

## Investigation of Stereo-dynamic Properties for the Reaction H+HLi by Quasi-classical Trajectory Approach

Yuliang Wang,\* Jinchun Zhang, Yanlan Jiang, Kun Wang, Mingyu Zhou, and Xiaorui Liang

Department of Basic Sciences, Naval Aeronautical and Astronautical University, Yantai 264001, P.R. China

\*E-mail: yarmiay@163.com

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Quasi-classical trajectory (QCT) calculations of H+HLi reaction have been carried out on a new potential energy surface of the ground state reported by Prudente *et al.* [*Chem. Phys. Lett.* **2009**, 474, 18]. The four polarization-dependent differential cross sections have been carried out in the center of mass (CM) frame at various collision energies. The reaction probability for the depletion channel has been studied over a wide collision energy range. It has been found that the collision energy decreases remarkably reaction probability, which shows the expected behavior of the title reaction belonging to an exothermic barrierless reaction. The results are in good agreement with previous RMP results. The  $P(\theta_r)$ ,  $P(\phi_r)$  and  $P(\theta_r, \phi_r)$  distributions, the  $\mathbf{k}-\mathbf{k}'-j'$  correlation and the angular distribution of product rotational vectors are presented in the form of polar plots. The average rotational alignment factor  $\langle P_2(j' \cdot \mathbf{k}) \rangle$  as a function of collision energy is also calculated. The results indicate that the collision energy has a great influence on the polarization of the product rotational angular momentum vector  $j'$ .

**Key Words :** Reaction stereo-dynamics, H+HLi  $\rightarrow$  H<sub>2</sub>+Li reaction, Quasi-classical trajectory, Vector correlations

### Introduction

The primordial molecules play an important role in observational cosmology, and it is believed that the formation and depletion of LiH system can offer useful perspectives for various studies about the early universe. Over the course of the past 30 years, efforts were made to understand the neutral and ionic chemistry of LiH.<sup>1,2</sup>

Recently, due to its importance, the LiH<sub>2</sub> systems received extensively attention and a large number of researches was presented on its potential energy surfaces (PESs).<sup>3-13</sup> The pioneer work can be traced to Clarke *et al.*,<sup>3</sup> where they firstly calculated the adiabatic LiH<sub>2</sub> potential energy surface using the spin-coupled valence bond (SCVB) non-orthogonal configuration interaction (CI) method, and found that cold LiH molecules can be depleted by reactive encounters with H atom at low collision energy. they also reported that there is a small barrier with the height of about 0.04 eV. After a short time, Lee *et al.*<sup>4</sup> reported a new ground state PES which shows a downhill descending shape from the initial state H+HLi to the final state H<sub>2</sub>+Li, and they found that <sup>1</sup>2 A' intermediate plays an important role in the reaction process. Dunne *et al.*<sup>5</sup> derived an analytical potential energy surface named DMJ PES by fitting a many-body potential to energies obtained from high quality *ab initio* (CI) calculations and carried out the reaction cross sections for reaction H+HLi  $\rightarrow$  H<sub>2</sub>+Li at various collision energies and selected rotational states. However, they found no barrier to the title reaction. Afterwards, Kim *et al.*<sup>6</sup> constructed the new PES for Li+H<sub>2</sub> with the high-level *ab initio* method and interpolated by the IMLS/Shepard scheme. The results

showed that there is no energy barrier for the H+HLi reaction in either of collinear (180°) and perpendicular (90°) approaches and the endoergicity of the H<sub>2</sub>+Li reaction is better overcome by high vibrational energy of H<sub>2</sub> molecules ( $v \geq 4$ ) than by high collision energy. Recently, Prudente *et al.*<sup>7</sup> improved the PES of Dunne *et al.*<sup>5</sup> by performing accurate *ab initio* full configuration interaction (FCI) calculations and fitting them to a slightly modified analytical DMJ function. At the same time Wernli *et al.*<sup>8</sup> provided a three-dimensional PES for the LiH<sub>2</sub> system and referred that there is no energy barrier along the reaction path which agrees with that of Dunne,<sup>5</sup> Kim<sup>6</sup> and Prudente<sup>7</sup> but opposite to that of Clarke.<sup>3</sup>

Based on these PESs, various quantum dynamical calculations have been carried out.<sup>13-28</sup> Padmanaban and Mahapatra<sup>14</sup> reported the reaction probabilities for both the collinear and the three-dimensional arrangements of the H+HLi ( $v = 0-3$ ,  $j = 0-3$ ) system with the aid of a time-dependent wave packet approach (TDWP), finding that for any ( $v, j$ ) state the HLi depletion probability is lower than the H exchange probability for any given energy. In their latter paper,<sup>15</sup> Padmanaban and Mahapatra calculated the cross section with the aid of the TDWP approach based on the DMJ PES for the title reaction up to a total energy of 0.9 eV. When compared to the results reported by Dunne *et al.*<sup>5</sup> a great difference was found. After two years, based on the TDWP approach, they<sup>16</sup> obtained the exact quantum scattering calculations to investigate the effect of Coriolis coupling (CC). The results were carried out up to  $J = 30$  and  $K_{\max} = 8$ . They indicated that the H+HLi reaction is a barrierless reaction. Recently, Prudente *et al.*<sup>7</sup> performed the calcu-

lations of the reaction probabilities in the collision energy range of 0.1–1.4 eV and indicated a decrease of the total reaction probability.

To date, however, it should be noticed that the previous work for LiH<sub>2</sub> system has dealt with the scalar properties. As we know, there are very rare reports for the title reaction vector properties which can provide the valuable information about chemical reaction stereo-dynamics. In order to shed light on investigating the title reaction dynamics, we present a quasi-classical trajectory (QCT) calculations to study the influence of the collision energy for the reaction H+HLi → H<sub>2</sub>+Li based on a new analytical PES reported by Prudente *et al.*<sup>7</sup> named PMM PES. The paper is organized in the following way: In Sec. 2 we describe the theory of the quasi-classical trajectory approach. In Sec. 3 we present the results obtained by the QCT method and interpret them. The paper is finished by summarizing the findings in Sec. 4.

### Computing Scheme

The PMM PES used in the present work for the H+HLi → H<sub>2</sub>+Li reaction is a relatively accurate adiabatic state. It was given by Prudente *et al.*,<sup>7</sup> who fitted a set of accurate *ab initio* points to many body polynomial expansion in the Murrell–Carter–Farantos–Huxley–Varandas functional form.<sup>29</sup> The detailed functional form and deduction process can be referred to Ref. 29.

The QCT method used here is specified elsewhere<sup>30–33</sup> and has been widely used to study dynamics of the chemical reactions.<sup>34–36</sup> The classical Hamilton's equations are integrated numerically for motion in three dimensions. Here, to deal with the drawback of QCT method which is unable to properly treat the zero-point energy, we employed a passive method which simply discards all reactive trajectories forming products with a total vibrational energy that is lower than the total harmonic zero-point energy of the products. All the calculations for the title reaction reported here are carried out at the vibrational and rotational ground state ( $v=0, j=0$ ), and the collision energies are 0.1 eV, 2.0 eV and 4.0 eV. For each collision energy, a batch of 20000 trajectories was run for the title reaction. The integration step size is chosen to be 0.1 fs. For  $J \neq 0$ , the appropriate value of the impact parameter,  $b_{\max}$ , was selected after preliminary running batches of 10000 trajectories at each collision energy. For  $J=0$  and  $b=0$ , the reaction probability is defined as  $P = N_r/N$ , which is the ratio of the number of reactive trajectories to the total number of trajectories.

The reference frame used in the present calculations is the center-of-mass (CM) frame.  $\mathbf{k}$  and  $\mathbf{k}'$  are the reagent relative velocity vector and product relative velocity, respectively.  $\mathbf{k}$  is parallel to the z axis and x-z plane containing the initial and final relative velocity vectors,  $\mathbf{k}$  and  $\mathbf{k}'$ . The final angular momentum is  $\mathbf{j}'$ , with its polar and azimuthal angles being  $\theta_r$  and  $\phi_r$ , respectively. Here we analyzed the correlations  $\mathbf{k}-\mathbf{j}'$  and  $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$  characterized by the angular distributions  $P(\theta_r)$  and angular distributions  $P(\phi_r)$ .

The  $\mathbf{k}-\mathbf{j}'$  angular distribution  $P(\theta_r)$  can be expanded into a

series of Legendre polynomials,

$$P(\theta_r) = \frac{1}{2} \sum_k [k] a_0^{(k)} P_k(\cos \theta_r) \quad (1)$$

The  $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$  angular distribution  $P(\phi_r)$  can be expanded in Fourier series as

$$P(\phi_r) = \frac{1}{2\pi} \left( 1 + \sum_{\text{even}, n \geq 2} a_n \cos n\phi_r + \sum_{\text{odd}, n \geq 1} a_n b_n \sin n\phi_r \right), \quad (2)$$

$$\text{where } a_n = 2 \langle \cos n\phi_r \rangle, \quad (3)$$

$$b_n = 2 \langle \sin n\phi_r \rangle, \quad (4)$$

In this work,  $P(\theta_r)$ ,  $P(\phi_r)$  and  $P(\theta_r, \phi_r)$  are expanded up to  $k=18, n=24, k=7$ , which show good convergence.

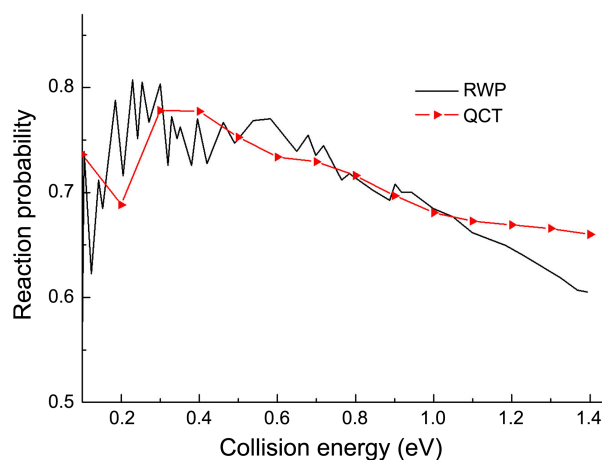
The fully correlated CM angular distribution is written as the sum

$$P(\omega_r, \omega_r) = \sum_{kq} \frac{[k]}{4\pi} \frac{1}{\sigma} \frac{d\sigma_{kq}}{d\omega_r} C_{kq}(\theta_r, \theta_r)^* \quad (5)$$

where  $(1/\sigma)(d\sigma_{kq}/d\omega_r)$  are the generalized polarization dependent differential cross-sections (PDDCSs). In this work,  $(2\pi/\sigma)(d\sigma_{00}/d\omega_r)$ ,  $(2\pi/\sigma)(d\sigma_{20}/d\omega_r)$ ,  $(2\pi/\sigma)(d\sigma_{22+}/d\omega_r)$  and  $(2\pi/\sigma)(d\sigma_{21-}/d\omega_r)$  are calculated. In addition, we also calculate the rotational alignment parameter  $\langle P_2(\mathbf{j}' \cdot \mathbf{k}) \rangle$  of the product since it has solely been measured in most of the experiments until now.

### Results and Discussion

Figure 1 shows a comparison between the reaction probability for  $J=0$  calculated by QCT method in this paper and reported with RWP method by Prudente *et al.*<sup>7</sup> The PMM PES we used did not reveal the existence of any barrier to the reaction, the collision favors the process at short times when H approaches LiH on the H side. As shown in the figure, both reaction probabilities display a similar trend over the whole collision energy range. The reaction is



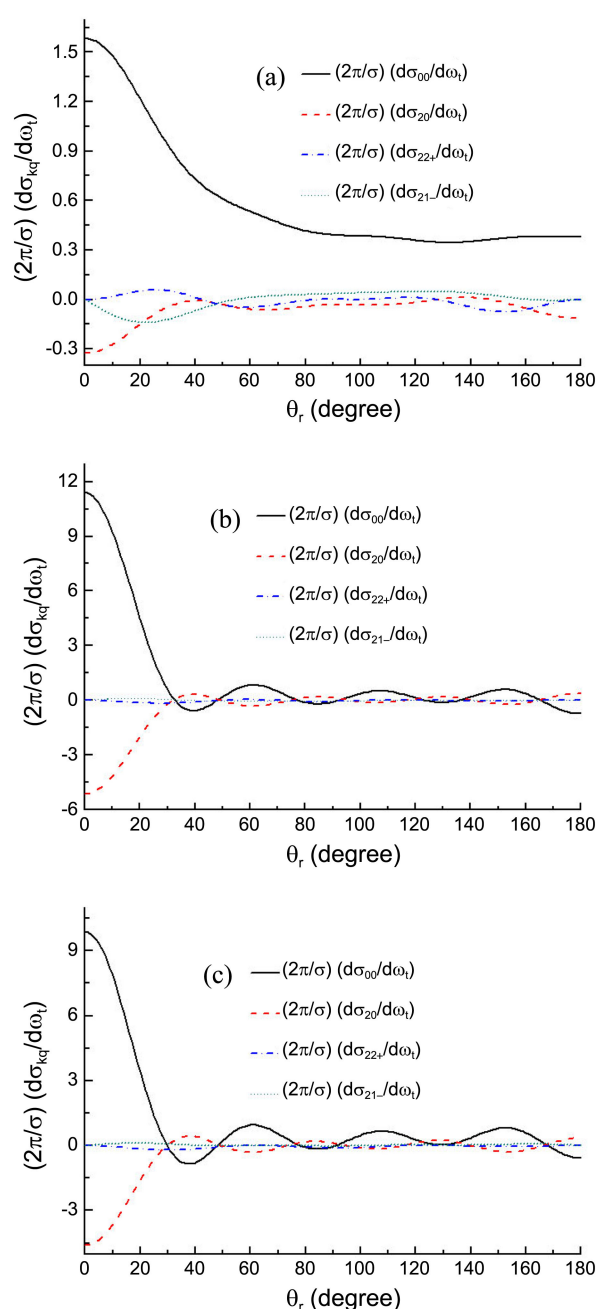
**Figure 1.** A comparison between the QCT-computed reaction probabilities in this work and the real wave packet (RWP) results calculated by Prudente *et al.*<sup>7</sup> for the depletion channel of the LiH+H reaction.

intrinsically barrierless and proceeds without any threshold, which is explicitly indicated in the  $J=0$  reaction probabilities. We also point out that the results indicate a decrease at high collision energy (about 0.3 eV), which shows the expected behavior of the title reaction belonging to an exothermic barrierless reaction.

The generalized polarization dependent differential cross-sections (PDDCSs) which describe the  $k-k'-j'$  correlation and the scattering direction of the product molecules have been calculated and the results are shown in Figure 2(a), (b), and (c) with the corresponding collision energy of 0.1 eV, 2.0 eV and 4.0 eV, respectively.

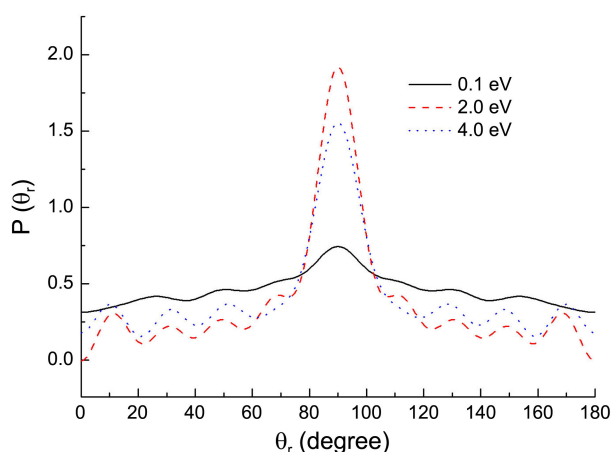
The PDDCS  $(2\pi/\sigma)(d\sigma_{00}/d\omega_r)$  is proportional to differential cross-section (DCS) which describes the angular distribution of the product molecule. As shown in the figure, the product molecules are strongly scattered forward (in the scattering angle range  $0-40^\circ$ ) for the three collision energies, and the tendency of forward scattering decreases with the increase in collision energy. Compared with the one at collision energy of 0.1 eV,  $(2\pi/\sigma)(d\sigma_{00}/d\omega_r)$  of the reaction at the collision energy of 2.0 eV and 4.0 eV indicates more obvious forward scattering, which is caused mainly by the collision effect of reactant atom. The PDDCS  $(2\pi/\sigma)(d\sigma_{20}/d\omega_r)$  is the expectation value of the second Legendre moment  $\langle P_2(\cos\phi_r) \rangle$ , and the trend of it is distinctly opposite to that of  $(2\pi/\sigma)(d\sigma_{00}/d\omega_r)$ . It indicates that the angular momentum of product molecules polarize along the direction at right angle to  $k$ . It is obvious that the PDDCSs with  $q \neq 0$  are zero at the extremities of forward and backward scatterings. The behavior of PDDCSs with  $q \neq 0$  at the scattering away from extreme forward and backward directions is more interesting and can provide abundant dynamic information.<sup>32</sup> The values are nonzero at scattering angles away from  $\theta_r = 0$  and  $\pi$ , which indicates the  $P(\theta_r, \phi_r)$  distribution is not isotropic for products molecules. The PDDCS  $(2\pi/\sigma)(d\sigma_{22+}/d\omega_r)$  is related to  $\langle \sin^2\theta_r \cos 2\phi_r \rangle$ , and the negative value indicates the product alignment along the  $y$ -axis, while the positive value indicates the product alignment along the  $x$ -axis. Moreover, the larger the absolute value is, the stronger is the degree of product alignment along the corresponding axis. In Figure 2, it can be seen that, with collision energy increasing, the degree of alignment along the  $y$ -axis becomes weaker at the high values of the scattering angle. When the collision energy is 0.1 eV, the value of  $(2\pi/\sigma)(d\sigma_{22+}/d\omega_r)$  is clearly positive at about  $20^\circ$  and nearly equal to zero at the other scattering angles, indicating the slight preference of product alignment along  $x$ -axis at  $20^\circ$  and almost no alignment at other scattering angles, respectively. However, when the collision energy is 2.0 eV or 4.0 eV, the product molecule shows no alignment at the wide range of scattering angles. The value of  $(2\pi/\sigma)(d\sigma_{21-}/d\omega_r)$  is related to  $\langle -\sin 2\theta_r \cos \phi_r \rangle$ , and it can be seen, for the three collision energies,  $(2\pi/\sigma)(d\sigma_{21-}/d\omega_r)$  are nearly zero indicating the product alignment is isotropic at the wide range of scattering angles.

In order to get a better graphical representation of the polarization of the product molecules of the title reaction, we

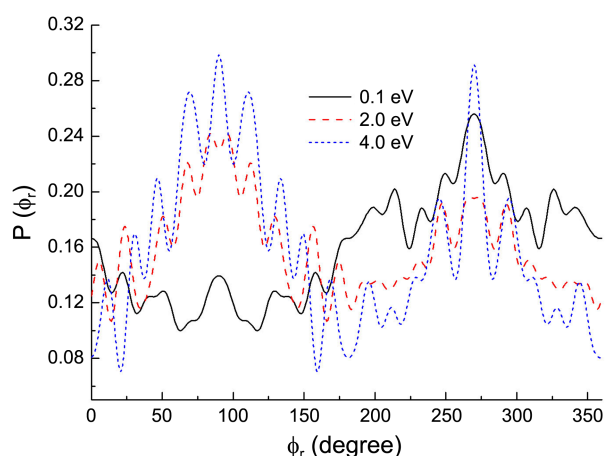


**Figure 2.** The four polarization dependent generalized differential cross-sections of the title reaction for the three different collision energies (a)  $E_c = 0.1$  eV (b)  $E_c = 2.0$  eV (c)  $E_c = 4.0$  eV.

have plotted  $P(\theta_r)$  and  $P(\phi_r)$  distributions in Figure 3 and Figure 4, respectively. The  $P(\theta_r)$  distribution describes the  $k-j'$  correlation, which is plotted in Figure 3. It clearly illustrates that  $P(\theta_r)$  for each collision energy has one peak at  $\theta_r = \pi/2$ . The  $P(\theta_r)$  distributions indicate that the product rotational alignment of the title reaction is strong, and the maximum value of the peaks appears at 2.0 eV, while the minimum value of the peaks appears at 0.1 eV. The  $P(\phi_r)$  distributions are shown in Figure 4. It describes  $k-k'-j'$  correlations. The  $P(\phi_r)$  tend to be very asymmetric with respect to the  $k-k'$  scattering plane (or about  $\phi_r = \pi$ ), directly reflecting the strong polarization of angular momentum for



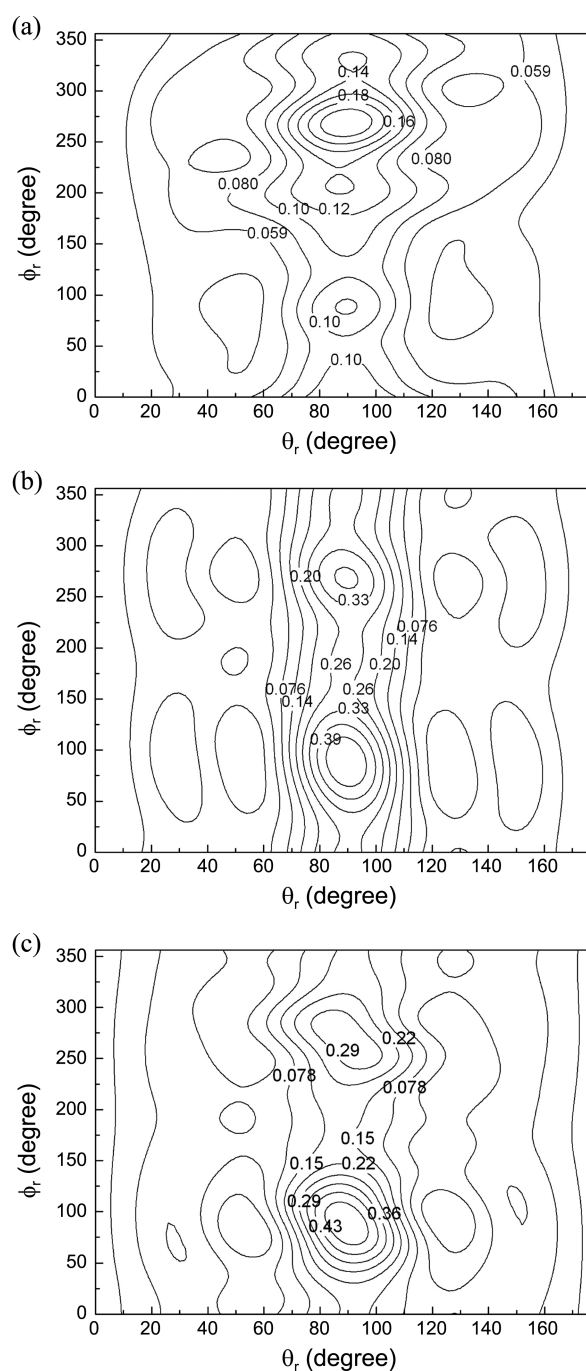
**Figure 3.** The distribution of  $P(\theta_r)$ , reflecting the  $k$ - $j'$  correlation at three collision energies.



**Figure 4.** The dihedral angle distribution of  $P(\phi_r)$  with respect to the  $k, k'$  plane at three collision energies.

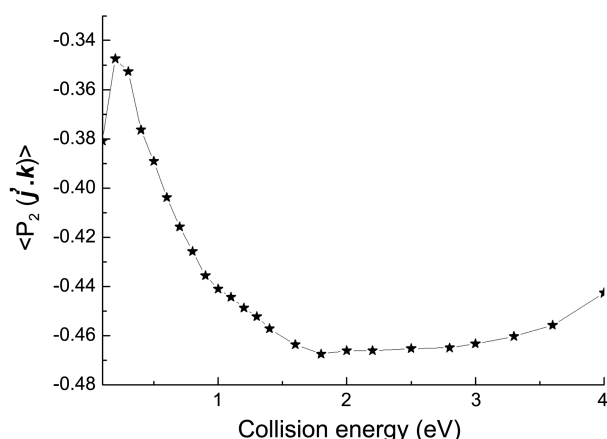
three different collision energies. As apparent from the figure, for 0.1 eV, the single peak appears at  $3\pi/2$ , and there is no obvious single peak of  $P(\phi_r)$  for 2.0 eV, while there are two peaks at  $\pi/2$  and  $3\pi/2$  for 4.0 eV, which indicates the trend of the product rotational angular momentum vector  $j'$  being oriented along the negative  $y$ -axis. However, for 2.0 and 4.0 eV, the average value of  $P(\phi_r)$  appearing at the angle close to  $\pi/2$  is slightly larger than  $3\pi/2$ , so that  $j'$  is oriented along the positive  $y$ -axis, but the degree of orientation is small. The broad distribution of  $P(\phi_r)$  indicates that the reaction is mainly dominated by out-of-plane mechanism, in which the product molecule prefers rotating in a plane perpendicular to the scattering plane.

In Figure 5, we also plot the angular momentum polarization in the form of polar plots in  $\theta_r$  and  $\phi_r$  averaged over all scattering angles for three collision energies. The distributions of  $P(\theta_r, \phi_r)$  indicate that the products are strongly polarized perpendicular to the scattering plane and the products of title reaction are mainly rotating in planes parallel to the scattering plane, which are in good accordance with the distributions of  $P(\theta_r)$  and  $P(\phi_r)$  of the product molecules.



**Figure 5.** Polar plots of  $P(\theta_r, \phi_r)$  distribution at three different collision energies (a)  $E_c = 0.1$  eV (b)  $E_c = 2.0$  eV (c)  $E_c = 4.0$  eV over averaged over all scattering angles.

In the present paper, we also calculated the average rotational alignment factor  $a_0^{(2)}$ , i.e.  $\langle P_2(j' \cdot k) \rangle$ . The dependence of the product rotational alignment on various collision energies is shown in Figure 6. It can be seen from the figure that the values of  $\langle P_2(j' \cdot k) \rangle$  decrease rapidly when the collision energies are below 1.9 eV and slightly increase above 2.8 eV. It indicates that the productional alignment becomes strong quickly to some extent and then weakens gradually.



**Figure 6.** The product rotational alignment  $P_2(j' \cdot k)$  for H+HLi  $\rightarrow$  H<sub>2</sub>+Li as a function of collision energy.

### Conclusions

The QCT calculations for the dynamics of the reaction H+HLi  $\rightarrow$  H<sub>2</sub>+Li at different collision energies based on the PMM PES have been performed. The reaction probability indicates a decrease at high collision energy (about 0.3 eV). The calculated PDDCSs indicate that the products are mainly forward scattering, and with the increasing collision energy, the tendency of forward scattering decreases to some extent. The values of  $\langle P_2(j' \cdot k) \rangle$  vary from decreasing to increasing when the collision energy increases. From the results, the product alignment and orientation are greatly influenced by collision energy. The overall variation of the stereodynamics corresponds well to the behavior of the barrierless reaction of LiH+H.

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