Electronic supplementary information (ESI) for

Experimental and Theoretical Studies of the Gas-Phase Reactions of O(^{1}D) with H$_2$O and D$_2$O at Low Temperature

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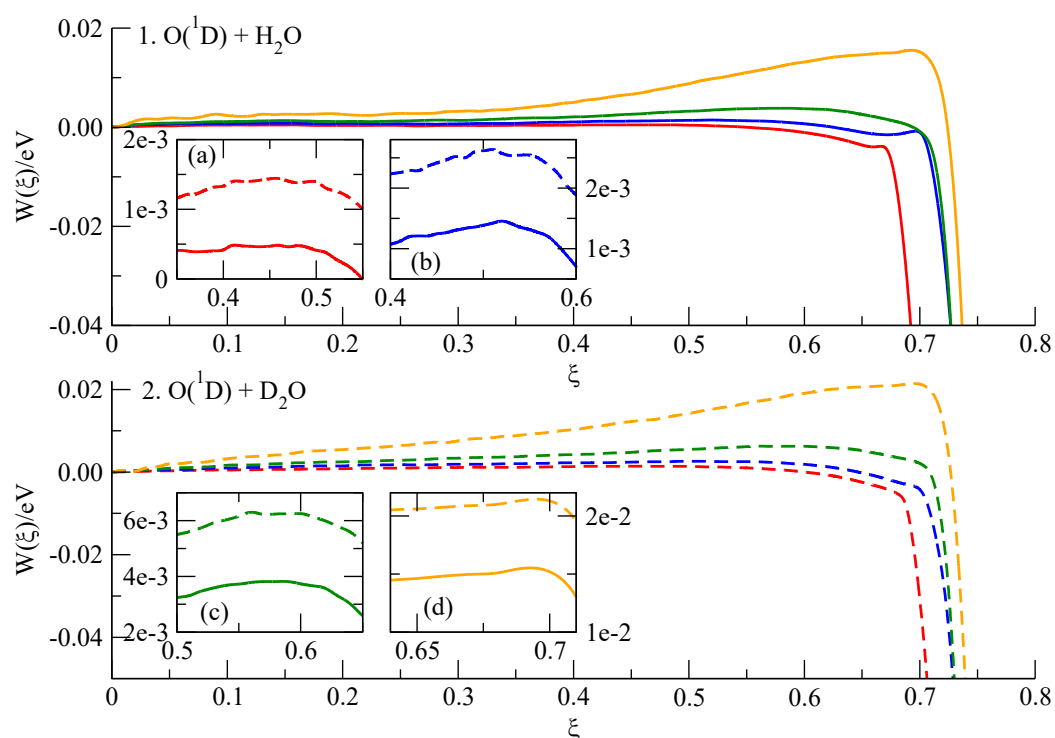
Figure S1. Ring polymer potentials of mean force ($W(\xi)$) along the reaction coordinate for the 1. O(^{1}D) + H$_2$O (top panel, solid lines) 2. O(^{1}D) + D$_2$O (bottom panel, broken lines) chemical reactions on the X ^{1}A PES at 50 K (red), 75 K (blue), 127 K (green) and 296 K (orange). Inset plots (a)-(d) are the magnification of the barrier region in the PMF profile and show the comparison between the O(^{1}D) + H$_2$O and O(^{1}D) + D$_2$O reactions at a particular temperature.
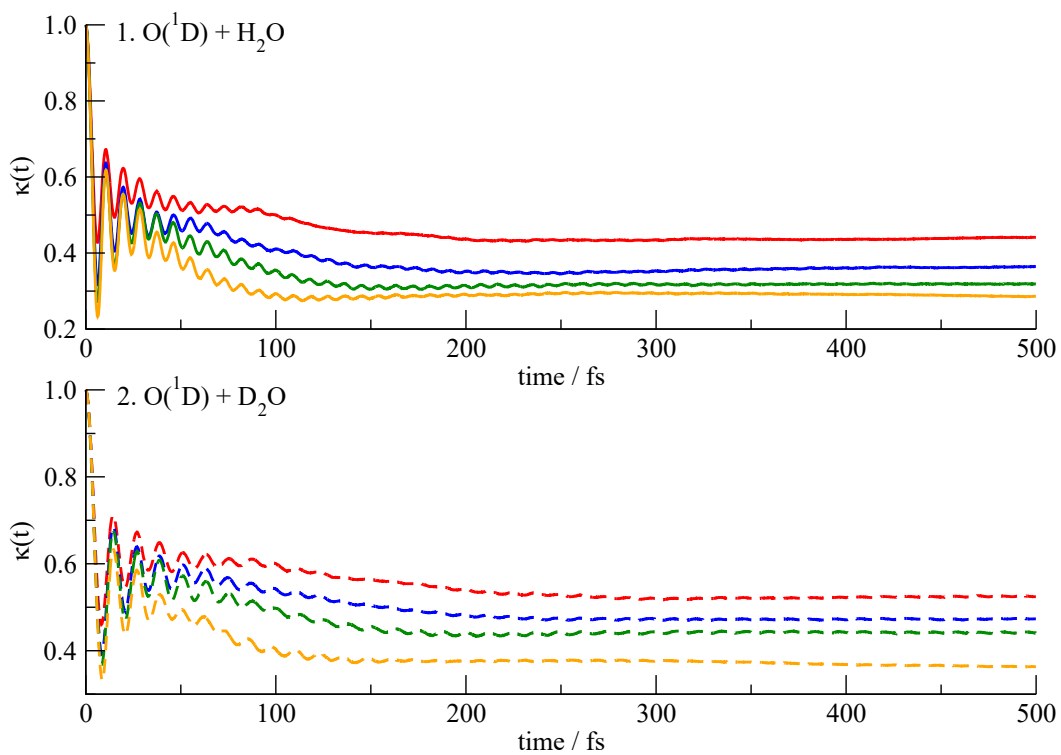
Figure S2. Ring polymer recrossing factor $\kappa(t)$ for the 1. $O(^1D) + H_2O$ (top panel, solid lines) 2. $O(^1D) + D_2O$ (bottom panel, broken lines) chemical reactions on the X ^1A PES at 50 K (red), 75 K (blue), 127 K (green) and 296 K (orange).

Table S1. Input parameters for the RPMDrate calculations on the O(^{1}D) + H_2O/D_2O reaction.

Parameter	Reaction		Explanation[a]
	O(^{1}D) + H_2O	O(^{1}D) + D_2O	
PES	X^1A		[EN:JB:PCCP2017][b]
Command Line Parameters			
temp	296		temperature (K)
	127		
	75		
	50		
N_{beads}	64		number of beads
Dividing Surface Parameters			
R_∞	15 Å		dividing surface parameter (distance)
N_{bond}	1		number of forming and breaking bonds
$N_{channel}$	2		number of equivalent product channels
thermostat	"Andersen"		thermostat option
Biased Sampling Parameters			
$N_{windows}$	111		number of Windows
ξ_1	-0.05		center of the first window
$d\xi$	0.01		window spacing step
ξ_N	1.05		center of the last window
dt	0.0001		time step (ps)
k_i	2.72		umbrella force constant ((T/K) eV)
$N_{trajectory}$	100		number of trajectories
$t_{equilibration}$	20		equilibration period (ps)
$t_{sampling}$	100		sampling period in each trajectory (ps)
Potential of Mean Force Calculation			
ξ_0	-0.02		start of umbrella integration
ξ	0.74		end of umbrella integration
N_{bins}	5000		number of bins
Recrossing Factor Calculation			
dt	0.0001		time step (ps)
$t_{equilibration}$	20		equilibration period (ps) in the constrained (parent) trajectory
$N_{totalchild}$	100000		total number of unconstrained (child) trajectories
$t_{childsampling}$	2		sampling increment along the parent trajectory (ps)
N_{child}	100		number of child trajectories per one initially constrained configuration
t_{child}	0.5		length of child trajectories (ps)

[a]The explanation of the format of the input file can be found in the RPMDrate code manual (http://rpmdrate.cyi.ac.cy).

[b][EN:JB:PCCP2017] Enhanced PES derived from D. V. Coelho and J. Brandão, *Phys. Chem. Chem. Phys.* **19**, 1378-1388 (2017).

Table S2. Results of RPMD calculations for the $O(^1D) + H_2O$ and $O(^1D) + D_2O$ reactions over the $X\,^1A$ PESs at 50, 75, 127, and 296 K, including centroid-density quantum transition state theory rate constant (k_{QTST}),[a] plateau value of the ring polymer transmission coefficients ($\kappa(t\to\infty)$), final RPMD rate constant (k_{RPMD}),[a] and the ratio between the $O(^1D) + H_2O$ and $O(^1D) + D_2O$ reaction rate constant (k_H / k_D).

T (K)	Reaction	k_{QTST}	$\kappa(t\to\infty)$	k_{RPMD} no correction (with correction)[b]	k_H / k_D
296	$O(^1D) + H_2O$	3.31×10^{-9}	0.29	9.45×10^{-10} (1.89×10^{-10})	1.02
	$O(^1D) + D_2O$	2.56×10^{-9}	0.36	9.30×10^{-10} (1.86×10^{-10})	
127	$O(^1D) + H_2O$	2.80×10^{-9}	0.32	8.96×10^{-10} (1.79×10^{-10})	0.93
	$O(^1D) + D_2O$	2.19×10^{-9}	0.44	9.64×10^{-10} (1.93×10^{-10})	
75	$O(^1D) + H_2O$	2.44×10^{-9}	0.36	8.91×10^{-10} (1.78×10^{-10})	0.95
	$O(^1D) + D_2O$	1.99×10^{-9}	0.47	9.40×10^{-10} (1.88×10^{-10})	
50	$O(^1D) + H_2O$	2.23×10^{-9}	0.44	9.84×10^{-10} (1.97×10^{-10})	1.08
	$O(^1D) + D_2O$	1.74×10^{-9}	0.52	9.14×10^{-10} (1.83×10^{-10})	

[a]All rate constants are given in $cm^3\ s^{-1}$.
[b]Corrected by electronic partition functions $Q_{el} = 5$.