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ARTICLE TYPE

Supplementary Material:

Rate coefficients for the O+H_2 and O+D_2 reactions: How well Ring Polymer Molecular Dynamics accounts for tunneling.

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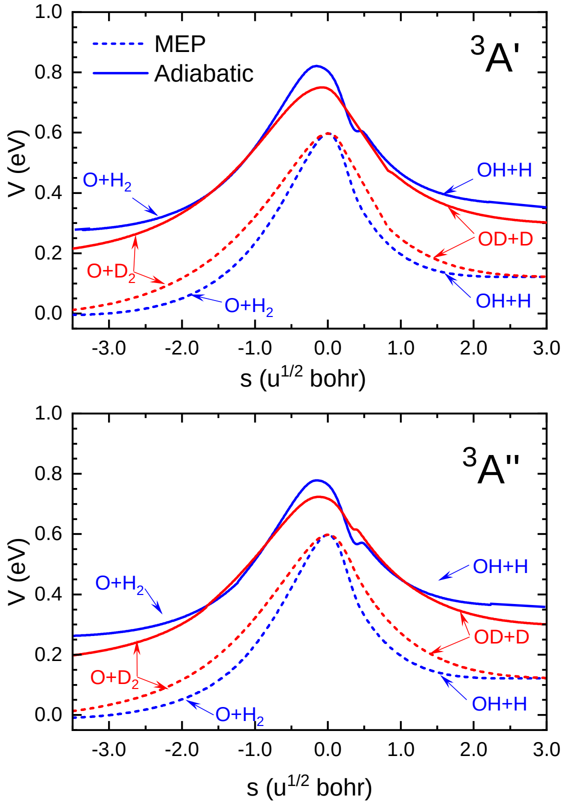

Figure S1. Minimum energy paths (dashed lines) as a function of the mass-scaled reaction coordinate (see text for definition) for the O(^3P)+H_2 (blue) and O(^3P)+D_2 (red) reactions on the $^3A'$ (upper panel) and $^3A''$ (bottom panel). The vibrationally adiabatic reaction paths including their respective zero point energies are also shown as solid lines. All the paths are referred to the minimum asymptotic isotopically invariant potential of H_2.

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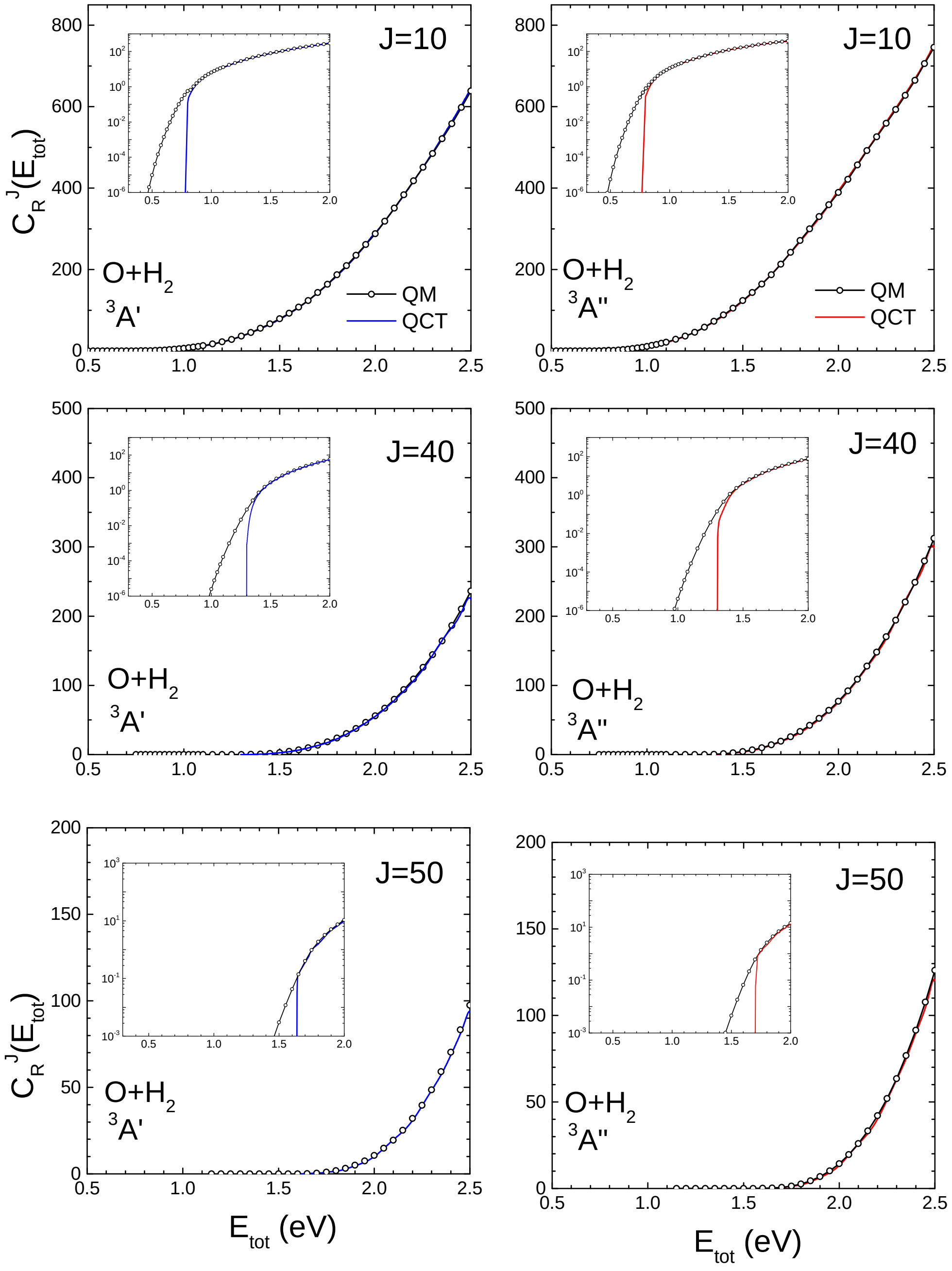

Figure S2. QM (black solid line with open circles) and QCT cumulative reaction probabilities resolved in J, as a function of the total energy for the O(^3P)+H$_2$ reaction on the $^3A'$ PES (blue line, left panels) and on the $^3A''$ PES (red line, right panels) at the indicated values of J. In each case, the inset depicts the low energy region in logarithmic scale.

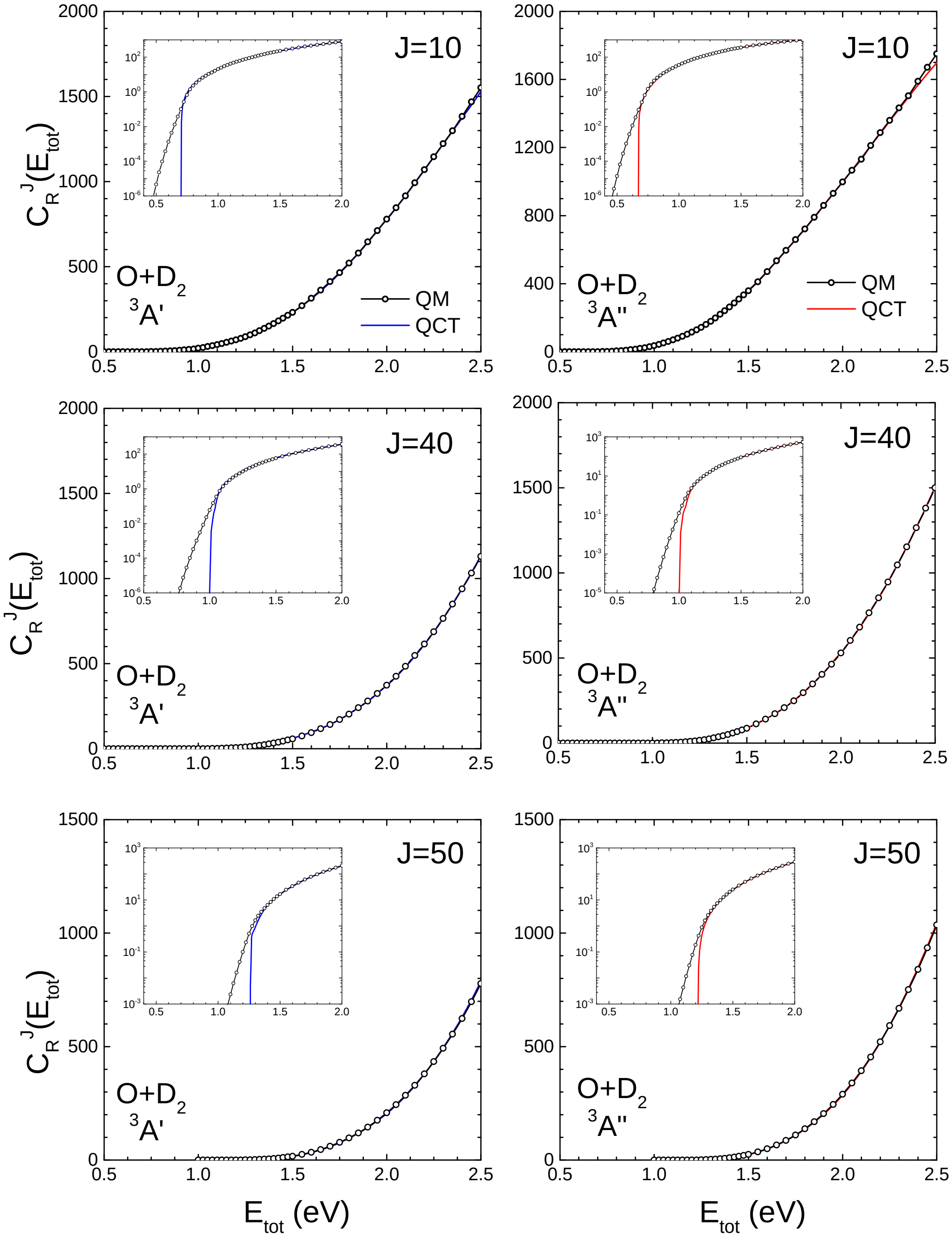

Figure S3. Same as Figure S2 for the O(^3P)+D$_2$ reaction.

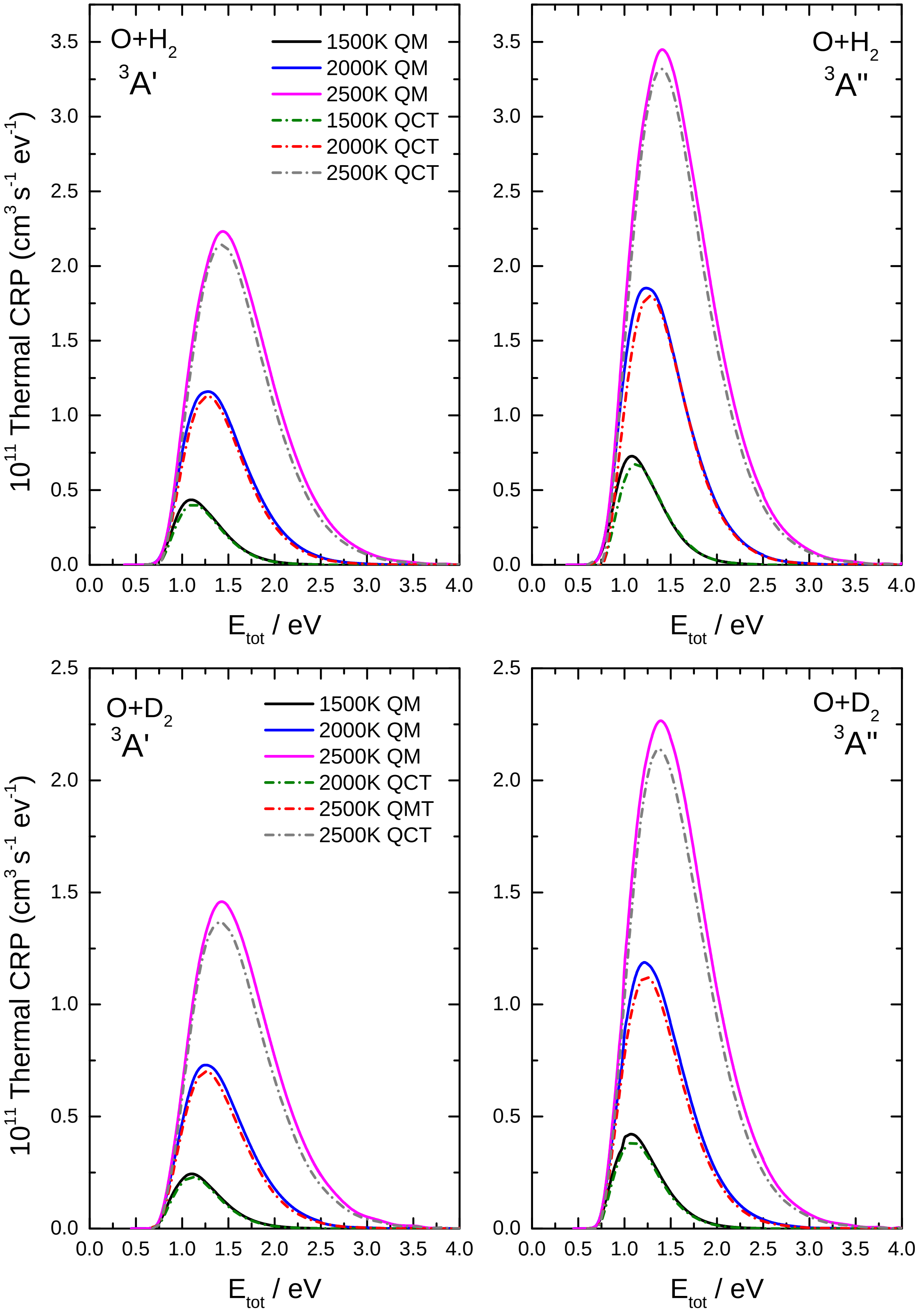

Figure S4. Comparison of QM (solid lines) and QCT (dash-dotted lines) thermal cumulative reaction probabilities at 1500 K, 2000 K and 2500 K for the O(^3P)+H$_2$ reaction (top panels) and for the O(^3P)+D$_2$ reaction (bottom panels). Left panels results are on the $^3A'$ and right panels on the $^3A''$. Integration of each of these curves renders the respective rate coefficients.

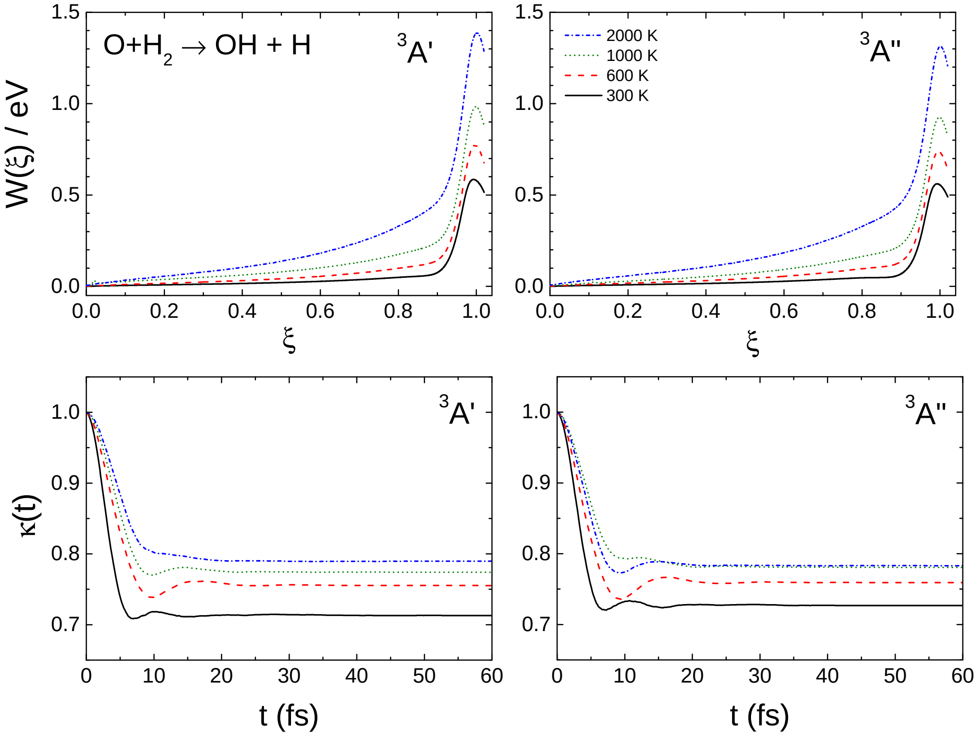

Figure S5. RPMD potential of mean force profiles (top panels) and time dependent transmission coefficients (bottom panels) for the O(^3P)+H_2 reaction on the $^3A'$ (left panels) and on the $^3A''$ (right panels) PESs at 300 K (black solid), 600 K (red dash), 1000 K (green dash–dot), and 2000 K (blue dash–dot-dash).

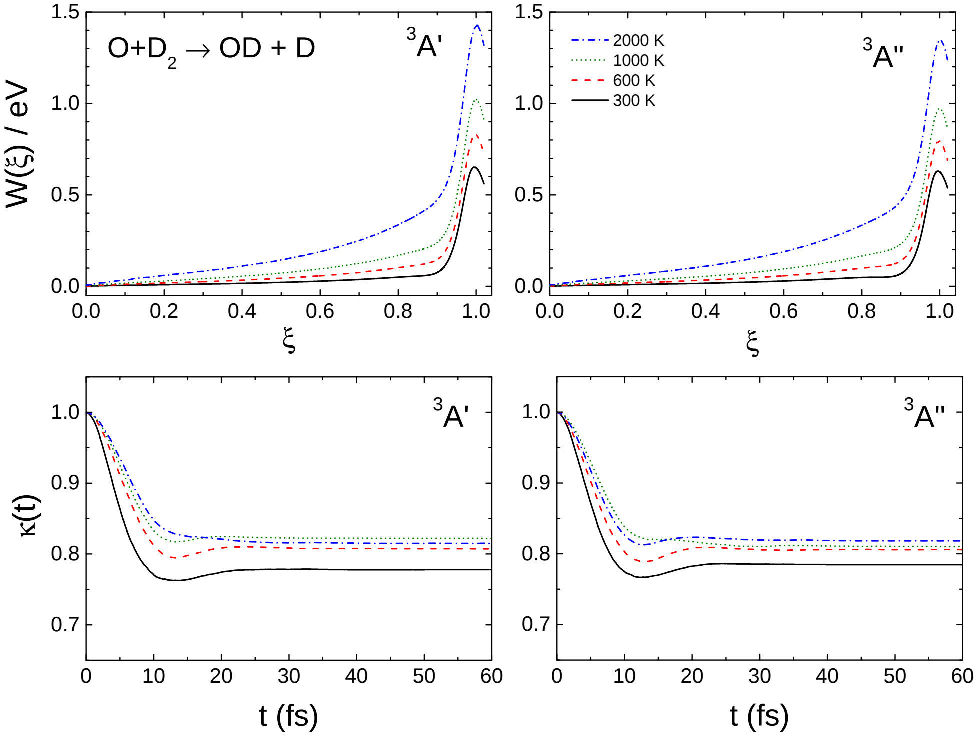

Figure S6. Same as Figure S5 for the O(^3P)+D_2 reaction.

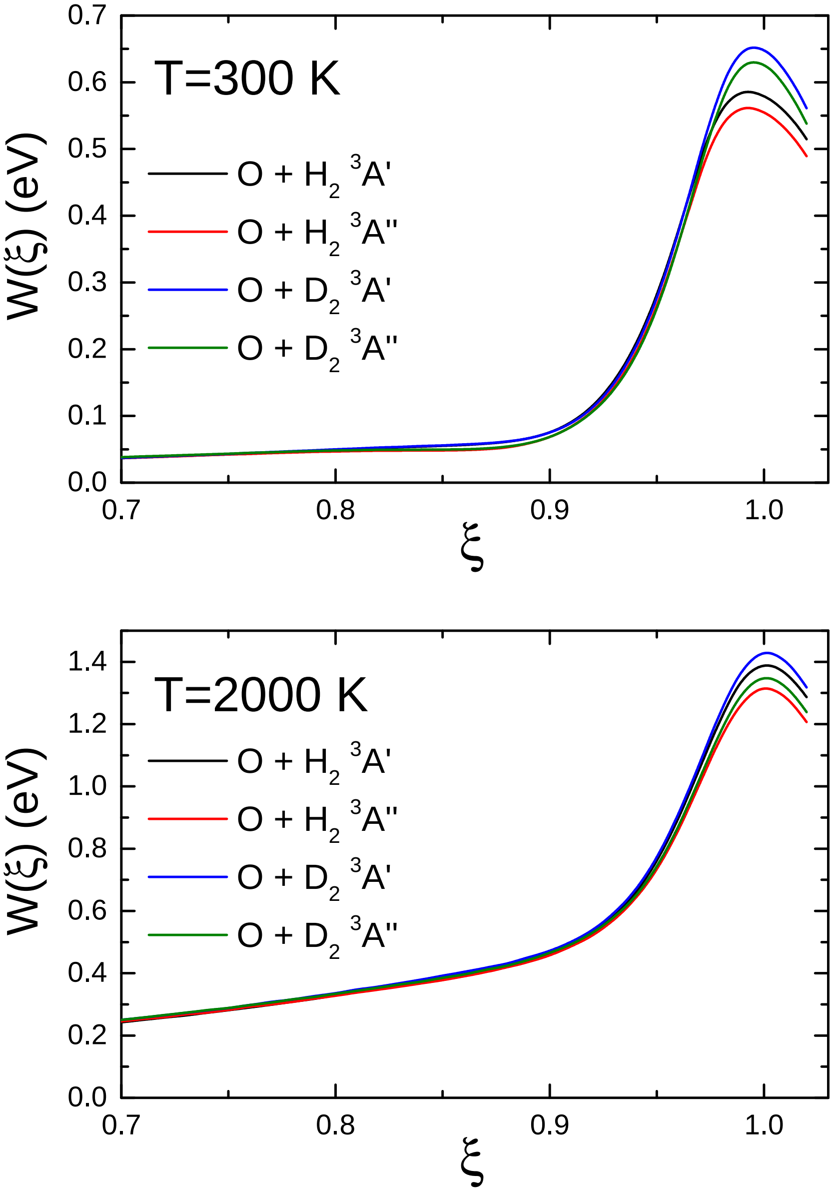

Figure S7. Comparison of RPMD potential of mean force profiles for the O(^3P)+H$_2$ and O(^3P)+D$_2$ reactions on the $^3A'$ and on the $^3A''$ PESs at 300 K (top panel), and 2000 K (bottom panel).

Table S1. RPMD Rate coefficients for the reaction O(^{3}P)+H$_2$, computed in the $^3A'$ and $^3A''$ PESs. The parenthesis denote powers of ten. Units are in cm^{3}s^{-1}.

$^3A'$					$^3A''$		
T/K	n_b	k_{QTST}	$\kappa(t \to \infty)$	k_{RPMD}	k_{QTST}	$\kappa(t \to \infty)$	k_{RPMD}
200	1	1.018(-26)	0.842	8.570(-27)	2.263(-26)	0.830	1.870(-26)
200	32	9.900(-21)	0.607	6.005(-21)	2.855(-20)	0.617	1.763(-20)
200	128	1.230(-20)	0.625	7.685(-21)	3.640(-20)	0.625	2.275(-20)
250	1	1.413(-23)	0.844	1.166(-23)	3.138(-23)	0.840	2.624(-23)
250	32	1.894(-19)	0.680	1.288(-19)	5.163(-19)	0.692	3.576(-19)
250	64	2.102(-19)	0.682	1.434(-19)	5.640(-19)	0.687	3.876(-19)
300	1	1.829(-21)	0.847	1.548(-21)	4.025(-21)	0.838	3.372(-21)
300	32	2.261(-18)	0.713	1.612(-18)	5.755(-18)	0.727	4.183(-18)
300	64	2.423(-18)	0.716	1.734(-18)	6.296(-18)	0.723	4.552(-18)
400	1	9.050(-19)	0.840	7.604(-19)	1.855(-18)	0.835	1.549(-18)
400	32	9.255(-17)	0.742	6.866(-17)	2.141(-16)	0.743	1.591(-16)
400	64	9.698(-17)	0.739	7.164(-17)	2.250(-16)	0.737	1.659(-16)
500	1	3.872(-17)	0.836	3.237(-17)	7.888(-17)	0.837	6.600(-17)
500	32	6.326(-16)	0.746	4.716(-16)	2.410(-15)	0.751	1.810(-15)
500	64	1.181(-15)	0.745	8.806(-16)	2.426(-15)	0.748	1.815(-15)
600	1	5.782(-16)	0.839	4.853(-16)	1.111(-15)	0.833	9.258(-16)
600	32	6.920(-15)	0.755	5.226(-15)	1.364(-14)	0.759	1.035(-14)
700	1	3.300(-14)	0.834	2.752(-15)	6.906(-15)	0.840	5.794(-15)
700	32	2.622(-14)	0.760	1.991(-14)	5.106(-14)	0.759	3.875(-14)
800	1	1.383(-14)	0.840	1.162(-14)	2.588(-14)	0.845	2.187(-14)
800	32	7.587(-14)	0.767	5.820(-14)	1.388(-13)	0.768	1.067(-13)
1000	1	1.060(-13)	0.834	8.829(-14)	1.894(-13)	0.834	1.580(-13)
1000	32	3.462(-13)	0.774	2.680(-13)	6.141(-13)	0.783	4.808(-13)
1200	1	4.454(-13)	0.824	3.670(-13)	7.417(-13)	0.820	6.088(-13)
1200	32	1.057(-12)	0.776	8.203(-13)	1.746(-12)	0.783	1.368(-12)
1500	1	1.883(-12)	0.821	1.546(-12)	3.148(-12)	0.816	2.570(-12)
1500	32	3.429(-12)	0.780	2.673(-12)	5.492(-12)	0.785	4.311(-12)
1800	1	5.100(-12)	0.817	4.166(-12)	8.345(-12)	0.813	6.785(-12)
1800	32	8.050(-12)	0.788	6.348(-12)	1.282(-11)	0.780	1.001(-11)
2000	1	8.729(-12)	0.818	7.140(-12)	1.370(-11)	0.805	1.104(-11)
2000	32	1.260(-11)	0.790	9.950(-12)	1.962(-11)	0.781	1.532(-11)
2200	1	1.365(-11)	0.810	1.104(-11)	2.126(-11)	0.801	1.702(-11)
2200	32	1.841(-11)	0.789	1.452(-11)	2.812(-11)	0.774	2.176(-11)
2500	1	2.313(-11)	0.794	1.836(-11)	3.664(-11)	0.784	2.874(-11)
2500	32	2.960(-11)	0.780	2.308(-11)	4.583(-11)	0.775	3.552(-11)

Table S2. RPMD Rate coefficients for the reaction O(^{3}P)+D$_2$, computed in the $^3A'$ and $^3A''$ PESs. The parenthesis denote powers of ten. Units are in cm^{3}s^{-1}.

$^3A'$					$^3A''$		
T/K	n_b	k_{QTST}	$\kappa(t \to \infty)$	k_{RPMD}	k_{QTST}	$\kappa(t \to \infty)$	k_{RPMD}
200	1	7.334(-27)	0.852	6.249(-27)	1.717(-26)	0.850	1.458(-26)
200	64	5.832(-23)	0.737	4.300(-23)	1.736(-22)	0.740	1.285(-22)
250	1	1.003(-23)	0.858	8.610(-24)	2.202(-23)	0.855	1.883(-23)
250	64	4.434(-21)	0.770	3.416(-21)	1.174(-20)	0.771	9.058(-21)
300	1	1.308(-21)	0.854	1.117(-21)	2.893(-21)	0.860	2.484(-21)
300	64	1.284(-19)	0.778	9.987(-20)	3.034(-19)	0.785	2.381(-19)
400	1	6.347(-19)	0.859	5.453(-19)	1.308(-18)	0.853	1.116(-18)
400	64	1.225(-17	0.785	9.618(-18)	2.680(-17)	0.791	2.120(-17)
500	1	2.830(-17)	0.858	2.426(-17)	5.604(-17)	0.860	4.812(-17)
500	64	2.370(-16)	0.802	1.900(-16)	4.407(-16)	0.800	3.766(-16)
600	1	4.10(-16)	0.858	3.522(-16)	7.736(-16)	0.854	6.607(-16)
600	64	1.760(-15)	0.807	1.421(-15)	3.455(-15)	0.806	2.784(-15)
700	1	2.397(-15)	0.856	2.051(-15)	4.914(-15)	0.850	4.177(-15)
700	64	8.244(-15)	0.821	6.768(-15)	1.542(-14)	0.818	1.262(-14)
800	1	9.856(-15)	0.854	8.415(-15)	1.811(-14)	0.850	1.540(-14)
800	64	2.660(-14)	0.821	2.185(-14)	4.884(-14)	0.820	4.004(-14)
1000	1	7.675(-14)	0.841	6.452(-14)	1.340(-13)	0.850	1.138(-13)
1000	64	1.583(-13)	0.822	1.301(-13)	2.623(-13)	0.818	2.146(-13)
1200	1	3.137(-13)	0.844	2.647(-13)	5.344(-13)	0.840	4.492(-13)
1200	64	5.102(-13)	0.820	4.182(13)	8.700(-13)	0.827	7.192(-13)
1500	1	1.335(-12)	0.840	1.121(-12)	2.200(-12)	0.840	1.847(-12)
1500	64	1.863(-12)	0.823	1.533(-12)	2.980(-12)	0.823	2.451(-12)
1800	1	3.584(-12)	0.831	2.980(-12)	5.885(-12)	0.834	4.908(-12)
1800	64	3.584(-12)	0.820	3.761(-12)	7.591(-12)	0.13	6.169(-12)
2000	1	6.266(-12)	0.830	5.198(-12)	9.981(-12)	0.823	8.217(-12)
2000	64	7.484(-12)	0.815	6.097(-12)	1.208(-11)	0.810	9.777(-12)
2200	1	7.484(-12)	0.827	8.202(-12)	1.495(-11)	0.821	1.228(-11)
2200	64	1.144(-11)	0.816	9.337(-12)	1.783(-11)	0.802	1.431(-11)
2500	1	1.144(-11)	0.816	1.379(-11)	2.570(-11)	0.807	2.075(-11)
2500	64	1.900(-11)	0.810	1.530(-11)	2.974(-11)	0.787	2.340(-11)

Recollection of rate coefficient ($cm^3\ s^{-1}$) expressions for $O+H_2$ and $O+D_2$

Sutherland et al.[1]

$$k_{H_2}(T) = 8.44 \cdot 10^{-20}\, T^{2.67} \exp(-3167/T)\,; \quad 297\,\mathrm{K} \le T \le 2495\,\mathrm{K} \tag{1}$$

Marshall and Fontijn[2]

$$k_{H_2}(T) = 7.30 \cdot 10^{-21}\, T^{2.93} \exp(-2980/T)\,; \quad 350\,\mathrm{K} \le T \le 1420\,\mathrm{K} \tag{2}$$

$$k_{H_2}(T) = 1.5 \cdot 10^{-12} \exp(-3540/T) + 3.7 \cdot 10^{-10} \exp(-7450/T)\,;\ 300\,\mathrm{K} \le T \le 2500\,\mathrm{K}$$

$$k_{D_2}(T) = 1.4 \cdot 10^{-12} \exp(-4250/T) + 3.6 \cdot 10^{-10} \exp(-7980/T)\,;\ 390\,\mathrm{K} \le T \le 2480\,\mathrm{K}$$

$$\frac{k_{H_2}(T)}{k_{D_2}(T)} = 6.5 \cdot 10^{-3}\, T^{0.64} \exp(1230/T)\,; \quad 390\,\mathrm{K} \le T \le 1420\,\mathrm{K} \tag{3}$$

Natarajan and Roth[3]

$$k_{H_2}(T) = 6.18 \cdot 10^{-18}\, T^{2.17} \exp(-4080/T).\,; \quad 1713\,\mathrm{K} \le T \le 3532\,\mathrm{K} \tag{4}$$

$$k_{H_2}(T) = 6.43 \cdot 10^{-20}\, T^{2.70} \exp(-3150/T).\,; \quad 300\,\mathrm{K} \le T \le 3532\,\mathrm{K} \tag{5}$$

Zhu et al.[4]

$$k_{D_2}(T) = 2.43 \cdot 10^{-16}\, T^{1.70} \exp(-4911/T)\,; \quad 343\,\mathrm{K} \le T \le 2487\,\mathrm{K} \tag{6}$$

$$k_{D_2}(T) = 4.78 \cdot 10^{-11} \exp(-5710/T)\,; \quad 343\,\mathrm{K} \le T \le 500\,\mathrm{K} \tag{7}$$

Michael[5]

$$k_{D_2}(T) = 1.95 \cdot 10^{-15}\, T^{1.45} \exp(-5250/T).\,; \quad 825\,\mathrm{K} \le T \le 2500\,\mathrm{K} \tag{8}$$

$$\frac{k_{H_2}(T)}{k_{D_2}(T)} = 3.47 \cdot 10^{-4}\, T^{0.97} \exp(1744/T)\,; \quad 350\,\mathrm{K} \le T \le 2500\,\mathrm{K} \tag{9}$$

Shin et al.[6]

$$k_{H_2}(T) = 1.31 \cdot 10^{-9} \exp(-9381/T).\,; \quad 1790\,\mathrm{K} \le T \le 2250\,\mathrm{K} \tag{10}$$

Yang et al.[7]

$$k_{H_2}(T) = 6.14 \cdot 10^{-10} \exp(-7818/T)\,; \quad 1600\,\mathrm{K} \le T \le 2500\,\mathrm{K} \tag{11}$$

$$k_{H_2}(T) = 6.42 \cdot 10^{-20}\, T^{2.70} \exp(-3150/T)\,; \quad 297\,\mathrm{K} \le T \le 3530\,\mathrm{K} \tag{12}$$

$$k_{D_2}(T) = 7.80 \cdot 10^{-10} \exp(-8900/T)\,; \quad 2370\,\mathrm{K} \le T \le 3390\,\mathrm{K} \tag{13}$$

$$k_{D_2}(T) = 1.99 \cdot 10^{-15}\, T^{1.72} \exp(-4480/T)\,; \quad 340\,\mathrm{K} \le T \le 3390\,\mathrm{K} \tag{14}$$

$$\frac{k_{H_2}(T)}{k_{D_2}(T)} = 3.1 \cdot 10^{-2}\, T^{0.45} \exp(800/T)\,; \quad 2400\,\mathrm{K} \le T \le 3400\,\mathrm{K} \tag{15}$$

Ryu el al.[8]

$$k_{\mathrm{H}_2}(T) = 3.12 \cdot 10^{-10} \exp(-6897/T).; \quad 1424\,\mathrm{K} \leq T \leq 2427\,\mathrm{K} \tag{16}$$

Baulch et al.[9]

$$k_{\mathrm{H}_2}(T) = 6.34 \cdot 10^{-12} \exp(-4000/T) + 1.46 \cdot 10^{-9} \exp(-9650/T) \tag{17}$$

$$298\,\mathrm{K} \leq T \leq 3300\,\mathrm{K}$$

Notes and references

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