Influence of reagent vibration on the stereodynamics of the Li + HF → LiF + H reaction*

Li Shu-Juan(李淑娟)[a)], Shi Ying(石 英)[a)†],
Xie Ting-Xian(解廷献)[b)], and Jin Ming-Xing(金明星)[a)]

[a)] *Institute of Atomic and Molecular Physics, Jilin University, Changchun* 130012, *China*
[b)] *Department of Physics, Dalian Jiaotong University, Dalian* 116028, *China*

(Received 6 May 2011; revised manuscript received 22 June 2011)

We investigate the influence of reagent vibration on the stereodynamics of the title reaction by the quasi-classical trajectory on the Aguado-Paniagua2-potential energy surface developed by Aguado *et al.* (*J. Chem. Phys.* 1997 **106** 1013). The cross sections and reaction probability as functions of the reagent vibration are calculated in the centre-of-mass frame. The product angular distributions of $p(\theta_r)$, $p(\phi_r)$, and $p(\theta_r, \phi_r)$, which reflect the vector correlation, are also presented and discussed. The results indicate that the vector properties are sensitively affected by the vibrational excitation.

Keywords: quasi-classical trajectory, vector correlation, cross sections, stereodynamics

PACS: 34.50.Lf, 82.20.Kh **DOI:** 10.1088/1674-1056/21/1/013401

1. Introduction

As a prototype of the heavy-heavy-light (HHL) system, and its reactive asymmetry, the Li+HF reaction would appear to be an excellent candidate for stereodynamical study.[1] One of the important aspects of the LiHF system is its rather deep van der Waals well in the entrance channel, which gives rise to the long-lived collision complexes and narrow scattering resonances in the energy-dependent reaction probabilities.[1] Its fundamental importance has led to reports of numerous experimental studies[2−5] and dynamic calculations[6−16] for this reaction over the last three decades. From an experimental point of view, differential cross sections of product LiF at different collision energies in a crossed molecular beam were measured by Becker *et al.*[2] Using crossed molecular beam apparatus, Loesch *et al.* reported the angular distributions of LiF for three different distributions of the internuclear axis of HF.[3] Recently, Hobel *et al.* have measured experimentally the double differential cross sections for the reaction at collision energies ranging from 88 to 378 meV in a crossed molecular beam experiment.[4] They considered that their experimental results were in good agreement with the quasi-classical trajectory (QCT) calculations.[15] In the theoretical aspect, in 1997, Aguado *et al.* constructed the potential energy surface (PES) of the reaction based on MRDCI *ab initio* energy points and carried out wave packet calculations.[16] Most recently, zero total angular momentum exact quantum probabilities for a Li atom reacting with HF and its isotopic variants have been reported by Lagana.[9] Wecka *et al.* presented the quantum reactive scattering calculations for the scattering process for zero total angular momentum at low and ultralow temperatures.[1]

With the rapid development of reaction dynamics, the research of stereodynamics of the title reaction has received plenty of attention. Insight into the chemical reaction dynamics of the Li+HF reaction can be provided by both the scalar and the vector properties. The vector properties, such as velocities and angular momentum, possess not only those related to magnitudes and rotational energies, but also directions. Therefore, it is necessary to calculate the polarization of the product angular momentum for the title reaction. The differential cross section has been measured, and the angular distribution of LiF with increasing collision energy has been calculated in order to obtain the stereodynamics of the title reaction.[4] Yuan and Zhao studied the vector properties of the products,

*Project supported by Jilin University, China (Grant No. 419080106440), the Chinese National Fusion Project for ITER (Grant No. 2010GB104003), and the National Natural Science Foundation of China (Grant No. 10974069).

†Corresponding author. E-mail: shi_ying@jlu.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

and investigated the variation of the rotational alignment with collision energy by QCT calculations on a Aguado-Paniagua2-potential energy surface (AP2-PES).[14] However, to the best of our knowledge, the vibration effects on the vector properties of the title reaction have never been carried out so far.

In this paper, we will conduct the calculations of product rotational polarization and explore the influence of the initial vibrational states of the reagent molecule on the product's vector correlations for the title reaction on AP2-PES. We expect that the analysis of the vector properties can reveal more dynamics information that is lost when the directional properties are not explicitly considered.

2. Theory

2.1. QCT calculations and potential energy surface

The QCT calculation method is similar to that previously described.[17−23] The classical Hamilton equations are numerically integrated in three dimensions. The product rotational polarization for the title reaction is employed on the AP2-PES constructed by Aguado *et al.*[17] This new fit lowers the saddle-point energy to 5.37 kcal/mol and removes the spurious features of the initial one[16] The trajectories are initiated at an Li–HF internucleus separation of 10 Å, the vibrational and rotational levels of the reactant molecules are taken to be $\nu = 0$–6 and $j = 0$, respectively. In this study, 20000 trajectories are sampled for each vibrational momentum at the collision energy of 8.76 kcal/mol above the reaction energy barrier The integration step size of 0.1 fs is used to ensure numerical stability. The accuracy of the numerical integration is verified by checking the conservation of the total energy and the total angular momentum for each trajectory.

2.2. Rotational alignment and cross section

The present QCT calculation is carried out within the centre-of-mass (CM) frame, in which the z-axis is parallel to the reagent velocity $\boldsymbol{k}$, and the y-axis is perpendicular to the xz plane containing the initial and the final relative velocity vectors $\boldsymbol{k}$ and $\boldsymbol{k}'$. The angles $\theta_{\rm r}$ and $\phi_{\rm r}$ are defined as the polar and azimuthal angles of the final rotational momentum $\boldsymbol{j}'$, respectively.[24−32] The reactive cross section is defined as $\sigma_{\rm r} = \pi b_{\rm max}^2 (N_{\rm r}/N)$. Specifically, $\langle P_2(\cos\theta_{\rm r})\rangle$ is the average rotational alignment factor and can be calculated over the vibrational momentum ($\nu = 0$–6) to investigate the variation of the rotational alignment with the increasing vibrational excitation.

3. Results and discussion

Figure 1 shows the total reaction cross section resulting from our QCT calculations. It is clear that the integral cross section increases monotonically with the vibrational quantum number ranging from $\nu = 0$ to $\nu = 6$. The average rotational alignment factor for the title reaction as a function of the vibrational reagent is presented in Fig. 2. It is observed that the $\langle P_2(\cos\theta_{\rm r})\rangle$ values are almost invariant with the increase of vibrational excitation, indicating that there are weak product rotational alignments. In this case, we can deduce that the angular momentum is large, which is consistent with the previous calculations of HHL mass combinations.[23,32,33]

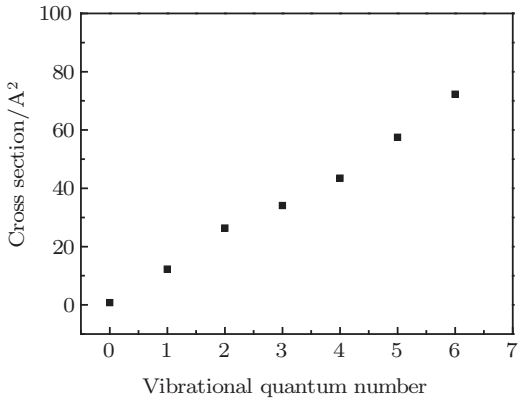


Fig. 1. QCT-computed reaction cross sections for Li + HF (ν = 0–6, j = 0) → LiF+H with vibrational number.

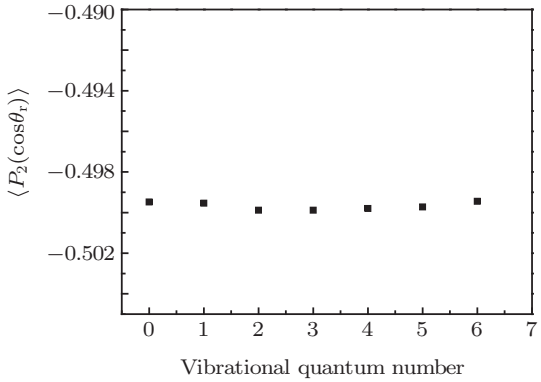


Fig. 2. Variation of rotational alignment parameter $\langle P_2(\cos\theta_{\rm r})\rangle$ with the vibrational quantum number for the title reaction.

The peaks of $p(\theta_r)$ and $p(\phi_r)$ on the AP2-PES are sensitive to the vibrational quantum number as shown in Figs. 3 and 4. The $p(\theta_r)$ distribution of the product is used to describe the $\boldsymbol{k}$–$\boldsymbol{j}'$ correlation. For seven vibrational states, it is clear that the peaks of $p(\theta_r)$ are distributed at $\theta_r = 90°$ and symmetric with respect to 90°, which shows that the product rotational angular momentum vector is distributed with a cylindrical symmetry in the product scattering plane and strongly aligned along the direction normal to the relative velocity. It is seen that there is a tiny discrepancy among the distributions of $p(\theta_r)$ of the seven reactions. The peaks of the $p(\theta_r)$ distribution of the reaction become narrower and higher when the reagent vibration is in the range of $\nu = 0$–6, indicating that the product rotational alignment effect becomes stronger when the reagent is in excited vibration states. The calculated results for the title reaction are in agreement with the distributions of $\langle P_2(\cos\theta_r)\rangle$.

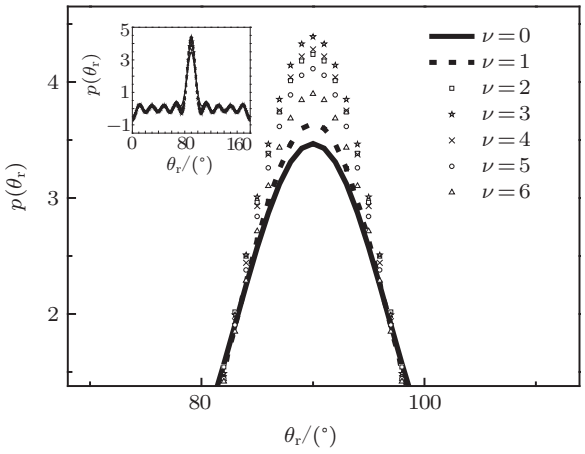


Fig. 3. Distributions of $p(\theta_r)$ reflecting $\boldsymbol{k}$–$\boldsymbol{j}'$ correlations at a collision energy of 8.76 kcal/mol for the reagent vibrational excitation.

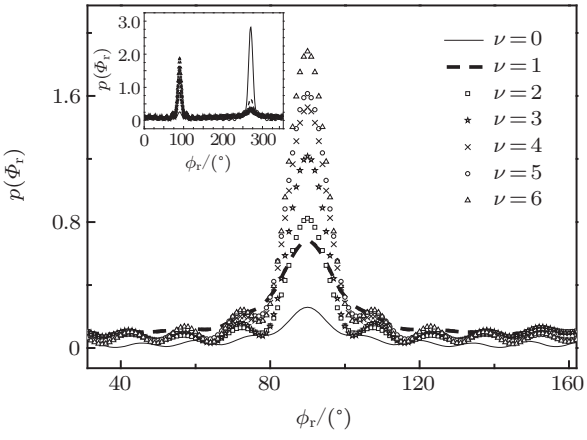


Fig. 4. The dihedral angle distribution of $p(\phi_r)$ with respect to the $\boldsymbol{k}$–$\boldsymbol{k}'$ plane, plotted at reagent vibrational excitation.

The dihedral angle distribution of $p(\phi_r)$ shown in Fig. 4 describes the $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ correlation. Those $p(\phi_r)$ which tend to be antisymmetric with respect to the $\boldsymbol{k}$–$\boldsymbol{k}'$ scattering plane directly reflect the strong polarization of the angular momentum for the title reaction. There are two peaks at $\phi_r = 90°$ and $\phi_r = 270°$, as shown in the inset, which might suggest that the reaction proceeds preferentially when the reactant velocity vector lies in a plane containing all three atoms. The peaks of $p(\phi_r)$ appear at $\phi_r = 90°$ and $\phi_r = 270°$, which reflect that $\boldsymbol{j}'$ is preferentially aligned along the direction of the y-axis. Because the peak at $\phi_r = 90°$ is different from that at $\phi_r = 270°$, which indicates that the rotational angular momentum vector of the products is not only aligned but also oriented along the y-axis. The peak at $\phi_r = 270°$ is much higher than that at $\phi_r = 90°$, when the reagent HF is in the vibration ground states as shown in the inset of Fig. 4. The peak at $\phi_r = 270°$ drops rapidly, while that at $\phi_r = 90°$ rises slowly. In order to show the peak change, we enlarge part of the peak at $\phi_r = 90°$. The peak at $\phi_r = 270°$ becomes smaller while the peak at $\phi_r = 90°$ becomes higher with increasing vibrational quantum number. In this case, the peak at $\phi_r = 90°$ becomes higher than that at $\phi_r = 270°$ at $\nu = 1$–6. This fact reflects that $\boldsymbol{j}'$ is oriented along the positive direction of the y-axis. It also can be seen that the degree of orientation is greatly conspicuous. In order to understand the behaviours of $p(\phi_r)$, more about product rotational orientation needs to be considered. According to the impulsive model about the molecular reaction for the reaction A+BC→AB+C,[34–37] the distribution of $\boldsymbol{j}'$ is expressed as $\boldsymbol{j}' = \boldsymbol{L}\sin^2\beta + \boldsymbol{J}\cos^2\beta + \boldsymbol{J}_1 m_A/m_B$, where $\boldsymbol{L}$ is the reagent orbital angular momentum and $\boldsymbol{J}_1 = (u_{BC}R)^{1/2}(\boldsymbol{r}_{AB} \times \boldsymbol{r}_{CB})$, with u_{BC} being the reduced mass of the BC molecular and R the repulsive energy. In the title reaction, the term of $\boldsymbol{L}\sin^2\beta + \boldsymbol{J}\cos^2\beta$ is symmetric, while the term $\boldsymbol{J}_1 m_A/m_B$ shows a preferred direction for the effect of repulsive energy, which leads to the change of orientation of the product LiF. References [38]–[43] have proved that the abstraction reaction causes $\boldsymbol{J}_1$ to orient along the positive direction of y-axis, whereas the insertion reaction to the opposite direction. The reason that the orientation along the positive direction of y-axis becomes stronger with the increasing vibrational quantum number may be explained as follows. As mentioned above, in the impulsive model, $\boldsymbol{J}_1$ plays a very important role in the product rotational orientation. It can be seen that a large $\boldsymbol{J}_1$ leads to a stronger tendency to orient along the $\boldsymbol{J}_1$ direction. The repulsive energy R

increases with the increase of vibrational quantum number, which leads to larger values of $\boldsymbol{J}_1$ at high vibrational quantum number. This influence plays a dominating role in product rotational orientation at high vibrational quantum number, which leads to the orientation along the positive direction of the y axis.

The product angular distributions which reflect the vector correlation contain rich information about the angular momentum polarization. In order to validate more information about the product molecule axis polarization, the values of $p(\theta_{\rm r}, \phi_{\rm r})$, averaged over all scattering angles at $\nu = 0$, 3, 6 are selected and plotted in Fig. 5. The distributions of $p(\theta_{\rm r}, \phi_{\rm r})$ with peaks at $(90°, 270°)$ are in good accordance with those of $p(\theta_{\rm r})$ and $p(\phi_{\rm r})$ of the LiF products for three vibrational states, although the shapes are somewhat different. The distributions of $p(\theta_{\rm r}, \phi_{\rm r})$ show that the products are preferentially polarised perpendicular to the scattering plane and the products of reactions rotate mainly in planes parallel to the scattering plane.

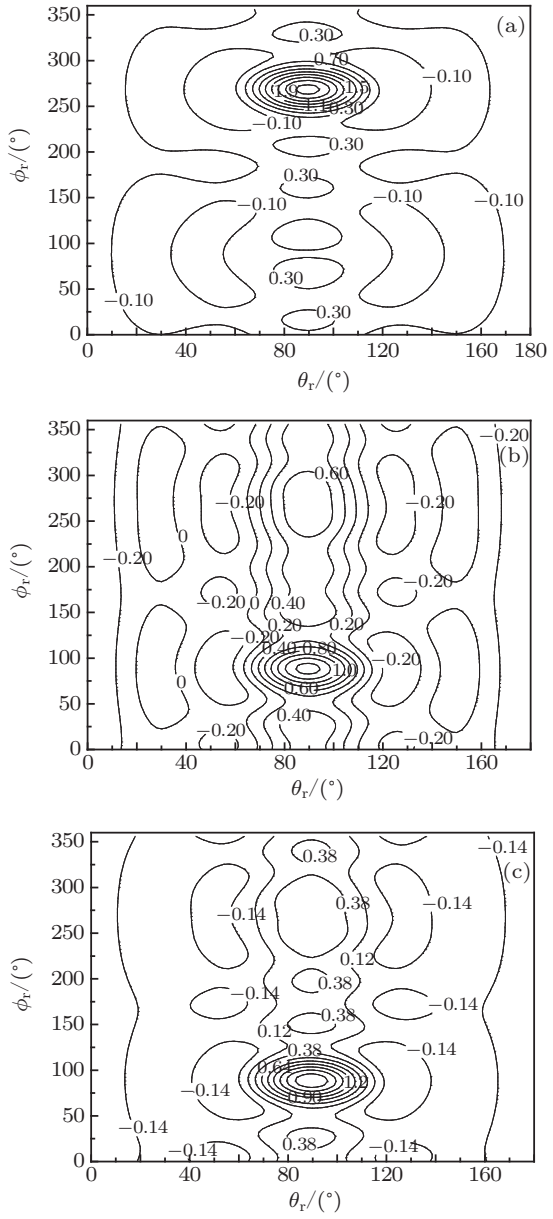


Fig. 5. Polar plots of the $p(\theta_{\rm r}, \phi_{\rm r})$ distribution for values of ν averaged over all scattering angles: (a) $\nu = 0$, (b) $\nu = 3$, (c) $\nu = 6$.

4. Conclusions

The product rotational polarization of the title reaction has been calculated by means of the QCT method for the collision energy 8.76 kcal/mol to study the influence of reagent vibrational excitation on the product vector properties. In addition, the distribution of $p(\theta_{\rm r})$ and $p(\phi_{\rm r})$ of the products for the title reactions Li + HF ($\nu = 0$–6, $j = 0$) $\rightarrow$ LiF + H is presented in this paper. The $p(\theta_{\rm r})$ distributions suggest that $\boldsymbol{j}'$ are strongly aligned perpendicular to $\boldsymbol{k}$. The distribution of $p(\phi_{\rm r})$ shows that the product rotational angular momentum vector $\boldsymbol{j}'$ is oriented along the positive direction of y-axis in the centre of mass frame, which implies a preference for right-handed product rotation. It can be well explained by the impulse model. The product rotational alignment effect tends to become stronger as the reagent vibrational momentum increases. The cross section increases monotonically with the increasing vibrational quantum number ranging from $\nu = 0$ to $\nu = 6$.

Acknowledgments

Many thanks to Prof. Haqn Ke-Li Han for providing the stereodynamics program.

References

[1] Wecka P F and Balakrishnan N 2005 *J. Chem. Phys.* **122** 234310

[2] Becker C H, Casavecchia P, Tiedemann P W, Valentini J J and Lee Y T 1980 *J. Chem. Phys.* **73** 2833

[3] Loesch H J and Stienkemeier F 1993 *J. Chem. Phys.* **98** 9570

[4] Hobel O, Bobbenkamp R, Paladini A, Russo A and Loesch H J 2004 *Phys. Chem. Chem. Phys.* **6** 2198

[5] Loesch H J and Stienkemeier F J 1993 *Chem. Phys.* **99** 9598

[6] Noorbatcha I and Sathyamurthy N 1982 *J. Am. Chem. Soc.* **104** 1766

[7] Noorbatcha I and Sathyamurthy N 1982 *Chem. Phys.* **76** 6447

[8] Weck P F and Balakrishnan N 2005 *J. Chem. Phys.* **122** 154309

[9] Lagana A, Bolloni A and Crocchianti S 2000 *Phys. Chem. Chem. Phys.* **2** 535

[10] Aguado A, Paniagua M, Sanz C and Roncero O 2003 *J. Chem. Phys.* **119** 10088

[11] Jasper A W, Hack M D, Chakraborty A, Truhlar D G and Piecuch P 2003 *J. Chem. Phys.* **116** 8353

[12] Wecka P F and Balakrishnan N 2005 *J. Chem. Phys.* **122** 154309

[13] Baer M, Last I and Loesch H J 1994 *J. Chem. Phys.* **101** 9648

[14] Yuan H and Zhao G J 2010 *Int. J. Quantum Chem.* **110** 1842

[15] Palmieri P and Laganà A 1989 *J. Chem. Phys.* **91** 7303

[16] Aguado A, Paniagua M, Lara M and Roncero O 1997 *J. Chem. Phys.* **106** 1013

[17] Aguado A, Paniagua M, Lara M and Roncero O 1997 *J. Chem. Phys.* **107** 10085

[18] Truhlar D G and Muckerman J T 1979 *A Guide for the Experimentalist* (New York: Plenum Press) p. 505

[19] Han K L, He G Z and Lou N Q 1996 *J. Chem. Phys.* **105** 8699

[20] Zhang W Q, Cong S L, Zhang C H, Xu X S and Chen M D 2009 *J. Phys. Chem.* A **113** 4192

[21] Chen M D, Han K L and Lou N Q 2003 *J. Chem. Phys.* **118** 4463

[22] Chu T S, Zhang Y and Han K L 2006 *Int. Rev. Phys. Chem.* **25** 201

[23] Zhao J, Xu Y, Yue D G and Meng Q T 2009 *Chem. Phys. Lett.* **471** 160

[24] Zhu T, Hu G D, Chen J Z, Liu X G and Zhang Q G 2010 *Chin. Phys.* B **19** 083402

[25] Liu Y F, Gao Y L, Shi D H and Sun J F 2009 *Chem. Phys.* **364** 46

[26] Xu Y, Zhao J, Yue D G, Liu H, Zheng X J and Meng Q T 2009 *Chin. Phys.* B **18** 5308

[27] Zhang C H, Zhang W Q and Chen M D 2009 *J. Theor. Comput. Chem.* **8** 403

[28] Han K L, He G Z and Lou N Q 1996 *J. Chem. Phys.* **105** 8699

[29] Chen M D, Han K L and Lou N Q 2002 *Chem. Phys. Lett.* **357** 483

[30] Xu Y, Zhao J, Wang J, Liu F and Meng Q T 2010 *Acta Phys. Sin.* **59** 3885 (in Chinese)

[31] Zhang W Q, Li Y Z, Xu X S and Chen M D 2010 *Chem. Phys.* **367** 115

[32] Wang M L, Han K L and He G Z 1998 *J. Phys. Chem.* A **102** 10204

[33] Zhao J and Luo Y 2011 *Chin. Phys.* B **20** 043402

[34] Li W L, Wang M S, Yang C L, Liu W W, Sun C and Ren T Q 2007 *Chem. Phys.* **337** 93

[35] Chu T S, Zhang H, Yuan S P, Fu A P, Si H Z, Tian F H and Duan Y B 2009 *J. Phys. Chem.* A **113** 3470

[36] Wei Q, Li X and Li T 2010 *Chem. Phys.* **368** 58

[37] Liu S L and Shi Y 2011 *Chin. Phys.* B **20** 013404

[38] Alexander A J, Aoiz F J, Bañares L, Brouard M and Simons J P 2000 *Phys. Chem. Chem. Phys.* **2** 571

[39] Duan L H, Zhang W Q, Xu, X S, Cong S L and Chen M D 2009 *Mol. Phys.* **107** 2579

[40] Yao L, Zhong H Y, Liu Y L and Xia W W 2009 *Chem. Phys.* **359** 151

[41] Xu W W, Liu X G, Luan S H, Zhang Q G and Zhang P Y 2008 *Chem. Phys. Lett.* **464** 92

[42] Yue X F, Cheng J, Li H, Zhang Y Q and Emilia L W 2010 *Chin. Phys.* B **19** 043401

[43] Liu X G, Sun H Z, Liu H R and Zhang Q G 2010 *Acta Phys. Sin.* **59** 7796 (in Chinese)