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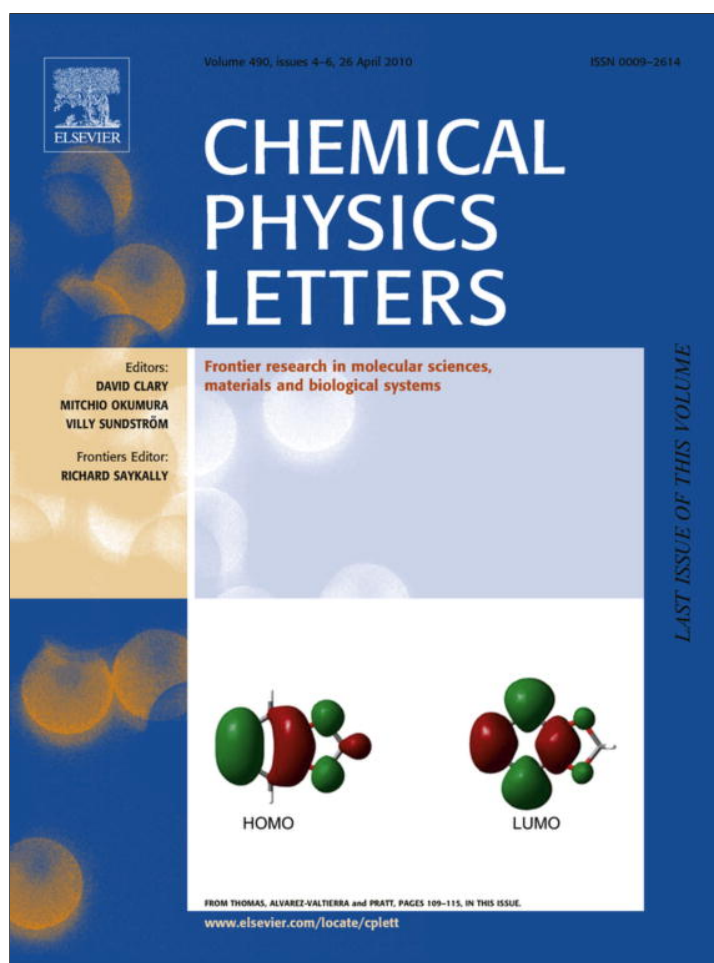


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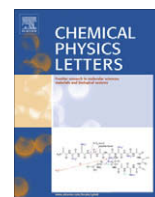
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ABSTRACT

We present a new accurate potential energy surface (PES) for the ground state $\text{H} + \text{Li}_2$ reaction from full configuration interaction and pseudo-potential calculations. The electronic energies were computed using an atomic orbital basis of 6-311G (2df, 2pd) quality. The results were fitted using a Bond Order polynomial expansion of eighth order. A topological study verified that the geometric configurations, energies, vibrational spectroscopic constants for the complex (HLi_2), reactant (Li_2), and the product (LiH) of the exothermic (about 34 kcal/mol) $\text{H} + \text{Li}_2$ fitted PES are in excellent agreement with the experimental data available in the literature. Furthermore, as a preliminary test, quasiclassical trajectories are integrated on the fitted surface to determine the reactive cross-section of the new PES.

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1. Introduction

Studies on mixed clusters, of metal plus another element, are an important way to investigate the chemisorption phenomena on metals. Addition of other atoms in the cluster can also modify its metallic properties. The Li_nH_m clusters (Li_2H being the one of them) are among the simplest mixed clusters from the electronic structure point of view. They can be used as a starting point to understand the chemistry of more complicated mixed clusters. Therefore, the reaction involving a hydrogen atom with the lithium molecule ($\text{H} + \text{Li}_2$) is of great interest to both theoreticians [1–3] and experimentalists [4–6].

Wu and Ihle [4], through mass spectroscopy measurements over dilute solutions of hydrogen in liquid lithium, proved the existence of the stable Li_2H molecule. From these measurements, they found a value of 89.7 ± 5.0 kcal/mol for the Li_2H atomization energy. From an adjusted potential energy surface Kim and Herschbach [7] obtained a binding energy value of about 87.9 kcal/mol. This value, according to Kim and Herschbach, is larger by approximately 3.0 kcal/mol than the published value of Wu and Ihle [4], which contained algebraic errors. The correction is comparable to the quoted experimental uncertainty of ± 3.0 kcal/mol.

Kim and Herschbach [7] obtained, from trajectory results, that the general rule of vibrational excitation of a reactant bond promoting reaction is some times contradicted. It happens when both the collision and internal excitation energies are low. From phase space calculations Shukla et al. [2] also found that vibrational excitation can cause vibrational inhibition. Siegbahn and Schaefer [8] calculated *ab initio* electronic energies to determine the HLi_2 po-

tential energy surface. They found Li_2 and LiH dissociation energies within 5 kcal/mol of experiment and that a minimum on the HLi_2 occurs for an isosceles triangle structure with $R_{\text{H-Li}} = 1.72$ Å and an LiHLi bond angle of 95° (or $\text{HLiLi} = 42.684^\circ$). This minimum lies 22.4 kcal/mol below the energy of the separated products $\text{Li} + \text{LiH}$. Furthermore, the linear HLiLi minimum is much shallower, lying only 4.2 kcal/mol below the products. These results are not in agreement with the available experimental data. This work presents a new $\text{H} + \text{Li}_2$ potential energy surface obtained from accurate *ab initio* electronic energies that are very close to experimental data. These energies were determined using full configuration interaction (CI) in combination with a norm-conserving pseudo-potential [9].

This article is organized as follows. In Section 2, we present the methods used to determine the *ab initio* energies and the fitting of $\text{H} + \text{Li}_2$ PES using polynomials in Bond Order coordinates. In this section, the topology of the $\text{H} + \text{Li}_2$ PES is also shown. A brief description of the quasiclassical trajectory (QCT) method and the $\text{H} + \text{Li}_2$ reactive cross-section calculations are shown in Section 3. Our conclusions are presented in Section 4.

2. The potential energy surface

The $\text{H} + \text{Li}_2$ *ab initio* electronic energies were determined using a pseudo-potential [9] to represent the lithium core and a full CI calculation on a 6-311G (2df, 2pd) basis set. All of the calculations were for the ground electronic states of the HLi_2 , Li_2 and LiH species. Preliminary results for Li_2 and LiH were reported in Refs. [10,11], where we showed that one could determine the PES containing atoms as small as Li using a pseudo-potential and still get spectroscopically accurate results. All the calculations reported here were carried out using the GAMESS package [12]. For the HLi_2

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system a regular grid of points, with a total of the 294 *ab initio* values, covering the relevant portion of the surface at θ , the angle formed by the LiH and LiH internuclear distances, equal to 30°, 60°, 90°, 120°, 150° and 180° was chosen (Supporting information available). To better characterize the collinear geometries 83 additional values considering θ equal to 0° (Supporting information available) were added. Furthermore, to well describe other important regions of the HLi₂ surface, another 17 geometries were considered, for a total of 394 nonequivalent *ab initio* energies.

To construct the Li₂ and LiH potential energy curves we considered 32 and 31 different internuclear configurations, respectively.

Analytical representations of the H + Li₂ system were obtained using a Bond Order (BO) polynomial expansion for both two- and three-body terms [13], following the standard many-body method [14]. Li₂ and LiH diatomic terms were determined by fitting a BO polynomial of the fourth order, while the three-body (computed by subtracting the diatomic potentials from the HLi₂ *ab initio* values) term was modeled using a BO polynomial expansion of the eighth order given by

$$V(R_{\text{LiH}}, R_{\text{LiH}}, R_{\text{Li}_2}) = \sum_{i=0}^6 \sum_{j=0}^6 \sum_{k=0}^6 C_{ijk} \eta_{\text{LiH}}^i \eta_{\text{LiH}}^j \eta_{\text{Li}_2}^k, \quad (1)$$

with $i + j + k \leq 8$ and at least two nonzero indices. The BO coordinates η_m are defined as $\eta_m = \exp[-\beta_m \rho_m]$, with $m = \text{LiH}$, LiH , and Li_2 . $\rho_m = R_m - R_{\text{eq}}(m)$ is the displacement from equilibrium distance (R_{eq}), β_m and C_{ijk} are adjustable parameters. Calculated coefficients and powers of the BO polynomial given by Eq. (1) are shown in the Supporting information available. These values were determined using the Powell method [15]. The parameters used for the BO variables were $R_{\text{eq}}(\text{Li}_2) = 2.6730 \text{ \AA}$, $R_{\text{eq}}(\text{LiH}) = 1.5955 \text{ \AA}$, $\beta_{\text{Li}_2} = 0.95975272 \text{ \AA}^{-1}$ and $\beta_{\text{LiH}} = 1.31779714 \text{ \AA}^{-1}$. The overall root-mean-square deviation value for the three-body term fitting was about 1.0 kcal/mol.

Table 1 shows the geometric configurations, energies, vibrational spectroscopic constants (ω_e , $\omega_e x_e$, and $\omega_e y_e$) for the (HLi₂) complex, the reactant (Li₂), and the product (LiH) of the H + Li₂ PES fitted in this work (theoretical and experimental data are shown in parenthesis). From this table, one can note that the diatomic internuclear distances, vibrational spectroscopic constants (ω_e , $\omega_e x_e$, and $\omega_e y_e$) and dissociation energies are in excellent agreement with the experimental data available in the literature. These features show that the Li₂ and LiH asymptotic channels are very well described in our new H + Li₂ PES.

When the minimum geometric configuration of our PES is considered, one can note that Li₂ and LiH internuclear distances are very close to the experimental data of Vezin et al. [5]. The differences found between our internuclear results and those obtained by Vezin et al. are 0.0135 Å and 0.0104 Å for Li₂ and LiH, respectively. The LiHLi bond angle (γ) found in our fitting was 94.65° (or 42.675° for HLiLi bond angle (θ)). This value is also in an excellent agreement with the value of 94.7° measured by Vezin et al. [5].

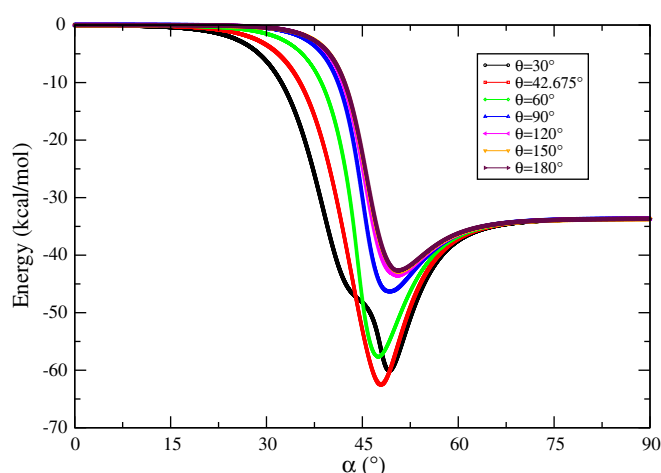


Fig. 1. Plots of an ensemble of minimum energy path calculated at different values of θ (see text for definition) for the H + Li₂ abstraction reaction given as a function of α (angle associated with the definition of the minimum energy path - see text for definition). The energy zero was set at the entrance channel asymptote (Li₂).

Theoretical (LiHLi) bond angle values calculated by Siegbahn and Schaefer ($\gamma = 95^\circ$) [8], Rao et al. ($\gamma = 95^\circ$) [16], Cardelino et al. ($\gamma = 94^\circ$) [17], Bonacić-Koutecký and Koutecký ($\gamma = 96^\circ$) [18], England et al. ($\gamma = 103^\circ$) [19], Allouche et al. ($\gamma = 94^\circ$) [20], Talbi and Saxon ($\gamma = 95.5^\circ$) [21], Yan et al. ($\gamma = 94.10^\circ$) [3] and Fang et al. ($\gamma = 94.42^\circ$) [22] agree (except the results obtained by England et al.) with the value reported in this work. However, our result is in better agreement with the reported experimental value. The depth of the potential minimum of our fitting is approximately 86.9 kcal/mol, relative to the H + Li + Li asymptote. This value is close to the value of 87.9 kcal/mol determined by Kim and Herschbach [7]. At last, we present in Table 1 the vibrational frequencies calculated using our adjusted PES. The values that we found are 341.6 cm⁻¹, 970.9 cm⁻¹ and 997.0 cm⁻¹. These frequencies are in qualitative agreement with the values (364.7 cm⁻¹, 1038.9 cm⁻¹ and 1037.6 cm⁻¹) found by Fang et al. [22] calculated at the UMP2/6-311G (p, spd) level.

Fig. 1 shows the minimum energy paths (MEPs), as a function of α , considering θ (the LiHLi angle) equal to 30°, 42.675° (minimum configuration), 60°, 90°, 120°, 150° and 180°. These MEPs were obtained by cutting the R_{Li_2} and R_{LiH} plane by straight lines centered on a high-in-energy turning point located on the ridge separating reactants and products channels. α describes the rotation of cutting line from 0 (the cutting line is parallel to R_{Li_2} – reactants), to 90° (the cutting line is parallel to R_{LiH} – products). In all these MEPs, the zero energy was set at the H + Li₂ entrance channel. From this topological study it was verified that this reaction is exothermic by about 34 kcal/mol. From these plots one can note that the H + Li₂ is essentially barrierless.

Table 1
Distances, potential energies, vibrational spectroscopic constants (ω_e , $\omega_e x_e$, and $\omega_e y_e$) for minimum configuration (HLi₂), reactant (Li₂), and product (LiH) of the H + Li₂ reaction. Experimental values are shown in parenthesis and other theoretical results are shown in square brackets.

Parameter	HLi ₂	Li ₂	LiH
$R_{\text{eq}}(\text{Li}_2)$ (Å)	2.5065 (2.5200) [5]	2.6730 (2.6730) [25]	
$R_{\text{eq}}(\text{LiH})$ (Å)	1.7046 (1.7150) [5]		1.5955 (1.5960) [25]
$\theta(\text{HLiLi})$	42.675° (42.708°) [5]		
Energy (kcal/mol)	86.9 (87.9 ± 3.0) [7]	24.438 (24.444) [26]	58.099 (58.112) [27]
ω_e (cm ⁻¹)	341.6 [364.7] [22] 970.9 [1038.9] [22] 997.0 [1037.6] [22]	351.48 (351.4) [25]	1405.7 (1405.6) [25]
$\omega_e x_e$ (cm ⁻¹)		2.652 (2.595) [25]	21.2 (23.2) [25]
$\omega_e y_e$ (cm ⁻¹)		0.0129 (0.0168) [26]	0.0245 (0.002) [27]

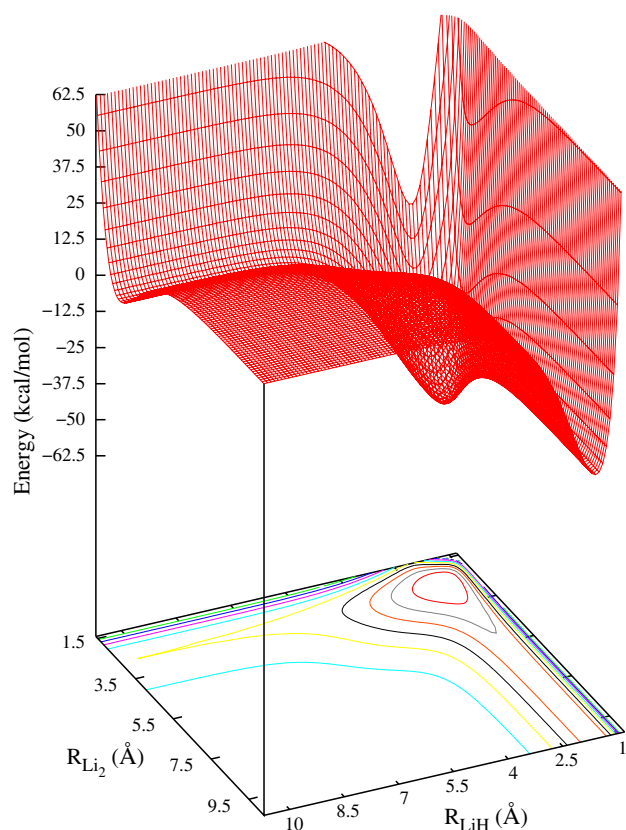


Fig. 2. Pseudo-three-dimensional plot of potential energy surface for H + Li₂ abstraction reaction calculated at $\theta = 42.675^\circ$ (minimum configuration). Isoenergetic contours are spaced by 12.5 kcal/mol. The energy zero was set at the entrance channel asymptote (Li₂).

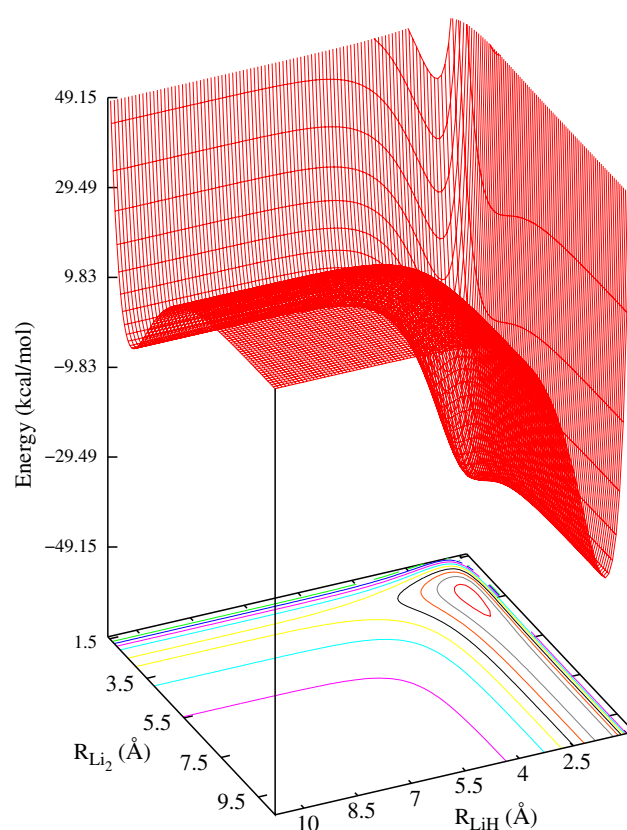


Fig. 3. Pseudo-three-dimensional plot of potential energy surface for H + Li₂ abstract reaction calculated at $\theta = 180.0^\circ$. Isoenergetic contours are spaced by 10.0 kcal/mol. The energy zero was set at the entrance channel asymptote (Li₂).

Pseudo-three-dimensional plots of potential energy surfaces for H + Li₂ abstraction reaction calculated at $\theta = 42.675^\circ$ (minimum configuration) and $\theta = 180.0^\circ$ (collinear configuration) are presented in Figs. 2 and 3, respectively. The energy zero was set at the entrance channel asymptote (Li₂) and isoenergetic contours are spaced by 12.5 kcal/mol at $\theta = 42.675^\circ$ and 10 kcal/mol at $\theta = 180.0^\circ$.

3. H + Li₂ reactive cross-sections

The H + Li₂ reactive cross-sections (RCS) were determined using the quasiclassical trajectory method [23]. In the present work, a modified version of BUNKER'S program [24] is used.

The H + Li₂ RCS were obtained integrating the trajectories considering the Li₂ reactant vibrational states $v = 0, 1, 2$ and 3, reactant rotational states $j = 0, 5$ and 10 and translational energy (E_{tr}) varying between 1.0 and 10.0 kcal/mol with a step of 1.0 kcal/mol.

For each pair of rovibrational and translational energy values, a batch of 50000 trajectory calculations was performed for initial and final atom–diatom distances of 14 Å (asymptotic region), and a time step of 5×10^{-17} s. This value was obtained checking the conservation of both mechanical energy and angular momentum. The maximum reactive impact parameter considered in this work was 8 Å. Tests with batches of one million trajectories were also performed and the obtained results are in a excellent agreement with those calculated with 50000 trajectories. Therefore, the final results are presented considering a batch of 50000 trajectories.

H + Li₂ RCS calculated at $j = 0$ (Li₂ reactant rotational state) and with v (Li₂ reactant vibrational state) equal to 0, 1, 2 and 3, are depicted in Fig. 4. The RCS is plotted as a function of reactant trans-

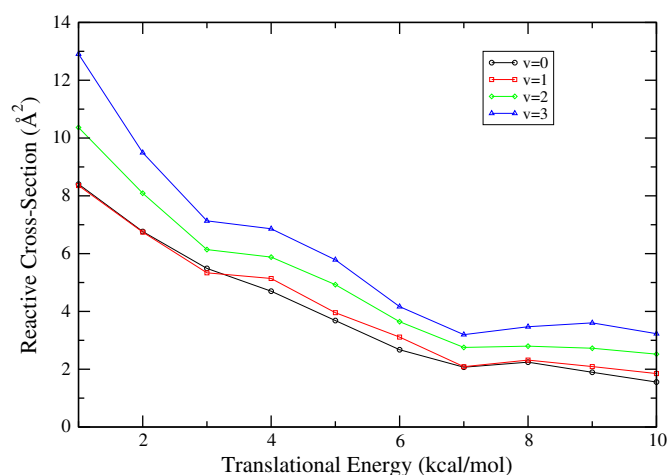


Fig. 4. H + Li₂ reactive cross-sections calculated at $j = 0$ (Li₂ rotational state) and with v (Li₂ vibrational state) equal to 0, 1, 2 and 3, plotted as a function of reactant translational energy.

lational energy (E_{tr}). From this Fig. 1 can note that the maximum RCS values varied from 8.36 ($v = 1$) to 12.91 Å² ($v = 3$) when the $E_{tr} = 1.0$ kcal/mol and $j = 0$ are considered. Furthermore, the RCS for $v = 0$ (8.40 Å²) is slightly larger than the RCS for $v = 1$ (8.36 Å²).

The maximum RCS values, at $j = 5$ and $E_{tr} = 1.0$ kcal/mol (Fig. 5), varied between 8.35 ($v = 1$) and 12.47 Å² ($v = 3$). When $j = 10$ and $E_{tr} = 1.0$ kcal/mol are considered (Fig. 6), the maximum RCS values are between 9.82 ($v = 1$) and 12.59 Å² ($v = 3$). These results show that the H + Li₂ exoergic reaction is not channeled into both Li₂

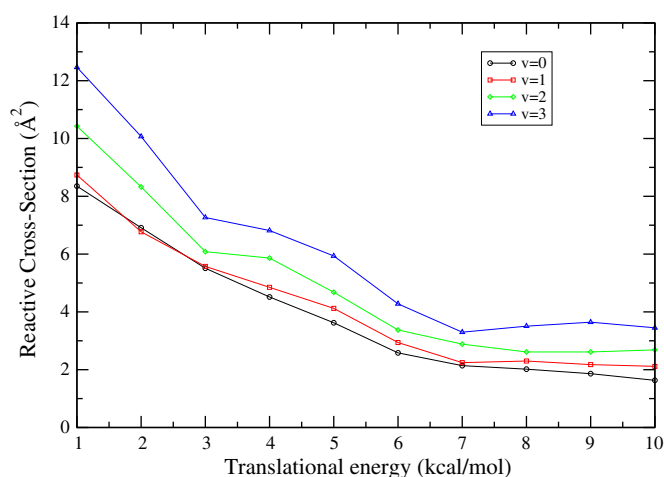


Fig. 5. H + Li₂ reactive cross-sections calculated at $j = 5$ (Li₂ rotational state) and with v (Li₂ vibrational state) equal to 0, 1, 2 and 3, plotted as a function of reactant translational energy.

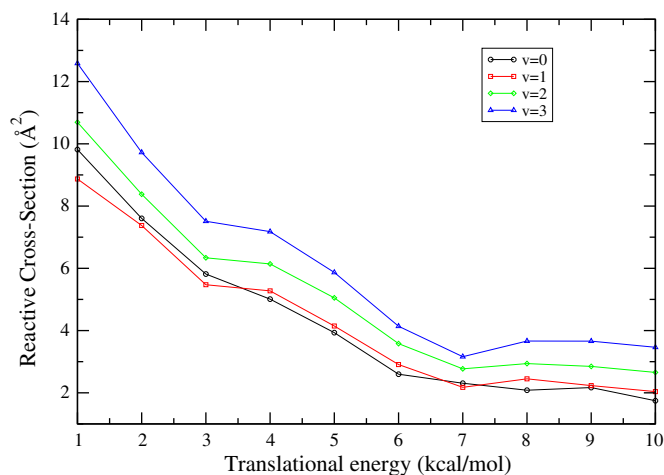


Fig. 6. H + Li₂ reactive cross-sections calculated at $j = 10$ (Li₂ rotational state) and with v (Li₂ vibrational state) equal to 0, 1, 2 and 3, plotted as a function of reactant translational energy.

vibration and rotation. This is consistent with the absence of a transition state in the present PES. These features are supported by experimental evidence [2,4,7].

4. Conclusions

This work presents a new potential energy surface for the H + Li₂ exoergic reaction. This new PES was built by fitting a polynomial Bond Order of eighth order to 394 calculated *ab initio* energies. All these energies were determined using a combination of a

norm-conserving pseudo-potential and full configuration interaction calculations with a 6-311G (2df, 2pd) basis set. Topological studies of the new PES showed that the geometry and energy of the global minimum configuration are very close to the available experimental data. Furthermore, it was found from QCT calculations that the reactant excited vibrational states do not substantially enhance cross-sections (absence of a threshold of reactivity). This fact is in accordance with the experimental data. In a future work, we will present dynamical studies of this new potential energy surface using exact quantum mechanical calculations.

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Appendix A. Supplementary material

CI in combination with a norm-conserving pseudo-potential energies values calculated with 6-311G (2df, 2pd) basis set and coefficients (in kcal/mol) and powers of the H + Li₂ potential energy surface. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2010.03.032.

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