

**Modulations of Transition-state Control of State-to-state Dynamics of the  $F + H_2O \rightarrow HF +$   
OH Reaction**

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**Supporting Information**

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## I. Hamiltonian and discretization

For state-to-state calculations of a tetra-atom reactive system using the TSWP approach, both the atom-triatom and diatom-diatom Jacobi coordinates need to be defined. As shown in Fig. S1, the A+BCD atom-triatom and AB+CD diatom-diatom Jacobi coordinates are denoted as  $(R, r_1, r_2, \theta_1, \theta_2, \varphi)$  and  $(R', r'_1, r'_2, \theta'_1, \theta'_2, \varphi')$ , respectively. The  $z$ -axis of the body-fixed (BF) frame for the A+BCD or AB+CD system is defined to coincide the  $\mathbf{R}$  or  $\mathbf{R}'$  vector, and the vector  $\mathbf{r}_1$  or  $\mathbf{r}'_1$  lies in the corresponding  $x$ - $z$  plane. We note that the triangle formed by A, B, and the CD center-of-mass (COM) spans a common plane in both coordinate systems and  $\mathbf{r}_2$  and  $\mathbf{r}'_2$  are the same vector. For the current system, A, B, C, and D are F, H, O and H', respectively.

Since the AB+CD and A+BCD Hamiltonians have the same form, we use below the latter Hamiltonian ( $\hbar=1$  hereafter):

$$\hat{H} = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{(\hat{J} - \hat{j}_{12})^2}{2\mu R^2} + \sum_{i=1}^2 \left[ \hat{h}_i(r_i) + \frac{\hat{j}_i^2}{2\mu_i r_i^2} \right] + V(R, r_1, r_2, \theta_1, \theta_2, \varphi). \quad (\text{S1})$$

For the A+BCD system,  $\mu$  is the reduced mass between A and the COM of BCD,  $\mu_1$  is the reduced mass between B and the COM of CD, and  $\mu_2$  is the reduced mass of CD.  $\hat{j}_{12}$  and  $\hat{j}_2$  are the rotational angular momentum operators of BCD and CD, respectively, and  $\hat{j}_1 = \hat{j}_{12} - \hat{j}_2$  is the orbital angular momentum operator of B relative to CD. For the AB+CD system,  $\mu'_1$  and  $\mu'_2$  are diatomic reduced masses for AB and CD,  $\mu'$  is the reduced mass between the COMs of AB and CD.  $\hat{j}'_1$  and  $\hat{j}'_2$  are the rotational angular momentum operators of AB and CD, respectively, and

they are coupled to form  $\hat{j}'_{12}$ . For both cases, the total angular momentum quantum number ( $J$ ) is conserved, and the reference vibrational Hamiltonians  $\hat{h}_i(r_i)$  are defined as

$$\hat{h}_i(r_i) = -\frac{1}{2\mu_i} \frac{\partial^2}{\partial r_i^2} + V_i(r_i), \quad (i=1,2), \quad (\text{S2})$$

where  $V_i(r_i)$  are the one-dimensional (1D) reference potentials. Note that the two arrangement channels have different 1D reference potentials and the potential term in Eq. (S1),  $V$ , is the total PES minus the reference potentials.

The wave functions is discretized in the terms of BF bases,

$$\Psi^{JM\varepsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, t) = \sum_{n,\nu,j,K} F_{n\nu jK}^{JM\varepsilon}(t) u_n^{\nu_1}(R) \phi_{\nu_1}(r_1) \phi_{\nu_2}(r_2) y_{jK}^{JM\varepsilon}(\hat{R}, \hat{r}_1, \hat{r}_2), \quad (\text{S3})$$

where  $M$  and  $K$  are the projections of  $J$  in the space-fixed (SF) and body-fixed (BF) frames, respectively. The composite index  $\nu$  denotes the two vibrational quantum numbers,  $\nu_1$  and  $\nu_2$ , and the vibrational eigenfunctions  $\phi_{\nu_i}(r_i)$  are the eigenfunctions of the reference vibrational Hamiltonians  $\hat{h}_i(r_i)$ , which define the potential optimized discrete variable representation (PODVR).<sup>1</sup> The translational basis  $u_n^{\nu_1}(R)$  is defined as<sup>2</sup>

$$u_n^{\nu_1}(R) = \begin{cases} \sqrt{\frac{2}{L_{asy}}} \sin \frac{n\pi(R-R_1)}{L_{asy}}, \nu_1 \leq \nu_{asy}, R \in (R_1, R_3) \\ \sqrt{\frac{2}{L_{int}}} \sin \frac{n\pi(R-R_1)}{L_{int}}, \nu_1 > \nu_{asy}, R \in (R_1, R_2) \end{cases}, \quad (\text{S4})$$

where  $L_{asy} = R_3 - R_1$  and  $L_{int} = R_2 - R_1$  are the lengths of the asymptotic and interaction regions along  $R$ , and the point  $R_2$  separates the  $R$  coordinate range  $(R_1, R_3)$  into the asymptotic and interaction regions in an  $L$ -shaped scheme.<sup>3</sup> Different translational bases are used in the two regions with the same grid points.  $\nu_{asy}$  is chosen to be the number of energetically open vibrational channels plus one or two closed channels. The composite index  $j$  denotes  $(j_1, j_2, j_{12})$ ,  $\varepsilon$  is the parity of the system defined as  $\varepsilon = (-1)^{j_1+j_2+l}$  with  $l$  being the quantum number for the orbital angular momentum  $\hat{l} = \hat{J} - \hat{j}_{12}$ . The parity-adapted BF rotational basis  $y_{jK}^{JM\varepsilon}(\hat{R}, \hat{r}_1, \hat{r}_2)$  is given as

$$y_{jK}^{JM\varepsilon}(\hat{R}, \hat{r}_1, \hat{r}_2) = \sqrt{\frac{2J+1}{8\pi(1+\delta_{K0})}} [D_{K,M}^{J*}(\alpha, \beta, \gamma) Y_{j_1 j_2}^{j_12 K}(\theta_1, \theta_2, \varphi) + \varepsilon(-1)^{j_1+j_2+j_{12}+J} D_{-K,M}^{J*}(\alpha, \beta, \gamma) Y_{j_1 j_2}^{j_12 -K}(\theta_1, \theta_2, \varphi)], \quad (S5)$$

where  $D_{K,M}^{J*}(\alpha, \beta, \gamma)$  is the Wigner rotation matrix<sup>4</sup> that rotates the SF frame to BF frame by three Euler angles  $(\alpha, \beta, \gamma)$ . The restriction,  $\varepsilon(-1)^{j_1+j_2+j_{12}+J} = 1$ , for  $K=0$  partitions the rotational basis set into even and odd parities. It again should be noted here that the definition of  $Y_{j_1 j_2}^{j_12 K}(\theta_1, \theta_2, \varphi)$  is different for the A+BCD and AB+CD arrangements. The A+BCD rotational basis  $Y_{j_1 j_2}^{j_12 K}(\theta_1, \theta_2, \varphi)$  is given by<sup>5</sup>

$$Y_{j_1 j_2}^{j_12 K}(\theta_1, \theta_2, \varphi) = \sum_m D_{Km}^{j_12*}(0, \theta_1, \varphi) \sqrt{\frac{2j_1+1}{4\pi}} \langle j_2 m j_1 0 | j_{12} m \rangle y_{j_2 m}(\theta_2, 0), \quad (S6)$$

where  $y_{jm}$  is the spherical harmonics, and  $\langle j_2 m j_1 0 | j_{12} m \rangle$  is the Clebsch-Gordan coefficient.<sup>4</sup>

The Wigner rotation matrix  $D_{Km}^{j_12*}(0, \theta_1, \varphi)$  rotates the BF frame to the MF frame (the  $z$  axis of

this frame lies along vector  $\mathbf{r}_1$ ) by the Euler angles  $(0, \theta_1, \varphi)$ . On the other hand, the AB+CD rotational basis  $Y_{j'_1 j'_2}^{j'_2 K'}(\theta'_1, \theta'_2, \varphi')$  is given by<sup>6</sup>

$$Y_{j'_1 j'_2}^{j'_2 K'}(\theta'_1, \theta'_2, \varphi') = \sum_{m'_1} \langle j'_1 m'_1 j'_2 K' - m'_1 | j'_2 K' \rangle y_{j'_1 m'_1}(\theta'_1, 0) y_{j'_2 K' - m'_1}(\theta'_2, \varphi'). \quad (\text{S7})$$

The radial kinetic energy operator in the Hamiltonian is expressed in a small and dense matrix, while the angular kinetic energy operator assumes a diagonal form.<sup>1</sup>

## II. Thermal flux eigenstates

The thermal flux eigenstates were determined in the diatom-diatom Jacobi coordinates using the Lanczos method implemented in ARPACK.<sup>7</sup> These eigenstates ( $|f_T^n\rangle$ ) come in pairs with eigenvalues ( $f_T^n$ ) of the same absolute value but opposite in sign.<sup>8</sup> The lowest ten pairs have been determined and their energies, defined as relative to the ground ( $n=1$ ) vibrational energy of the activated complex:

$$E_n \approx -k_B T (\ln |f_T^n| - \ln |f_T^1|), \quad (\text{S8})$$

where the approximate energy of this ground state is  $E_1 \approx -k_B T \ln |f_T^1|$ , represent approximately the excitation energies of higher thermal flux eigenstates relative to  $E_1$ . They can be considered as energies of the activated complex and listed in Table S1.

## III. Convergence

Parameters used in the final calculations are given as follows. The propagation of the TSWPs was carried out using the second order split-operator method<sup>53</sup> with a time step of 10 au. The total propagation time is 90000 and 50000 au for the reactant and product arrangement channels, respectively. The long propagation is due to the resonances in the pre- and post-

reaction wells. In the atom-triatom arrangement channel, a total of 333 sine basis functions covering a range from 2.5 to 23.0 bohr were used for  $R$ , with 48 for the interaction region. 32 and 9 PODVR basis functions in the range from 0.7 to 5.0 bohr were used for  $r_1$  in the interaction and asymptotic regions, respectively. Only 4 PODVR basis functions in the range from 0.7 to 5.0 bohr were used for  $r_2$ . The size of the rotational basis functions was controlled by the parameters,  $j_{1\max} = 28$ ,  $j_{2\max} = 20$ . The reactant asymptotic dividing surface was placed at  $R_r^\infty = 16.0$  bohr. The absorption potentials use following form:

$$V(q) = -iC \left( \frac{q - q_0}{L} \right)^n \quad (\text{S9})$$

where  $C$ ,  $q_0$  and  $L$  are the strength, length and starting point of the absorption potential. For  $R$ ,  $C_R = 0.0025$  au,  $R_0 = 17.1$  au,  $L_R = 5.9$  au and  $n_R = 1.5$ ; for  $r_1$ ,  $C_{r_1} = 0.045$  au,  $r_{1,0} = 2.7$  au,  $L_{r_1} = 2.3$  au and  $n_{r_1} = 1.5$ .

In the diatom-diatom arrangement channel, a total number of 309 sine basis functions covering a range from 2.5 to 23.0 bohr were used for  $R'$ , with 48 for the interaction region. 32 and 6 PODVR basis functions in the range from 0.7 to 5.0 bohr were used for  $r'_1$  in the interaction and asymptotic regions, respectively. Similarly, 4 PODVR basis functions in the range from 0.7 to 5.0 bohr were used for the OH bond length  $r'_2$ . The size of the rotational basis functions was controlled by the parameters,  $j'_{1\max} = 42$ ,  $j'_{2\max} = 18$ . The product asymptotic dividing surface was located at  $R_p^\infty = 16.0$  bohr. The absorption potentials use the same form as in Eqn. (S9). For  $R'$ ,  $C_{R'} = 0.0025$  au,  $R'_0 = 17.1$  au,  $L_{R'} = 5.9$  au and  $n_{R'} = 1.5$ ; for  $r'_1$ ,  $C_{r'_1} = 0.05$  au,  $r'_{1,0} = 3.5$  au,  $L_{r'_1} = 1.5$  au and  $n_{r'_1} = 1.5$ .

We first examine the convergence of initial state-selected reaction probabilities with respect to the number of thermal flux eigenstates. As shown in Fig. S1 for three rotational states of H<sub>2</sub>O in its ground vibrational state, the reaction probabilities with eight pairs of thermal flux eigenstates are indistinguishable from the corresponding ones with ten pairs, indicating convergence for the initial state-selected reaction probabilities in the current energy range.

The convergence of state-to-state reaction probabilities is then examined by comparing the  $J=0$  initial state-selected total reaction probability of the F + H<sub>2</sub>O(000, 0<sub>00</sub>) reaction obtained from three different methods: (1) the TSWP method with propagation only in the reactant rearrangement channel; (2) the sum of TSWP state-to-state reaction probabilities over all product states; (3) an initial state specific wave packet (ISSWP) method using the reactant coordinates, which can be considered as a benchmark. The TSWP calculations were performed with the lowest eight pairs of thermal flux eigenstates. It can be seen from Fig. S3 that the agreement among the three calculations is excellent in the energy range, which validates the implementation.

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Table S1. Excitation energies of the activated complex.

$n$	$E_n$ (cm <sup>-1</sup> )
1	0.0
2	311.0
3	499.9
4	612.0
5	812.3
6	925.4
7	968.5
8	1142.2
9	1258.0
10	1270.5

**Figure S1.** The A+BCD ( $R, r_1, r_2, \theta_1, \theta_2, \varphi$ ) and AB+CD Jacobi coordinates ( $R', r'_1, r'_2, \theta'_1, \theta'_2, \varphi'$ ) for tetra-atomic reactions. The angle between the two BF  $z$  axes  $R$  and  $R'$  is denoted as  $\Delta$ .

**Figure S2.** Convergence of the initial state-selected reaction probability with respect to the number of thermal flux eigenpairs for three initial rotational states of vibrationless H<sub>2</sub>O: a. 0<sub>00</sub>, b. 1<sub>01</sub>, and c. 4<sub>04</sub>.

**Figure S3.** Initial state-selected total reaction probabilities of the F + H<sub>2</sub>O(000, 0<sub>00</sub>) reaction obtained from the TSWP method with only reactant propagation (black solid) and the sum of TSWP state-to-state reaction probabilities over all product states (red solid). For comparison, the reaction probability obtained by the ISSWP method is also shown (green dashed). The TSWP calculations use eight pairs of thermal flux eigenstates.



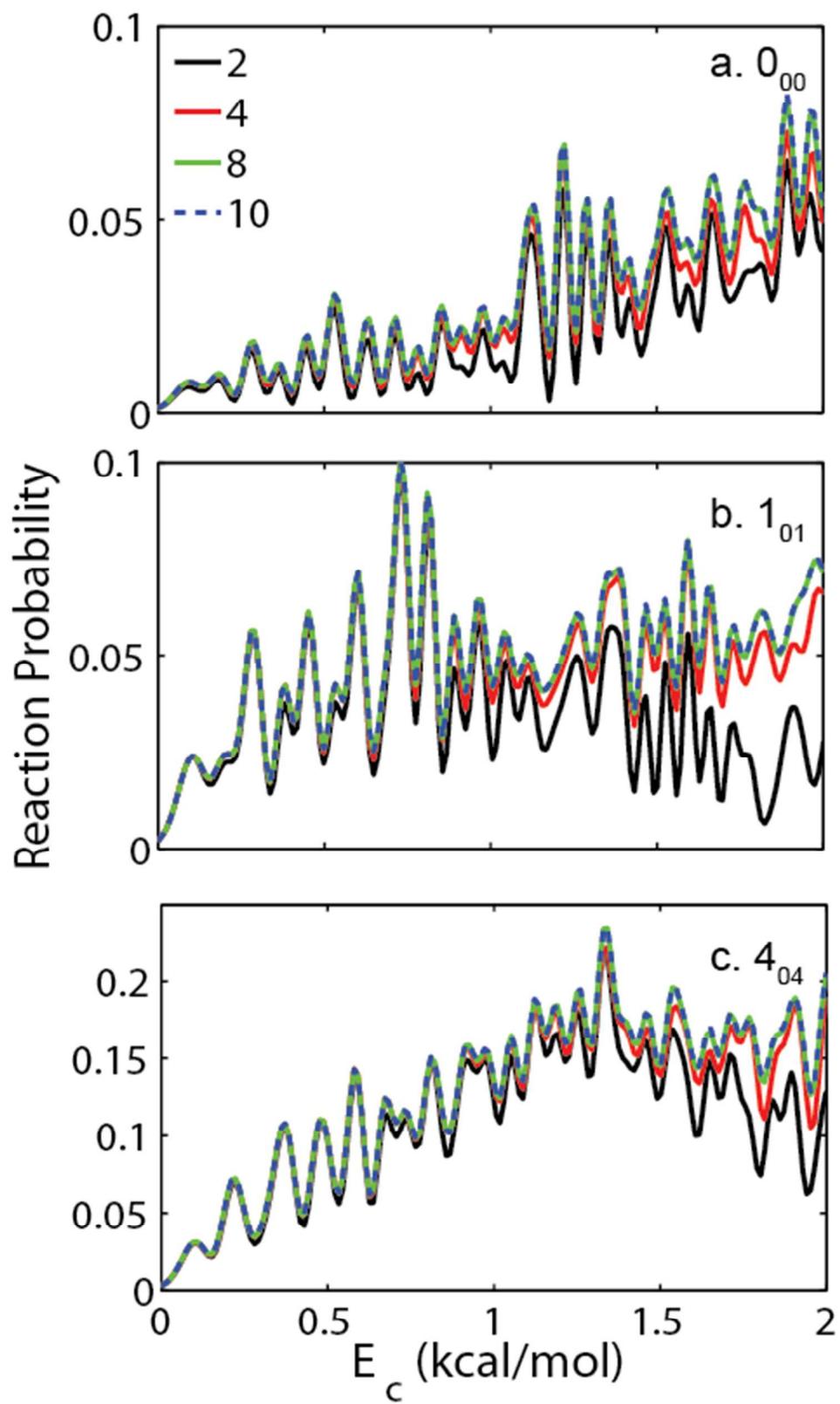


Figure S2

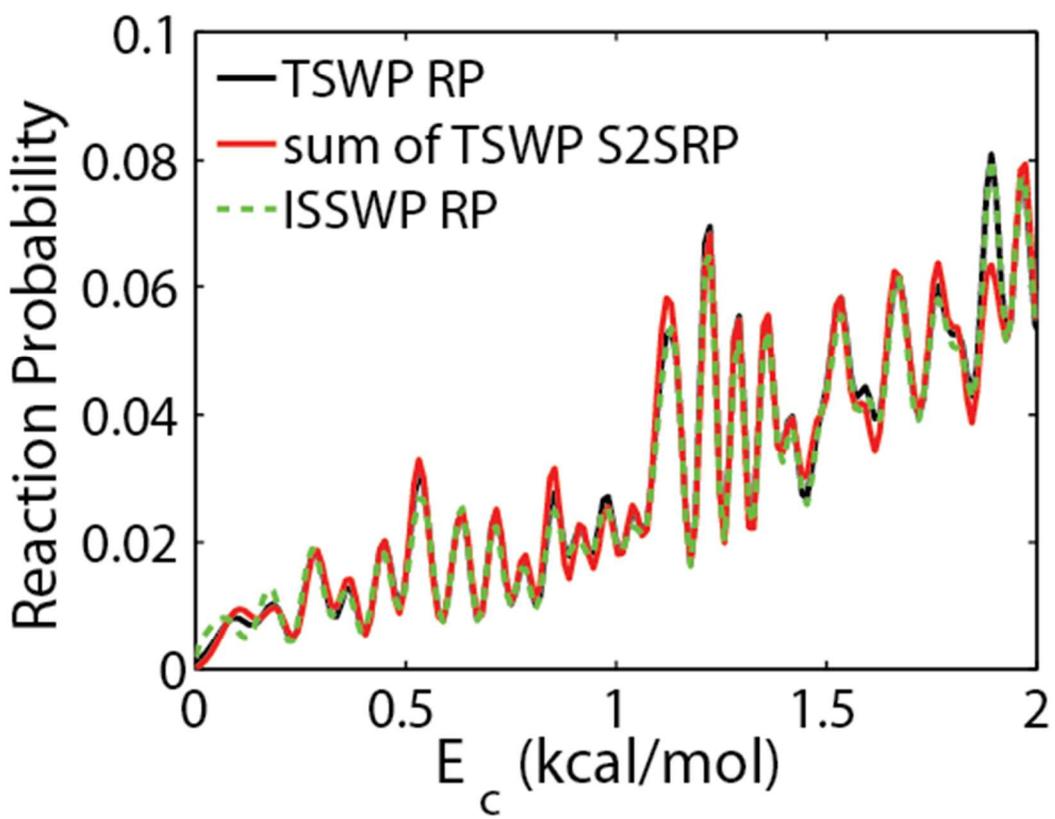


Figure S3