The quantum threshold behavior of the Na+HF reaction

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Full three dimensional quantum calculations of reactive properties of the Na+HF system have been performed at zero total angular momentum (J=0) to investigate the energy dependence of the reactive probability of this reaction. The effect of increasing the vibrational excitation of reactants is also discussed. © 1998 American Institute of Physics. [S0021-9606(98)02015-7]

I. INTRODUCTION

Recently, a new potential energy surface (PES) based on an extended *ab initio* calculation has been reported in the literature¹ for reaction of sodium atoms with hydrogen fluoride in the ground electronic state

$$Na(3 {}^{2}S_{1/2}) + HF(X {}^{1}\Sigma^{+}) \rightarrow NaF(X {}^{1}\Sigma^{+}) + H({}^{2}S_{1/2}).$$
(1)

This PES (BO5) has been constructed using a polynomial in the bond order (BO) coordinates.² BO5 is highly endoergic and has a bent transition state. This makes a full dimensional investigation of the Na+FH reaction quite challenging from a theoretical point of view, since a large number of states is required to carry out reactive scattering calculations even for energy values around the reactive threshold.

The Na+HF reaction has been experimentally investigated using different techniques.^{3–6} The first experimental investigation of this reaction was carried out by Polanyi and collaborators using a Chemiluminescence Depletion Method (CMD).³ The experiment provided a measurement of the rate constant for different values of the reactant vibrational quantum state v and an estimate for the reactive cross section.³ The rate constant is inappreciable at v=0 then it increases linearly with v starting from v=1. Measurements of the reactive cross section of this reaction have also been carried out by Lee and co-workers using a crossed molecular beam apparatus.⁴ They found that for HF in the ground vibrational state (v=0) the system is not reactive. Similar conclusions were drawn from experiments of Loesch and collaborators⁵ and Düren and co-workers.⁶

Dynamical calculations for this reaction using quasiclassical trajectory techniques on BO5 have already been performed.¹ In agreement with the CMD experiment these calculations indicate that an increase of the reactant vibrational excitation is quite effective in promoting reactivity.

In the present paper we discuss our efforts to carry out a 3D quantum calculation of the Na+HF reactive probabilities and comment results obtained.

The paper is organized as follow: The potential energy surface is discussed in Sec. II. The calculation of surface functions and eigenvalues is illustrated in Sec. III. The propagation of the coupled channel scattering equations and the main characteristics of the calculated reactive probabilities are discussed in Sec. IV.

II. THE POTENTIAL ENERGY SURFACE

As already mentioned, the PES used for calculations is a polynomial in the BO coordinates. Details of the determination of the *ab initio* potential energy values and of the BO interpolation procedure are given in Ref. 1. Here we confine the description of the PES to the main features of BO5 by paying particular attention not only to the usual critical regions (wells, barriers, etc.) but also to the location in the hyperangle space of the various arrangement channels since their accurate description is critical for obtaining converged results. The BO5 PES has a well depth of 0.44 eV located early in the entrance channel and a large barrier to reaction mainly due to the endoergicity of the process. To better illustrate the overall shape of the PES, we plot in Fig. 1 the ensemble of fixed angle (Φ) minimum energy paths (MEP) of the reactive process using a pseudo three dimensional representation and related isoenergetic contours. In this type of plots Φ , the angle formed by the NaF and HF internuclear distances, is kept fixed to draw individual MEPs by varying α (the rotation angle associated with the definition of the reaction coordinate).⁷ Such a representation clearly evidences the possibility of forming an intermediate complex having a preferred collinear geometry though easy to distort to bent geometries. It also shows that there is a barrier to reaction which has a minimum for a bent geometry (Φ $=77^{\circ}$). The analysis of these plots is made easier by the isometric contours given in the underlying map. Plots of the BO5 PES are also given as stereographic projections of the fixed hyper-radius hyperspherical representations. Figures 2, 4, 3, and 5 give fixed ρ (ρ =35.0, 6.85, 7.29, 6.0 a_o) representations of the PES as a function of the Cartesian coordinates X and Y defined as $X = \tan(\theta/2)\cos \chi$ and Y $= \tan(\theta/2) \sin \chi$. The variables ρ , θ and χ are the internal adiabatically adjusting principal axis of inertia hyperspherical (APH) coordinates defined as

$$\rho^2 = S_{\tau}^2 + s_{\tau}^2, \tag{2}$$

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FIG. 1. Pseudo three dimensional plot of the fixed Φ minimum energy paths calculated at different values of α for the Na+FH \rightarrow NaF+H reaction given (see the text for the definition of Φ and α). In the underlying map the related energy contours are shown. The energy zero was set at the entrance channel asymptote. Isoenergetic contours are spaced by 0.28 eV.

$$\tan \theta = \frac{\left[(S_{\tau}^2 - s_{\tau}^2)^2 + 4S_{\tau}^2 s_{\tau}^2 \cos^2 \Theta_{\tau} \right]^{1/2}}{2S_{\tau} s_{\tau} \sin \Theta_{\tau}},$$
(3)

$$\sin(2\chi_{\tau}) = \frac{2S_{\tau}s_{\tau}\cos\Theta_{\tau}}{[(S_{\tau}^2 - s_{\tau}^2)^2 + 4S_{\tau}^2s_{\tau}^2\cos^2\Theta_{\tau}]^{1/2}},$$
(4)

$$\cos(2\chi_{\tau}) = \frac{S_{\tau}^2 - s_{\tau}^2}{\left[(S_{\tau}^2 - s_{\tau}^2)^2 + 4S_{\tau}^2 s_{\tau}^2 \cos^2 \Theta_{\tau}\right]^{1/2}}$$
(5)

with S_{τ} , s_{τ} and Θ_{τ} being the usual mass scaled Jacobi coordinates of the arrangement τ .

In these figures, as θ goes from zero at the center of figure (X=Y=0) to $\theta=90^{\circ}$ at the periphery, the triangle flattens from a geometry for which the two principal moments of inertia lying in the plane of the triatom are equal into a linear geometry. As χ goes from zero to 360° (circling counterclockwise) all possible arrangements are described twice.⁸

At large ρ values (see Fig. 2 for $\rho = 35 a_o$), the graph shows that the different energetically allowed asymptotic regions of the potential are well separated and confined into a small portion of the plane (this is due to the polar nature of the hyperspherical coordinates). The small structure located around $X = \pm 1$, Y = 0 is associated with the reactant Na+HF arrangement channel. A larger portion of the graph is associated with the product NaF+H channel (around X=0, $Y=\pm 1$). The closed NaH+F arrangement channel does not show up in the figure because it is much higher in energy. Only the encircled area of the graph has physical meaning.

At ρ values around the transition state (see Fig. 3 for $\rho = 6.85 a_o$) the reactant Na+HF and the product NaF+H channel partly merge leading to a saddle. Near the saddle there is a small pocket corresponding to the fixed ρ cut of the well shown in Fig. 1. The large shaded areas near $\chi = \pm \pi/2$ correspond to the repulsive region of the interaction for the NaF+H arrangement channel while the small shaded areas near $\chi = 0$ and π correspond to the repulsive regions of the Na+HF interaction. The small shaded areas near χ



FIG. 2. Stereographic projection of contour plots of the Na+HF potential energy surface given as a function of APH hyperangles θ (the circle radius) and χ (the circle angle) for fixed hyper-radius (ρ =35.0 a_o). The dotted contour is taken at 0.79 eV. Regions where the potential energy is larger than 2.0 eV are shaded (see the text for discussion).

 $=\pi/6$ and $7\pi/6$ are due to the repulsive region of the NaH arrangement channel (closed at the energies investigated here). No rotations of NaF with respect to H are allowed. The same considerations are valid also for the smallest ρ (ρ_{switch}) value (ρ =7.29 a_o) at which, as for the asymptotes, the channel quadratures easily converge using arrangement channel based coordinates. In this case, however (see Fig. 4) rotations of NaF around H are allowed.

At shorter ρ values (see Fig. 5 for $\rho = 6 a_o$) the various channels are no longer distinct and the potential energy surface shows a well corresponding to a triatomic NaHF geometry located in the highly repulsive region.



FIG. 3. As in Fig. 2 for $\rho = 6.85 a_o$, which is the hyper-radius value for the transition state. The dotted contours are taken at 0.81, 0.87 and 0.93 eV (regions where the potential energy is larger than 1.10 eV are shaded). The system goes from the reactant to the product arrangement (at χ about 0 or π) as θ decreases, by passing over the entrance channel well, the barrier and a small pocket in the strong interaction region (see the text for discussion). Rotations of NaF around H are hindered.



FIG. 4. As in Fig. 2 for $\rho = 7.29 a_o$. The dotted contours are taken at 0.79, 0.86 and 0.93 eV and regions where the potential energy value is larger than 1.10 eV are shaded (see the text for discussion). As in Fig. 3 the system reacts by flying over the well, the barrier and a pocket in the strong interaction region. NaF rotations are now allowed.

III. THE CONSTRUCTION OF SURFACE FUNCTIONS

The theoretical approach used here is based on APH coordinates, and is described in detail in Ref. 8. A key part of the approach is the partitioning of the hyper-radius ρ range into a large number of sectors. At a given total angular momentum **J** within each sector ξ , the wave function Ψ^{JMpn} is expanded about the sector midpoint ρ_{ξ} as follows

$$\Psi^{JMpn} = 4 \sum_{t,\Lambda} \rho^{-5/2} \psi^{Jpn}_{t\Lambda}(\rho) \Phi^{Jp}_{t\Lambda}(\theta,\chi;\rho_{\xi})$$
$$\times \hat{D}^{Jp}_{\Lambda M}(\alpha_{Q},\beta_{Q},\gamma_{Q}). \tag{6}$$

In Eq. (6) the $\hat{D}_{\Lambda M}^{J_p}(\alpha_Q, \beta_Q, \gamma_Q)$ are the Wigner rotation functions of the three Euler angles $(\alpha, \beta, \text{ and } \gamma)$, the $\Phi_{i\Lambda}^{J_p}(\theta, \chi_i; \rho_{\xi})$ are the surface functions of two internal hy-



FIG. 5. As in Fig. 2 for $\rho = 6.0 a_o$, (the initial propagation ρ value). The dotted contours are taken at 0.79 and 1.48 eV. Regions above 1.80 eV are shaded (see the text for discussion).

perangles (θ, χ) , the $\psi_{t\Lambda}^{Jpn}(\rho)$ are the functions of the hyperradius which carry the scattering information.

At **J=0** the sector APH surface functions Φ_t are eigensolutions of the two-dimensional Schrödinger equation

$$\left[T_{h}+\frac{15\hbar^{2}}{8\mu\rho_{i}^{2}}+V(\rho_{i},\theta,\chi)-\mathscr{E}_{t}(\rho_{i})\right]\Phi_{t}(\theta,\chi;\rho_{i})=0,\quad(7)$$

where T_h is

$$T_{h} = -\frac{\hbar^{2}}{2\mu\rho^{2}} \left(\frac{4}{\sin 2\theta} \frac{\partial}{\partial\theta} \sin 2\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^{2}\theta} \frac{\partial^{2}}{\partial\chi^{2}} \right). \quad (8)$$

The method used to integrate Eq. (7) is the Analytic Basis Method (ABM).¹⁰ The ABM method is based on an expansion of Φ_t in terms of rotation-vibration analytic functions centered on each of the arrangement channels

$$\Phi_t = \sum_f A_{ft} \phi_{\nu_f}(z_f) \hat{P}_{j_f \Lambda}(\Theta_f), \qquad (9)$$

where the coefficients A_{ft} are determined by the variational principle, $\hat{P}_{j_f}(\Theta_f)$ are the associated Legendre polynomials and ϕ is a simple harmonic oscillator function of z_f

$$\phi_{\nu_f}(z_f) = \frac{1}{\left[\pi^{1/2} 2^{\nu_f}(\nu_f!)\right]^{1/2}} H_{\nu_f}(z_f) e^{-(1/2)z_f^2}.$$
 (10)

In Eq. (10) H_{ν_f} is the Hermite polynomial and z_f is a variable defined as

$$z_f = a_f \tan \vartheta_f - \frac{b_f}{\tan \vartheta_f} + c_f \tag{11}$$

in terms of the Delves hyperangle ϑ_f . The parameters a_f , b_f , and c_f (chosen to make the oscillator basis functions ϕ to behave approximately like Morse eigenfunctions) are defined as

$$a_f = \cos^4 \vartheta_{Mf} \left(g_2^{1/2} + \frac{g_3}{6g_2^{1/2}} \tan \vartheta_{Mf} \right),$$
 (12)

$$b_f = \sin^4 \vartheta_{Mf} \left(g_2^{1/2} - \frac{g_3}{6g_2^{1/2}} \cot \vartheta_{Mf} \right),$$
 (13)

$$c_f = b_f \cot \vartheta_{Mf} - a_f \tan \vartheta_{Mf}. \tag{14}$$

In these equations g_i is the *i*th derivate of g at ϑ_{Mf}

$$g_2 = \gamma_f^2 k_f e^{-\gamma_f(\vartheta_{Mf} - \vartheta_{mf})} + \zeta_f \sec^2 \vartheta_{Mf}, \qquad (15)$$

$$g_3 = -\gamma_f^3 k_f e^{-\gamma_f (\vartheta_{Mf} - \vartheta_{mf})} + 2\zeta_f \sec^2 \vartheta_{Mf} \tan \vartheta_{Mf},$$
(16)

where ϑ_{Mf} can be determined by solving the equation

$$g_1 = 0 = -\gamma_f k_f e^{-\gamma_f (\vartheta_{Mf} - \vartheta_{mf})} + (k_f - \frac{1}{2})\gamma_f + \zeta_f \tan \vartheta_{Mf},$$
(17)

with k_f and γ_f being defined at the initial propagation ρ value.¹⁰ Thus given any initial choice of the variational parameters δ_f and ζ_f the parameters a_f , b_f , and c_f can be determined by solving a simple transcendental equation for ϑ_{Mf} . The parameters a_f and b_f can be written as a product between two scaling parameters c_{α} and a_n , where c_{α} essentially scales the frequency and a_n scales the anharmonicity of the oscillator. The final values of the parameters a_f , b_f , and

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TABLE I. Parameters for the ABM calculation.

Arrangement	Na+HF	F+NaH	H+NaF
mass (amu)	22.98977	18.9984032	1.00782503
ω_e (a.u.)	0.01885557	0.00534093	0.00244219
$\omega_e x_e$ (a.u.)	0.00040952	0.000089850	0.000015491
$r_e(a_o)$	1.732517	3.5666692	3.6395124
$v_{\rm max}$	6	0	4
$j_{\rm max}$	14	3	33
nhermt	96	96	96
<i>n</i> glegn	96	96	96
c _α	0.956	1.0005	0.962
r_x	1.036	1.003	1.002
a _n	1.034	1.030	0.868
δ	1.190	0.01	0.170
ζ	0.001	1.0	1.19

 c_f are determined by optimizing the vibrational energy levels in each arrangement by varying the scaling parameters c_{α} , r_x [the scaled equilibrium distance $(r_{xf}r_{ef}/d_f)$] and a_n cyclically in that order until the average energy of all the open vibrational levels is minimum. The values of these parameters and ABM basis dimension are given in Table I. They were chosen to give the energies of the asymptotically open channels with an accuracy better than 0.1 meV and the energies of all locally open channels with an accuracy better than 0.2 meV.

As indicated by the v_{max} and j_{max} values given in Table I, the ABM calculations for the Na+HF reaction made use of a total of 279 primitive basis functions to include enough closed channels to prevent a loss of flux. At the highest energy considered here, 0.93 eV, there are 105 asymptotically open channels. The large number of primitive bases was made necessary by the high endoergicity of the Na+FH reaction and by the bent geometry of the intermediate that induces a strong angular momentum coupling. The integral between the 279 primitive basis functions were evaluated using various numerical quadratures. At ρ values larger than $\rho = 7.29 a_o (\rho_{\text{switch}})$ the quadratures were performed in the arrangement channel Delves space.¹⁰ At ρ values smaller than ho_{switch} the quadratures were performed in the APH space.¹⁰ In this case, θ was divided in three sectors (0.0, 0.583), (0.583, 1.36) and (1.36, $\pi/2$), containing, respectively, a total of 10, 50 and 100 grid points and χ was divided into the six sectors $(-(\pi/2), -0.41)$, (-0.41), -0.20, (-0.20, 0.0), (0.0, 0.31), (0.31, 0.71) and (0.71, 0.71) $\pi/2$), containing, respectively, 16, 14, 52, 100, 30, 16 grid points. These intervals and grid points were determined by analyzing the stereographic projections¹¹ of the potential energy surface taken at $\rho = 6.0$, 6.85 and 7.29 a_o .

IV. DYNAMICAL CALCULATIONS AND RESULTS

The APH coupled channel differential equations read

$$\left[\frac{\partial^2}{\partial\rho^2} + \frac{2\mu E}{\hbar^2}\right] \psi_{t\Lambda}^{Jpn}(\rho) = \frac{2\mu}{\hbar^2} \sum_{t'\Lambda'} \left\langle \Phi_{t\Lambda}^{Jp} \hat{D}_{\Lambda M}^{Jp} |H_i| \Phi_{t'\Lambda'}^{Jp} \hat{D}_{\Lambda'M}^{Jp} \right\rangle \\ \times \psi_{t'\Lambda'}^{Jpn}(\rho), \tag{18}$$



FIG. 6. Adiabatic surface function eigenvalues plotted as a function of the hyper-radius.

$$H_{i} = T_{h} + \frac{15\hbar^{2}}{8\mu\rho^{2}} + V(\rho, \theta, \chi_{i}).$$
(19)

The numerical integration of the 279 coupled equations was carried out for 230 sectors from $\rho = 6.0 a_o$ to ρ = 35.0 a_o using a logarithmic derivative method with 40 propagation steps per smallest propagation wavelength¹² and for 80 energy values from 0.79 to 0.93 eV with a step of 0.0017 eV. The number of ρ_i values considered was determined using the relationship

$$\rho_i = [\rho_{\min} + (i-1)\Delta\rho_1](1+\Delta\rho_2)^{i-1}, \qquad (20)$$

where $\rho = 6.0 a_o$, $\Delta \rho_1 = 0.020 a_o$, and $\Delta \rho_2 = 5.238049180$ 328 $3 \cdot 10^{-3} a_o$. The resulting adiabatic curves are plotted in Fig. 6. The number of quadrature points were increased to produce the surface functions $\Phi_t(\theta, \chi; \rho_i)$ accurate to 4 significant figures. The asymptotic analysis was performed at $\rho = 35 a_o$ where corresponding **S** matrix elements were evaluated. The convergence of the calculations has been tested by varying the surface functions basis set from 254 to 279 functions. The resulting probabilities are accurate to within one percent at threshold energy and the error increases to about ten percent at the higher energies.

The related computer program was developed on workstations. The production runs were performed on an eight node SP2 machine working in a nondedicated mode. On a dedicated single Power2 SP2 node the average calculation time of the surface functions for this type of problem at a given ρ value is about 9 minutes. As shown also in the study of Ref. 13, the efficiency of the section of the code devoted to the calculation of the surface functions does not exceed 60% when running the program concurrently on a 32 node dedicated machine using a single program multiple data parallel model. The efficiency is lower in a nondedicated environment when, as in our case, the assignment of the work is managed by the "load leveler" of the machine. The propa-

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FIG. 7. Reactive probabilities summed over all open product j' and v' states for the ground reactant vibrational state (v=0) at various reactant j values plotted as a function of total energy.

gation section can be parallelized in a more efficient way by using a task farm model dynamically assigning the workload.¹⁴

The reactive probabilities for initial v=0 and different initial j values summed over the product vibrational and rotational states v' and j' are plotted in Fig. 7 (primed quantities for products, unprimed for reactants) as a function of the total energy E. Increments of some kcal/mol in energy are unable to raise the reaction probability above 2%. In this range of energy only the lowest rotational states seem to contribute to the reactivity of the system. The calculated quantum threshold energy coincides with the endoergicity of



FIG. 8. Reactive probabilities summed over all open product j' and v' states for the first reactant vibrational state (v=1) at various reactant j values plotted as a function of total energy.



FIG. 9. Product vibrational distributions (probability vs v') calculated at E = 0.905 eV (left-hand column), 0.910 eV (center column) and 0.915 eV (right-hand column) for the first excited vibrational state (v = 1) and various reactant rotational states j summed over all open product rotational states.

the process indicating that low energy reactivity is associated with a tunneling of H out of the NaFH transition state. This agrees also with the fact that most of the contribution to reaction comes from the lowest reactant rotational states. The fact that an increase of the rotational excitation of reactants increases the threshold energy implies also that the fraction of energy supplied as HF rotation is largely unsuitable for enhancing reaction. Trajectory studies indicate that a deviation of the reaction path from the minimum energy approach



FIG. 10. Product rotational distributions (probability vs j') calculated at E = 0.905 eV (left-hand column), 0.910 eV (center column) and 0.915 eV (right-hand column) for the first reactant vibrational state (v = 1) and various reactant rotational states j summed over all open product vibrational states.

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at the preferred angle of attack can be responsible for this effect.

As for Li+HF in the threshold region the reactive probability shows a definite resonant structure. Some of these peaks persist for different rotational states and are located around E = 0.845 and E = 0.873 eV. These peaks can be associated with the existence of almost bound states of the transition aggregate. A sharper peak of this type can also be found at about E = 0.910 eV.

Another important feature of this reaction is the role played by vibrational excitation in an enhancing reaction. A plot of the reactive probability of the type given in Fig. 7 for v=0 is shown in Fig. 8 for v=1. The reactive probability at v=1 is about one order of magnitude larger than that calculated at v=0. This is typical of endoergic reactions when vibrational energy increases as confirmed by classical trajectory calculations.

Also different with respect to the behavior of this reaction at v=0 is the role played by rotational excitation in promoting reactivity when v is 1. Reactivity increases with j to reach a maximum at j=5 and then suddenly decrease at larger j values. In the already used trajectory language this effect can be understood in terms of the fact that at v=1 the best matching between the velocity of the incoming atom and the orientation of the window to reaction occurs when the target has a non-negligible rotational energy.

Other reactive properties we have investigated are the final state distributions of the products at fixed energy. Product vibrational distribution (PVD) summed over all j' for reactants in v = 1 at the three values of E 0.905, 0.910 and 0.915 eV going from the left to the right-hand side columns are shown in Fig. 9. PVDs are unimodal at all energies and at all values of j (j increases from 0 to 7 going from the lower to the upper panels). An increase of E leads to a shift of the maximum of the distribution to smaller v' values. Such a result seems to be in contrast with the increasingly direct nature of the reactive collision as energy increases. Although a full rationalization of this result needs an extended ad hoc

trajectory investigation aimed at figuring out how the reaction mechanism partitions the available energy among the various molecular modes, it is fairly intuitive that a reduction of the interaction time associated with a higher collision energy may reduce the amount of energy allocated as vibration of the product molecule. On the contrary, product rotational distributions (PRD) shown in Fig. 10 for the same reactant vibrational state do not vary significantly with energy. Despite their rather structured shape, they are always inverted with the most populated product being close to j' = 5.

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