REGULAR ARTICLE

The Dynamics of the Reaction of LiH (X¹Σ⁺) with H(²S) on a New Potential Energy Surface

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Abstract: The dynamics of the reaction H + LiH are studied with the aid of Quasi-classical trajectory (QCT) method, based on a new ground electronic state global potential energy surface(PES) of Yuan et al.[Phys. Chem. Chem. Phys. 2015, 17(17):11732-11739]. The influence of collision energy on the dynamic properties of the title reaction is discussed from 0.01eV to 0.8eV. The results show that the variation trend of the dynamics of the H + LiH reaction at low collision energy is markedly different from that of high collision energy. The rotational angular momentum j' of product H_2 is oriented along the positive y-axis all the time. The distributions of PDDCS are calculated and find that the polarized degree of the rotational angular momentum j' is stronger in the forward hemisphere.

1. Introduction

Considerable attention has been paid to the lithium chemistry because of its importance in the evolution of the primordial universe [1-4]. Particularly the LiH formation (via the process of radiative association) and LiH depletion (via the collision with hydrogen atom to form H_2), which leave the important imprint on the spectrum of the cosmic background radiation from early epochs, are frequently reported during the past decades [5-7]. For the LiH formation, the nascent

rotational population distribution of LiH (v=0) in the Li (2 ^2P_J) with H$_2$ reaction was studied by Chen et al. [8] using a pump-probe technique in 2000. The results suggested that the reaction be dominated by the insertion mechanism. Bililign et al. [9] observed the LiH formation in the Li*+H collisions for the atomic states from Li (^{2}s) to Li (^{3}d). Moreover, the LiH$_2$ system shows the complex features of the more complicated chemical species. Therefore, a series of studies have been carried out about this attractive system recently.

It is well known that the construction of the accurate PES for a reaction system is fundamental to investigate its dynamic properties. So great efforts have been made to construct the PES [10, 11, 18-21, 27, 30, 36] and investigate dynamical properties [10, 12-17, 22-36] for LiH$_2$ system in the last few decades. Clarke et al. [10] firstly calculated the collinear arrangement PES (CA PES) of the ground-state of LiH$_2$ system, and carried out classical trajectory calculations and time-dependent wave packet propagation studies. Their results showed that the LiH depletion reaction was exothermic with nearly 2.0 eV and existed a small barrier of 0.036 eV in the LiH + H entrance. Dunne et al. [11] constructed an ab initio global PES (DMJ PES) of the lowest state (^{2}A′) of LiH$_2$ system using the many body expansion method and the root mean square error (RMSE) of the fitting result was 0.09 eV. It should be noted that the barrier that existed in the LiH + H entrance channel on CA PES couldn't be found in DMJ PES. Based on DMJ PES, a series of quantum mechanical (QM) calculation had been carried out to investigate the dynamics of this reaction in detail [12-17]. Bodo et al. studied the interaction between LiH and H in low energy collision regimes with the Coupled Cluster method when the strength of the coupling between the impinging atom and the ro-vibrational states of LiH was taken into account [18]. Kim et al. [19] constructed an interpolations of accurate ab initio PES and did trajectory calculation to investigate dynamics properties of the LiH formation and depletion reaction. Berriche and Tlili [20] developed an ab initio PES of LiH$_2$ system, in which they observed the presence of a double well for the angles around 11º. Wernli et al. [21] developed a global three-dimensional PES (Wernli PES), which was fitted by large scale calculated energy data in the modified Aguado-Paniagua function and the RMSE was 0.022 eV. Based on the Wernli PES, Bovino et al. [22-26] calculated total reaction probabilities, rate coefficients, and channel reactivity of the reaction LiH + H → Li + H$_2$ using a time-independent quantum mechanical close-coupling (TIQM-CC) or Time Dependent Wave Packet(TDWP) method. Prudente et al. [27] developed an analytical PES (Prudente PES) and the RMSE was 0.064 eV. Besides, they calculated the reaction probabilities for both exothermic (Li + H$_2$) and thermal-neutral (H + LiH) reaction by using real wave packet (RWP) method. Based on the Prudente PES, Jiang et al. [28-34] investigated the dynamics of the reaction H + LiH using QCT or QM method. Hsiao et al. [35] constructed ab initio PES of the ground 1^{2}A′ and excited 2^{2}A′ states of LiH$_2$ system. Recently, Yuan et al. [36] employed neural network method to construct a new ground electronic state global PES (YHC PES) of LiH$_2$ system. The accuracy of fitting procedure of the YHC PES is fairly high with only 0.004eV. The spectroscopic constants of LiH (X$^1\Sigma^+$) and H$_2$ (X$^1\Sigma_g^+$) obtained from the YHC PES agreed very well with the experimental data.