Reaction Rate Coefficients of Atmospheric Reactions

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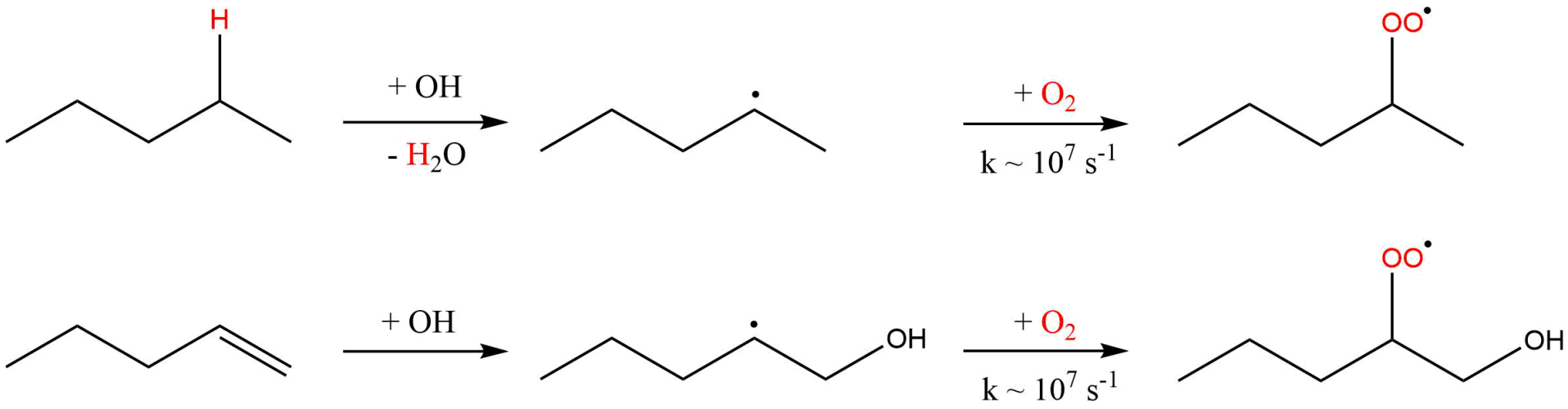
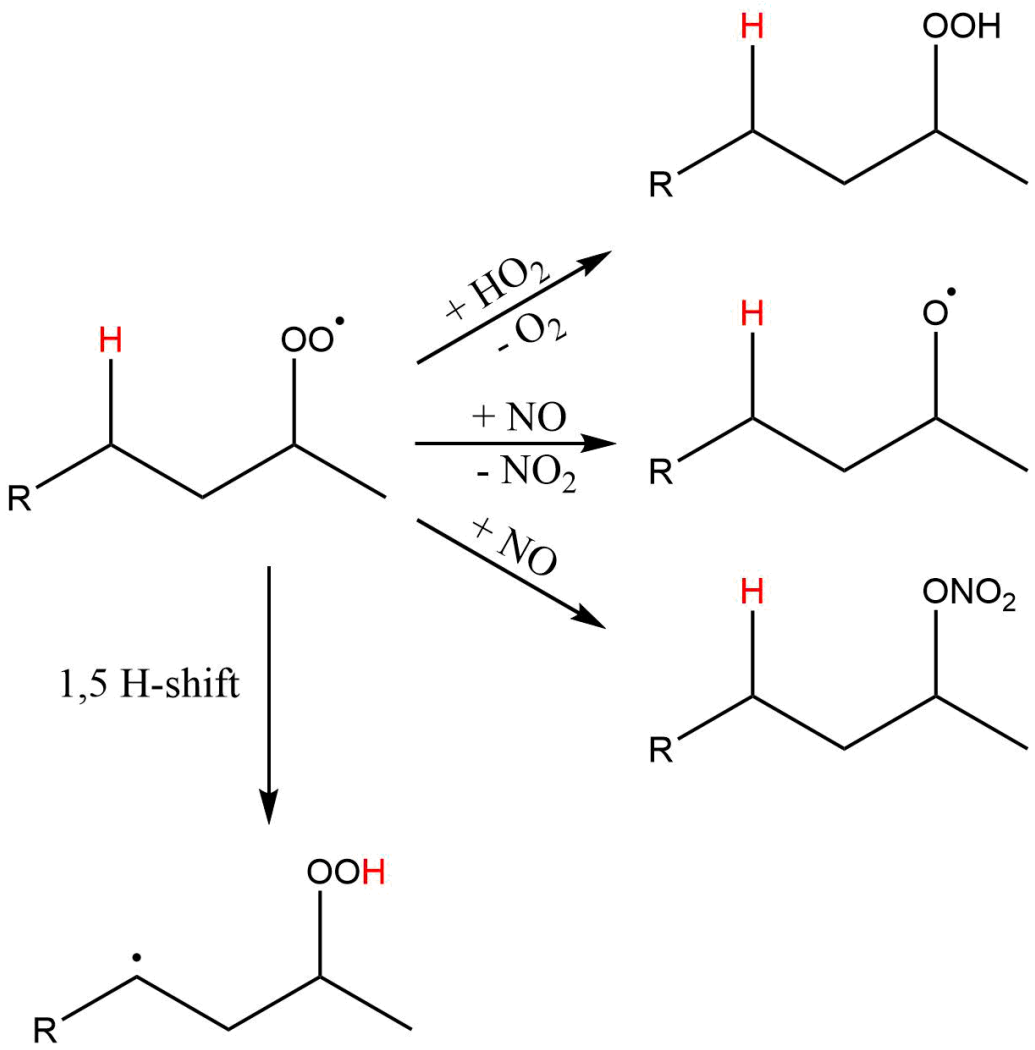
Atmospheric Oxidation of VOC

Important oxidation agents: OH, NO_3, O_3 and Cl



Park et al., *J. Phys. Chem. A*, 108, **2004**
Atkinson et al., *Atmos. Environ.*, 37, **2003**

Peroxy Radical Reactions



Pseudo first-order reaction rate coefficients

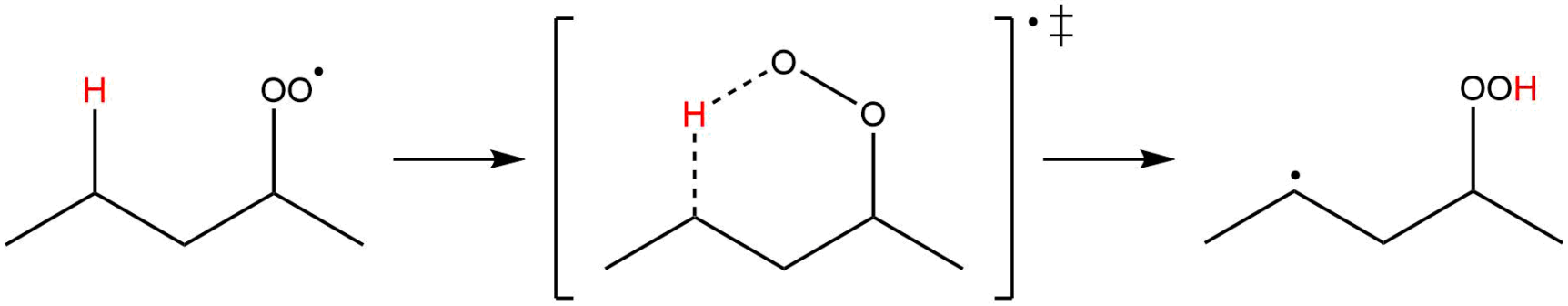
Pristine	Urban
~10^{-2} s^{-1}	~10^{-2} s^{-1}

~10^{-3} s^{-1}	~10 s^{-1}

10^{-11} s^{-1} - 10^{7} s^{-1}

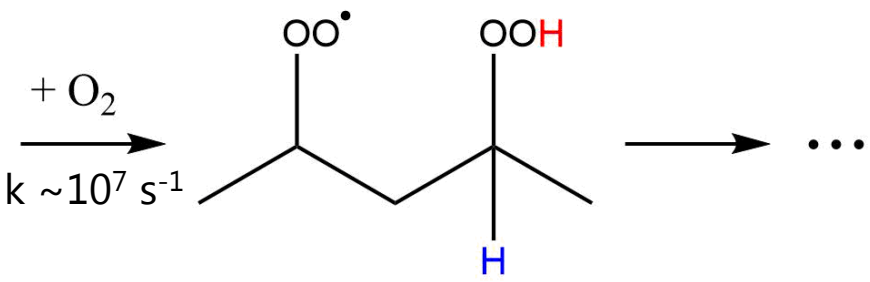
McAdam et al., *Chem. Phys. Lett.*, 133, **1987**
Plumb et al., *Int. J. Chem. Kinet.*, 14, **1982**
Crounse et al., *J. Phys. Chem. Lett.*, 4, **2013**

Hydrogen Shifts and Autoxidation



O/C ratio:
2/5

1,5 H-shift



O/C ratio:
4/5

Secondary Organic Aerosol (SOA)

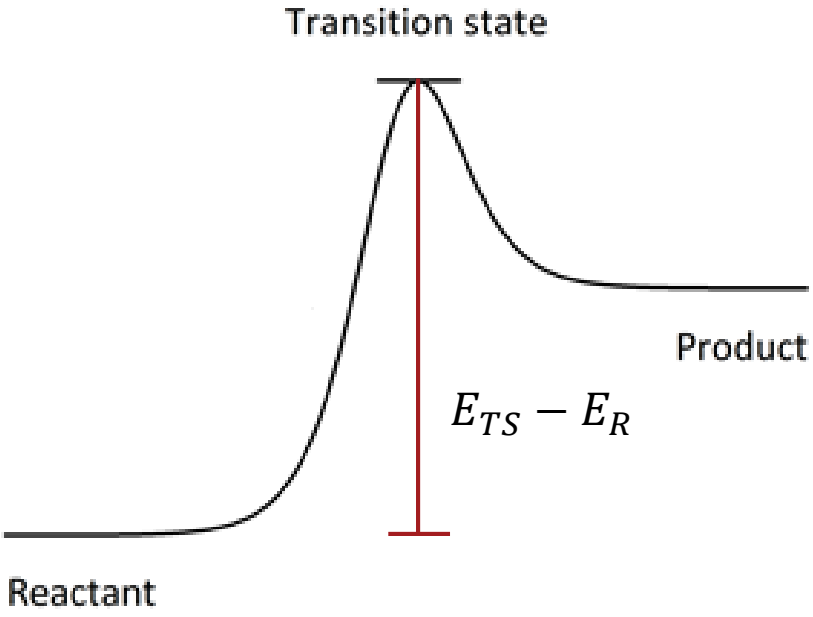
Crounse et al., *J. Phys. Chem. Lett.*, 4, **2013**

Transition State Theory

Unimolecular reaction:

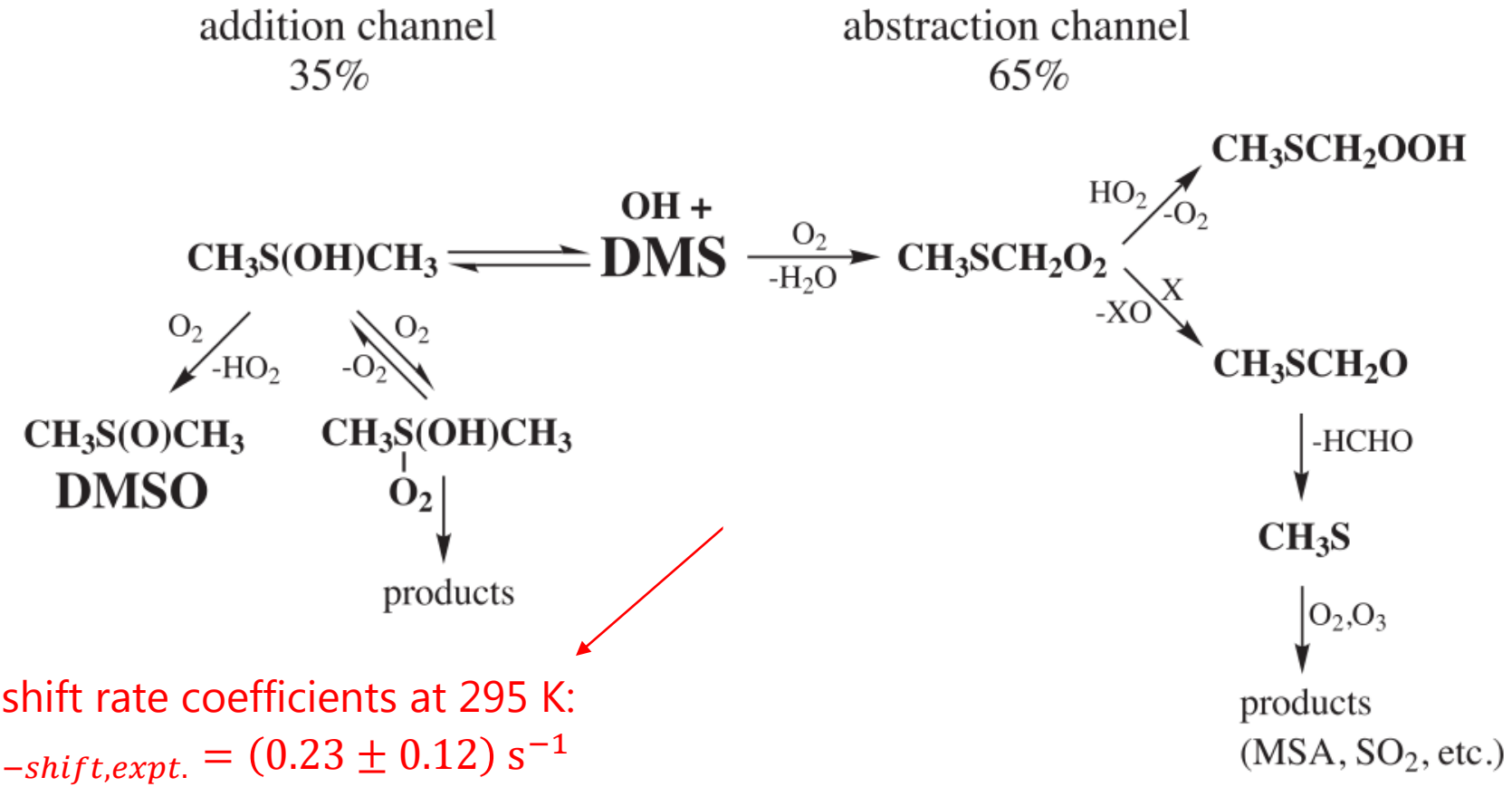
$$k = \kappa \frac{k_B T}{h} \frac{Q_{TS}}{Q_R} e^{\frac{-(E_{TS}-E_R)}{k_B T}}$$

- κ: Tunneling correction, Eckart
- Q: Partition function
- E: ZPVE-corrected energy



H-shifts in Dimethylsulfide Oxidation

Annual DMS emission: ~20 × 10^6 tons



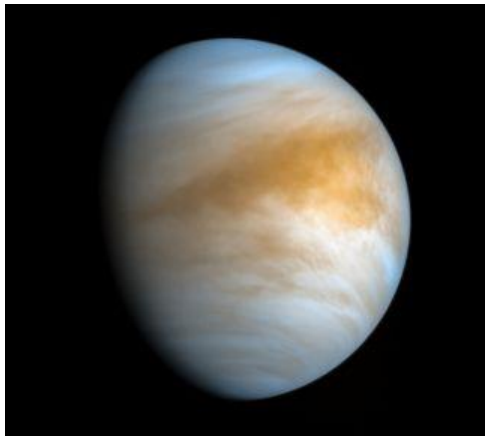
H-shift rate coefficients at 295 K:

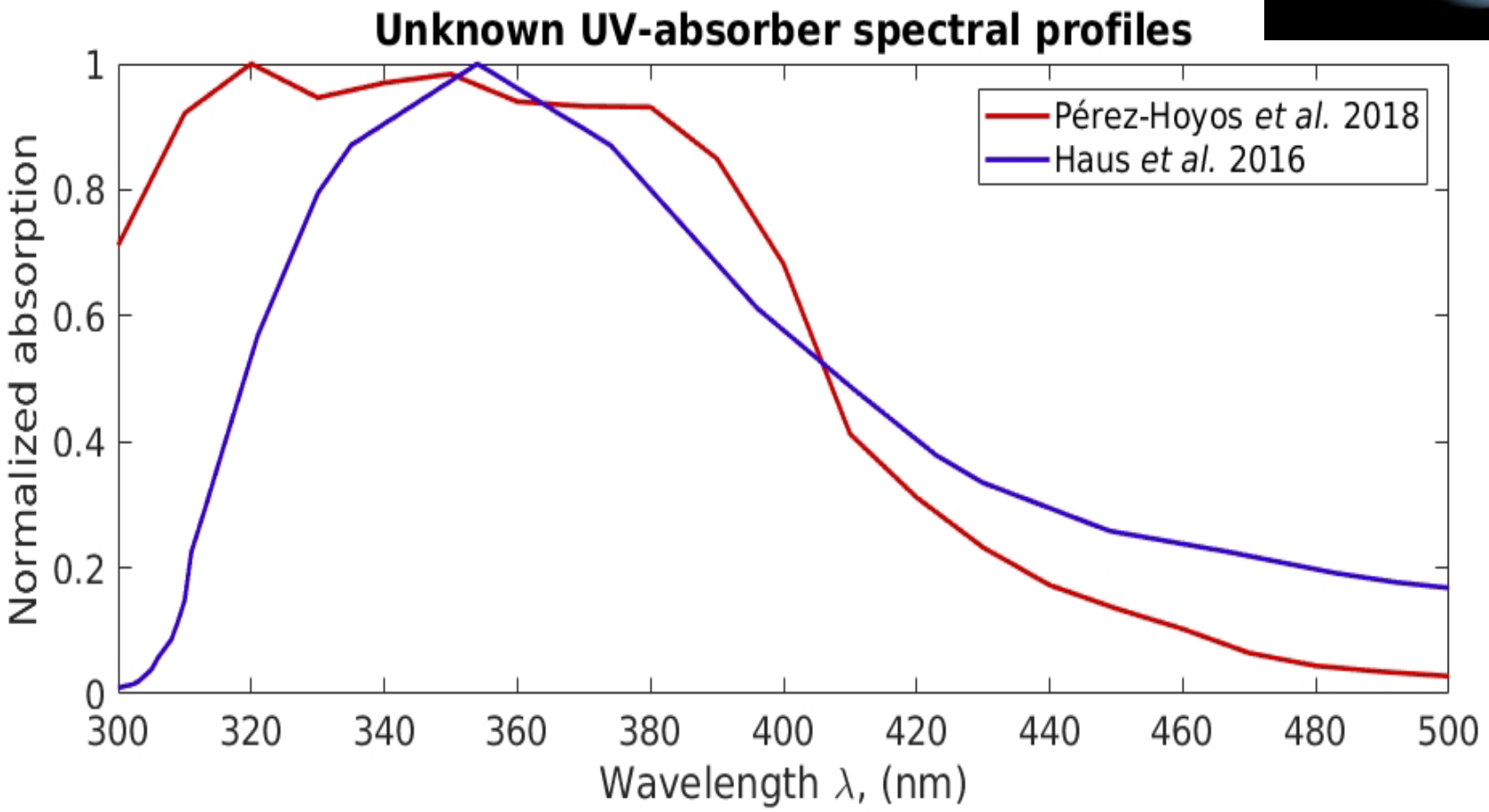
$k_{H-shift,expt.} = (0.23 \pm 0.12)\ s^{-1}$

$k_{H-shift,calc.} = 0.047\ s^{-1}$

Veres et al., *Proc. Natl. Acad. Sci.,* 4, 117, **2020**
Berndt et al., *J. Chem. Phys. Lett.*, 10, **2019**

Unknown UV-Absorber on Venus





Frandsen et al., submitted to J. Phys. Chem. A

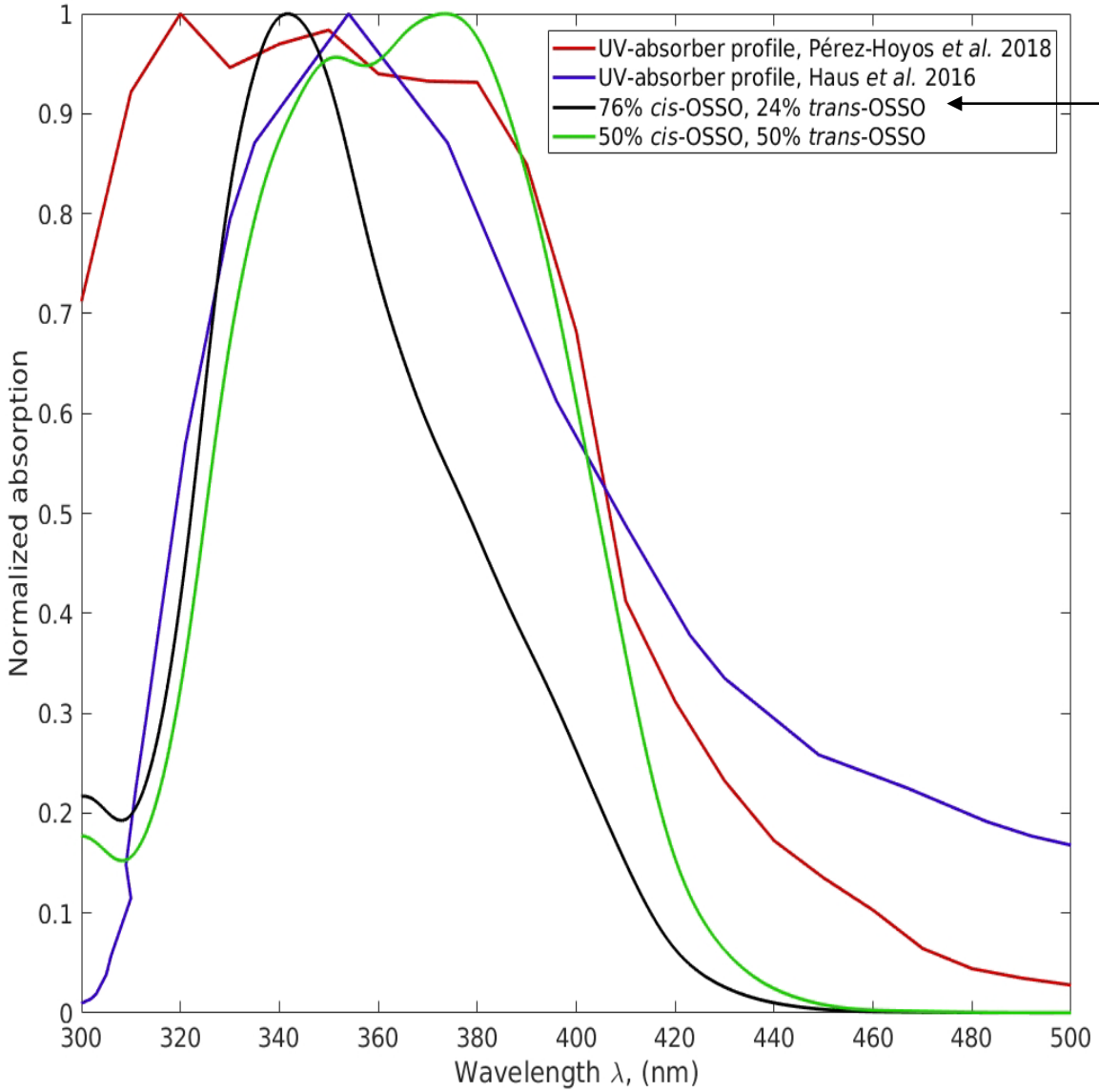
OSSO as a Candidate

- UV absorption coincides with SO_2 on Venus

$$SO_2 + h\nu \rightarrow SO + O$$

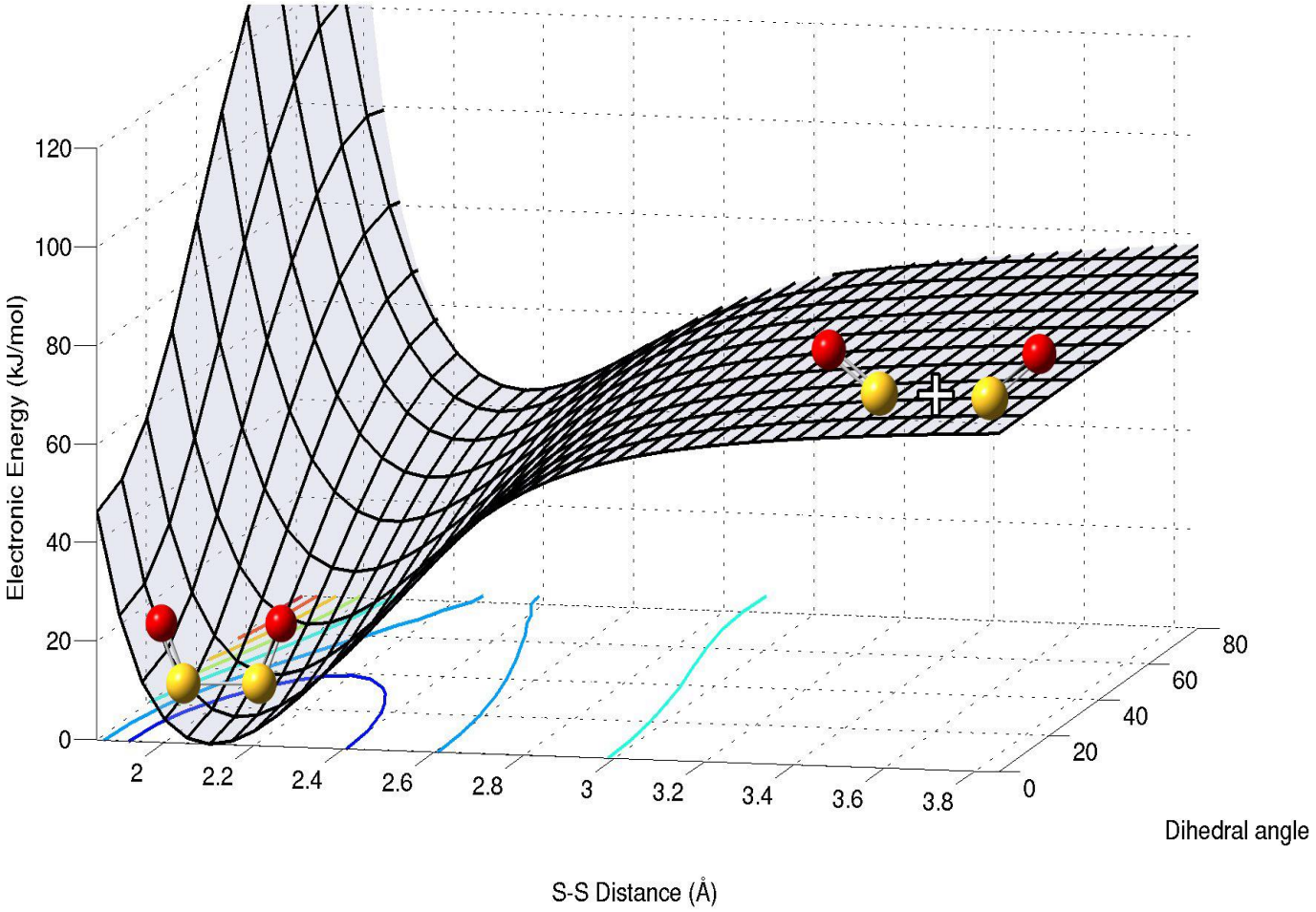
$$SO + SO \rightarrow OSSO$$

Calculated OSSO Absorption Spectra



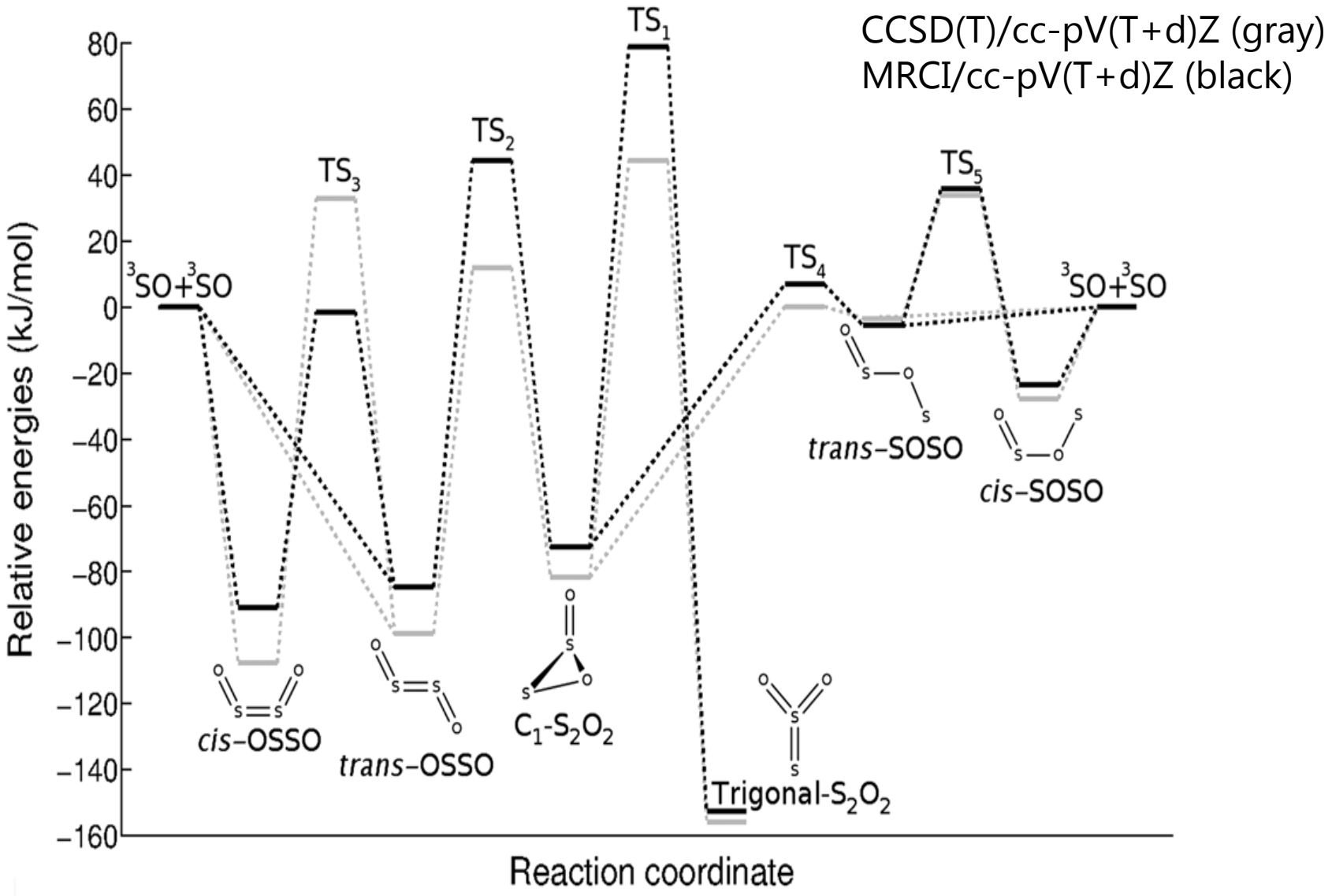
Based on estimated photolysis rate coefficients

SO + SO



Frandsen et al., *Geophys. Res. Lett.*, 43, 11, 146-155, 2016

Potential Energy Surface



SO + SO Rate Coefficient

High-pressure limit:

$$\frac{d[OSSO]}{dt} = k[SO]^2$$

Calculated high-pressure rate coefficients at T = 245 K:

$$k_{\infty,collision} = 1.4 \times 10^{-11}\ \text{molecule}^{-1}\ \text{cm}^3\ \text{s}^{-1}$$
$$k_{\infty,VTST} = 1.7 \times 10^{-11}\ \text{molecule}^{-1}\ \text{cm}^3\ \text{s}^{-1}$$

Slight negative temperature dependence

Frandsen et al., *Geophys. Res. Lett.*, 43, 11, 146-155, 2016
Frandsen et al., submitted to J. Phys. Chem. A

Implementation into Venus Model