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Product angular and rovibrational state distributions of the Li + HF(v=0, j=0) → LiF(v′, j′) + H reaction

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Abstract. A state-to-state dynamics analysis of the title reaction has been investigated via the quasiclassical trajecory method. Results of the product state resolved differential cross sections, polarization parameters, as well as rovibrational state distributions were revealed and discussed, most of which agree well with the recent quantum mechanics study by Roncero and co-workers. It was found that more than 82.28% of reactive trajectories undergo the direct reaction mechanism. The title reaction occurs predominantly in the head-end collision.

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Key words: reaction mechanism, quasiclassical trajectory, differential cross section, polarization, product state distribution.

1 Introduction

As one of the simplest collision systems involving three different atoms, the Li + HF → LiF + H reaction has become a benchmark for the study of molecular reaction dynamics [1-35]. Experimentally, Becker *et al.* [1] have measured the laboratory angular distribution and time-of-flight spectra of LiF products in the reaction Li + HF → LiF + H at several collision energies by employing the crossed molecular beam (CMB) method. The analysis of their results in the center-of-mass (CM) frame demonstrates that the differential cross section (DCS) is nearly a forward-backward symmetry at the collision energy (E_c) of 130 meV, while a strongly forward peaked distribution at E_c=377 meV. Their observations on different DCSs were interpreted as a change in reaction mechanisms from the formation of a long lived complex at the low collision energy of 130 meV to a direct process at the

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high collision energy of 377 meV [1]. Loesch and co-workers [2-6] have performed a lot of CMB experiments on influences of reagent alignment [2], translational energy [3-4], vibrational [2, 5] and rotational excitations [6] on the Li + HF $\rightarrow$ LiF + H reaction. In their studies, the alignment of the reagent HF internuclear axis was achieved by changing the direction of the guiding field. The product angular distributions, the partition of available energy and integral reaction cross sections (ICSs) showed a marked difference for three different alignments of the HF internuclear axis (namely an isotropic distribution, two others with the molecular axis preferentially aligned along and perpendicular to the relative velocity vector of reagents). Recently, Bobbenkamp *et al.* [4] have implemented the effect of the excitation function (collision energy) on the ICS for the Li + HF $\rightarrow$ LiF + H reaction using a new CMB apparatus. A monotonous rise of the excitation function was found with the increase of energies ranging from 25 to 131 meV. This predicates that a possible translational energy threshold to the title reaction is significantly smaller than 25 meV, which supports the recent quantum mechanics (QM) study by Zanchet *et al.* [7] who have found a threshold of 10 meV.

Theoretically, a series of semi-empirical and *ab initio* potential energy surfaces (PESs) [8-14] have been constructed for the LiFH system. In 1980, Chen and Schaefer [8] have carried out the first *ab initio* PES calculation for this system by using the self-consistent field (SCF) and configuration interaction. The height of the barrier at the transition state (R_{LiF}=1.699Å, R_{HF}=1.291Å, θ_{LiFH}= 74°) was found to be 0.434 eV, which is too large for a realistic description of the reaction. Since then, a lot of *ab initio* calculations were dedicated to reduce the height of this reaction barrier. Carter and Murrell [9] reduced the barrier down to 0.17 eV. Laganà and co-workers [10] obtained the barrier of 0.182 eV at the bent transition state located in the exit channel. Aguado *et al.* [11-14] carried out multireference single and double excitation configuration interaction calculations of the LiFH PES. The number of 2323 *ab initio* points was computed and used to fit the PES. This PES shows a saddle point energy of 0.233 eV (from the minimum of the asymptotic entrance potential) located in the exit channel (R_{LiF}=1.692Å, R_{HF}=1.301Å, θ_{LiFH}= 71.4°). Availability of these reliable PESs has promoted numerous QCT [5-6, 15-20], time-independent quantum dynamics [21-26], and time-dependent wave packet [24-35] calculations to explore reaction dynamics of the Li + HF reaction. Most of these studies have verified that the title reaction contains rich and complex dynamics, and therefore further studies on reaction mechanisms are needed to carry out to elucidate dynamics of the Li + HF reaction.

At the present work, we carried out the state-to-state dynamics study on the Li + HF(v=0, j=0) $\rightarrow$ LiF(v', j') + H reaction at E_c = 97 meV by employing the QCT method. The product state resoled DCSs, first real polarization parameters, product rovibrational state distributions, and variations of internuclear distances and angles along the propagation time were calculated and presented. According to the direct interaction with product repulsion (DIPR) mode [36], we proposed a possible reaction mechanism which has rationally interpreted most of our calculated results.