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Potential-energy surfaces for the $\text{Li} + \text{HF}$ reaction. MRDCI study of the ground- and lower excited-states for doublet LiFH

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Abstract

Ab initio electronic energy calculations are reported for 570 nuclear configurations of LiFH in C_s symmetry (three dimensional potential energy surface). The lower five doublet spin-state eigenfunctions (three $^2A'$ and two $^2A''$) for LiFH have been determined using a multiple reference single and double excitations configuration-interaction (MRDCI) method and an extended triple-zeta-plus-polarization contracted Gaussian basis set. As the Li atom approaches the HF diatomic, it first forms a bent complex (106°) with 28 kJ/mol of stabilization energy before reaching the transition state. The latter, also bent (73°) was located in the exit channel and is predicted to be 24 kJ/mol above the reactants. We argue that laser catalysis of the $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$ reaction would be possible and irradiation in the $6000\text{--}9000\text{ cm}^{-1}$ range is predicted to enhance the reaction.

1. Introduction

A fundamental problem in chemical physics is to understand reaction kinetics in terms of the molecular dynamics induced by the electronic forces. Under the Born–Oppenheimer nonrelativistic approximation the motion of the nuclei is governed by potential energy surfaces (PES) for the manifold of electronic states that are involved. The simple atom exchange reaction, namely $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$, has received much attention from the very first successful crossed molecular beam experiment performed by Taylor and Datz [1] in 1955 on the reaction $\text{K} + \text{HBr} \rightarrow \text{KBr} + \text{H}$. However, a few studies have employed accurate ab initio potentials as a consequence of the significant computational effort in calculating an accurate PES (the potential depends on three coordinates, each of which

must vary over a wide range) that increases when several electronic states are involved. Moreover, it is a difficult task to find a global and faithful functional representation of the PES.

The LiFH system is a new benchmark in molecular reaction dynamics for both experimental and theoretical reasons [2]. From the experimental viewpoint the HF molecule can be completely state prepared with respect to the nuclear motion and the products ($\text{LiF} + \text{H}$) are easily detectable via surface ionization. Therefore, the elementary atom exchange reaction $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$ has been studied experimentally [3–5]. From the theoretical viewpoint LiFH is the lightest system corresponding to the $\text{M} + \text{HX} \rightarrow \text{MX} + \text{H}$ (M = alkali metal atom, X = halogen) reactions. Then, the LiFH system has been studied also theoretically (PES calculations [6–13], PES fits [14–17], classi-

cal trajectory studies [18–21] and most recently three dimensional quantum calculations [22–25]). In previous *ab initio* configuration-interaction (CI) calculations of the LiFH PES [10] the barrier to reaction (42 kJ/mol) was found to be too high to explain the large reactivity measured at low collision energy. Moreover, the authors of the previous CI calculations found a shallow well in the reactants channel (complex) with a depth of about 19 kJ/mol [10], while the more recent measured experimental well depth is about 29 kJ/mol (see the last paper in Ref. [5]).

For a realistic description of the intramolecular motion, several semiempirical adjustments to the *ab initio* energies [10] of this reaction have been proposed [14,15], the most important one being a Gaussian-type correction added in the transition state region with an amplitude adjusted to match computed and experimental reactive cross sections. However, in a very recent investigation [12] for the ground- and lowest excited-state of the ${}^2A'$ LiFH collinear system we pointed out that the subtraction of a Gaussian function with an amplitude of 13 kJ/mol [14] (or about 21 kJ/mol [20]) centered at the LiFH transition state it produces a higher preference for the bent collisions than that corresponding to the true computed one. In fact, in our preliminary LiFH investigation [12], we conclude that the Gaussian function must be maximum for the collinear approach where we found a difference of about 22 kJ/mol with respect to previous results [10], while for the bent transition state the difference is about 18 kJ/mol [12].

Moreover, we found [12] that the barrier located on the reaction surface is due to an avoided crossing between the ionic ($\text{Li}^+ + \text{HF}^-$) and covalent ($\text{Li} + \text{HF}$) structures, as suggested previously by Balint-Kurti and Yardley [7] and Chen and Schaefer III [10]. In our previous work [12] we found the presence of a minimum in the first excited adiabatic state ($2^2A'$) located very close to the avoided crossing, near to the collinear saddle point, at about 100 kJ/mol higher than the ground state ($1^2A'$) that would be of very important dynamical implications. Excited states have been a topic of great theoretical interest in laser catalysis [26–30]. Moreover, the implication of excitation to a bound molecular state whose role is to “shuttle” the reactants to the products’ side has not been considered in detail [29].

In this paper we present an accurate *ab initio*

multiple reference single and double excitations configuration-interaction (MRDCI) [31] study of three ${}^2A'$ and two ${}^2A''$ electronic states of LiFH. We report here the results of an extensive *ab initio* calculation of a full-dimensional grid (in C_s symmetry) for the LiFH system.

2. Computational details

In the choice of an efficient coordinate system, in the sense of providing the most useful surface information, becomes an important consideration that the greatest amount of information is needed in regions of rapid energy change such as occur near minima, inflections and avoided crossings on PESs. Following this consideration we adopt a coordinate system consisting of two bond distances R_{LiF} and R_{HF} and one bond angle θ (the interior angle between the two bond distances, $\theta(\text{LiFH}) = 180^\circ$ being the collinear approach). The choice of bond distances allows a selection of grid points derived from diatomic energy curves. The choice of a bond angle presumes that the angular dependence of the potential energy would be less pronounced than the dependence on the internuclear distance, thus requiring fewer grid points to determine the PES behavior.

The basic grid of geometries at which the *ab initio* calculations were done was selected with respect to the SCF diatomic equilibrium distances (in atomic units):

$$R_{\text{HF}} = 1.70 + 0.5i \quad (i = -1, 0, 1, 2, 3, 4, 5), \quad (1)$$

$$R_{\text{LiF}} = 2.96 + 0.5j \quad (j = -1, 0, 1, 2, 3, 4, 5), \quad (2)$$

and $\theta = 180^\circ, 135^\circ, 90^\circ, 74^\circ, 45^\circ$. We also investigate the two different collinear sections corresponding to $\theta = 0^\circ$. One of these sections corresponds to the approach of the Li atom from the H end of the HF molecule giving the reaction: $\text{Li} + \text{HF} \rightarrow \text{HLi} + \text{F}$. For this collinear reaction the distance R_{HF} was varied using the values given by Eq. (1) and the distance R_{HLi} was varied independently using the following values:

$$R_{\text{HLi}} = 3.00 + 0.5k \quad (k = -2, -1, 0, 1, 2, 3, 4). \quad (3)$$

The other section for $\theta = 0^\circ$ corresponds to the Li atom located between the H and F atoms; the corresponding collinear reaction being: $\text{HLi} + \text{F} \rightarrow \text{H} + \text{LiF}$. Here, the distance R_{LiF} was varied using the values given by

Eq. (2) and the distance R_{HLi} was varied using the values given by Eq. (3).

This grid was chosen to provide more detailed information in the regions of the minima of neutral diatomics HF, LiF and HLi. However, there is no assurance that the minima remain localized when a third atom is brought near the diatomic. This is particularly true for excited states with the additional complication that avoided crossings may not be adequately covered by the grid. Therefore, we consider this grid (343 points) as preliminary because interesting regions on the surface may not be anticipated and require closer investigation. Then, we decide to add more points mainly at the crossing regions and in the minimum energy paths for all the θ values and also in the saddle regions and exit channels for new $\theta = 60^\circ, 70^\circ, 80^\circ$ values, to get a better characterization of the true transition state and to investigate the presence of a further barrier, located later in the exit channel [25]. The total number of grid points was 570 that are available from the authors by electronic mail [32]. We must stress that previous ab initio (configuration interaction with only one reference configuration) calculations [10] included only the ground state at 214 grid points.

We adopt as basis set the extended basis set described in a previous study [11] of the basis set size plus correlation effects on the LiFH PES, using density functional methods. The corresponding calculated values of the equilibrium frequencies and distances, the reaction endoergicity, and the nonrelativistic total energies, for the HF, HLi and LiF diatomics, and their comparison with the experimental data, have been reported in a previous paper [13].

However, if we try to obtain a “chemical accuracy” PES (about 4–8 kJ/mol or 0.002 a.u. of differences error, about 0.002% of the total LiFH energy) with the basis set adopted here, and also with more extended basis sets, we must consider that we have absolute errors in the total energies about 0.2 a.u. (or 525 kJ/mol). This absolute error has been estimated by performing the difference between the total MRDCI energy for the LiF diatomic and its “experimental” non-relativistic energy (these two values are in Table I in Ref. [13]), here, we assume that the correlation energy error for the H atom is zero (this assumption is true only for the products asymptote). However, we are not interested in total energies but in energy differences, which are usually small quantities. In forming

Table 1
Reference configurations for MRDCI calculations

$2A'$					
...	$(4a')^2$	$(1a'')^2$	$(5a')^2$	$(6a')^1$	
...	$(4a')^1$	$(1a'')^2$	$(5a')^2$	$(6a')^2$	
...	$(4a')^2$	$(1a'')^2$	$(5a')^2$	$(7a')^1$	
...	$(4a')^2$	$(1a'')^2$	$(5a')^2$	$(8a')^1$	
...	$(4a')^2$	$(1a'')^2$	$(5a')^2$	$(11a')^1$	
...	$(4a')^1$	$(1a'')^2$	$(5a')^2$	$(6a')^1$	$(7a')^1$
...	$(4a')^2$	$(1a'')^2$	$(5a')^1$	$(6a')^1$	$(13a')^1$
...	$(4a')^2$	$(1a'')^2$	$(5a')^1$	$(6a')^1$	$(7a')^1$
...	$(4a')^2$	$(1a'')^2$	$(5a')^1$	$(6a')^1$	$(14a')^1$
...	$(4a')^2$	$(1a'')^1$	$(5a')^2$	$(6a')^1$	$(4a'')^1$
$2A''$					
...	$(4a')^2$	$(1a'')^1$	$(5a')^2$	$(6a')^2$	
...	$(4a')^2$	$(1a'')^1$	$(5a')^2$	$(7a')^2$	
...	$(4a')^2$	$(1a'')^2$	$(5a')^2$	$(2a'')^1$	
...	$(4a')^2$	$(1a'')^2$	$(6a')^2$	$(2a'')^1$	
...	$(4a')^2$	$(1a'')^2$	$(5a')^2$	$(3a'')^1$	
...	$(4a')^2$	$(1a'')^2$	$(5a')^2$	$(4a'')^1$	
...	$(4a')^2$	$(1a'')^1$	$(5a')^2$	$(6a')^1$	$(7a')^1$
...	$(4a')^2$	$(1a'')^1$	$(5a')^2$	$(6a')^1$	$(9a')^1$
...	$(4a')^1$	$(1a'')^1$	$(5a')^2$	$(6a')^2$	$(7a')^1$
...	$(4a')^1$	$(1a'')^2$	$(5a')^2$	$(6a')^1$	$(2a'')^1$

the difference between two large quantities of similar size, the absolute accuracy of each term will be of essential importance. We must consider that errors at each term of the difference are similar and will cancel to a large extent, with a final result that may be good. In our calculations we estimate that the differences error, relative to a zero energy (reactants Li + HF in its ground state), in our final energies is about 5 to 9 kJ/mol for the ground state surface [12]. For the lower excited-state surfaces this error is about 18 kJ/mol [12] if we consider the errors in the ionization potential of atomic lithium and the electron affinity of atomic fluorine.

All calculations were carried out using the same procedure outlined in our previous study for the collinear section of the Li + HF reaction [12]. The electronic energy was calculated using the MRDCI method of Buenker and co-workers [31]. In Table 1 we present the reference configurations used to construct the CI space of A' symmetry for all the geometries. All the electrons (13) of LiFH are then distributed among the remaining MOs through single and double excitations relative to the reference con-

figurations. These have been chosen so as to give a final contribution of more than 90% to the CI wavefunctions for the three lowest roots of A' symmetry. The CI space of A'' symmetry was constructed using also 10 reference configurations (see Table 1). The reference configurations have been chosen to give a final contribution of more than 90% to the CI wavefunctions for the two lowest roots of A'' symmetry. The configuration generation process was similar to that for the corresponding A' roots and resulted in 601 776 configuration symmetry-adapted functions. Then, for both A' and A'' symmetries 7 000 to 18 000 configurations were selected for the final CI calculation by employing an energy selection criterion with a threshold of 5 μ hartree with respect to the selected roots. We obtain the full CI extrapolated energy as in our previous collinear study [12].

Since a MRDCI with a careful selected set of reference configurations and a low threshold was chosen for the calculations, it may be assumed that there is minimal loss of accuracy due to truncation of the CI expansion. Nevertheless, we have made test calculations including up to 20 reference configurations with a selection threshold of 2 μ hartree resulting in energy differences of only 1 to 2 kJ/mol.

3. Results and discussion

To obtain a graphical representation of the $2A'$ and $2A''$ LiFH PESs we report fixed θ contour maps of the calculated adiabatic energies. Isoenergetic contours of these two-dimensional cuts of the PES were obtained by means of a cubic spline interpolation. Figs. 1–7 are maps of horizontal cuts at $\theta = 180^\circ$, 135° , 90° , 74° , 45° and the two different collinear sections mentioned above for $\theta = 0^\circ$. In all of these figures the left-hand side top panel corresponds to the ground-state ($1^2A'$), while the first excited-state ($2^2A'$) is plotted at the right-hand side top panel. We must stress that these two adiabatic states correspond to an avoided crossing between the two lowest diabatic states, where the crossing region is close to the ground-state saddle [12]. The $3^2A'$ and $1^2A''$ excited-states (see the left- and right-hand middle panels in Figs. 1–7) are the two components of the $1^2\Pi$ state for the linear geometries (Figs. 1, 6, 7). These two states differ slightly for geometries apart from linearity. Finally, the left-

hand side bottom panel in Figs. 1–7 corresponds to the $2^2A''$ excited-state, that has a very high energy with respect to all the calculated states and it is probably contaminated by energy crossings corresponding to higher excited-states.

An examination of these contour maps and further calculations (see Section 2) around critical features reveal that the ground-state minimum energy path begins with the Li atom being attracted towards the fluoride end of HF (the zero energy at the reactants channel, see the left-hand side top panels, Figs. 1–7). When the incoming particle approaches to intermediate distances, the path has begun its descent to smaller θ passing through a well (28 kJ/mol below the reactants, $\theta = 106^\circ$, this value is in excellent agreement with the experimental one [5]). The HF diatomic is forced to move adiabatically through the crossing in the direction of increasing R_{HF} until the collision, by mixing the two electronic states, makes the energy difference between them sufficiently small for the transition from covalent to ionic surface to take place, near the true transition barrier clearly located in the exit channel of the reaction (24 kJ/mol above the reactants, $\theta = 73^\circ$, this value makes possible the large reactivity measured at low collision energy [3]), after which the system, if the collision energy is enough, passes over the barrier into the products channel. This barrier increases smoothly toward larger angles and rises rapidly toward smaller angles of approach.

The path goes to smaller θ and begins to turn as the HF distance stretches and the LiF distance ceases to contract. A further well in the product channel has been detected (5 kJ/mol above the reactants, $\theta = 70^\circ$), but as the difference with respect to the separated products is only of the order of 5 kJ/mol (within the calculations uncertainty), it hardly seemed justified to talk of a $\text{LiF} \cdots \text{H}$ complex as had been noted by Chen and Schaefer III [10].

However, we have not been able to detect an additional barrier also in the product channel, in a clear discrepancy with that obtained in a very recent fit of Parker et al. [25] to “scaled” ab initio energies [10]. An explanation of this behaviour may be that the scaling procedure (the subtraction of a gaussian function centered at the transition state) has a non-negligible effect only in the vicinity of the true transition state, producing a new barrier in the product channel (as high as the true barrier [25]) and a higher preference

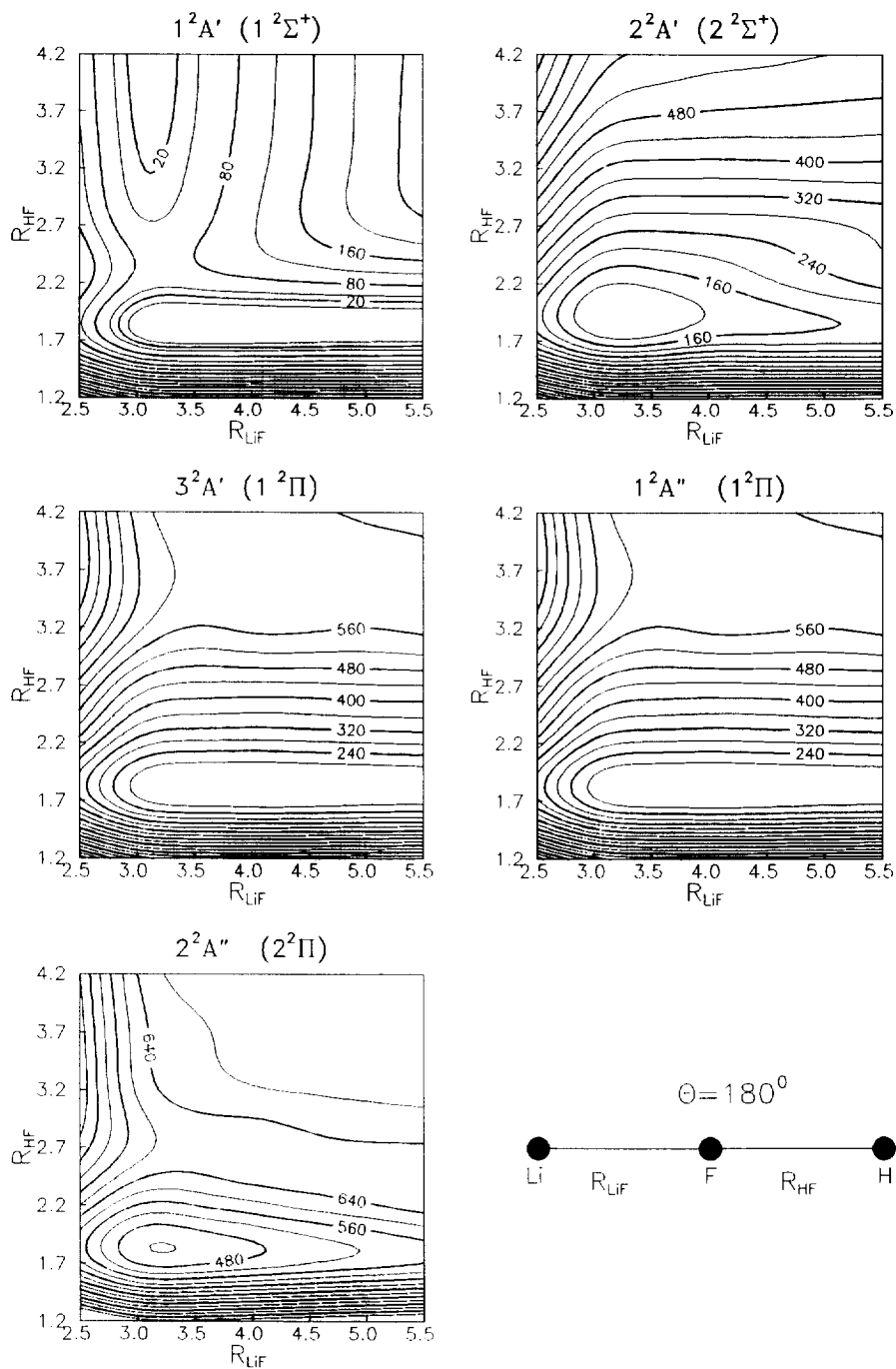


Fig. 1. Potential contours for $\theta = 180^\circ$ (the collinear section) as indicated by arrangement of nuclei at the right-hand bottom. Contour labels are in kJ/mol with respect to the selected zero energy (reactants), all the distances are in atomic units.

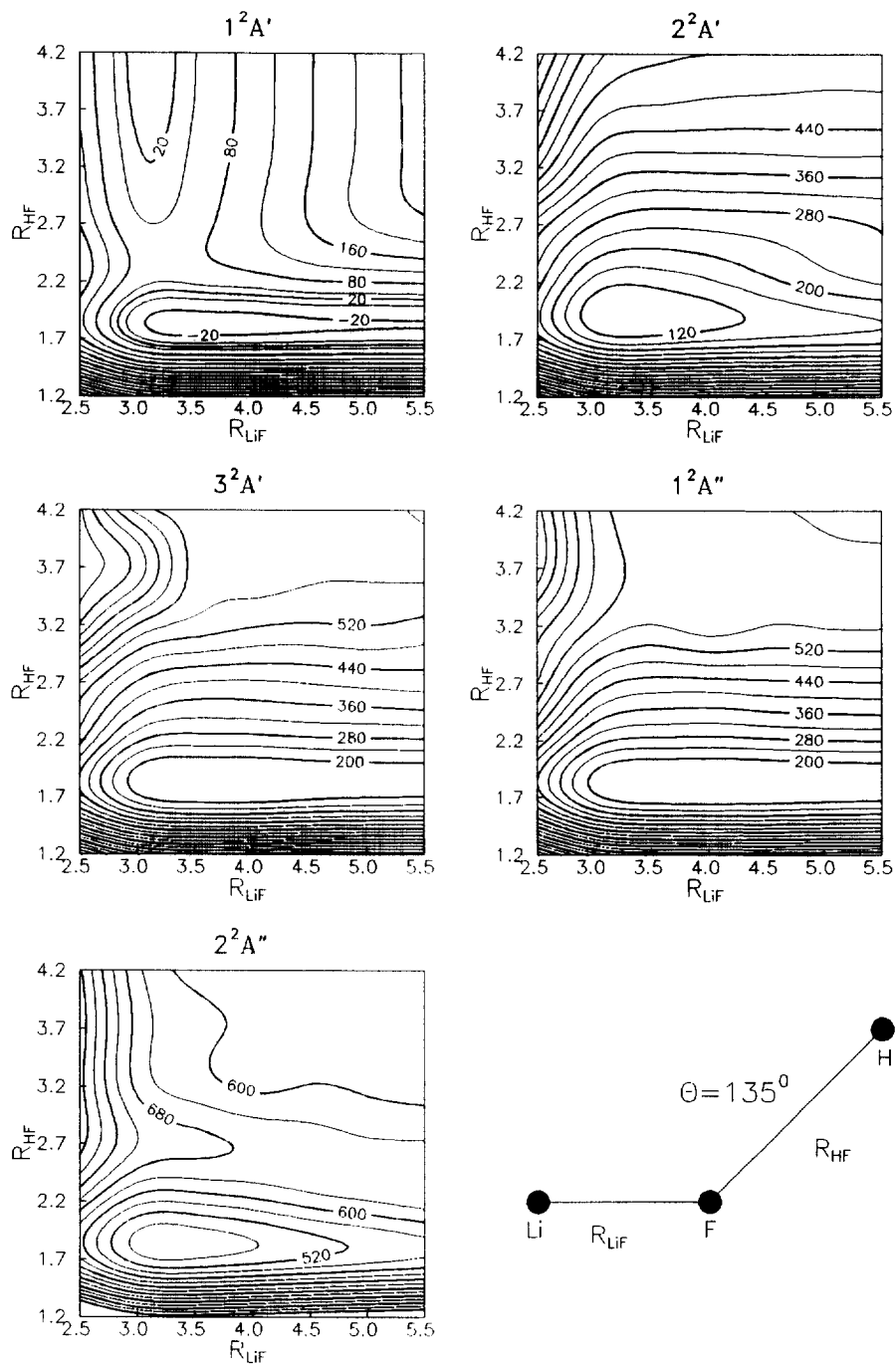


Fig. 2. Potential contours for $\theta = 135^\circ$ as indicated by arrangement of nuclei at the right-hand bottom. Units as in Fig. 1.

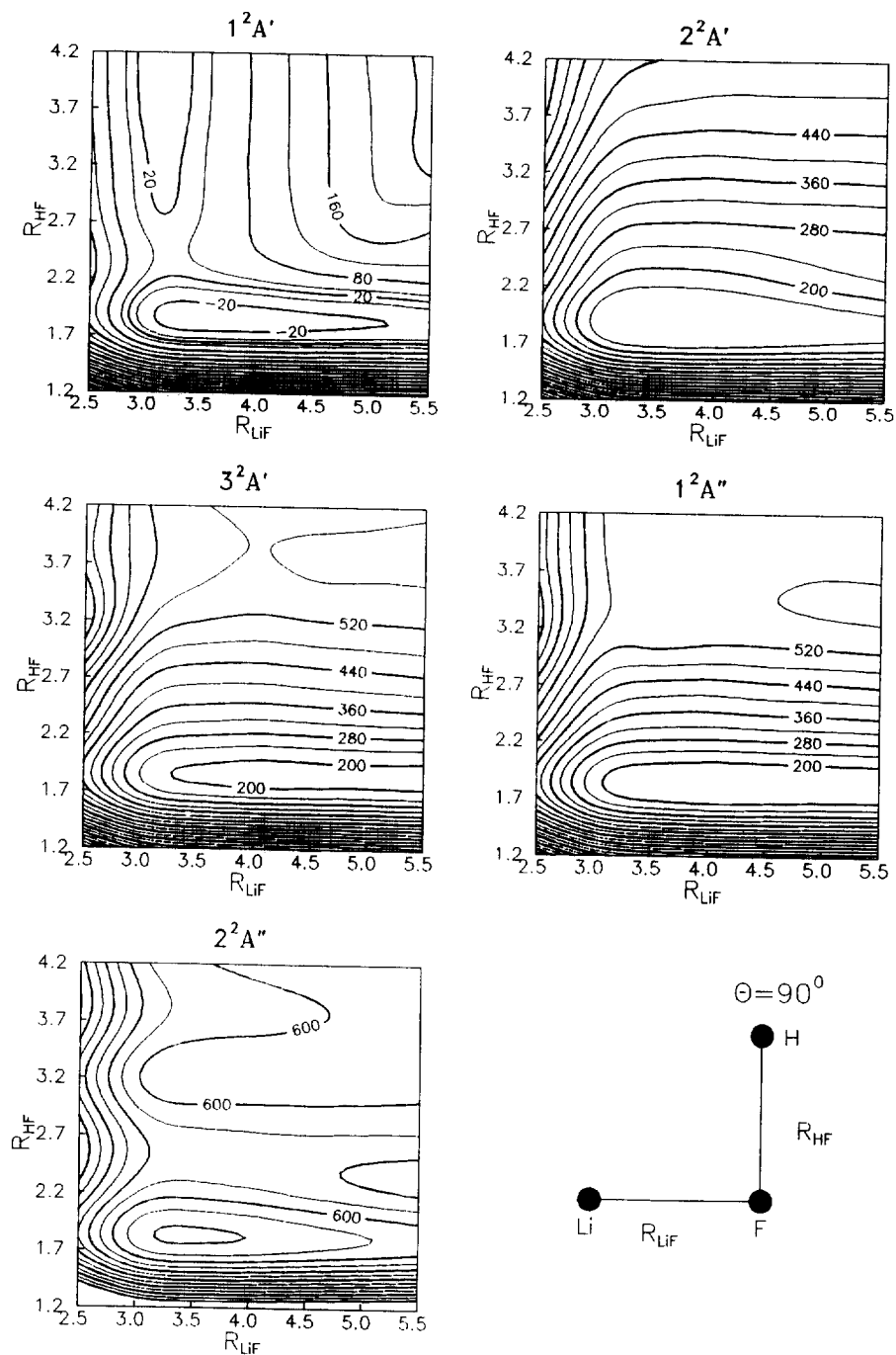


Fig. 3. Potential contours for $\theta = 90^\circ$ as indicated by arrangement of nuclei at the right-hand bottom. Units as in Fig. 1.

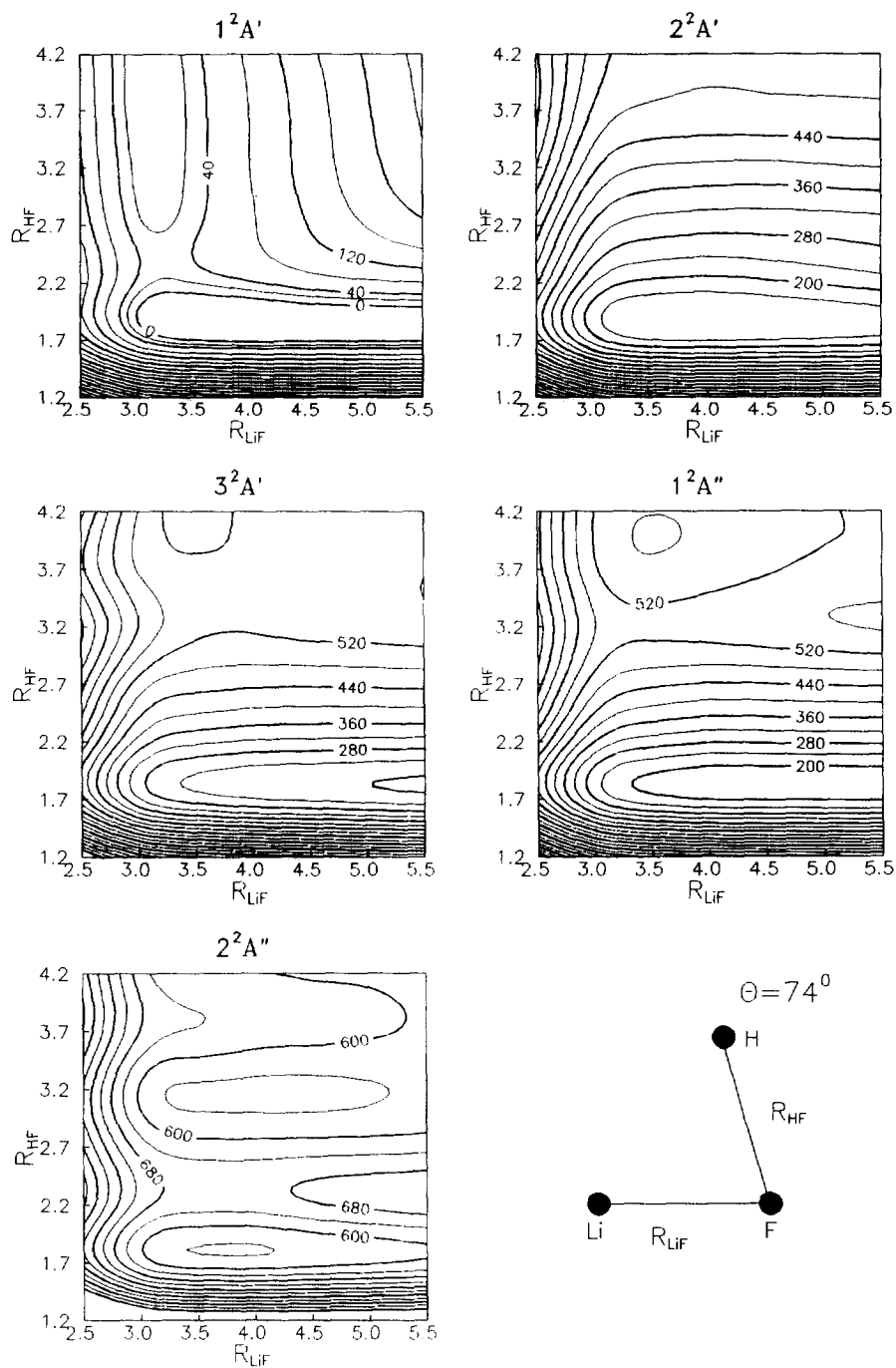


Fig. 4. Potential contours for $\theta = 74^\circ$ as indicated by arrangement of nuclei at the right-hand bottom. Units as in Fig. 1.

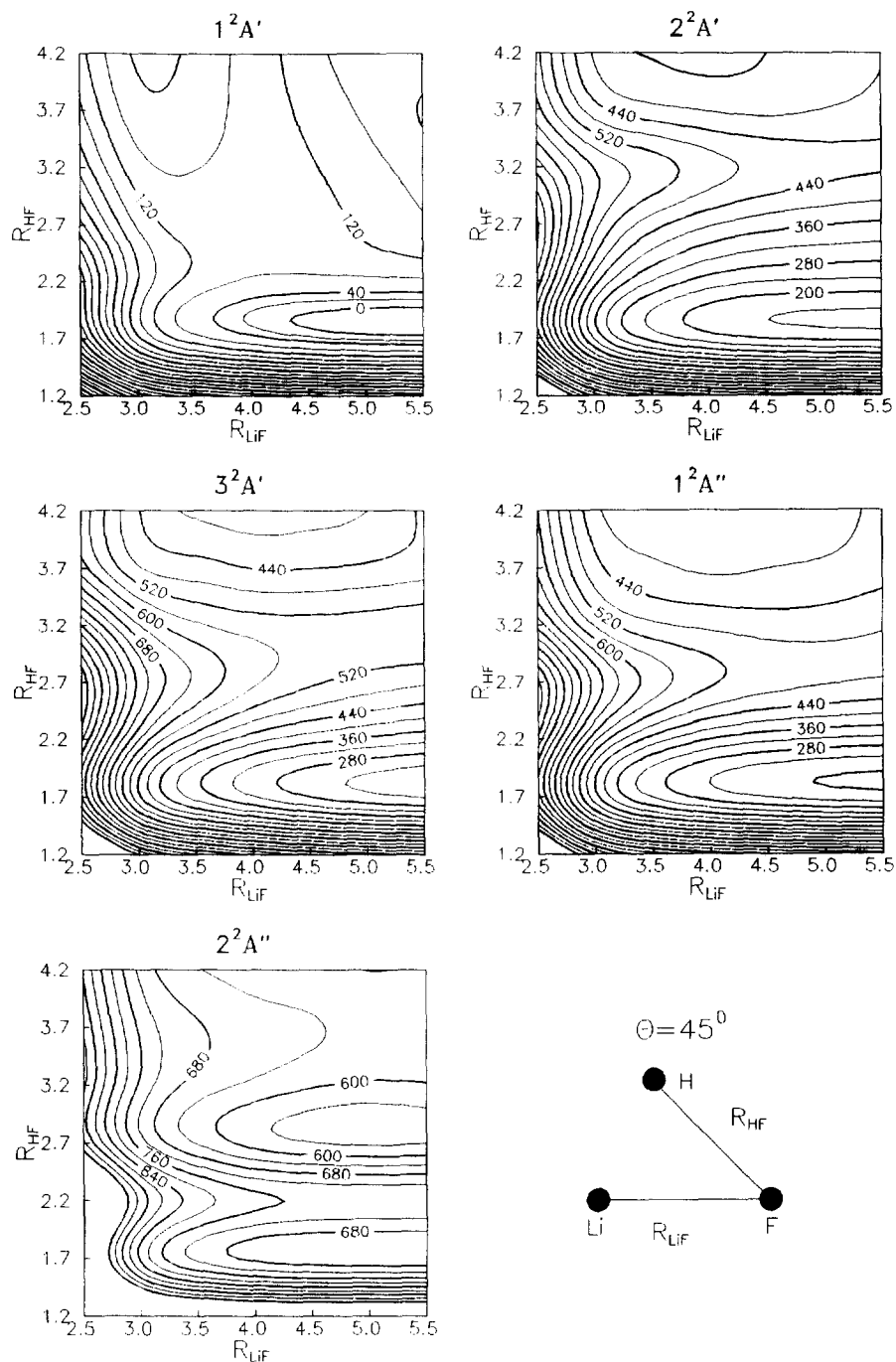


Fig. 5. Potential contours for $\theta = 45^\circ$ as indicated by arrangement of nuclei at the right-hand bottom. Units as in Fig. 1.

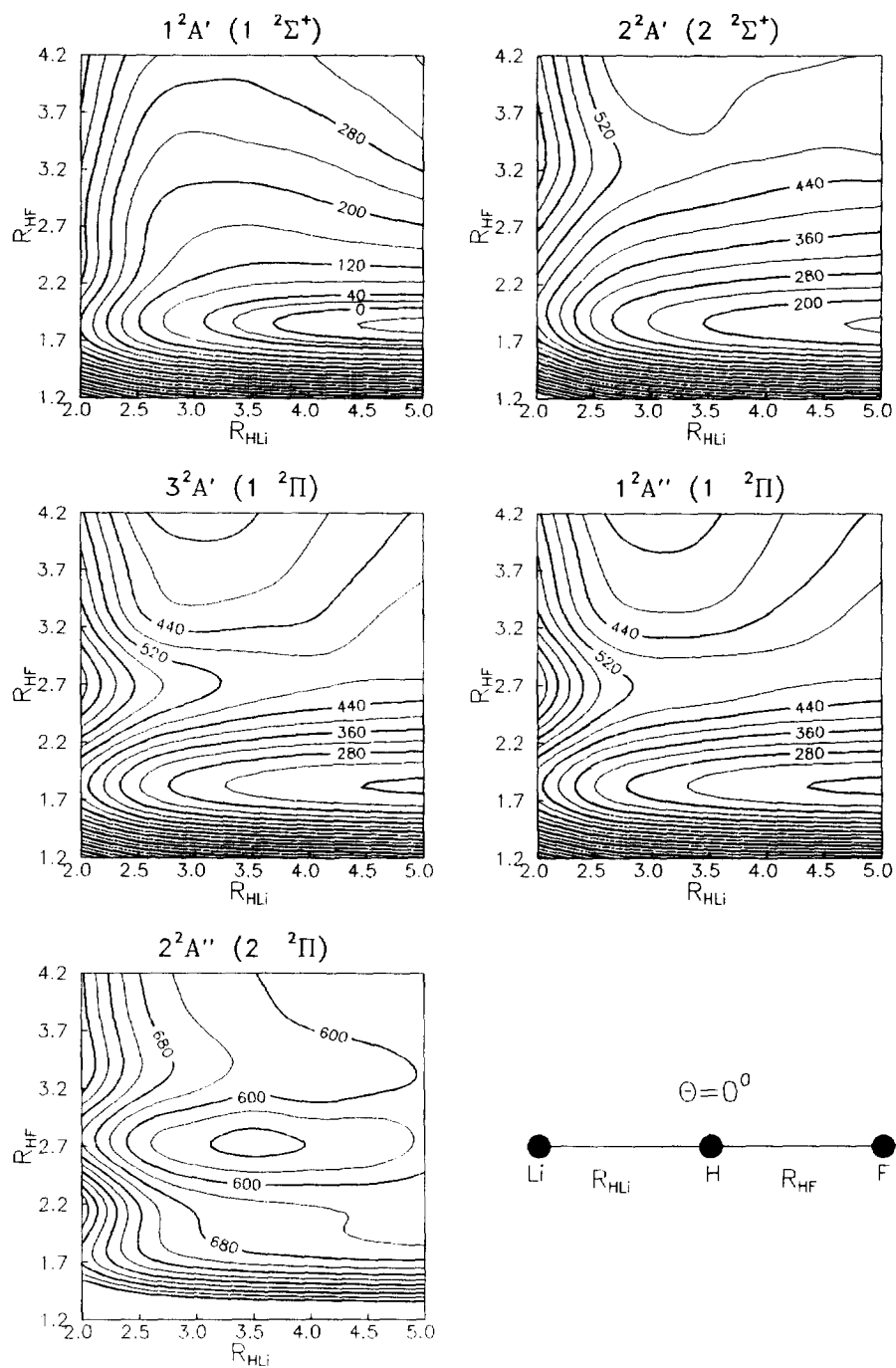


Fig. 6. Potential contours for $\theta = 0^\circ$ as indicated by arrangement of nuclei at the right-hand bottom. Units as in Fig. 1.

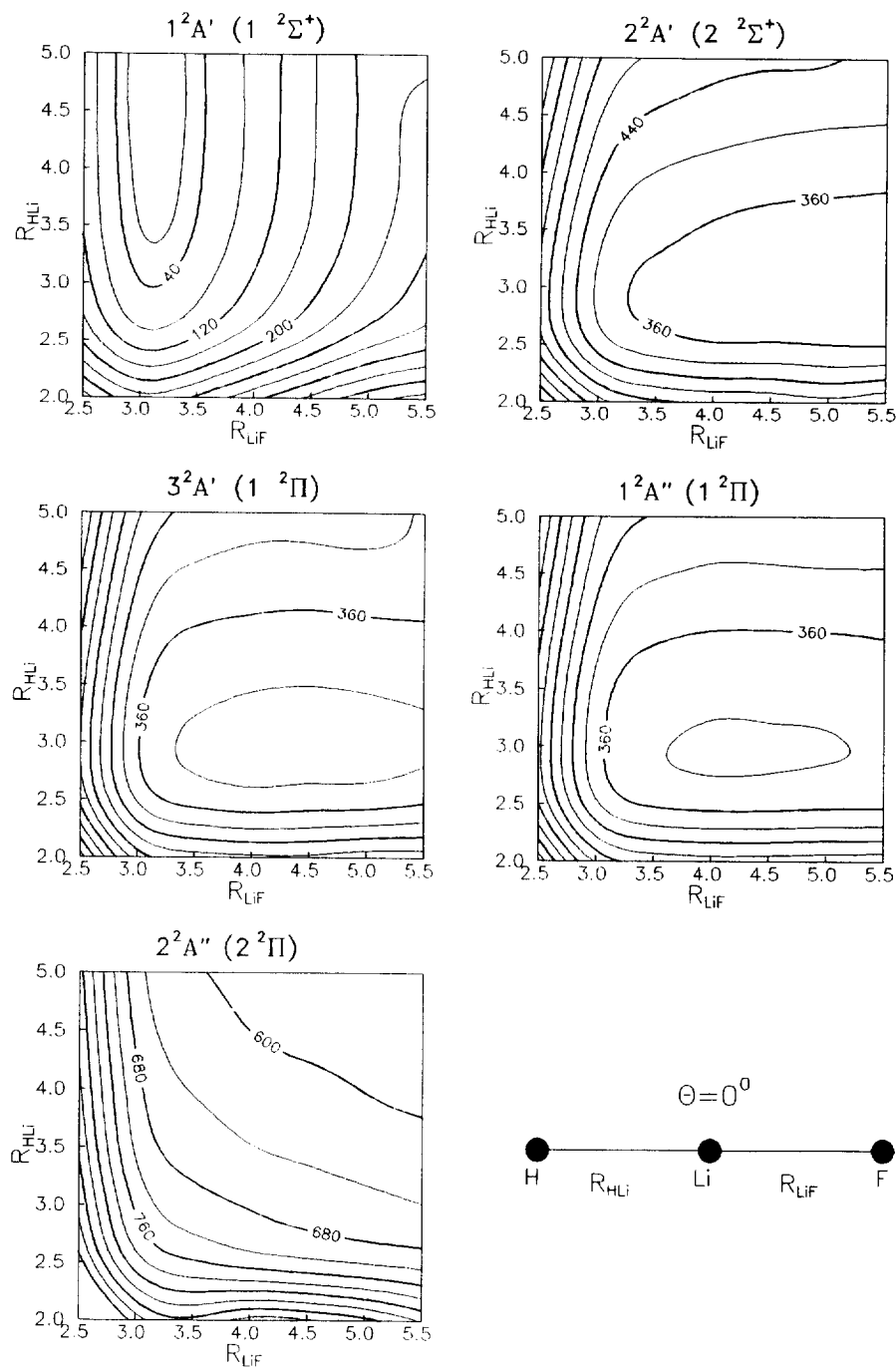


Fig. 7. Potential contours for $\theta = 0^\circ$ (Li atom insertion) as indicated by arrangement of nuclei at the right-hand bottom. Units as in Fig. 1.

for the bent collisions than that corresponding to the true computed one.

After the transition state, the path rises back to the collinear encounters ($\theta = 180^\circ$) as the HF distance goes to infinity (products LiF + H), corresponding to an energy about 10 kJ/mol above the reactants, or 9 kJ/mol below the reactants if we take into account the zero point vibration for HF and LiF. This last result is in a good agreement with the experimental exoergicity ($\Delta H = -4.6 \pm 8$ kJ/mol) [3].

The contour PES maps corresponding to the first excited-state are shown in the right-hand side top panels in Figs. 1–7. In contrast to the ground-state, the first excited-state ($2^2A'$) PES has essentially no barrier. As shown in Figs. 1–7 it is predicted to have an elongated well at somewhat extended configurations ($R_{\text{HF}} = 2.06$ a.u., $R_{\text{LiF}} = 3.25$ a.u.). The minimum of the well lies about 110 kJ/mol above the reactants asymptote (our zero energy, corresponding to Li + HF in their ground states). It is the existence of this well which is so important for laser catalysis [29,30]. Another important requirement for laser catalysis is a strong transition dipole in the transition region. Basically, the transition dipole is strongest near an ionic-covalent crossing (or “electron-jump” region). As we have shown in a previous paper [12], this last condition is fulfilled by the LiFH system.

A possible mechanism for the photon catalysis involves the collision between Li and HF on the ground electronic state ($1^2A'$), the system is slowed down near the “electron-jump” region (very close to the saddle at the collinear approach [12]), following the photon absorption at $6\,000\text{--}9\,000\text{ cm}^{-1}$ to the first excited-state ($2^2A'$). Then, the bound motion on the first excited-state, leading from the reactants side of the transition state to its products side, allows a stimulated emission to the ground-state occurring on the products side where the system reaches the H + LiF asymptotic region. We also look for a strong transition dipole in the saddle region. The squared transition dipole between the ground and the first excited state (μ_{12}^2) is depicted in Fig. 8 for the collinear section. As pointed out above, we can see from Fig. 8 that the transition dipole is strongest near the crossing region characterized in our previous collinear study [12].

The contour PES maps corresponding to the second excited-state are shown in the left-hand side middle panels in Figs. 1–7. As for the first excited-state the

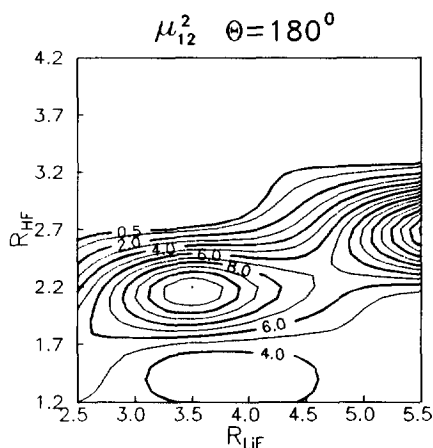


Fig. 8. Squared transition dipole (μ_{12}^2) between the ground and first excited $2^2A'$ states, as a function of the LiF and HF distances in the collinear configuration ($\theta = 180^\circ$). All the distances and transition dipoles are in atomic units.

second excited-state ($3^2A'$) PES has essentially no barrier. As shown in Figs. 1–7 it is predicted to have a well in the reactants asymptote. The minimum of the well lies about 170 kJ/mol above the reactants asymptote. However, the laser catalysis it is no possible here due to the weak values of the computed squared transition dipole (μ_{13}^2). The contour PES maps corresponding to the first A'' excited-state ($1^2A''$) are shown in the right-hand side middle panels in Figs. 1–7. From these figures we can see that the $3^2A'$ is degenerate with respect to the $1^2A''$ for linear arrangements of the nuclei (Figs. 1, 6 and 7). Moreover, the contour PES maps corresponding to the second A'' excited-state ($2^2A''$) are depicted in the left-hand side bottom panels in Figs. 1–7. All the energy values for this state are too high with respect to the reactants asymptote, involving a negligible effect on the Li + HF reactivity.

In Table 2 we present a summary of the outstanding points for the $1^2A'$, $2^2A'$, $3^2A'$ and $1^2A''$ states of the LiFH system. We can see from this table the main points mentioned above. We can also see from Table II that the corresponding points for the $3^2A'$ and $1^2A''$ states are degenerate at linear arrangements of the Li, F and H atoms (see also Figs. 1, 6 and 7, as pointed out above).

Finally, we conclude that there is a need for a fit of the accurate ab initio LiFH PES points reported here without “scaling” procedures that involve an ad hoc

Table 2
Outstanding points on the LiFH MRDCI PES^a

State	R_{LiF}	R_{HF}	R_{HLi}	V	Identity
$1^2A'$	∞	1.74	∞	0	Li (2S) + HF ($X^1\Sigma^+$), reactants asymptote
$1^2A'$	3.00	∞	∞	10	LiF ($X^1\Sigma^+$) + H (2S), products asymptote
$1^2A'$	∞	∞	3.04	320	HLi ($X^1\Sigma^+$) + F (2P), products asymptote
$1^2A'$	3.79	1.74	5.43	-16	well for $\theta = 180^\circ$
$1^2A'$	3.67	1.74	5.05	-22	well for $\theta = 135^\circ$
$1^2A'$	3.65	1.76	4.47	-28	well for $\theta = 106^\circ$
$1^2A'$	3.68	1.78	4.09	-24	well for $\theta = 90^\circ$
$1^2A'$	3.80	1.80	3.73	-11	well for $\theta = 74^\circ$
$1^2A'$	3.06	3.56	3.82	5	well for $\theta = 70^\circ$
$1^2A'$	3.14	2.42	5.56	60	saddle point for $\theta = 180^\circ$
$1^2A'$	3.13	2.46	5.17	54	saddle point for $\theta = 135^\circ$
$1^2A'$	3.14	2.52	4.03	32	saddle point for $\theta = 90^\circ$
$1^2A'$	3.20	2.46	3.42	24	transition state for $\theta = 73^\circ$
$1^2A'$	3.89	2.66	2.75	89	saddle point for $\theta = 45^\circ$
$2^2A'$	∞	1.74	∞	198	Li (2P) + HF ($X^1\Sigma^+$), reactants asymptote
$2^2A'$	3.18	1.95	5.13	112	well for $\theta = 180^\circ$
$2^2A'$	3.25	1.99	4.87	115	well for $\theta = 135^\circ$
$2^2A'$	3.61	1.89	4.07	127	well for $\theta = 90^\circ$
$2^2A'$	3.81	1.79	3.74	141	well for $\theta = 74^\circ$
$3^2A'$	∞	1.74	∞	198	Li (2P) + HF ($X^1\Sigma^+$), reactants asymptote
$3^2A'$	3.96	1.79	5.75	172	well for $\theta = 180^\circ$
$3^2A'$	3.56	1.79	4.99	170	well for $\theta = 135^\circ$
$1^2A''$	∞	1.74	∞	198	Li (2P) + HF ($X^1\Sigma^+$), reactants asymptote
$1^2A''$	3.96	1.79	5.75	172	well for $\theta = 180^\circ$
$1^2A''$	3.76	1.79	5.55	169	well for $\theta = 135^\circ$
$1^2A''$	3.76	1.79	4.16	181	well for $\theta = 90^\circ$

^a Energies in kJ/mol referred to $V = 0$ fixed at the ground state ($1^2A'$) reactants asymptote. Distances in atomic units.

modification of the true PES. We are in the process of fitting new analytic LiFH PESs to our ab initio energies (ground- and lower excited-states), that will be reported in a forthcoming paper [33].

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