Topic 2

Measurement of rate coefficients for elementary reactions

Measurement of rates of elementary reactions 1

- Concentrate on reactions of atoms and radicals; say something briefly about reactions that don't involve radicals and are involved in initiation steps

- Need to cover a range of T from 1000 to 3000 K for reactions involved in high temperature combustion reactions; 600 – 1000 K for low T oxidation in the autoignition regime; 200 – 300 K for reactions of combustion generated pollutants in the lower atmosphere (the troposphere)

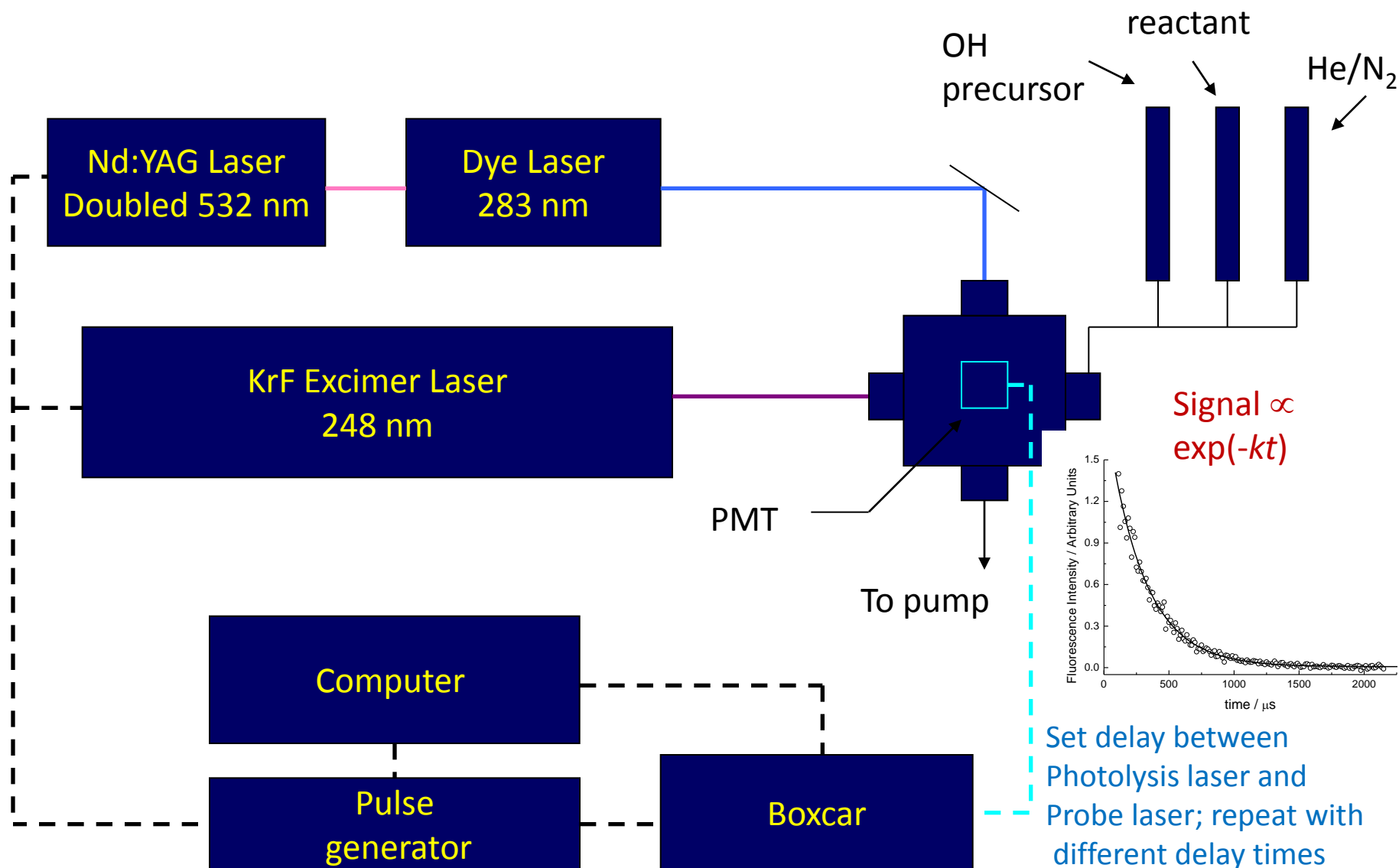# Measurement of rates of elementary reactions 2

- Ideally, isolate the individual reaction and study it at the appropriate combustion conditions.

- Not always possible:

  – May have to model the system to extract rate coefficients of interest

  – May need to extrapolate to appropriate T, p. Ideally achieve this with the help of theory (see Topic 3).
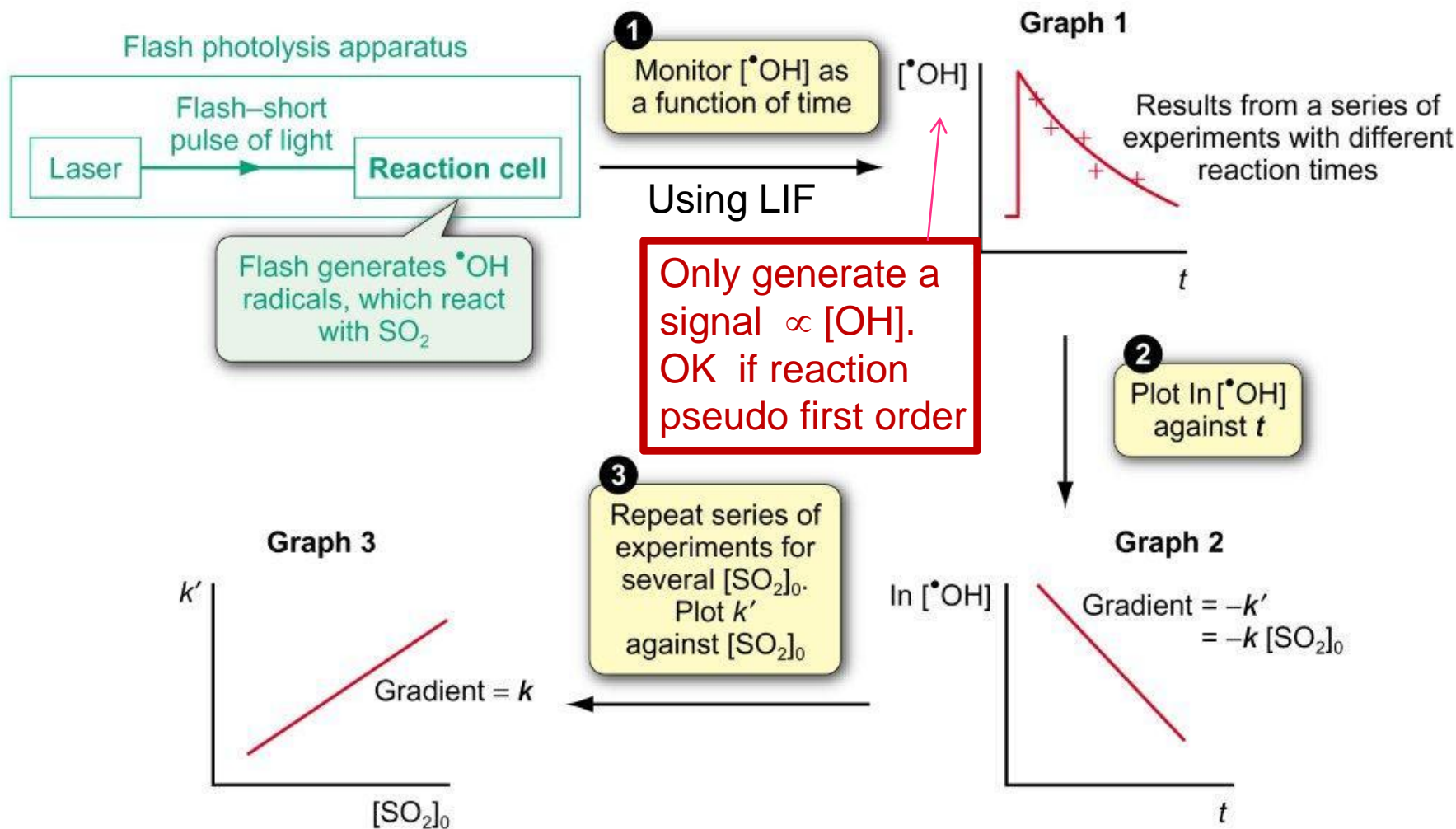
Techniques

- Pulsed laser photolysis (laser flash photolysis)
- Shock tubes
- Flow tubes for elementary reactions and whole systems
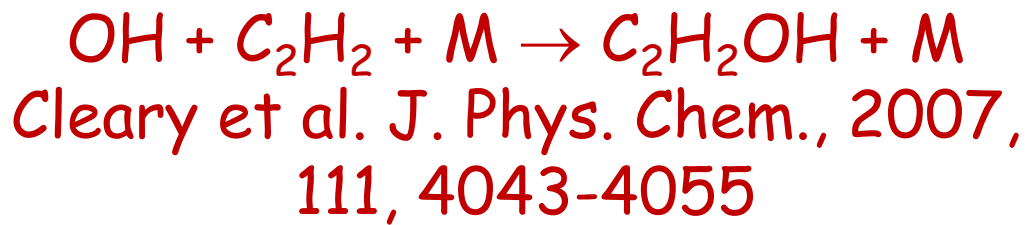- Static studies of whole systems

Pulsed laser photolysis

Laser flash photolysis (LFP) / laser induced fluorescence (LIF) for the study of OH + reactant

OH precursor

reactant

He/N$_2$

Nd:YAG Laser Doubled 532 nm	Dye Laser 283 nm

KrF Excimer Laser 248 nm

Signal $\propto$ exp($-kt$)

PMT

To pump

Computer

Pulse generator

Boxcar

Set delay between Photolysis laser and Probe laser; repeat with different delay times

Procedure for determining rate coefficients for pseudo first order reactions using LFP for OH + SO_2

Flash photolysis apparatus

Flash–short pulse of light

Laser ⟶ **Reaction cell**

Flash generates $^\bullet$OH radicals, which react with SO_2

① Monitor [$^\bullet$OH] as a function of time

Using LIF

Only generate a signal $\propto$ [OH]. OK if reaction pseudo first order

Graph 1

[$^\bullet$OH]

Results from a series of experiments with different reaction times

t

② Plot ln [$^\bullet$OH] against t

③ Repeat series of experiments for several [SO_2]$_0$. Plot k' against [SO_2]$_0$

Graph 3

k'

Gradient = k

[SO_2]$_0$

Graph 2

ln [$^\bullet$OH]

Gradient = $-k'$ = $-k$ [SO_2]$_0$

t

OH + C$_2$H$_2$ + M $\rightarrow$ C$_2$H$_2$OH + M
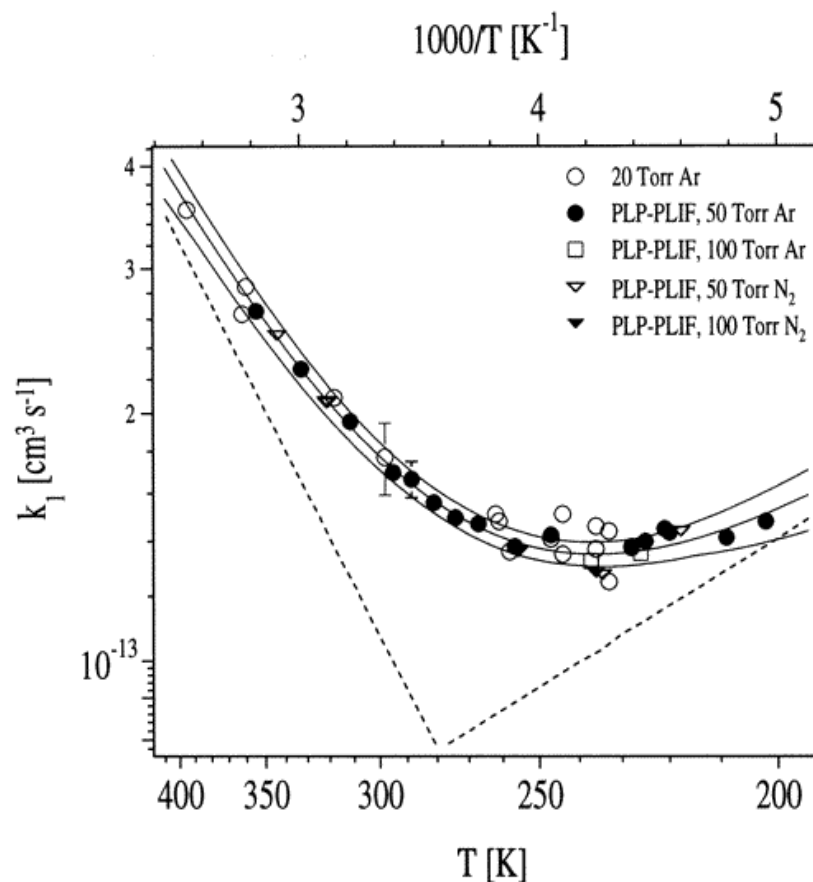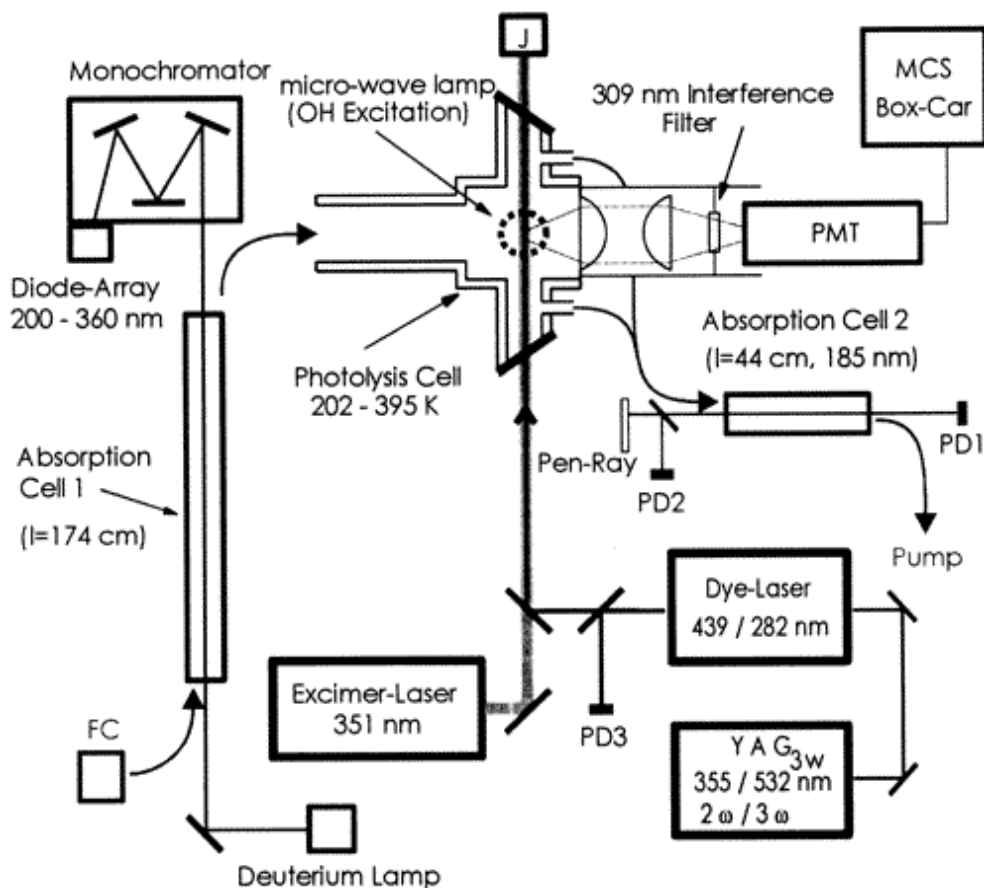## Cleary et al. J. Phys. Chem., 2007, 111, 4043-4055

- Pressure dependent (association) reaction.
- Study as a function of temperature and pressure
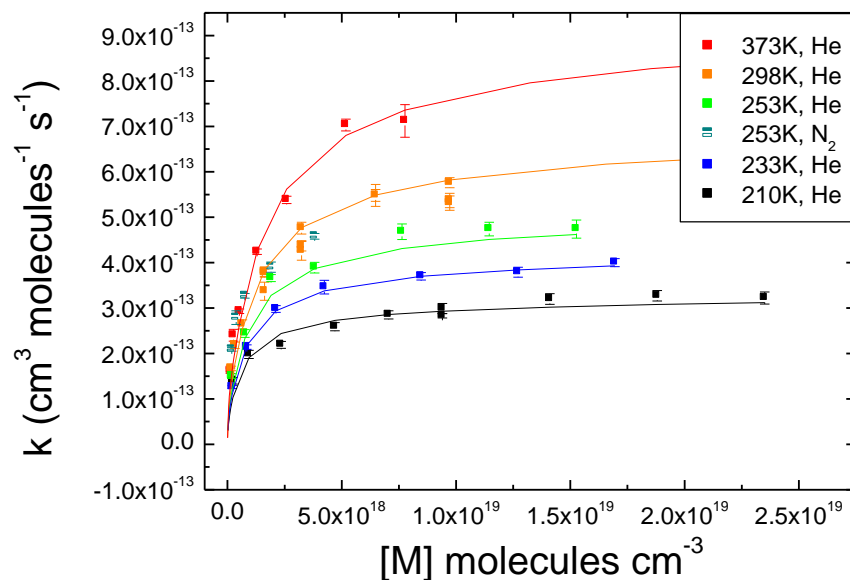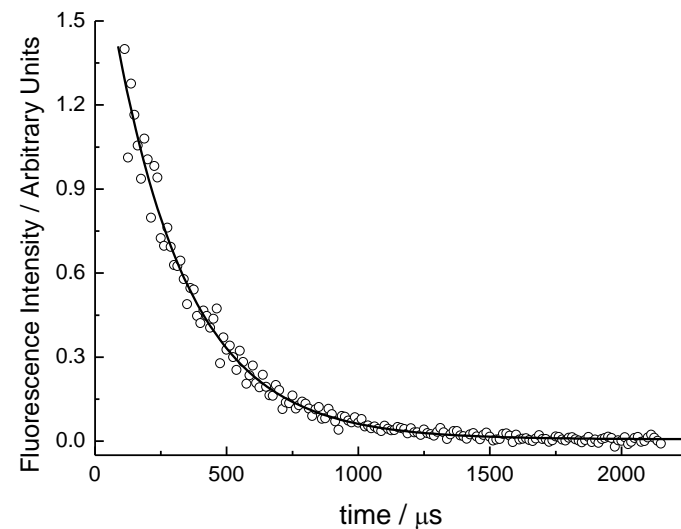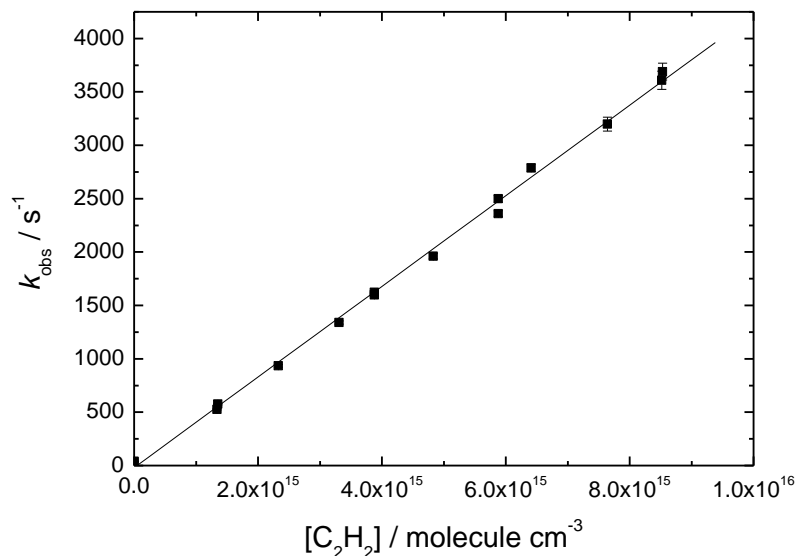
OH + acetone, J N Crowley, JPCA, 2000, **104**,2695

laser flash photolysis, resonance fluorescence/laser induced fluorescence to measure [OH] (relative). Optical measurement of [acetone] before and after reactor.
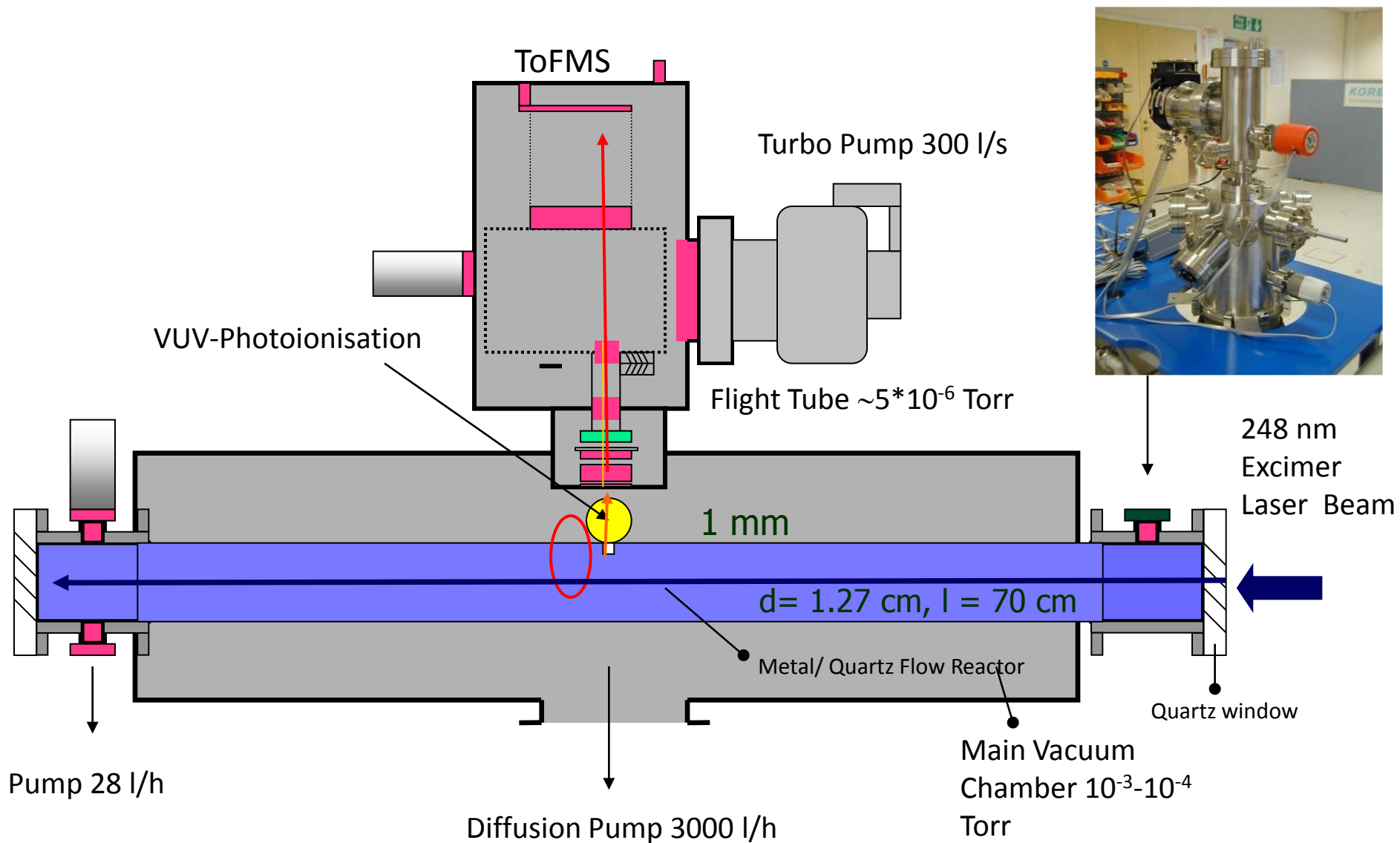
Minimising secondary reactions

- In order to be able to use a simple pseudo first order approach to the analysis of the data, secondary reactions must play a negligible role.
- This involves keeping the initial radical concentration low.
- See Vaghjiani and Ravishankara (Nature, 1991, 350, 406) for a classic experimental analysis of this problem for OH + $CH_4 \rightarrow CH_3 + H_2O$.
- Typical radical decay timescales in pulsed photolysis reactions are ~ 0.1 – 1 ms
- k(OH + CH_3) is ~ 10^{-10} cm^3 molecule^{-1} s^{-1}. The timescale for removal of OH by this reaction is ~ 0.1 s for $[CH_3]$ = 10^{11} cm^{-3} and 1 ms for $[CH_3]$ = 10^{13} cm^{-3} . So it is essential to keep the amount of OH generated in the photolysis pulse low if this secondary reaction is to make a negligible contribution to the observed decay of OH.
- Need a sensitive detection technique – LIF is ideal.

# Detection using time of flight mass spectrometry
Blitz et al. Rev. Sci. Inst. 2007, 78, 034103

ToFMS

Turbo Pump 300 l/s

VUV-Photoionisation

Flight Tube ~5*10⁻⁶ Torr

248 nm Excimer Laser Beam

1 mm

d= 1.27 cm, l = 70 cm

Metal/ Quartz Flow Reactor

Quartz window

Pump 28 l/h

Diffusion Pump 3000 l/h

Main Vacuum Chamber 10⁻³-10⁻⁴ Torr

Application of synchrotron radiation for photoionization (SVUV-PIMS) to distinguish isomers in flames
1. ALS, USA

- ALS is tuneable and so it is feasible to distinguish isomers, which have the same mass, through their differing photoionization efficiency curves.

- Traces show m/z=44 for different flames:
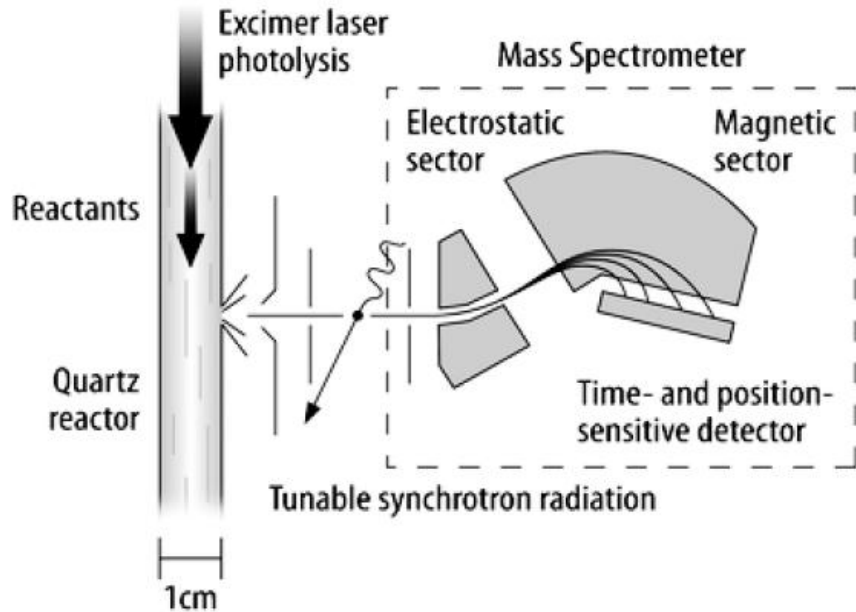
  acetaldehyde: CH_3CHO

  ethenol: $CH_2=CHOH$
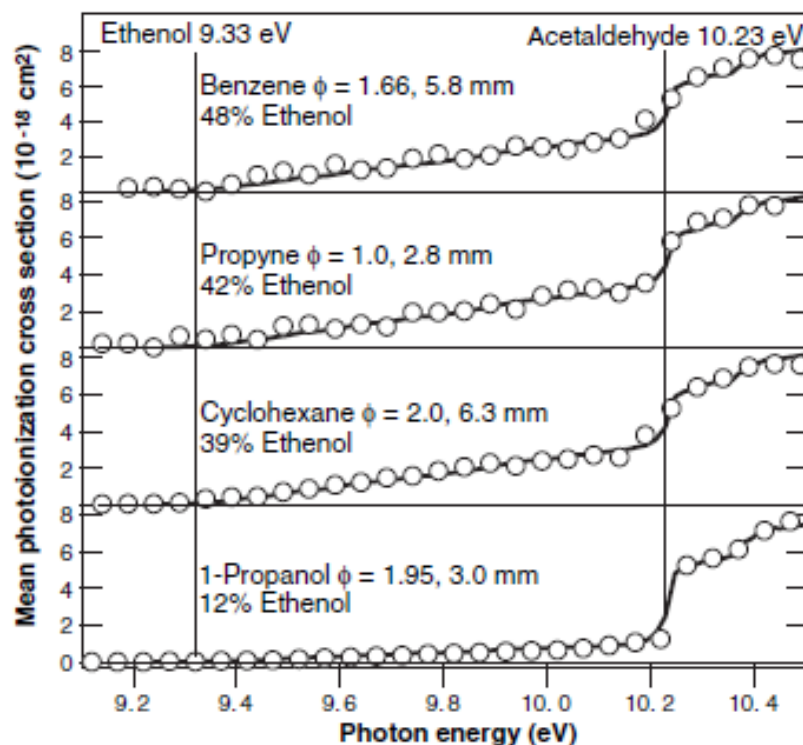
Taatjes et al. *Science* 2005, **308**, 1887

2. NSRL China
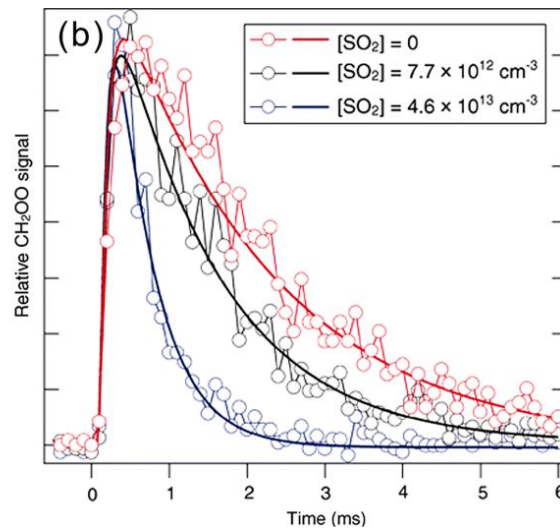## Various butanol flames,

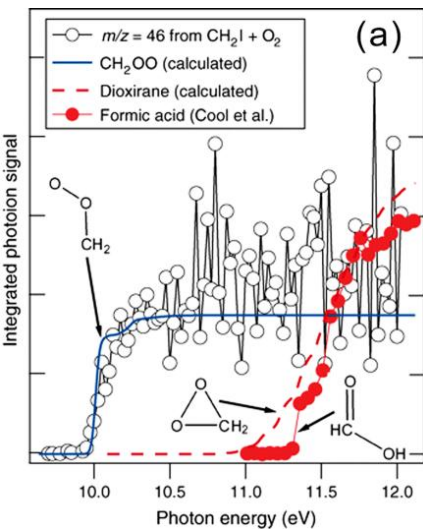- Yang et al.Combust. Flame 148 (2007) 198-209.
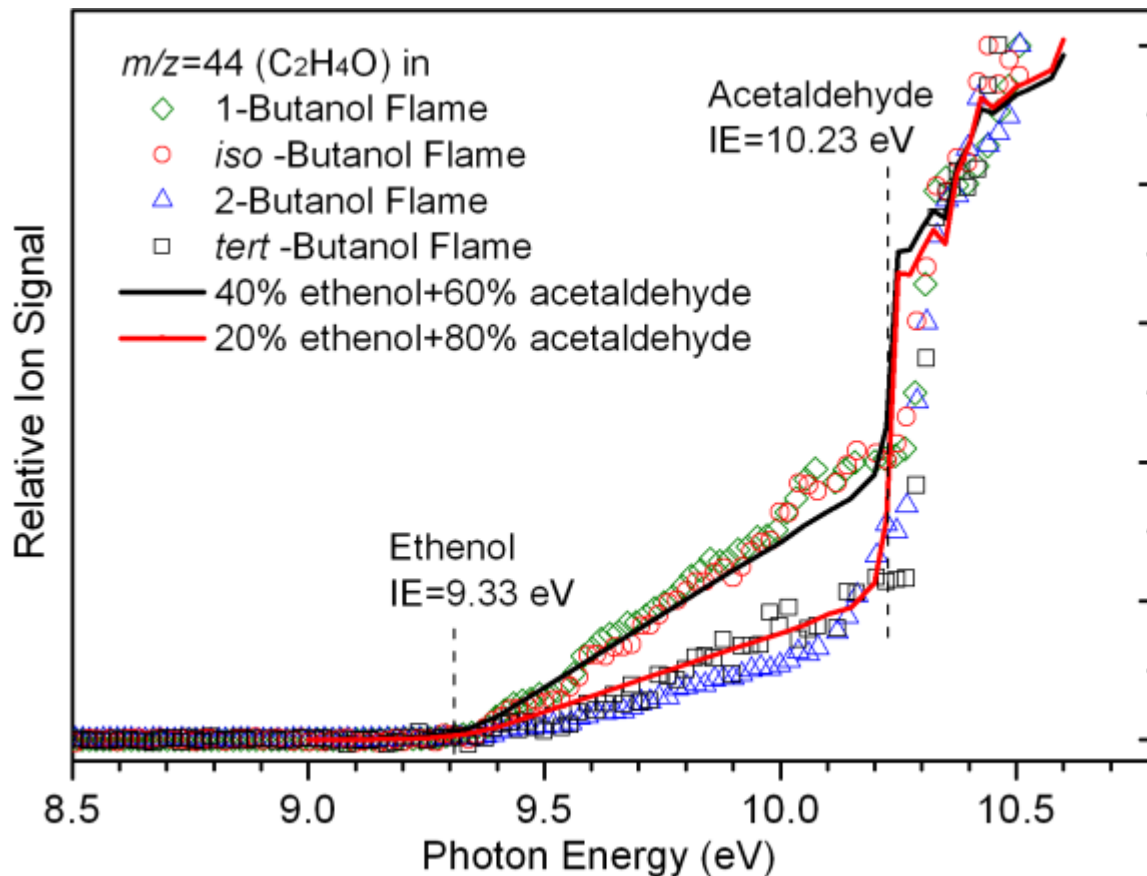
SVUV-PIMS for kinetics
Taatjes et al., PCCP,
2008, 10, 20 – 34

(a) The calculated photoionization spectra of the Criegee intermediate CH_2OO and dioxirane, the experimental photoionization spectrum for formic acid, as well as schematic chemical structures, are shown.

(b) Time-dependent CH_2OO signals for various concentrations of SO_2. Solid lines represent fits to the data traces, including convolution with a measured instrument response function, from which pseudo–first order decay constants are derived Welz et al. Science 335, 204-207

Radical detection using absorption spectroscopy: $C_3H_5 + C_3H_5$
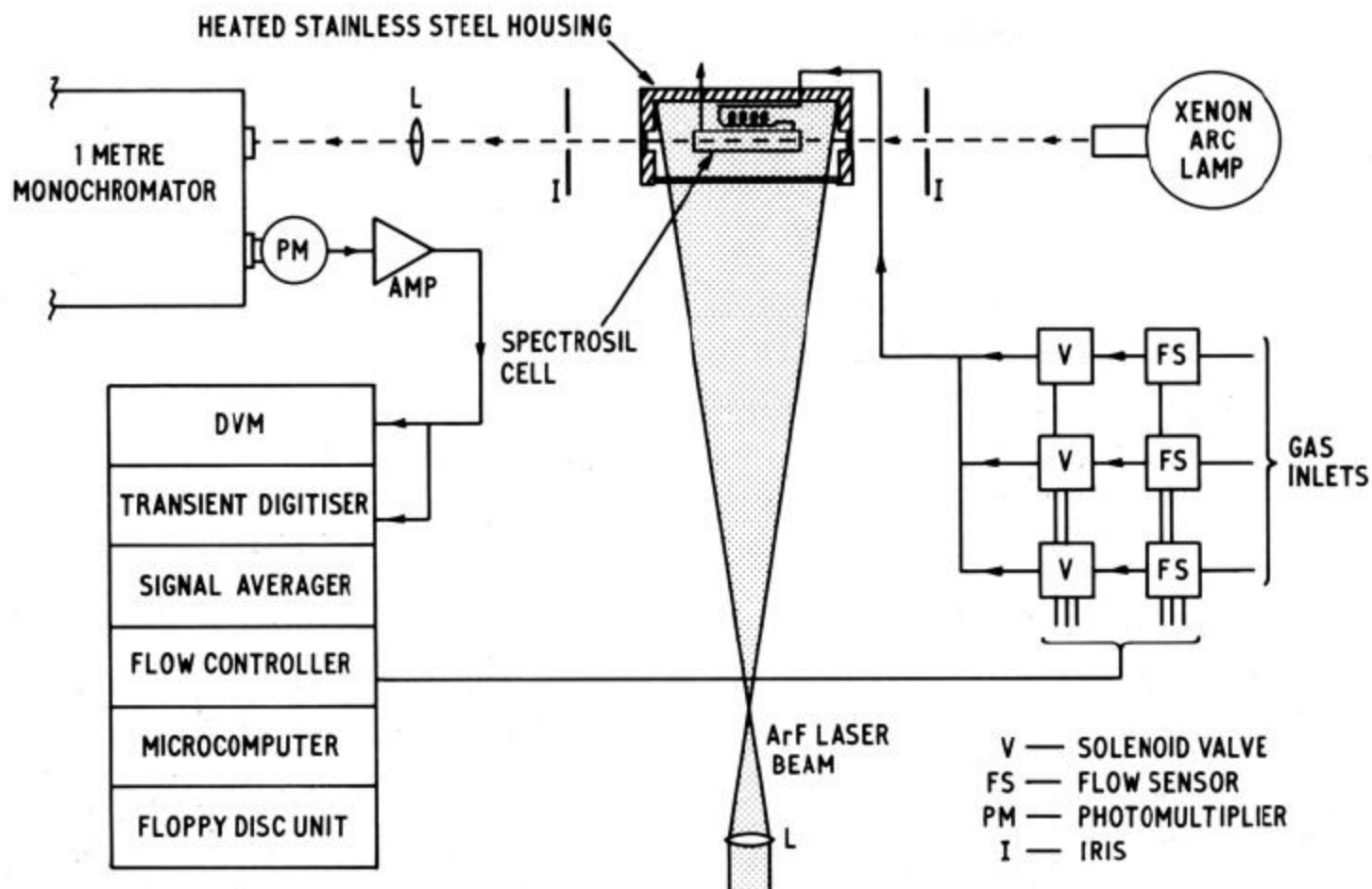
Reaction is <u>second order</u> in the radical – need the <u>absolute</u> concentration to determine k.

Tulloch et al. *J. Phys. Chem.* l982, 86, 3812-3819

C$_3$H$_5$ + C$_3$H$_5$:Absorption spectroscopy 2

- Reaction is second order in C$_3$H$_5$
- Need to know absolute concentration of radical – absorption spectroscopy provides a good route to this. (see J. Phys. Chem. 1985, 89, 2268-2274 for discussion for CH$_3$)
- I/I$_0$ = exp(-σ[C$_3$H$_5$]L) where I$_0$ is the incident and I the transmitted light intensity, σ is the absorption cross section and L is the path length.
- Similar method applied to CH$_3$ + CH$_3$. See Topic 3 for analysis of multiple determinations using master equation approach..
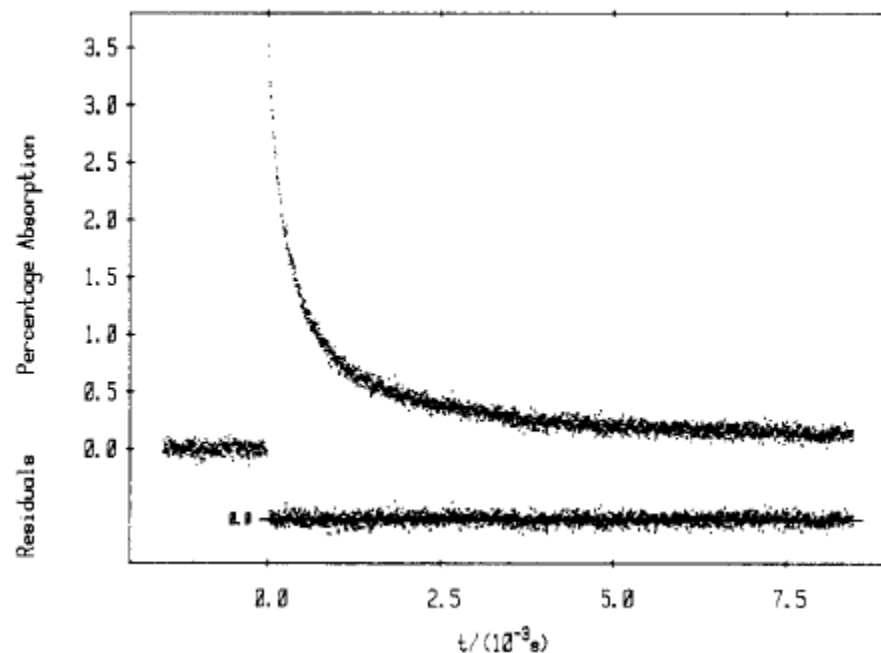
Experimental determination of k(CH$_3$ + H))

- This reaction presents an additional problem – the need to detect two radicals

- Laser flash photolysis producing H and CH$_3$ with [H]<<[CH$_3$]

- H by resonance fluorescence, CH$_3$ by absorption. Need absolute [CH$_3$], since k(H) = k[CH$_3$]

- Brouard et al. J. Phys. Chem. 1989, 93, 4047-4059
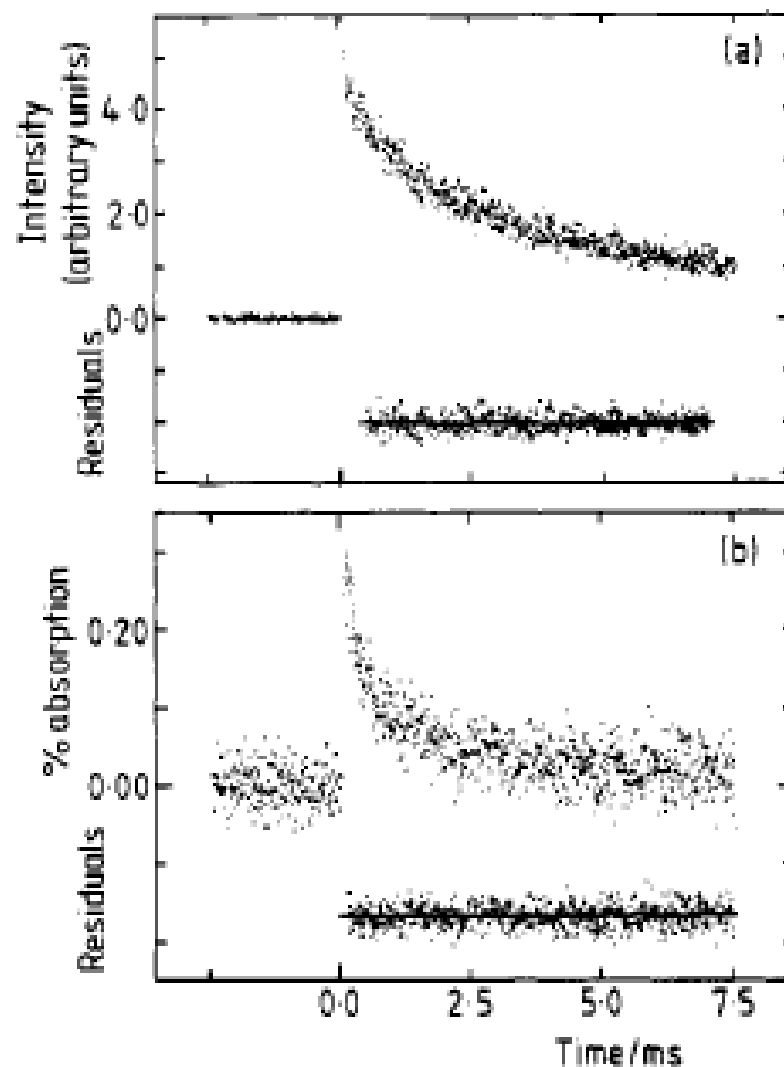
Experimental results for CH_3 + H

CH_3 absorption analysed via

$$\Delta_0 = \sigma[CH_3]_0 L$$

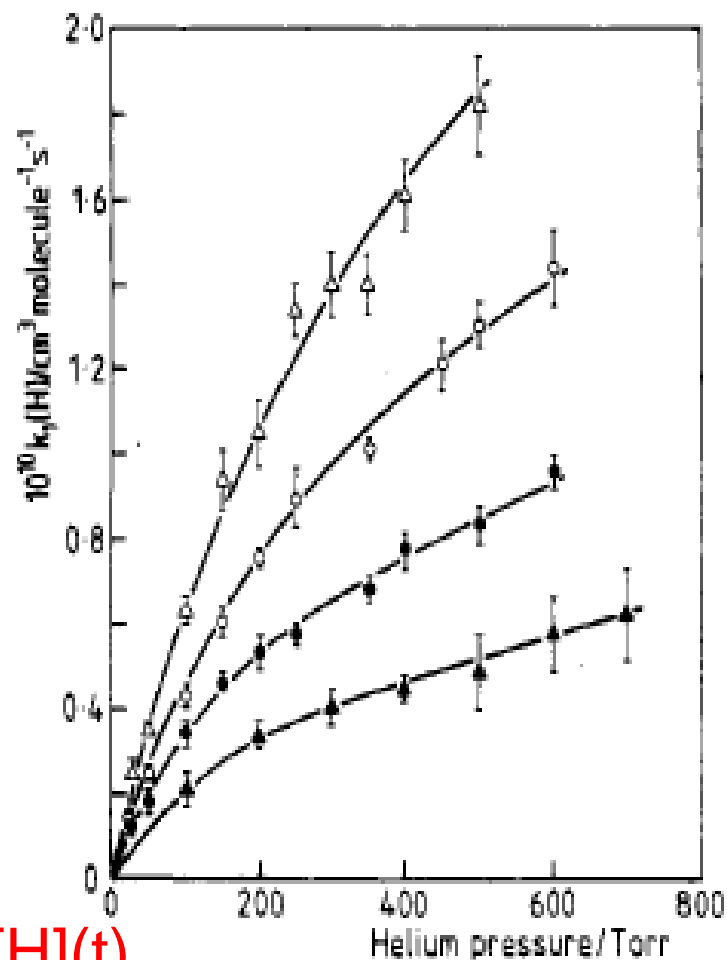$$D(t) = 1 - \exp\left\{-\left(\Delta_0^{-1} - \frac{2k_2t}{\sigma L}\right)^{-1}\right\}$$

Where $D(t) = \Delta I/I_0$, Δ_0 is the peak optical density, σ is the absorption cross section and L is the path length.

H fluorescence analysed via

$$[H] = [H]_0\left\{1 + \frac{2k_2\Delta_0t}{\sigma L}\right\}^{-\frac{k_1}{2k_2}}\exp(-k_3t)$$

- Where k_2 refers to CH_3 + CH_3 and k_3 to other 1st order loss processes for

- Plot shows rate coefficients vs p at 300, 400, 500, 600 K.

From $d[H]/dt = -k_1[H](t)[CH_3](t) - k_3[H](t)$

# CH$_3$ + H. Parameterisation and determination of k$^\infty$

- Parameterisation using Troe method (next slide)
- Also determined k$^\infty$ using master equation method coupled with inverse Laplace transform (see later)

TABLE III: Limiting Rate Coefficients Obtained from Fitting the Data for k_1(H) Using the Troe Factorization Procedure[36,37]

T/K	$10^{10}k_1^\infty$(H)/ cm^3 molecule^{-1} s^{-1}	$10^{29}k_1^0$(H)/ cm^3 molecule^{-1} s^{-1}	F_{sc}^{cent}	β_c
300	7.6 ± 1.6	2.7 ± 0.4	0.659	0.45
400	4.7 ± 1.2	3.1 ± 0.6	0.627	0.39
500	3.1 ± 0.6	3.0 ± 0.5	0.599	0.34
600	1.8 ± 0.6	2.5 ± 0.8	0.566	0.30

Recall earlier slide: Pressure dependent association reactions

$$A + B \quad \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \quad AB^* \quad \overset{k_s[M]}{\rightarrow} \quad AB.$$
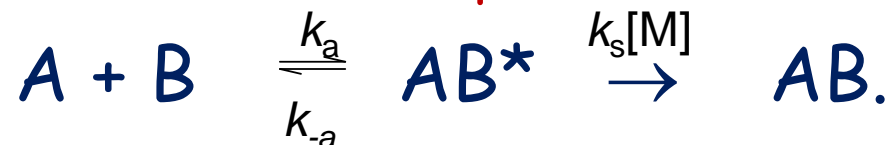
$$k = \frac{k_a \, k_s[M]}{k_{-a} + k_s[M]}$$

As $[M] \rightarrow \infty, k \rightarrow k_a = k^\infty$

As $[M] \rightarrow 0, k \rightarrow \frac{k_a k_s[M]}{k_{-a}} = k_0[M]$

$$k = \frac{k_0[M]k^\infty}{k^\infty + k_0[M]}$$

Similar treatment for dissociation reactions

- This is the Lindemann-Hinshelwood model of pressure dependent unimolecular reactions.
- The treatment is an approximation because (i) k_{-a} depends on the energy of AB* (ii) deactivation of AB* takes place in a number of steps.
- These have the effect of *broadening* the fall-off curve (k vs [M]). These effects have been incorporated in a fitting procedure developed by Troe that is widely used in parameterising rate coefficients for use in combustion modelling

Troe Fitting

Need to represent k(T,P) for Global Models

Standard is Troe Fitting

$$k(T,p) = \frac{k_0[M]k^\infty}{k^\infty + k_0[M]} F \qquad \log_{10} F = \frac{\log_{10} F_{cent}}{1 + \left[\frac{\log_{10}(p^*) + c}{N - d\left(\log_{10}(p^*) + c\right)} \right]^2}$$

$$p^* = k_0[M]/k^\infty \qquad d = 0.14$$

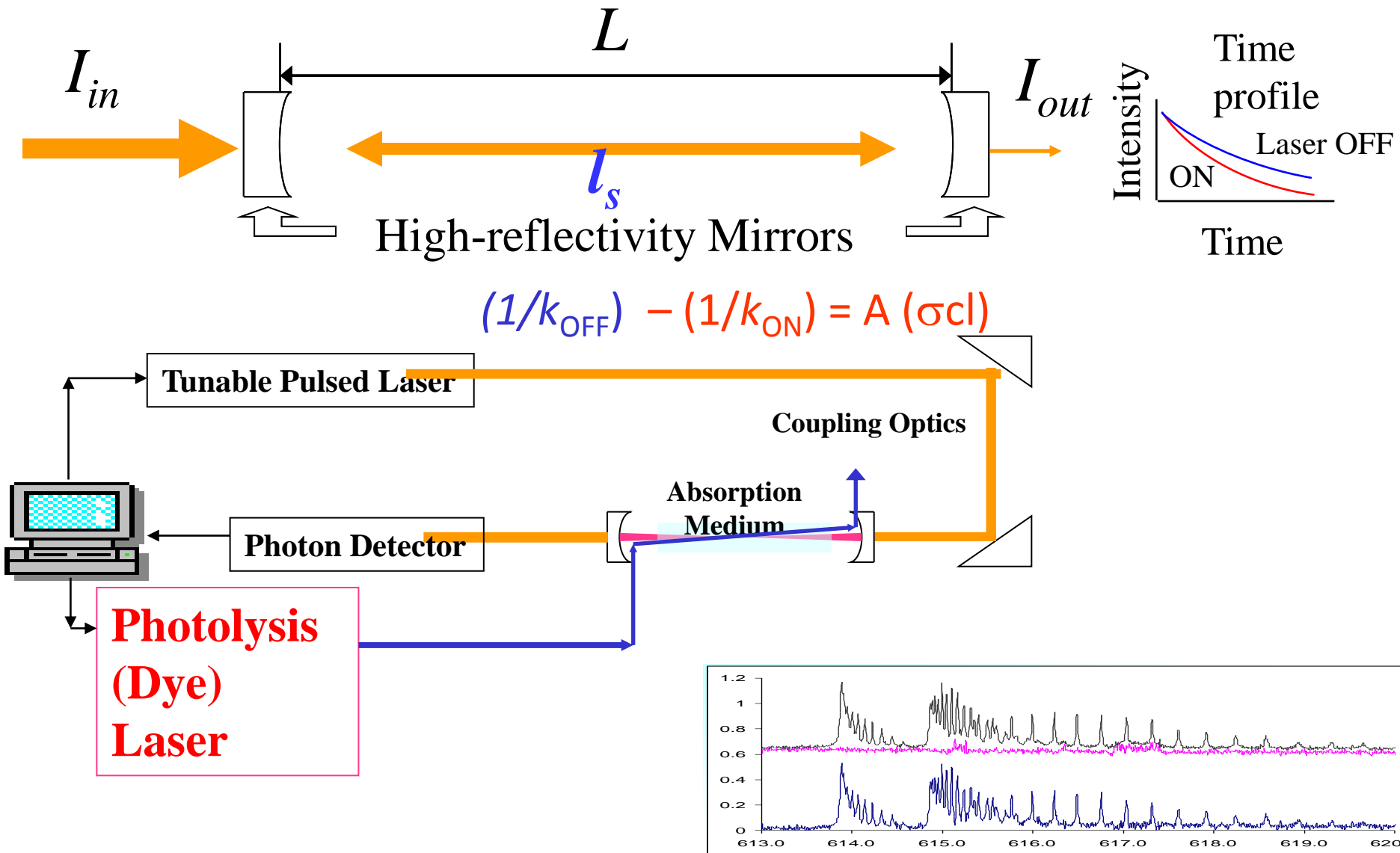$$c = -0.4 - 0.67 \log_{10} F_{cent} \qquad N = 0.75 - 1.27 \log_{10} F_{cent}$$

Fit k_0 & k^∞ to modified Arrhenius $\quad k_0 = A_0 T^{n_0} \exp(-E_0/T)$

Fit F_{cent} to:

$$F_{cent} = (1-a)\exp\left(-T/T^{***}\right) + a\exp\left(-T/T^*\right) + \exp\left(-T^{**}/T\right)$$

For the most recent formulation of the broadening term see
***Zeitschrift für Physikalische Chemie*, 2014; Vol. 228, p 1**

Detection of HCO using cavity ring down spectroscopy (CRDS)
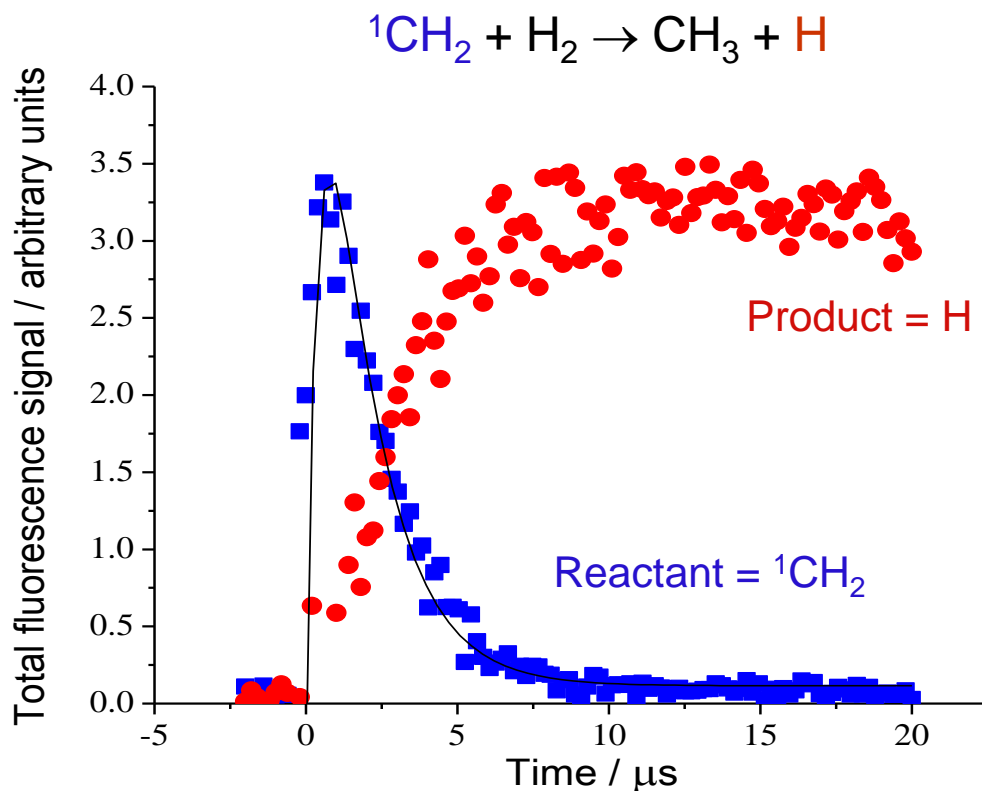

$$(1/k_{OFF}) - (1/k_{ON}) = A\,(\sigma cl)$$

Determination of product yields by Laser Flash Photolysis 1

- Use laser pulse to generate radical on short timescale (~10 ns)
- Observe radical concentration vs time. Obtain kinetics from decay time constant
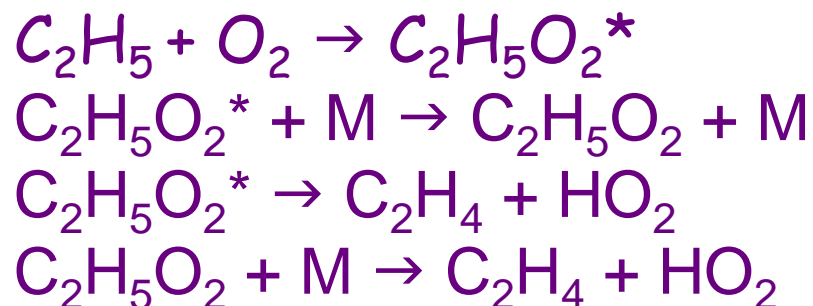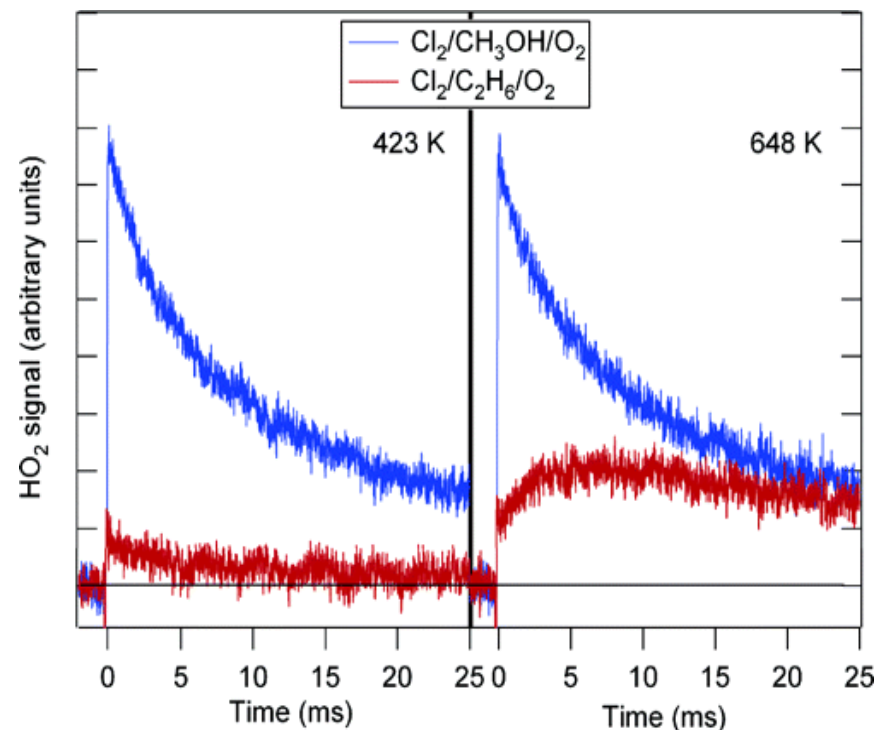- Also observe product – calibration gives channel yield for a multi channel reaction:

$$A + B \rightarrow C + D$$
$$\rightarrow E + F$$
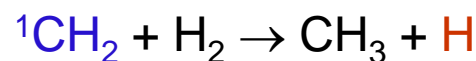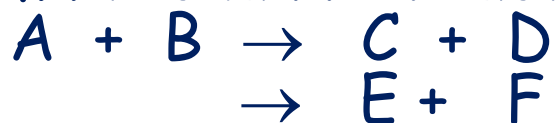
Detection technique :
laser induced
fluorescence
for CH_2 and H
Need to calibrate signals

$^1CH_2 + H_2 \rightarrow CH_3 + H$

Product = H

Reactant = $^1CH_2$

Total fluorescence signal / arbitrary units

Time / μs

Determination of product yields by Laser Flash Photolysis 2: $C_2H_5 + O_2$

- Taatjes et al. (J. Phys. Chem. A 104 (2000) 11549 – 11560) observed the formation of OH and HO_2, determining the fractional yields. Used 100% yield of HO_2 from $CH_2OH + O_2$ to calibrate the system.

- HO_2 yield↑ as T↑ and p↓

- Two timescales at higher T

- OH yield is small.

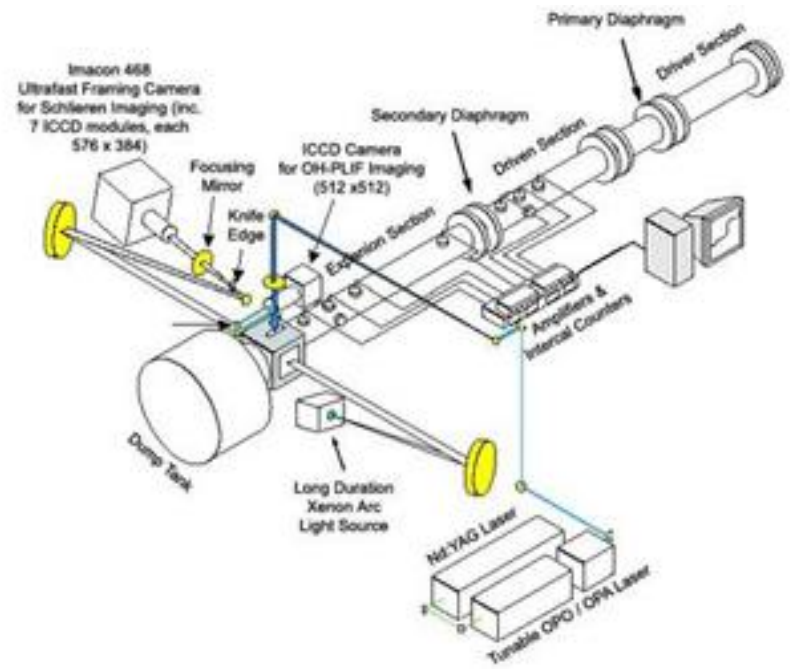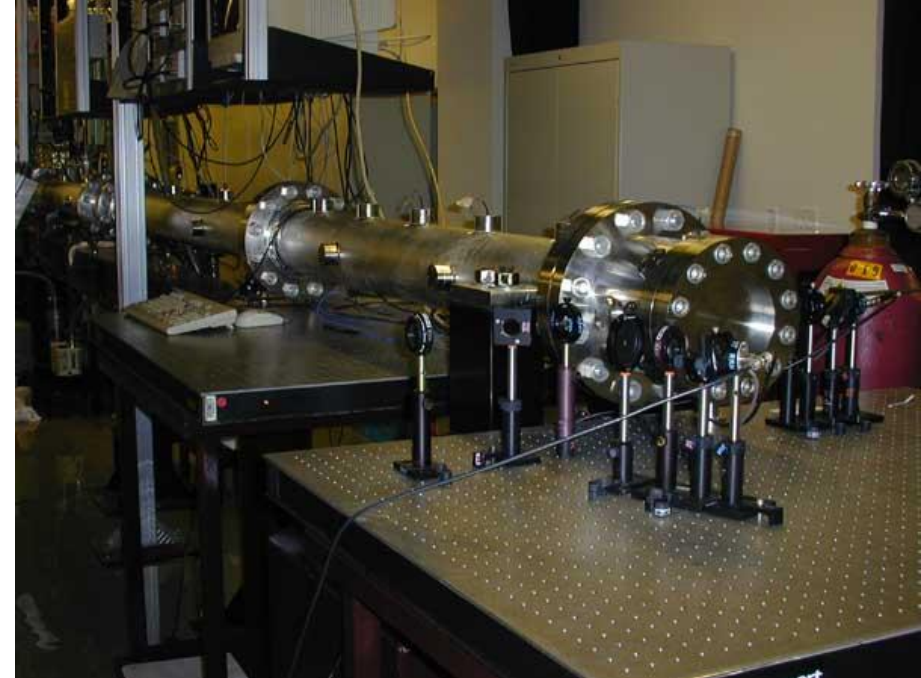- Theoretical interpretation and relevance to autoignition chemistry will be discussed later

$C_2H_5 + O_2 \rightarrow C_2H_5O_2{}^*$
$C_2H_5O_2{}^* + M \rightarrow C_2H_5O_2 + M$
$C_2H_5O_2{}^* \rightarrow C_2H_4 + HO_2$
$C_2H_5O_2 + M \rightarrow C_2H_4 + HO_2$

Shock tubes

Shock tube - basics
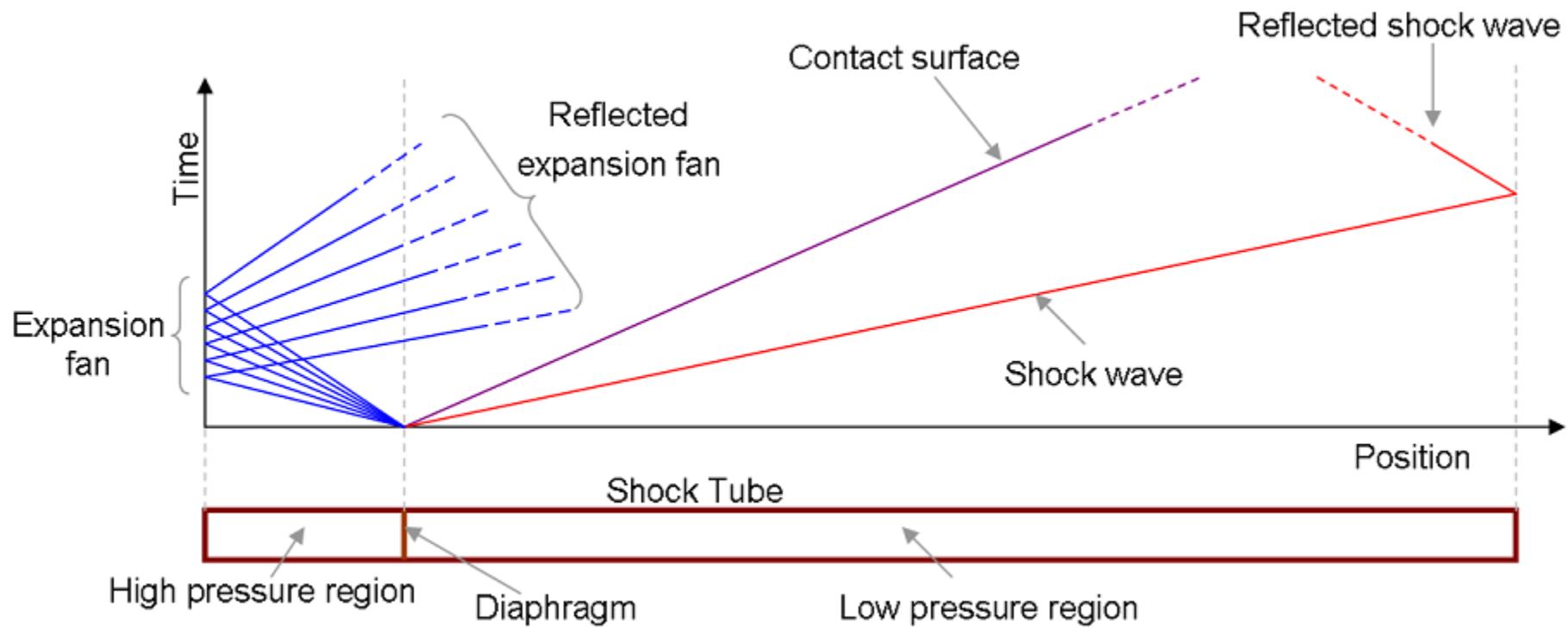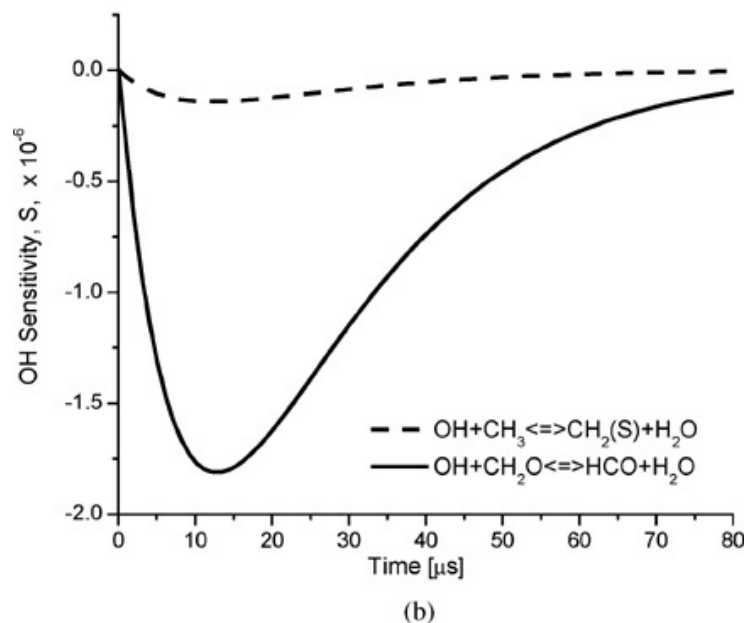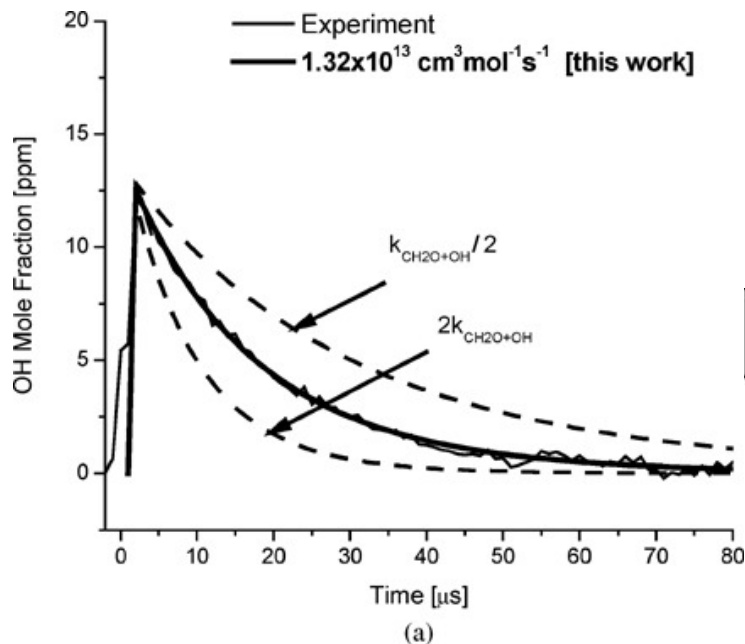
Shock tube:
Hanson lab at Stanford

Shock tubes

– Compressive heating of reaction mixture

– Radicals generally formed from thermal dissociation of precursor

– Single shot, so no signal averaging, but impressive optimisation of signal

– Generally need to assess secondary reactions and use numerical chemical model with sensitivity analysis to show viability of measurements.

– Example: Measurement of $CH_3 + OH$ by the Hanson group

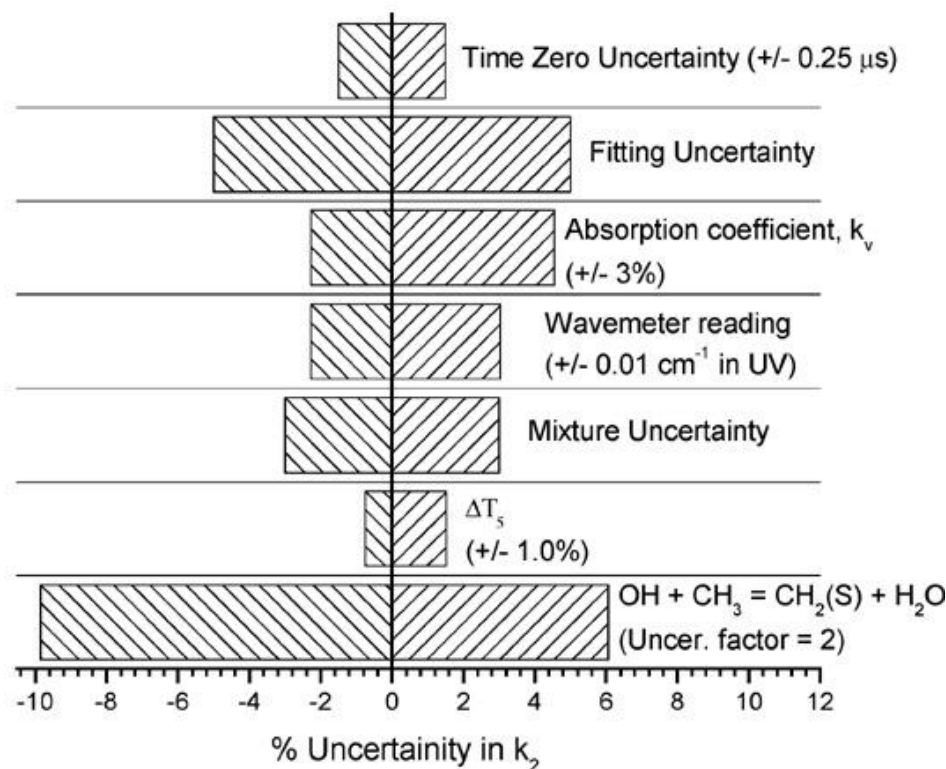Vasudevan et al, International Journal of Chemical Kinetics (2008), 40(8), 488-495.
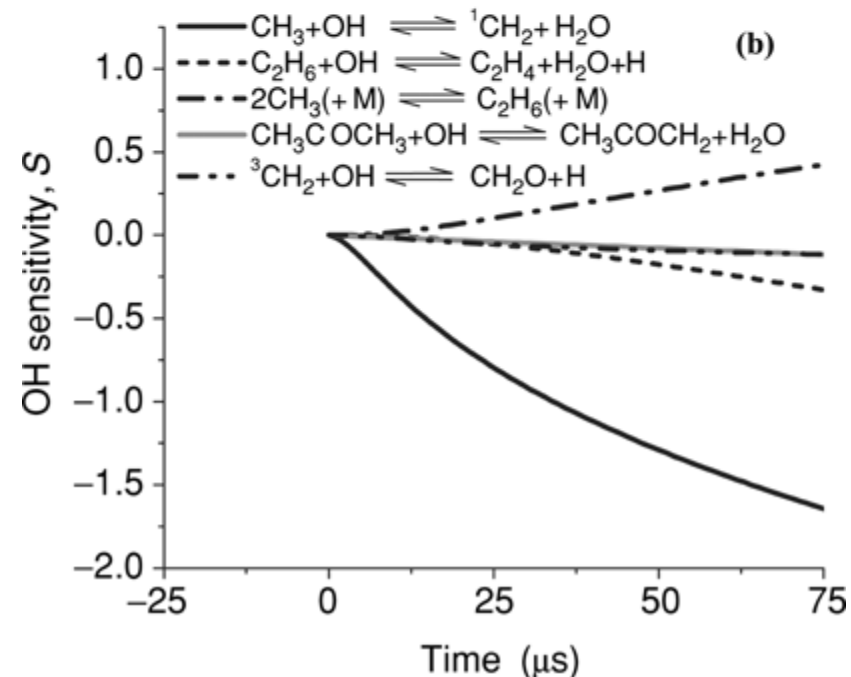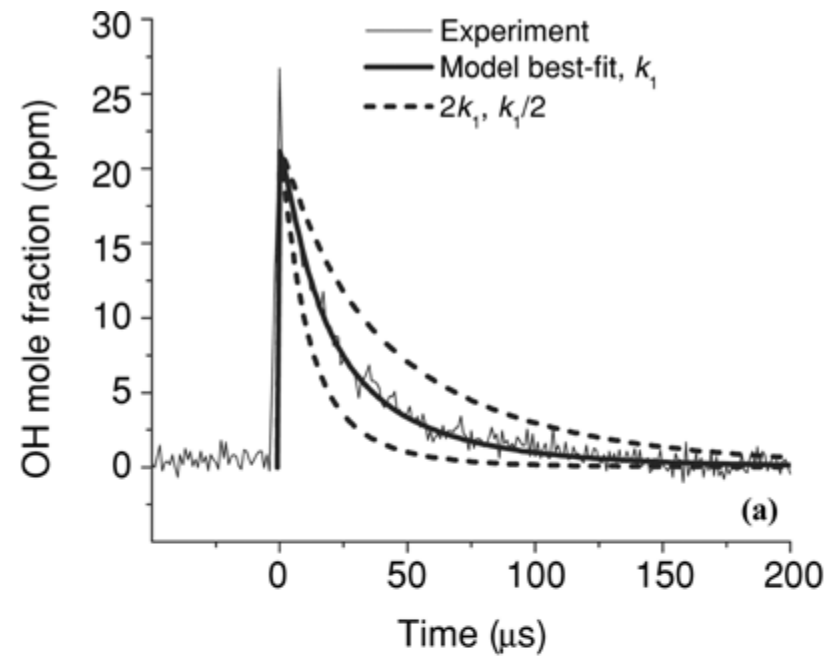
OH + HCHO, 934 K to 1670 K, 1.6 atm
Int J Chem Kinet 37: 98–109, 2005

- Behind reflected shock waves. OH radicals shock-heating tert-butyl hydroperoxide

- OH concentration time-histories were inferred from laser absorption using the R1(5) line of the OH A-X (0, 0) band near 306.7 nm.

- Other reactions contribute to the OH time profile, especially CH_3 + OH.

- Rate coefficient determined by fitting to detailed model (GRI-Mech – see Wednesday), with addition of acetone chemistry, deriving from dissociation of OH precursor (t-butylhydroperoxide). Detailed uncertainty analysis
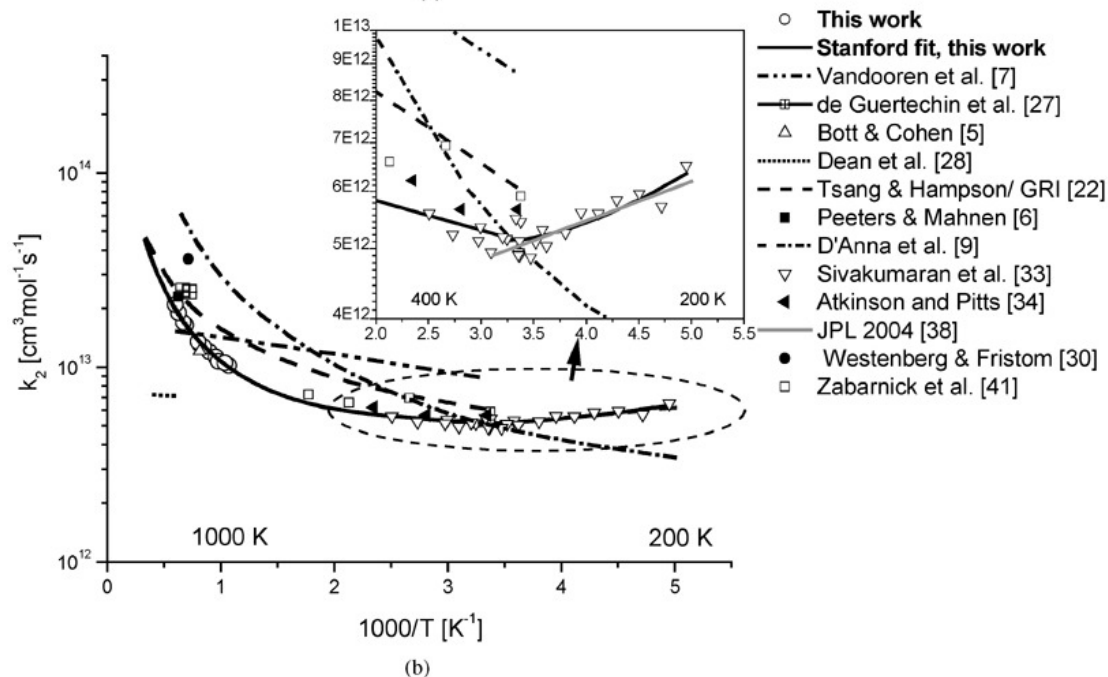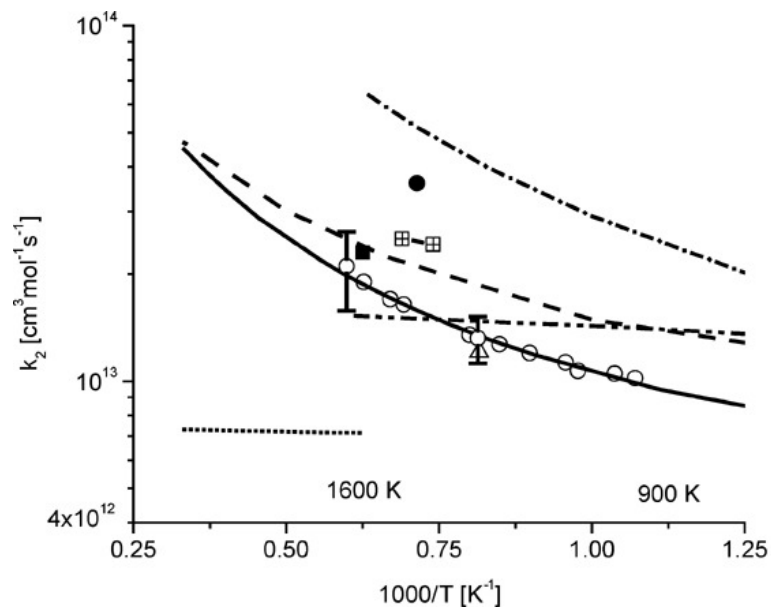
Determination of *k* and uncertainty analysis

(a)

(b)

1229 K, 1.64 atm
Combined uncertainty on k_2: +13.3% / - 15.2%

Time Zero Uncertainty (+/- 0.25 μs)

Fitting Uncertainty

Absorption coefficient, k_v (+/- 3%)

Wavemeter reading (+/- 0.01 cm^{-1} in UV)

Mixture Uncertainty

ΔT_s (+/- 1.0%)

$OH + CH_3 = CH_2(S) + H_2O$ (Uncer. factor = 2)
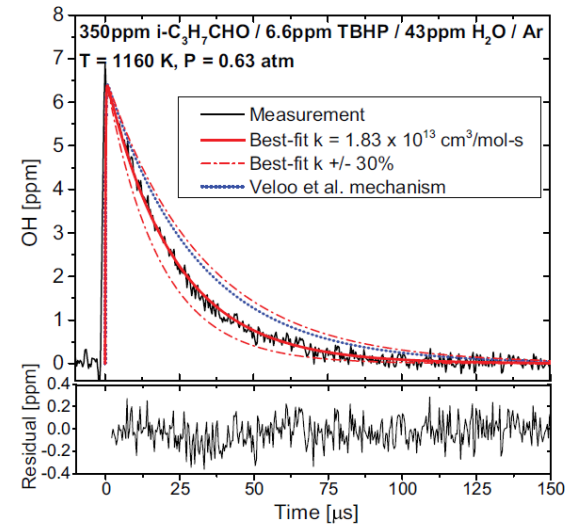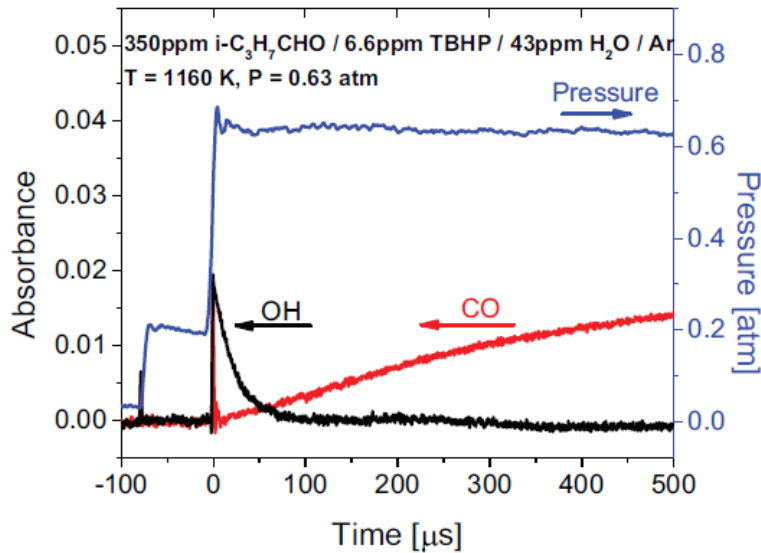
% Uncertainty in k_2

Arrhenius plot for OH + HCHO

- $k_2 = 7.82 \times 10^7\, T^{1.63} \exp(531/T)\ /\ cm^3\ mol^{-1}\ s^{-1}$
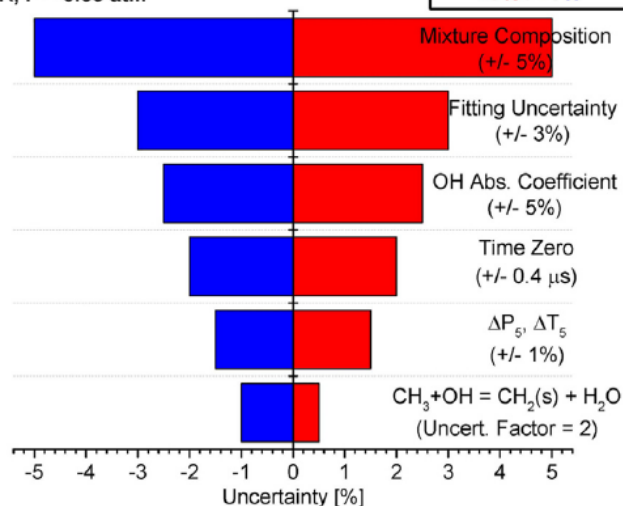
OH + Aldehydes

(Wang et al. Proceedings of the Combustion Institute 36 (2017) 151–160)

- Same absorption technique; 976 – 1346 K, 0.6 atm. Some dissociation of aldehyde at higher T. Monitor by CO absorption.

OH + aldehydes contd.

350ppm i-C_3H_7CHO / 6.6ppm TBHP / 43ppm H_2O / Ar
T = 1160 K, P = 0.63 atm

Overall Uncertainty
+7% / - 7%

Mixture Composition (+/- 5%)
Fitting Uncertainty (+/- 3%)
OH Abs. Coefficient (+/- 5%)
Time Zero (+/- 0.4 μs)
ΔP_5, ΔT_5 (+/- 1%)
$CH_3+OH = CH_2(s) + H_2O$ (Uncert. Factor = 2)

Uncertainty [%]

$k_{iC_3H_7CHO+OH} = 7.70 \times 10^{13} \exp(-1700 \text{ K/T}) \pm 7\%;$

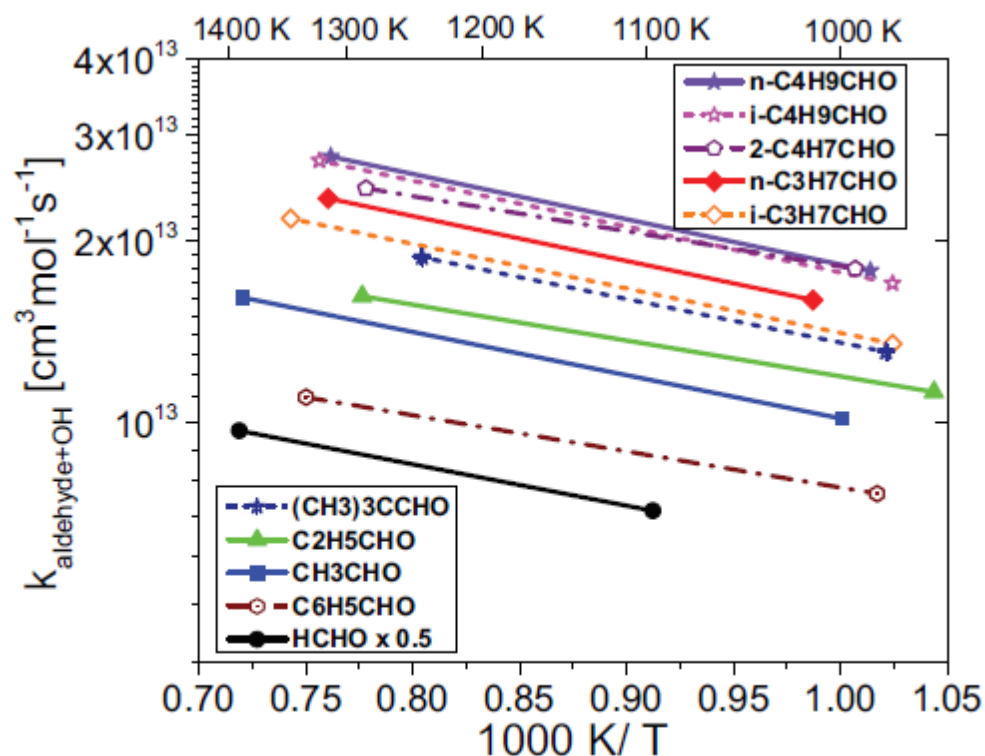$k_{nC_4H_9CHO+OH} = 1.03 \times 10^{14} \exp(-1730 \text{ K/T}) \pm 7\%;$

$k_{iC_4H_9CHO+OH} = 1.02 \times 10^{14} \exp(-1750 \text{ K/T}) \pm 10\%;$

$k_{(CH_3)_3CCHO+OH} = 7.20 \times 10^{13} \exp(-1670 \text{ K/T}) \pm 8\%;$

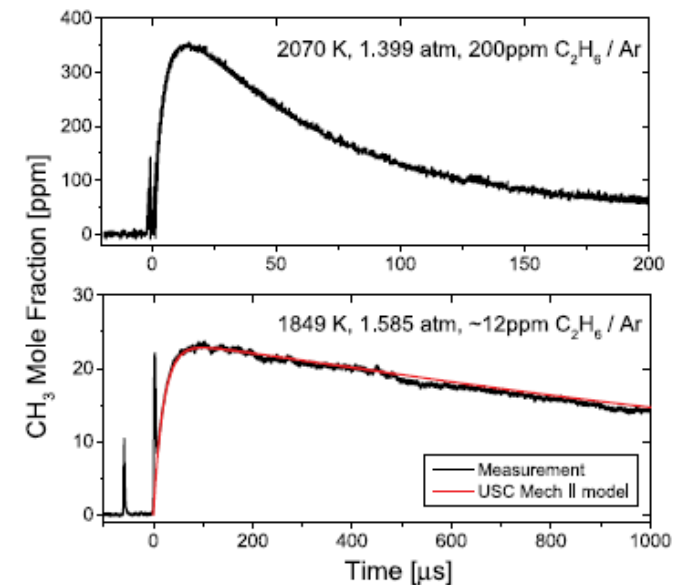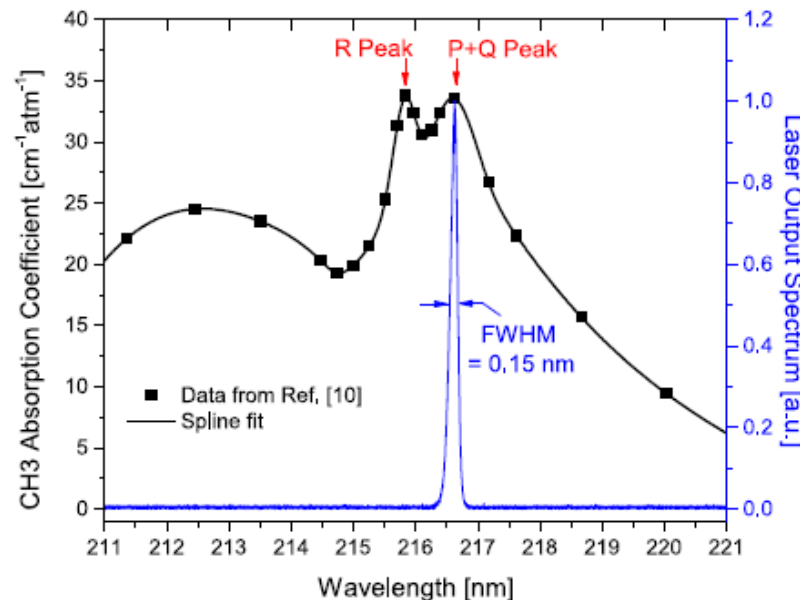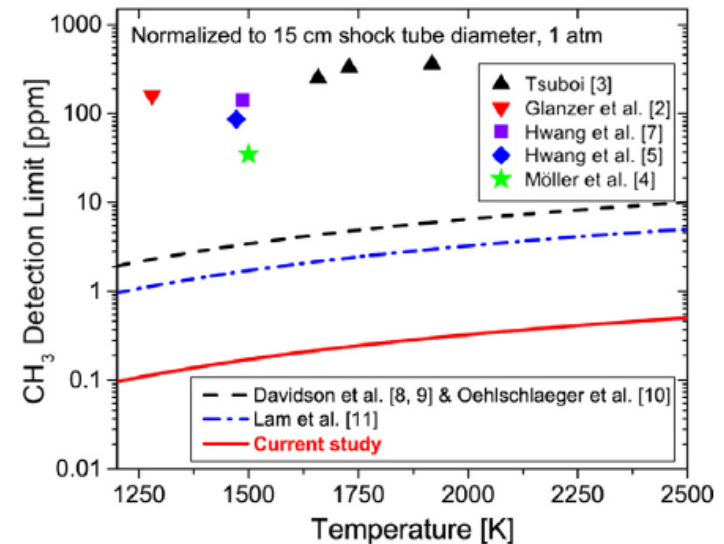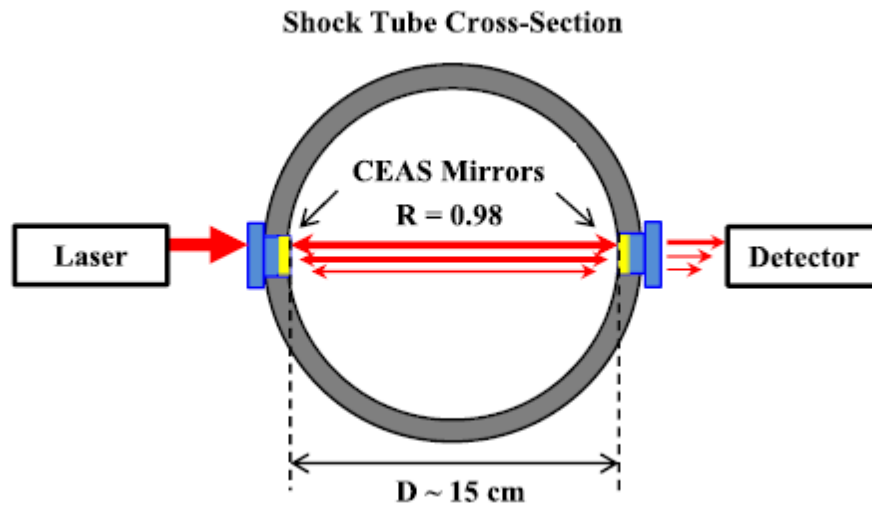$k_{C_2H_5CHCHCHO+OH} = 6.93 \times 10^{13} \exp(-1340 \text{ K/T}) \pm 8\%;$

$k_{C_6H_5CHO+OH} = 3.10 \times 10^{13} \exp(-1380 \text{ K/T}) \pm 8\%.$

Sub ppm CH₃ detection by cavity enhanced absorption spectroscopy (CEAS)
## (Wang et al Proceedings of the Combustion Institute 36 (2017) 4549–4556)

Shock Tube Cross-Section

CEAS Mirrors

R = 0.98

Laser

Detector

D ~ 15 cm

Normalized to 15 cm shock tube diameter, 1 atm

- ▲ Tsuboi [3]
- ▼ Glanzer et al. [2]
- ■ Hwang et al. [7]
- ◆ Hwang et al. [5]
- ★ Möller et al. [4]

- — — Davidson et al. [8, 9] & Oehlschlaeger et al. [10]
- — · — Lam et al. [11]
- —— **Current study**

CH_3 Detection Limit [ppm] vs Temperature [K]

R Peak   P+Q Peak

CH3 Absorption Coefficient [cm⁻¹atm⁻¹] / Laser Output Spectrum [a.u.] vs Wavelength [nm]

FWHM = 0.15 nm

- ■ Data from Ref. [10]
- —— Spline fit

2070 K, 1.399 atm, 200ppm C_2H_6 / Ar

1849 K, 1.585 atm, ~12ppm C_2H_6 / Ar

CH_3 Mole Fraction [ppm] vs Time [µs]

- —— Measurement
- —— USC Mech II model

Shock tube study of the thermal decomposition of $C_2D_5I/CH_3I/Kr$ mixtures which generated D atoms and CH_3 radicals. [H] and [D] were monitored by ARAS. A rate constant of $2.20 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} was measured for the reaction $CH_3 + D \rightarrow CH_2D + H$. This rate constant was converted to the high pressure limit for $CH_3 + H \rightarrow CH_4$ using the ratio of 1.6 determined theoretically by Klippenstein, Georgieskii, and Harding. (Proc. Comb. Inst. 2002, **29**, 1229.)

Flow tubes for elementary reactions and whole systems
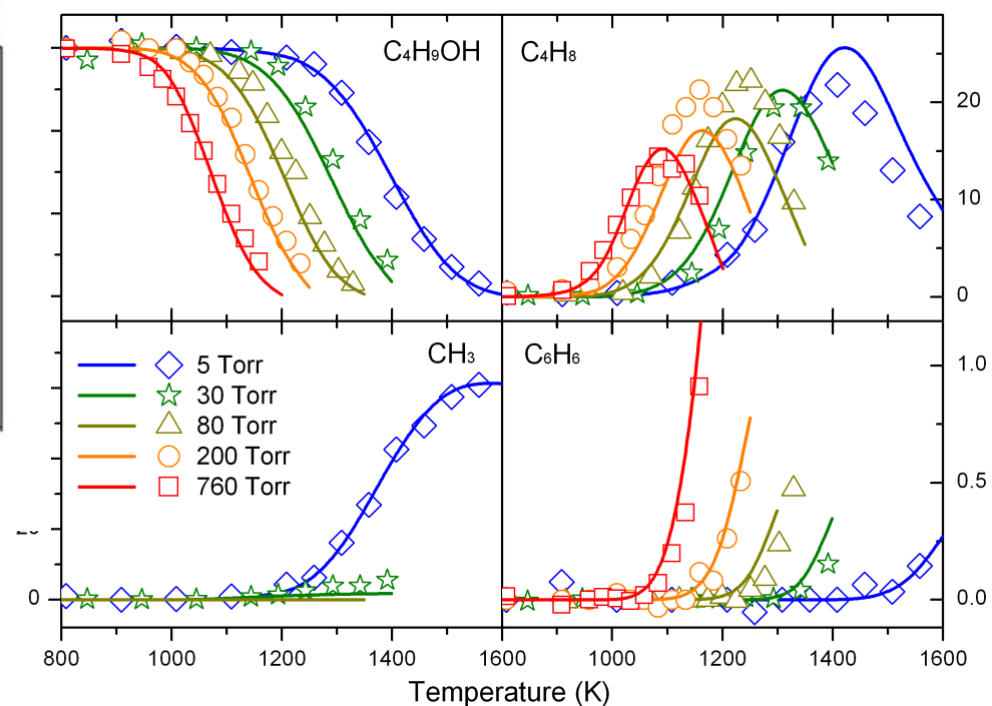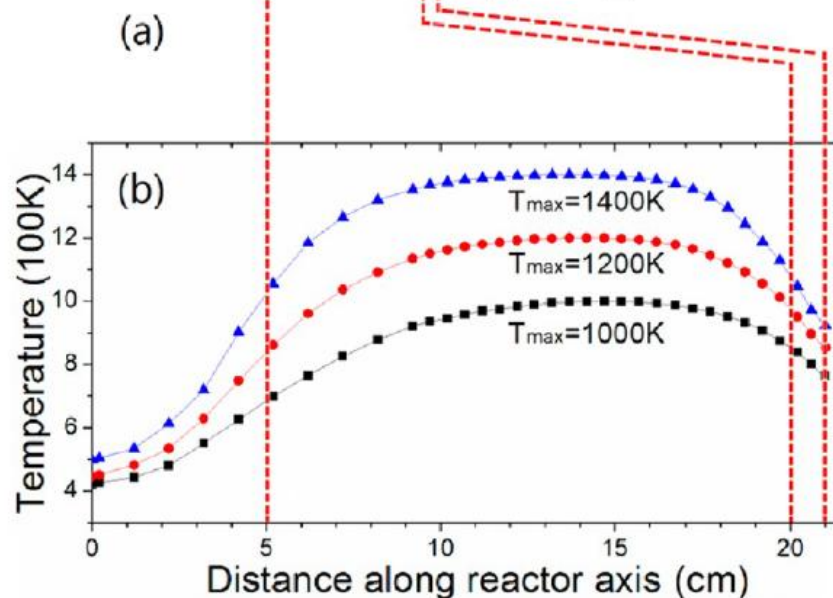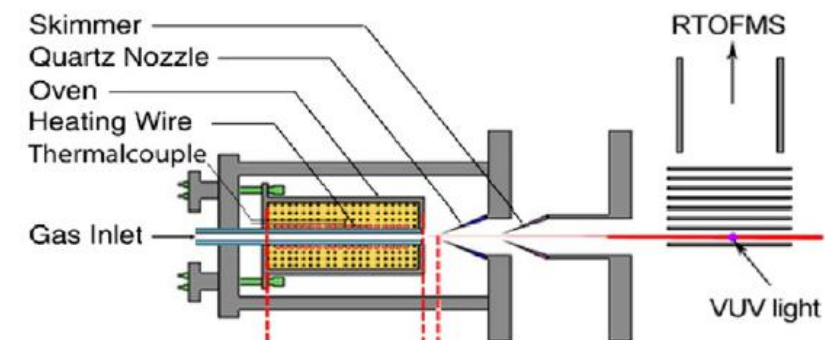
Combined flow tube and pulsed photolysis: O + OH
Howard and Smith, J. Chem. Soc Faraday Trans. 2, 1981,77,997-1008
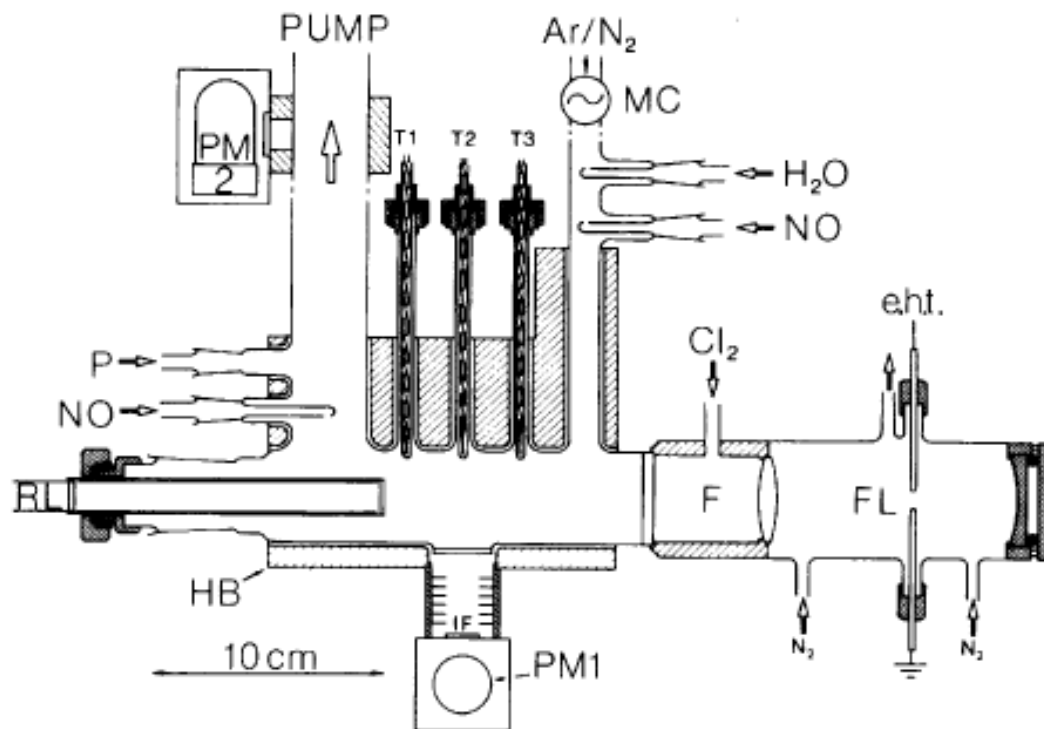
- O generated in discharge, OH by pulsed photolysis, with [O]>> [OH]. [O] generated from N + NO and concentration determined by titration.
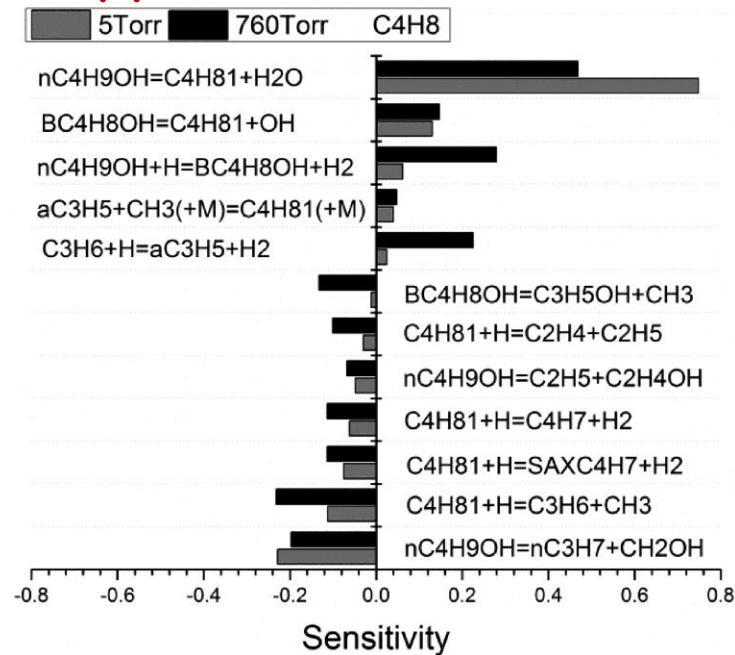
Pyrolysis of butanol using molecular beam sampling from a plug flow reactor

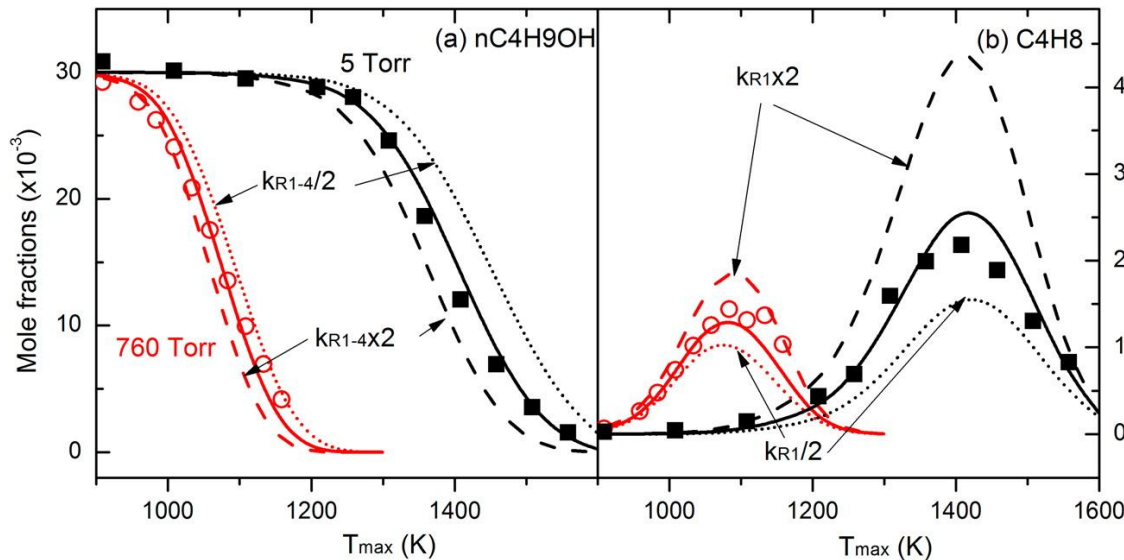Cai et al. (Energy & Fuels, 26, 5550-5568 (2012))

Use of species concentrations in flow reactor to determine rate coefficients: butanol dissociation

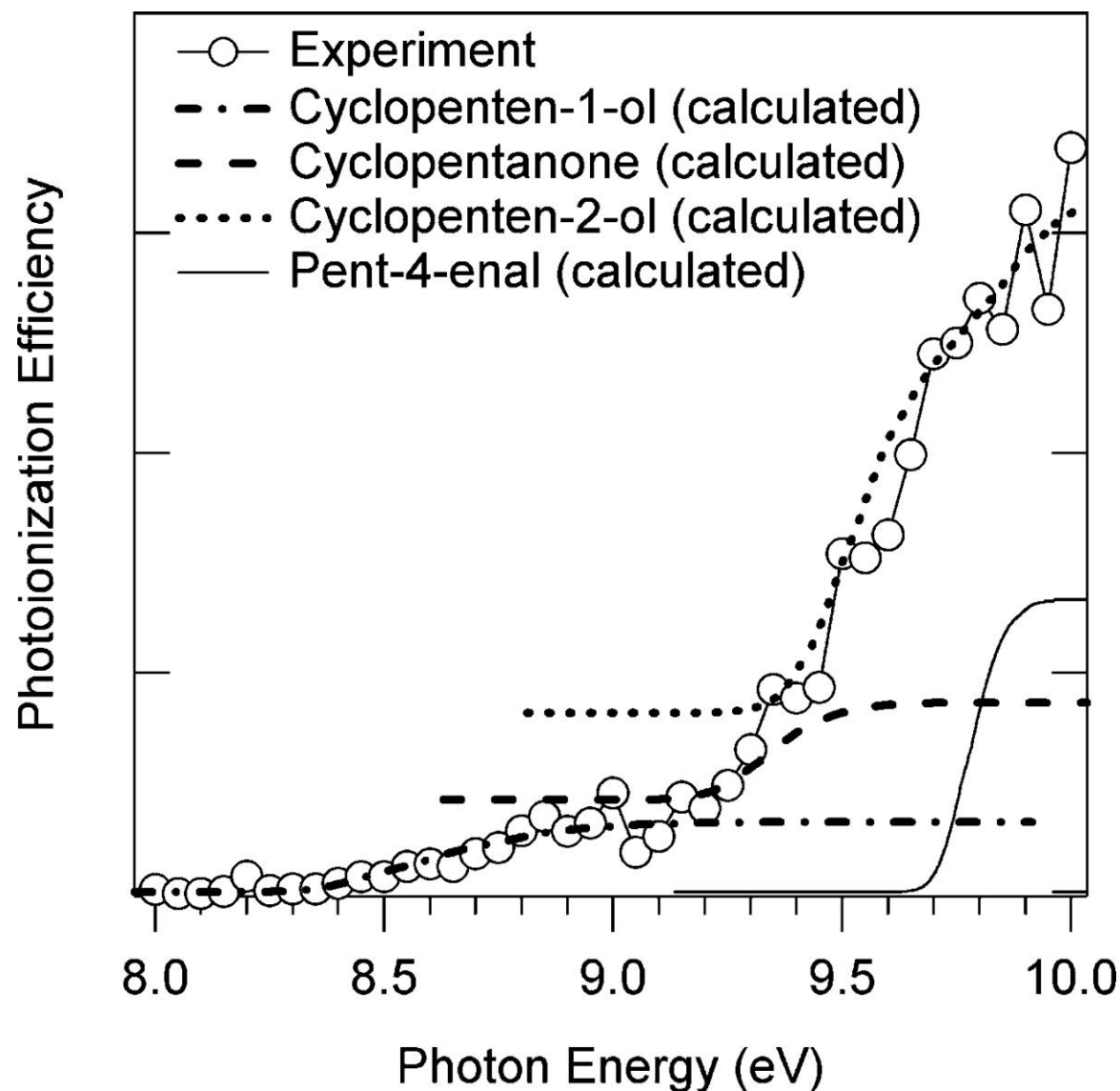Cai et al. (Energy & Fuels, 5550-5568 (2012))

C_4H_8 sensitivity
T_{max} = 1450 K under 5 Torr (gray) and
T_{max} = 1100 K under 760 Torr (black)

Experimental mole fraction profiles (symbols) and modeling results (lines) of nC_4H_9OH pyrolysis at 5 and 760 Torr.

Decomposition of photoionization curves in a flow tube study of cyclopentene oxidation *J. Phys. Chem. A* 2008, *112,* 13444–13451

Schematic decomposition of the best fit to the experimental photoionization efficiency spectrum into the substituent calculated photoionization efficiency curves of the three isomers: 1-c-C_5H_7OH, c-C_5H_8O, and 2-c-C_5H_7OH. The isomeric photoionization efficiency curves are scaled by their weighting in the fit to the overall spectrum and vertically displaced for clarity.

Static reactors: Early studies of alkane oxidation kinetics and mechanism by Baldwin, Walker and co-workers

- The techniques rely on end product analysis using gas chromatography. Three techniques were used:
  - Addition of small amounts of alkane, RH, to a slowly reacting $H_{2+}O_2$ mixture at ~ 750 K allowed measurements of, e.g. OH, H, HO_2 + RH. $H_2 + O_2$ provides a well-controlled environment containing the radicals. (JCS Faraday Trans 1., 1975, 71, 736)
  - Oxidation of aldehydes (550 – 800 K). Aldehydes act as a source of alkyl radicals, e.g. $2\text{-}C_3H_7$ from $2\text{-}C_3H_7CHO$ (JCS Faraday Trans 2., 1987, 83, 1509)
  - Decomposition of tetramethylbutane (TMB) in the presence of O_2. System acts as a source of $HO_{2.}$ (JCS Faraday Trans 1., 1986, 82, 89)

Examples from the $H_2 + O_2$ system

# Reminder Interaction of elementary reactions in $H_2 + O_2$

- There are three ignition (explosion) limits. In each case, there is a competition between a termination reaction (removing radicals, decelerating the rate) and a branching reaction (accelerating the rate)

- First limit – competition between termination at the wall e.g. $H \rightarrow$ wall (rate $\uparrow$ as pressure $\downarrow$) and $H + O_2 \rightarrow OH + O$.

- Second limit – competition between $H + O_2 + M \rightarrow HO_2 + M$ (rate $\uparrow$ as pressure $\uparrow$) and $H + O_2 \rightarrow OH + O$. HO_2 is an unreactive radical and reacts mainly by $HO_2 + HO_2 + M \rightarrow H_2O_2 + M$.

- Third limit – H_2O_2 dissociates generating OH radicals ($H_2O_2 + M \rightarrow 2OH$) and propagation and branching recommence
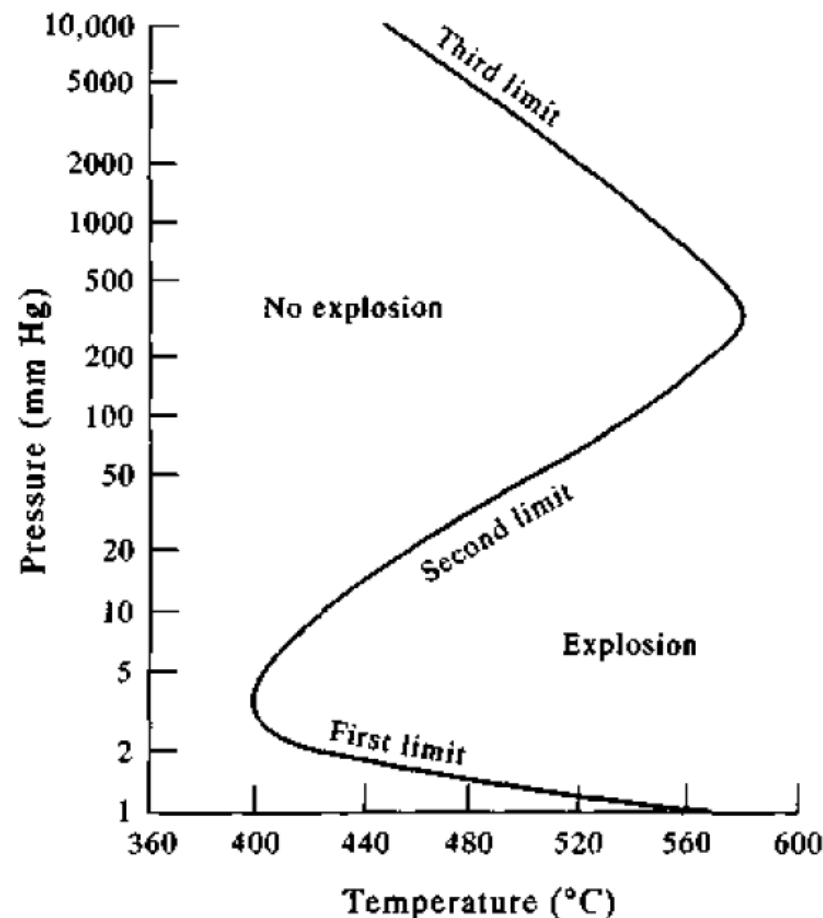
Hydrogen oxygen system

- Review by Miller et al. (Proc Comb. Inst., 2005, 30, 45-88)

- Slide shows sensitivities for ignition delay times (8% H_2, 2% O_2, 90% Ar, 1 bar).

- Note the significance of the $H + O_2$ branching step, the termination step $H + O_2 + M$ and the $H + HO_2$ steps

H + O$_2$ → OH + O
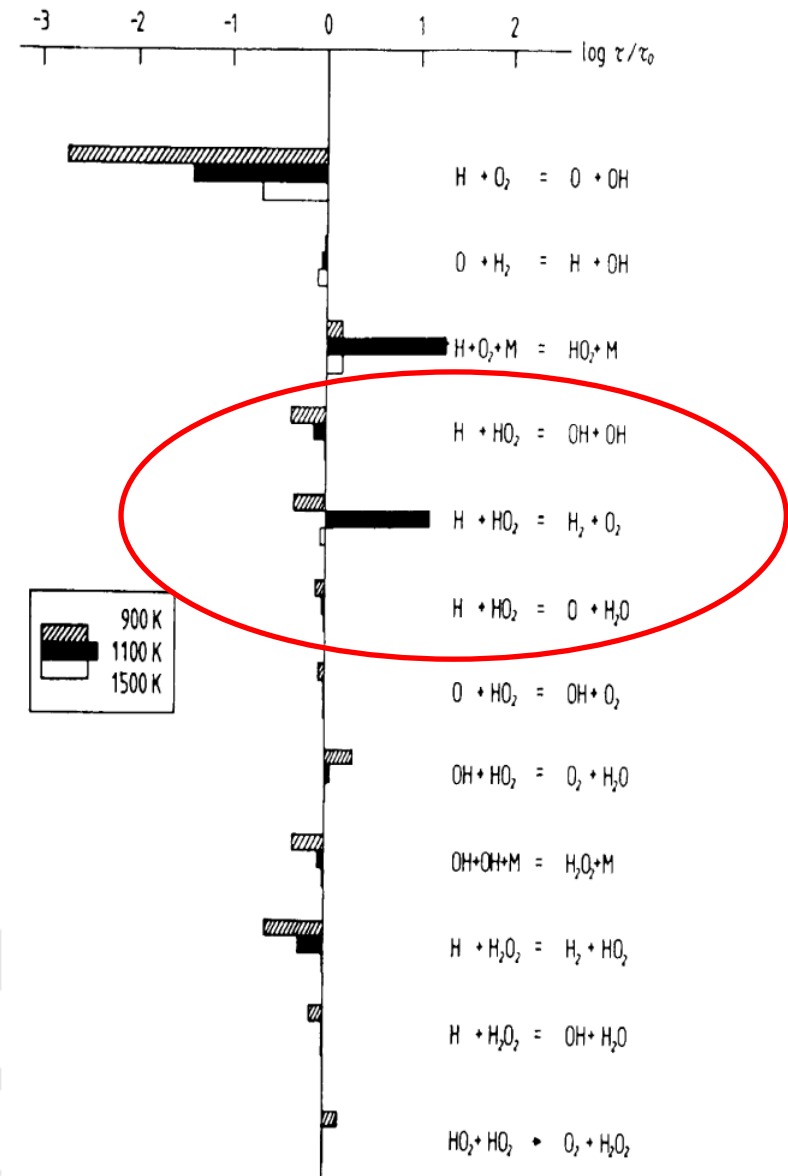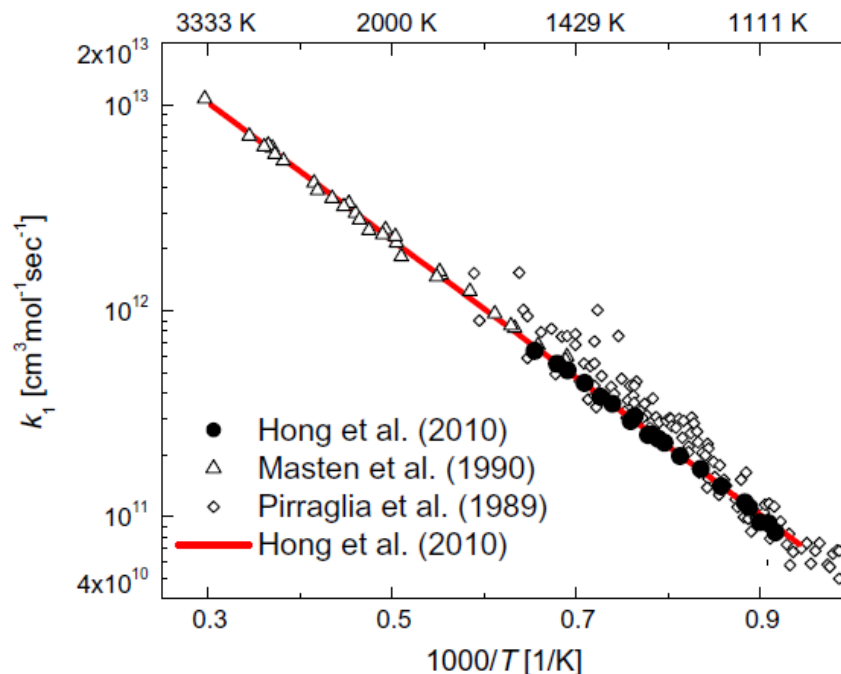

- From Hong et al., shock tube measurements. Comb Flame 2011, 158,633, $k = 1.7 \times 10^{-10} \exp(-7670/T)$ (1100 – 3370 K). Uncertainty ± 10%.
- See Burke et al. Int J Chem Kinet, 2012, 44, 444, who support the rate coefficient
- See discussions on evaluation in later lectures.

Reverse reaction: O + OH → H + O$_2$
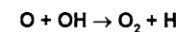
- Studied 150 – 500 K, mainly by discharge flow / laser flash photolysis.

- Not of great importance in combustion, but provides additional information on reverse reaction through thermodynamics

- k = 2.00x10^{-10} T$^{-0.352}$ exp(113/T) cm^3 molecule^{-1} s^{-1} over the range 250–3000 K.

- Δlog k = ± 0.2 over the range 250–3000 K.

O + OH → O$_2$ + H
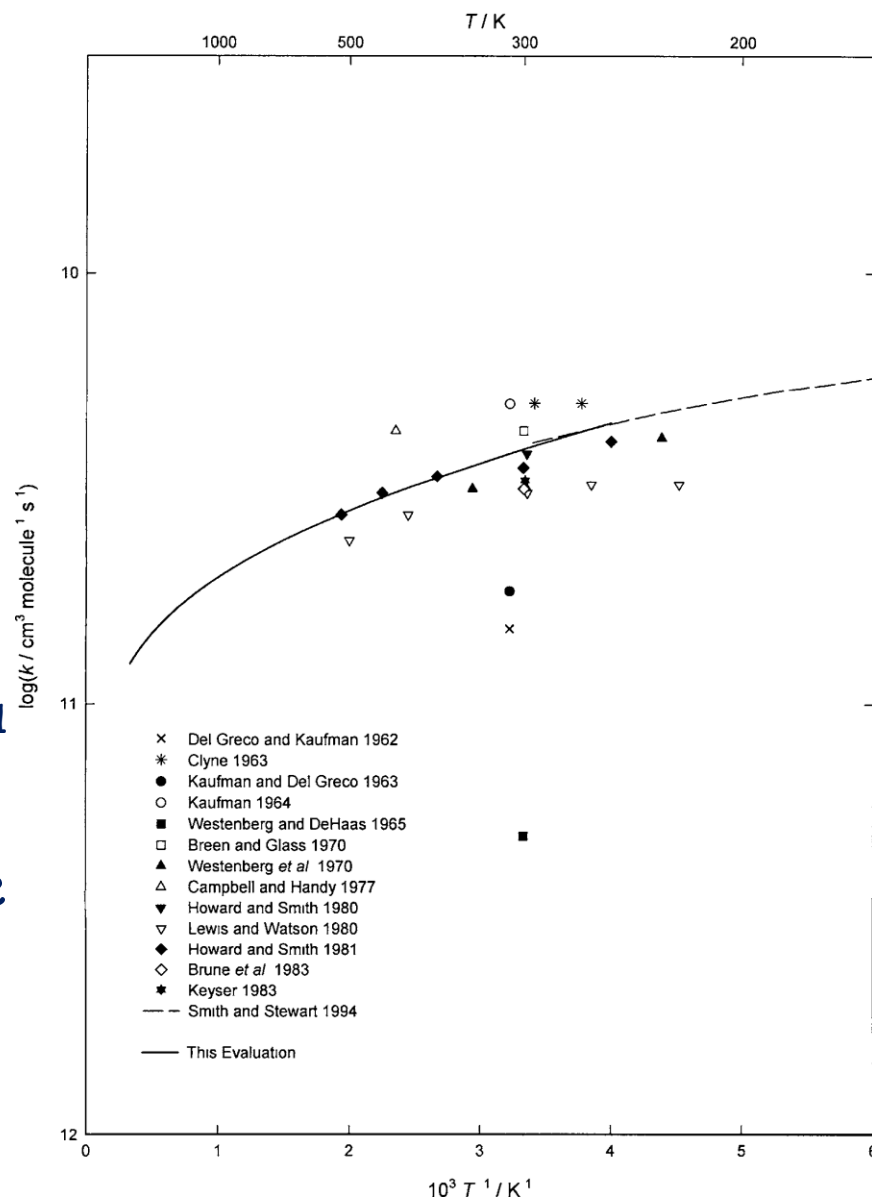
Second branching step
$O + H_2 \rightarrow OH + H$

- Sutherland et al. (21st Symp(Int) Comb, 1986, 929). Used flash photolysis, monitoring O by resonance fluorescence, and shock tube, generating O by flash photolysis of NO and monitoring by ARAS. ()

- Davidson and Hanson (Comb and Flame, 1990, 82, 445) used shock tube, generating O by laser flash photolysis of NO and by pyrolysis of N_2O. O monitored by ARAS. 2120 – 2750 K.

- Javoy et al, (Int J Chem Kinet, 2000, 32, 686 and Expt. Thermal Fluid Sci. 2003, 27, 371). ARAS 2021 – 3356 K.
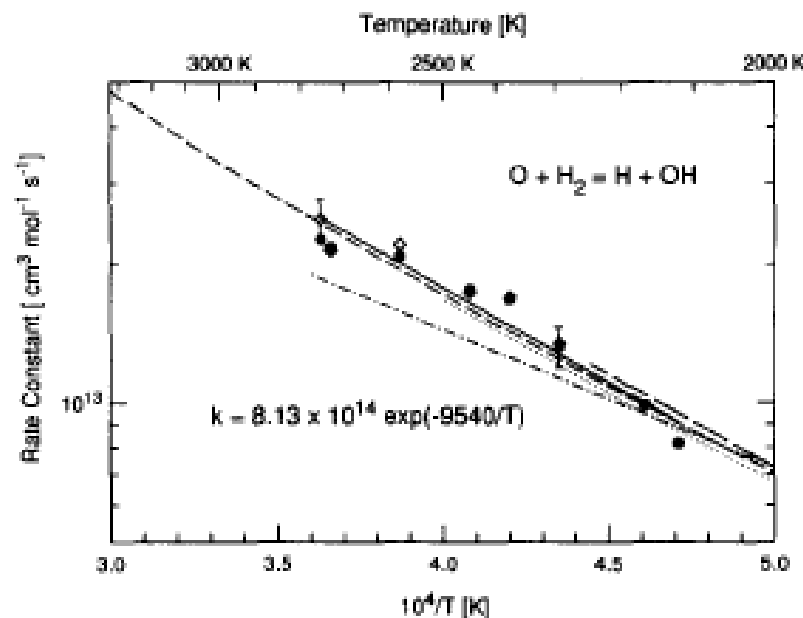
Fig. 2. Arrhenius diagram: $O + H_2 \rightarrow OH + H$. Filled circles—data derived from photolysis method. Open diamonds—data derived from pyrolysis method. Error bars represent ± 10%. Solid line—best fit to present data. Dotted line—Sutherland et al. [8]. Dashed line—Nataranjan and Roth [9]. Dot-dashed line—Pamidimukkala and Skinner [10]. Long-dashed line—Shin et al. [11].

Sutherland et al

H + O$_2$ + M → HO$_2$ + M

- Termination step at lower T, converting reactive H into less reactive HO$_2$. Acts as a route to branching through formation of H$_2$O$_2$ through HO$_2$ + HO$_2$ (and HO2 + RH in hydrocarbon combustion)

- Reaction is at the third order limit except at higher pressures.

- Michael et al. J. Phys. Chem. A 2002, 106, 5297-5313 used flash photolysis at room T for a wide range of third bodies, and a shock tube at higher T for Ar,. O$_2$ and N$_2$. Showed that H$_2$O is an unusually effective third body.

- Detailed analysis of collision frequencies and energy transfer parameters.

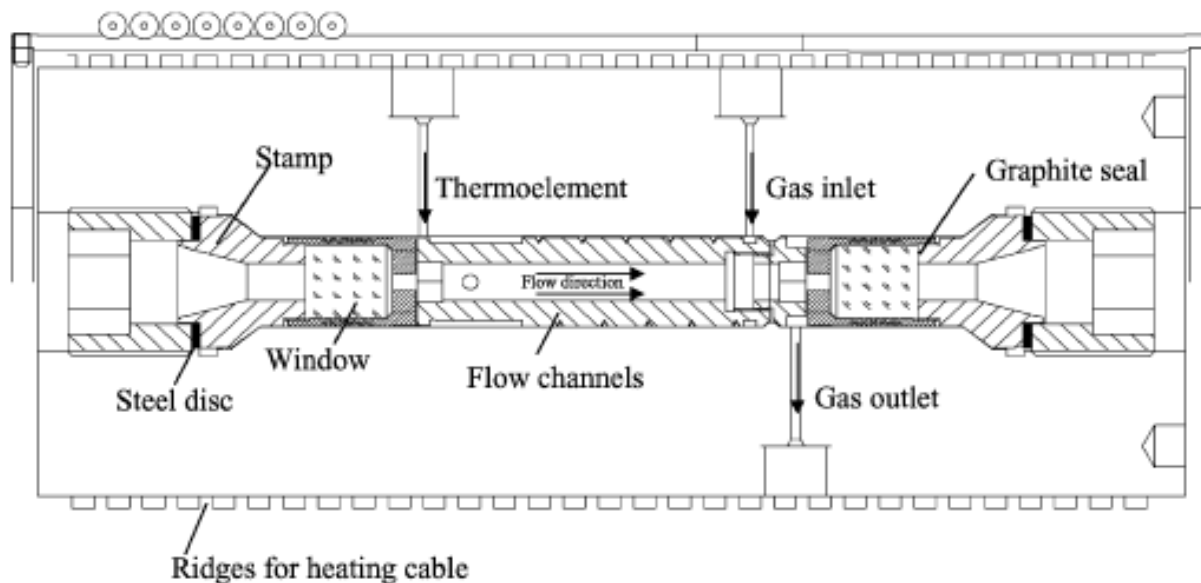$$A + B \rightleftharpoons AB^* \rightarrow AB$$

$$k = \frac{k_0[\text{M}]k^\infty}{k^\infty + k_0[\text{M}]}$$
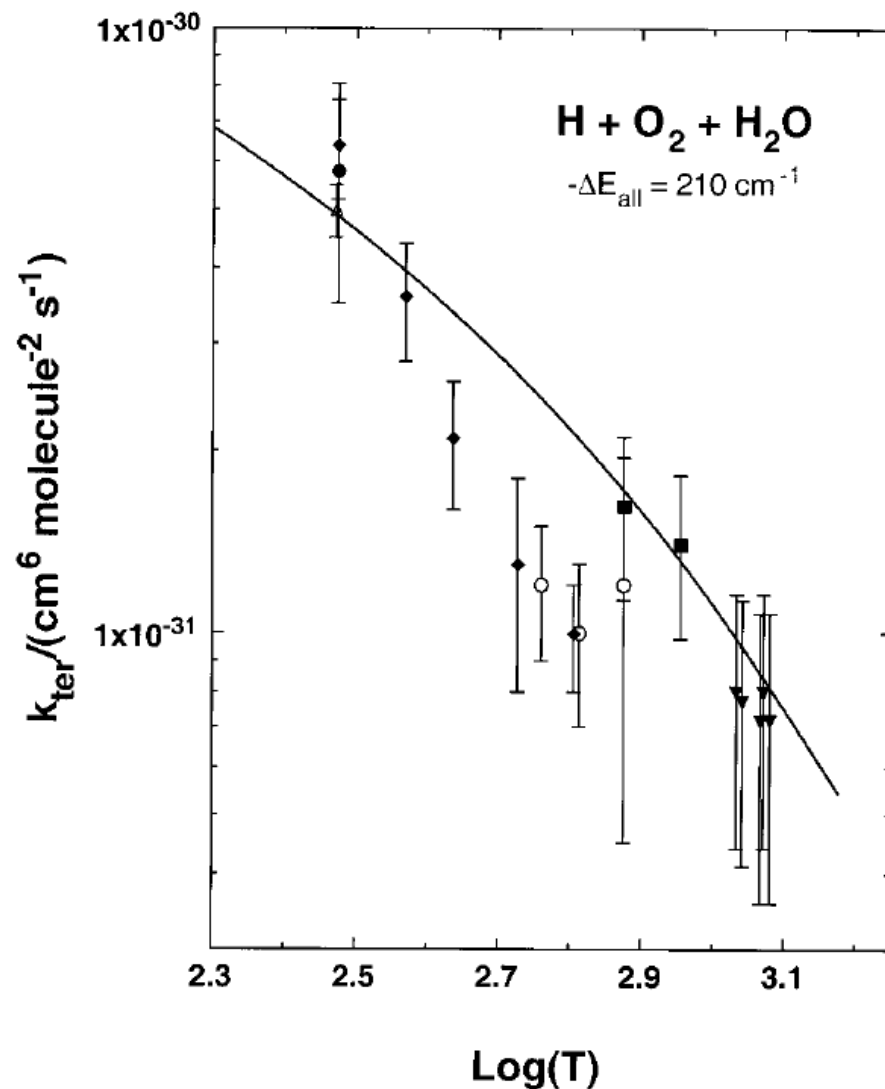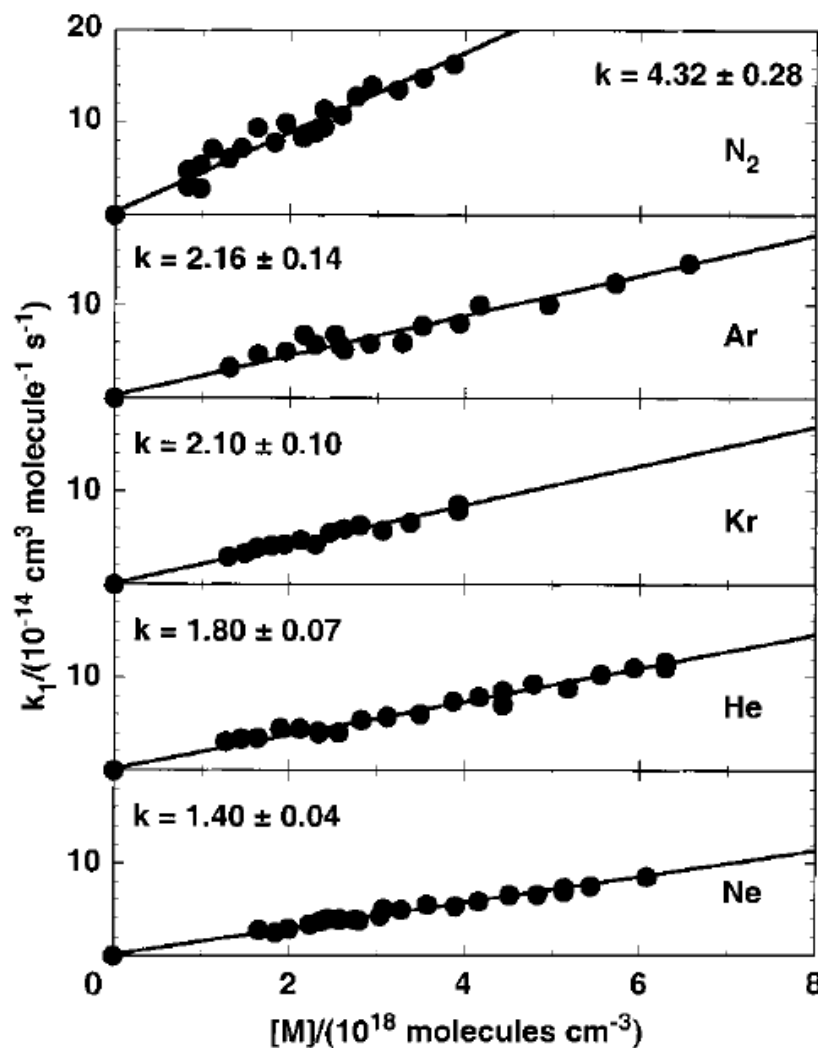
H + O₂ + M → HO₂ + M

Units of k: 10^{-32} cm^6 molecule^{-2} s^{-1}

High pressure pulsed photolysis / flow reactor
Fernandes et al. Phys. Chem. Chem. Phys., 2008, 10, 4313–4321

- H + O_2 + M → HO_2 + M, 300 – 900 K, 1.5 – 950 bar
- H from photolysis NH_3 at 193 nm
- HO_2 detected by absorption spectroscopy at 230 nm.
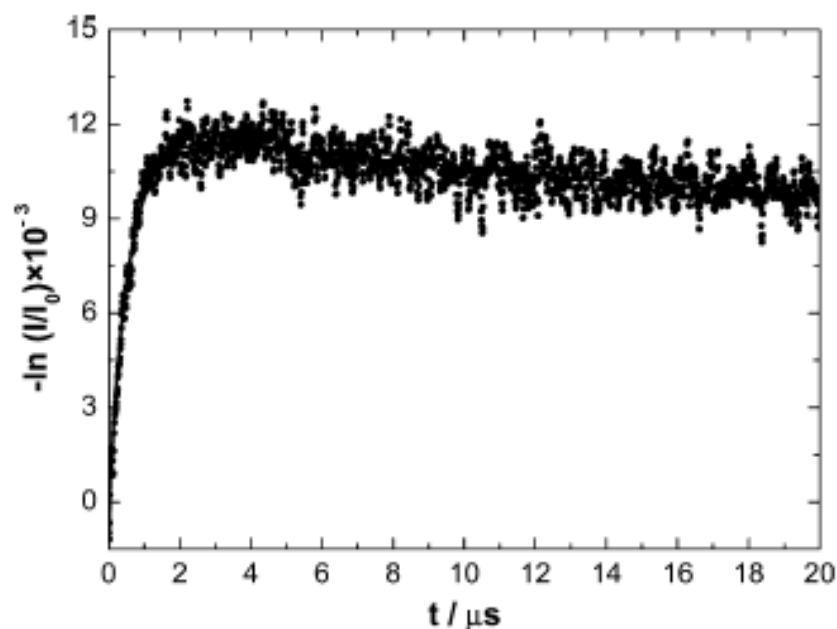- At these higher pressures, the reaction moves into the fall-off region

H + O$_2$ + M → HO$_2$ + M

Fig. 2 Absorption–time profile of HO$_2$ ($\lambda = 230$ nm, $T = 600$ K, $p = 300$ bar, M = N$_2$).
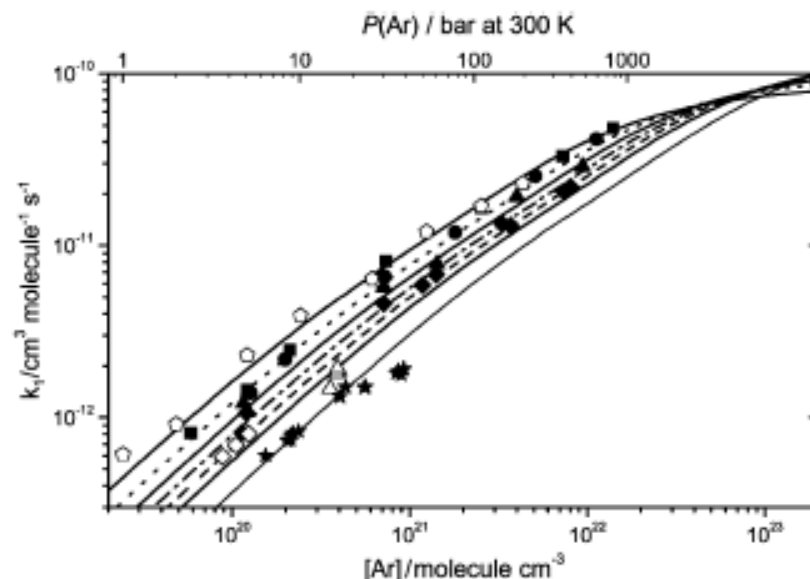
Fig. 5 Falloff curves for the recombination H + O$_2$ (+Ar) → HO$_2$ (+Ar) (representative upper pressure scale for 300 K; $T/K = 300$ (■), 400 (●), 500 (▲), and 600 (♦) from this work; 300 (⬠, ref. 19), 820 (◇, ref. 20), 1200 (★, ref. 22), and 1325 (△, ref. 21); the fitted curves at left from top to bottom are for $T/K = 300, 400, 500, 600, 700, 820,$ and 1200, resp.).

H + O$_2$ + M → HO$_2$ + M

- Data for different third bodies and temperatures can be rationalised and placed on the same plot using reduced falloff curves. Requires calculation of high pressure limiting rate coefficient (that isn't accessible to experiment for this reaction.)
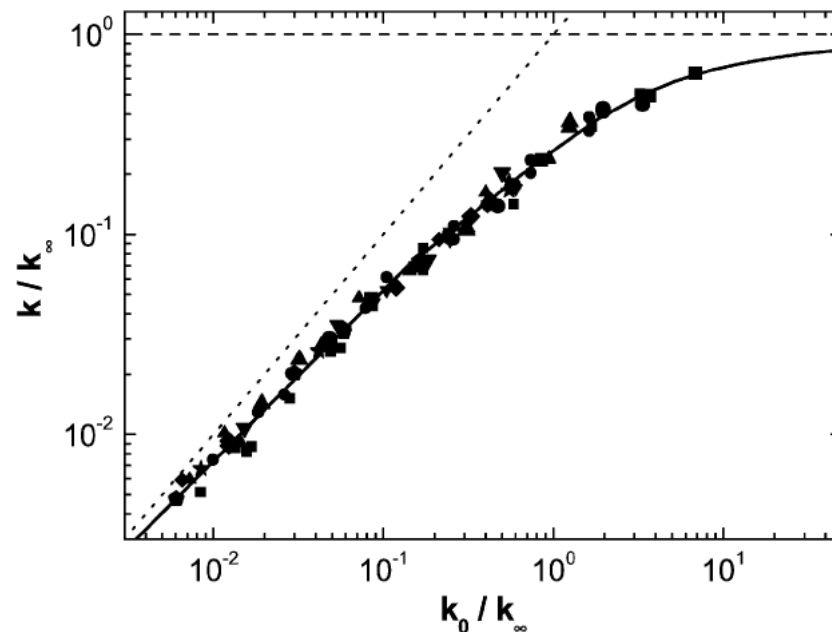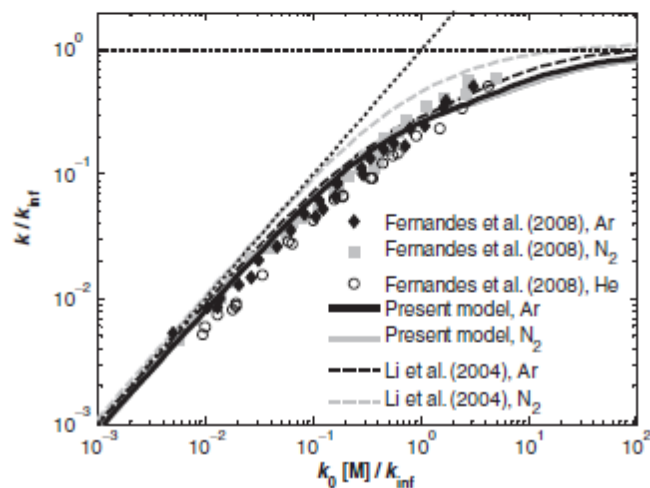

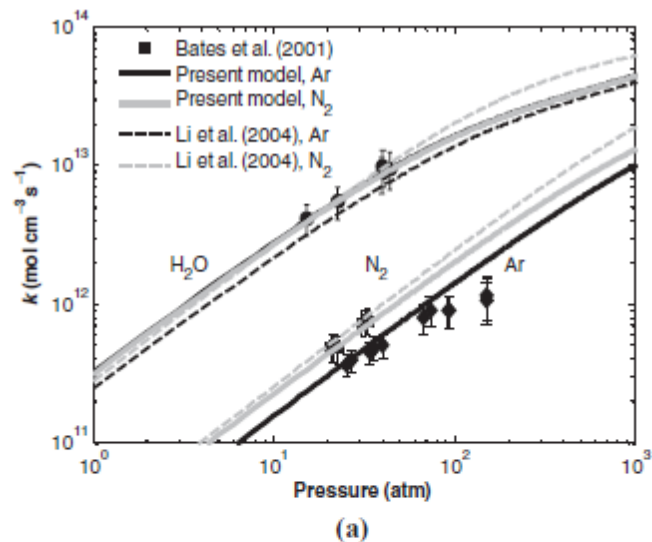Fig. 7 Doubly reduced falloff curves for the recombination H + O$_2$ (+M) → HO$_2$ (+M) in the bath gases M = He, Ar, and N$_2$ (experimental points from this work from Tables 1–3; T/K = 300 (■), 400 (●), 500 (▲), 600 (▼), 700 (♦), 800 (★), and 900 (⬠), see text).

- See paper for detailed discussion of Troe parameters (next slide), uncertainties etc.

Troe Fitting

Need to represent k(T,P) for Global Models

Standard is Troe Fitting

$$k(T,p) = \frac{k_0[M]k^{\infty}}{k^{\infty} + k_0[M]} F \qquad \log_{10} F = \frac{\log_{10} F_{cent}}{1 + \left[\dfrac{\log_{10}(p^*) + c}{N - d\left(\log_{10}(p^*) + c\right)}\right]^2}$$

$$p^* = k_0[M]/k^{\infty} \qquad d = 0.14$$

$$c = -0.4 - 0.67\log_{10} F_{cent} \qquad N = 0.75 - 1.27\log_{10} F_{cent}$$

Fit k_0 & k^{∞} to modified Arrhenius $\qquad k_0 = A_0 T^{n_0} \exp(-E_0/T)$
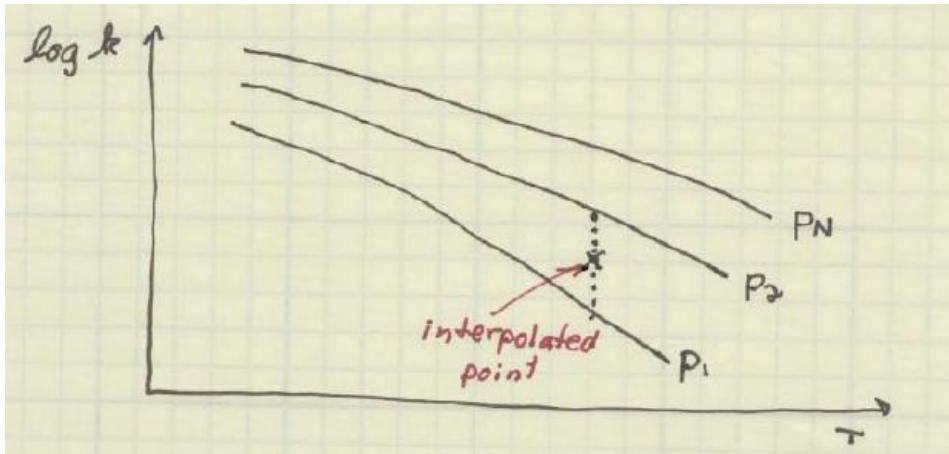
Fit F_{cent} to:

$$F_{cent} = (1-a)\exp\left(-T/T^{***}\right) + a\exp\left(-T/T^{*}\right) + \exp\left(-T^{**}/T\right)$$

Alternative generalized polynomial approach: PLOG

Gou, J.A. Miller, W. Sun and Y. Ju, http://engine.princeton.edu, 2011.

$$k(T, p_i) = \sum_{j=1}^{M} A_{ij} T^{nij} \exp\left(-\frac{E_0^{ij}}{RT}\right),$$

$$i = 1, \ldots N, \quad M \geq 1$$

at a set of pressures, $p = p_1, p_2, \ldots p_N$. M (which determines the order of the polynomial)and N are user specified numbers. The extrapolation is bounded by the two pressure limits, p_1 and p_N.
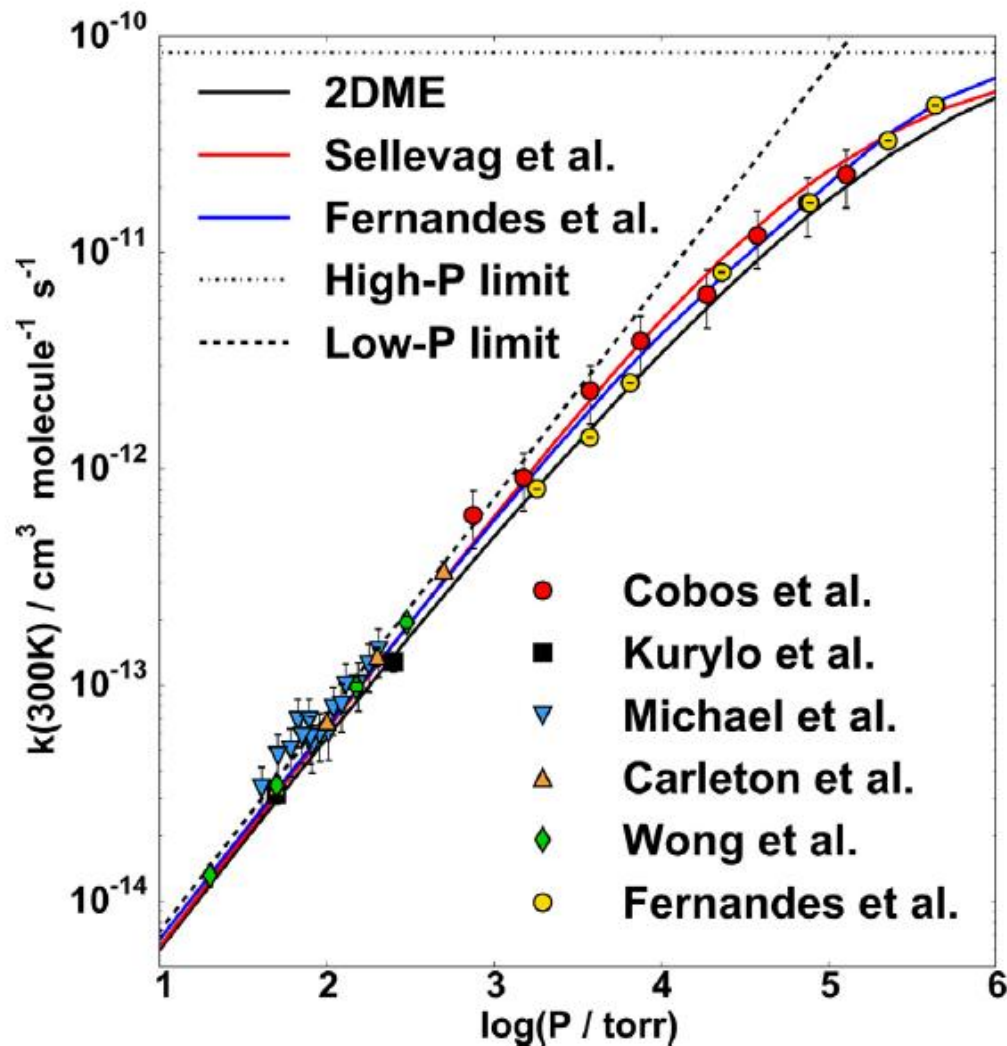

Linear extrapolation of lg$k$ vs lg$p$ is used to determine k at other p.

Code available, programmed in CHEMKIN PRO – see link above

Latest comparison of purely *a priori* theory and experiment, M=Ar
Klippenstein, Proc Comb Inst, 2017, 36, 217

1. solid black line: *a priori* energy transfer based 2DME predictions, coupled with dynamically corrected variable reaction coordinate TST based on a high accuracy well-validated MRCI PES

2: solid red line: fitted master equation results of Sellevag et al. J Phys Chem A 2008, 112, 5085.

3. solid blue line: analytic fit of Fernandes et al. Phys Chem Chem Phys 2008, 10, 4313

HO$_2$ + HO$_2$ $\rightarrow$ H$_2$O$_2$ + O$_2$

- < 800 K. Flash photolysis, absorption spectroscopy
- Open circles: shock tube, absorption spectroscopy (Kappel et al, Phys Chem Chem Phys, 2002, 4, 4392)
- Reference 5: Hippler et al. J Chem Phys 1990, 93, 1755
- Significant disagreement > 1000 K
- Burke etal. 'Difficult to discern which, if any, (of the high T) determinations is reliable.' More measurements needed under combustion conditions.
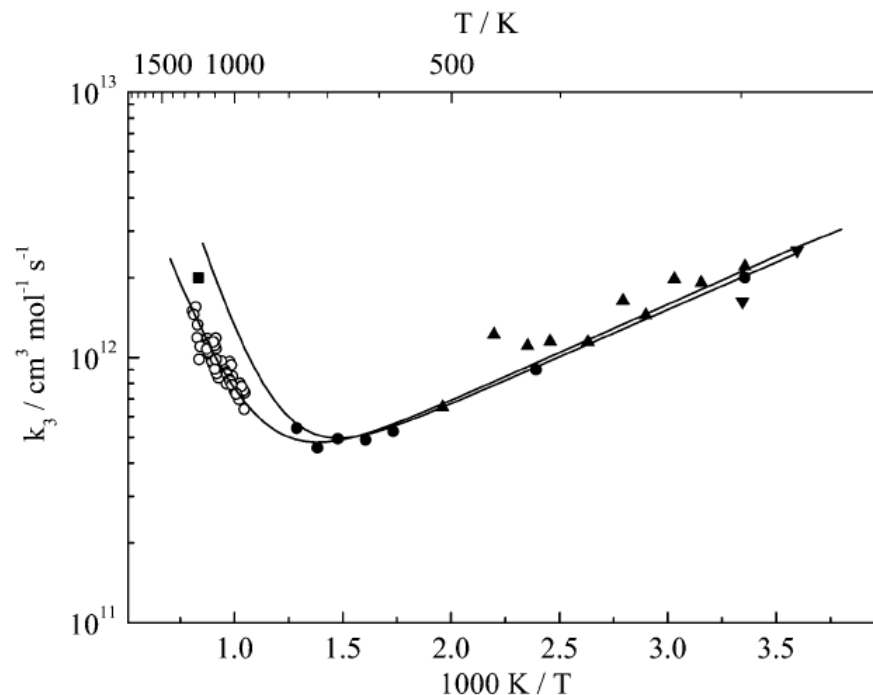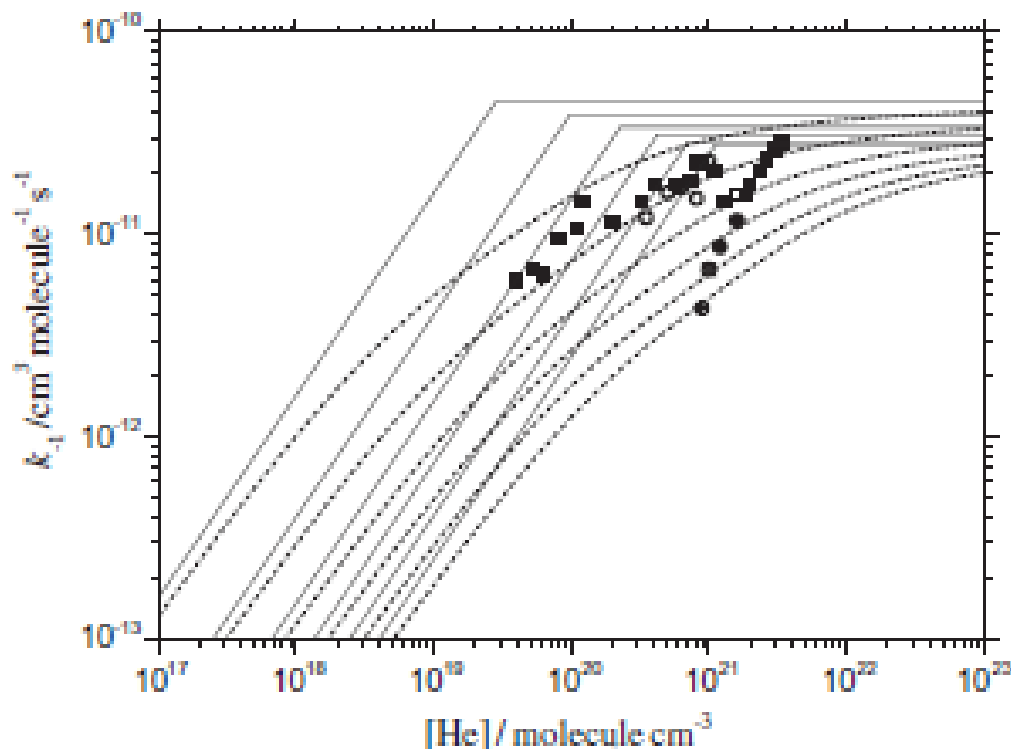- See Topic 3 - Theory

Fig. 10 Rate constants k_3 (■: ref. 2, ▲: ref. 35, ▼: ref. 36, ●: ref. 37, ○ and lower line: this work, upper line: ref. 5).

$H_2O_2 + M \rightarrow 2OH + M$

- Troe, Combustion and Flame 2011, 158, 594–601 The thermal dissociation/recombination reaction of hydrogen peroxide $H_2O_2 \rightleftharpoons 2OH$Analysis and representation of the temperature and pressure dependence over wide ranges.

- Reaction is far from the high pressure limit. To obtain a representation of k(T,p), Troe used the statistical adiabatic channel model to calculate k_∞, using an ab initio surface (Phys. Chem. Chem. Phys. 10 (2008) 3915; J. Chem. Phys. 111 (1999) 2565.

- An important aspect of this work was the use of thermodynamics to relate forward and reverse reactions, using the revised enthalpy of formation of OH – see Wednesday lecture on thermodynamics

Association reaction

- Flash photolysis coupled with saturated LIF.
- Use pressure dependence to separate from $O + H_2O$ channel
- Also problems with secondary reactions (see paper)

Fig. 3. Experimental recombination rate coefficients k_{-1} and their modelled falloff representation (M = He, experimental points from Refs. [30,31] at T/K = 210 (○), 298 (■), 406 (□), 510 (●), 614 (⊘), and 694 (⊕); full lines = modelled limiting low and high pressure rate coefficients from Section 5 of this work; dashed lines = falloff representation by Eq. (3.3) with F_c = 0.37 and N = 1.32).

Reaction is second order in radical, so absolute concentration is needed

Dissociation reaction

Overall reaction

- Flow reactor and static studies at lower T and shock tube measurements above 950 K (see below)
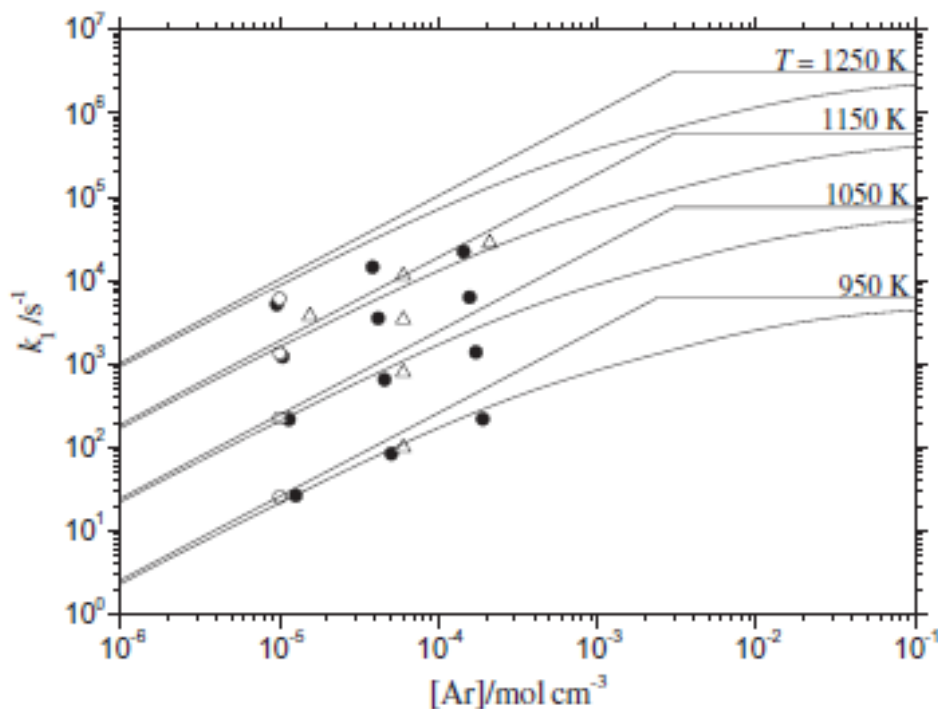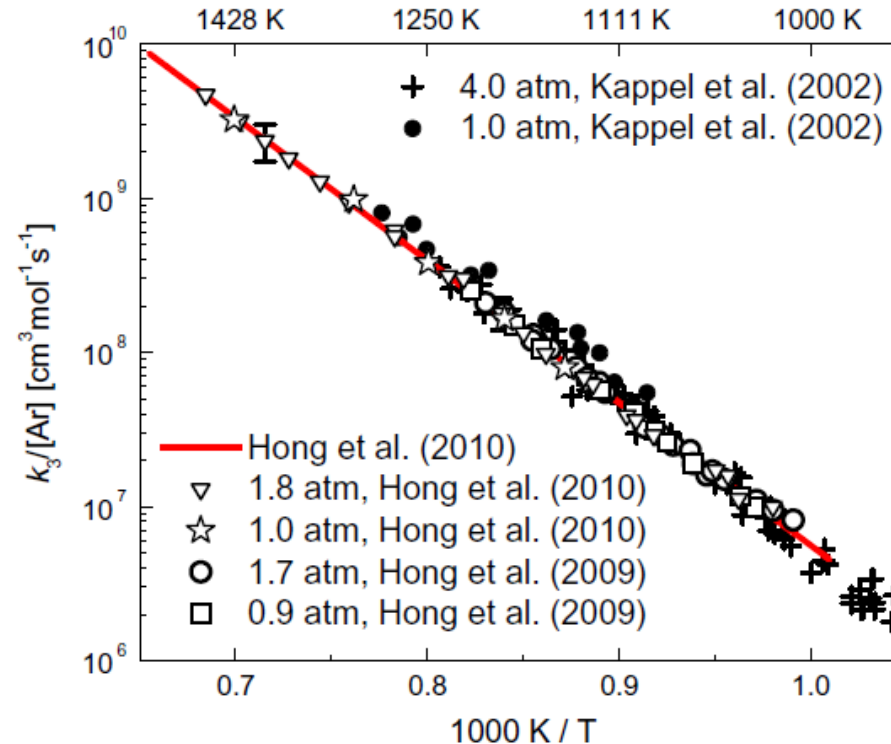
- Dissociation and association data fitted to Troe expression (see earlier) using theoretical high pressure limit and equilibrium constant

H₂O₂ dissociation
Hong et al. Comb Flame 2011, 158, 633

- Data refer to low pressure limit. Used shock tube with laser absorption detection of H_2O and OH