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

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Why are we interested?

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

Figure from: [http://chemed.purdue.edu/genchem/topicreview/bp/ch22/activate.html](http://chemed.purdue.edu/genchem/topicreview/bp/ch22/activate.html)
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:

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- Reaction should be relevant to ozone chemistry.

Selected reactions for this study:

\[
\begin{align*}
\text{OH}(v=0\ldots9) + \text{O}_3 & \rightarrow \text{O}_2 + \text{HO}_2 \\
\text{OH}(v=0\ldots9) + \text{O} & \rightarrow \text{O}_2 + \text{H}
\end{align*}
\]
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 vibrational levels 1 to 9.
Effective rate coefficient:

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

\[ k_{\text{eff}} = \frac{1}{[\text{OH}(v = 0...9)]} \sum_{v=0}^{9} k_v[\text{OH}(v)]. \]
How large is $k_{eff}$?
How important is this?  
Comparison with competing reactions

Ox loss:

\[ \text{OH}(v = 0...9) + \text{O}_3 \rightarrow \text{O}_2 + \text{HO}_2 \]  
(R1)

\[ \text{O}_3 + \text{O}^3\text{P} \rightarrow 2\text{O}_2 \]  
(R3)

\[ \text{O}_3 + \text{O}^1\text{D} + \text{M} \rightarrow 2\text{O}_2 + \text{M} \]  
(R4)

\[ \text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M} \]  
(R5)

\[ \text{H} + \text{O}_3 \rightarrow \text{O}_2 + \text{OH}(v = 1...9) \]  
(R2)

\[ \text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H} \]  
(R6)

\[ \text{HO}_2 + \text{O} \rightarrow \text{O}_2 + \text{OH} \]  
(R7)

\[ \text{HO}_2 + \text{O}_3 \rightarrow 2\text{O}_2 + \text{OH} \]  
(R8)

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  
(R9)

\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \]  
(R10)

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]  
(R11)

\[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \]  
(R12)

\[ \text{H}_2\text{O}_2 + \text{O} \rightarrow \text{OH} + \text{HO}_2 \]  
(R13)

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]  
(R14)
Excess relative Ox sink strength

\[ \text{OH}(v=0\ldots9) + \text{O}_3 \]

- midlat. day
- midlat. night
- tropic
- polar winter
- polar summer

Altitude / km

Excess relative Ox sink / %
How important is this?
Comparison with competing reactions

O$_3$ loss: R1-4, R8-9, R11, R14, and additionally:

\[ O_3 + h\nu \rightarrow O_2 (^3\Sigma_g^-) + O (^3P) \] (R15)

and

\[ O_3 + h\nu \rightarrow O_2 (^1\Delta_g) + O (^1D), \] (R16)
Excess O$_3$ sink strength

OH$(v=0...9) +$ O$_3$

Altitude /km

Excess relative O$_3$ sink/%
How important is this?  
Comparison with competing reactions

**OH loss:**

\[ \text{OH}(v = 0...9) + O_3 \rightarrow O_2 + HO_2 \]  \hspace{1cm} \text{(R1)}

\[ \text{OH} + O \rightarrow O_2 + H \]  \hspace{1cm} \text{(R6)}

\[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + H, \]  \hspace{1cm} \text{(R17)}

\[ \text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}, \]  \hspace{1cm} \text{(R18)}

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2, \]  \hspace{1cm} \text{(R19)}

\[ \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + H, \]  \hspace{1cm} \text{(R20)}

\[ \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2, \]  \hspace{1cm} \text{(R21)}

and

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}. \]  \hspace{1cm} \text{(R22)}
Excess OH sink strength

OH($v=0...9$) + O$_3$

Altitude /km

Excess relative OH sink/%

midlat. day
midlat. night
tropic
polar winter
polar summer
Is this important?
Comparison with competing reactions

HO₂ sources

\[
\begin{align*}
H₂O₂ + O & \rightarrow OH + HO₂ \quad \text{(R13)} \\
OH + H₂O₂ & \rightarrow H₂O + HO₂, \quad \text{(R21)} \\
H + O₂ + M & \rightarrow HO₂ + M, \quad \text{(R25)}
\end{align*}
\]
Excess HO$_2$ source strength

OH($v=0...9$) + O$_3$

Altitude / km

Excess relative OH sink/%

midlat. day
midlat. night
tropic
polar winter
polar summer
Caveat:

\[ \text{OH}(v=0\ldots9) + \text{O}_3 \rightarrow \text{O}_2 + \text{HO}_2 \]

- Resulting \( \text{HO}_2 \) 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:
  - \( \text{O}_2 + \text{H} + \text{O}_2 \)
  - \( \text{O}_2 + \text{OH} + \text{O} \)
- Source strength of \( \text{HO}_2 \) may be overestimated.
- Sink strengths of \( \text{Ox} \) and \( \text{OH} \) may be overestimated.
- How does vibrationally excited \( \text{HO}_2 \) react?
Next reaction:

\[ \text{OH}(v=0\ldots9) + \text{O} \rightarrow \text{O}_2 + \text{H} \]
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, O₃, CO, HO₂ etc may also be an issue
Thank you!