Potential energy surfaces of LiH$_2$ for singlet and triplet states and quasiclassical trajectory study of LiH$^+$ + H and LiH + H$^+$

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Introduction

A gas formed of H, He, Li and some of their isotopes generated the first stellar objects according to the Big Bang model. The depletion and formation of LiH and LiH$^+$ are suggested as contributors to the cosmic background radiation. The reactions producing LiH and LiH$^+$, in their different electronic states, have been widely studied but only for the two first singlet states$^{1,2}$. In this study we have studied six reactions involving three singlet and three triplet electronic states of LiH$^+$.

Results

Potential Energy Surfaces

A total of 45,645 energy points per state were computed using the MOLPRO package of programs, using a correlation-consistent polarized quadruple-ζ basis set (cc-pVQZ-F12), and the i-MRCI-F12 method. The ab initio i-MRCI-F12 energy points for the six states are fitted using the GTFSEC procedure.

Quasiclassical trajectory (QCT) calculations

In absence of important quantum contributions to reactivity the QCT method is ideal to investigate the dynamics and kinematics of chemical reactions in gas phase and condensed media. In order to obtain converged results we have considered the following for each initial condition:

- \( r_0 \) (initial H-Li center of mass distance) = 30 Å
- Total energy conservation: 1 part in 10$^{13}$
- \( \Delta t \) (integration time step) = 0.1 10$^{-16}$ s
- \( E_{coll} = 0.01-1.0 \text{eV} \) \([0.1-1.0 \text{eV}]/a^3 \text{LiH}^+ \text{PES}\)
- Number of trajectories calculated for each \( E_{coll} = 0 \) to \( 10^{-16} \) = 10,000-20,000

The studied reactions (H or H$^+$ transfer) correspond with the inverse of the indicated at the introduction. Among these, exchange and collision induced dissociation reaction channels are studied.

H transfer (PEs $^1 \Sigma^G$ and $^1 \Delta^G$ or H$^+$ transfer (PEs $^1 \Sigma^G$) reaction channel

- The cross section decreases as collision energy \( E_{coll} \) increases what is expected due to the barrierless character of the PESs along the MEP.
- This channel (H transfer) is not possible on the PES $^1 \Delta^G$ as it leads to $^2 \Sigma^G^+$ that is a repulsive state of $^2 \Sigma^+$.

Exchange reaction channel

- The initial increase of \( \sigma_E \) with \( E_{coll} \) results from the existence of a threshold energy that corresponds with the H-Li-H exchange transition state that is present in all the PESs.
- For the PES $^1 \Delta^G$ the strong decrease of \( \sigma_E \) vs \( E_{coll} \) that occurs after the maximum correlates with the opening of the CID channel.

Collision induced dissociation (CID) reaction channel

- This channel is closed for the PES $^2 \Sigma^G^+$ for the collision energies considered. This state is the only with a reactant diatomic molecule of LiH($^2 \Sigma^+$) that has not a weak bond.
- For the other PESs there is a small threshold energy after which \( \sigma_E \) increases substantially with \( E_{coll} \) and reaches a plateau at the higher \( E_{coll} \) values.

Minimum Energy Paths

The corresponding Minimum Energy Paths (MEPs) are shown in Figure 4.a with all the energies relative to the LiH$^+$(NâH) + H(1s) + H(1s) asymptote (0.27993 a.u.). The two MEPs corresponding to $^1 \Lambda^G$ and $^1 \Delta^G$ are found to be very similar to that obtained previously$^1$.

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References