Quantum dynamics of the Li + HF → H + LiF reaction at ultralow temperatures

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Abstract

Quantum mechanical calculations are reported for the Li + HF($v = 0, 1, j = 0$) → H + LiF($v', j'$) bimolecular scattering process at low and ultralow temperatures. Calculations have been performed for zero total angular momentum using a recent high accuracy potential energy surface for the $X^2A'$ electronic ground state. For Li + HF($v = 0, j = 0$), the reaction is dominated by resonances due to the decay of metastable states of the Li⋯F−H van der Waals complex. Assignment of these resonances has been carried out by calculating the eigenenergies of the quasibound states. We also find that while chemical reactivity is greatly enhanced by vibrational excitation the resonances get mostly washed out in the reaction of vibrationally excited HF with Li atoms. In addition, we find that at low energies, the reaction is significantly suppressed due to the formation of rather deeply bound van der Waals complexes and the less efficient tunneling of the relatively heavy fluorine atom.

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I. INTRODUCTION

The past few years have witnessed an extremely prolific research effort in the experimental and theoretical investigation of ultracold molecules. The rapid development of techniques for cooling, trapping, and manipulating molecules at ultracold temperatures led recently to the creation of Bose-Einstein condensates (BEC) of diatomic molecules. This major achievement opens new perspectives in the exploration of the crossover regime between BEC and Bardeen-Cooper-Schrieffer (BCS) superfluidity, as well as in the conception of qubits in quantum computers using electric dipole moment couplings between ultracold polar molecules.

Among the wealth of techniques developed for producing ultracold molecules, photoassociation of ultracold atoms has proven its success in creating ultracold ($T \simeq 100 \mu K$) polar neutral molecules. Indeed, using that technique, magneto-optical trapping of ultracold polar neutral ground state KRb and NaCs molecules, as well as formation of RbCs* molecules from a laser-cooled mixture of $^{85}$Rb and $^{133}$Cs atoms were recently reported. Exothermic chemical reactions and vibrational relaxation triggered by collisions are important factors limiting the lifetime of molecules created by photoassociation in highly excited vibrational levels. Although collisional studies of ultracold molecules have been a matter of active research in recent years, relatively few progress has been reported on chemical reactivity of polar molecules at ultralow temperatures.

In this work, we report quantum scattering calculations for the Li+HF $\rightarrow$ H+LiF reaction at cold and ultracold translational energies. Since methods for cooling and trapping alkali metal atoms have reached high degree of sophistication and creation of BEC of alkali metal atoms has become rather widespread, collisions of ultracold alkali metal atoms with polar molecules are being explored as a possible method for creating ultracold polar molecules. Thus, cross sections for elastic and ro-vibrationally inelastic collisions of Li+HF system are of significant interest. Moreover, from a chemical dynamics point of view the Li+HF collision is especially interesting due to the unusually deep van der Waals minimum of about 0.24 eV (1936 cm$^{-1}$) in the entrance channel of the collision. Since Li+HF $\rightarrow$ LiF + H involves the transfer of the relatively heavy F atom (the LiH+F channel is highly endoergic and is not open at low energies), it will be particularly interesting to see whether the reaction...
will occur with significant rate coefficient at ultralow energies.

The Li$^+$HF reaction has been the topic of a large number of experimental and theoretical studies. After the pioneering crossed beam work of Taylor and Datz [34], the Li$^+$HF reaction became a prototype system for experimental studies of the “harpoon” mechanism in reactions between alkali or alkaline earth metal atoms and hydrogen halide molecules [35]. Thus, a large amount of experimental information has been reported for key observables such as integral and differential reactive cross sections [36, 37, 38, 39, 40, 41, 42, 43, 44]. On the theoretical front, numerous quantum mechanical [38, 39, 40, 43, 45, 46, 47, 48, 49, 50, 51, 52, 53] as well as classical trajectory [40, 54] scattering calculations have been performed on the ground state potential energy surface (PES). The relative simplicity of the LiHF system, with only 13 electrons, makes it very suitable for accurate \textit{ab initio} calculations. Consequently, a rich variety of analytic global fits to the $X^2A'$ symmetry electronic ground state PES have been proposed [52, 53, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70]. As mentioned above, one of the unique aspects of the LiHF system is the rather deep van der Waals well in both the Li$^+$HF and H$^+$LiF channels. Unlike the well studied F$^+$H$_2$ and Cl$^+$H$_2$ systems where the van der Waals well depth is about 100 − 200 cm$^{-1}$, the van der Waals well in the Li$^+$HF is an order of magnitude deeper, giving rise to long-lived collision complexes and narrow scattering resonances in the energy dependent reaction probabilities. The presence of the deep van der Waals well in the Li$(^2S)$ + HF$(X^1\Sigma^+; v = 0, 1, j = 0)$ entrance valley was confirmed by backward glory scattering experiment of Loesch and Stienkemeier [37] and by spectroscopic measurements of Hudson et al. [71].

The $X^2A'$ LiHF PESs used in previous scattering studies were based on a relatively restricted sets of \textit{ab initio} data, thus limiting the accuracy of the calculations. Furthermore, the energy range investigated did not cover the translationally cold and ultracold regimes. Here, we report quantum scattering calculations for Li$(^2S)$ + HF$(X^1\Sigma^+; v = 0, 1, j = 0) \rightarrow$ H$^+$LiF$(X^1\Sigma^+; v', j')$ collisions, for a total molecular angular momentum $J = 0$, using the recent high accuracy global PES of the LiHF ground state calculated by Aguado et al. [70]. A brief review of the basic characteristics of the PES is given in Sec. II, together with a summary of the quantum scattering approach with illustrative convergence tests assessing the validity of our calculations. In Sec. III, we present state-to-state and initial-state-selected probabilities, cross sections, and rate coefficients for both reactive and non-reactive open channels of the collision. We discuss the effect of vibrational excitation on chemical
reactivity at low temperatures and provide a summary of our findings in Sec. IV.

II. CALCULATIONS

A. $X^2A'$ state potential energy surface

Calculations reported in the present study have been carried out using the recent LiHF ground state PES of Aguado et al. [70]. This chemically accurate PES was computed for about 6000 nuclear geometries using internally contracted multireference configuration interaction (MRCI) wave functions including all single and double excitations and Davidson size consistency correction (+Q). A large atomic basis set was used to adequately describe the Li$^+$ + HF$^-$ and Li$^+$ + H$^-F$ ionic configurations responsible for the curve crossing leading to the LiF products in the adiabatic representation of the electronic ground state. A saddle point results from the crossing between the Li$^+$ + HF$^-$ ionic state and a covalent configuration correlating to Li($^2S$) + HF($X^1\Sigma^+$). On the basis of these MRCI+Q results, an analytic global PES was constructed using the modified many-body expansion of Aguado and Paniagua [72]. Major features of this PES are as follows: a $-0.241$ eV deep van der Waals well corresponding to the Li···FH complex in the entrance channel due to strong dipole electric fields of the reagents followed by a saddle point at $+0.251$ eV. The formation of the LiF···H complex takes place in a late shallow van der Waals well with a minimum at $+0.118$ eV in the product valley, connecting with the H($^2S$) + LiF($X^1\Sigma^+$) products asymptote at $+0.186$ eV. All energies are relative to the Li($^2S$) + HF asymptote with energy $E = 0$ corresponding to the bottom of the HF potential. Thus, the Li + HF $\rightarrow$ H + LiF reaction is endoergic with exclusion of the zero-point energy of the reactants and products. The reaction becomes exoergic with ground state reagents if the zero-point energy of the reactants and products is included. The exoergicity is 0.01122 eV with ground state reagents. The LiH($X^1\Sigma^+$) + F($^2P$) products lie at 3.57 eV and this reaction channel is closed for the energy range covered in this study.

B. Quantum scattering calculations

Quantum reactive scattering calculations have been performed using the ABC program developed by Skouteris, Castillo and Manolopoulos [73]. This implementation of the coupled-
channel hyperspherical coordinate method solves the Schrödinger equation in Delves hyperspherical coordinates for the motion of the three nuclei on the parametric representation of a single Born-Oppenheimer PES with reactive scattering boundary conditions applied exactly.

Parity-adapted $S$–matrix elements, $S^{J,P}_{v'j'k',vjk}$, are computed for all the arrangements of the collision products for each given $(J, P, p)$ triple, where $J$ is the total angular momentum quantum number and $P$ and $p$ are the triatomic and diatomic parity eigenvalues, respectively; $v$ and $j$ are the usual diatomic vibrational and rotational quantum numbers and $k$ is the helicity quantum number for the reactants, their primed counterparts referring to the products. After transformation of the parity-adapted $S$–matrix elements into their standard helicity representation, $S^J_{v'j'k',vjk}$, initial state selected cross sections are calculated as a function of the kinetic energy, $E_{\text{kin}}$, according to

$$
\sigma_{vj}(E_{\text{kin}}) = \frac{\pi}{k^2_{vj}(2j + 1)} \sum_{J=0}^{J_{\text{max}}} (2J + 1) \sum_{v'j'k'} |S^J_{v'j'k',vjk}(E_{\text{kin}})|^2,
$$

where $k_{vj}$ is the incident channel wave vector and the helicity quantum numbers $k$ and $k'$ are restricted to the ranges $0 \leq k \leq \min(J, j)$ and $0 \leq k' \leq \min(J, j')$. Let us note that for zero total molecular angular momentum and $s$–wave scattering in the incident channel, Eq. (1) merely reduces to a summation over the quantum number $v'$ and $j'$.

C. Convergence tests

At very low temperatures, quantum tunneling becomes the dominant mechanism of chemical reaction when energy barriers are present. As a consequence, the reaction probabilities are usually very small and particular care must be paid to the convergence of scattering calculations. We have performed extensive convergence tests of the initial-state-selected and state-to-state reaction probabilities with respect to the maximum rotational quantum number, $j_{\text{max}}$, and cut-off energy, $E_{\text{max}}$, that control the basis set size, the maximum value of the hyperradius, $\rho_{\text{max}}$, and the size of the log derivative propagation sectors, $\Delta \rho$.

The energy dependence of the Li+HF($v = 0, j = 0$) $\rightarrow$ H+LiF($v', j'$) reaction probability is shown in Fig. 1 for different values of $\rho_{\text{max}}$ and $\Delta \rho$. Convergence with an accuracy better than $10^{-10}$ was achieved over the range $10^{-5} - 10^{-3}$ eV using the values $\rho_{\text{max}} = 50.0$ a.u. and $\Delta \rho = 0.005$ a.u. A more stringent convergence test consisted in the analysis of the product rotational distribution represented in Fig. 2. The same values of $\rho_{\text{max}}$ and $\Delta \rho$ as
above were used to calculate the state-to-state reaction probabilities for \( \text{Li} + \text{HF}(v = 0, j = 0) \rightarrow \text{H} + \text{LiF}(v' = 0, j') \) at a fixed incident kinetic energy of \( 10^{-5} \text{ eV} \). Using the results obtained with \( j_{\text{max}} = 25 \) and \( E_{\text{max}} = 3.2 \text{ eV} \) as a reference, similar accuracy was found using \( j_{\text{max}} = 20 \) and a cut-off internal energy \( E_{\text{max}} = 2.9 \text{ eV} \) in any channel. The basis set corresponding to these values was composed of 771 local basis functions. As Fig. 2 illustrates, the state-to-state reactive probability is particularly sensitive to the size of the basis set at low translational energies. On the basis of these convergence tests, values of \( \rho_{\text{max}} = 50.0 \text{ a.u.}, \Delta \rho = 0.005 \text{ a.u.}, j_{\text{max}} = 20 \) and \( E_{\text{max}} = 2.9 \text{ eV} \) were adopted for the calculations reported hereafter.

III. RESULTS AND DISCUSSION

The initial state-selected reaction probability for LiF formation in \( \text{Li} + \text{HF}(v = 0, j = 0) \) collisions is shown in Fig. 3 as a function of the total energy. Our results are presented along with the recent time-independent quantum coupled channel hyperspherical calculations of Laganà, Crocchianti, and Piermarini [51] obtained with a scaled PES of Parker et al. [45]. Both sets of results are consistent with respect to the magnitude of the predicted probability, i.e., both exhibit small values for the reaction probability. This merely reflects the fact that for collisions with HF molecules initially in their ground vibrational state the reaction proceeds mainly by quantum tunneling through the barrier. The unusually large well depth of the van der Waals potential in the entrance valley effectively raises the reaction barrier, thus leading to small values of the reaction probability. Our results confirm that there is indeed a dense resonance structure at low energies associated with quasibound states of the \( \text{Li} \cdots \text{F} - \text{H} \) van der Waals complex [50, 51]. However, the positions of the peaks predicted by our calculations are noticeably different from the quantum scattering results of Laganà et al. As discussed by Aguado et al. [53], the PES of Parker et al. used in most of the LiFH dynamical calculations performed until 1997, is based on a limited set of \textit{ab initio} data and \textit{ad hoc} modifications introduced to reproduce experimental properties resulted in artificial features in the PES. In addition, the total energy threshold for the time-independent calculations of Laganà et al. [51] is higher than our value of 0.2535 eV corresponding to the energy of the HF(\( v = 0, j = 0 \)) state. However, their time-dependent calculation carried out using wavepacket methods is in line with our prediction of the threshold position [see
Comparison of our results presented in Fig. 3 with the recent quantum mechanical scattering calculations of Wei, Jasper, and Truhlar [50] is also very revealing of the quantitative discrepancies introduced by the PES in dynamical studies at low temperatures. Their time-independent quantum calculations using the variational method employed the global \textit{ab initio} PES of Jasper et al. [67]. Briefly, this ground-state PES is characterized by a reactant van der Waals well at $-0.21 \text{ eV}$ relative to the Li($^2S$) + HF asymptote, followed by a saddle point at $+0.35 \text{ eV}$, a product van der Waals well at $+0.167 \text{ eV}$ and finally a product asymptote at $+0.21 \text{ eV}$. This potential also exhibits a second saddle point in the product valley at $+0.224 \text{ eV}$. Compared to our results, the reaction probability obtained by Wei et al. for LiF formation is smaller by more than an order of magnitude. This reflects the effect of a 0.1 eV higher barrier in the reactant channel as well as the presence of a second saddle point in the product valley of the PES of Jasper et al.

Fig. 4 shows the state-to-state reaction probabilities for LiF($v', j'$) formation as a function of the product rotational quantum number, $j'$, in Li + HF($v = 1, j = 0$) collisions. For a fixed incident kinetic energy of $10^{-5} \text{ eV}$, 5 vibrational levels are energetically accessible in the diatomic products of the reactions, each of these levels supporting 20 rotational states as restricted by our cut-off value for $j_{\text{max}}$. The probability for LiF formation is larger for intermediate-$j'$ product channels of the $v' = 0$ and $v' = 1$ vibrational levels. A broad peak centered at $j' = 10$ appears in the population distribution of these vibrational states, corresponding to an exoergicity of $4.85 \times 10^{-1} \text{ eV} = 11.183 \text{ kcal/mol}$ and $3.74 \times 10^{-1} \text{ eV} = 8.629 \text{ kcal/mol}$ for the reaction to $v' = 0$ and $v' = 1$, respectively. Vibrational excitation of the reactants significantly increases the reaction probability, as can be seen from the comparison of Fig. 2 and Fig. 4.

Initial-state-selected cross sections for LiF formation and for nonreactive scattering in Li + HF($v = 0, 1, j = 0$) collisions are displayed in Fig. 5 for incident translational energies covering the range $10^{-7} - 10^{-1} \text{ eV}$. The reaction cross section is rather small for HF molecules initially in their ground vibrational state since quantum tunneling of the relatively heavy fluorine atom is the dominant reaction mechanism. For energies below $10^{-5} \text{ eV}$, the reaction cross section reaches the Wigner regime [74] where it varies inversely as the velocity. However, a strong peak centered at $5 \times 10^{-4} \text{ eV}$ is observed where the cross section increases by about six orders of magnitude. This feature suggests that reactivity may be more important at low temperatures than generally recognized. For translational energies beyond
$10^{-3}$ eV, the reaction cross section is characterized by resonant spikes due to metastable states of the Li····F−H van der Waals complex in the initial channel. Nonreactive channels of the Li + HF($v = 0, j = 0$) collisions are open only for translational energies larger than $5.06 \times 10^{-3}$ eV, thereby explaining the sharp rise in the nonreactive cross section at this value corresponding to the energy for rotational excitation to the first excited state of the product, HF($v = 0, j = 1$). Beyond this energy threshold, nonreactive scattering becomes more favorable than LiF formation, as shown in the lower panel of Fig. 5. On the contrary, in Li + HF($v = 1, j = 0$) collisions the reactive channel dominates the nonreactive processes, with a LiF/HF product branching ratio reaching 20 at low and ultralow temperatures. This is especially interesting as the reaction involves quantum tunneling of the relatively heavy fluorine atom. Moreover, chemical reactivity is greatly enhanced by vibrational excitation. In the Wigner regime, where cross section ratios become constant, the reaction cross section involving excited HF($v = 1, j = 0$) reactants are 635 times larger than for collisions with HF reactants in their rovibrational ground state.

Further characterization of the peaks represented in the lower panel of Fig. 5 has been carried out by calculating the bound- and quasi-bound states of the Li····F−H van der Waals potential that correlate with the HF($v = 0$) manifold. The adiabatic potentials are obtained by constructing the matrix elements of the interaction potential in a basis set of the rovibrational levels of the HF molecule and diagonalizing the resulting diabatic potentials as a function of the atom-molecule separation, $R$. The resonance energies and the corresponding wave functions are computed using the Fourier grid Hamiltonian method [75, 76]. For constructing the adiabatic potentials, we used a 20-term Legendre expansion of the interaction potential, 25 angular orientations to project out the expansion coefficients, 17 Gauss-Hermite quadrature points for the vibrational wave functions and a grid of 1000 points for the atom-molecule separation. As reported in Table II and Fig. 6, the excellent agreement found between the energy eigenvalues and the peak positions from our scattering calculations suggests that peaks A to H in Fig. 5 are resonances due to the decay of metastable states of the Li····HF van der Waals complex. The resonances correspond to quasibound states of the adiabatic potentials correlating with $j = 1 − 4$ of the Li····HF($v = 0$) molecule. Each of the adiabatic potential supports a number of quasibound complexes due to the relatively deep van der Waals interaction in the entrance channel. Only high-lying stretching vibrational states of the van der Waals complex generate resonances for $j = 1 (t = 10, 11)$ and $j = 2$
While low-\( t \) channels give rise to resonances for \( j = 3, 4 \). However, we have not been able to assign the strong peak centered at \( E = 2.539 \times 10^{-1} \) eV to a reactant van der Waals complex. Nevertheless, time-delay calculations show that it is a reactive scattering resonance.

Elastic cross sections for \( s \)-wave scattering in Li + HF(\( v = 0, 1, j = 0 \)) collisions are presented in Fig. 7 as a function of the incident translational energy. For translational energies below \( 10^{-3} \) eV elastic cross sections for \( v = 0 \) and 1 are nearly identical. Above this energy value, the results for \( v = 1 \) are less oscillatory compared to those of \( v = 0 \). The real part of the scattering length has been calculated for \( v = 0 \) and 1 in the ultracold limit according to

\[
\alpha = -\lim_{k \to 0} \frac{\text{Im}(S^{el})}{2k},
\]

where \( S^{el} \) is the elastic component of the scattering matrix and \( k \) is the wavevector corresponding to the initial kinetic energy. We found \( \alpha_{v=0} = +11.551 \) Å and \( \alpha_{v=1} = +11.535 \) Å for the real part of the scattering length for \( v = 0 \) and 1, respectively.

Fig. 8 shows the \( J = 0 \) contribution to the reaction rate coefficients for LiF(\( v', j' \)) formation in Li + HF(\( v = 0, 1, j = 0 \)) collisions, evaluated as the product of the cross section and the relative velocity, as a function of the translational temperature, \( T = E_{\text{kin}}/k_B \), where \( k_B \) is the Boltzmann constant. The unusually large well depth of the van der Waals potential in the entrance channel (\( -0.2407 \) eV, relative to the Li(\( ^2S \)) + HF asymptote of the PES) effectively raises the reacton barrier and lead to small values of the reaction rate coefficients at low energies. For HF(\( v = 0, j = 0 \)) reactants, the rate coefficient reaches the Wigner regime for temperatures below 0.03 K, with a constant value of \( 4.5 \times 10^{-20} \) cm\(^3\) s\(^{-1}\) in the zero-temperature limit. Vibrational excitation to the \( v = 1 \) state enhances reactivity by 3 orders of magnitude in the ultracold limit, as depicted in the upper panel of Fig. 8, where a constant value of \( 2.8 \times 10^{-17} \) cm\(^3\) s\(^{-1}\) is attained for the reaction rate coefficient for temperatures below 0.005 K. For both \( v = 0 \) and 1, the reactivity rapidly increases beyond 1 K. However, accurate prediction of rate coefficients for higher temperatures requires calculations for \( J > 0 \) which is beyond the scope of this work.
IV. CONCLUSION

Quantum reactive scattering calculations have been performed for the \( \text{Li}^+ + \text{HF}(v = 0, 1, j = 0) \rightarrow \text{H} + \text{LiF}(v', j') \) bimolecular scattering process for zero total angular momentum, at low and ultralow temperatures. The energy dependence of state-to-state and initial-state-selected probabilities and cross sections, as well as limiting values of the rate coefficients have been evaluated using the coupled-channel hyperspherical coordinate method. For \( \text{Li}^+ + \text{HF}(v = 0, j = 0) \) collisions, our calculations, using the most recent PES for the LiHF electronic ground state, clearly illustrate the dominance of the resonance tunneling mechanism due to the decay of metastable states of the Li\cdots HF van der Waals complex in the entrance valley into the LiF\((v' = 0)\) product manifold. Comparison of our calculations with previous quantum scattering results emphasizes the extreme sensitivity of scattering matrix elements to the details of the PES and therefore the desirability for high accuracy analytic fits to correctly describe the collision dynamics and the interplay among the various energy modes in the cold and ultracold regimes. We also find that chemical reactivity is dramatically enhanced by vibrational excitation for cold and ultracold translational energies, with a 3-order of magnitude increase between the \( v = 0 \) and \( v = 1 \) rate coefficients in the zero-temperature limit, consistent with our findings for the \( \text{H} + \text{HCl} \) and \( \text{H} + \text{DCl} \) reactions [32]. Moreover, our results show that the LiF formation dominates the nonreactive processes in \( \text{Li}^+ + \text{HF}(v = 1, j = 0) \) collisions, with a LiF/HF product branching ratio reaching 20 at low and ultralow temperatures.

The rich resonance features characterizing the energy dependence of the \( \text{Li}^+ + \text{HF} \) cross sections make the LiHF system particularly attractive for the study of coherent control of resonance-mediated reactions. In fact, recent advances in the control of bimolecular processes have shown that cross sections resulting from scattering that proceeds via an intermediate resonance are exceptionally controllable [77]. This offers new possibility for tuning chemical reactivity at the single quantum state level of resolution. The present study shows that vibrational excitation may be used to circumvent reaction barriers at cold and ultracold temperatures even when the reaction involves tunneling of a heavy atom such as fluorine.
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TABLE I: Assignment of the resonances in the total energy dependence of the cross sections for LiF formation in Li + HF\(v = 0, j = 0\) collisions (energies in eV).

| Resonance | Peak position | Binding energy of Li···HF\((v, j)\) complex\(^a\) | Quantum numbers |
|-----------|---------------|------------------------------------------------|-----------------|
| A         | 0.2549        | 0.2549                                          | 0 2 5           |
| B         | 0.2554        | 0.2553                                          | 0 1 10          |
| C         | 0.2568        | 0.2568                                          | 0 3 2           |
| D         | 0.2579        | 0.2578                                          | 0 1 11          |
| E         | 0.2587        | 0.2585                                          | 0 4 0           |
| F         | 0.2597        | 0.2596                                          | 0 2 6           |
| G         | 0.2656        | 0.2646                                          | 0 3 3           |
| H         | 0.2665        | 0.2664                                          | 0 2 8           |

\(^a\)Energies are calculated with the Fourier grid Hamiltonian method. Energies are relative to separated Li + HF system with energy zero corresponding to the bottom of the HF potential.

\(^b\)HF vibrational quantum number.

\(^c\)HF rotational quantum number.

\(^d\)Quantum number for the Li – HF\((v, j)\) van der Waals stretching vibration.
FIG. 1: Translational energy dependence of the reaction probability for LiF($v', j'$) formation in Li + HF($v = 0, j = 0$) collisions for different values of $\rho_{\text{max}}$ and $\Delta \rho$.

FIG. 2: State-to-state reaction probability for LiF($v' = 0, j'$) formation as a function of the product rotational quantum number, $j'$, in Li + HF($v = 0, j = 0$) collisions. Results are presented for various values of $E_{\text{max}}$ and $j_{\text{max}}$, at a fixed incident kinetic energy of $10^{-5}$ eV, $\rho_{\text{max}} = 50.0$ a.u., and $\Delta \rho = 0.005$ a.u.

FIG. 3: Initial state-selected reaction probability for LiF formation in Li + HF($v = 0, j = 0$) collisions as a function of the total energy. Solid curve: present calculations; dotted curve: quantum scattering calculation of Laganà et al. [51] (extracted graphically from Fig. 3 of ref. [51]).

FIG. 4: State-to-state reaction probabilities for LiF($v', j'$) formation in Li + HF($v = 1, j = 0$) collisions as a function of the product rotational number $j'$ for a fixed incident kinetic energy of $10^{-5}$ eV.

FIG. 5: Cross sections for LiF formation and nonreactive scattering in Li + HF($v, j = 0$) collisions, for $v = 0$ (lower panel) and $v = 1$ (upper panel), as a function of the incident kinetic energy. Dashed curve: nonreactive scattering; solid curve: LiF product channel.

FIG. 6: Adiabatic potential energy curves and corresponding quasibound levels of the Li· · ·HF($v = 0, j$) van der Waals complex (left panel); cross section for LiF formation in Li + HF($v = 0, j = 0$) collisions as a function of the total energy (right panel). The resonances A to H in the cross section appear as a result of the decay of quasibound states of the Li· · ·HF van der Waals complex.

FIG. 7: Elastic cross sections for $s$–wave scattering in Li + HF($v = 0, 1, j = 0$) collisions as a function of the incident kinetic energy. Solid curve: $v = 0$; dashed curve: $v = 1$.

FIG. 8: Temperature dependence of reaction rate coefficients for LiF formation in Li + HF($v = 0, 1, j = 0$) collisions.
\[ \Delta \rho_{\text{max}} = 50 \text{ a.u., } \Delta \rho = 1 \times 10^{-3} \text{ a.u.} \]

\[ \Delta \rho_{\text{max}} = 50 \text{ a.u., } \Delta \rho = 5 \times 10^{-3} \text{ a.u.} \]

\[ \rho_{\text{max}} = 100 \text{ a.u., } \Delta \rho = 5 \times 10^{-3} \text{ a.u.} \]

\[ \rho_{\text{max}} = 35 \text{ a.u., } \Delta \rho = 5 \times 10^{-3} \text{ a.u.} \]
Product (LiF) rotational level $j'$

- $E_{\text{max}} = 2.0 \text{ eV}, j_{\text{max}} = 20$
- $E_{\text{max}} = 2.9 \text{ eV}, j_{\text{max}} = 15$
- $E_{\text{max}} = 2.9 \text{ eV}, j_{\text{max}} = 20$
- $E_{\text{max}} = 3.2 \text{ eV}, j_{\text{max}} = 25$
