Acetonylperoxy/Hydroperoxy Self and Cross Reaction Rate Constants Via Infrared Kinetic Spectroscopy

Discovery of Acetone•Hydroperoxy Adduct Chaperone Effect

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(All work carried out at JPL and funded by NASA)

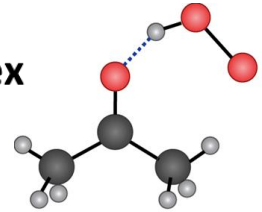
Importance: Rate parameters of volatile organic compounds' reactions with HO_2 for atmospheric HO_2/OH budget & subsequent product reactions

Upper troposphere → need T-dependence !

Our case: HO_2 with acetone and acetonylperoxy radical

3 major rxns:

H-Bonded Complex



k_1 $2\ HO_2 \rightarrow H_2O_2 + O_2$ Self

$k'[CH_3OH]$ $HO_2 + CH_3OH \bullet HO_2 \rightarrow H_2O_2 + O_2 + CH_3OH$ Chaperone

$k''[(CH_3)_2CO]$ $HO_2 + (CH_3)_2CO \bullet HO_2 \rightarrow H_2O_2 + O_2 + (CH_3)_2CO$ Chaperone

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$k_{HO_2AO_2}$ $HO_2 + CH_3C(O)CH_2OO \rightarrow CH_3C(O)OOH + O_2$ Cross

$\rightarrow CH_3C(O)CH_2O + O_2 + OH$

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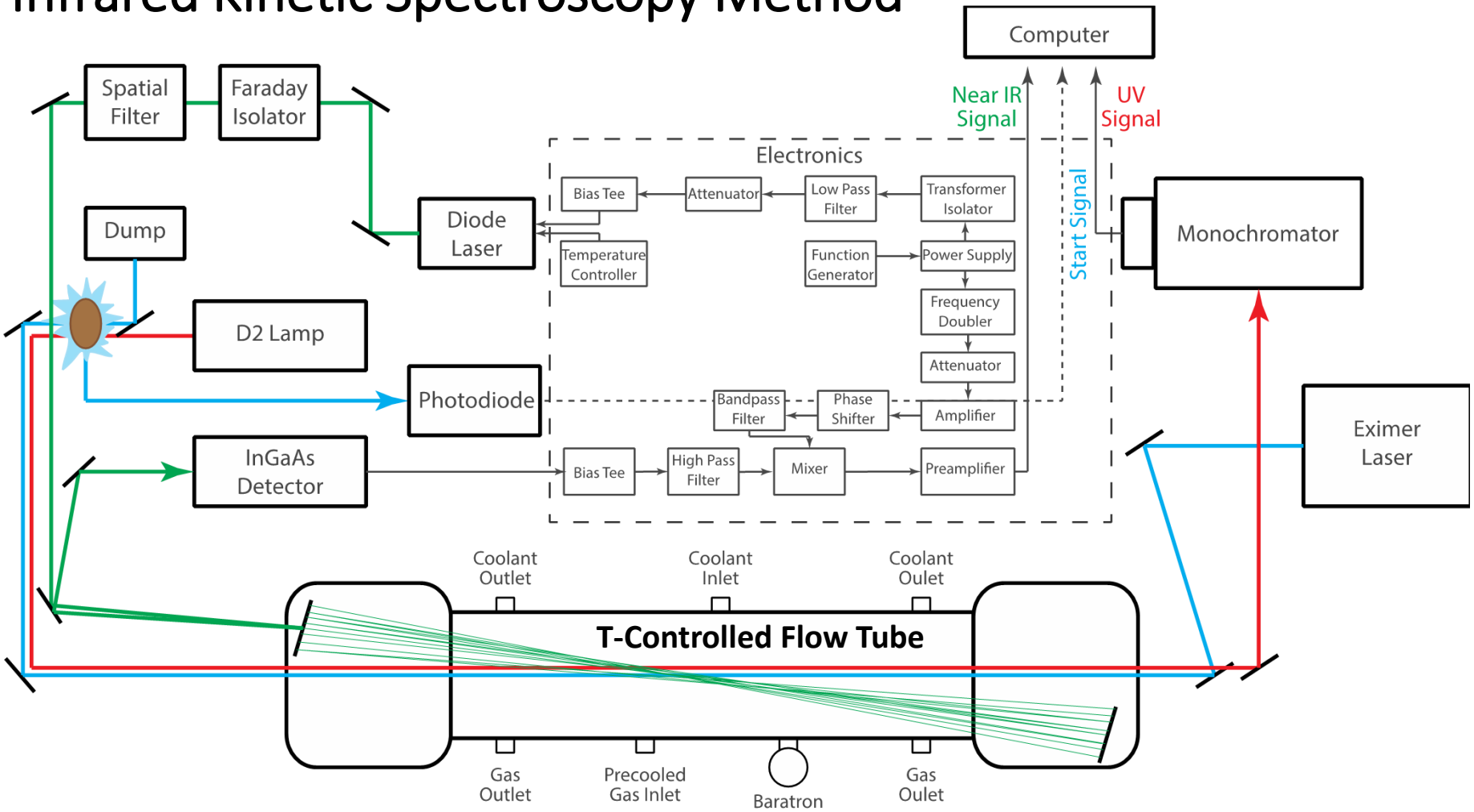
k_{AO_2self} $2\ CH_3C(O)CH_2OO \rightarrow 2CH_3C(O)OO + 2CH_2O$ Self

$\rightarrow CH_3C(O)CHO + CH_3C(O)CH_2OH$

We previously measured k_{AO_2self} = (5.2 ± .25) E-12 cm^3 $molecule^{-1}$ s^{-1}

Overall reaction kinetics scheme > 30 rxns (Full Model)

Infrared Kinetic Spectroscopy Method



Laser flash photolysis (351 nm)

$Cl_2/CH_3OH/O_2 \rightarrow HO_2$

$Cl_2/(CH_3)_2CO/O_2 \rightarrow CH_3C(O)CH_2OO$

(All experiments at 100 Torr)

IR diode laser

λ modulation

Herriot cell

→ good S/N

IR/UV combination

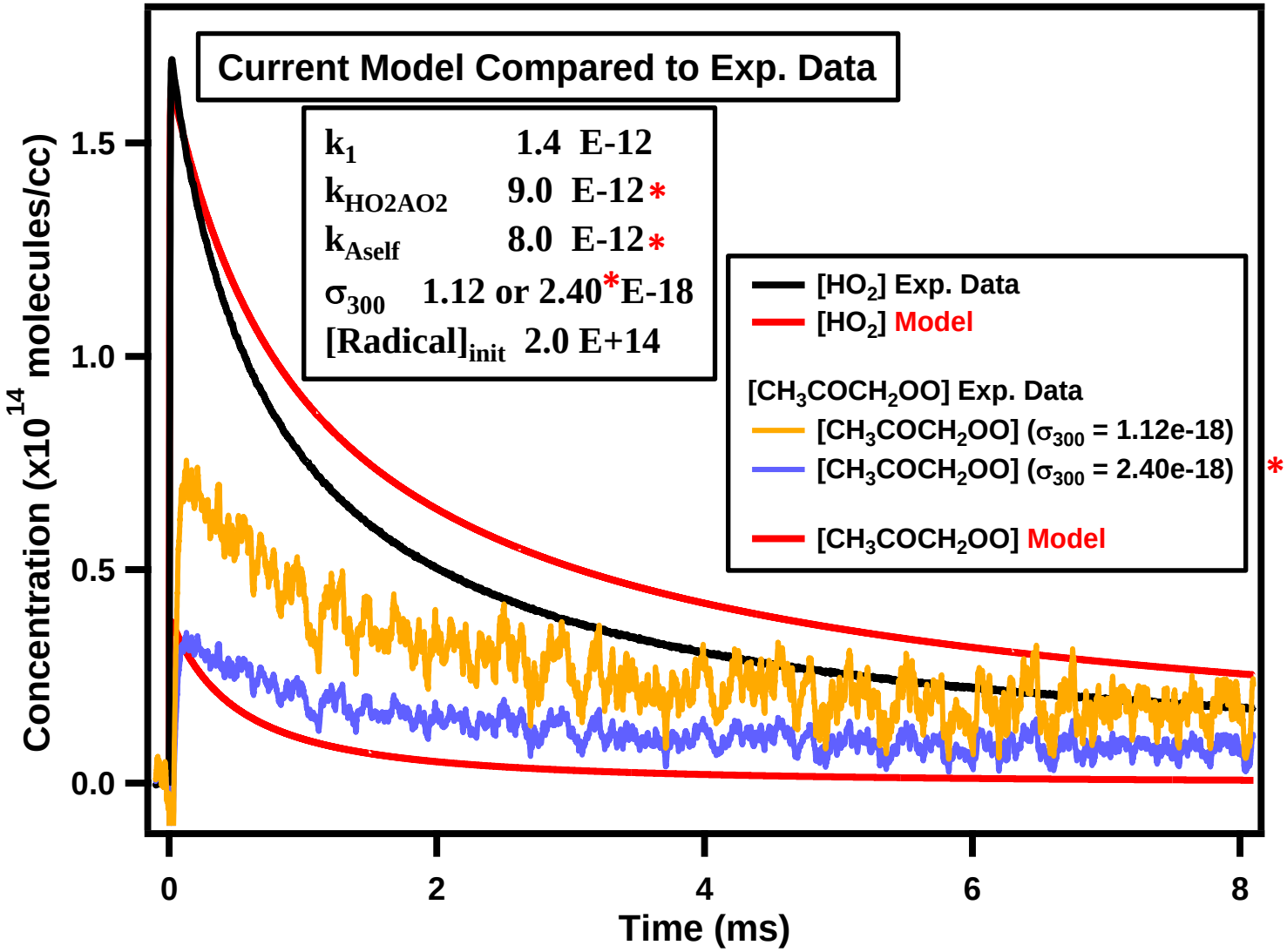
→ $[HO_2]$

→ Initial [Radical]

→ $[CH_3C(O)CH_2OO]$

(isolated UV band at 300 nm)

Model w/ Recommended Values Doesn't Fit Our Data



*Bridier, I., Veyret, B., Lesclaux, R., Jenkin, M. *J. Chem. Soc. Faraday Trans.* **1993**, 89, 2993.

J. B. Burkholder, S. P. Sander, J. Abbatt, J. R. Barker, R. E. Huie, C. E. Kolb, M. J. Kurylo, V. L. Orkin, D. M. Wilmouth, and P. H. Wine Evaluation No. 18, JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, 2015 http://jpldataeval.jpl.nasa.gov.

Acetonylperoxy/Hydroperoxy Rate Constant

Primary reactions: 1) HO_2 self reaction with chaperone effect

$$2\ HO_2 \rightarrow H_2O_2 + O_2$$
$$HO_2 + CH_3OH{\bullet}HO_2 \rightarrow H_2O_2 + O_2 + CH_3OH$$
$$HO_2 + (CH_3)_2CO{\bullet}HO_2 \rightarrow H_2O_2 + O_2 + (CH_3)_2CO$$

$$k_{1obs} = k_1 + k'[CH_3OH] + k''[(CH_3)_2CO] = k^M + k''[(CH_3)_2CO]$$

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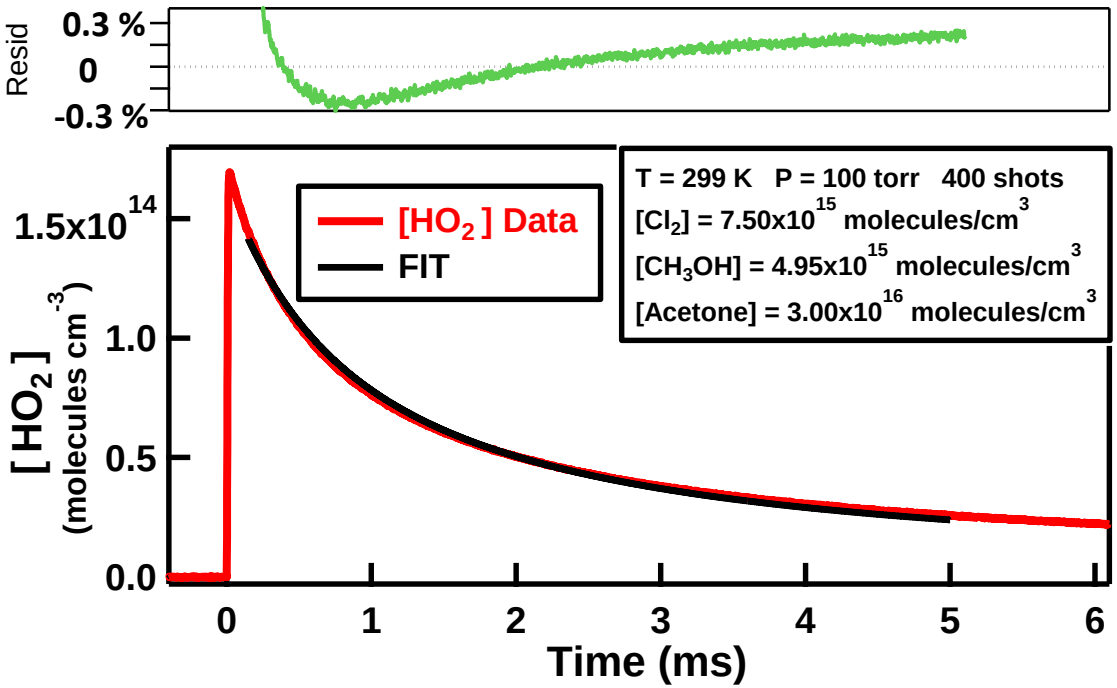
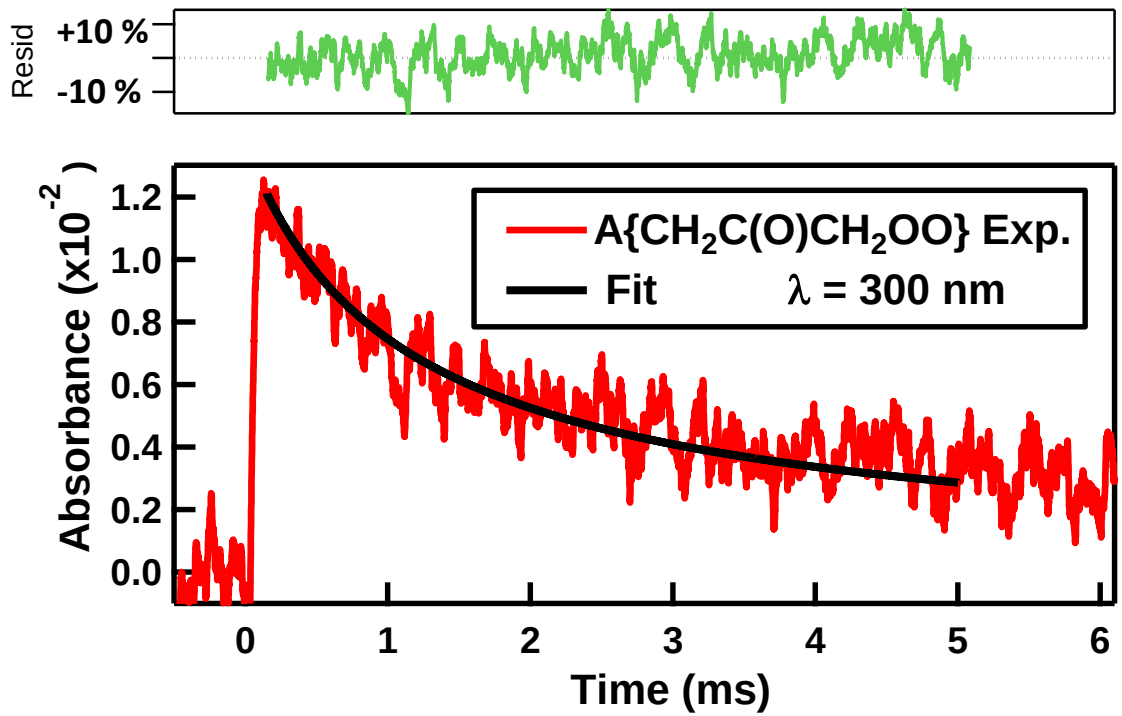
2) $HO_2/CH_3C(O)CH_2OO$ cross reaction

$$HO_2 + CH_3C(O)CH_2OO \xrightarrow{k_{HO_2AO_2}} CH_3C(O)OOH + O_2$$
$$\rightarrow CH_3C(O)CH_2O + O_2 + OH$$

- Simultaneously measure & fit HO_2 IR & $CH_3C(O)CH_2OO$ UV signals
- Vary $[CH_3OH]$ & $[(CH_3)_2CO]$ to vary $[HO_2]$ & $[CH_3C(O)CH_2OO]$ & to test chaperone effect
- Use full model kinetics with our k_{AO_2self} in FACSIMILE fits (5 msec)
- Determine k_{1obs}, $k_{HO_2AO_2}$, σ_{300}, $[Radical]_{initial}$

$CH_3C(O)CH_2OO/HO_2$ typical full model fits

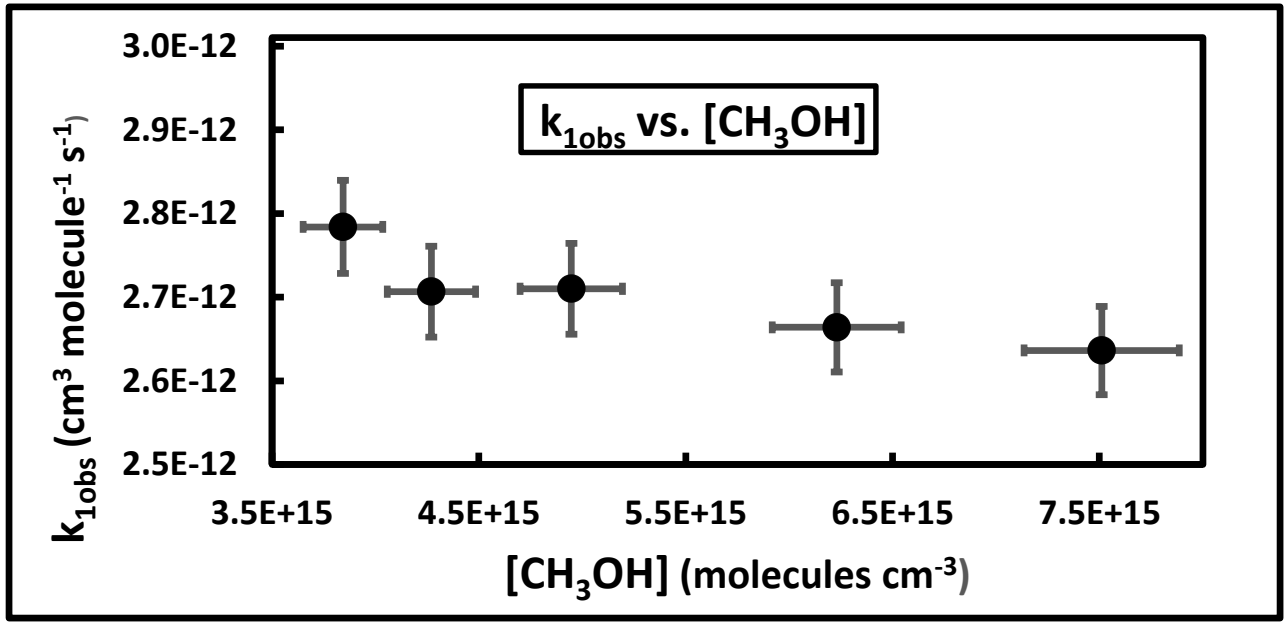




	Value	uncrtnty
k_{1obs}	2.71E-12	0.28%
k_{HO2AO2}	3.27E-12	1.77%
σ_{300}	2.44E-18	0.64%
$[Radical]_{init}$	2.00E+14	0.16%

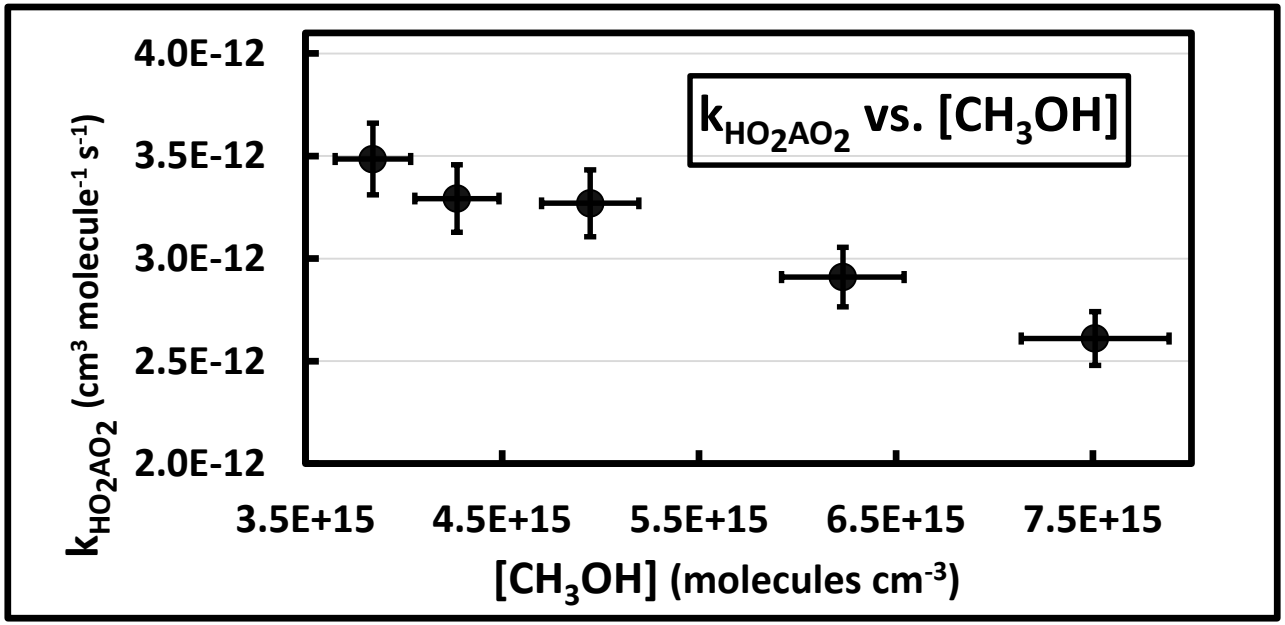
acetonylperoxy/HO_2 Results Vary [CH_3OH]

[$(CH_3)_2CO$] = 3.0E16 constant



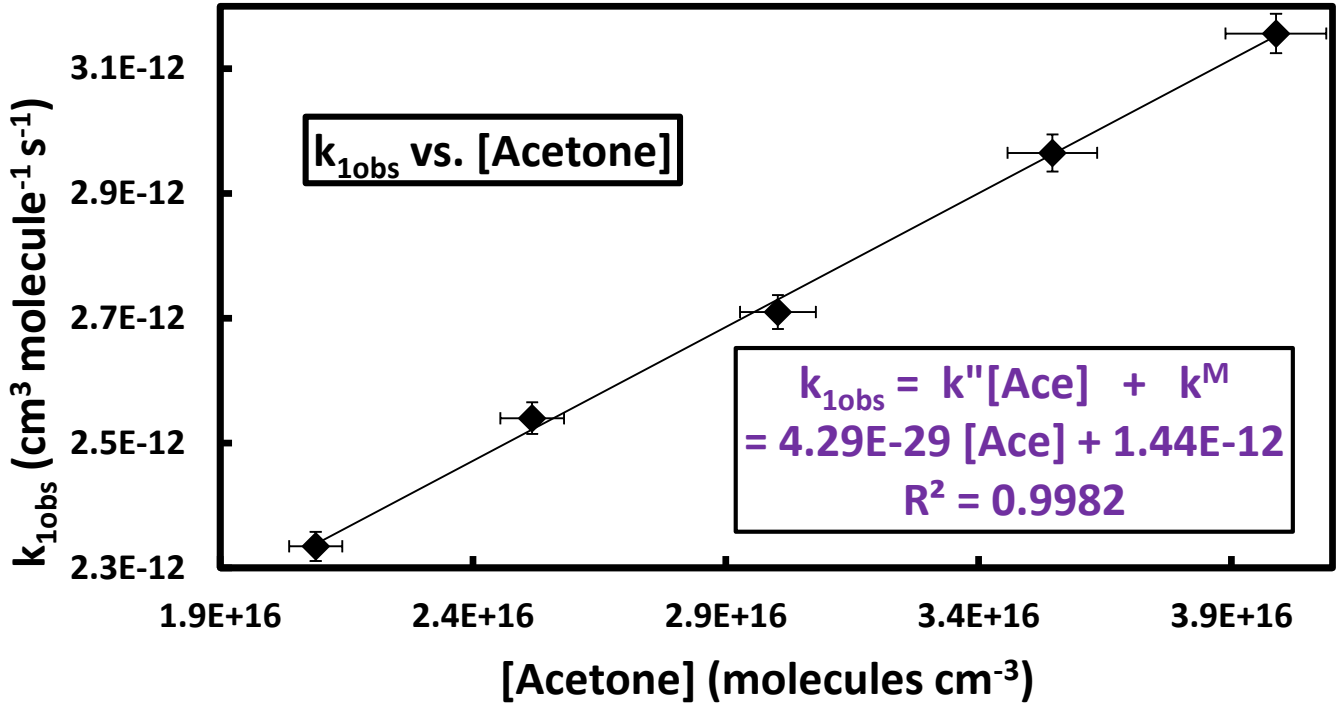
k_{1obs} = (2.70 ± 0.06)E-12 cm^3 $molecule^{-1}$ s^{-1}

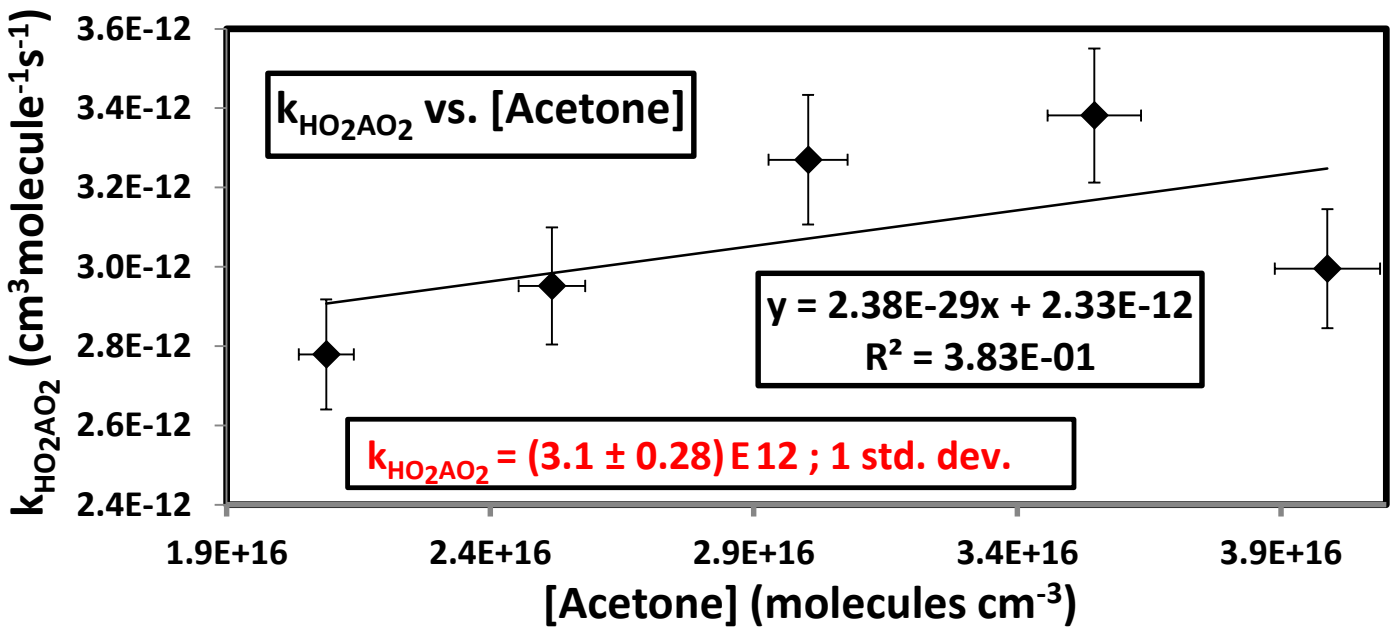
$k_{HO_2AO_2}$ = (3.11 ± 0.35)E-12 cm^3 $molecule^{-1}$ s^{-1}



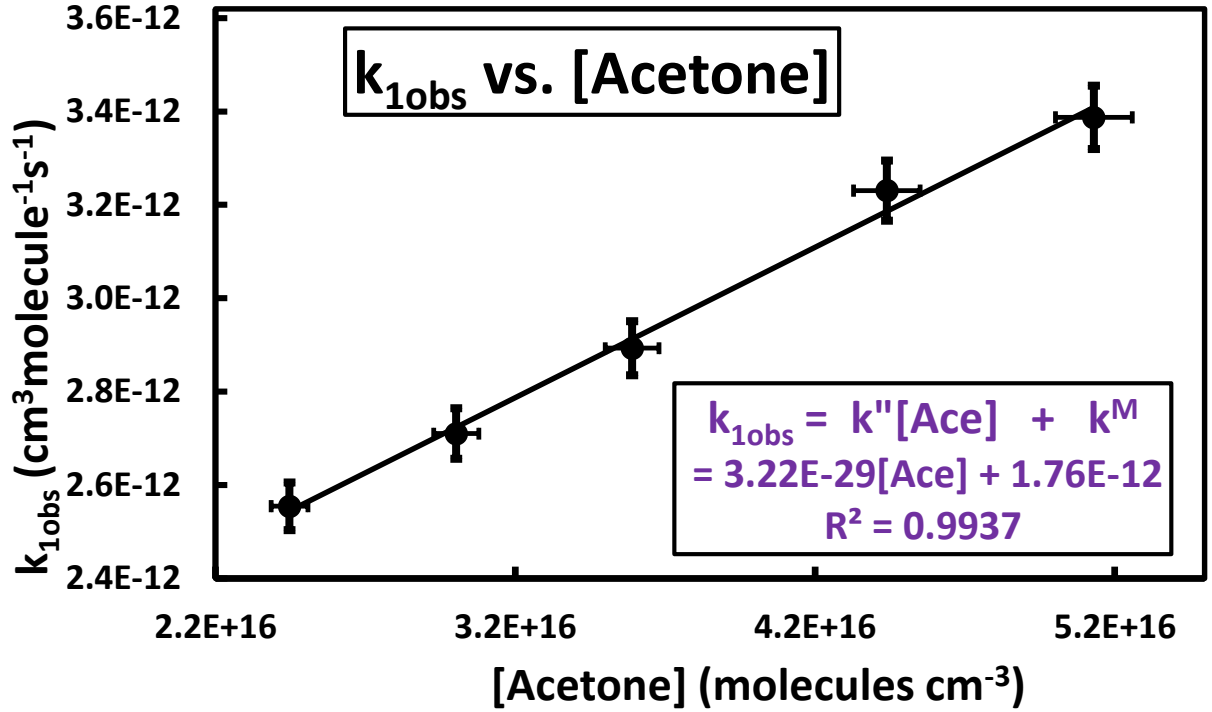
Vary $[(CH_3)_2CO]$

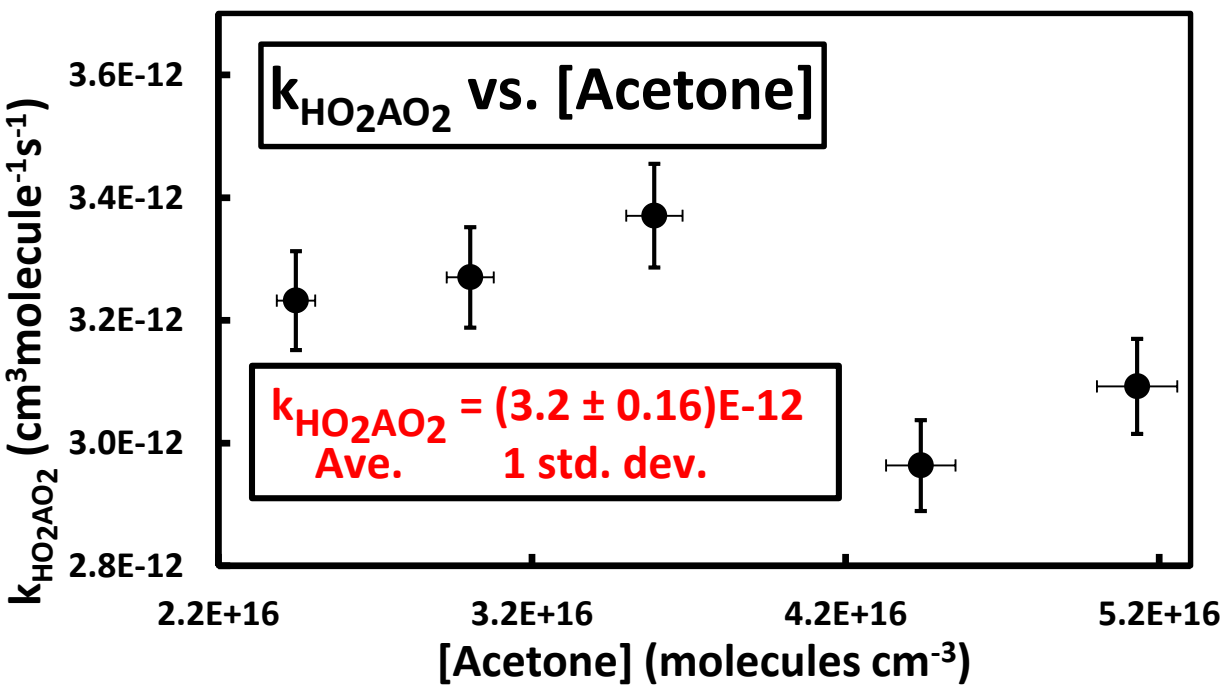
$[CH_3OH] = 3.0E15$ constant





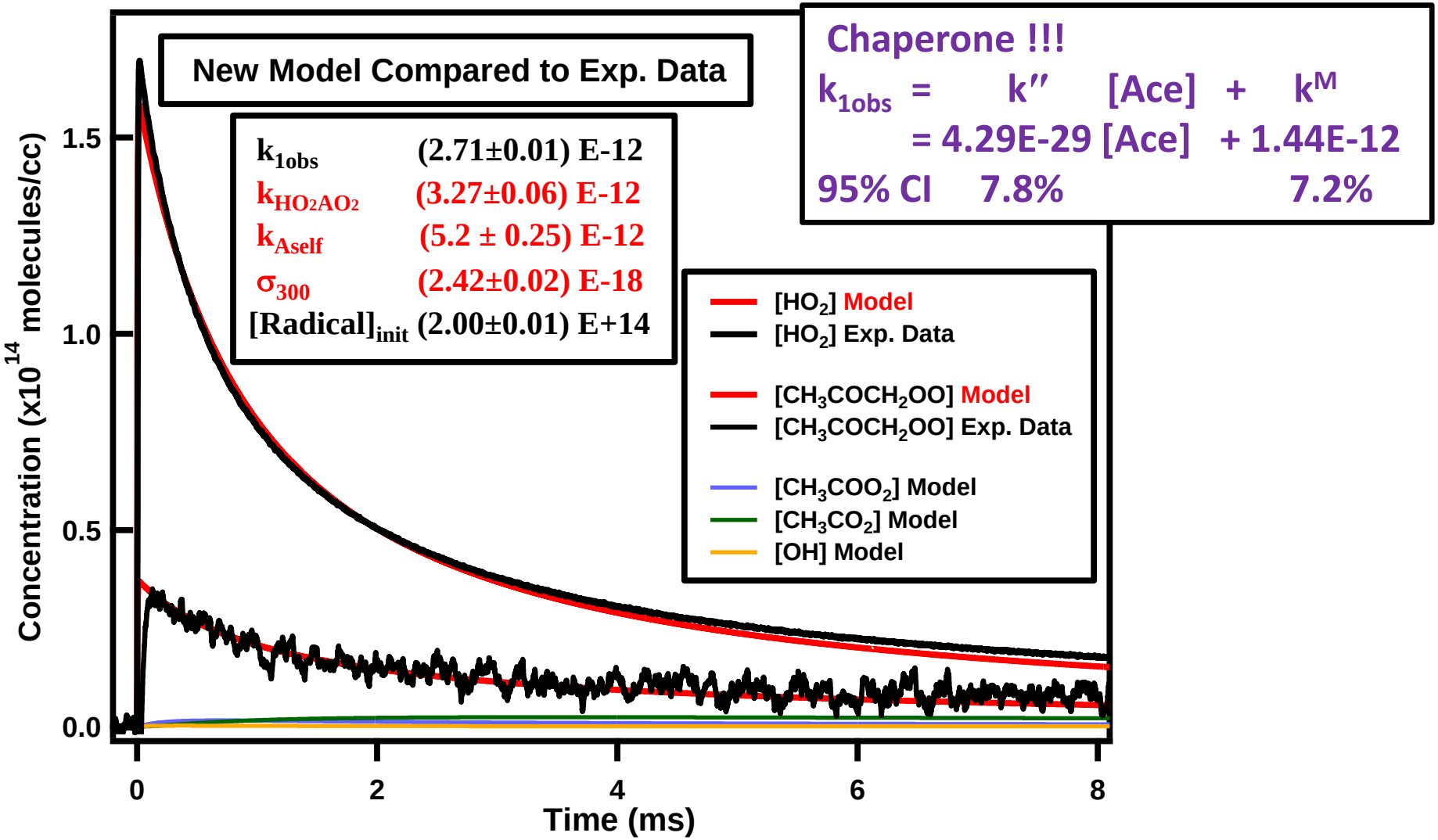
Vary both
$[(CH_3)_2CO]$ & $[CH_3OH]$
at constant ratio = 6.0





Results

Parameter	Our Work	Recommended
$k_{HO_2AO_2}$ (cm^3 $molecule^{-1}$ s^{-1})	(3.12 ± 0.21) E-12	(9 ± 1) E-12
k_{AO_2self} (cm^3 $molecule^{-1}$ s^{-1})	(5.2 ± 0.25) E-12	(8 ± 2) E-12
σ_{300} (cm^2)	(2.46 ± 0.08) E-18	(1.12) E-18



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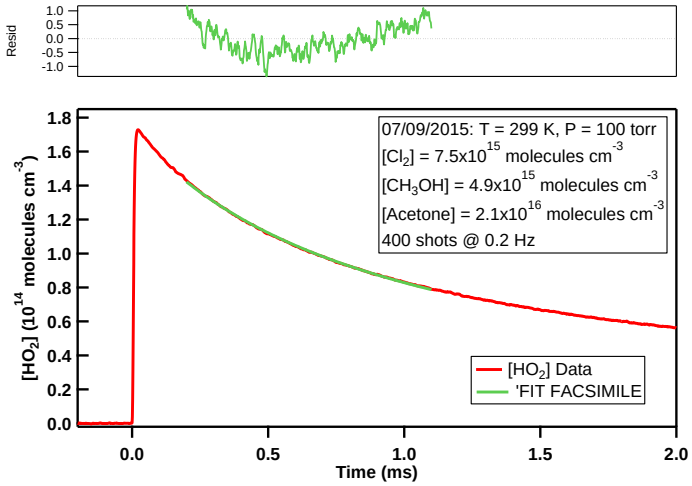
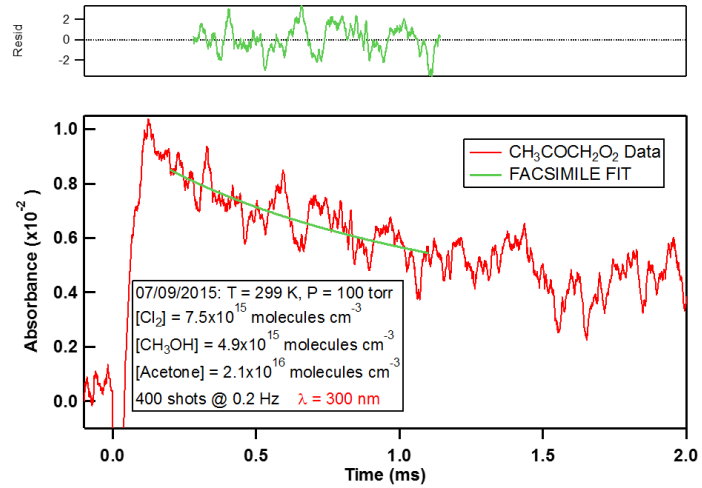
For low T work: k(T) full model unknown

- Fit over short time scale (~ 1 msec) to minimize subsequent product reactions
- Fit to simple reaction scheme (k_1 , $k_{HO_2AO_2}$, k_{AO_2self})

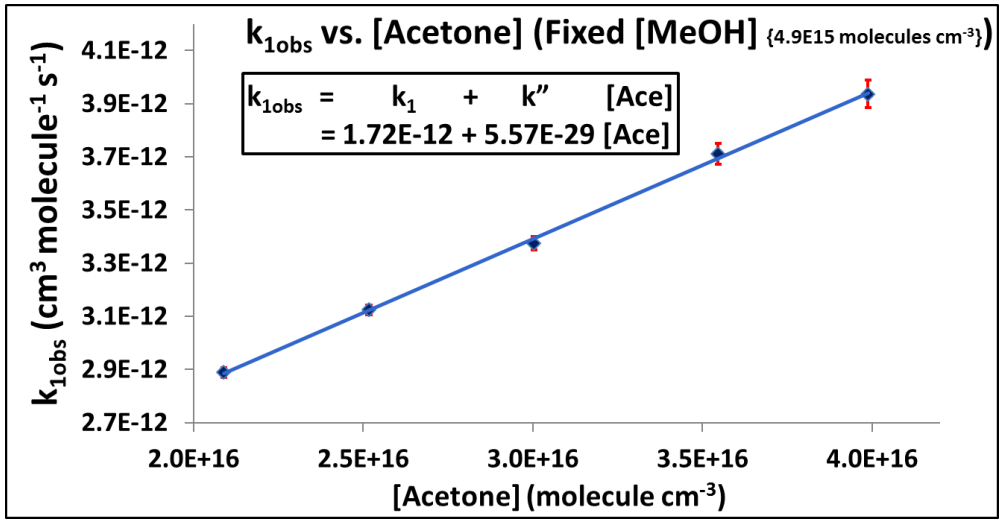




- No dependence of $k_{HO_2AO_2}$ on $[CH_3OH]$ or $[(CH_3)_2CO]$ as before
- Averaged value (all runs):

$k_{HO_2AO_2}$ = (2.8 ± 0.53) E-12 cm^3 $molecule^{-1}$ s^{-1}

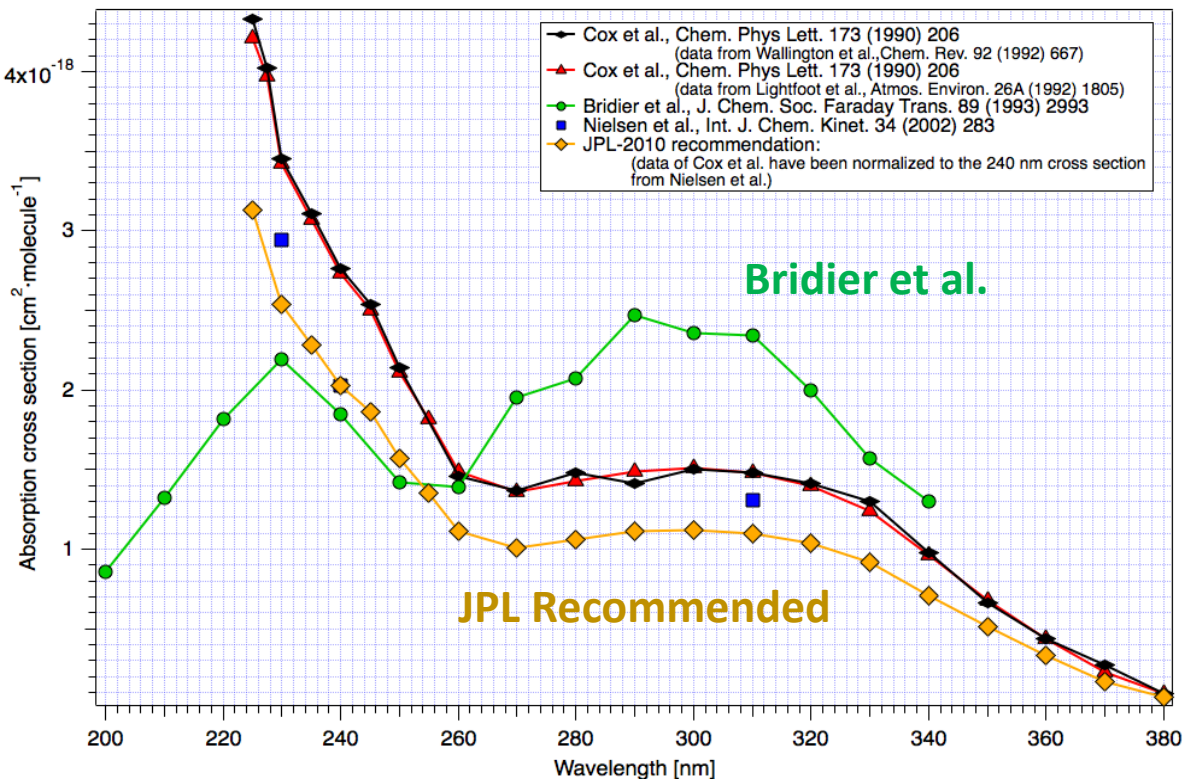
- k_{1obs}? chaperone



1st Acetonylperoxy Self Reaction: Method

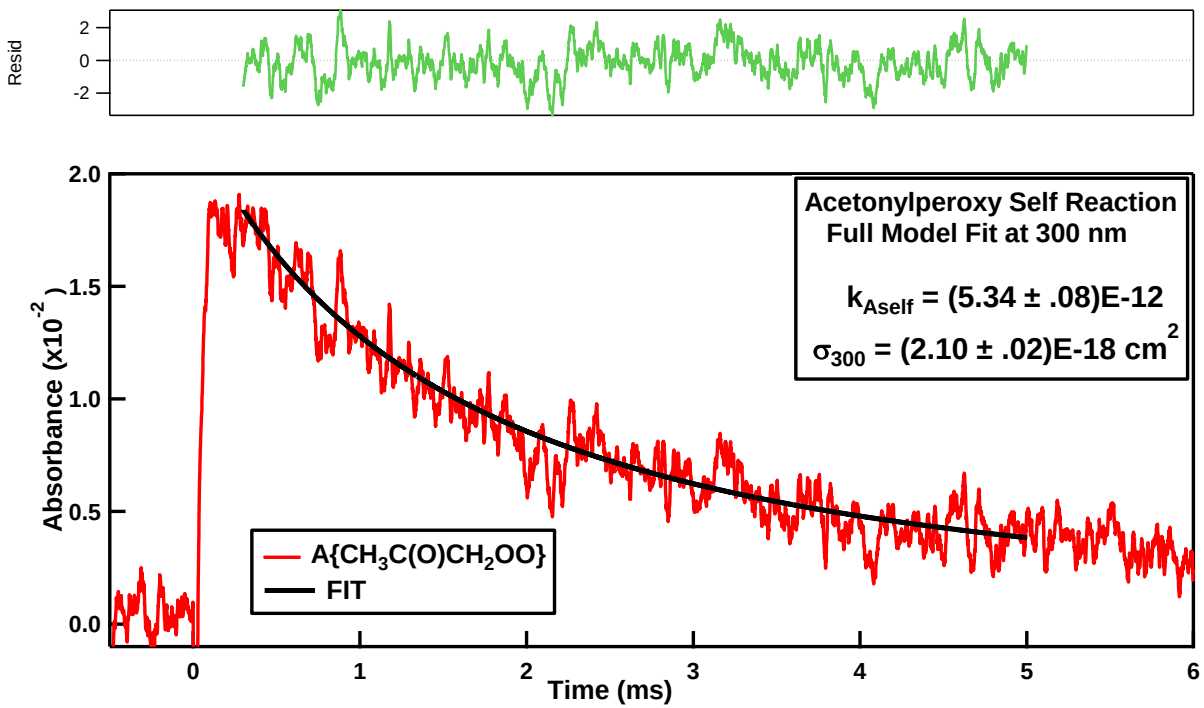
$$2\ CH_3C(O)CH_2OO \xrightarrow{k_{AO_2self}} 2CH_3C(O)OO + 2CH_2O$$
$$\rightarrow CH_3C(O)CHO + CH_3C(O)CH_2OH$$

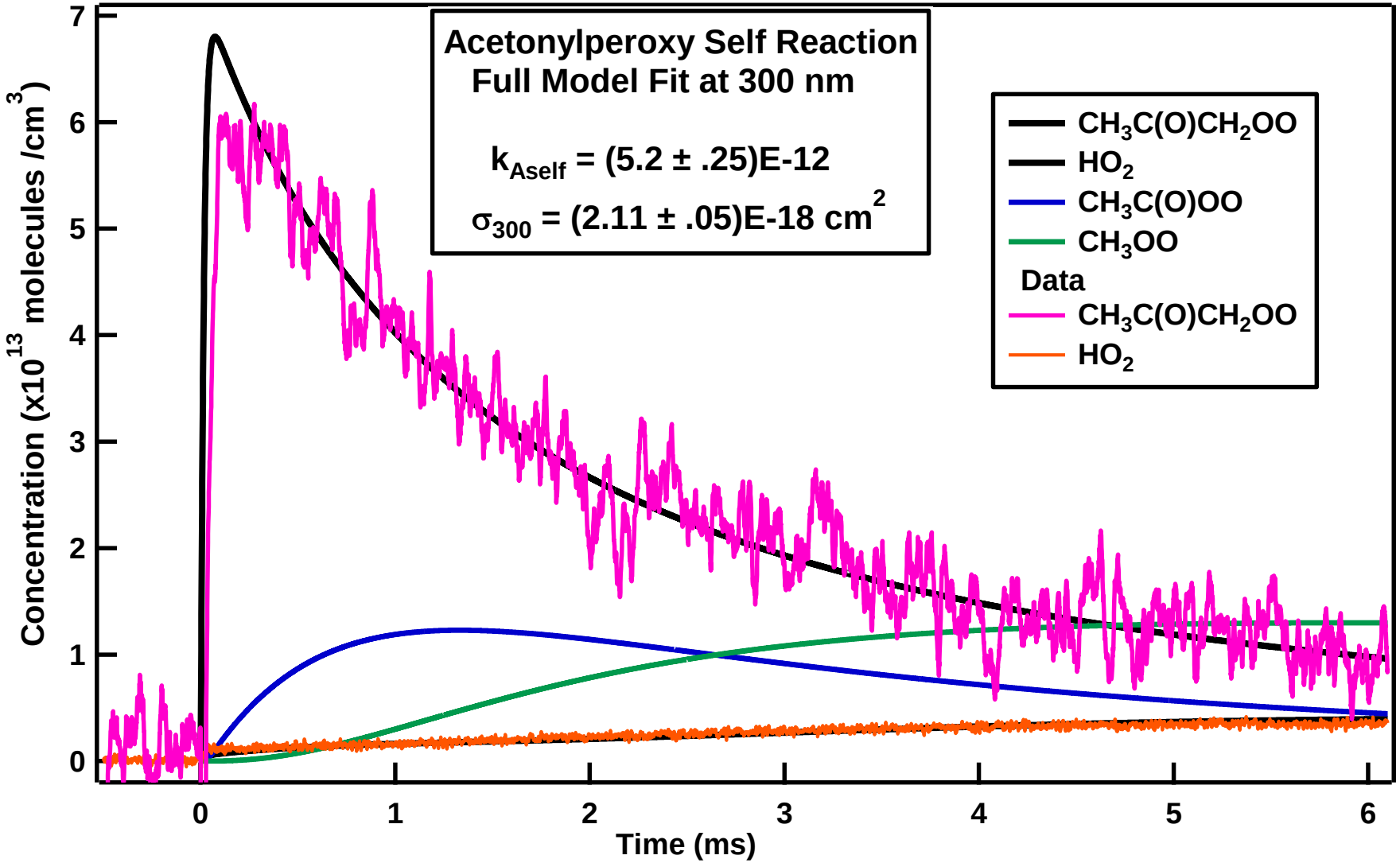
- **Determine [Radical}$_{init}$ (via HO_2) = [$CH_3C(O)CH_2OO$]$_{initial}$**
- **Measure Absorbance of $CH_3C(O)CH_2OO$ at 300 nm**
  ~ isolated band, but uncertain σ_{300}
- **Fit with Full Model at various σ_{300}**



Acetonylperoxy Self Reaction via UV at 300 nm

$[Radical]_{init}$ (molecule/cc)	σ_{300} (cm^2)	Source	k_{Aself} (cm^3 /molecule/s
7.20E+13	–	Our Exp.	–
12.7E+13	1.12E-18	JPL rec.	2.59E-12
6.12E+13	2.36E-18	Bridier et al.	5.83E-12
7.20E+13	2.11E-18	Our Fit	5.20E-12



k_{Aself} = (5.2 ± .25)E-12 cm^3 $molecule^{-1}$ s^{-1}

{k_{Aself} = (8.0 ± 2.0)E-12 cm^3 $molecule^{-1}$ s^{-1} Bridier et al.}