

Supplementary Information for

**Comparison of Experimental and Theoretical Quantum-state-selected Integral Cross Sections for the  $\text{H}_2\text{O}^+ + \text{H}_2$  ( $\text{D}_2$ ) Reactions in the Collision Energy Range of 0.04-10.00 eV**

Hongwei Song,<sup>a)</sup> Anyang Li,<sup>b)</sup> Hua Guo\*

*Department of Chemistry and Chemical Biology, University of New Mexico,  
Albuquerque, NM 87131*

Yuntao Xu, Bo Xiong, Yih-Chung Chang, and C. Y. Ng\*

*Department of Chemistry, University of California,  
Davis, CA 95616*

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- a) Present address: State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China  
b) Present address: College of Chemistry and Materials Science, Northwest University, Xi'an, 710069, China  
\* Email addresses: Hua Guo <[hguo@unm.edu](mailto:hguo@unm.edu)> and C. Y. Ng <[cyng@ucdavis.edu](mailto:cyng@ucdavis.edu)>

## S-I. THEORY

### S-IA. Quantum dynamics

The parity ( $\varepsilon$ ) adapted wave function is expanded in terms of the body-fixed (BF) ro-vibrational basis functions:

$$\psi^{J_{\text{tot}}M\varepsilon}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3) = \sum_{n, \nu_1, j, K} F_{n\nu_1 j K}^{J_{\text{tot}}M\varepsilon} u_n^{\nu_1}(R) \phi_{\nu_1}(r_1) \Phi_{jK}^{J_{\text{tot}}M\varepsilon}(\hat{R}, \hat{r}_1, \hat{r}_2, \hat{r}_3), \quad (1)$$

where  $n$  labels the translational basis functions,  $\nu_1$  is the basis index for  $r_1$ ;  $j$  denotes  $(j_1, l_2, j_3, J_{23}, J)$ . The translational basis function,  $u_n^{\nu_1}$ , is dependent on  $\nu_1$  due to the use of an  $L$ -shaped grid.  $\Phi_{jK}^{J_{\text{tot}}M\varepsilon}$  in Eq. (1) is the parity-adapted coupled BF total angular momentum eigenfunction, which can be written as

$$\Phi_{jK}^{J_{\text{tot}}M\varepsilon} = (1 + \delta_{K0})^{-1/2} \sqrt{\frac{2J_{\text{tot}} + 1}{8\pi}} [D_{K,M}^{J_{\text{tot}}} Y_{j_1 j_2 j_3}^{JK} + \varepsilon (-1)^{j_1 + l_2 + j_3 + J + J_{\text{tot}}} D_{-K,M}^{J_{\text{tot}}} Y_{j_1 j_2 j_3}^{J-K}], \quad (2)$$

where  $D_{K,M}^J$  is the Wigner rotation matrix.<sup>1</sup>  $M$  is the projection of  $J_{\text{tot}}$  on the space-fixed  $z$  axis, and  $K$  is its projection on the body-fixed  $z$  axis that coincides with  $R$ .  $Y_{j_1 j_2 j_3}^{JK}$  is the eigenfunction of  $\hat{J}$  defined as

$$Y_{j_1 j_2 j_3}^{JK} = \sum_{\omega} \langle j_1 \omega j_2 3 K - \omega | JK \rangle y_{j_1 \omega}(\hat{r}_1) Y_{j_2 j_3 K - \omega}(\hat{r}_2, \hat{r}_3), \quad (3)$$

and

$$Y_{j_{23}l_2j_3K-\omega}(\hat{r}_2, \hat{r}_3) = \sum_m D_{K-\omega m}^{j_{23}}(\hat{r}_2) \sqrt{\frac{2l_2+1}{2j_{23}+1}} \langle j_3 m l_2 0 | j_{23} m \rangle y_{j_3 m}(\hat{r}_3), \quad (4)$$

where  $\omega$  is the projection of  $j_1$  on the BF  $z$  axis and  $y_{jm}$  denotes the spherical harmonics. Note the restriction that  $\varepsilon(-1)^{j_1+l_2+j_3+J+J_{tot}} = 1$  for  $K = 0$  in Eq. (2).

Within the centrifugal-sudden (CS) approximation,<sup>2,3</sup> the centrifugal term, *i.e.*  $(\hat{J}_{tot} - \hat{J})^2$  in the Hamiltonian, is given by

$$\langle \Phi_{jK}^{J_{tot}M\varepsilon} | (\hat{J}_{tot} - \hat{J})^2 | \Phi_{j'K'}^{J_{tot}M\varepsilon} \rangle \approx \delta_{jj'} \delta_{KK'} [J_{tot}(J_{tot}+1) + J(J+1) - 2K^2]. \quad (5)$$

In this case,  $K$  becomes a good quantum number and is conserved.

The initial wave packet  $|\chi_i\rangle$  is chosen as the direct product of a localized Gaussian wave packet in the scattering coordinate and a specific  $(J_{tot}K\varepsilon)$  state of the reactive system with specific internal ro-vibrational states of both  $H_2$  and  $H_2O^+$ .

$$|\chi_i\rangle = \left(\frac{1}{\pi\delta^2}\right)^{1/4} e^{-(R-R_0)^2/2\delta^2} e^{-ik_i R} |v_{1i}\rangle |j_{1i}j_{23i}J_iK_i\tau; J_{tot}\varepsilon\rangle \quad (6)$$

where  $R_0$  and  $\delta$  are the mean position and width of the Gaussian function and  $k_i$  is the mean momentum given by  $E_i$  via  $k_i = \sqrt{2\mu_R E_i}$ ,  $j_{1i}, j_{23i}, J_i$  and  $K_i$  are the initial angular quantum numbers and  $\tau$  is the parity of  $H_2O^+$ . The latter were obtained by diagonalizing the individual ro-vibrational Hamiltonians. The triatomic Hamiltonian of  $H_2O^+$  by fixing the two non-reactive OH bonds can be written as

$$\hat{H} = \frac{\hat{l}_2^2}{2\mu_2 r_{20}^2} + \frac{\hat{j}_3^2}{2\mu_3 r_{30}^2} + \hat{V}(R = \infty, r_{10}, r_{20}, r_{30}, \theta_{10}, \theta_{20}, \theta_3, \varphi_{10}, \varphi_{20}) \quad (7)$$

when  $R$  is sufficiently large, the interaction potential only depends on the coordinate  $\theta_3$ .

This wave packet is then propagated in time using the split-operator method.<sup>4</sup> The flux through the dividing surface,  $S[r_1 = r_1^F]$ , is obtained from the energy-dependent scattering wavefunction,  $\psi_i^+(E)$ , which is determined by Fourier transforming the wave packet at the dividing surface. To impose outgoing boundary conditions, the wave packet is absorbed at the edge of the grid using an absorbing potential as follows:

$$D(x) = -\alpha \left( \frac{x - x_a}{x_{\max} - x_a} \right)^n, \quad (8)$$

where  $x = R$  and  $r_1, x_a$  is the starting point of the absorption potential.

The integral cross section (ICS) from a specific initial state is obtained by summing the reaction probabilities over all the partial waves (total angular momentum  $J_{tot}$ ),

$$\begin{aligned} \sigma_{v_1^v H_2 O^+ j_1 j_{23}}(E) &= \frac{1}{(2j_1 + 1)(2j_{23} + 1)} \sum_{JK\varepsilon} \frac{\pi}{k^2} \sum_{J_{tot} \geq K} (2J_{tot} + 1) P_{v_1^v H_2 O^+ j_1 j_{23} JK}^{J_{tot} \varepsilon}(E) \\ &= \frac{1}{(2j_1 + 1)(2j_{23} + 1)} \sum_{JK\varepsilon} \sigma_{v_1^v H_2 O^+ j_1 j_{23}}^{JK\varepsilon}(E) \end{aligned} \quad (9)$$

where  $\sigma_{v_1^v H_2 O^+ j_1 j_{23}}^{JK\varepsilon}$  is defined as the  $J, K$  and  $\varepsilon$  specific cross section and  $K$  is taken from 0 to  $\min(J, J_{tot})$ . In the quantum dynamical study, we focus on the dynamics from the reactant ground vibrational states, *i.e.*  $v_{H_2} = 0, v_{H_2 O^+} = (0, 0, 0)$ .

The numerical parameters employed in the quantum dynamics calculations on an  $L$ -shaped grid are given in Table S1. For the scattering coordinate  $R$ , 106 sine discrete variable representation (DVR) basis/points are used in the whole range from 1.0 to 15.0  $a_0$  and 40 sine DVR basis/points are used in the interaction region. For the dissociating H-H bond of  $r_1$ , 24 PODVR basis/points are used in the interaction region, and 3 PODVR basis/points are used in the asymptotic region. The propagation time is around  $40000a.u.$  with a time step of  $10a.u.$

The calculated rotational energies of  $H_2O^+$  by fixing the two OH bonds are given in Table S2 and compared with the experimental values.<sup>5</sup> Clearly, they agree with each other reasonably well.

### **S-IB. Quasi-classical trajectory method**

The trajectories were initiated with a reactant separation of 10.0 Å, and terminated when products reached a separation of 6.0 Å, or when reactants are separated by 10.0 Å for non-reactive trajectories. During the propagation, the gradient of the PES was obtained numerically by a central-difference algorithm. The propagation time step was selected to be 0.02 fs, which conserves the energy better than 0.04 kcal/mol for most trajectories. A few trajectories which failed to converge energy to 0.04 kcal/mol or were nonreactive after 4.0 ps were discarded. The maximal impact parameter ( $b_{\max}$ ) was determined using small batches of trajectories with trial values.

The total integral cross section (ICS) for the reaction was computed by:

$$\sigma_r(E_c) = \pi b_{\max}^2(E_c) P_r(E_c), \quad (10)$$

where the reaction probability at the specified collision energy  $E_c$  is given by the ratio between the number of reactive trajectories ( $N_r$ ) and total number of trajectories ( $N_{total}$ ):

$$P_r(E_c) = N_r / N_{total}. \quad (11)$$

The standard error is given by:  $\Delta = \sqrt{(N_{total} - N_r) / N_{total} N_r}$ .

In the QCT calculations, the maximal impact parameter ( $b_{\max}$ ) ranges from 6.0 Å at 0.05 eV to 4.0 Å at 1.0 eV. 100 000 trajectories were run for each  $E_c$ , with the standard errors of these cross sections less than 1%.

**Table S1.** Numerical parameters used in the wave packet calculations. (Atomic units are used unless stated otherwise.)

$\text{H}_2 + \text{H}_2\text{O}^+ \rightarrow \text{H} + \text{H}_3\text{O}^+$	
Grid/basis range and size:	$R \in [1.0, 15.0]$ $N_R^{tot} = 106, N_R^{int} = 40$ $N_{r_1}^{int} = 24, N_{r_1}^{asy} = 3$ $j_{1max} = 28, j_{23max} = 30, j_{3max} = 22$ $l_{2max} = 24, J_{max} = 36$
Initial wave packet:	$R_0 = 12.0, \delta = 0.4, E_i = 0.25 \text{ eV}$
Damping term:	$R_a = 12.0, \alpha_R = 0.05, n_R = 2.5$ $r_{1a} = 4.0, \alpha_{r_1} = 0.035, n_{r_1} = 2.0$
Flux position:	$r_1^F = 3.5$

**Table. S2:** Comparison of experimental and theoretical rotational energies of  $\text{H}_2\text{O}^+$ . The two OH bonds are fixed in the theoretical calculations. The energy is given in  $\text{cm}^{-1}$ .

$(J,\tau,n)^a$	Theo	Exp <sup>b</sup>	Assignment
(1,+1,1)	21.37		$1_{01}$
(1,+1,2)	38.93	37.45	$1_{11}$
(1,-1,1)	42.90		$1_{10}$
(2,+1,1)	63.48	60.93	$2_{02}$
(2,+1,2)	77.72		$2_{12}$
(2,-1,1)	89.62	86.82	$2_{11}$
(2,-1,2)	141.81		$2_{21}$
(2,+1,3)	142.41		$2_{20}$

<sup>a</sup>:  $J$  and  $\tau$  are the angular quantum number and parity of  $\text{H}_2\text{O}^+$ .  $n$  denotes the  $n$ th eigenstate of triatomic Hamiltonian with given  $J$  and  $\tau$ .

<sup>b</sup>: The experimental values are taken from Ref. 5.

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