Accurate 3D quantum reactive probabilities of Li+FH

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Accurate three-dimensional quantum reactive scattering calculations have been carried out at zero total angular momentum (J=0) for the "three-different-atom non-collinearly dominated" Li+HF reaction. The main features of the reactive probability for reactants in the ground vibrational state are discussed.

1. Introduction

The calculation of accurate detailed quantum 3D reactive probabilities for the Li+HF system is interesting both per se and as a case study of the reactive dynamics of generic elementary atom-diatom reactions. In fact, the reaction

$$Li + HF(v, j) \rightarrow LiF(v', j') + H, \qquad (1)$$

in addition to being of interest for modelling chemical components of some modern technologies [1], has one of the lightest "three-different-atom mass combinations and a non-collinear" transition state. These two features make the Li + FH system a fairly general prototype of the A + BC elementary reactions presently affordable using available computer technology.

Experimental investigations of this reaction have been carried out using molecular beams. Reactive differential cross sections and time of flights for v=0have been measured [2]. The effects on the reactivity of this system of increasing the vibrational energy and aligning the target have also been investigated [3]. On the theoretical side, ab initio calculations have been carried out at a number of nuclear geometries sufficient to give a detailed representation of the potential energy surface (PES) [4] and fitted using different analytical representations [5-8]. Several dynamical investigations have been performed on these surfaces using both quasiclassical and reduced dimensionality quantum techniques [9-26].

More recently, improved estimates of the potential energy at the stationary points of the surface have been obtained from new ab initio calculations [27] and incorporated into a new fitted PES. On this PES, when Li approaches FH, a weakly bound triatom stabilized by a -0.302 eV well (the energy zero is set at the reactant asymptote) located early in the entrance channel can be formed. When the Li atom gets closer, the minimum energy path goes through a barrier of 0.182 eV. Before reaching the product asymptote (0.157 eV) the minimum energy path goes through both an other little well and another small barrier confined within a narrow window around the transition state angle. However, when the zero-point energies are included, the product asymptote lies 0.043 eV below that of reactants, meaning that the reactive process is quantally exoergic.

In this Letter we report the first converged, accurate quantum calculations of the reactive probabilities of reaction (1) and a preliminary discussion of their main features.

2. The calculations

In our approach, scattering equations are written using the APH formalism [28-30]. The related Schrödinger equation is solved by expanding the global wavefunction in terms of a product of Wigner rotational functions times surface functions of the two hyperangles θ and χ . After averaging over the five hyperangles, the resulting coupled differential equations in ρ are integrated by propagating the solution through the different sectors (via an intrasector adiabatic propagation).

The related computational procedure is articulated in the following steps:

(1) computation of fixed ρ surface functions and eigenvalues;

(2) construction of the overlap matrix between surface functions of adjacent sectors;

(3) evaluation of the coupling matrix for all values of the propagation grid;

(4) propagation of the solution along ρ from near the origin to the asymptotes;

(5) determination of the fixed energy (E) detailed state (vj) to state (v'j') zero total angular momentum probability $P_{vj,v'j'}(E)$.

The PES used, the computational procedure followed and the results obtained will be discussed in detail elsewhere [31]. Here, we describe the parameters used for the converged calculation and attempt a rationalization of the main features of the results using simple models.

To compute fixed ρ surface functions of step (1), the analytical basis method (ABM) [32] was adopted for the whole ρ range. For the energy range of interest convergence was obtained using 75 vibrotational basis functions for the HF channel, 4 rotational basis functions for the LiH channel and 198 vibrotational-rotational basis functions for the LiF channel.

In steps (2) and (3), integrals relevant to the assembling of the energy independent part of the coupling matrix were calculated at 230ρ values and then interpolated for all other points of the integration grid.

In step (4), the propagation of the solution for zero total angular momentum was carried out from $\rho=3$ to $\rho=35$ bohr using a logarithmic derivative method [33].

In step (5), at $\rho = 35$ bohr, a switch to Delves coordinates was performed and asymptotic boundary conditions imposed to determine the desired **S** matrix elements and detailed reaction probabilities. Steps (4) and (5) were repeated for all the energy values going from near the threshold to 0.600 eV (in steps of 0.005 eV) to obtain **S** matrix elements and reaction probabilities at 681 different values of the scattering energy.

3. The surface function energies

Energies associated with fixed ρ surface functions calculated in step (1) on the Li+FH potential energy surface are given in fig. 1. The upper panel of the figure shows these energies for an interval of the hyperradius values going from 4 to 20 bohr.

At large ρ values the curves associated with the three lowest LiF vibrational states (and the related rotational manifold) as well as several rotational levels of the HF ground vibrational state can be easily singled out, the graph being a mere superposition of the reactant and product channel asymptotic values. At shorter ranges, the graph becomes more difficult to read because of the occurrence of several avoided crossings. However, the coupling between the reactant and product channels being still small, channel diabatic curves can be worked out merely by connecting different adiabatic curves of the graph at the crossings. In this way (see the lower panel of fig. 2), the manifold of the entrance channel Li+FH rotational barriers becomes apparent, and the significant lowering in energy of the excited LiF vibrational states at short range also becomes apparent. Other characteristics of the system are the HF nature of the lowest states at short range (this is confirmed by inspection of the calculated surface functions) and the limited effect on the calculated surface function energies of the exit channel well located immediately past the saddle (such an effect is significant only for



Fig. 1. Upper panel: Surface function energies plotted as a function of the hyperradius ρ . Lower panel: Some diabatic curves derived from the energy plots of the upper panel (dashed lines: ground vibrational Li + FH states for *j* ranging from 0 to 6; dotted lines: ground rotational LiF + H states for *v* ranging from 0 to 2).

the lowest rotational level of each vibrational state).

Obviously, as already mentioned, to compute accurate reaction probabilities the coupling matrix of step (2) was evaluated and the propagation of step (4) performed. However, to rationalize calculated dynamical effects it is often sufficient to inspect the diabatic curves constructed, as mentioned above, assuming a unit non-adiabatic coupling at the crossings. For illustrative purposes some of these diabatic curves are shown in the lower panel of fig. 1. In particular, the lowest seven vibrotational states of HF (dashed lines) and the lowest rotational state of LiF (dotted lines) at v=0, 1 and 2 are shown.



Fig. 2. State to state reactive probabilities for HF(v=0, j=0)LiF(v=0, j') plotted as a function of the total energy *E*. Individual plots are given in fig. 4.

4. Energy dependence of the reactive probability

A first important feature of the Li+FH reactive probability is apparent from the plot of fig. 2 where the reactive probability from v=j=0 to different j' values is plotted: there is virtually no translational energy threshold. The probability becomes non-zero at E=0.260 eV (the reactant zero-point energy is 0.256 eV). This agrees with the fact that the experiment measures a non-negligible cross section even at collision energies lower than 0.1 eV. Such a feature can be easily rationalized by inspecting fig. 1. As already mentioned, in fact, the Li+FH reaction is quantally exoergic: the lowest reactant vibrotational state has an energy of 0.256 eV and correlates with the ground product vibrational state having an energy of 0.213 eV. Though such a decrease is nonmonotonic (the PES minimum energy path has a barrier to reaction of 0.182 eV), the lowest reactant and product diabatic curves match at an energy lower than that of the reactant ground state. This allows the Li+FH reaction to behave as a no barrier exoergic process.

A second peculiar feature of the reactive probability plot is that in the investigated energy range two main types of reactive behaviour can be singled out. As shown in fig. 2, the first one is dominant at low energy and has a spiked, short-spaced, long-lived resonant nature. The second one has a more background nature and a more slowly oscillatory behaviour.

It is possible to associate peaks of the long-lived resonant structure to the eigenvalues of the entrance channel wells. By approximating the seven wells shown in the lower panel of fig. (1) as Morse curves, related eigenenergies can be given by a simple analytical formulation. The structure of the calculated eigenvalues is similar to that of the resonant spikes and has the same decreasing trend with E. These bound states physically correspond to hindered rotations of Li+FH implying that low energy reactivity can be rationalized in terms of leaks from incomplete rotations of the system as Li approaches HF.

Reactivity associated with a HF back-and-forth bouncing when H and Li get close in hindered rotations has already been evidenced in a graphical study of Li+FH classical trajectories carried out to rationalize the fact that attacks on the H side were found to be more effective than those on the F side [23]. Present quantum results obtained on a PES having a lower barrier to reaction and a more attractive long range tail confirm that the importance of the contribution of hindered rotations to reactivity is a typical feature of the system rather than a byproduct of a structure of the surface introduced by the fitting procedure. Further support of such a rationalization is given by the isotopic effect [23]. In fact, when D or T was substituted for H in the Li+FH reaction reorientation was found to be almost nonexistent and the maximum reactivity to take place at values of the angle of attack corresponding to that of the bent transition state. On the contrary, when substituting H with Mu, the effect was highly enhanced because of the lighter reduced mass of MuF.

As far as the background oscillatory energy dependence of the reactive probability is concerned, it has to be pointed out that fixed angle reduced dimensionality quantum results also show a clear oscillating structure [17,18] whose amplitude and phase increase with energy. These features were rationalized in terms of an interference effect between components of the scattered wavefunction traveling on different reaction paths (say α and β) but degenerate at long range. In this approach the reaction probability can be formulated as

$$P(E) = P^{0}(E) \sin^{2}[\Delta_{\alpha,\beta}(E)], \qquad (2)$$

with $P^{0}(E)$ being a smooth background function enveloping the P(E) maxima and $\Delta_{\alpha,\beta}(E)$ the difference in phase shift between the α and β components of the scattering wavefunction. When applying this formula, the oscillatory behaviour was reasonably well reproduced. For simplicity, the portions of α and β paths giving rise to the dephasing were assumed to be constant and have the same length.

It is known form the literature [34] that little reminiscence of reduced dimensionality structures can be found in 3D estimates of scattering quantities because of the smoothing induced by angular momentum and collision angle averaging. Our results show that for Li+FH the angular averaging (when correctly introduced as is in a full 3D quantum treatment) does not wipe out the oscillatory structure of the reactive probability. Therefore, any smoothing of the full 3D quantum result must be due to the angular momentum averaging.

5. State to state specificity of the reactive probability

An important dynamical feature singled out by the plots of the detailed reactive probability is its strong state specificity.

First of all, our results show that rotational energy plays a selective role in promoting reaction. The effect on the reactive probability of atom-diatom systems of increasing the rotational excitation of the reactant diatom has already been discussed in the literature mainly by making use of quasiclassical arguments [11,35,36]. In the case of the Li+FH reaction, the rotational energy dependence of the reactive probability was found to first decrease with j and then increase [11]. Lately, however, this effect was found to be caused by a spurious structure of the potential energy surface used for the calculations. Calculations performed on a smoothed PES led to a monotonic trend [15]. An investigation of the dependence of the reactive probability on the rotational energy of the reactant diatom was also carried out using quantum means in ref. [37]. There, for the reactions $X+H_2$ (X=O, Cl, H) it was shown that at low collision energy quantum calculations give a reactive probability decreasing with the initial rotational number.

Our calculations suggest (as can be seen from fig. 3) that for Li+FH the effect on reactivity of increasing the rotational excitation of the reactant diatom depends on the value of E. In particular, at low E values the spiked shape of the reactive probability may make its *j* dependence behave randomly before dying off when total and rotational energy coincide. At these energy values, the reactive probability (averaged over a finite interval of E) increases when going from j=0 to larger js before dying off. At larger E values (when the main contribution to reactivity is smoother) the state selected reactive probability at first rises with *i*. At large *i* values it decreases and rises again before falling off. Such a behaviour is therefore more complex than expected from previous studies and different from that of collinearly dominated systems. This means that our calculations, while confirming that an increase of *i* shifts the probability curve to higher energy values, indicate a state specific alteration of the structure of the curve.

We found also another state specific feature of the

Li+HF reactive probability. As shown in fig. 4, the amplitude of the reactive probability and its energy dependence are strongly sensitive to the value of the final product rotational state involved. Resonant peaks seem to be particularly enhanced when the product rotational excitation is moderately high. On the other hand, the highest probability is obtained for j' = 0 and j' = 3 at higher energy when the reactivity is mainly determined by interference. At the same time, at higher j' values reactivity is almost zero.

6. Conclusions

In the present Letter we discuss the results of the first converged accurate 3D quantum calculation of the Li + FH detailed reactive probabilities. To carry out the calculations a highly modular computer program designed to run on workstations and making use of the APH formalism was used. Particular care was dedicated to the selection of the optimum calculation parameters due to the particular nature of the Li + FH reaction.

Plots of the detailed reactive probabilities show



Fig. 3. Reactive probabilities for HF(v=0, j) summed over all final states plotted as a function of the total energy E.



LIFH Transition Probabilities

Fig. 4. Reactive probabilities for HF(v=0, j=0) to LiF(v'=0, j') plotted as a function of the total energy E.

several interesting properties that can be rationalized in terms of vibrotational adiabatic curves. The first of them is the absence of a threshold value for the collision energy even if the reaction is classically endoergic and its minimum energy path has a clear barrier. Such a feature is due to the fact that the zeropoint energy of the reactants is higher than that of both the transition state and the products i.e. the reaction is quantally exoergic and without a zero-point energy barrier.

The second important feature of the probability plots for HF in its ground vibrational state reacting to give the ground vibrational LiF state is the structure of its energy dependence. A rationalization of this feature in terms of the shape of non-adiabatic vibrotational curves was able to give a proper account of both the low energy spiked long-lived resonant structure as well as the higher energy oscillating behaviour. Both features are reminiscent of quasiclassical and reduced dimensionality quantum structures.

Two other features of the Li + FH detailed reactive probability plots were found to be of interest: the reactant and product rotational state specificity. These features largely differ from those of collinear dominated reactions and seem to be peculiar to full 3D reactivity of three different atom systems. Though difficult to rationalize in terms of simple dynamical models, they clearly indicate the coming into play of some kind of selection rule.

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