

Experimental and theoretical studies of $O(^1D) + H_2O/D_2O$ gas-phase reactions

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The reactions of atomic oxygen in its first electronically excited state, $O(^1D)$, play important roles in the chemistry of several planetary atmospheres, including Earth and Mars, where oxygen bearing molecules are among the major atmospheric constituents. In this work,¹ we report an experimental and theoretical study of the gas-phase reactions between $O(^1D)$ and H_2O and $O(^1D)$ and D_2O at room temperature and below. On the experimental side, the kinetics of these reactions have been investigated over the 50–127 K range using a continuous flow Laval nozzle apparatus, coupled with pulsed laser photolysis and pulsed laser induced fluorescence for the production and detection of $O(^1D)$ atoms respectively. On the theoretical side, the existing full-dimensional ground X^1A potential energy surface for the H_2O_2 system involved in this process has been reinvestigated and enhanced to provide a better description of the barrierless H-atom abstraction pathway.² Based on this enhanced potential energy surface, quasiclassical trajectory calculations and ring polymer molecular dynamics simulations have been performed to obtain low temperature rate constants.

Experimental results: Table 1 and Fig 1

Table 1 Measured second-order rate constants for the $O(^1D) + H_2O$ and $O(^1D) + D_2O$ reactions

T/K	N^b	$[H_2O]/10^{13} \text{ cm}^{-3}$	$k_{O(^1D)+H_2O}/10^{-10} \text{ cm}^3 \text{ s}^{-1}$	N^b	$[D_2O]/10^{13} \text{ cm}^{-3}$	$k_{O(^1D)+D_2O}/10^{-10} \text{ cm}^3 \text{ s}^{-1}$	k_H/k_D
296	45	0–44.3	$(2.00 \pm 0.21)^c$	36	0–13.1	$(1.87 \pm 0.23)^c$	1.07
127 ± 2^a	50	0–19.8	(2.61 ± 0.28)	36	0–11.4	(2.09 ± 0.27)	1.25
75 ± 2	18	0–9.13	(4.56 ± 0.55)	34	0–12.5	(2.53 ± 0.27)	1.81
50 ± 1	26	0–8.5	(4.84 ± 0.84)	32	0–4.76	(3.71 ± 0.75)	1.30

^a Uncertainties on the calculated temperatures represent the statistical (1σ) errors obtained from Pitot tube measurements of the impact pressure.

^b Number of individual measurements. ^c Uncertainties on the measured rate constants represent the combined statistical (1σ) and estimated systematic (10%) errors.

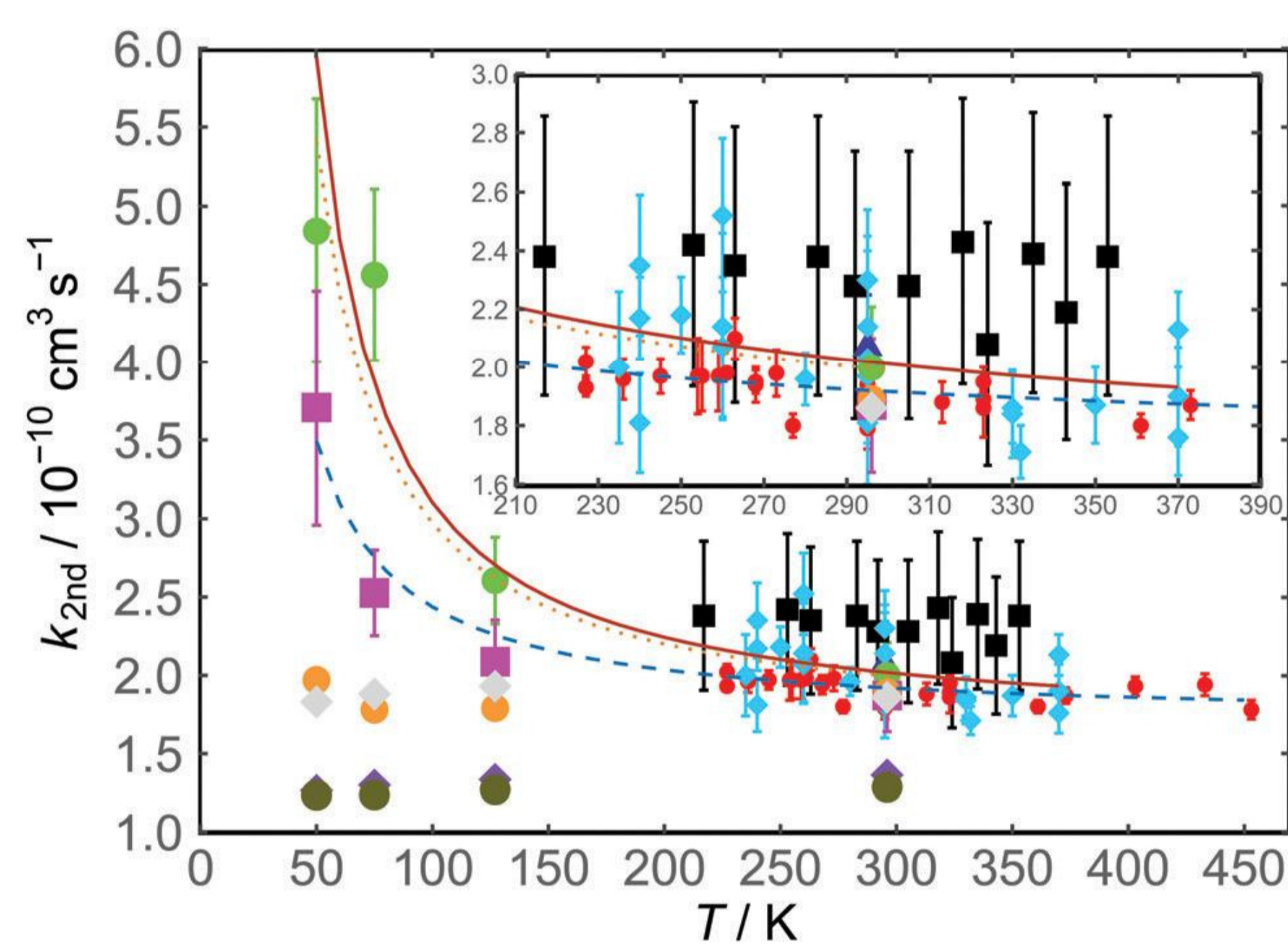


Fig. 2 Second-order rate constants for the $O(^1D) + H_2O$ and $O(^1D) + D_2O$ reactions

In Fig. 1 the upper panel is for the $O(^1D) + H_2O$ reaction the lower panel is for the $O(^1D) + D_2O$ reaction. Solid lines represent weighted fits to the individual datasets.

In Fig. 2, for the $O(^1D) + H_2O$ reaction: green circles-- This experimental work; purple diamonds -- our QCT calculations; black squares, light blue diamonds, red circles, dark blue triangle, orange circles are results from other authors;³ solid brown line, dashed blue line and dotted brown line are Arrhenius fit for some experimental recommendation.⁴ For the $O(^1D) + D_2O$ reaction: purple squares -- This experimental work; olive green circles -- this work QCT calculations. Error bars on the present measurements represent the combined statistical and estimated systematic uncertainty.

The inset shows an expanded view of the congested region between 210 K and 390 K.

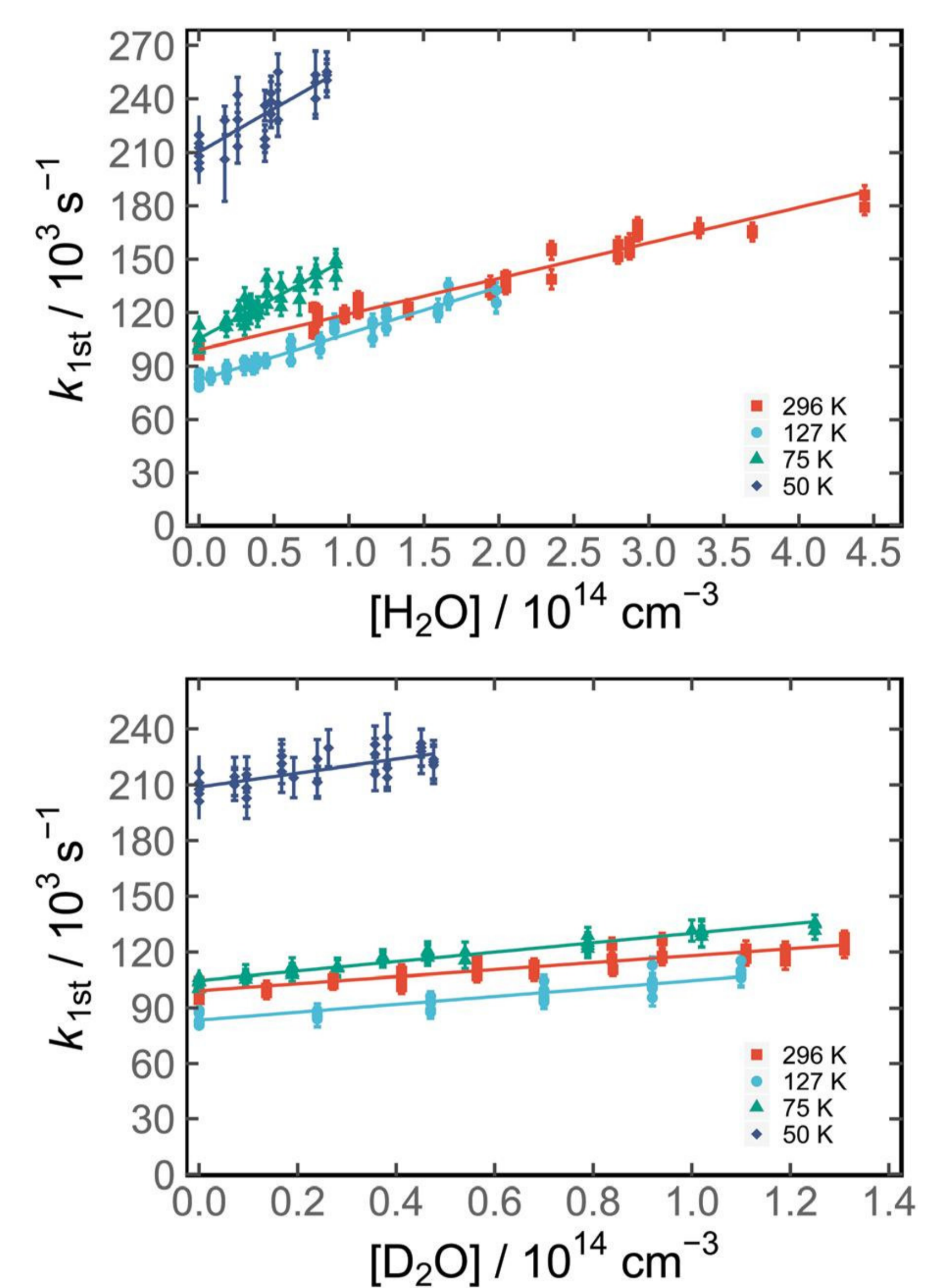


Fig. 1 Pseudo-first-order rate constant as a function of the concentration

Theoretical Calculations: Table 2, Table 3 and Fig 2

Table 2 Summary of the quasiclassical trajectory results obtained in this study

	T/K	$b_{\text{max}}/\text{\AA}$	N_{total}^a	N_{react}^b	$\sigma_r/\text{\AA}^2$	$k/10^{-10} \text{ cm}^3 \text{ s}^{-1c}$	k_H/k_D
$O(^1D) + H_2O$	50	14.0	39 586	11 331	176.3 ± 1.4	1.25 ± 0.01	1.03 ± 0.01
$O(^1D) + D_2O$	50	14.0	37 925	10 747	174.5 ± 1.4	1.20 ± 0.01	
$O(^1D) + H_2O$	75	13.0	14 612	4 125	149.9 ± 2.0	1.30 ± 0.02	1.05 ± 0.02
$O(^1D) + D_2O$	75	13.5	12 523	3 201	146.4 ± 2.2	1.24 ± 0.02	
$O(^1D) + H_2O$	127	12.0	18 775	4 914	118.4 ± 1.5	1.33 ± 0.02	1.05 ± 0.02
$O(^1D) + D_2O$	127	12.0	17 082	4 363	115.6 ± 1.5	1.27 ± 0.02	
$O(^1D) + H_2O$	296	10.5	30 109	6 891	79.3 ± 0.8	1.36 ± 0.01	1.06 ± 0.02
$O(^1D) + D_2O$	296	10.0	31 626	7 717	76.7 ± 0.8	1.29 ± 0.01	

^a Total number of trajectories performed. ^b Number of reactive trajectories. ^c Total rate constant divided by the electronic partition function.

Table 3 Reactive trajectory behaviour at short times for the $O(^1D) + X_2O$ reactions

	T/K	0 fs (%)	< 50 fs (%)
$O(^1D) + H_2O$	50	5.8	67.6
$O(^1D) + D_2O$	50	5.0	58.2
$O(^1D) + H_2O$	75	6.2	67.0
$O(^1D) + D_2O$	75	5.2	57.3
$O(^1D) + H_2O$	127	6.0	66.1
$O(^1D) + D_2O$	127	5.2	57.9
$O(^1D) + H_2O$	296	6.3	67.6
$O(^1D) + D_2O$	296	4.7	57.3

Conclusions:

The theoretical constants display a similar temperature independent behaviour to the experimental ones above 100 K, with the theoretical values derived by the ring polymer molecular dynamics method being closer to the measured values. In contrast, while the theoretical rate constants remain relatively constant below 100 K, the experimental values for both reactions increase significantly. Plausible explanations for the discrepancy between experiment and theory are presented, including a possible increased contribution of quenching losses during the low temperature measurements and/or the contribution of excited potential energy surfaces to the reaction which are not accounted for by the present calculations.

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