Supplementary Information File for

"An Experimental and Theoretical Study of the O(^{1}D) + HD Reaction"

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The supplementary information file contains:

Supplemental discussion of the reaction dynamics. Supplemental figures S1-S4. Supplemental tables S1-S3.

Supplementary discussion of the reaction dynamics

Supplementary evidence for a complex-forming mechanism for the O(^{1}D) + HD reaction is obtained when the vibrational distributions for the product OH(v') fragments are analysed. The corresponding statistical predictions can be compared with those cross sections from the work by Yuan *et al.*[14] As shown in Figure S1 both QM and experimental populations of the OH(v') states are not far from a monotonical decrease as the vibrational excitation v' increases.

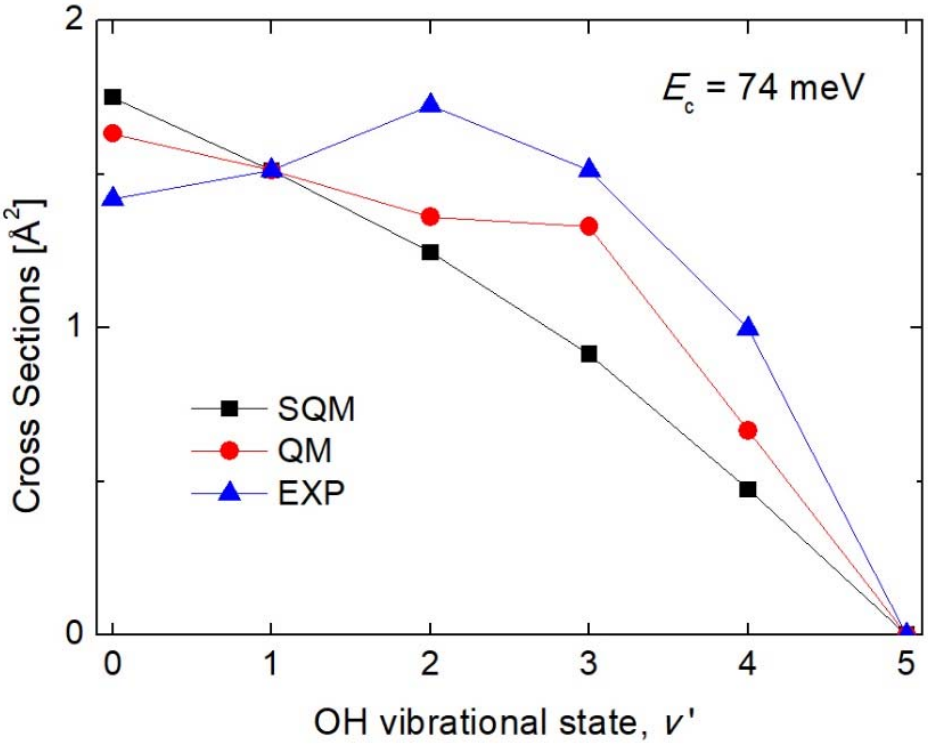

Figure S1. Cross sections measured in Å^2 for the OH(v')+D formation process at E_c = 74 meV. (Black squares) Present SQM distributions are compared with (red circles) QM and (blue triangles) experimental results both reported by Yuan *et al.*[14] QM and experimental distributions, originally in arbitrary units in Ref. (14) have been scaled here for comparison with the statistical cross sections.

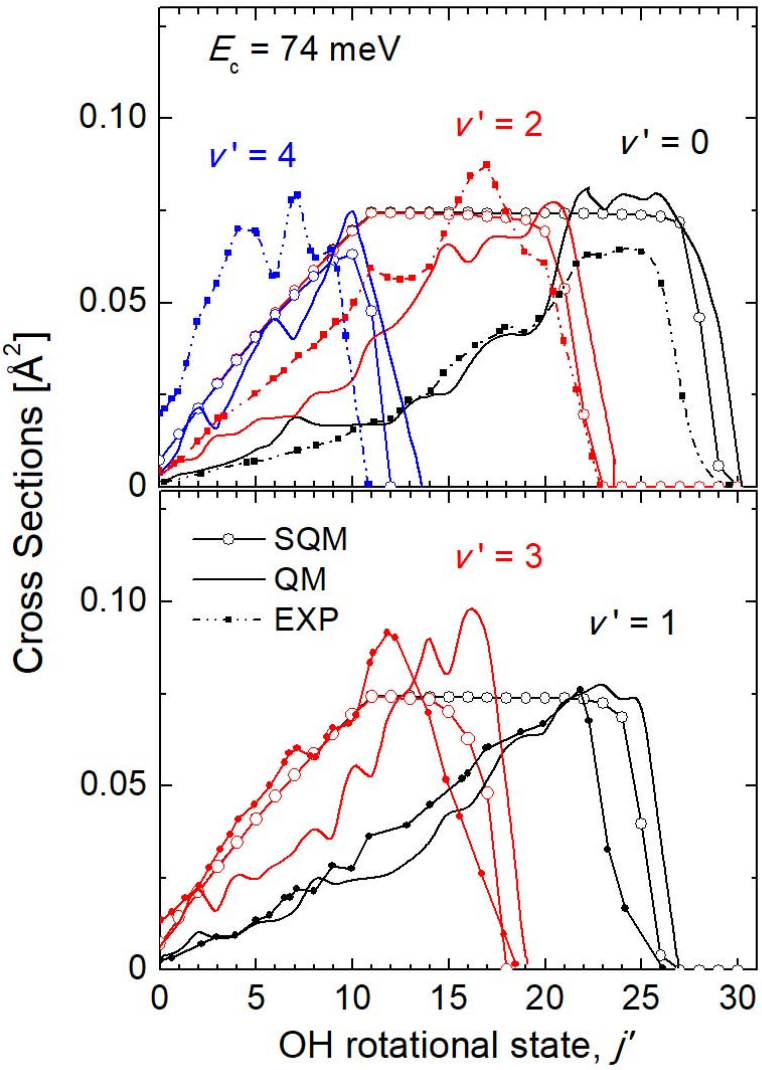

Figure S2. Rotationally resolved cross sections measured in Å^2 for the O(^1D) + HD → OH(v', j')+D process at at E_c = 74 meV. (Open circles and solid lines) SQM distributions are compared with (solid) QM[14] and (solid circles and dashed-dotted lines) experimental[14] results for (top panel) v' = 0, 2, 4, and (bottom panel) v' = 1, 3. Results from Ref. (14) have been scaled here.

A much more demanding comparison can be established at the O(^1D) + HD → OH (v', j') + D state to state level. Thus, we have calculated the rovibrational distributions (v', j') of the product OH by means of the SQM method in Figure S2. The corresponding comparison has been made with the QM and experimental results by Yuan *et al.*[14] Although the measured cross sections extend up to slightly lower rotational j' states for all possible final v' states than the theoretical calculations, the present SQM predictions are possibly in a better agreement with experiment than the QM values. However the almost equally distributed cross sections seen in

the statistical investigation for the most populated rotational states seem to be too crude in view of both the experimental and QM distributions obtained by Yuan *et al.*[14]

Figure S3. Ring polymer potentials of mean force ($W(\xi)$) along the reaction coordinate for the O(^1D) + HD chemical reaction on the 1 ^{1}A′ (top panel) and 1 ^{1}A″ (bottom panel) PESs at 50 and 296 K. Legends correspond to both panels.

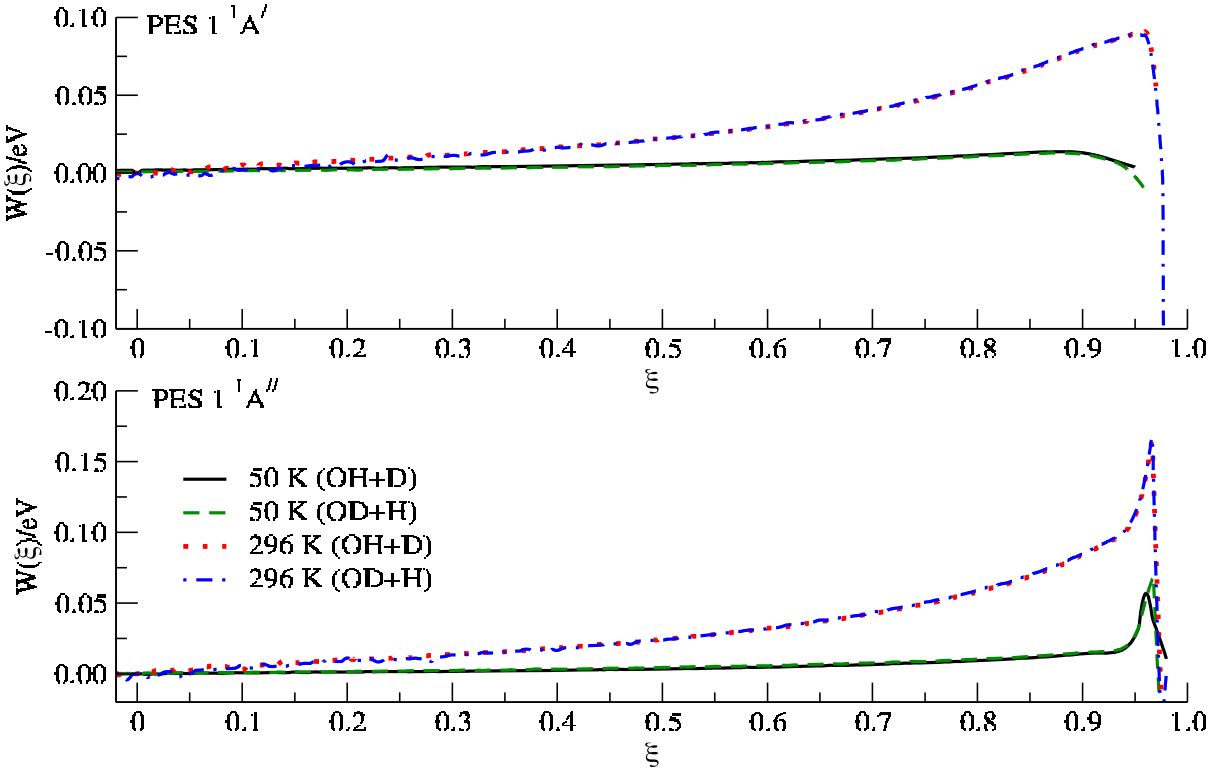

Figure S4. Ring polymer recrossing factor $\kappa(t)$ along the reaction coordinate for the O(^1D) + HD chemical reaction on the 1 ^{1}A′ (top panel) and 1 ^{1}A″ (bottom panel) PESs at 50 and 296 K. Legends correspond to both panels.

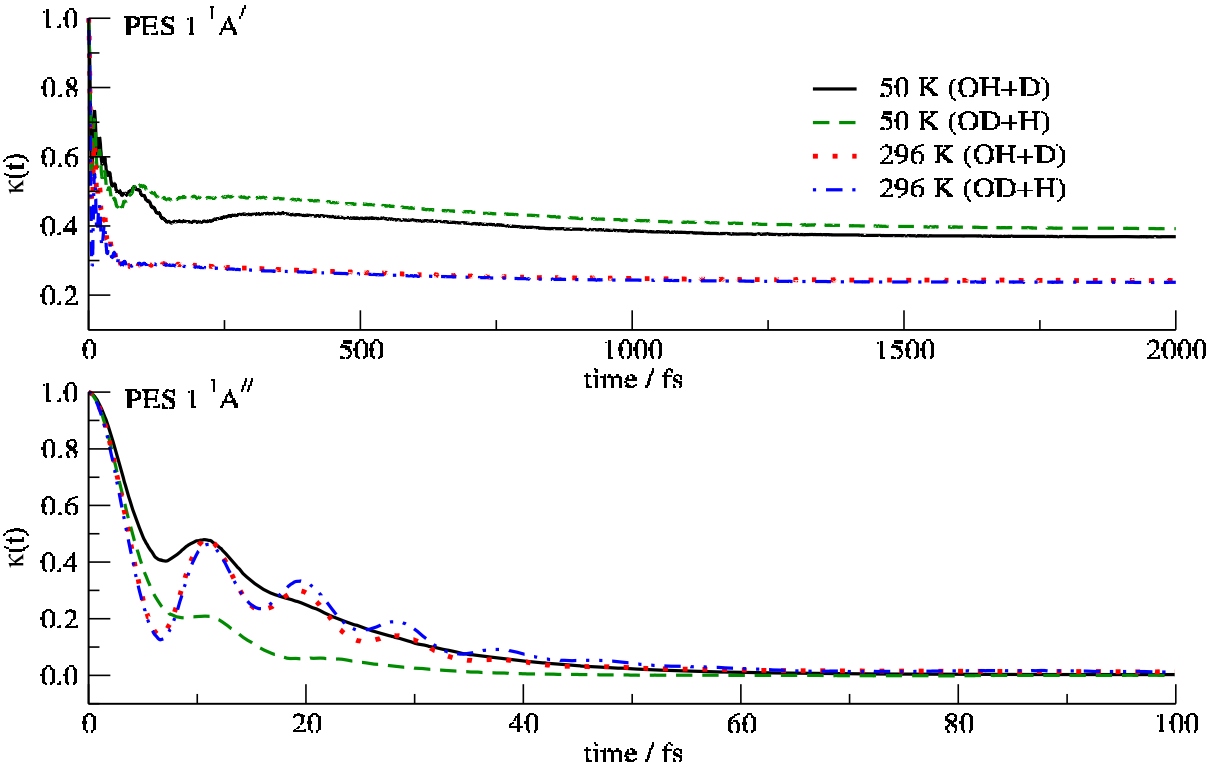

Table S1. Input parameters for the RPMDrate calculations on the O(^1D) + HD reaction**.**

Parameter	Product Channel				Explanation[a]
	OH + D		OD +H		
PES	^{1}A′	^{1}A″	^{1}A′	^{1}A″	[DK:MP1997, DK:FD98][b]
Command Line Parameters					
temp	296				temperature (K)
	50				
N_{beads}	128 (296 K); 296 (50 K)				number of beads
Dividing Surface Parameters					
R_∞	60 a_0				dividing surface parameter (distance)
N_{bond}	1				number of forming and breaking bonds
$N_{channel}$	1				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
dξ	0.01				window spacing step
ξ_N	1.05				center of the last window
dt	0.0001				time step (ps)
k_i	20.41 (296 K); 53.06 (50 K)		20.41 (296 K); 54.42 (50 K)		umbrella force constant ((T/K) eV)
$N_{trajectory}$	200				number of trajectories
$t_{equilibration}$	20				equilibration period (ps)
$t_{sampling}$	100				sampling period in each trajectory (ps)
N_i	2×10^8				total number of sampling points
Potential of Mean Force Calculation					
ξ_0	−0.02				start of umbrella integration
$\xi^\ddagger$	1 ^{1}A′: 0.96 (296 K); 0.88 (50 K) 1 ^{1}A″: 0.96 (OH + D/50 K); 0.97				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}	2 (1 ^{1}A′); 0.1 (1 ^{1}A″)				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][DK:MP97] A. J. Dobbyn and P. J. Knowles, *Mol. Phys.* **91**, 1107-1124 (1997). [DK:FD98] A. J. Dobbyn and P. J. Knowles, *Farad. Discuss.* **110**, 247 (1998).

Table S2. Results of RPMD calculations for the O(^1D) + HD reaction over the ^{1}A′ and ^{1}A″ PESs at 50 and 296 K, including ring polymer transmission coefficients (κ) and final RPMD rate constants (k_{RPMD}).[a]

T (K)	Product Channel	κ	k_{RPMD} no correction (with correction)[b]
		PES 1 ^{1}**A′**	
296	OH + D	2.42×10^{-1}	3.41×10^{-10} (0.68×10^{-10})
	OD + H	2.37×10^{-1}	3.66×10^{-10} (0.73×10^{-10})
50	OH + D	3.69×10^{-1}	3.16×10^{-10} (0.63×10^{-10})
	OD + H	3.92×10^{-1}	4.06×10^{-10} (0.81×10^{-10})
		PES 1 ^{1}**A″**	
296	OH + D	1.27×10^{-2}	1.20×10^{-12} (2.40×10^{-13})
	OD + H	1.23×10^{-2}	8.79×10^{-13} (1.76×10^{-13})
50	OH + D	2.94×10^{-3}	1.11×10^{-16} (2.22×10^{-17})
	OD + H	3.42×10^{-4}	2.04×10^{-17} (4.08×10^{-18})

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

Table S3. Thermal rate constants k_{RPMD} for the O(^1D) + HD reaction and branching ratios (OD + H / OH + D) calculated by the RPMD method.

T (K)	$k_{RPMD\ (OH + D)}$[a,b]	$k_{RPMD\ (OD + H)}$[a,b]	$k_{RPMD\ (O(^1D)+HD)}$[a,b]	branching ratio[b]
296	0.68×10^{-10}	0.73×10^{-10}	1.41×10^{-10}	1.07
50	0.63×10^{-10}	0.81×10^{-10}	1.44×10^{-10}	1.28

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