## **Electronic Supplementary Information**

## Enhancement of bimolecular reactivity by a pre-reaction van der Waals complex: the case

of  $F + H_2O \rightarrow HF + HO$ 

Jun Li, Bin Jiang, and Hua $\operatorname{Guo}^*$ 

Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New

Mexico 87131, USA

<sup>\*:</sup> corresponding author, email: hguo@unm.edu

# **Table of Contents**

A.	Potential energy surfaces	<b>S</b> 3
B.	Quasi-classical trajectory method	<b>S</b> 4
C.	Quantum dynamics method	S5

### A. The potential energy surfaces

The PES for the title reaction has been discussed at length in our earlier work.<sup>1</sup> Briefly, ~30,000 points were calculated at the level of two-state multi-reference configuration interaction (MRCI), which used the initial guess from the dynamically-weighted state-averaged complete active space self-consistent field (DW-SA-CASSCF) method.<sup>2-3</sup> Dunning's AVTZ basis set was used. To account for higher excitations, the rotated reference Davidson correction  $(Q_{rot})^4$  was adapted. Note that this correction can only be calculated at multi-state ( $\geq 2$ ) MRCI. The final PES consists of two parts: the first part ( $V_{fit}$ ) was a fit to *ab initio* points using the permutation invariant polynomial method of Bowman and coworkers,<sup>5</sup> and the second part ( $V_{dip}$ ) describes the long range interaction between the two products HF and HO. These two parts were connected with a switching function.

In order to test the effect of the pre-reaction van der Waal complex on reactivity, a modified PES was constructed and denoted mod-PES, in which the van der Waals complex was removed. This is done with an additional switching function S defined as follows (in Å):

$$S' = \left(\frac{1 + \tanh\left[5\left(R_{\rm FH_1} - 1.8\right)\right]}{2}\right) \left(\frac{1 + \tanh\left[5\left(R_{\rm FH_2} - 1.8\right)\right]}{2}\right) \left(\frac{1 + \tanh\left[8\left(R_{\rm FO} - 1.7\right)\right]}{2}\right)$$
(1)

which modifies the PES in the entrance channel:

$$V' = S'V(R_{\rm HF} = \infty) + (1 - S')V \tag{2}$$

The switching function allows an approximate removal of the entrance channel van der Waals complex with minimal impact on the transition state and the product channel. As shown in Fig. S1, the van der Waals wells are essentially eliminated.

## B. QCT calculations

Standard QCT calculations were performed using VENUS.<sup>6-7</sup> The trajectories were initiated with a reactant separation of 7.0 Å, and terminated when products reached a separation of 15.0 Å, or when reactants are separated by 7.0 Å for non-reactive trajectories. The maximal impact parameter ( $b_{max}$ ) was determined using small batches of trajectories with trial values. The other scattering parameters (impact parameter, vibrational phases and spatial orientation of the initial reactants) were selected *via* a Monte Carlo approach. In particular, the angle variables for the H<sub>2</sub>O normal modes were selected randomly and then converted to the initial coordinates and momenta along with fixed action variables.<sup>6-7</sup> To test the influence of the reactant rotational excitation, two rotational temperatures were used for H<sub>2</sub>O. During the propagation, the gradient of the PES was obtained numerically by a central-difference algorithm. The propagation time step was selected to be 0.10 fs. Energy conservation of the trajectories was better than 0.04 kcal/mol with the chosen time step. Almost all trajectories conserved energy to within a chosen criteria (0.04 kcal/mol), which confirms the smoothness of the PES.

The total integral cross section (ICS) for the title reaction was computed according to the following formula:

$$\sigma_r(E_c) = \pi b_{\max}^2(E_c) P_r(E_c), \tag{3}$$

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 ( $N_{total}$ ):

$$P_r(E_c) = N_r / N_{total}.$$
(4)

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

#### B. Quantum mechanical calculations

In this work, we focus on quantum scattering with zero total angular momentum (*J*=0). The Hamiltonian ( $\hbar = 1$ ) is given in the Jacobi coordinates:

$$\hat{H} = -\frac{1}{2\mu_{1}}\frac{\partial^{2}}{\partial r_{1}^{2}} - \frac{1}{2\mu_{2}}\frac{\partial^{2}}{\partial r_{2}^{2}} - \frac{1}{2\mu_{3}}\frac{\partial^{2}}{\partial r_{3}^{2}} + \frac{\hat{j}^{2}}{2\mu_{1}r_{1}^{2}} + \frac{\left(\hat{J}_{H_{2}O} - \hat{j}\right)^{2}}{2\mu_{2}r_{2}^{2}} + \frac{\left(\hat{J}_{H_{2}O}\right)^{2}}{2\mu_{3}r_{3}^{2}} + V\left(r_{1}, r_{2}, r_{3}, \theta_{1}, \theta_{2}, \varphi\right),$$
(5)

where the  $r_1$  is the bond length of OH<sub>a</sub> bond,  $r_2$  the distance between the centre of mass of OH<sub>a</sub> and H<sub>b</sub>, and  $r_3$  the distance between F and the centre of mass of H<sub>2</sub>O.  $\mu_i$  (*i*=1, 2, 3) are the corresponding reduced masses,  $\hat{j}$  and  $\hat{J}_{H_2O}$  are the angular momentum operators for OH<sub>a</sub> and H<sub>2</sub>O, respectively.

As discussed in our previous work,<sup>8-9</sup> the wave packet calculations were performed within a mixed discrete variable representation (DVR) and finite basis representation (FBR).<sup>10</sup> Due to the early barrier in the title reaction, both OH bonds have to be treated as reactive, which significantly increases the computational difficulties. An *L*-shape grid was used in order to achieve computational savings, in which vibrational basis functions used for both  $r_1$  and  $r_2$  in the asymptotic region can be relatively reduced. The interaction region is defined as  $r_1$ =[1.0,5.0] bohr,  $r_2$ =[1.0,5.0] bohr, and  $r_3$ =[2.0,6.2] bohr, while the asymptotic region which is defined as  $r_3$ =[6.2-18.0] bohr. A non-direct product FBR basis was used to evaluate the rotational kinetic energy terms,<sup>12</sup> which is consisted of normalized associated Legendre polynomials ( $\bar{P}_j^K(\cos \theta_1)$ and  $\bar{P}_{J_{HO}}^K(\cos \theta_2)$ ) and the exponential Fourier function ( $\exp(iK\varphi)$ ), where *j*,  $J_{H_2O}$ , and *K* are the angular momentum quantum numbers associated with OH<sub>a</sub>, H<sub>2</sub>O, and the projection of  $\hat{j}$  and  $\hat{J}_{H_2O}$  on the molecule-fixed (BF) *z*-axis, which is defined along the vector  $\bar{r}_2$ . 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  $\varphi$ . For *J*=0, we can further take advantage of the inversion symmetry of the potential to separate a wave function with even or odd parity, which can be expanded in terms of  $\cos(K\varphi)$  or  $\sin(K\varphi)$  basis functions, respectively.<sup>12</sup>

To compute initial state selected reaction probabilities, a modified version of the transition-state wave packet approach<sup>13-14</sup> based the Chebyshev propagator<sup>15</sup> was used. Since extensive derivation can be found in our recent work,<sup>8-9</sup> only brief description will be given here. In our scheme, an initial wave packet located in the reactant asymptote with  $r_3=r_{3\text{flux}}$ , is constructed on the first dividing surface  $S_1$  as a direct product of the positive one-dimensional eigenstate of the flux operator<sup>16-17</sup> and the specific rovibrational eigenstate for the reactant. The initial state selected reaction probabilities are computed by evaluating the flux through the second dividing surface  $S_2$ , placed near the transition state:

$$P_{n_{\rm l}}(E) = 4\pi^2 \lambda_{\rm l} \left\langle \phi_{n_{\rm l}}^+ \middle| \delta(E - \hat{H}) \hat{F}_2 \delta(E - \hat{H}) \middle| \phi_{n_{\rm l}}^+ \right\rangle, \tag{6}$$

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  $S_1(\hat{F}_1 | \pm \rangle = \pm \lambda_1 | \pm \rangle$ ), 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>14</sup>

Expressing the Dirac delta function in terms of the Chebyshev polynomials:<sup>18</sup>

$$\delta(E - \hat{H}) = \frac{1}{\Delta H \pi \sin \theta} \sum_{k=0}^{\infty} (2 - \delta_{k0}) \cos(k\theta) \cos(k\hat{\Theta}), \tag{7}$$

where the Chebyshev angle and the corresponding angular operator are defined in terms of normalized energy ( $\theta = \arccos(E_{norm})$ ) and Hamiltonian ( $\hat{\Theta} = \arccos(\hat{H}_{norm})$ ), which are normalized by the mean ( $\bar{H} = (H_{max} + H_{min})/2$ ) and half-width ( $\Delta H = (H_{max} - H_{min})/2$ ) of the Hamiltonian; and substituting Eq. (7) back to Eq. (6) and executing the second flux operator, we have

$$P_{n_{1}}(E) = \frac{4\lambda_{1}}{\mu_{\xi}\Delta H^{2}\sin^{2}\theta} \operatorname{Im}\left[\left\langle\sum_{k=0}^{\infty} (2-\delta_{k0})\cos(k\theta)\psi_{k}\right| \times \delta(\xi-\xi_{f})\frac{\partial}{\partial\xi}\left|\sum_{k'=0}^{\infty} (2-\delta_{k'0})\cos(k'\theta)\psi_{k'}\right\rangle\right],$$
(8)

where  $\xi = \xi_f$  defines the second dividing surface with  $\mu_{\xi}$  as the corresponding reduced mass.  $|\psi_k\rangle = \cos(\hat{k\Theta}) |\phi_{n_1}^+\rangle$  is the Chebyshev wave packet, which is propagated with a modified Chebyshev recursion scheme:<sup>19</sup>

$$\left|\psi_{k}\right\rangle = D(2\hat{H}_{norm}\left|\psi_{k-1}\right\rangle - D\left|\psi_{k-2}\right\rangle), \qquad k \ge 2$$

$$\tag{9}$$

where  $|\psi_0\rangle = |\phi_{n_1}^+\rangle$  and  $|\psi_1\rangle = D\hat{H}_{norm}|\psi_0\rangle$ . *D* is defined as an exponential form to damp spurious reflection of the wave packet at the edges of the grid,

$$D(\zeta) = \begin{cases} 1 & \zeta < \zeta_d, \\ e^{-\alpha \left(\frac{\zeta - \zeta_d}{\zeta_{\max} - \zeta_d}\right)^2} & \zeta \ge \zeta_d. \end{cases}$$
(10)

Here,  $\zeta$  is defined in three radial coordinates.

Finally, the energy functions defined on an energy grid ({  $E_i$  }) can be assembled on the fly from the Chebyshev wave packets.

$$\left|\Psi_{n_{i}}(E_{i})\right\rangle = \frac{1}{\Delta H \pi \sin \theta_{i}} \sum_{k=0}^{\infty} (2 - \delta_{k0}) \cos(k\theta_{i}) \left|\psi_{k}\right\rangle \tag{11}$$

The parameters used to converge the reaction probability up to 15 kcal/mol are listed in Table S-I.

**Table S-I.** Numerical parameters used in quantum wavepacket calculations. (Atomic units are used unless stated otherwise.)

Parameters	Original PES	Modified PES
Grid size and range in $r_3$	200 sine-DVR, [2.0-18.0]	144 sine-DVR, [2.0-10.0]
Basis function in $r_2$ in the interaction region	25 vibrational bases	25 vibrational bases
Basis function in $r_2$ in the asymptotic region	16 vibrational bases	16 vibrational bases
Basis function in $r_1$ in the interaction region	25 vibrational bases	25 vibrational bases
Basis function in $r_1$ in the asymptotic region	16 vibrational bases	16 vibrational bases
Quadrature points in $(\theta_1, \theta_2, \varphi)$	(18,30,18)	(18,30,18)
Initial wavepacket $(S_1)$	15.8	7.8
Flux analysis $(S_2)$	2.8	2.8
	$r_{3d}$ =16.0, $\alpha$ =0.10	$r_{3d}$ =8.0, $\alpha$ =0.10
Absorbing potential parameters	$r_{2d}$ =3.0, $\alpha$ =0.10	$r_{2d}=3.0, \alpha=0.10$
	$r_{1d}$ =3.0, $\alpha$ =0.10	$r_{1d}=3.0, \alpha=0.10$
Potential cut-off	4 eV	4 eV
Propagation step	5500	5500

### References:

- 1 J. Li, R. Dawes and H. Guo, J. Chem. Phys. (2012).
- 2 M. P. Deskevich, D. J. Nesbitt and H.-J. Werner, J. Chem. Phys. **120**, 7281 (2004).
- 3 R. Dawes, A. W. Jasper, C. Tao, C. Richmond, C. Mukarakate, S. H. Kable and S. A. Reid, J. Phys. Chem. Lett. **1**, 641 (2010).
- 4 H. J. Werner, M. Kallay and J. Gauss, J. Chem. Phys. **128**, 034305 (2008).
- J. M. Bowman, G. Czakó and B. Fu, Phys. Chem. Chem. Phys. **13**, 8094 (2011).
- 6 X. Hu, W. L. Hase and T. Pirraglia, J. Comp. Chem. **12**, 1014 (1991).
- W. L. Hase, R. J. Duchovic, X. Hu, A. Komornicki, K. F. Lim, D.-H. Lu, G. H. Peslherbe, K. N. Swamy,
   S. R. V. Linde, A. Varandas, H. Wang and R. J. Wolf, Quantum Chemistry Program Exchange
   Bulletin 16, 671 (1996).
- 8 B. Jiang, D. Xie and H. Guo, J. Chem. Phys. **135**, 084112 (2011).
- 9 B. Jiang, X. Ren, D. Xie and H. Guo, Proc. Natl. Acad. Sci. USA **109**, 10224 (2012).
- 10 J. C. Light and T. Carrington Jr., Adv. Chem. Phys. **114**, 263 (2000).
- 11 D. T. Colbert and W. H. Miller, J. Chem. Phys. **96**, 1982 (1992).
- 12 R. Chen, G. Ma and H. Guo, J. Chem. Phys. **114**, 4763 (2001).
- 13 W. H. Miller, S. D. Schwartz and J. W. Tromp, J. Chem. Phys. **79**, 4889 (1983).
- 14 D. H. Zhang and J. C. Light, J. Chem. Phys. **104**, 6184 (1996).
- 15 D. Xie, S. Li and H. Guo, J. Chem. Phys. **116**, 6391 (2002).
- 16 T. P. Park and J. C. Light, J. Chem. Phys. **85**, 5870 (1985).
- 17 T. P. Park and J. C. Light, J. Chem. Phys. **88**, 4897 (1988).
- 18 W. Zhu, Y. Huang, D. J. Kouri, C. Chandler and D. K. Hoffman, Chem. Phys. Lett. **217**, 73 (1994).
- 19 V. A. Mandelshtam and H. S. Taylor, J. Chem. Phys. **103**, 2903 (1995).

Fig. S1. Contour plot of the modified PES for F and  $H_2O$  in the entrance channel. The system is arranged the same way as in Fig. 3. It is clear that the van der Waals wells are absent on this PES.

