

## Vibrationally Mediated Bond Selective Dissociative Chemisorption of HOD on Cu(111)

### Supporting Information

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## SI-Theory

The Hamiltonian in Eq. (1) was discretized in a mixed discrete variable representation (DVR) and finite basis representation (FBR).<sup>1</sup> The  $z$  and  $r_2$  coordinates were discretized using the sine DVR,<sup>2</sup> while  $r_1$  was treated as non-reactive with a potential optimized DVR (PODVR).<sup>3-</sup>  
<sup>4</sup> This is possible because the transition state is “late” and the flux passing through a particular transition state is unlikely to reach the other equivalent one. The potential energy operator is diagonal in the DVR representation. To evaluate the rotational kinetic energy terms in the Hamiltonian, a non-direct product FBR basis was used,

$$|jJK\rangle = |jK\rangle |JK\rangle = \bar{P}_j^K(\cos\theta_1)\bar{P}_J^K(\cos\theta_2)\Phi_K(\varphi), \quad (\text{S1})$$

where  $j$ ,  $J$ , and  $K$  are the angular momentum quantum numbers associated with diatom, the triatom, and the projection of  $\hat{J}$  on the molecular-fixed  $z$ -axis which is along  $r_2$ .  $\bar{P}_j^K(\cos\theta_1)$  and  $\bar{P}_J^K(\cos\theta_2)$  are normalized associated Legendre polynomials, and  $\Phi_K(\varphi)$  is the normalized exponential Fourier function ( $\frac{1}{\sqrt{2\pi}}\exp(iK\varphi)$ ). The angular kinetic energy operator has a tridiagonal form in this basis.<sup>5</sup> The corresponding angular grid is a direct product of the Gauss-Legendre quadrature points in  $\theta_1$  and  $\theta_2$ , and a Fourier grid in  $\varphi$ . While there is no inversion symmetry in  $\varphi$  for a molecule on a real surface, such symmetry is present in our model Hamiltonian. Hence, we took advantage of the inversion symmetry of the potential with respect to  $\varphi$  by expanding the wave function of even parity in terms of  $\cos(K\varphi)$  basis functions. In the propagation, the wave packet was transformed to the angular grid by three one-dimensional pseudo-spectral transformations,<sup>6</sup> which allow the evaluation of the action of the potential energy operator at each grid point.

The reaction probabilities were calculated using the Chebyshev wave packet approach recently proposed by the current authors.<sup>7-8</sup> This method is based on the well-known quantum transition-state theory introduced by Miller and coworkers,<sup>9</sup> which uses the following trace formula to calculate the cumulative reaction probability  $N(E)$  :

$$N(E) = 2\pi^2 \text{Tr}[\hat{F}_1 \delta(E - \hat{H}) \hat{F}_2 \delta(E - \hat{H})], \quad (\text{S2})$$

where  $\hat{H}$  is the Hamiltonian of the reaction system,  $\hat{F}_1$  and  $\hat{F}_2$  are the flux operators defined at two dividing surfaces  $S_1$  and  $S_2$ , and  $\delta(E - \hat{H})$  is the Dirac's delta function.

The two dividing surfaces in Eq. (S2) can coincide with each other or be defined in different positions, as long as they separate the reactant channel from the product channel. The former arrangement is convenient for computing the cumulative reaction probability,<sup>10-12</sup> and the latter is useful when initial state selected reaction probabilities are desired.<sup>7, 13-14</sup> In our work,  $S_1$  is located in the reactant asymptote with  $z=z_0$ , which defines naturally the initial wave packets associated with various reactant internal states. The initial state selected reaction probabilities are computed by evaluating the flux through the second dividing surface  $S_2$ , placed beyond the transition state:

$$P_{n_1}(E) = 4\pi^2 \lambda_1 \langle \phi_{n_1}^+ | \delta(E - \hat{H}) \hat{F}_2 \delta(E - \hat{H}) | \phi_{n_1}^+ \rangle, \quad (\text{S3})$$

where  $\lambda_1$  is the absolute value of the two non-zero eigenvalues of the flux operator  $\hat{F}_1$  defined at the first dividing surface  $S_1$  ( $\hat{F}_1 |\pm\rangle = \pm \lambda_1 |\pm\rangle$ ),<sup>15-16</sup> and  $|\phi_{n_1}^+\rangle \equiv |+\rangle |n_1\rangle$  is a product of the positive flux eigenstate and a ro-vibrational state for the reactant labeled by  $n_1$ .<sup>10</sup>

To compute the reaction probability in Eq. (S3), the Dirac delta function was expanded:<sup>17-18</sup>

$$\delta(E - \hat{H}) = \frac{1}{\Delta H \pi \sin \theta} \sum_{k=0}^{\infty} (2 - \delta_{k0}) T_k(E_{norm}) T_k(\hat{H}_{norm}), \quad (\text{S4})$$

where  $T_k(\hat{H}_{norm}) \equiv \cos(k\hat{\Theta})$  is the Chebyshev propagator,<sup>17-18</sup> and the Chebyshev angle and the corresponding angular operator are given in terms of normalized energy and Hamiltonian, respectively,

$$\theta = \arccos(E_{norm}) = \arccos\left(\frac{E - \bar{H}}{\Delta H}\right), \quad \hat{\Theta} = \arccos(\hat{H}_{norm}) = \arccos\left(\frac{\hat{H} - \bar{H}}{\Delta H}\right). \quad (\text{S5})$$

Here, the mean and half-width of the Hamiltonian are determined as  $\bar{H} = (H_{max} + H_{min})/2$  and  $\Delta H = (H_{max} - H_{min})/2$ , where  $H_{max}$  and  $H_{min}$  define the spectral range of the Hamiltonian, which can be estimated from the kinetic energy and potential on the grid.

Substituting Eq. (S4) back to Eq. (S3), we have

$$P_{n_1}(E) = \frac{4\lambda_1}{\mu_2 \Delta H^2 \sin^2 \theta} \text{Im} \left[ \left\langle \sum_{k=0} (2 - \delta_{k0}) \cos(k\theta) \psi_k \right| \delta(r_2 - r_{2f}) \frac{\partial}{\partial r_2} \left| \sum_{k'=0} (2 - \delta_{k'0}) \cos(k'\theta) \psi_{k'} \right\rangle \right], \quad (\text{S6})$$

where  $r_2 = r_{2f}$  defines the second dividing surface.

The Chebyshev wave packet  $|\psi_k\rangle = T_k(\hat{H}_{norm})|\phi_{n_1}^+\rangle$  is propagated with a modified Chebyshev recursion scheme:<sup>19</sup>

$$|\psi_k\rangle = D(2\hat{H}_{norm}|\psi_{k-1}\rangle - D|\psi_{k-2}\rangle), \quad k \geq 2 \quad (\text{S7})$$

where  $|\psi_0\rangle = |\phi_{n_1}^+\rangle$  and  $|\psi_1\rangle = D\hat{H}_{norm}|\psi_0\rangle$ .  $D$  is a damping function designed to avoid spurious reflection of the wave packet at grid edges, which generally has the following exponential form,

$$D(\zeta) = \begin{cases} 1 & \zeta < \zeta_d, \\ e^{-\alpha\left(\frac{\zeta - \zeta_d}{\zeta_{max} - \zeta_d}\right)^2} & \zeta \geq \zeta_d. \end{cases} \quad (\text{S8})$$

Here,  $\zeta$  is defined in both the  $z$  and  $r_2$  coordinates.

To calculate the reaction probability as a function of the energy, the wavefunctions defined on an energy grid ( $\{E_i\}$ )

$$|\Psi_{n_1}(E_i)\rangle = \frac{1}{\Delta H \pi \sin \theta_i} \sum_{k=0} (2 - \delta_{k0}) \cos(k\theta_i) |\psi_k\rangle \quad (\text{S9a})$$

$$|\Psi'_{n_1}(E_i)\rangle = \frac{1}{\Delta H \pi \sin \theta_i} \sum_{k=0} (2 - \delta_{k0}) \cos(k\theta_i) \frac{\partial}{\partial r_2} |\psi_k\rangle \quad (\text{S9b})$$

are assembled on the fly from the Chebyshev wave packets. Note that only the wave functions on the dividing surface ( $S_2$  or  $r_2 = r_{2f}$ ) are needed. The differentiation of the Chebyshev wave packet in Eq. (S9b) can be carried out analytically on the sine basis. All parameters used in this work have been listed in Table I.

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