E. *Appl. Phys. B*, **1986**, **36**: 203
- 15 Jonah C D, Zare R N, Ottinger C. *J. Chem. Phys.*, **1972**, **56**: 263
- 16 Jalink H, Parker D H, Stolte S. *J. Chem. Phys.*, **1986**, **85**: 5372
- 17 Prisant M G, Rettner C T, Zare R N. *Chem. Phys. Lett.*, **1982**, **88**: 27
- 18 Vander W, Zhang R, Mckendrick K G, *et al.* *J. Phys. Chem.*, **1991**, **95**: 8205
- 19 Polanyi J C, Wong W H. *J. Chem. Phys.*, **1969**, **51**: 1439
- 20 Hijazi N H, Polanyi J C. *Chem. Phys.*, **1975**, **11**: 1
- 21 Hijazi N H, Polanyi J C. *J. Chem. Phys.*, **1975**, **63**: 2249
- 22 Li R J, Han K L, Li F E, *et al.* *Chin. Chem. Phys.*, **1993**, **6**: 1
- 23 Han K L, He G Z, Lou N Q. *Chin. Chem. Lett.*, **1993**, **4**: 517
- 24 Alvarino J M, Lagana A J. *Chem. Phys.*, **1991**, **95**: 998
- 25 Prisant M G, Rettner C T, Zare R N. *J. Chem. Phys.*, **1984**, **81**: 269
- 26 Hartree W S, Simons J P, Gonzalez-Urena A. *J. Chem. Soc. Faraday*, **1990**, **86**: 17
- 27 Barnwell J D, Loeser J G, Herschbach D R. *J. Phys. Chem.*, **1983**, **8**: 2781
- 28 Blais N C, Truhlar D G. *J. Chem. Phys.*, **1997**, **67**: 1540
- 29 Cai M Q, Zhang L, Tang B Y, *et al.* *Chemical Physics*, **2000**, **225**: 283
- 30 Cai M Q, Tang B Y, Yang G W, *et al.* *Natural Science Journal of Xiangtan University*, **2001**, **23**(1): 138 [蔡孟秋,唐璧玉,杨国伟等. 湘潭大学自然科学学报 (*Xiangtan Daxue Ziran Kexue Xuebao*), **2001**, **23**(1): 138]
- 31 Cai M Q, Tang B Y, Yang G W, *et al.* *Natural Science Journal of Xiangtan University*, **2000**, **22**(4): 131 [蔡孟秋,唐璧玉,杨国伟等. 湘潭大学自然科学学报 (*Xiangtan Daxue Ziran Kexue Xuebao*), **2000**, **22**(4): 131]
- 32 Prisant M Q, Rettner C T, Zare R N. *J. Chem. Phys.*, **1981**, **75**: 22

碰撞能量对反应 $\text{Sr} + \text{HF}$ 转动取向的影响

蔡孟秋 唐璧玉 杨国伟 杨益明 韩克利¹

(湘潭大学物理系, 湘潭 411105; ¹ 中国科学院大连化学物理研究所 分子反应动力学国家重点实验室, 大连 116023)

摘要 在推广 LEPS 势能面上, 用经典轨线方法, 研究了反应碰撞能量对反应 $\text{Sr} + \text{HF}$ 的转动取向的影响. 计算结果与产物轨道角动量模型进行比较. 计算结果表明, 随着碰撞能量的增加, 产物转动取向越强烈.

关键词: 轨线计算, 推广 LEPS 势能面, 碰撞能量, 转动取向