

REGULAR ARTICLE

Quasi-Classical Trajectory Study of the Effects of Reactant Ro-Vibrational Excitation on the $\text{H} + \text{LiH}^+ \rightarrow \text{Li}^+ + \text{H}_2$ Reaction

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Abstract: Theoretical studies of the dynamics of the $\text{H} + \text{LiH}^+ \rightarrow \text{Li}^+ + \text{H}_2$ reaction have been performed using quasiclassical trajectory (QCT) method via a three-dimensional potential energy surface (PES) structured by Martinazzo et al. [J. Chem. Phys., 119 (2003), 11241]. The differential cross section (DCS) and reaction probability branching ratio between dissociation channel and the title channel are strongly affected by the vibrational excitation and translational energy. There is a Vander Waals well about 0.286eV in the product valley of the PES, which is too shallow to form a long-lived complex in the transition state, and the lifetime of the LiH_2^+ complex becomes shorter with collision energy increasing. The calculation of stereodynamics indicates that rotational angular momentum (j') polarization of the product molecule is sensitive to both rotational and vibrational excitations at the collision energy 0.03eV. With the increasing vibrational energy of reactant, the j' polarization increases and the molecular rotation of the products prefers an in-plane reaction mechanism rather than the out-of-plane mechanism. However, the opposite conclusion has been drawn for rotation excitation.

AMS subject classifications: 68U05, 74F25, 81v55

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1 Introduction

Recently, the title reaction has attracted a lot of attentions because of the importance of LiH molecule and related reactions in the early universe [1-6]. According to the standard Big Bang model, the primordial universe is full of radiation at a quite high temperature. During this time, the universe is opaque [7], and a majority of moleculars are ionized including the LiH⁺ ion [8-9]. Generally, the LiH molecule and its ionic variant are thought to be a coolant because they can absorb thermal energy by internal ro-vibrational excitations and release it through emission of photons [10]. When the temperature of the galaxy is reduced, the universe gets transparent. The time is called recombination epoch, during which the lithium chemistry has played a vital role [11]. That is why people focus on the LiH molecule and its ionic related reaction.

In order to get an accurate three-dimensional potential energy surface (PES) of LiH₂⁺ system, Bodo and co-workers have made a significant progress in past decade [10, 12-17]. Ro-vibrational levels of the ground electronic state LiH₂⁺ have also been studied [18-20]. Haxton et al have reviewed the indirect dissociative recombination of LiH₂⁺, they showed that LiH⁺ complex is weakly bounded with dissociation energy of 0.112 eV, therefore this ion is easily broken up [21]. Much work has been done in LiH molecule related reaction recently [22-24], and this work has been performed on accurate three-dimensional potential energy surfaces which allowed reactions within the two lowest-lying electronic states of the LiH₂⁺ system [17]. The ground-state H+LiH⁺→Li⁺+H₂ reaction is a barrierless, exoergic process. The exoergicity of the title reaction is 4.365(4.609) eV with (without) the zero-point energy corrections. For this reaction, the first quantum mechanical (QM) calculations were implemented for the collinear geometries by Bodo and coworkers [25]. They argued that a direct reactive dynamics should be expected. Afterwards, Pino and coworkers studied the thermal rate constants and integral cross sections of different ro-vibrational states for three channels by QCT method [26]. They found that this reaction was well described by the classical capture model, and the break-up channel at energies of a few tenths of eV should be considered. The influence of the low energy collision induced dissociation (CID) channel has been discussed by Roy and coworkers using a time-dependent wave packet approach [27].

As mentioned above, much effort has been made in the title reaction. However, most of the work is concerning the scalar properties, in order to get a whole dynamics of a reaction, the vector properties should also be taken into account. Stereodynamics of the title reaction had been carried out by our previous work [28]. We stressed that the reaction mainly behaves as an exoergic reaction rather than an insertion mechanism because of a shallow Vander Waals well about 0.286eV. We also calculated the changes of j' polarization with