

Supplementary Information

**New *ab initio* potential energy surface of NaFH (1A') system and
quantum dynamics studies for the Na + HF (*v, j*) → NaF + H reaction**

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Computational methods: Quantum wave packet calculation

In our calculations, the Hamiltonian and wavepacket are expressed in the reactant (Na + HF) body-fixed Jacobi coordinates (R, r, θ) , which are the distance between Na and the center-of-mass of HF (R), the length of the HF internuclear distance (r) and the angle enclosed by R and r (θ), respectively. The \vec{R} vector is also coincided with the body-fixed z axis. The Hamiltonian is expressed in atomic units as

$$\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \frac{\hat{j}^2}{2\mu_r r^2} + \frac{\hat{l}^2}{2\mu_R R^2} + V(R, r, \theta) \quad (1)$$

where μ_R and μ_r are the corresponding reduced masses. \hat{j} donates the diatomic rotational angular momentum operator and \hat{l} donates the orbital angular momentum operator. The operator \hat{l}^2 can be further expressed as

$$\hat{l}^2 \equiv (\hat{J} - \hat{j})^2 = \hat{J}^2 + \hat{j}^2 - 2\hat{J}_z \hat{j}_z - \hat{J}_+ \hat{j}_- - \hat{J}_- \hat{j}_+ \quad (2)$$

where \hat{J} is the total angular momentum operator. \hat{J}_z and \hat{j}_z are their corresponding projections onto the body-fixed z axis and \hat{J}_+ (\hat{J}_-) and \hat{j}_+ (\hat{j}_-) are the corresponding raising (lowering) operators which represent the Coriolis coupling [1,2]. $V(R, r, \theta)$ is obtained from our fitted potential surface.

We use a discrete variable representation (DVR) for the radial coordinates and a finite basis representation (FBR) for the angular coordinates [3]. We define equidistant grids labeled by χ_1 and χ_2 for R and r and use the following parity (p) - adapted BF-FBR for θ [4].

$$|j\Omega; Jp\rangle = (2 + 2\delta_{\Omega,0})^{-1/2} (|J\Omega\rangle |j\Omega\rangle + p(-1)^J |J-\Omega\rangle |j-\Omega\rangle) \quad (3)$$

where $|j\Omega\rangle \equiv \Theta_{j\Omega}(\gamma, 0)$ are normalized associate Legendre functions with the Condon-Shortley phase convention [5]. The overall rotation is represented by $|J\Omega\rangle = \sqrt{(2J+1)/8\pi^2} D_{\Omega,0}^{J*}$ where $D_{\Omega,0}^{J*}$ is the Wigner rotation matrix [6]. In the body-fixed frame, Ω is the projection of J and j onto z axis and restricted to be non-negative. Thus, the wavepacket can be expressed as

$$|\psi^{Jp}\rangle = \sum_{\chi_1 \chi_2 j \Omega} \Psi_{\chi_1 \chi_2 j \Omega}^{Jp} |\chi_1\rangle |\chi_2\rangle |j\Omega; Jp\rangle \quad (4)$$

In the dynamic calculations, the wavepacket is propagated using the modified Chebyshev recursion relation [7-9]

$$|\psi_{k+1}\rangle = D(2H_{scaled} |\psi_k\rangle - D |\psi_{k-1}\rangle), \quad k \geq 1 \quad \text{and} \quad |\psi_1\rangle = D \hat{H}_{scaled} |\psi_0\rangle \quad (5)$$

The scaled Hamiltonian is defined by the spectral width and mean of the Hamiltonian, $\hat{H}_{scaled} = (\hat{H} - H^+) / H^-$, where $H^\pm = (H_{max} \pm H_{min}) / 2$ with H_{max} , H_{min} as the upper and lower spectral bound [10], respectively. The wavepacket is absorbed by damping function D at the edges of grids to enforce the outgoing boundary condition

$$D(x) = \begin{cases} 1, & \text{for } x \leq x_d \\ e^{-d_x(x-x_d)^2}, & \text{for } x > x_d \end{cases} \quad x = R \text{ or } r \quad (6)$$

The initial wavepacket is constructed as a product of a one-dimensional Gaussian-shaped wavepacket along R , a well-defined rovibrational eigenfunction of reactant HF and a space-fixed (SF) angular momentum eigenstate in the coupled representation.

$$|\psi_0\rangle = N e^{-(R-R_0)^2/2\delta^2} \cos(k_0 R) |\varphi_{v_i j_i}\rangle |JMj_i l_i\rangle \quad (7)$$

where k_0 , R_0 , δ and N are the mean momentum, mean position, width, and normalization constant, respectively.

The actions of the first two kinetic energy operators (KEOs) in eq 1 are performed by fast sine Fourier transform. The third KEO term is diagonal in the BF-FBR

$$\langle j' \Omega'; Jp | \hat{j}^2 | j \Omega; Jp \rangle = j(j+1) \delta_{j',j} \delta_{\Omega',\Omega} \quad (8)$$

The fourth KEO term is tri-diagonal in the BF-FBR and we can also calculate straightforward

$$\begin{aligned} \langle j' \Omega'; Jp | \hat{l}^2 | j \Omega; Jp \rangle &= [J(J+1) + j(j+1) - 2\Omega^2] \delta_{j',j} \delta_{\Omega',\Omega} - \\ & \left[(1 + \delta_{\Omega',0})(1 + \delta_{\Omega,0}) \right]^{-1/2} \left\{ \lambda_{j\Omega}^+ \lambda_{j\Omega}^+ \delta_{\Omega',\Omega+1} + \lambda_{j\Omega}^- \lambda_{j\Omega}^- \left[\delta_{\Omega',\Omega-1} + p(-1)^j \delta_{\Omega',-\Omega+1} \right] \right\} \delta_{j',j} \end{aligned} \quad (9)$$

where $\lambda_{jm}^\pm = \sqrt{j(j+1) - m(m \pm 1)}$.

Herein, we first transform the wavepacket in the BF-FBR $|j\Omega; Jp\rangle$ to the SF-FBR $|jl; Jp\rangle$ using the formula below [11] because that the spectral range is unmanageable

when the corresponding rotational energy constant becomes very large with $R \rightarrow 0$ in the BF frame.

$$|j\Omega; Jp\rangle = \sum_l (-1)^{j-l+\Omega} \sqrt{(2-\delta_{\Omega,0})(2l+1)} \begin{pmatrix} j & l & J \\ \Omega & 0 & -\Omega \end{pmatrix} |jl; Jp\rangle \quad (10)$$

where $\begin{pmatrix} l \\ \Omega \end{pmatrix}$ is the 3-j symbol. We can control the spectral range conveniently by truncating the rotational energy as the fourth KEO is diagonal in the SF-FBR. The wavepacket is then transformed back to the original BF-FBR after this.

The action of the fifth term in eq 1 (potential energy operator) is diagonal at DVR points. In this case, the angular DVR is defined by the angular Gauss-Legendre quadrature points associated with rotational basis. We transform the wavepacket from the FBR to angular DVR through a pseudospectral transform [12,13]

$$T_{j\alpha}^{(\Omega)} = \sqrt{\omega_\alpha} \Theta_{j\Omega}(\gamma_\alpha) \quad (11)$$

where α is the index of the Gauss-Legendre quadrature points for the Jacobi angular coordinate and ω_α is the corresponding weight.

The initial-state-selected reaction probability is extract by flux method using the following equation [14,15]

$$P(E) = \frac{1}{2\pi\mu_r |a_i(E)|^2 (H^-)^2 \sin^2 \theta} \times \text{Im} \left\langle \sum_k (2-\delta_{k0}) e^{-ik\theta} \psi_k \left| \sum_{k'} (2-\delta_{k'0}) e^{-ik'\theta} \left[\delta(r-r_f) \frac{\partial}{\partial r} \psi_{k'} \right] \right. \right\rangle \quad (12)$$

r_f defines the dividing surface in the product channel where we calculate the outgoing flux. $a_i(E) = \langle i\sqrt{\mu_R k_i / 2\pi R h_\Lambda^{(2)}}(k_i R) | g(R) \rangle$ is the energy amplitude [16], where $h_\Lambda^{(2)}(k_i R)$ is the spherical Hankel function of the second kind.

The integral cross section (ICS) is obtained by partial wave summation over J and an average over l ($l \in [|J - j_i|, J + j_i]$)

$$\sigma_{v_i j_i}(E) = \frac{f\pi}{(2j_i+1)k_{v_i j_i}^2} \sum_{J, l_i} (2J+1) P_{v_i j_i}^J(E) \quad (13)$$

where $k_{v_i j_i}^2 = 2\mu_R E_c$, E_c is the collision energy and f is the electronic degeneracy factor

which is set to 1 for this reaction.

The rate constant is obtained by integrating of the ICS over the collision energy with the Boltzmann weight

$$k_{v_i, j_i}(T) = \frac{1}{k_B T} \left(\frac{8}{\pi \mu_R k_B T} \right)^{1/2} \int_0^{\infty} \sigma_{v_i, j_i}(E_c) e^{-E_c/k_B T} E_c dE_c \quad (14)$$

where k_B is the Boltzmann constant and T is temperature.

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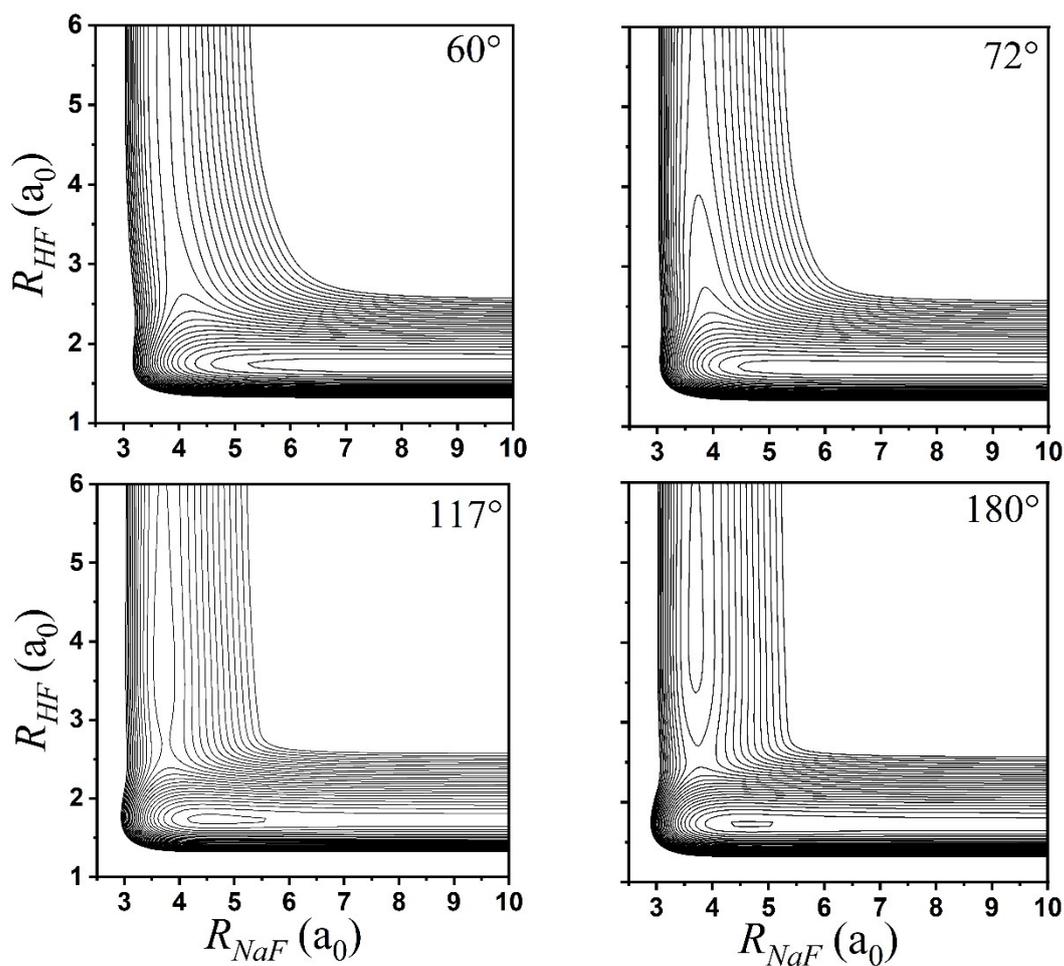


Fig. S1 The contour plots of potential energy surfaces in terms of Na-F bond length (x-axis) and H-F bond length (y-axis) for several fixed bond angles, $\theta_{NaFH} = 60^\circ, 72^\circ, 117^\circ, 180^\circ$. Isoenergetic contours are drawn every 0.1 eV from 0 to 2.5 eV with respect to the energy of the global minimum of the PES.

Table S1. The eigen-energies of the $v = 0-5, j = 0-7$ rovibrational states of the reactant and product. All the energies are given in eV.

(v, j)	HF	NaF	(v, j)	HF	NaF
(0, 0)	0.2555	1.2773	(3, 0)	1.6892	1.4648
(0, 1)	0.2606	1.2774	(3, 1)	1.6938	1.4649
(0, 2)	0.2709	1.2776	(3, 2)	1.7030	1.4651
(0, 3)	0.2862	1.2779	(3, 3)	1.7167	1.4654
(0, 4)	0.3067	1.2784	(3, 4)	1.7351	1.4658
(0, 5)	0.3323	1.2789	(3, 5)	1.7580	1.4663
(0, 6)	0.3629	1.2795	(3, 6)	1.7853	1.4670
(0, 7)	0.3985	1.2802	(3, 7)	1.8172	1.4677
(1, 0)	0.7582	1.3408	(4, 0)	2.1204	1.5256
(1, 1)	0.7631	1.3409	(4, 1)	2.1248	1.5257
(1, 2)	0.7730	1.3411	(4, 2)	2.1337	1.5259
(1, 3)	0.7877	1.3414	(4, 3)	2.1470	1.5262
(1, 4)	0.8073	1.3418	(4, 4)	2.1647	1.5266
(1, 5)	0.8318	1.3423	(4, 5)	2.1867	1.5271
(1, 6)	0.8611	1.3430	(4, 6)	2.2131	1.5277
(1, 7)	0.8953	1.3437	(4, 7)	2.2439	1.5284
(2, 0)	1.2360	1.4032	(5, 0)	2.5316	1.5855
(2, 1)	1.2408	1.4033	(5, 1)	2.5358	1.5856
(2, 2)	1.2503	1.4035	(5, 2)	2.5444	1.5858
(2, 3)	1.2646	1.4039	(5, 3)	2.5572	1.5861
(2, 4)	1.2835	1.4043	(5, 4)	2.5742	1.5865
(2, 5)	1.3072	1.4048	(5, 5)	2.5954	1.5870
(2, 6)	1.3355	1.4054	(5, 6)	2.6209	1.5876
(2, 7)	1.3685	1.4061	(5, 7)	2.6504	1.5883