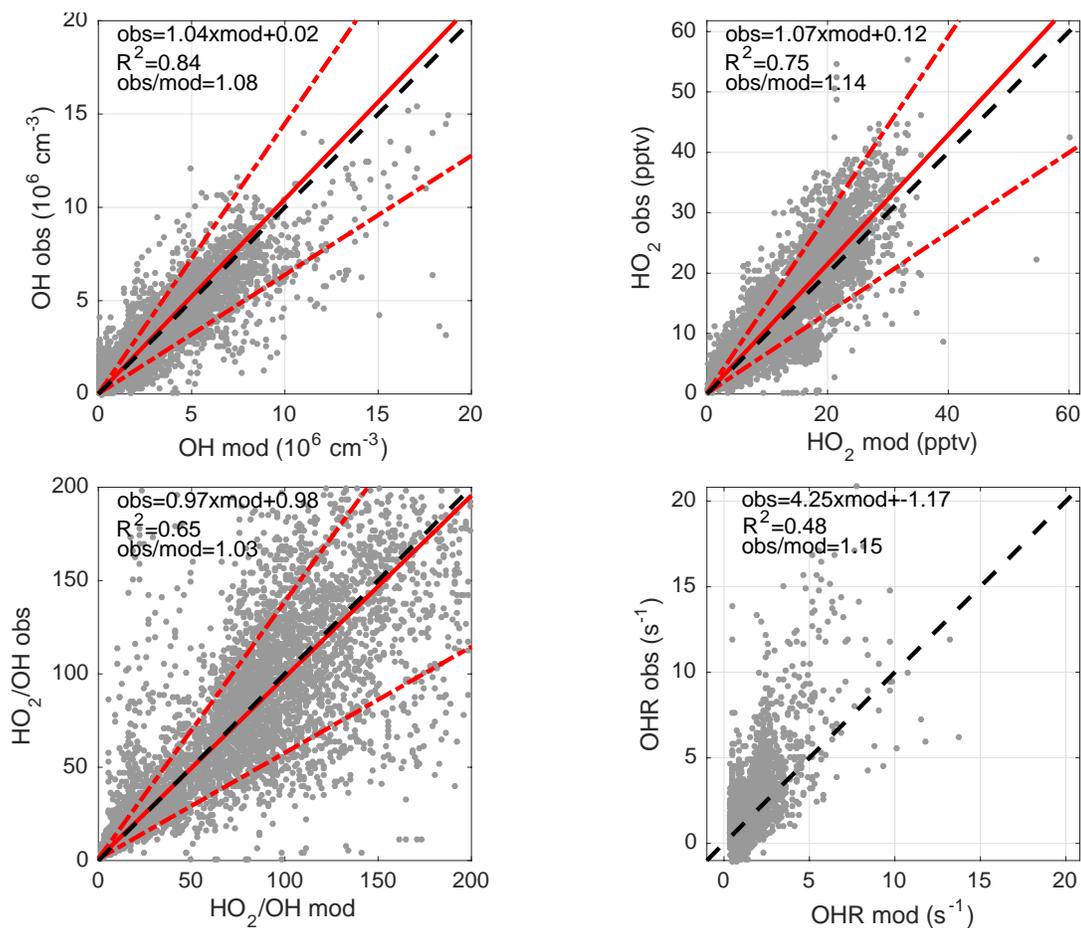
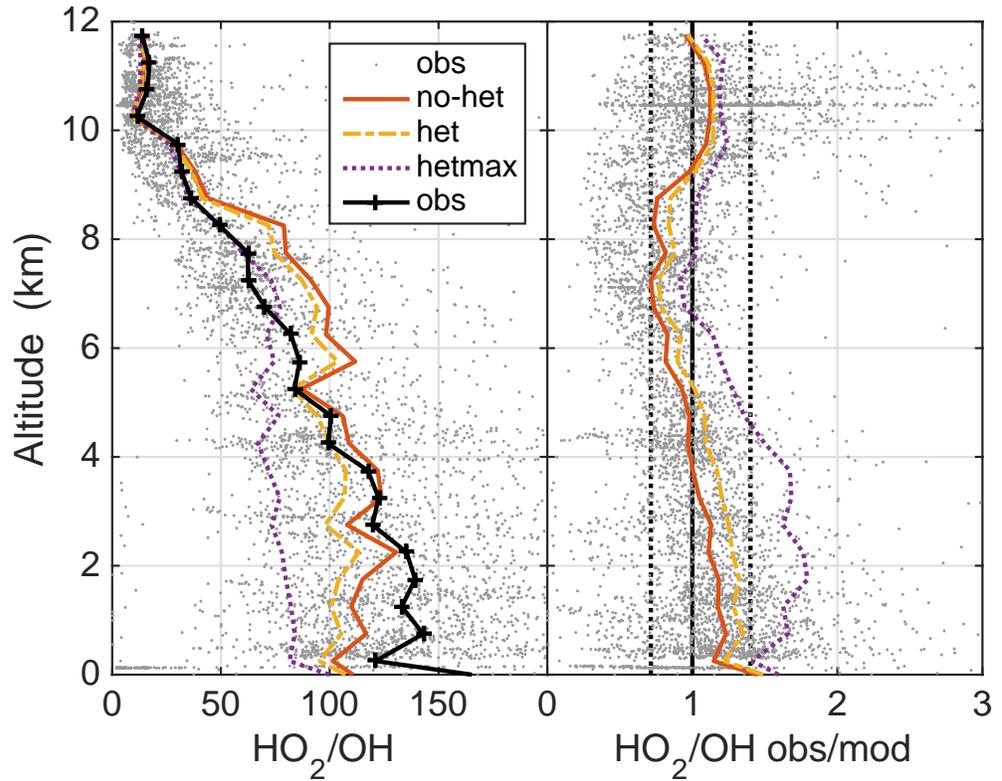


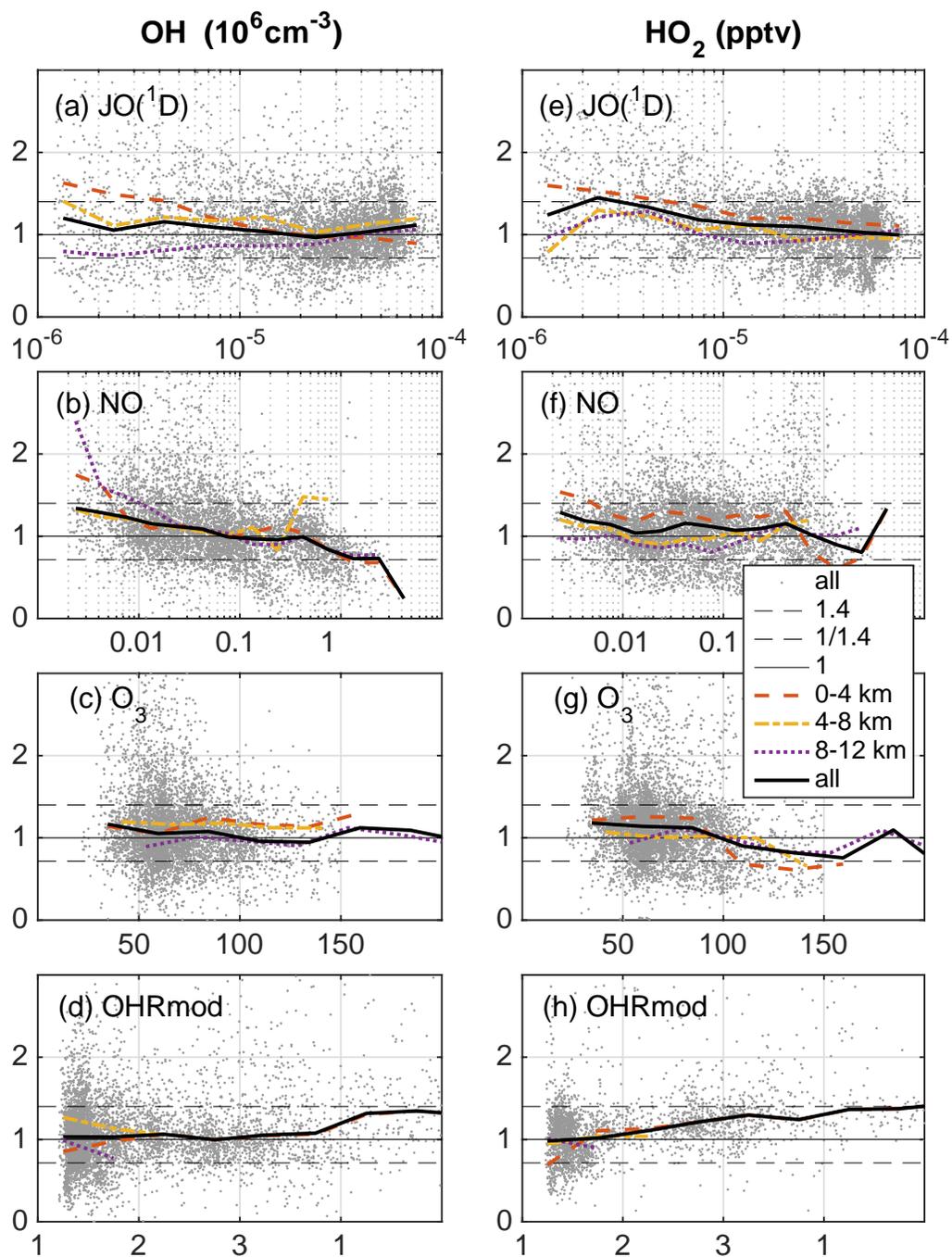
## Supplementary Material



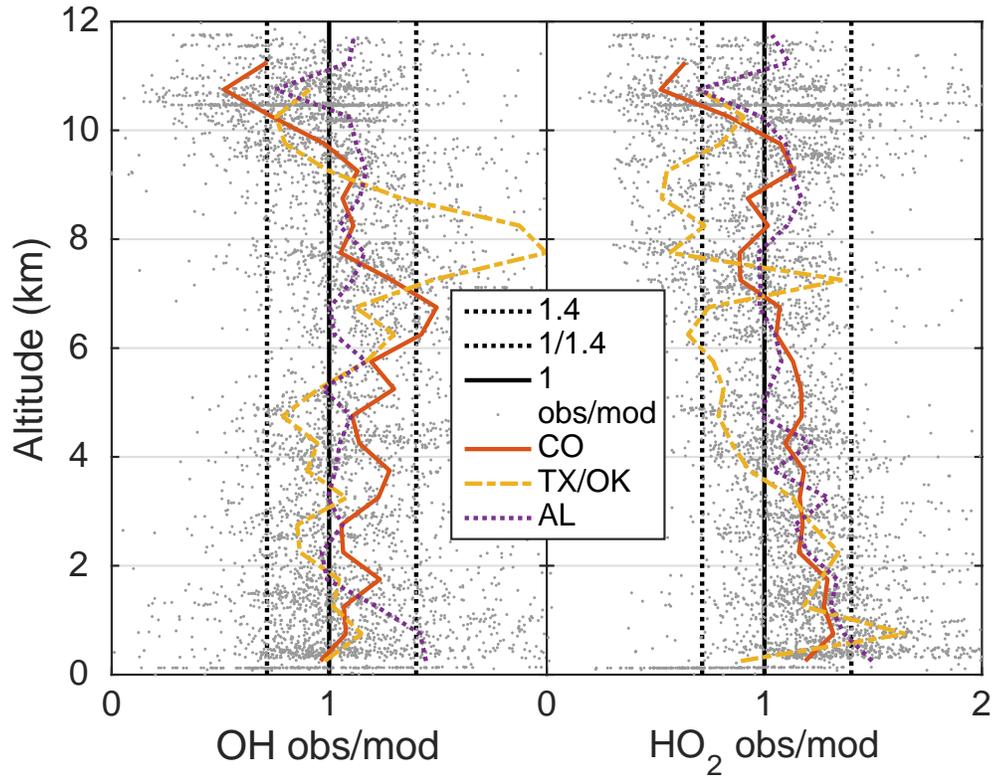
**Figure S1.** Observations versus the no-het model. Scatter plots of observed versus modeled OH (upper right), HO<sub>2</sub> (upper left), HO<sub>2</sub>/OH (lower left), and OH reactivity (lower right). Gray points are one-minute averages. Dashed red lines are factors of 1/1.4 and 1.4 times the fitted line (solid red).



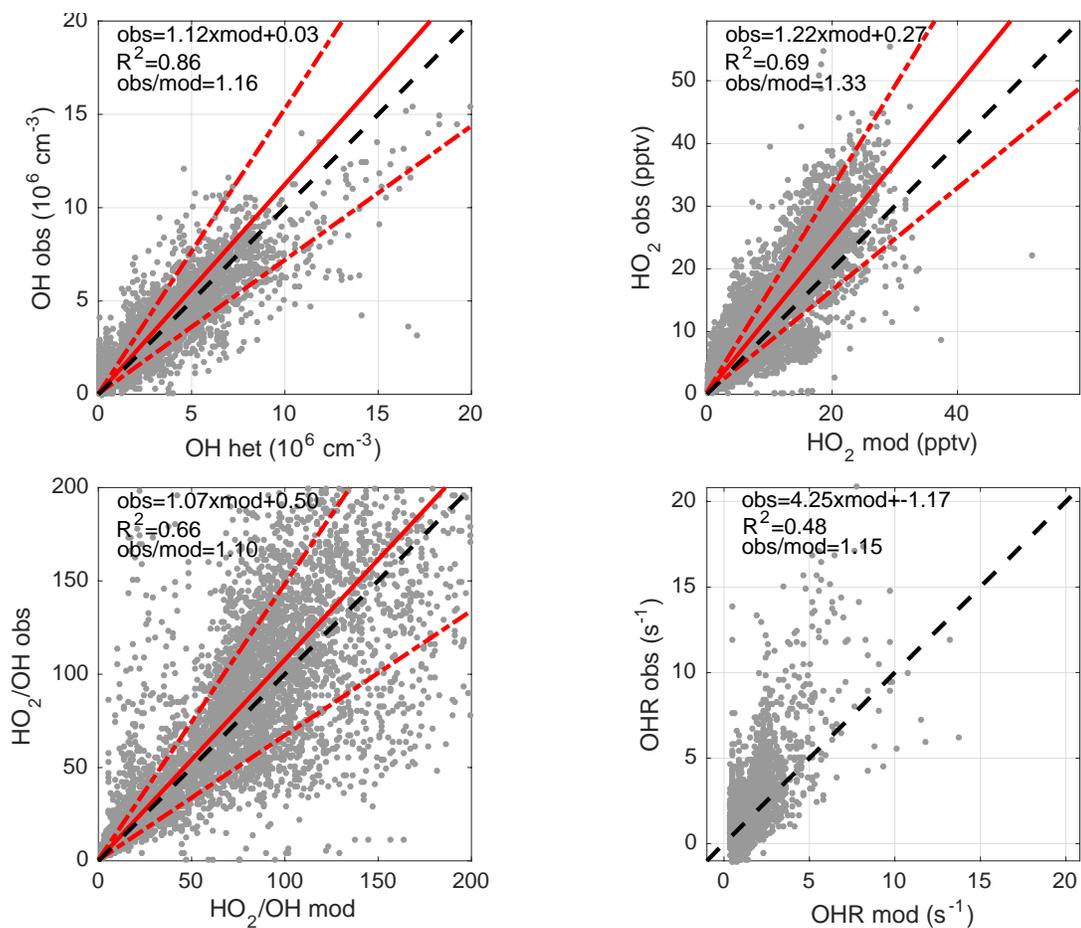
**Figure S2.** Median measured and modeled HO<sub>2</sub>/OH as a function of altitude (left); median ratio of observed-to-modeled HO<sub>2</sub>/OH for the three models as a function of altitude. Gray points are individual 1-minute HO<sub>2</sub>/OH observations and ratios of observed-to-no-heterogeneous modeled HO<sub>2</sub>/OH. Dotted vertical red lines on right are approximate indicators of observation and model agreement.



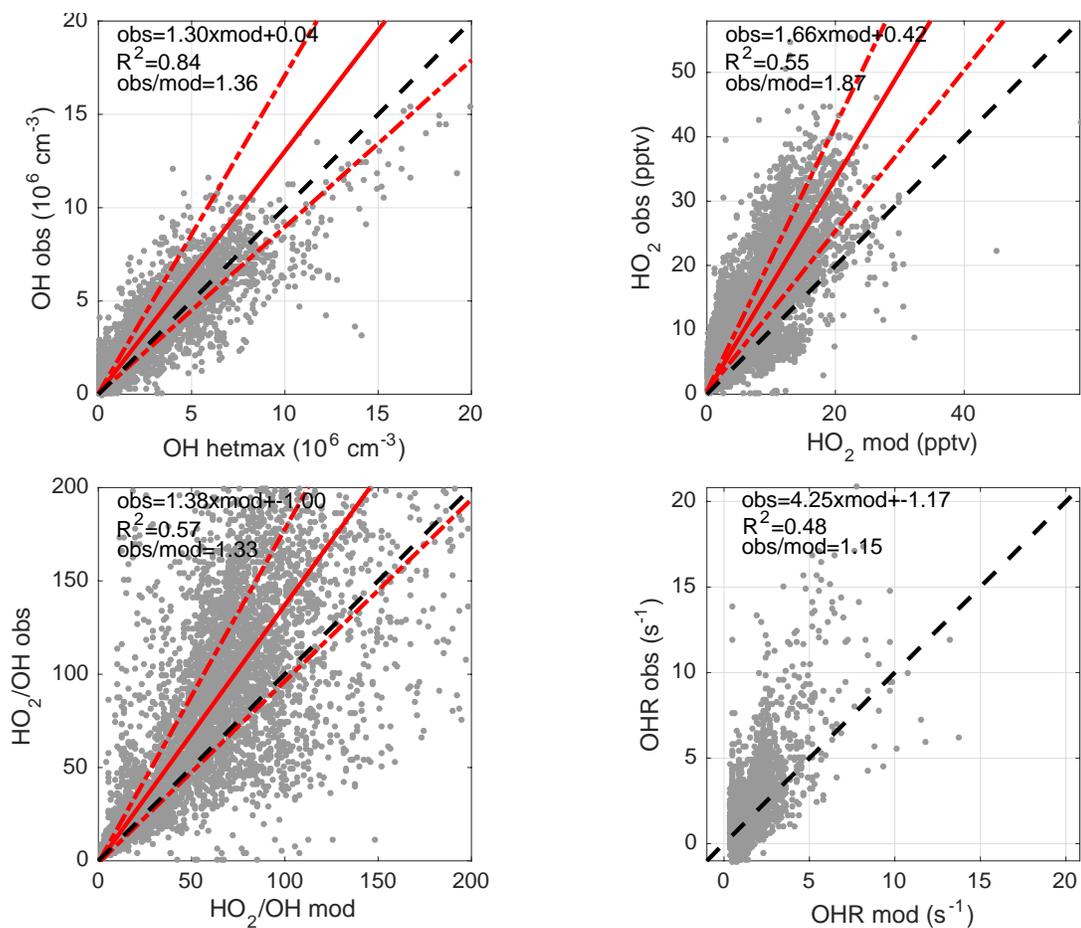
**Figure S3.** Measured/modelled OH (left) and HO<sub>2</sub> (right) as a function of controlling variables: JO(<sup>1</sup>D) in s<sup>-1</sup>, NO in ppbv, O<sub>3</sub> in ppbv, and modeled OH reactivity in s<sup>-1</sup>. Ratios are averaged for three different altitude bands and all the data. Dotted horizontal lines are approximate indicators of observation and model agreement.



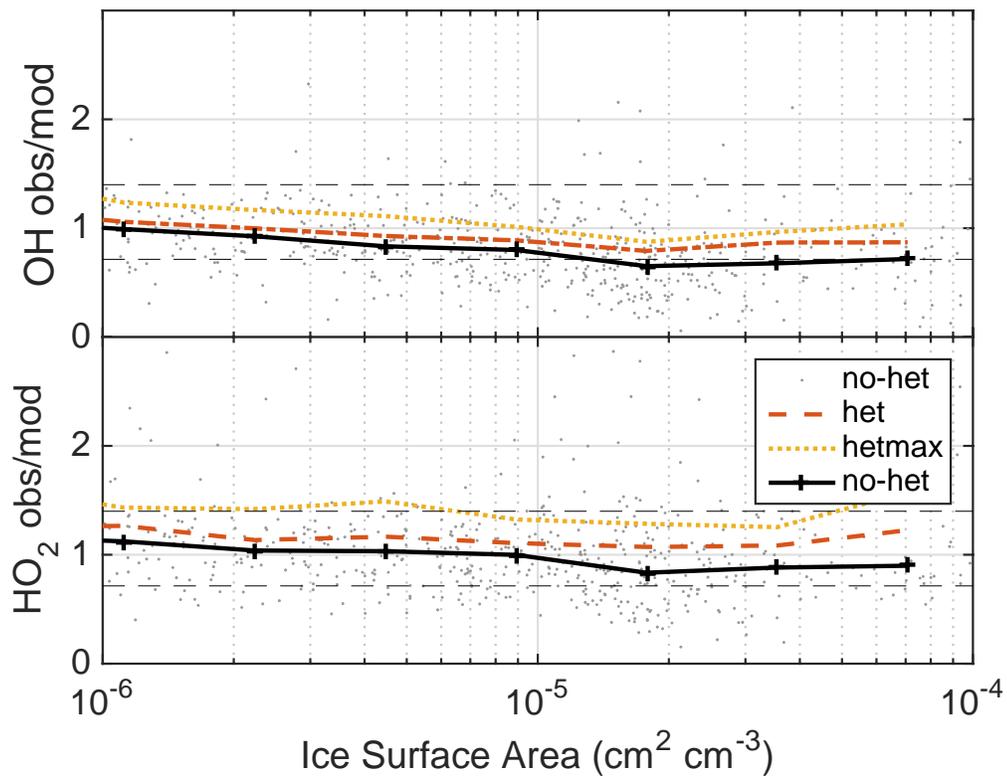
**Figure S4.** Median observed-to-modeled OH (left) and HO<sub>2</sub> (right) with the no-het model, as a function of altitude for the three regions: Colorado, Texas/Oklahoma, and Alabama. Dotted vertical black lines on right are approximate indicators of observation and model agreement.



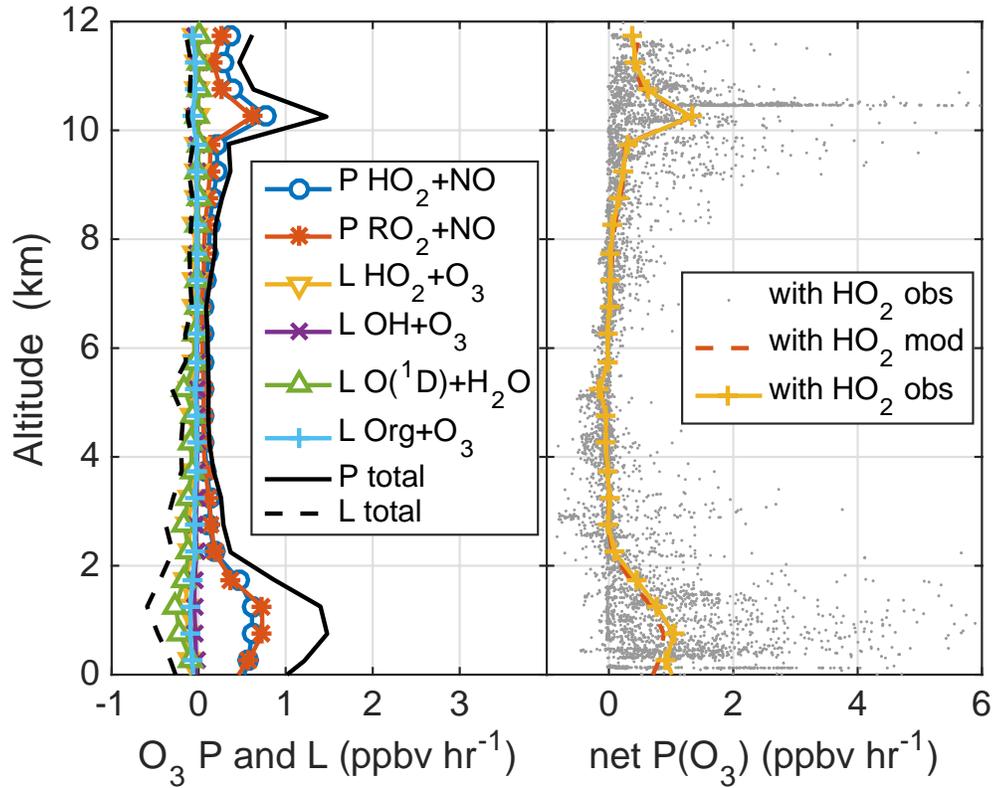
**Figure S5.** Observations versus the het model. Scatter plots of observed versus modeled OH (upper right), HO<sub>2</sub> (upper left), HO<sub>2</sub>/OH (lower left), and OH reactivity (lower right). Gray points are one-minute averages. Dashed red lines are factors of 1/1.4 and 1.4 times the fitted line (solid red).



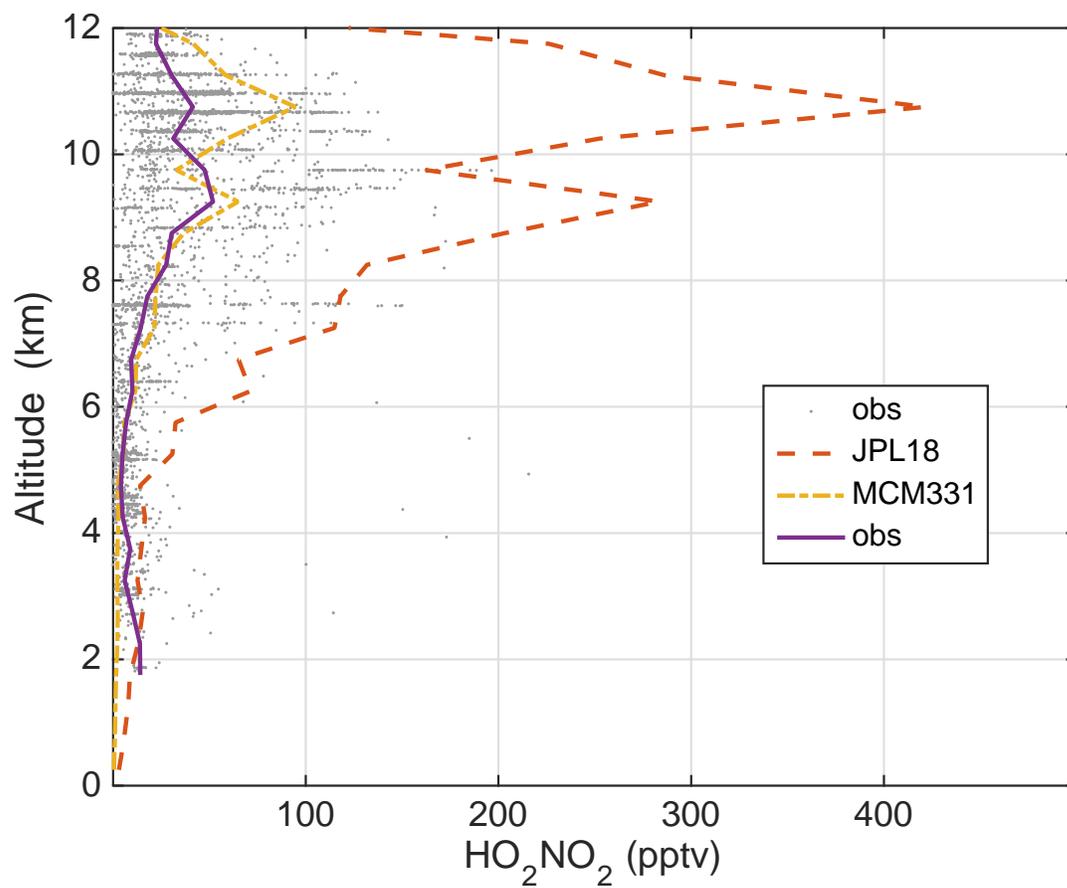
**Figure S6.** Observations versus the hetmax model. Scatter plots of observed versus modeled OH (upper right),  $\text{HO}_2$  (upper left),  $\text{HO}_2/\text{OH}$  (lower left), and OH reactivity (lower right). Gray points are one-minute averages. Dashed red lines are factors of 1/1.4 and 1.4 times the fitted line (solid red).



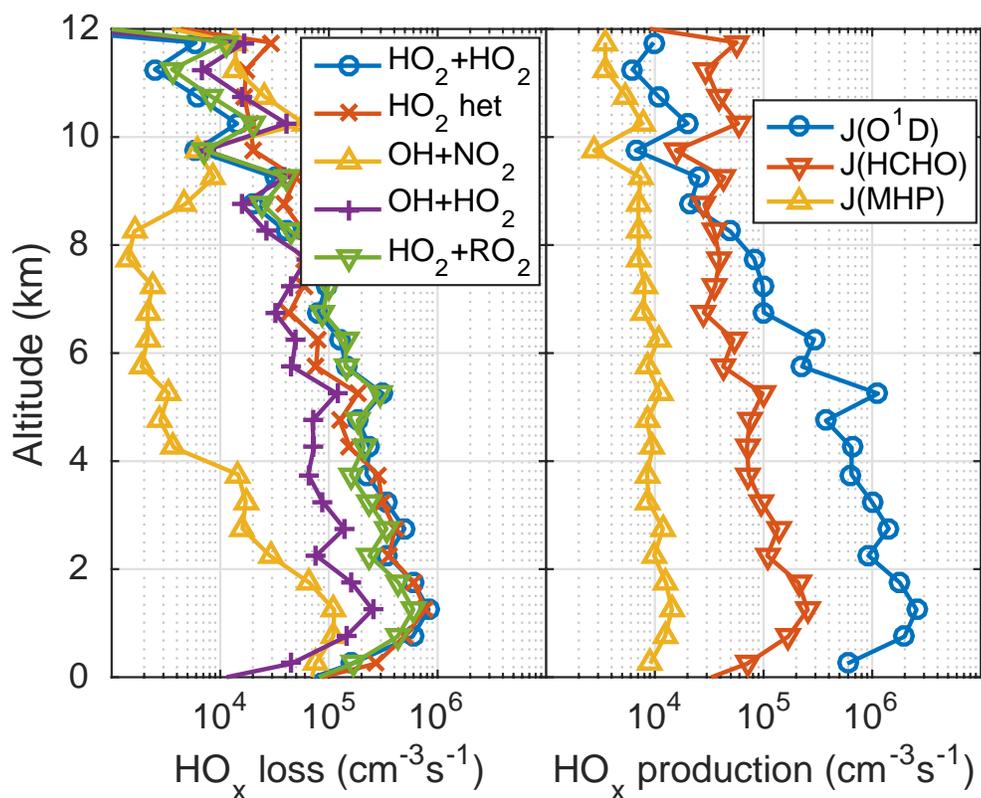
**Figure S7.** Median observed-to-modeled OH (top) and HO<sub>2</sub> (bottom) versus ice surface area concentration. Dotted horizontal black lines are indicators of observation and model agreement.



**Figure S8.** Calculated ozone production ( $\text{P}(\text{O}_3)$ ). Rates of production (P) and loss (L) are on the left. Individual rates are shown, along with the total. Net  $\text{P}(\text{O}_3)$  is shown on the right.



**Figure S9.** HO<sub>2</sub>NO<sub>2</sub> as a function of altitude. MCM331 was run the reaction rate coefficient for HO<sub>2</sub>+NO<sub>2</sub>+M from JPL18 (Burkholder et al., 2015) and from MCMv3.1.1 (Saunders et al., 2003).



**Figure S10.** Median modeled HO<sub>x</sub> loss (right) and production (left) as a function of altitude. MHP is Methyl hydroperoxide. The HO<sub>2</sub> heterogeneous loss was calculated with the het model.

**Table S1.** Scatter plot statistics for OH and HO<sub>2</sub> with ~10% of total one-minute data (661/6817)

case	molecule	units	slope	intercept	R <sup>2</sup>	ratio
no-het	OH	10 <sup>6</sup> cm <sup>-3</sup>	0.96	0.19	0.76	1.08
	HO <sub>2</sub>	pptv	1.13	0.21	0.88	1.14
het	OH	10 <sup>6</sup> cm <sup>-3</sup>	1.09	0.20	0.83	1.16
	HO <sub>2</sub>	pptv	1.33	0.19	0.79	1.33
hetmax	OH	10 <sup>6</sup> cm <sup>-3</sup>	1.33	0.21	0.80	1.36
	HO <sub>2</sub>	pptv	1.90	0.27	0.62	1.87