Li+FH reactive cross sections from $J=0$ accurate quantum reactivity

A. Laganà
Dipartimento di Chimica, Università di Perugia, Perugia, Italy
R. T Pack
Theoretical Division T12, MS B268, Los Alamos National Laboratory, Los Alamos, New Mexico 87545
G. A. Parker
Department of Physics and Astronomy, University of Oklahoma, Norman, Oklahoma 73019-0225

(Received 11 March 1993; accepted 27 May 1993)

Accurate three dimensional quantum calculations have been carried out for the Li+HF reaction at zero total angular momentum J on a potential energy surface fitted to *ab initio* points. By adopting a J shifting approximation reactive cross sections are estimated and compared with the experiment. The agreement is very good.

I. INTRODUCTION

Recently, we have reported accurate quantum calculations[1] of the detailed state (vj) to state $(v'j')$ reactive probabilities for the Li+HF $(vj) \rightarrow$ LiF $(v'j')$+H reaction at zero total angular momentum J. The calculations were carried out using a computer code based on the adiabatically adjusting principal axes of inertia hyperspherical coordinate (APH) formalism.[2] In the APH approach, reactive probabilities of atom–diatom reactions are computed by expanding the global wave function in terms of a product of eigenfunctions (surface functions) of the angular coordinates calculated at fixed values of the hyperradius ρ and Wigner rotation functions, then propagating coupled differential equations obtained by substituting the expansion into the Schrödinger equation. The propagation in ρ is carried out from near the origin where the wave function is zero to a value of the hyperradius large enough to allow a projection of the wave function into reactant and product channel states. Such a procedure has been already employed successfully for the calculation of detailed reactive probabilities of several collinearly dominated reactive systems.[3] The present reaction has a bent transition state.

Experimental crossed molecular beam results for the Li+HF reaction obtained for HF in the ground vibrational state and a rotational temperature of 60 K were published[4] in 1980. In particular, estimates of the total integral reactive cross section $\sigma_v(E_{\rm tr})$ from the reactant ground vibrational state $v=0$ were derived[4] from the measured product beam intensity at the translational energies ($E_{\rm tr}$) of 3 and 8.7 kcal/mol giving, respectively, 0.8 and 0.94 Å^2. At the same time, a non-negligible reactivity was measured for collision energies as low as 1.9 kcal/mol establishing that the translational energy threshold, if any, must be lower than 0.1 eV. Because of the characteristics of the experimental apparatus and of the procedure used to recover the integral cross section from the amount of Li detected in the mass spectrometer, an error factor of 2 for the absolute value and of 30% for the relative one were indicated as plausible by the authors.

The aim of this paper is to compare approximate cross section values derived from $J=0$ accurate quantum reactive probabilities with the experiment.

II. CALCULATIONS AND RESULTS

As will be discussed in detail elsewhere,[5] the surface functions and related eigenvalues for the Li+HF system were calculated using the analytic basis[6] method (ABM). The propagation in ρ was performed using the logarithmic derivative method.[7] Due to the strongly bent geometry of the transition state and the hindered nature of FH rotations, the propagation had to be extended to very large values of the hyperradius before switching to Delves coordinates and applying asymptotic scattering boundary conditions to obtain the needed S matrix elements. The potential energy surface used for the calculations[5] was derived from *ab initio* values reported in Ref. 8.

To evaluate the cross section, reactive probabilities need to be converged for a large number of total angular momentum J. However, approximate estimates of the reactive cross sections can be obtained from the $J=0$ reactive probabilities by invoking the J shifting approximation.[9] This approximation assumes that nonzero total angular momentum probabilities $P^J_{vj,v'j'}(E_{\rm tr})$ can be derived from $J=0$ ones using the following relationship

$$P^J_{vj,v'j'}(E_{\rm tr}) \simeq P^{J=0}_{vj,v'j'}(E^J_{\rm tr}) \tag{1}$$

with $vj(v'j')$ being the reactant (product) vibrotational state quantum numbers and $E^J_{\rm tr}$ being defined as

$$E^J_{\rm tr} = E_{\rm tr} - BJ(J+1). \tag{2}$$

In Eq. (2), $B=\hbar^2/2I_B=\hbar^2/2\mu_{\rm LiF}r^2=3.59\cdot 10^{-3}$ kcal/mol is the rigid diatomic rotor constant of LiF computed at the saddle point ($r=1.62$ Å) and $\mu_{\rm LiF}$ is the LiF reduced mass. Properties of the transition state of the Li+FH system were derived by calculating the minimum energy path at a value of the collision angle corresponding to that of the transition state. Transition state bond lengths were found to be 1.62, 1.21, and 1.73 Å for the LiF, HF, and LiH pairs, respectively, showing that the displacement of the center of mass of the triatom from the LiF internuclear axis is negligible (0.043 Å) and, therefore, a diatomlike treatment reasonable.

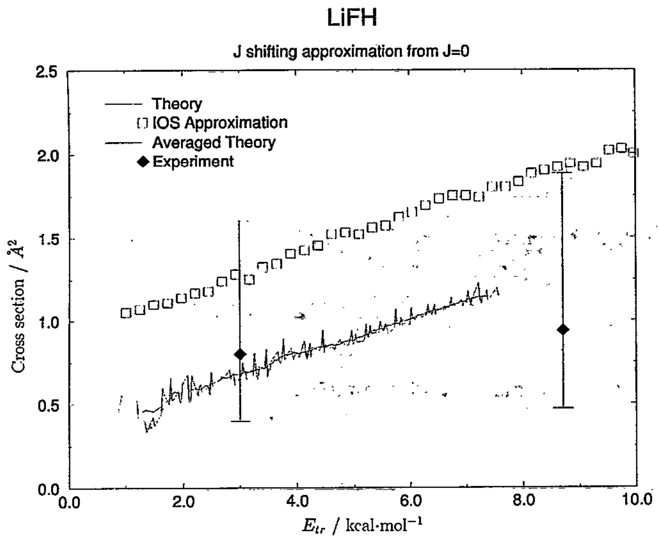

FIG. 1. Quantum integral cross section plotted as a function of the collision energy. 3D*JS* and its smoothing (solid line): infinite order sudden approximation (squares); experiment (diamonds and related error bars).

As a result, for a given rotational temperature T, the three dimensional J shifting (3D*JS*) quantum reactive cross section $\sigma_v^{3DJS}(E_{tr})$ from a given vibrational state v reads as

$$\sigma_v^{3DJS}(E_{tr}) = \sum_j \frac{\pi(2j+1)e^{-\epsilon_j/kT}}{k_{vj}^2 Q_{ROT}} \times \sum_J (2J+1) \sum_{v'j'} P_{vj,v'j'}^{J=0}(E_{tr}^J), \qquad (3)$$

where, as usual, ϵ_j is the energy associated with the reactant rotational state j, k is the Boltzmann constant, $k_{vj}^2 = 2\mu E_{tr}$, $Q_{ROT} = \Sigma_j(2j+1)e^{-\epsilon_j/kT}$, and μ the reduced mass of Li+FH.

The 3D*JS* calculated cross section (solid line) is plotted in Fig. 1 as a function of the collision energy E_{tr}. The plot shows a structure which, though smoother than that of individual state-to-state reactive probabilities, is still quite rich because of the simplifications introduced in treating the triatomic rotations. To mimic the smoothing caused by a proper treatment of triatomic rotations, we averaged calculated values over the six nearest points (the smoothed curve is also shown in the figure).

As apparent from the figure, the computed 3D*JS* values show an excellent agreement with measured cross sections (given as diamonds) falling well within the error bars shown. Compared with the infinite order sudden approximation estimates[10] (plotted in the same figure as squares) 3D*JS* results, though having a similar slope, are about 50% lower leading to a better agreement with the experiment.

In addition to experimental uncertainties, the single energy nature of theoretical calculations and the J shifting model used to derive the cross section from the $J=0$ probability are all sources of discrepancy between calculated and measured data. The validity of the J shifting approximation has been tested in the past mainly for collinear dominated systems. Here we see that it works surprisingly well for a reaction with a bent transition state.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U. S. Department of Energy under the Laboratory Directed Research and Development Program. Financial support was also given by CNR (Italy), ENEA (Italy), and NATO (Grant No. CRG 920051).

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