How important is excess vibrational energy for modelling upper atmospheric chemistry?

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Why are we interested?

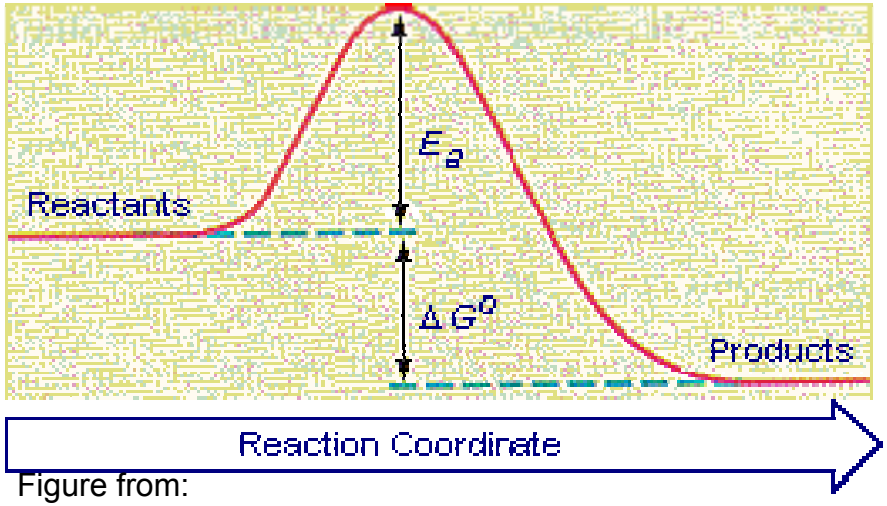


Figure from:
http://chemed.purdue.edu/genchem/topicreview/bp/ch22/activate.html

- Usually, k(T) is calculated with the Arrhenius equation.
- Upper atmosphere: Non-local thermodynamic equilibrium.
- Does excess vibrational energy change reaction rates?

Selection of case studies:

- Reactants should be abundant in the middle/upper atmosphere.
- Reactants should be in strong non-local thermodynamic equilibrium. Chemical non-LTE preferable over radiative non-LTE (larger population of vibrational excited states)
- Reaction should be relevant to ozone chemistry.
- Literature on k(v) needed.

Selection of case studies:

- Reactants should be abundant in the middle/upper atmosphere.
- Reactants should be in strong non-local thermodynamic equilibrium. Chemical non-LTE preferable over radiative non-LTE (larger population of vibrationally excited states)
- Reaction should be relevant to ozone chemistry.
- Literature on k(v) needed (we use: Varandas and Zhang, Chem. Phys. Lett. 340, 62-70, 2001; Varandas, Chem Phys Lett. 396, 182-190, 2004)

Selected reactions for this study:

$$OH(v=0\ldots9) + O_3 \rightarrow O_2 + HO_2$$
$$OH(v=0\ldots9) + O \rightarrow O_2 + H$$

Populations of vibrational states of OH

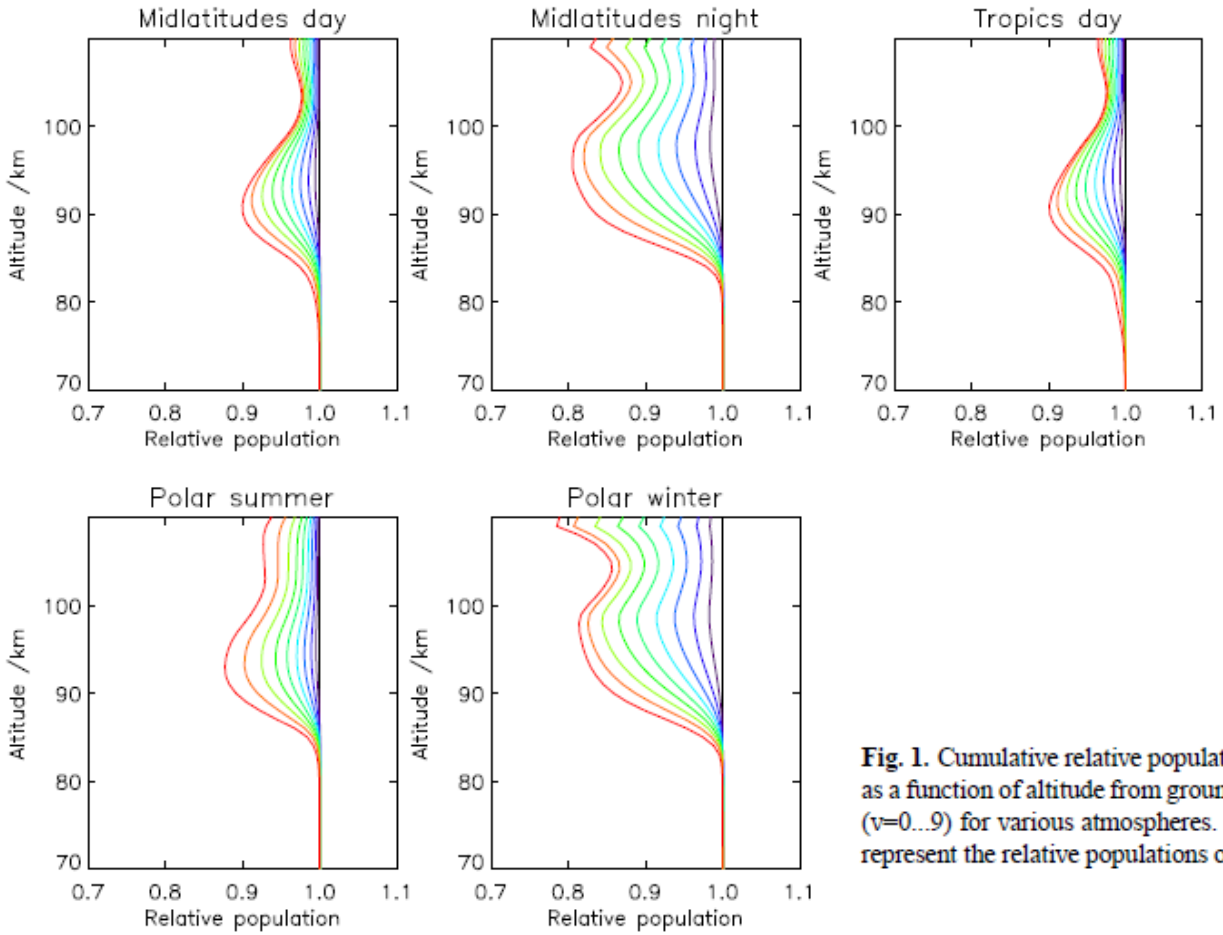


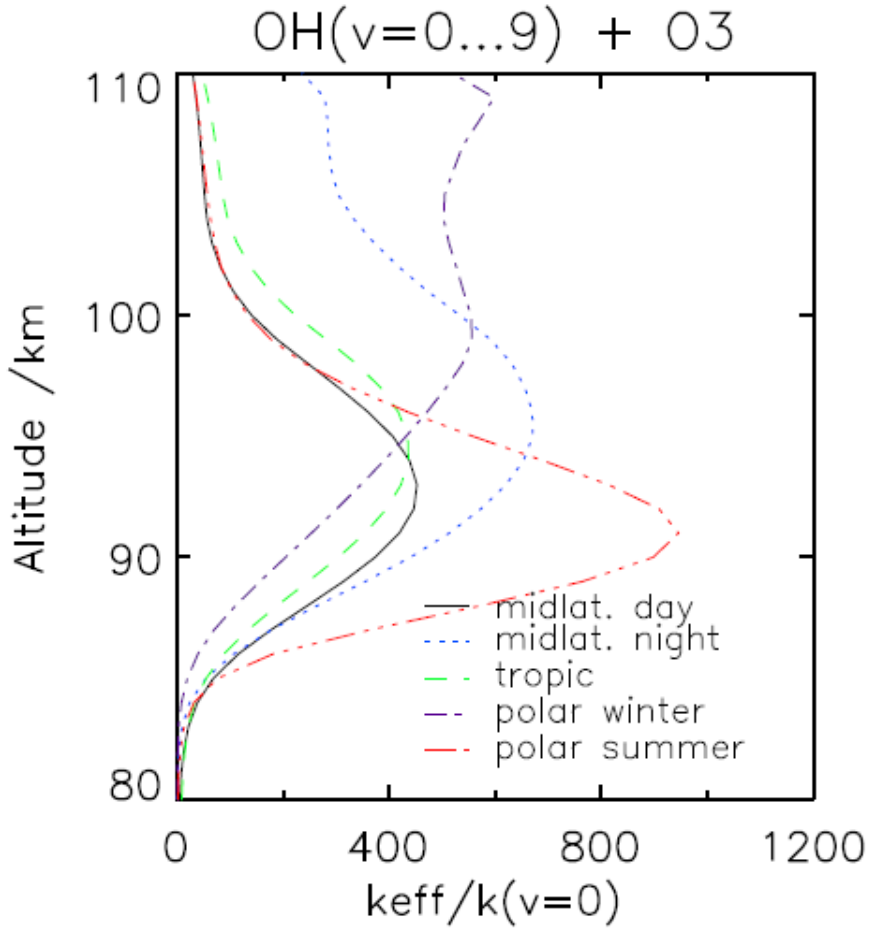
Fig. 1. Cumulative relative populations of the OH vibrational states as a function of altitude from groundstate (leftmost line) to total OH (v=0...9) for various atmospheres. The distances between the lines represent the relative populations of of vibrational levels 1 to 9.

Effective rate coefficient:

The effective rate coefficient is the population-weighted mean of vibrational state dependent rate coefficients.

$$k_{eff} = \frac{1}{[\mathrm{OH}(v = 0...9)]} \sum_{v=0}^{9} k_v [\mathrm{OH}(v)].$$

How large is k_{eff}?



How important is this?
Comparison with competing reactions

Ox loss:

$$\mathrm{OH}(v=0...9) + \mathrm{O_3} \rightarrow \mathrm{O_2} + \mathrm{HO_2} \quad \text{(R1)}$$

$$\mathrm{O_3} + \mathrm{O}(^3\mathrm{P}) \rightarrow 2\mathrm{O_2} \quad \text{(R3)}$$

$$\mathrm{O_3} + \mathrm{O}(^1\mathrm{D}) + \mathrm{M} \rightarrow 2\mathrm{O_2} + \mathrm{M} \quad \text{(R4)}$$

$$\mathrm{O} + \mathrm{O} + \mathrm{M} \rightarrow \mathrm{O_2} + \mathrm{M} \quad \text{(R5)}$$

$$\mathrm{H} + \mathrm{O_3} \rightarrow \mathrm{O_2} + \mathrm{OH}(v=1...9) \quad \text{(R2)}$$

$$\mathrm{OH} + \mathrm{O} \rightarrow \mathrm{O_2} + \mathrm{H} \quad \text{(R6)}$$

$$\mathrm{HO_2} + \mathrm{O} \rightarrow \mathrm{O_2} + \mathrm{OH} \quad \text{(R7)}$$

$$\mathrm{HO_2} + \mathrm{O_3} \rightarrow 2\mathrm{O_2} + \mathrm{OH} \quad \text{(R8)}$$

$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2} + \mathrm{O_2} \quad \text{(R9)}$$

$$\mathrm{NO_2} + \mathrm{O} \rightarrow \mathrm{NO} + \mathrm{O_2} \quad \text{(R10)}$$

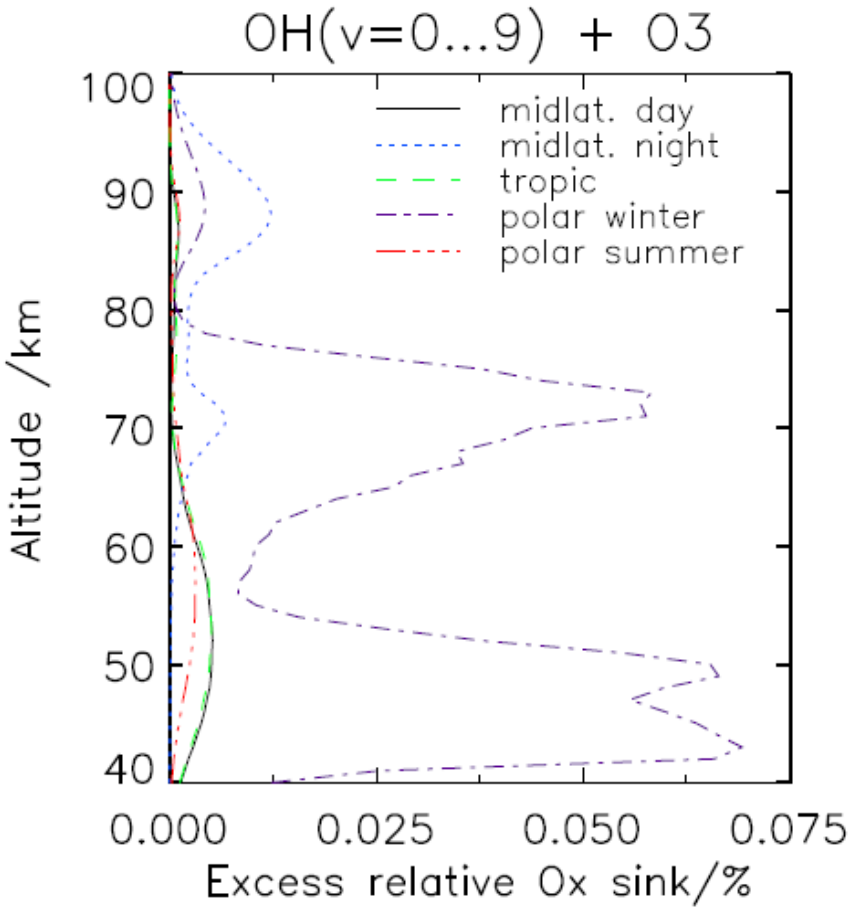
$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2} \quad \text{(R11)}$$

$$\mathrm{ClO} + \mathrm{O} \rightarrow \mathrm{Cl} + \mathrm{O_2} \quad \text{(R12)}$$

$$\mathrm{H_2O_2} + \mathrm{O} \rightarrow \mathrm{OH} + \mathrm{HO_2} \quad \text{(R13)}$$

$$\mathrm{NO_2} + \mathrm{O_3} \rightarrow \mathrm{NO_3} + \mathrm{O_2} \quad \text{(R14)}$$

Excess relative Ox sink strength



How important is this? Comparison with competing reactions

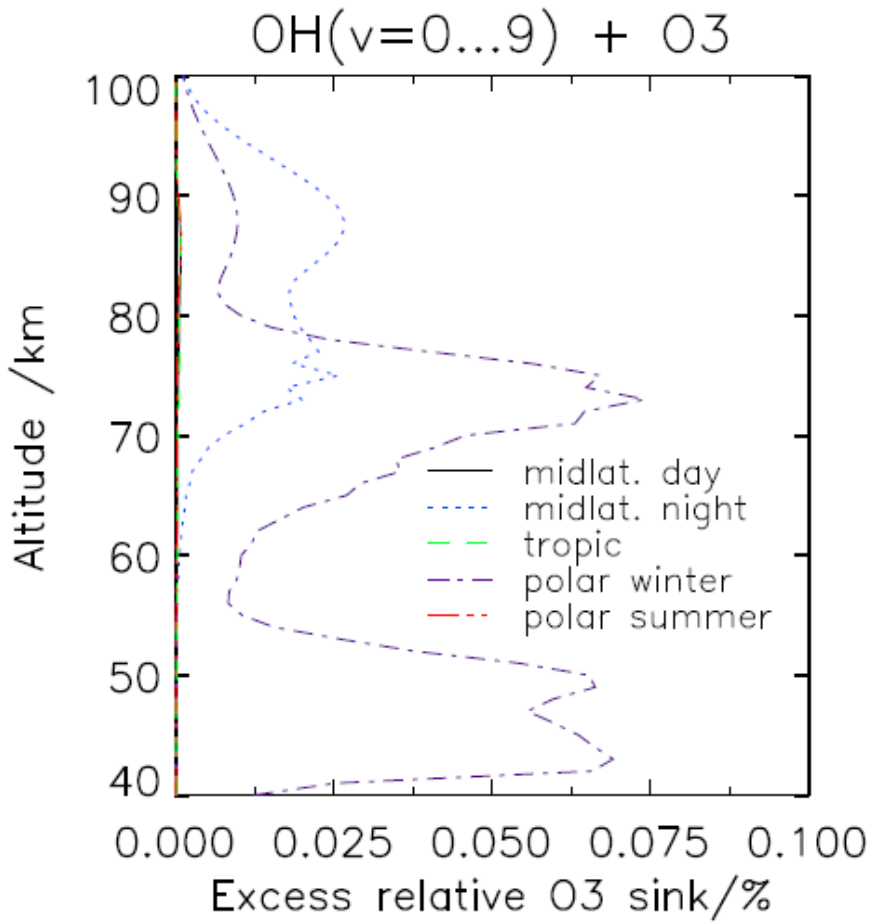
O_3 loss: R1-4, R8-9, R11, R14, and additionally:

$$\mathrm{O_3} + h\nu \rightarrow \mathrm{O_2}(^3\Sigma_g^-) + O(^3P) \qquad \text{(R15)}$$

and

$$\mathrm{O_3} + h\nu \rightarrow \mathrm{O_2}(^1\Delta_g) + O(^1D), \qquad \text{(R16)}$$

Excess O_3 sink strength



How important is this? Comparison with competing reactions

OH loss:

$$\mathrm{OH}(v = 0...9) + \mathrm{O_3} \rightarrow \mathrm{O_2} + \mathrm{HO_2} \quad \text{(R1)}$$

$$\mathrm{OH} + \mathrm{O} \rightarrow \mathrm{O_2} + \mathrm{H} \quad \text{(R6)}$$

$$\mathrm{OH} + \mathrm{CO} \rightarrow \mathrm{CO_2} + \mathrm{H}, \quad \text{(R17)}$$

$$\mathrm{OH} + \mathrm{OH} + \mathrm{M} \rightarrow \mathrm{H_2O_2} + \mathrm{M}, \quad \text{(R18)}$$

$$\mathrm{OH} + \mathrm{HO_2} \rightarrow \mathrm{H_2O} + \mathrm{O_2}, \quad \text{(R19)}$$

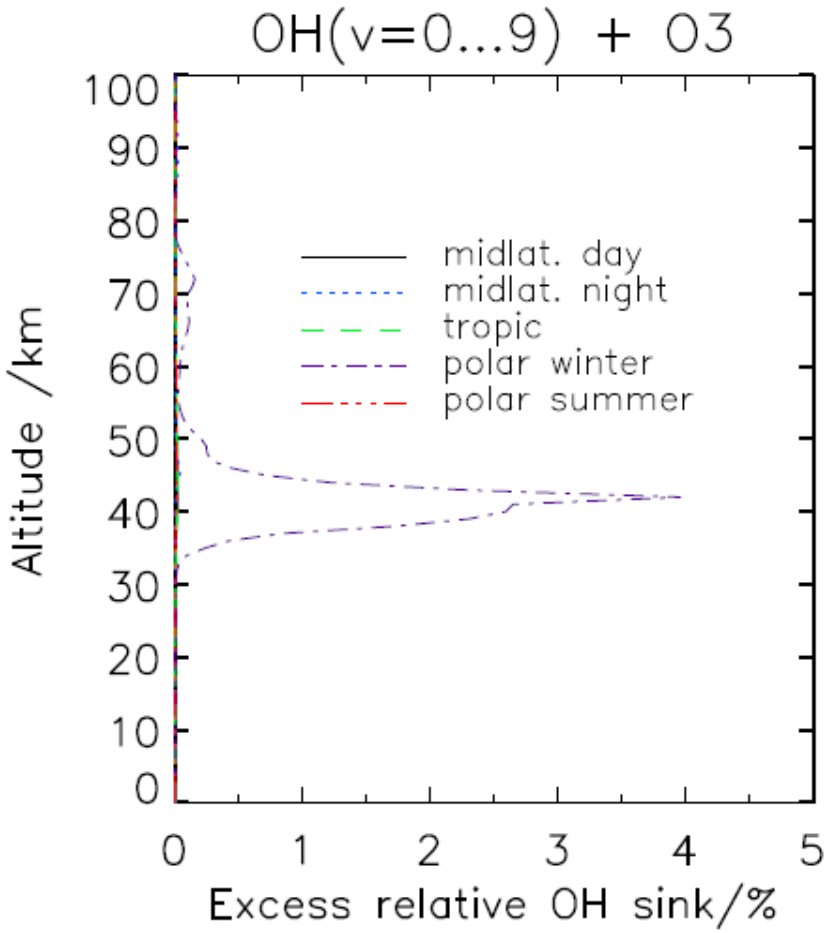
$$\mathrm{OH} + \mathrm{H_2} \rightarrow \mathrm{H_2O} + \mathrm{H}, \quad \text{(R20)}$$

$$\mathrm{OH} + \mathrm{H_2O_2} \rightarrow \mathrm{H_2O} + \mathrm{HO_2}, \quad \text{(R21)}$$

and

$$\mathrm{OH} + \mathrm{OH} \rightarrow \mathrm{H_2O} + \mathrm{O}. \quad \text{(R22)}$$

Excess OH sink strength



Is this important?
Comparison with competing reactions

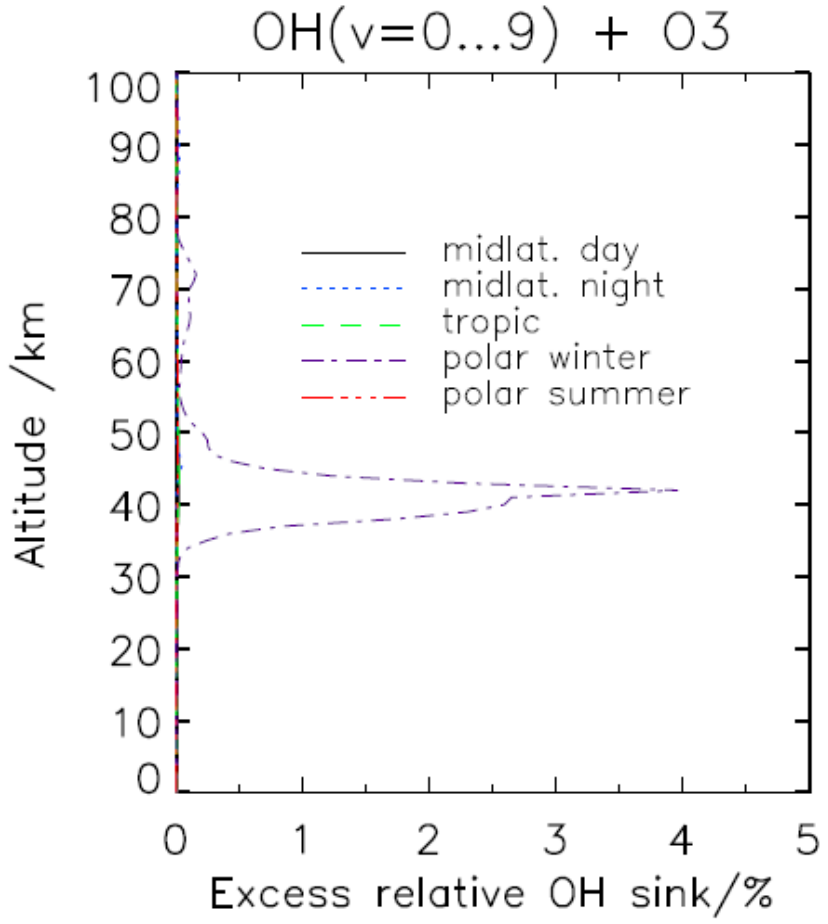
HO_2 sources

$$H_2O_2 + O \rightarrow OH + HO_2 \qquad \text{(R13)}$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2, \qquad \text{(R21)}$$

$$H + O_2 + M \rightarrow HO_2 + M, \qquad \text{(R25)}$$

Excess HO_2 source strength



Caveat:

$$OH(v=0\ldots9) + O_3 \rightarrow O_2 + HO_2$$

- Resulting HO_2 is predicted to be in a vibrational state beyond its dissociation limit.
- Quantum yields for this reaction path are less than unity.
- Other possible products are:

  $O_2 + H + O_2$

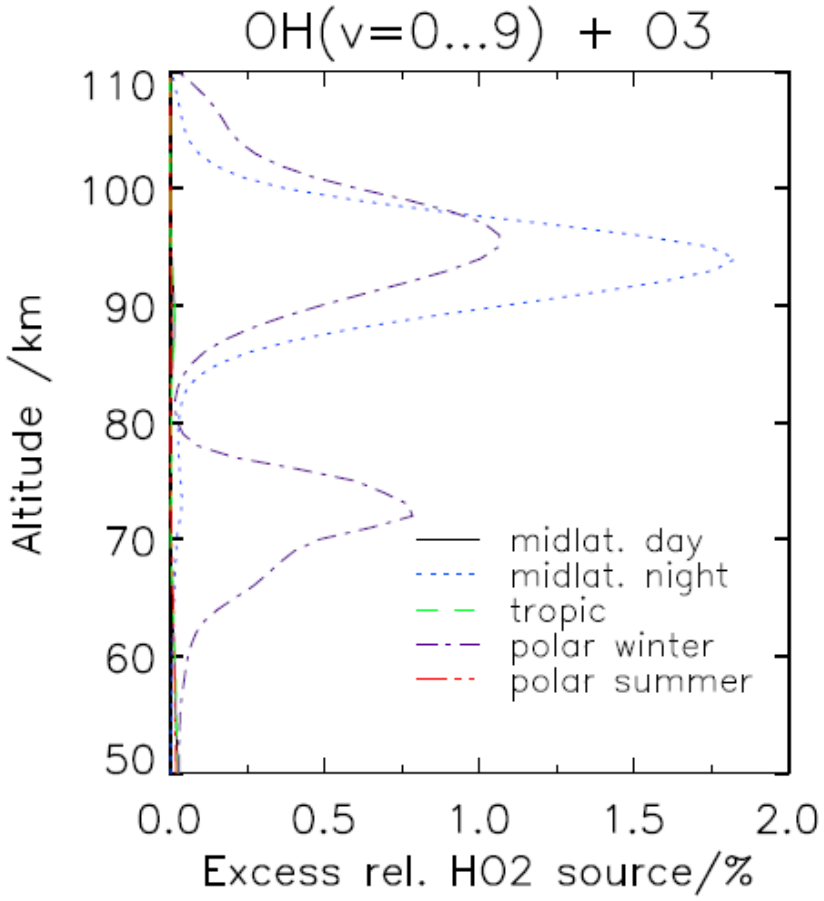
  $O_2 + OH + O$

- Source strength of HO_2 may be overestimated.
- Sink strengths of Ox and OH may be overestimated.
- How does vibrationally excited HO_2 react?

Next reaction:

$$OH(v=0\ldots9) + O \rightarrow O_2 + H$$

k_{eff}


OH(v=0...9) + O3
110
100
90
80
70
60
50
Altitude /km
0.0
0.5
1.0
1.5
2.0
Excess rel. HO2 source/%
midlat. day
midlat. night
tropic
polar winter
polar summer

Conclusion:

☹ Bad news: this research topic won't make me rich and famous, nor will it considerably increase my h-index

Conclusion:

☹Bad news (for me): this research topic won't make me rich and famous, nor will it considerably increase my h-index

☺ Good news (for you): by now there is no evidence that anything is wrong with conventional (Arrhenius-type, LTE) chemistry modelling.

- Caveat: SPE conditions have not yet been investigated.
- Caveat: vibrationally excited NO, O_3, CO, HO_2 etc may also be an issue

Thank you!