

# Potential energy surfaces of $\text{LiH}_2^+$ for singlet and triplet states and quasiclassical trajectory study of $\text{LiH}^+ + \text{H}$ and $\text{LiH} + \text{H}^+$

Javier Hernández<sup>1†</sup>, Cristina Sanz<sup>1</sup>, Pedro A. Enríquez<sup>2</sup>, Miguel González<sup>3</sup> and Miguel Paniagua<sup>1</sup>

<sup>1</sup>Dept. de Química Física Aplicada, Univ. Autónoma de Madrid, Spain

<sup>2</sup>Dept. de Química, Univ. de La Rioja, Spain

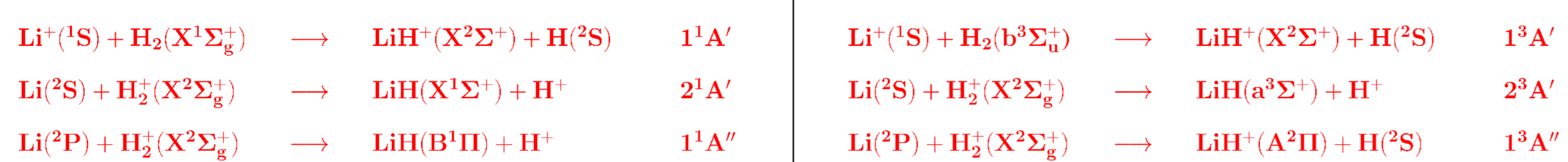
<sup>3</sup>Dept. de Ciència dels Materials i Química Física and IQTC, Univ. de Barcelona, Spain

† email: javier.hernandezr@estudiante.uam.es

## 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  $\text{LiH}^+$  are suggested as contributors to the cosmic background radiation.

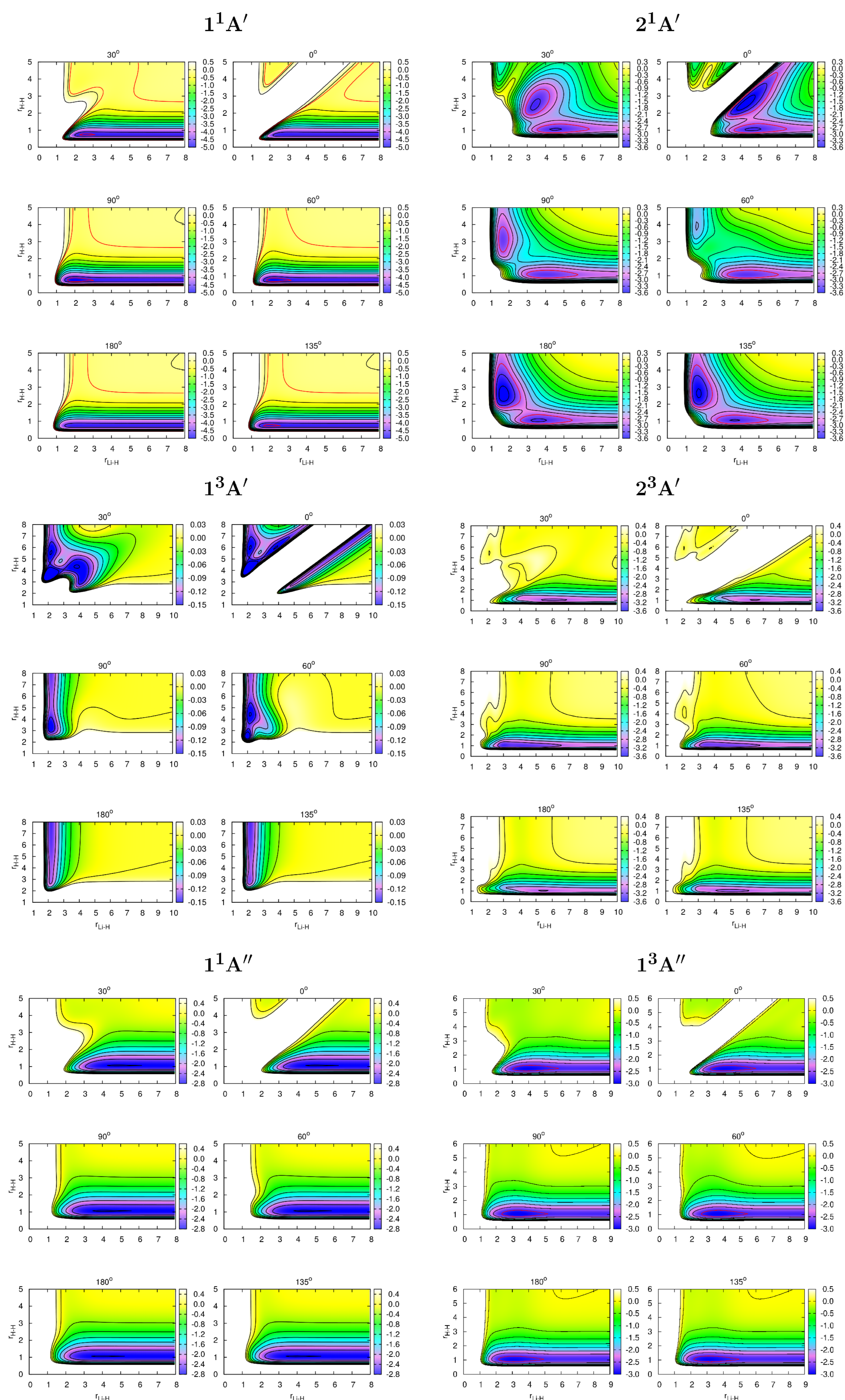
The reactions producing LiH and  $\text{LiH}^+$ , in their different electronic states, have been widely studied but only for the two first singlet states<sup>1,2</sup>. In this study we have studied six reactions involving three singlet and three triplet electronic states of  $\text{LiH}_2^+$ .



## Results

### Potential Energy Surfaces

A total of 45,645 energy points per state were computed using MOLPRO package of programs, using a correlation-consistent polarized quadruple- $\zeta$  basis set (cc-pVQZ-F12), and the ic-MRCI-F12 method. The *ab initio* ic-MRCI-F12 energy points for the six states are fitted using the GFIT3C procedure.



### Minimum Energy Paths

The corresponding Minimum Energy Paths (MEPs) are shown in Figure 4.a with all the energies relative to the  $\text{Li}^+(^1\text{S}) + \text{H}(^1\text{S}) + \text{H}(^1\text{S})$  asymptote (-8.27993 a.u.). The two MEPs corresponding to  $1^1\text{A}'$  and  $2^1\text{A}'$  are found to be very similar to that obtained previously<sup>2</sup>.

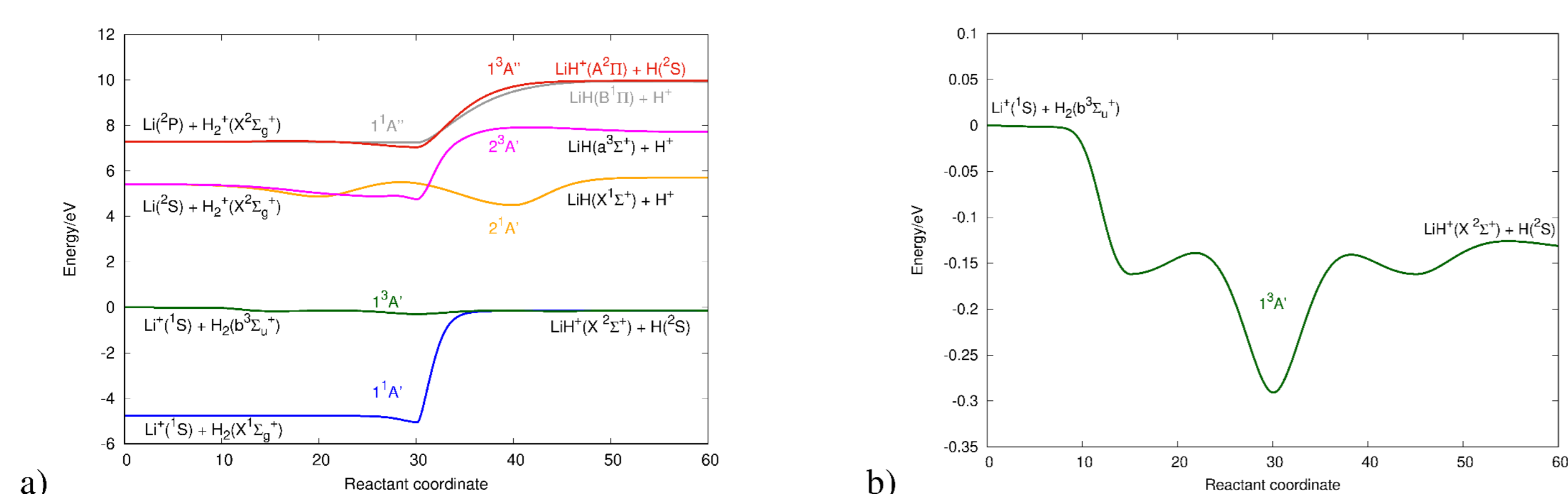


Figure 1: a) Minimum energy paths on the PES for the six states of  $\text{LiH}_2^+$ . b) In detail MEP of the  $1^3\text{A}'$  state.

## Quasiclassical trajectory (QCT) calculations

In absence of important quantum contributions to reactivity the QCT method is ideal to investigate the dynamics and kinetics of chemical reactions in gas phase and condensed media.

In order to obtain converged results we have considered the following for each initial condition:

- $\rho_0$  [initial H-(LiH center of mass) distance] =  $30\text{\AA}$
- Total energy conservation criterion: 1 part in  $10^5$
- $\Delta t$  [integration time step] = 0.1 10-16 s
- $E_{\text{col}} = 0.01-1.0$  eV [(0.1-1.0 eV) for  $1^3\text{A}''$  PES]
- Number of trajectories calculated for each ( $E_{\text{col}}, v=0, j=0$ ) = 10000-20000

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

### H transfer [PESs $1^1\text{A}'$ and $2^1\text{A}'$ ] or $\text{H}^+$ transfer [PES $1^3\text{A}''$ ] reaction channel

- The cross section decreases as collision energy ( $E_{\text{col}}$ ) 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  $1^3\text{A}'$  as it leads to  $\text{H}_2(\text{b}^3\Sigma_u^+)$  that is a repulsive state of  $\text{H}_2$ .

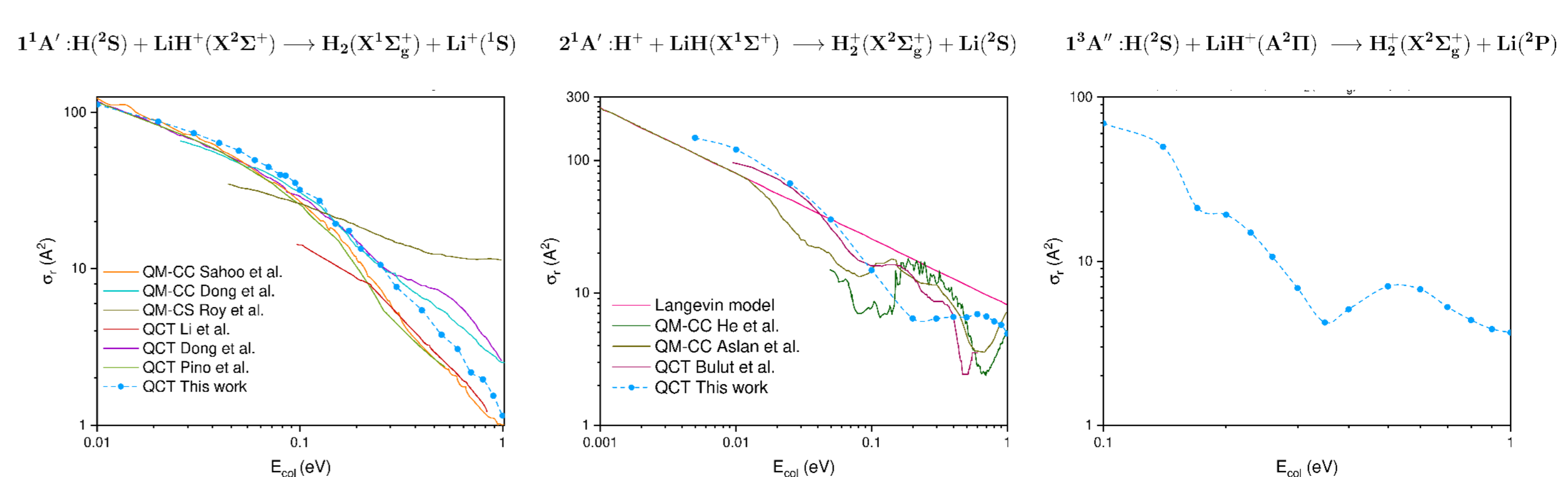


Figure 2: QCT cross-sections for the H transfer for each indicated reaction. Previous results from literature are included for comparison<sup>2-8</sup>.

### Exchange reaction channel

- The initial increase of  $\sigma_T$  with  $E_{\text{col}}$  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.

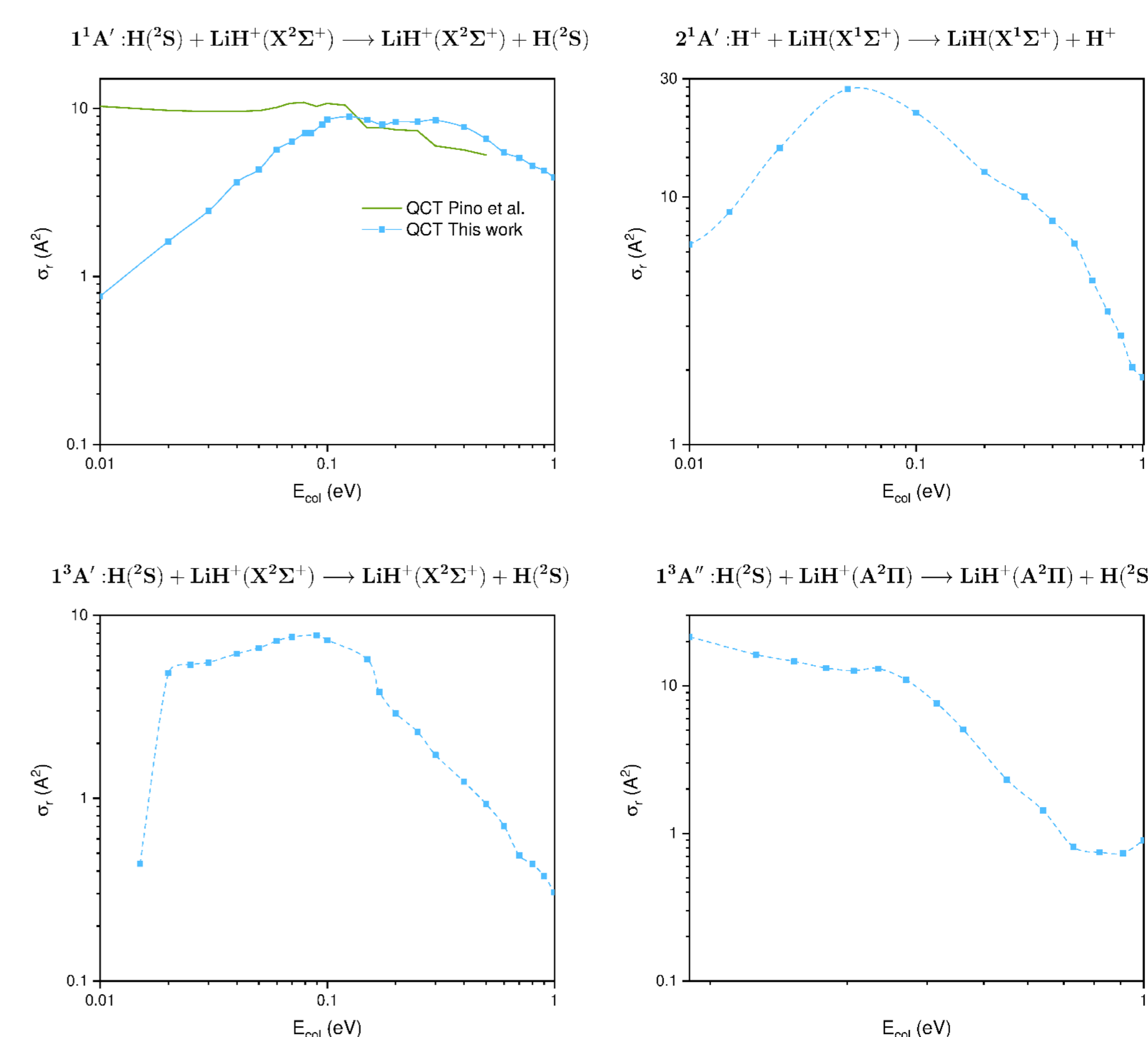


Figure 3: QCT cross-sections for the exchange reaction channel for each indicated reaction. Previous results from literature are included for comparison<sup>3</sup>.

### Collision induced dissociation (CID) reaction channel

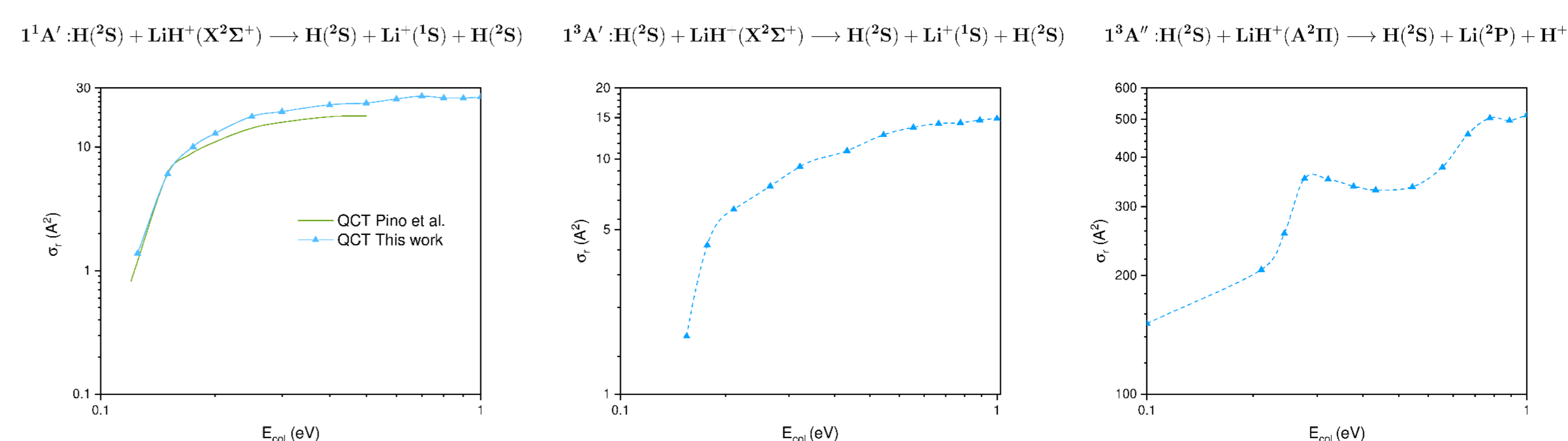


Figure 4: QCT cross-sections for the CID reaction channel for each indicated reaction. Previous results from literature are included for comparison<sup>3</sup>.

- This channel is closed for the PES  $2^1\text{A}'$  for the collision energies considered. This state is the only with a reactant diatomic molecule of  $\text{LiH}(\text{X}^1\Sigma^+)$  that has not a weak bond.

- For the other PESs there is a small threshold energy after which  $\sigma_T$  increases substantially with  $E_{\text{col}}$  and reaches a plateau at the higher  $E_{\text{col}}$  values.

## References

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