Attack and Recoil Angle Dependence of the Li + HF → LiF + H Reaction at $J = 0$

Marcelo P. de Miranda*

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154,
13083-970 Campinas, SP, Brazil

Stefano Crocchianti and Antonio Laganà

Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy

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This article presents a quantum theoretical study of the attack-angle dependence and the recoil-angle selectivity in the title reaction. Two complementary approaches were used: the preferred attack angle method and the examination of spatial distributions of molecular axes associated with either minimal- or maximal-probability reactions. These approaches were extended so that recoil angles could be included in the stereodynamical analysis. Our results were compared to those obtained by Alvariño et al. with the stereodirected representation (*J. Phys. Chem. A* **1998**, *102*, 9638). This allowed for an assessment of the advantages and disavantages of each method. The reaction was confirmed to be highly dependent on the attack angle and highly selective with regard to the recoil angle. The attack angle dependence is itself highly dependent on the total energy and on the product vibrational state, but the recoil angle selectivity is not.

1. Introduction

What are the roles of mutual orientations and relative directions of motion of reagents and products in the molecular mechanisms of chemical reactions? This is the basic question we ask ourselves while studying chemical reaction stereodynamics, and it is currently addressed in one of two different ways.[1−3] In the "rotational polarization" scheme, the reagent-approach and product-recoil directions are correlated to the spatial distributions of the rotational angular momenta of reagents and products.[3−7] If these rotational angular momentum distributions are anisotropic, we can say that the reaction mechanism favors particular planes and directions of molecular rotation.[5−7] In the "molecular polarization" scheme, on the other hand, the reagent-approach and product-recoil directions are correlated to the spatial distributions of the molecular axes of reagents and products, not to the spatial distributions of their rotational angular momenta.[1,2,7−12] If the molecular axes distributions are anisotropic, we can say that the reaction mechanism favors particular relative orientations among the molecules of reagents and products.[9−11]

In this article, we report a quantum theoretical study of the stereodynamics of the atom−diatom reaction

$$\mathrm{Li}(^2\mathrm{S}) + \mathrm{HF}(^1\Sigma^+) \rightarrow \mathrm{LiF}(^1\Sigma^+) + \mathrm{H}(^2\mathrm{S}) \qquad (1)$$

at total angular momentum $J = 0$ and total energy $E_\mathrm{T} = 0.45$−0.54 eV. We have analyzed the reaction stereodynamics according to the molecular polarization scheme and used two complementary approaches recently introduced by Miranda and Gargano:[11] the "preferred attack angle" (PAA) method and the exam of spatial distributions of molecular axes associated with either minimal- or maximal-probability reactions. Our goal was to study the correlations tying the reaction probability to the attack angle Θ^k of Li relative to HF, and to the recoil angle $\Theta^{k'}$ of H relative to LiF (see Figure 1 for a sketch of the definitions of the attack angle Θ^k and the recoil angle $\Theta^{k'}$).

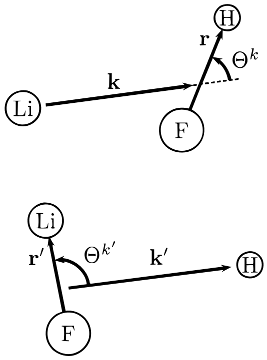

Figure 1. Definitions of the attack angle Θ^k and recoil angle $\Theta^{k'}$. **k** and **k′** are the reagent-approach and product-recoil directions, respectively, while **r** and **r′** are the interatomic axes of HF and LiF. Li attack on the F end of HF corresponds to $\Theta^k = 0$, while Li attack on the H end of HF corresponds to $\Theta^k = 180°$. H recoil from the Li end of LiF corresponds to $\Theta^{k'} = 0$, while H recoil from the F end of LiF corresponds to $\Theta^{k'} = 180°$.

The stereodynamics of the Li + HF reaction has been the subject of both experimental[13−16] and theoretical[9,10,15−18] studies, and it is now known that the reaction probability can be strongly dependent on the attack angle. Different aspects of such dependence have been observed experimentally,[14−16] in quasi-classical trajectory calculations[16,17] and in quantum studies either at zero total angular momentum[9,10] or within the framework of the centrifugal sudden approximation.[18] The results by Alvariño et al.[9,10] are particularly relevant to the present work, for those authors have also calculated the attack-angle dependence and the recoil-angle selectivity of the reaction at $J = 0$. Furthermore, their calculations, just like our own, were based on the scattering

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* Corresponding author. Present address: Department of Chemistry, New York University, New York, NY 10003-6688. E-mail: miranda@quantum.chem.nyu.edu.

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matrices obtained by Parker and co-workers (see refs 19 and 20; the latter also describes the potential energy surface for the reaction). In their stereodynamical analysis, however, Alvariño et al. have used the "stereodirected" (SD) representation developed by Aquilanti and co-workers.[8] The results obtained by Alvariño et al. are directly comparable to ours, and such comparison provides an ideal test case for the different methods of stereodynamical analysis since the dynamical calculations are the same. A similar comparison has been made for the Na + HF reaction, but in that case only the attack angle was considered.[11]

This paper is organized as follows. In section 2 we present the methods we used to extract stereodynamical information from the scattering matrices. We describe the PAA method and the procedure used in the exam of minimal- and maximal-probability reactions and show how they can be used when one also wants to study the recoil angle selectivity. Because of its relevance for the comparison of our results to those by Alvariño et al., we also give a short description of the SD representation. In section 3 we present and discuss our results, and concluding remarks close the paper in section 4.

2. Stereodynamical Analysis

In classical mechanics the specification of well-defined spatial orientations of molecular axes and well-defined attack angles poses no problem. In quantum mechanics this is not the case.[12] The best one can do is to specify spatial distributions of the molecular axis that *according to chosen criteria* can be related to particular, "nominal" values of the attack angle.[8,12]

There are three quantum methods currently used to study the attack angle dependence of the reaction probability: the stereodirected representation,[8−10] the prefered attack angle method,[11] and the exam of the spatial distributions of the molecular axis associated to either minimal- or maximal-probability reactions.[11] These three methods also allow for the exam of the recoil angle selectivity and are described below.

2.1. Stereodirected (SD) Representation. The transformation between the helicity representation and the stereodirected representation scattering matrices reads[8−10]

$$S^{J}_{\Omega'\nu',\Omega\nu} = \sum_{j,j'} G^{j'_{\max}\Omega'}_{j'\nu'}\, S^{J}_{j'\Omega',j\Omega} G^{j_{\max}\Omega}_{j\nu} \tag{2}$$

where J, j, Ω, and ν are the total angular momentum, rotational angular momentum, helicity, and steric quantum numbers, and $j_{\max}$ is the maximum value j can take considering all open channels at a given total energy. Unprimed symbols apply to reagents and primed symbols apply to products. Although not explicit in the notation, the scattering matrix elements are also labeled by total energy, parity and vibrational quantum numbers. The transformation coefficients $G^{j_{\max}\Omega}_{j\nu}$ are given by[8−10]

$$G^{j_{\max}\Omega}_{j\nu} = (-1)^{j-\nu+[(j_{\max}-\Omega)/2]} \sqrt{\frac{2}{1+\delta_{\nu 0}}} \left\langle \frac{j_{\max}-\Omega}{2}\nu, \left(\frac{j_{\max}+\Omega}{2}-\nu\right) \middle| j\, 0 \right\rangle \tag{3}$$

where $\langle ..,..|..\rangle$ is a Clebsch−Gordan coefficient in the notation of Zare.[21]

Note that in the stereodirected representation the definition of quantum states involves helicity and steric quantum numbers, but not rotational quantum numbers. The stereodirected states are coherent superpositions of rotational states.

Equations 2 and 3 imply that in the SD formalism the spatial distribution of the interatomic axis of the diatomic at given values of ν and Ω is given by

$$\rho_{\mathrm{SD}}(\Theta^k,\Phi^k) = |\sum_{j} G^{j_{\max}\Omega}_{j\nu} Y_{j\Omega}(\Theta^k,\Phi^k)|^2 \tag{4}$$

where $Y_{j\Omega}(\Theta^k,\Phi^k)$ are spherical harmonics and the polar angles Θ^k and Φ^k are defined in a body-fixed frame where the z axis is parallel to the reagent-approach direction. According to Aquilanti and co-workers,[8−10] in the classical limit this distribution tends to a δ function centered on

$$\cos \Theta^k_\nu = \frac{2\nu}{j_{\max}+1} \tag{5}$$

This relation defines the nominal value of the attack angle that corresponds to a given steric quantum number ν, and equations entirely analogous to (3)−(5) define the nominal value of the recoil angle corresponding to the product steric quantum number ν'. The (ν, ν')-dependent reaction probability can be obtained from the squared moduli of the scattering matrix elements in the usual way,[8−10] and describes the attack and recoil angle dependence of the reaction.

2.2. Preferred Attack Angle (PAA) Method. The PAA method is based on an alternative definition of the distribution function $\rho(\Theta^k,\Phi^k)$, also related to a coherent superposition of rotational states. If the reagents' state is

$$|\Psi^{\mathrm{R}}_{v}\rangle = \sum_{j,\Omega} c_{j\Omega} |j\Omega\rangle \tag{6}$$

(where $c_{j\Omega}$ are coefficients satisfying $\sum_{j,\Omega}|c_{j\Omega}|^2 = 1$), then the spatial distribution of the internuclear axis of the reagent diatomic is given by

$$\rho(\Theta^k,\Phi^k) = |\sum_{j,\Omega} c_{j\Omega} Y_{j\Omega}(\Theta^k,\Phi^k)|^2 \tag{7}$$

and the formula for the reaction probability (at a given vibrational level of the reagent and for a particular product state) reads

$$P_{v'j'\Omega'\leftarrow v} = |\sum_{j,\Omega} c_{j\Omega} S^{J}_{j'\Omega',j\Omega}|^2 \tag{8}$$

If the $c_{j\Omega}$ coefficients are those that maximize $\rho(\Theta^k,\Phi^k)$ *at chosen values of* Θ^k and Φ^k, then this distribution function is related to a preferred attack angle even in the quantum regime. We represent the distribution functions thus obtained by $\rho_{\mathrm{PAA}}(\Theta^k,\Phi^k)$. Note that in the PAA method the nominal value of the attack angle is not quantized: unless the maximization fails, $\rho_{\mathrm{PAA}}(\Theta^k,\Phi^k)$ can be obtained at any Θ^k_{nom} value.

Figure 2 compares the distribution functions $\rho_{\mathrm{SD}}(\Theta^k,\Phi^k)$ and $\rho_{\mathrm{PAA}}(\Theta^k,\Phi^k)$ at four different nominal values of the attack angle. These distributions were obtained with $j_{\max} = 9$ (that is the actual value of $j_{\max}$ for the Li + HF reaction at $E_{\mathrm{T}} = 0.50-0.53$ eV) and $\Omega = 0$ (which makes them Φ^k-independent). The figure shows that the two distributions are quite similar when Θ^k_{nom} is close to 90°, but quite different when Θ^k_{nom} is not close to 90°.

If the products' state is written as

$$|\Psi^{\mathrm{P}}_{v'}\rangle = \sum_{j',\Omega'} c_{j'\Omega'} |j'\Omega'\rangle \tag{9}$$

(where $c_{j'\Omega'}$ are coefficients satisfying $\sum_{j',\Omega'}|c_{j'\Omega'}|^2 = P_{v'}$), comparison with eq 8 shows that

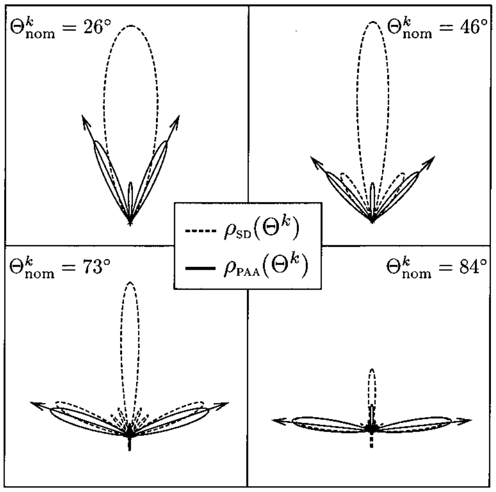


Figure 2. Polar plots of the axial distribution functions $\rho_{\rm SD}(\Theta^k)$ and $\rho_{\rm PAA}(\Theta^k)$ at four different nominal values of the attack angle, with arrows giving a pictorial indication of the $\Theta^k_{\rm nom}$ value. The $\rho_{\rm SD}(\Theta^k)$ function is used in the stereodirected (SD) representation, while $\rho_{\rm PAA}(\Theta^k)$ is used in the preferred attack angle (PAA) method. The distributions shown here were obtained with $j_{\max} = 9$ (which is the actual $j_{\max}$ value for the Li+HF reaction at $E_{\rm T} = 0.50-0.53$ eV) and $\Omega = 0$, and are Φ^k-independent. In the classical limit all distributions tend to δ functions centered on the nominal value of the attack angle.

$$c_{j'\Omega'} = \sum_{j,\Omega} c_{j\Omega} S^J_{j'\Omega',j\Omega} \qquad (10)$$

Given the coefficients $c_{j'\Omega'}$, the recoil angle distribution $\rho_{\rm PAA}(\Theta^{k'},\Phi^{k'})$ can be calculated by use of an expression analogous to eq 7. Notice that in this case the PAA method deals with the actual recoil angle distribution, not with nominal values of $\Theta^{k'}$ and $\Phi^{k'}$. This is another difference between the PAA method and the SD representation.

The SD and PAA representations are both exact in some sense and can be expected to give qualitatively similar descriptions of the reaction stereodynamics. We have just seen, however, that there are important conceptual differences between them. These differences will in general lead to a quantitative disagreement that will be larger in the quantum regime and at nearly collinear configurations (attack or recoil angles far from 90°), and smaller in the correspondence principle limit and at nearly perpendicular configurations (attack or recoil angles close to 90°).

If the quantitative disagreement between the SD and PAA results becomes relevant, it becomes necessary to pay more attention to the interpretation of the results. It will then be useful to remember in what sense are the SD and PAA results are exact. The SD results are exact if stated in terms of steric quantum numbers, but not if stated in terms of attack and recoil angles. This is so because the expression relating steric quantum numbers to attack or recoil angles, eq 5, is not strictly valid unless the correspondence principle limit has been attained. On the other hand, the PAA method expresses the stereodynamics directly in terms of attack and recoil angles. Therefore, and in contrast to the SD case, PAA results *are* exact if expressed in terms of attack and recoil angles. It must, however, be kept in mind that a nominal value of Θ^k does not imply a single value for it. Rather, what one actually has is a distribution of attack angles which has a maximum at $\Theta^k_{\rm nom}$.

2.3. Minimal- and Maximal-Probability Reactions. Choosing the coefficients $c_{j\Omega}$ in eqs 6−8 so that *the reaction probability* is either minimum or maximum, one can use eq 7 to examine the attack angle distributions $\rho_{\min}(\Theta^k,\Phi^k)$ and $\rho_{\rm MAX}(\Theta^k,\Phi^k)$ associated with minimal- or maximal-probability reactions. One can also use eq 10 and the products-side equivalent of eq 7 to examine the recoil angle distributions $\rho_{\min}(\Theta^{k'},\Phi^{k'})$ and $\rho_{\rm MAX}(\Theta^{k'},\Phi^{k'})$. Note that here neither attack nor recoil angles are defined in terms of nominal values.

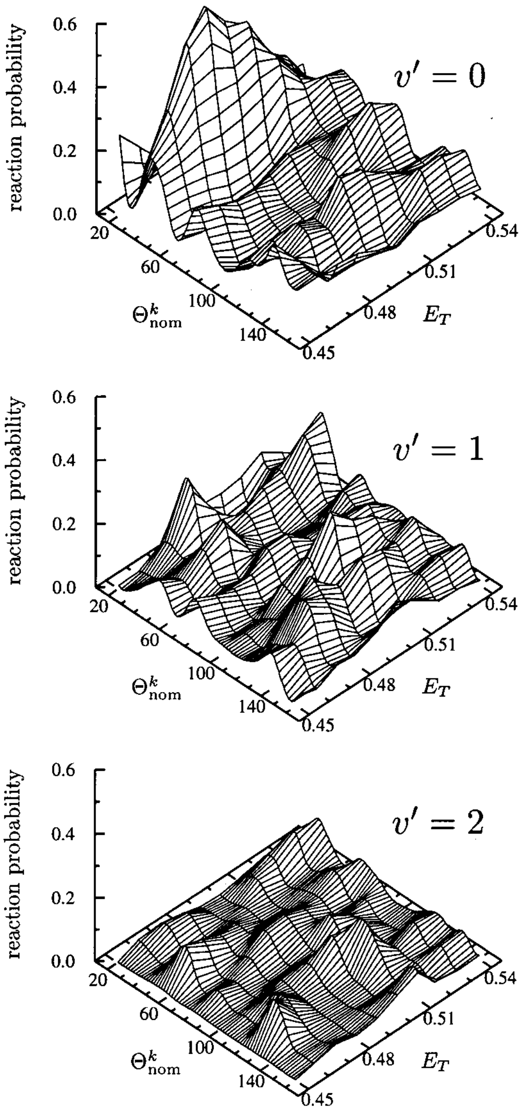


Figure 3. Li + HF(v=0) → LiF(v') + H reaction probability as a function of total energy and nominal attack angle according to the PAA method. Total energies in eV, attack angles in degrees.

3. Results

The results we present below refer to the Li + HF → LiF + H reaction with HF in its ground vibrational state and are summed over LiF rotational states but resolved with regard to LiF vibrational state. In the total energy range we have considered ($E_{\rm T} = 0.45-0.54$ eV) HF cannot be vibrationally excited. The $J = 0$ condition imposes $\Omega = \Omega' = 0$, which in turn implies that all our results are Φ^k- and $\Phi^{k'}$-independent.

Figure 3 presents plots of the reaction probability as a function of total energy and nominal attack angle according to the PAA method. The nominal values of the attack angle are restricted to the range $20° \le \Theta^k_{\rm nom} \le 160°$ because for values of $\Theta^k_{\rm nom}$ closer to 0 or 180° the maximization procedure led to $\rho_{\rm PAA}(\Theta^k)$ distributions whose maxima were at $\Theta^k = 0$ or 180°, not at the specified $\Theta^k_{\rm nom}$ values.

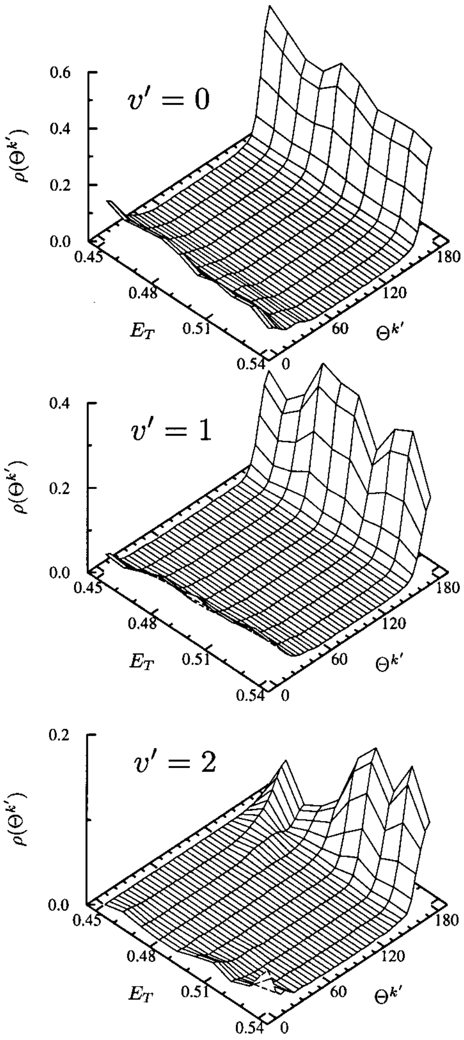


Figure 4. Recoil angle distributions produced by Li + HF(v=0) → LiF(v') + H reactions as a function of total energy. The reagents state was taken to be an incoherent superposition of HF rotational states in which each j level was equally probable. Total energies in eV, recoil angles in degrees.

Figure 3 shows that the reaction probability decreases with product vibrational excitation and that the strongest steric effect is found when reactions at $E_T = 0.48$ eV form LiF in its ground vibrational state. In this case the reaction probability has a pronounced peak at $\Theta^k_{nom} \approx 40°$ and is relatively low at other nominal attack angles within the 20°−160° range. This indicates preference for Li attack on the F end of HF. Note, however, that we are not considering head-on collisions; this attack angle of 40° is intermediate between the head-on ($\Theta^k = 0$) and side-on ($\Theta^k = 90°$) limits.

We now turn to the recoil angle distribution. Figure 4 shows results for Li + HF(v=0) → LiF(v') + H reactions in which the reagents' state is an incoherent superposition of HF rotational states with each j level being equally probable. It is clear that the reaction favours collinear or nearly-collinear recoil configurations, and in particular those in which the H atom exits from the F side of LiF.

The results in Figures 3 and 4 can be compared to those obtained by Alvariño and co-workers with the stereodirected representation.[9,10] This is done in Figure 5. It is seen that the qualitative description of the stereodynamics is the same, but that there are quantitative disagreements. Since both calculations have used the same set of scattering matrices, the only source of disagreement is the stereodynamical representation.

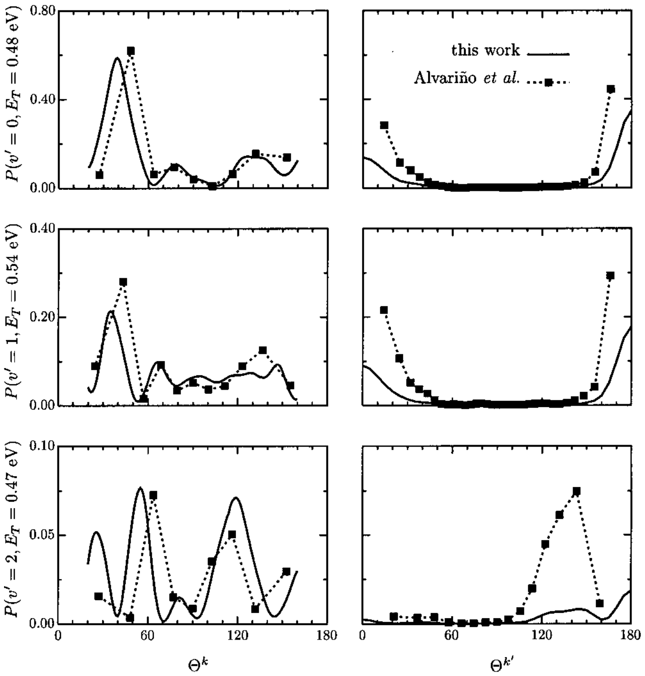


Figure 5. Attack angle dependence (left column) and recoil ngle distributions (right column) of Li + HF(v=0) → LiF(v') + H reactions at selected values of the total energy. Solid lines represent results obtained with the PAA method, squares and dotted lines represent the results obtained by Alvariño and co-workers with the stereodirected representation.[9,10] Attack and recoil angles in degrees.

In the case of the attack-angle dependence, the quantitative disagreement between the results obtained with the PAA method and the SD representation is due to the differences between the attack-angle distributions $\rho_{SD}(\Theta^k)$ and $\rho_{PAA}(\Theta^k)$ associated with a given nominal value of the attack angle. As seen in section 2 and Figure 2, these two distributions get increasingly different as Θ^k_{nom} gets further away from 90°.

In the case of recoil-angle distributions, the quantitative disagreement can also be attributed to the different stereodynamical representations. While in our approach the actual recoil angle distribution generated by the reaction is directly considered, in the SD representation the recoil angles are represented by nominal values $\Theta^{k'}_{nom}$ and their corresponding $\Theta^{k'}$ distributions in exactly the same way as the attack angles. As in the attack-angle case, the two representations become identical only when eq 5 becomes strictly valid: in the correspondence principle limit.

Let us now consider the correlation between the attack and recoil angles. Figure 6 shows the recoil angle distributions obtained when the nominal value of the attack angle (determined according to the PAA method) is varied between 20° and 160°. The total energies and final vibrational states selected for this figure are the same ones considered in Figure 5.

We have already mentioned the strong steric effect found for reactions leading to $v' = 0$ at $E_T = 0.48$ eV, which are favored by attack angles close to 40°. Figure 6 shows that such reactions favor recoil angles close to 180° but that recoil angles close to 0 are also relevant for the reaction mechanism. This suggests that a simple and direct mechanism (Li attack on the F side of HF, H exit on the F side of LiF) dominates the reaction but that a more complex mechanism (involving LiF rotation before the H atom is expelled) is also relevant.

In the $E_T = 0.54$ eV, $v' = 1$ case, side-on attack correlates with H exit on the F side of LiF, while head-on attack on either

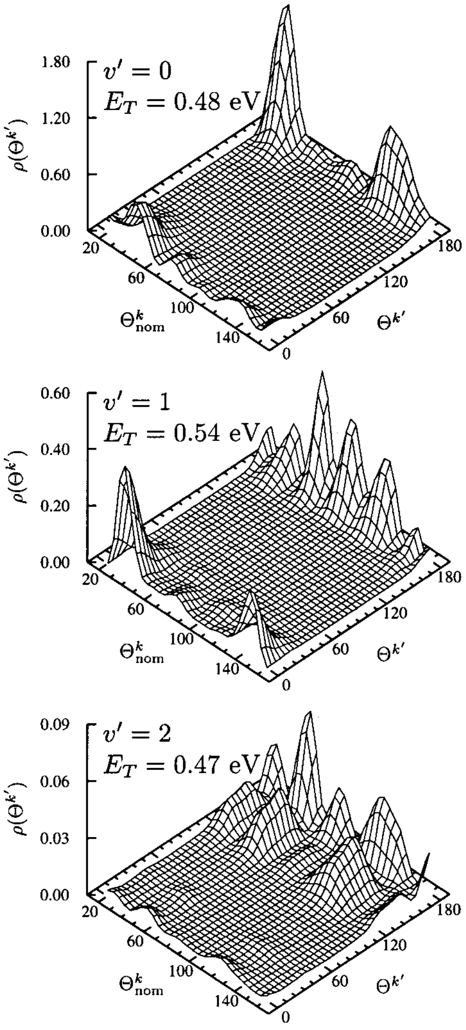


Figure 6. Recoil angle distributions as functions of nominal attack angle (determined according to the PAA method) for Li + HF(v=0) → LiF(v') + H reactions at selected values of the total energy.

end of HF correlates with H exit on the Li side of LiF. This is further evidence for the presence of a relatively complex mechanism.

We have found that recoil angles close to 180° are typical of the Li + HF reaction under the conditions we have considered and that recoil angles close to zero, although seldom dominant, are also often observed. What is not typical is the behavior found for reactions leading to $v' = 2$ at $E_T = 0.47$ eV. The curious appearance of maxima of $\rho(\Theta^{k'})$ at recoil angles in the 120°–150° range has not been observed for other combinations of total energy and product vibrational state.

Let us now consider the reaction stereodynamics from the point of view of minimal- and maximal-probability reactions. We start with the influence of stereochemical effects on the reaction probability: Figure 7 shows Li + HF(v=0) → LiF(v') + H reaction probabilities calculated with or without maximization (the reagents' state in the "unmaximized" case is an incoherent superposition of HF rotational states with each j level being equally probable). Minimized reaction probabilities are all of the order of 10^{-5} or smaller and are not shown in Figure 7.

From the data we have just presented it is clear that a suitable choice of the reagents' state can dramatically change the reaction probability. In the $v' = 0$ case this is particularly so: the probability can vary from a minimum of less than 10^{-5} to a maximum value close to unity.

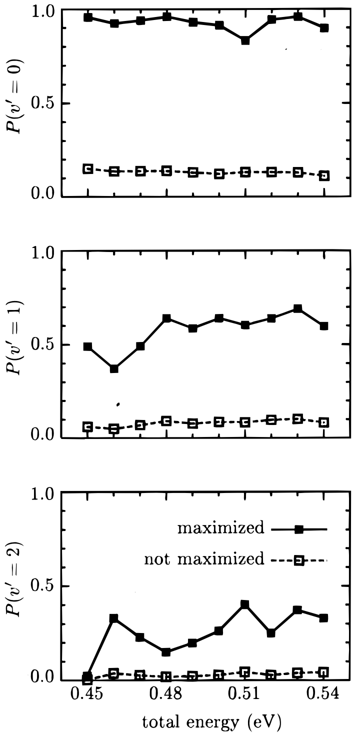


Figure 7. Li + HF(v=0) → LiF(v') + H reaction probabilities obtained with and without use of the reaction probability maximization procedure described in section 2. Minimized reaction probabilities (not shown in the figure) are of the order of 10^{-5} or smaller.

Are there stereochemical effects associated with these large variations of the reaction probability? Figures 8–10 help us answer this question. They present the attack and recoil angle distributions associated with minimal and maximal-probability reactions.

Comparison between the attack or recoil angle distributions associated with either minimum or maximum reaction probability shows that stereochemical effects do play an important role in the reaction dynamics. Consider, for instance, the recoil angle distributions. Reactions whose probability is maximum invariably lead to preferential collinear H recoil from the F side of LiF ($\Theta^{k'} = 180°$). In the case of minimal-probability reactions this is not necessarily so: H recoil from the F side of LiF becomes less important, and for several combinations of E_T and v' one finds minimal-probability reactions dominated by H recoil from the Li (not F) side of LiF ($\Theta^{k'} = 0$).

Figures 8–10 also show that HF orientation can have an important effect on the reaction probability. At $E_T = 0.48$ eV, for instance, reactions producing LiF in its ground vibrational state with maximum probability ($P = 0.96$) are dominated by Li attack on the F side of HF. The preferred attack angle is $\Theta^k = 0$, and the contribution of attack angles $\Theta^k \approx 40°$ is also important. On the other hand, minimal-probability reactions leading to the $v' = 0$ state of LiF at $E_T = 0.48$ eV (they have $P = 2 \times 10^{-5}$) are dominated by Li attack on the H (not F) side of HF ($\Theta^k = 180°$). Similar observations about the influence of the attack angle on the reaction probability can be made for other combinations of E_T and v' values.

It is also interesting to correlate the results in Figures 8–10 to those in Figures 3 and 4. According to Figure 3, at $E_T = 0.48$ eV there is a maximum of the $v' = 0$ reaction probability as a function of the nominal attack angle at $\Theta^k_{\rm nom} \approx 40°$. Figure 8 shows that at this energy the maximal-probability $v' = 0$ reaction indeed has a strong contribution of attack angles

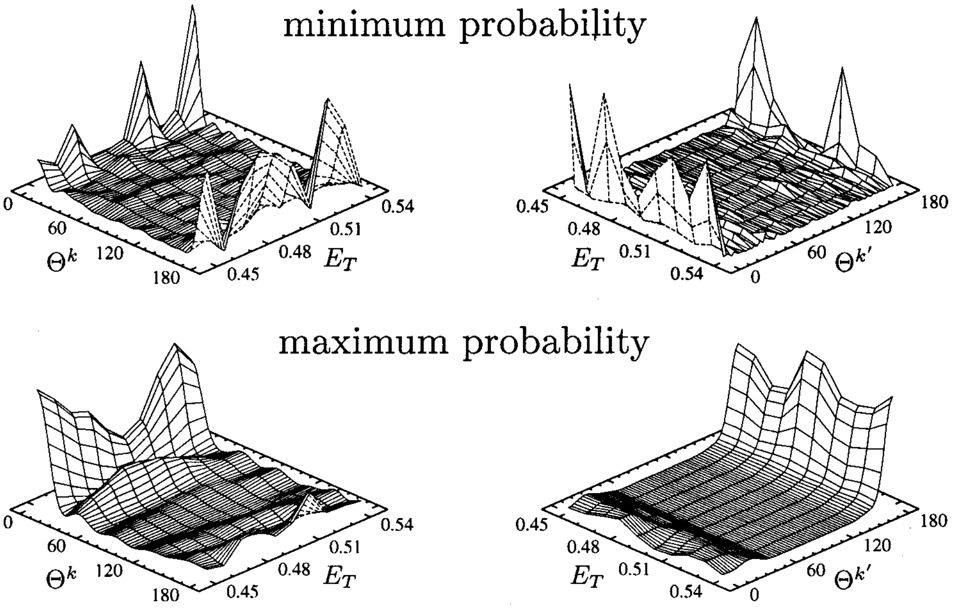


Figure 8. Attack (Θ^k) and recoil ($\Theta^{k'}$) angle distributions associated with minimal- and maximal-probability Li + HF(v=0) → LiF(v'=0) + H reactions as a function of total energy. Total energies in eV, angles in degrees.

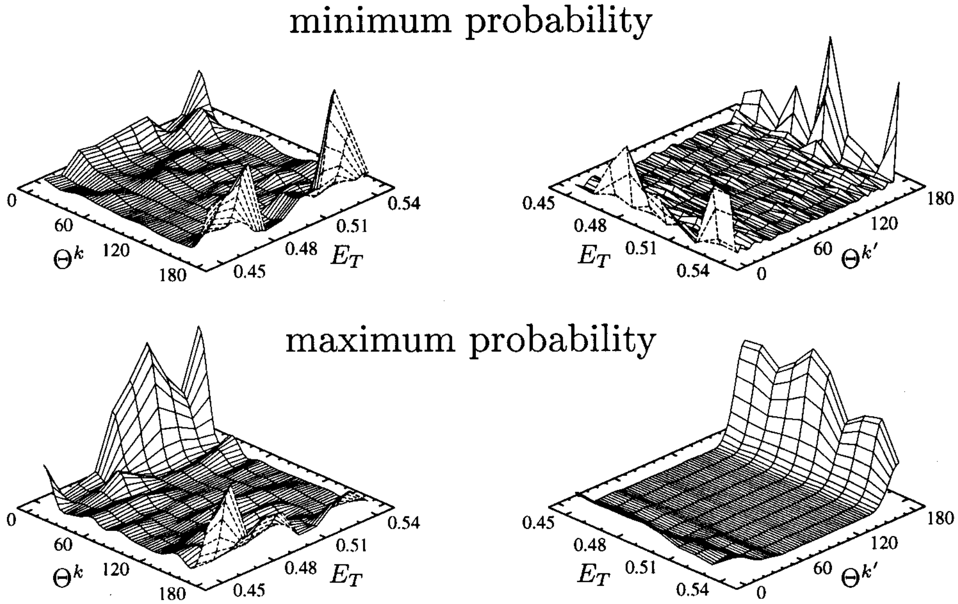


Figure 9. As in Figure 8, but for the $v' = 1$ state of LiF.

around $\Theta^k = 40°$, while in the case of the minimal-probability $v' = 0$ reaction the contribution of attack angles around $\Theta^k = 40°$ is very small. Analogous observations can be done at other energies, product states, and attack or recoil angles. The results obtained with the PAA method are consistent with those obtained by analysis of minimal- and maximal-probability reactions.

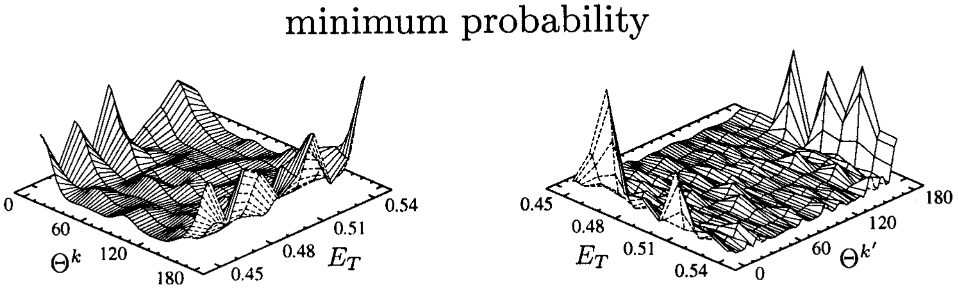
4. Conclusion

Our results confirm the main observations made by Alvariño et al. in their previous studies of the stereodynamics of the Li+HF reaction at $J = 0$:[9,10] the reaction is highly dependent on the attack angle, and highly selective with respect to the recoil angle. The attack-angle dependence of the reaction is itself strongly dependent on total energy and product vibrational state. The recoil-angle selectivity, on the other hand, is not seriously affected by E_T or v'; collinear H recoil from the F end of LiF is always dominant.

The results obtained with the prefered attack angle (PAA) method are qualitatively similar to those obtained with the stereodirected (SD) representation by Alvariño et al.,[9,10] but in quantitative terms the agreement is not as good. Since our calculations were based on the same set of scattering matrices as those by Alvariño and co-workers, the only sources of disagreement are the different stereodynamical representations.

The quantitative disagreement between the PAA and SD results becomes more pronounced for attack and recoil angles not close to 90° and appears because under the conditions we have considered the Li + HF reaction is far from the classical limit. Under such regime the criterion used in the SD representation for relating the steric quantum numbers to nominal values of the attack and recoil angles, eq 5, cannot be totally satisfactory. In the classical limit the PAA and SD approaches should lead to identical results.

The examination of minimal- and maximal-probability reactions furnished a complementary picture of the correlation tying



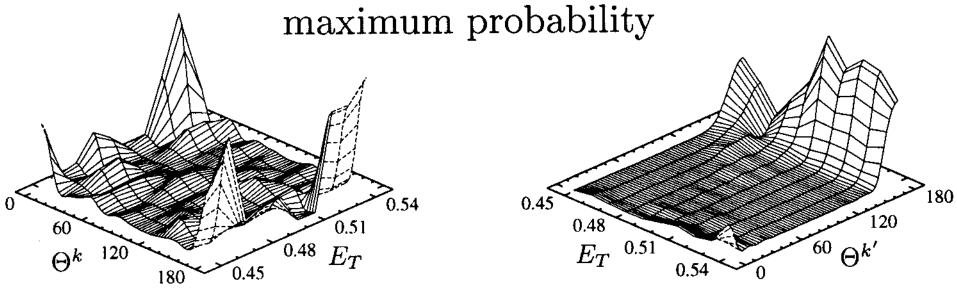


Figure 10. As in Figure 8, but for the $v' = 2$ state of LiF.

the reaction probability to the attack and recoil angles. On one hand, it allowed us to access the importance of head-on collisions between the lithium atom and either the hydrogen or the fluorine ends of HF; this could not be done with the stereodirected representation or the PAA method. On the other hand, the exam of minimal- and maximal-probability reactions allowed us to consider actual attack angles, not only their nominal values.

The methods of stereodynamical analysis we have used (the PAA method and the analysis of minimal- and maximal-probability reactions) were first introduced in ref 11. Here we have extended them so that recoil angles could also be considered. In our opinion these methods have some advantages when compared to the SD representation. The analysis of minimal- and maximal-probability reactions allows for a direct consideration of the actual attack and recoil angles and does not require the definition of "nominal" values of such angles. Furthermore, it also allows for the examination of collinear or nearly-collinear reagent-approach and product-recoil conformations, which may not be possible when the PAA method is used for the analysis of attack angles or the SD representation for the analysis of attack or recoil angles. As for the PAA method, its main advantages with regard to the SD representation are that (i) it does not require the definition of nominal recoil angles, (ii) the definition of nominal attack angles is valid regardless of the proximity of the classical limit, and (iii) it describes the reaction probability as a continuous function of the attack angle.

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