Heavy atom tunneling in chemical reactions: study of H + LiF collisions

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Abstract

The H + LiF($X^1\Sigma^+, v = 0 - 2, j = 0$) → HF($X^1\Sigma^+, v', j'$) + Li($^2S$) bimolecular process is investigated by means of quantum scattering calculations on the chemically accurate $X^2A'$ LiHF potential energy surface of Aguado et al. [J. Chem. Phys. 119, 10088 (2003)]. Calculations have been performed for zero total angular momentum for translational energies from $10^{-7}$ to $10^{-1}$ eV. Initial-state selected reaction probabilities and cross sections are characterized by resonances originating from the decay of metastable states of the H···F – Li and Li···F – H van der Waals complexes. Extensive assignment of the resonances has been carried out by performing quasi-bound states calculations in the entrance and exit channel wells. Chemical reactivity is found to be significantly enhanced by vibrational excitation at low temperatures, although reactivity appears much less favorable than non-reactive processes due to the inefficient tunneling of the relatively heavy fluorine atom strongly bound in van der Waals complexes.

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I. INTRODUCTION

Quantum mechanical tunneling through an energy barrier has long been recognized as an important process in a variety of chemical reactions [1]. Recently, evidences for tunneling in reactions have been reported, for instance, in enzymology [2], organic [3], atmospheric [4], and interstellar chemistry [5]. This mechanism is also being investigated at cold and ultra-cold temperatures in the context of chemical reactivity involving Bose-Einstein condensates (BEC) of diatomic molecules [6, 7, 8] where tunneling is thought to be the dominant reactive process [9, 10, 11, 12].

Analysis of subthreshold resonances in the energy dependence of reaction cross sections can provide important insight into the reaction mechanism as illustrated recently for \( \text{FH}_2 \) [13, 14], \( \text{HOCl} \) [15, 16], \( \text{HCl}_2 \) [17] and \( \text{LiHF} \) [18, 19, 20]. For these systems, resonances were attributed to the decay of quasibound van der Waals complexes in the entrance and/or exit channels of the reaction. The LiHF system is especially interesting since at low temperatures where tunneling is preponderant, the reaction pathway between the \( \text{H} + \text{LiF} \) and \( \text{Li} + \text{HF} \) arrangements involves the transfer of the relatively heavy F atom. The \( \text{LiH} + \text{F} \) product channel is highly endoergic and is not accessible at low energies. The LiHF system has been extensively studied experimentally and theoretically. Indeed, after the original crossed beam measurement of Taylor and Datz [21], the \( \text{Li} + \text{HF} \) reaction became a prototype for experimental investigation of the “harpoon” mechanism [22] and many measurements of the integral and differential reactive cross sections have been reported [23, 24, 25, 26, 27, 28, 29, 30, 31]. Moreover, LiHF is particularly amenable to \textit{ab initio} calculations of chemical accuracy, therefore explaining the variety of potential energy surfaces (PESs) available for the \( X^2A' \) symmetry electronic ground state [32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49]. A large number of quantum mechanical [19, 20, 25, 26, 27, 28, 32, 33, 50, 51, 52, 53, 54, 55] and classical trajectory [27, 56] scattering calculations have been performed on these PESs for the \( \text{Li} + \text{HF} \) collision. In contrast, the \( \text{H} + \text{LiF} \) collision has received no theoretical and experimental attention, to the best of our knowledge. The lack of experimental results may be explained by the difficulty in working with metastable hydrogen atom sources in crossed beams experiments.

In this work, we present quantum scattering calculations on the \( X^2A' \) LiHF electronic ground state for the \( \text{H} + \text{LiF}(X^1\Sigma^+, v = 0 \rightarrow 2, j = 0) \rightarrow \text{HF}(X^1\Sigma^+, v', j') + \text{Li}^2S \) reaction.
Calculations have been performed for zero total angular momentum using the recent high accuracy global PES of Aguado et al. 49. In the context of our study of the reverse reaction [20], particular effort is made here to assign resonances due to the decay of metastable states in van der Waals wells of the entrance and exit channels. The LiHF electronic ground state is typical of alkali metal halides with a saddle point resulting from the crossing of the Li$^+$ + HF$^-$ ionic state and a covalent configuration correlating to Li($^2S$) + HF($^1\Sigma^+$). The strong dipole electric field of the products is at the origin of an exceptionally deep van der Waals minimum of about 0.24 eV for the Li···F − H complex, while the H···F − Li complex in the entrance channel is about 0.07 eV deep. These van der Waals wells give rise to long-lived collision complexes and narrow scattering resonances in the energy dependence of reaction probabilities. Since H + LiF → HF + Li involves the transfer of the relatively heavy F atom, it will be of particular interest to see whether the reaction will occur with significant rate coefficient at low energies and how resonances due to tunneling affect reaction rates.

In Sec. II, we give a summary of the principal features of the PES of Aguado et al. 49, followed by a concise review of quantum scattering theory and convergence tests assessing the validity of our numerical results. Initial-state-selected probabilities, cross sections, cumulative reaction probabilities as well as rate coefficients for both reactive and non-reactive open channels of the collision are presented in Sec. III. We also provide a detailed analysis of the resonances present in the energy dependence of cross sections by means of quasibound state calculations of the van der Waals complexes formed in the reagent and product channels. The effect of vibrational excitation on chemical reactivity at low temperatures and the contribution of resonances in reaction rates are discussed. Finally, a summary of our findings is given in Sec. IV.

II. CALCULATIONS

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

The $X^2A'$ LiHF ground state PES of Aguado et al. 49 was used for the present scattering calculations. Ab initio calculations were performed for 6000 nuclear geometries at the multireference configuration interaction (MRCI) level of theory, using internally contracted
wave functions including all single and double excitations and the Davidson correction (+Q). The Li$^+$ + HF$^-$ and Li$^+$ + H$^-$F ionic configurations, responsible for the curve crossing leading to the LiF products in the adiabatic $X^2A'$ state, were adequately described using a large atomic basis set. The crossing between the Li$^+$ + HF$^-$ ionic state and a covalent configuration correlating to Li$(2S) +$ HF$(X^1\Sigma^+)$ was found to produce a pronounced saddle point in the Born-Oppenheimer electronic ground state. The resulting analytic PES constructed using the modified many-body expansion of Aguado and Paniagua [57] exhibits deep van der Waals wells of 0.2407 eV (5.551 kcal/mol) and 0.0686 eV (1.582 kcal/mol) corresponding to the Li···F − H and H···F − Li complexes, respectively. The saddle point and the Li$(2S) +$ HF products asymptote are at +0.0642 eV and −0.1861 eV, respectively, relative to the H$(2S) +$ LiF$(X^1\Sigma^+)$ asymptote with $E = 0$ corresponding to the bottom of the LiF potential. The LiH$(X^1\Sigma^+) +$ F$(2P)$ products channel lies at +3.3839 eV relative to the energy origin, thus this reaction channel is closed for the energy range considered in this study. The PES of Aguado et al. [49] significantly improves on the widely used PES of Parker et al. [50] constructed from a limited set of $ab$ initio data. It is also markedly different from the recent $ab$ initio PES of Jasper et al. [46], which exhibits a +0.076 eV higher saddle point separating the H···FLi and Li···FH complexes and an additional saddle point at +0.014 eV in the reagent valley. Using the PES of Aguado et al. [49], we found that, when the zero-point energies of reactants and products are included, the H + LiF($v = 0, j = 0$) → Li + HF($v' = 0, j' = 0$) reaction has an endothermicity of 0.0112 eV (0.2588 kcal/mol), while for vibrationally excited LiF($v = 1, j = 0$) and LiF($v = 2, j = 0$) reagents the reaction producing HF($v' = 0, j' = 0$) becomes exothermic by 0.0998 eV (2.3011 kcal/mol) and 0.2089 eV (4.8170 kcal/mol), respectively.

B. Quantum scattering calculations

Quantum reactive scattering calculations were carried out using the coupled-channel hyperspherical coordinate method as implemented in the ABC program [58]. In this method, the Schrödinger equation for the motion of three nuclei on the parametric representation of a single Born-Oppenheimer PES is solved in Delves hyperspherical coordinates with exact reactive scattering boundary conditions. For all arrangements of the collision products, parity-adapted $S$—matrix elements, $S_{v'j'k'}^{J,P_{vjk}}$, are calculated for each $(J, P, p)$ triple. Here, $J$ is the
total angular momentum quantum number, $P$ 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, $S_{v'j'k',vjk}$, initial state selected cross sections are computed as a function of the kinetic energy, $E_{\text{kin}}$, according to

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

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 $0 \leq k' \leq \min(J, j')$. 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 $j'$. The cumulative reaction reaction probability (CRP) is also computed using the formula

$$N_{J=0}(E) = \sum_{v'j'k',vjk} |S_{v'j'k',vjk}(E)|^2,$$

where $E$ is the total energy and the summation is over all open channels of the reactant and product molecules. For $J = 0$, reaction rate coefficients are further 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.

Owing to the predominance of quantum tunneling in reactions involving energy barriers at low temperatures, reaction probabilities are generally small for translationally cold and ultracold collisions. Therefore, extensive convergence tests have been carried out for the initial-state-selected and state-to-state reaction probabilities of the exothermic $\text{H} + \text{LiF}(v = 1, 2, j = 0) \rightarrow \text{Li} + \text{HF}(v', j')$ reactions. Convergence of our scattering calculations was checked with respect to the maximum rotational quantum number, $J_{\text{max}}$, the 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, $\Delta \rho$.

Converged reaction probability for LiF formation in $\text{H} + \text{LiF}(v = 1, 2, j = 0)$ collisions were obtained over the range $10^{-5} - 10^{-3}$ eV using the values $\rho_{\text{max}} = 25.0$ a.u. and $\Delta \rho = 0.01$ a.u. The accuracy of our numerical results over this energy range was better than $10^{-10}$ using a large basis set size constrained with the values of $J_{\text{max}} = 25$ and $E_{\text{max}} = 2.5$ eV. Using
the same values of $\rho_{\text{max}}$ and $\Delta \rho$ as above, the size of the basis set was further optimized by adjusting the value of the cut-off energy. In general, the reaction probabilities are more sensitive to the basis set parameters at low energies. We performed the basis set optimization at an incident kinetic energy of $10^{-5}$ eV. We found that the state-to-state reactions $\text{Li} + \text{HF}(v = 1, 2, j = 0) \rightarrow \text{H} + \text{LiF}(v' = 0, j')$ with $E_{\text{max}} = 2.5$ eV and $E_{\text{max}} = 2.0$ eV resulted in nearly identical values of the reaction probabilities. The basis set corresponding to $E_{\text{max}} = 2.0$ eV was composed of 634 basis functions. Based on these convergence tests, values of $\rho_{\text{max}} = 25.0$ a.u., $\Delta \rho = 0.01$ a.u., $j_{\text{max}} = 25$ and $E_{\text{max}} = 2.0$ eV were adopted in the calculations reported hereafter.

III. RESULTS AND DISCUSSION

Fig. 1 shows the initial state-selected reaction probability for HF formation in $\text{H} + \text{LiF}(v = 0 - 2, j = 0)$ collisions as a function of the translational energy. For LiF reagent initially in the rovibrational ground state, the reaction leading to HF formation has an endoergicity of 0.0112 eV (0.2588 kcal/mol), thus explaining the presence of the kinetic energy threshold in the lower panel of Fig. 1. Probability for nonreactive collisions also exhibits a threshold near $3 \times 10^{-4}$ eV (0.007 kcal/mol) associated with rotational excitation to LiF($v = 0, j = 1$). At low energies, the reaction probabilities are small, because quantum tunneling of the fluorine atom is the main reaction pathway. Vibrational excitation of LiF significantly enhances the reaction probability in the ultracold and cold regimes, for instance, an energy increase of 0.109 eV from LiF($v = 1, j = 0$) to LiF($v = 2, j = 0$) translates in a 350% increase of the reaction probability in the zero temperature limit. Our results also show a dense resonance structure in the energy dependence of the reaction probability at low energies associated with quasibound states of the $\text{H} \cdots \text{F} - \text{Li}$ and $\text{Li} \cdots \text{F} - \text{H}$ van der Waals complexes. Assignment of these resonances will be presented further in this study.

Cross sections for $s$-wave elastic scattering in $\text{H} + \text{LiF}(v = 0 - 2, j = 0)$ collisions are displayed in Fig. 2 as a function of the incident kinetic energy. For low translational energies, only $s$-wave scattering is expected to play a significant role. For collisions involving excited LiF reagents, elastic cross sections are found to have similar values for kinetic energies below $5 \times 10^{-3}$ eV. The nearly identical values of the limiting elastic cross sections for $v = 1$ and 2 suggest that vibrational excitation does not affect the isotropic
part of the interaction potential. In the zero-temperature limit, the scattering length can be expressed as a complex number, \( a_{vj} = \alpha_{vj} - i\beta_{vj} \), where the real and imaginary parts are related to the elastic component of the \( S \)-matrix, \( S_{vj}^{el} \), according to

\[
\alpha_{vj} = -\lim_{k_{vj}\to 0} \frac{\text{Im}(S_{vj}^{el})}{2k_{vj}},
\]

\[
\beta_{vj} = \lim_{k_{vj}\to 0} \frac{1 - \text{Re}(S_{vj}^{el})}{2k_{vj}},
\]

where \( k_{vj} \) is the wave vector in the incident channel. We found \( \alpha_{10} = +9.100 \, \text{Å} \) and \( \alpha_{20} = +9.159 \, \text{Å} \) for \( v = 1 \) and \( v = 2 \), respectively. However, for numerical reasons, the Wigner’s threshold law for inelastic reactive and nonreactive collisions, i. e.

\[
\sigma_{vj}^{in} = \frac{4\pi \beta_{vj}}{k_{vj}},
\]

is preferred over Eq. (4) to evaluate the imaginary part of the scattering length. In Eq. (5), \( \sigma_{vj}^{in} \) is the sum of the nonreactive and reactive cross sections. Using Eq. (5), we found \( \beta_{10} = 2.365 \times 10^{-4} \, \text{Å} \) and \( \beta_{20} = 3.478 \times 10^{-3} \, \text{Å} \) for \( v = 1 \) and \( v = 2 \), respectively. The total elastic cross section in the zero energy limit is given by

\[
\sigma_{vj}^{el} = 4\pi |a_{vj}|^2,
\]

which yields \( \sigma_{20}^{el} = 1054.05 \times 10^{-16} \, \text{cm}^2 \) and \( \sigma_{10}^{el} = 1040.58 \times 10^{-16} \, \text{cm}^2 \).

Initial-state-selected cross sections for HF formation and for nonreactive scattering in \( \text{H} + \text{LiF}(v = 0-2, j = 0) \) collisions are displayed in Fig. 3 as a function of the incident translational energy. For \( v = 1 \) and \( v = 2 \), reaction cross sections reach the Wigner regime \[60\] for kinetic energies below \( 10^{-5} \, \text{eV} \) in accordance with Eq. (5). Nonreactive scattering dominates over the complete kinetic energy range investigated, with a LiF/HF product branching ratio of 4 for \( v = 1 \) and 15 for \( v = 2 \) in the Wigner regime. For translational energies beyond \( 10^{-4} \, \text{eV} \), reaction cross sections are characterized by resonant spikes due to metastable states of the \( \text{H} \cdots \text{F} - \text{Li} \) and \( \text{Li} \cdots \text{F} - \text{H} \) van der Waals complexes. These resonances tend to be washed out for reactions with vibrational excited reactants.

Assignments of the resonances in the energy dependence of the reactive cross sections in \( \text{H} + \text{LiF}(v = 0-2, j = 0) \) collisions are presented in Table I. Bound- and quasi-bound states calculations have been performed for the \( \text{H} \cdots \text{F} - \text{Li} \) van der Waals potentials correlating
with the LiF(\(v = 0 - 2\)) 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 LiF 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 (FGH) method \[61, 62\]. 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 2000 points in the atom-molecule separation ranging from \(R = 0.1 - 100\) a\(_0\). Similar calculations for the Li···F−H exit channel complexes have been carried out previously \[20\] and results for the van der Waals potential correlating with the HF(\(v = 0\)) manifold were reported. Total energy values given in Table I are relative to separated H + LiF system with energy origin at the bottom of the LiF potential. Eigenenergies of the reactant and product diatoms calculated using the FGH and ABC codes were found to be consistent within an error margin of \(10^{-6}\) eV for both H + LiF and Li + HF asymptotes. The resonances in the H···LiF entrance channel van der Waals well are characterized by quantum numbers \((v, j, t)\), where \(v\) and \(j\) are the LiF vibrational and rotational quantum numbers, respectively, and \(t\) refers to the H−LiF(\(v, j\)) van der Waals stretching vibration; their primed counterparts refer to resonances originating from the Li···HF exit channel well. As shown in Table I the agreement between the FGH energy eigenvalues and the peak positions from our scattering calculations is excellent. For \(v = 0\), resonances are mostly due to the decay of \((v' = 0, j', t')\) metastable states of the Li···HF exit channel van der Waals complex, with \(j'\) and \(t'\) ranging from relatively high \(t'\)-values for \(j' = 1\) to the lowest-lying stretching vibrational states of \(j' = 5\). Resonances attributed to the H···LiF(\(v = 0, j = 10 - 15, t = 1 - 2\)) states also appear for reactants in this vibrational state. For \(v = 1\) and \(v = 2\), this tendency is reverted with a dominant imprint of resonances corresponding to low−\(t\) quasibound states of the adiabatic potentials correlating with \(j = 2 - 12\) of the entrance channel H···LiF complex. For these vibrationally excited states of the reagents, only few high-lying stretching vibrational states of the Li···HF exit channel van der Waals complex give rise to resonances: \(j' = 6\) for \(v = 1\) and \(j' = 9\) for \(v = 2\). Although the exit channel van der Waals well is much deeper than the entrance channel well, the Li···HF exit channel complex dominates only for \(v = 0\), while for higher vibrational levels of the reagents, the entrance channel complex plays the major role and the
signature of the exit channel quasi-bound states tends to disappear. It is also interesting to note that the resonances appear mostly in the reactive cross sections despite the fact that for \( v = 1 \) and 2 it is the entrance channel van der Waals potential that supports the resonances. Thus, it appears that the long lived resonances decay mostly by vibrational pre-reaction of the quasibound states by tunneling of the F atom.

The cumulative reaction probability for HF formation in \( H + LiF(v = 0−2, j = 0) \) collisions is depicted in Fig. 4 as a function of the total energy. CRP is represented over an energy range of 0.1 eV starting from the total energy values of the LiF \((v, j = 0)\) reagents, thus explaining the presence of thresholds at 0.0675 eV, 0.1673 eV and 0.2764 eV, respectively, for \( v = 0−2 \). The resonance structure still subsists in the CRP, but becomes less sharper with increase in energy and vibrational excitation.

The \( J = 0 \) contribution to the reaction rate coefficients for HF formation in \( H + LiF(v = 1, 2, j = 0) \) collisions is shown in Fig. 5. For \( v = 1 \), the reaction rate coefficient reaches the Wigner regime for temperatures below 0.1 K, with a finite value of \( 3.86 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \) in the zero-temperature limit. Vibrational excitation of HF to the \( v = 2 \) level enhances reactivity by about a factor of 4 in the cold and ultracold regimes. Although rate coefficients appear to be small at low temperatures, the values are not negligible compared to those for reactions involving tunneling of atoms lighter than fluorine. This suggests that heavy atom tunneling may play a major role at low energies, as observed recently by Zuev et al. for carbon tunneling in ring expansion reactions of 1-methylcyclobutylhalocarbenes at 8 to 25 K. In Fig. 5, for \( v = 1 \) and \( v = 2 \), the reactivity rapidly increases beyond 3 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

We have investigated the scattering dynamics of the \( H + LiF(X^1\Sigma^+, v = 0−2, j = 0) \rightarrow HF(X^1\Sigma^+, v', j') + Li(2S) \) reaction for zero total angular momentum. Using the coupled-channel hyperspherical coordinate method, probabilities, cross sections, and rate coefficients have been computed from the zero-temperature limit up to a translational energy of 0.1 eV using the most recent PES for the LiHF electronic ground state. Extensive calculations have been carried out for quasibound states in the entrance and exit channel van der Waals wells
to characterize the rich resonance structure observed in our scattering calculations. We found that the resonances arise from the decay of metastable states of both H···F−Li and Li···F−H van der Waals complexes. In particular, the quasibound states of the deep Li···F−H van der Waals well were found to strongly imprint the resonance structure for reactions involving LiF($v = 0, j = 0$). For vibrationally excited reagents, however, resonances are mainly originating from tunneling of metastable states of H···F−Li into the HF($v’ = 0$) product manifold. Consistent with our recent findings for the reverse reaction [20], chemical reactivity for H+LiF → HF+Li is enhanced by vibrational excitation of the reagents at low and ultralow temperatures. In contrast to Li+HF($v = 1, j = 0$), nonreactive processes dominate over HF formation in H+LiF($v = 0 − 2, j = 0$) collisions. However, quasibound states of the entrance channel van der Waals potential do decay through vibrational prereaction by tunneling of the fluorine atom. The results suggest that heavy atom tunneling at low temperatures may be more important than generally recognized, as observed recently by Zuev et al. [3] for carbon tunneling in ring expansion reactions.

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TABLE I: Assignment of the resonances in the energy dependence of the cross sections for HF formation in H + LiF\((v = 0 – 2, j = 0)\) collisions (energies in eV).

| \(v^a\) | Position\(^b\) | \(\text{H} \cdots \text{LiF}(v, j, t)\) | \(\text{Li} \cdots \text{HF}(v', j', t')\) |
|---|---|---|---|
| | | \(E_{v,j,t}^c\) | \(j^d\) | \(t^e\) | \(E_{v',j',t'}^c\) | \(v'^f\) | \(j'^g\) | \(t'^h\) |
| 0 | 0.0127 | 0.0690 | 0.0689 | 0 | 2 | 6 |
| 0 | 0.0132 | 0.0695 | 0.0692 | 10 | 1 | 11 |
| 0 | 0.0146 | 0.0709 | 0.0709 | 0 | 3 | 3 |
| 0 | 0.0157 | 0.0720 | 0.0718 | 0 | 1 | 12 |
| 0 | 0.0165 | 0.0728 | 0.0725 | 0 | 4 | 1 |
| 0 | 0.0175 | 0.0738 | 0.0737 | 0 | 2 | 7 |
| 0 | 0.0222 | 0.0785 | 0.0787 | 12 | 1 | 0.0786 | 0 | 3 | 4 |
| 0 | 0.0244 | 0.0807 | 0.0809 | 13 | 1 | 0.0804 | 0 | 2 | 9 |
| 0 | 0.0264 | 0.0827 | 0.0826 | 0 | 2 | 10 |
| 0 | 0.0272 | 0.0835 | 0.0836 | 0 | 4 | 1 |
| 0 | 0.0280 | 0.0843 | 0.0843 | 0 | 3 | 5 |
| 0 | 0.0298 | 0.0861 | 0.0868 | 14 | 1 |
| 0 | 0.0357 | 0.0920 | 0.0922 | 15 | 2 | 0.0920 | 0 | 5 | 1 |
| 0 | 0.0397 | 0.0960 | 0.0957 | 0 | 3 | 8 |
| 0 | 0.0437 | 0.1000 | 0.0992 | 0 | 4 | 4 |
| 0 | 0.0477 | 0.1040 | 0.1043 | 0 | 5 | 2 |
| 1 | 0.0003 | 0.1676 | 0.1675 | 2 | 2 |
| 1 | 0.0007 | 0.1680 | 0.1679 | 6 | 2 |
| 1 | 0.0018 | 0.1691 | 0.1690 | 3 | 2 |
| 1 | 0.0028 | 0.1701 | 0.1701 | 0 | 6 | 8 |
| 1 | 0.0033 | 0.1706 | 0.1705 | 4 | 2 |
| 1 | 0.0049 | 0.1722 | 0.1726 | 0 | 6 | 9 |
| 1 | 0.0061 | 0.1734 | 0.1733 | 8 | 1 |
| 1 | 0.0093 | 0.1766 | 0.1766 | 9 | 1 |
| 1 | 0.0131 | 0.1804 | 0.1802 | 10 | 1 |
| 1 | 0.0177 | 0.1850 | 0.1856 | 11 | 1 |
| 1 | 0.0235 | 0.1908 | 0.1896 | 12 | 1 |
| 2 | 0.0010 | 0.2774 | 0.2772 | 6 | 1 |
| 2 | 0.0029 | 0.2793 | 0.2794 | 7 | 1 |
| 2 | 0.0046 | 0.2810 | 0.2807 | 0 | 9 | 6 |
| 2 | 0.0056 | 0.2820 | 0.2822 | 8 | 1 |
| 2 | 0.0095 | 0.2859 | 0.2854 | 9 | 1 |
| 2 | 0.0118 | 0.2882 | 0.2889 | 10 | 1 | 0.2880 | 0 | 9 | 8 |
| 2 | 0.0168 | 0.2932 | 0.2936 | 11 | 1 |
| 2 | 0.0225 | 0.2989 | 0.2985 | 12 | 1 |

\(^a\)LiF vibrational quantum number.

\(^b\)Position of the observed resonances. Total energy, \(E_{\text{tot}}\), is relative to separated H + LiF system with energy zero corresponding to the bottom of the LiF potential.

\(^c\)Binding energies \(E_{v,j,t}^c\) and \(E_{v',j',t'}^c\) are calculated with the Fourier grid Hamiltonian method in the H\(\cdots\)LiF and Li\(\cdots\)HF van der Waals wells, respectively.

\(^d\)LiF rotational quantum number.

\(^e\)Quantum number for the H – LiF\((v, j)\) van der Waals stretching vibration.

\(^f\)HF vibrational quantum number.

\(^g\)HF rotational quantum number.

\(^h\)Li rotational quantum number.
FIG. 1: Initial state-selected probability for HF formation (solid curve) and for non-reactive scattering (dashed curve) in H + LiF\((v = 0 - 2, j = 0)\) collisions as a function of the total energy.

FIG. 2: Elastic cross sections for \(s\)-wave scattering in H + LiF\((v = 0 - 2, j = 0)\) collisions as a function of the incident kinetic energy. Solid curve: \(v = 0\); dotted curve: \(v = 1\); dashed curve: \(v = 2\).

FIG. 3: Cross sections for HF formation and nonreactive scattering in H + LiF\((v = 0 - 2, j = 0)\) collisions as a function of the incident kinetic energy. solid curve: HF product channel; dashed curve: nonreactive scattering.

FIG. 4: Cumulative reaction probability for HF formation in H + LiF\((v = 0 - 2, j = 0)\) collisions as a function of the total energy. Solid curve: \(v = 0\); dotted curve: \(v = 1\); dashed curve: \(v = 2\).

FIG. 5: Temperature dependence of reaction rate coefficients for HF formation and nonreactive vibrational quenching in Li + HF\((v = 1, 2, j = 0)\) collisions.
Cross section ($10^{-16}$ cm$^2$)

Kinetic energy (eV)

$\nu = 0$

$\nu = 1$

$\nu = 2$
