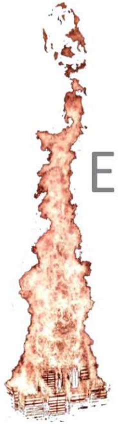
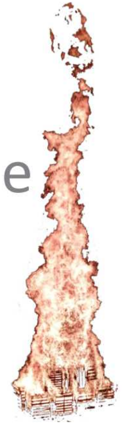
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2018-7926C



Estimating the joint distribution of rate parameters across multiple reactions in the absence of experimental data



Tiernan Casey, Habib Najm

Combustion Research Facility, Sandia National Laboratories, Livermore CA

Sandia National Laboratories

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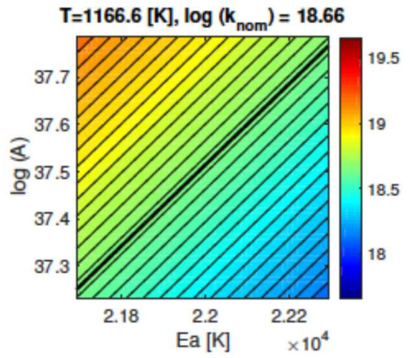
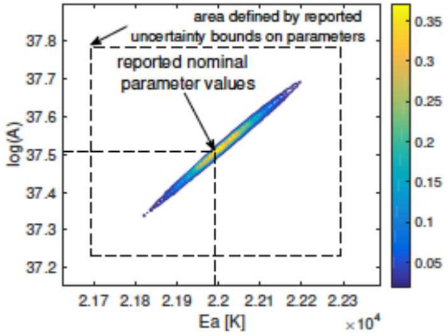
Uncertain chemical model parameters

- chemical kinetic rate parameters (e.g. Arrhenius A, n, E) are uncertain due to the noise and bias in supporting experimental data, motivating uncertainty quantification (UQ)
- UQ hindered by incomplete reporting of uncertainties, e.g. reported uncertainty on A only, or A and E, or error bars on k values for different experiment temperatures
- ideally, using the raw noisy experimental data along with models for the both the kinetics and noise, to learn a joint density on the model parameters. However data are typically missing or unavailable, we only have statistics of the data
- Is it possible to reconstruct the missing data given the available information from the experiment?



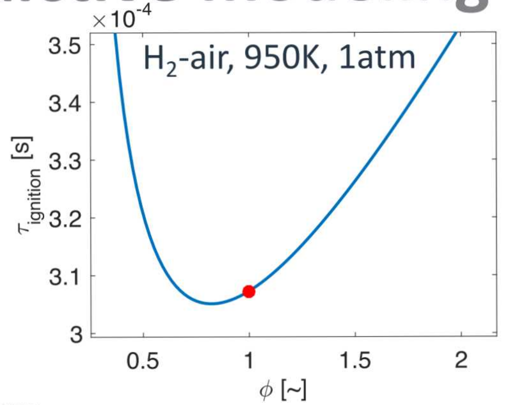


Uncertainty quantification and predictive modeling

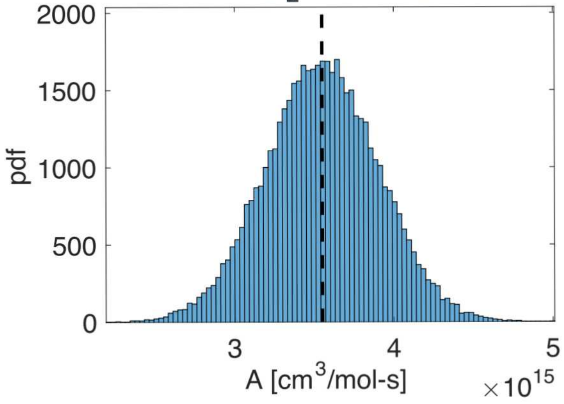
What are the consequences of uncertainty for predictive modeling?

What is the ignition time corresponding to the most likely rate parameter values?

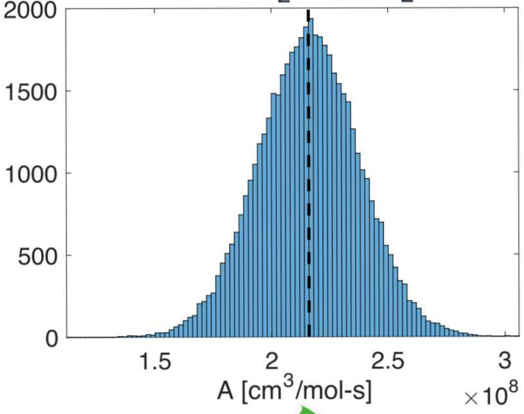
What is the most likely ignition time given the available information about the rate parameters?

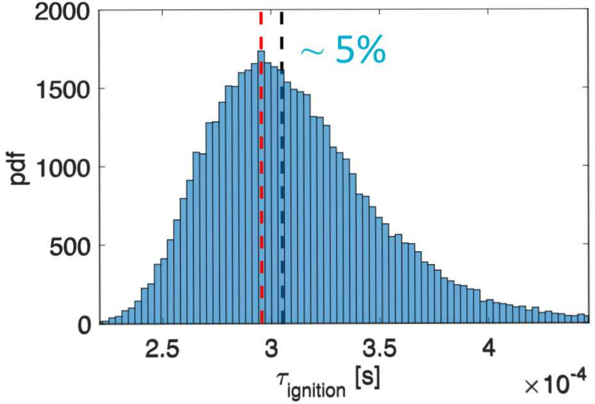


$H+O_2$->$OH+O$



$OH+H_2$->$H+H_2O$

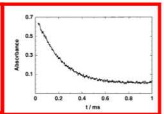




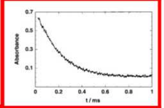
CRF

Chemical kinetic modeling: mechanism

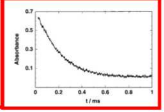
Pirraglia et al. [1990]
shock tube, T



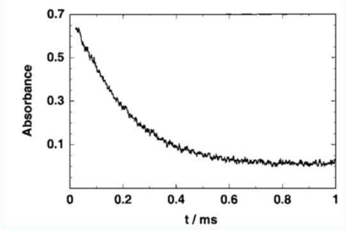
Masten et al. [1990]
shock tube, T>



Du & Hessler [1992]
shock tube, T>>

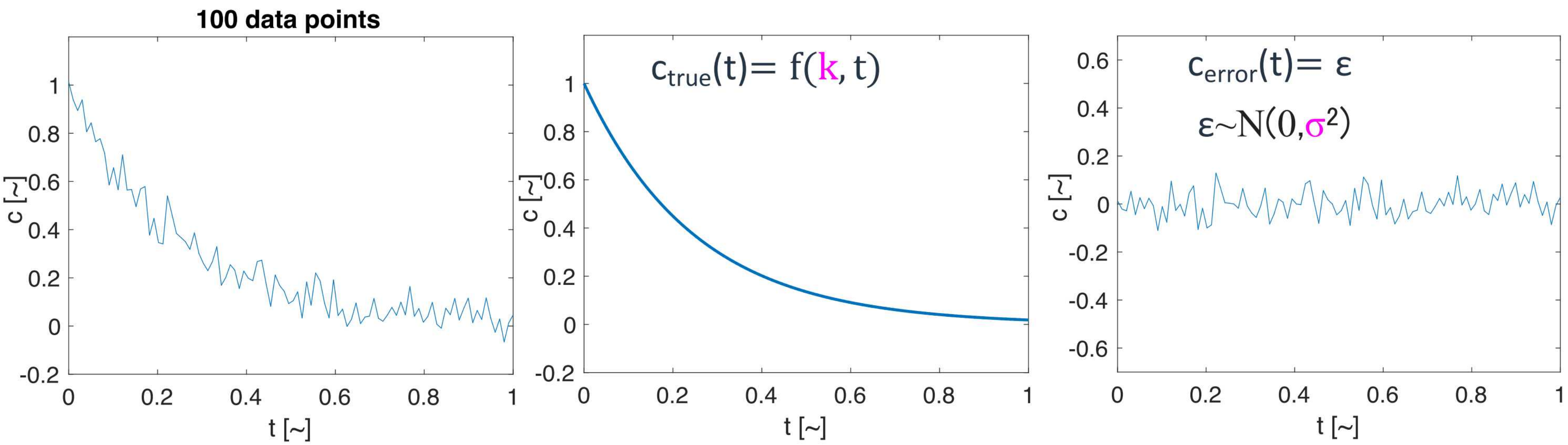


#	Reaction	A	n	E_a	Reference
	H_2/O_2 reactions				
1	$H + O_2 = O + OH$	3.55E+15	−0.40	1.66E+04	[87]
2	$O + H_2 = H + OH$	5.08E+04	2.70	6.29E+03	[88]
3	$H_2 + OH = H_2O + H$	2.16E+08	1.50	3.43E+03	[89]
4	$O + H_2O = OH + OH$	2.97E+06	2.00	1.34E+04	[90]
5	$H_2 + M = H + H + M$	4.58E+19	−1.40	1.04E+05	[81]



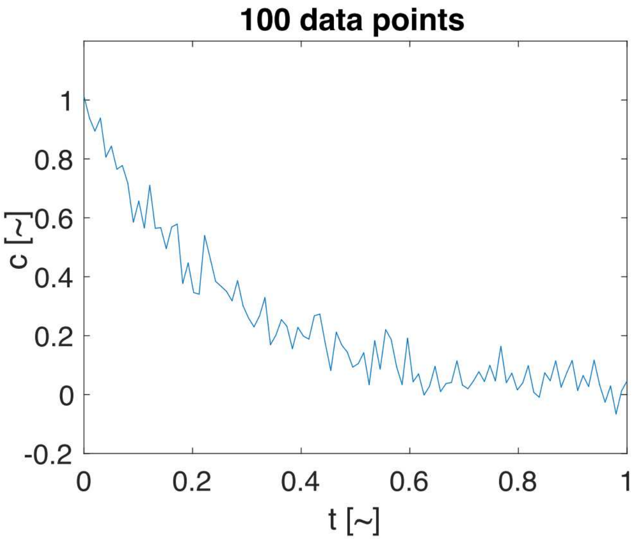
No.	Reaction	A	n	E_a [cal/mol]	Reference
1	$H + O_2 = OH + O$	1.04E+14		15,286	[11]
9	$O + H_2 = H + OH$	3.82E+12		7948	[45]
10	$H_2 + OH = H_2O + H$	2.16E+08	1.50	3.43E+03	
8	$OH + OH = H_2O + O$	3.57E+04	2.4	−2111	[74]
18	$H_2 + M = H + H + M$	5.84E+18	−1.1	104,380	[4]

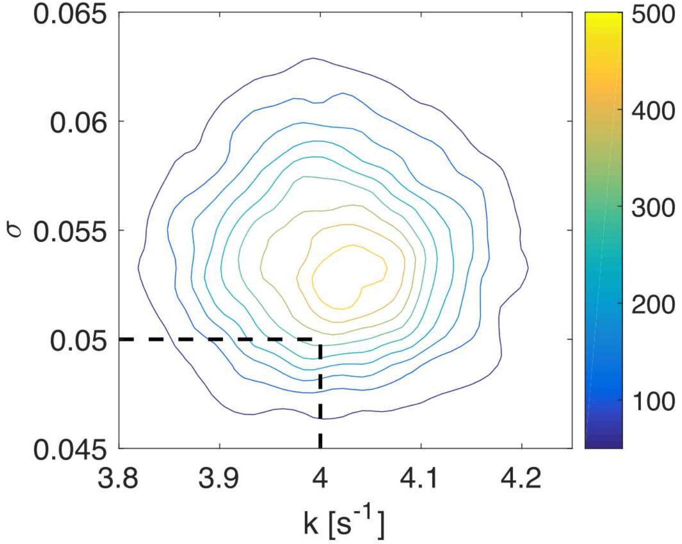
$$c(t) = c_{true}(t) + c_{error}(t)$$



Bayesian inference

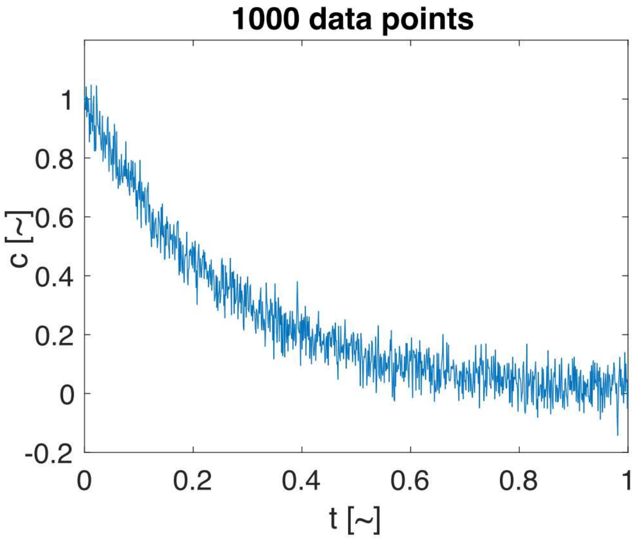
n=100 $\quad p(\mathrm{k}, \sigma | \mathrm{c_n}) \propto p(\mathrm{c_n} | \mathrm{k}, \sigma)$

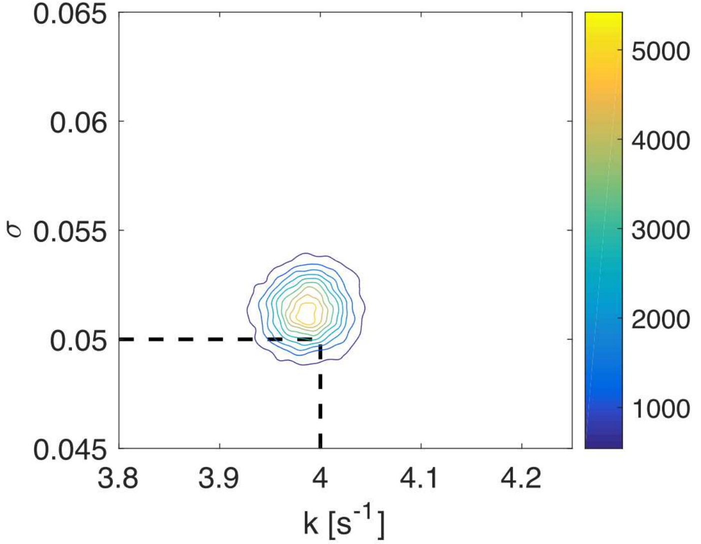




Bayesian inference

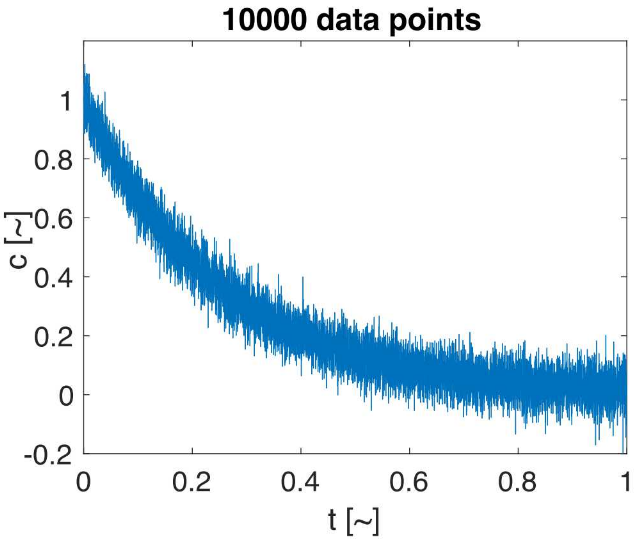
n=1000 $p(\mathrm{k}, \sigma|\mathrm{c_n}) \propto p(\mathrm{c_n}|\mathrm{k}, \sigma)$

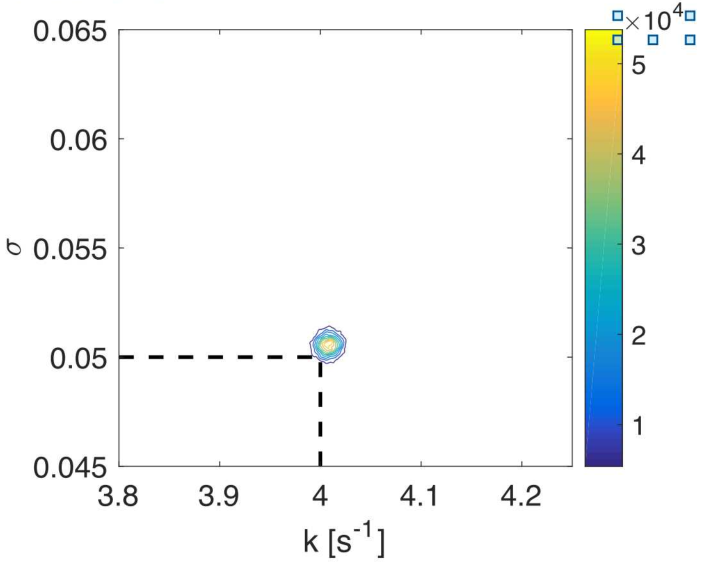




Bayesian inference

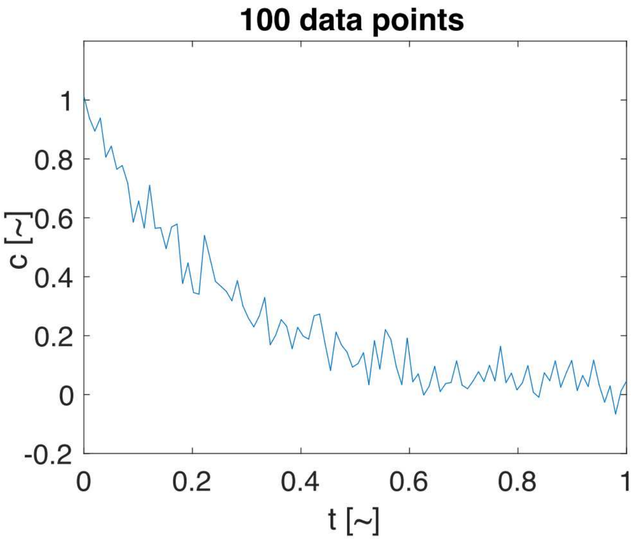
n=10000 $p(\mathrm{k},\sigma|\mathrm{c_n}) \propto p(\mathrm{c_n}|\mathrm{k},\sigma)$

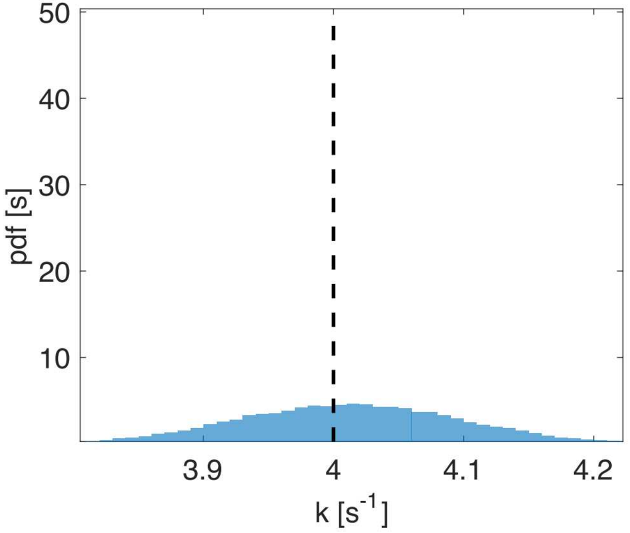




Bayesian inference

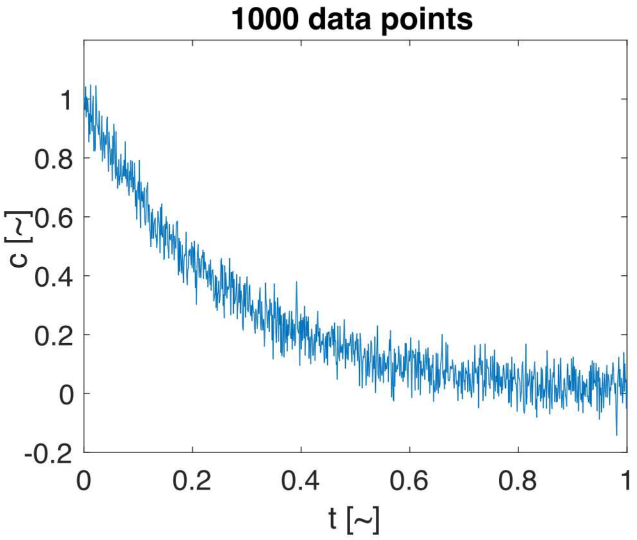
n=100 $\quad p(\text{k}, \sigma|\text{c}_\text{n}) \propto p(\text{c}_\text{n}|\text{k}, \sigma)$

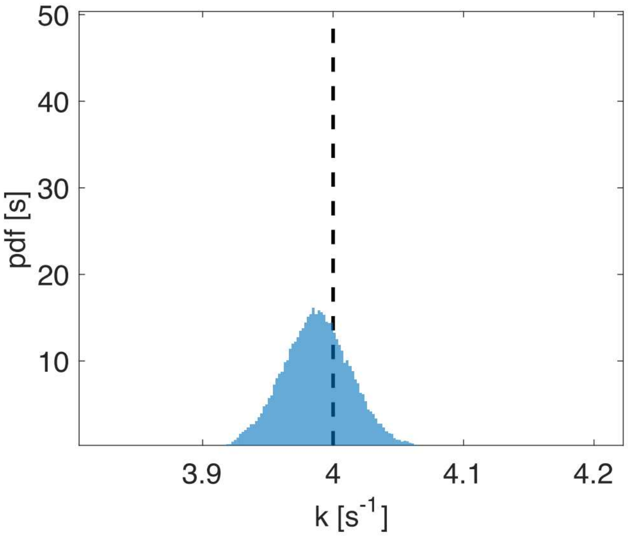




Bayesian inference

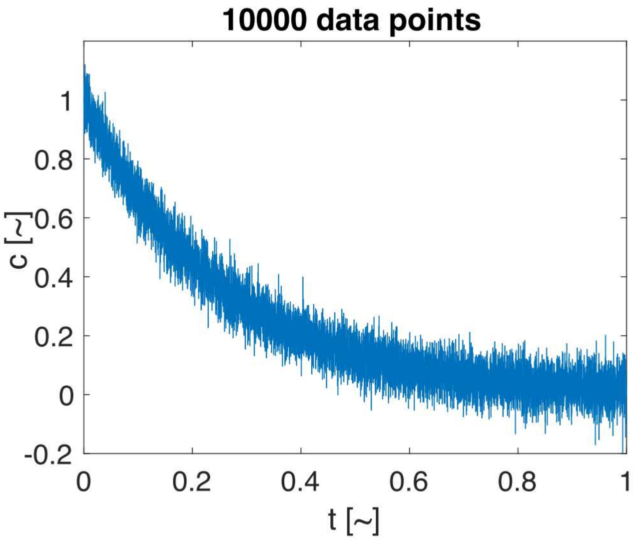
n=1000 $p(\mathrm{k}, \sigma|\mathrm{c_n}) \propto p(\mathrm{c_n}|\mathrm{k}, \sigma)$

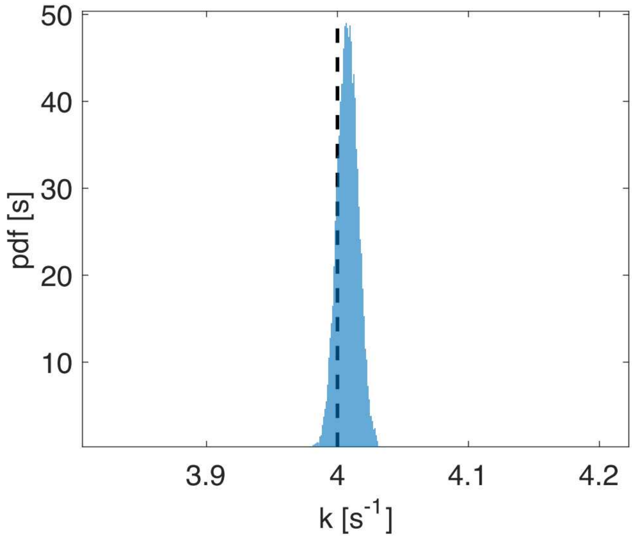




Bayesian inference

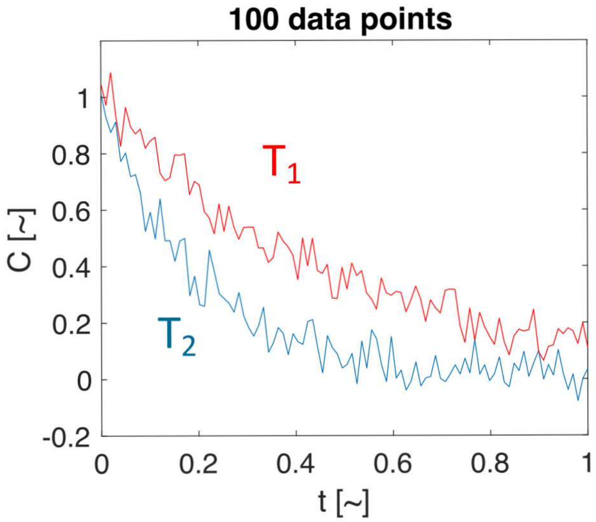
n=10000 $p(\mathrm{k}, \sigma | \mathrm{c_n}) \propto p(\mathrm{c_n} | \mathrm{k}, \sigma)$

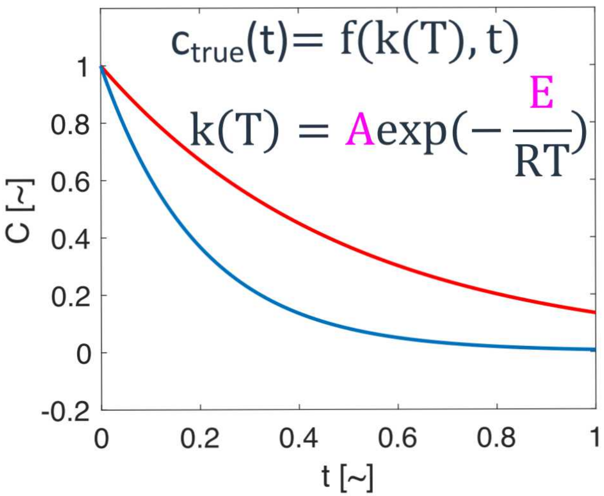


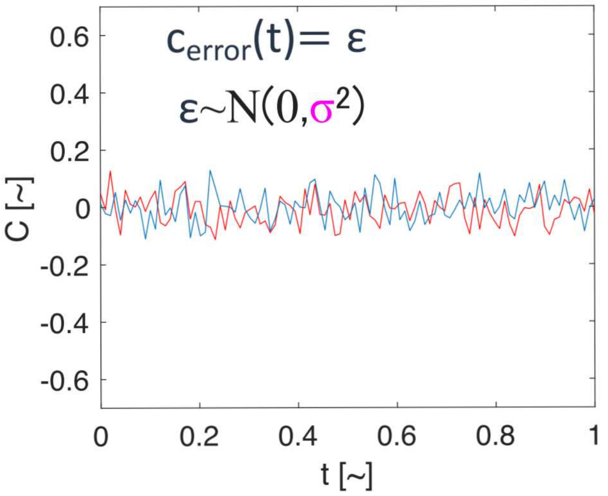


Bayesian inference: hierarchical model

$$c(t) = c_{true}(t) + c_{error}(t)$$

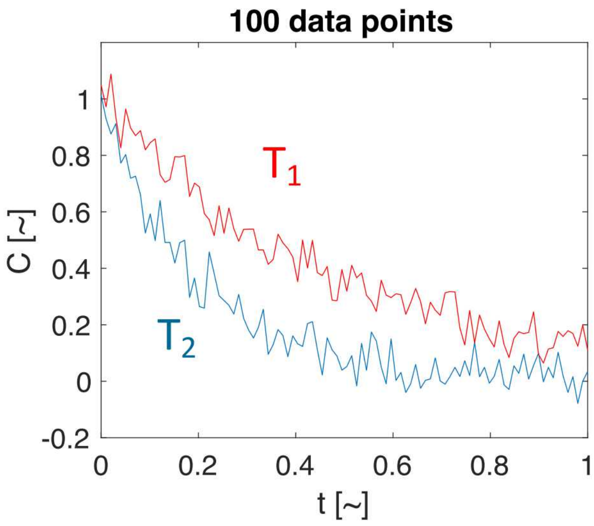


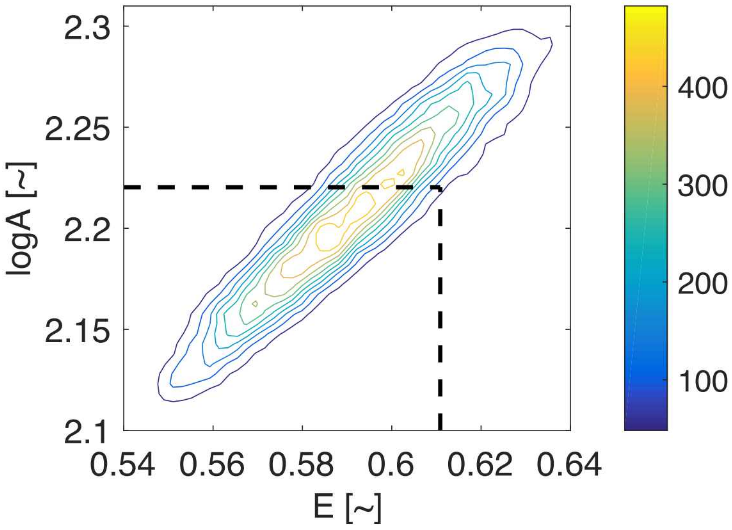




Bayesian inference: hierarchical model

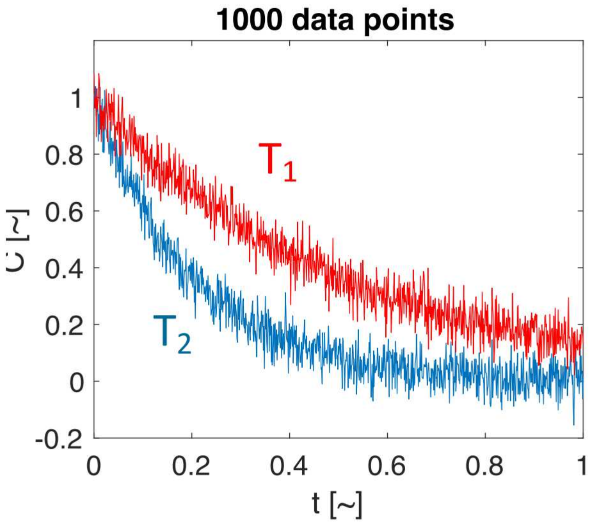
n=100 $\quad p(\mathrm{A}, \mathrm{E}, \sigma | \mathrm{c_n}) \propto p(\mathrm{c_n} | \mathrm{A}, \mathrm{E}, \sigma)$

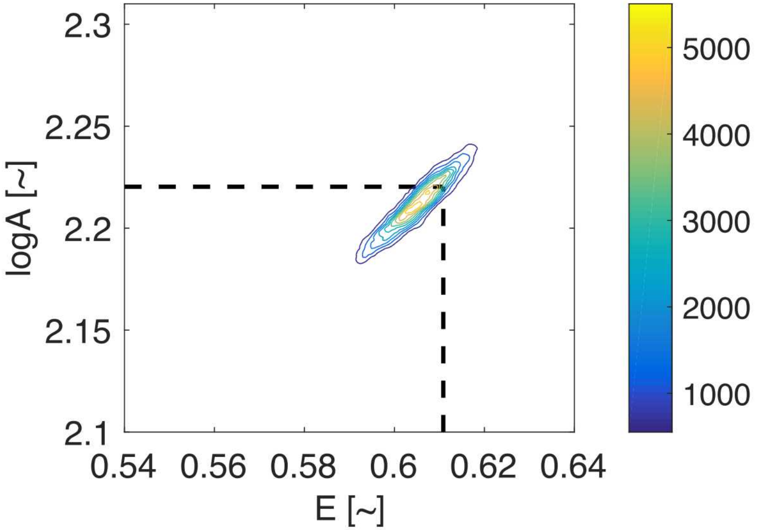




Bayesian inference: hierarchical model

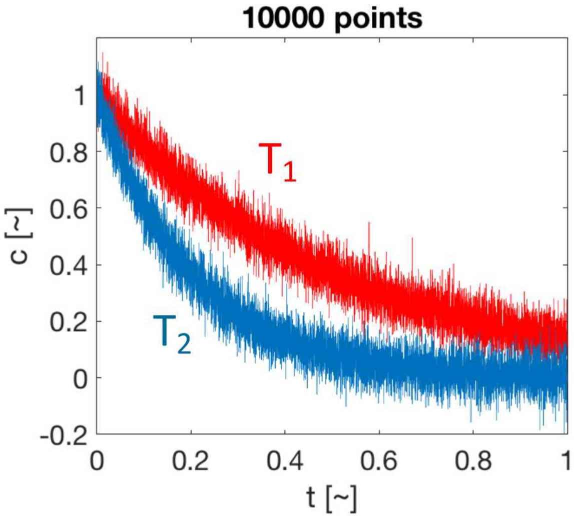
n=1000 $\quad p(A, E, \sigma | c_n) \propto p(c_n | A, E, \sigma)$

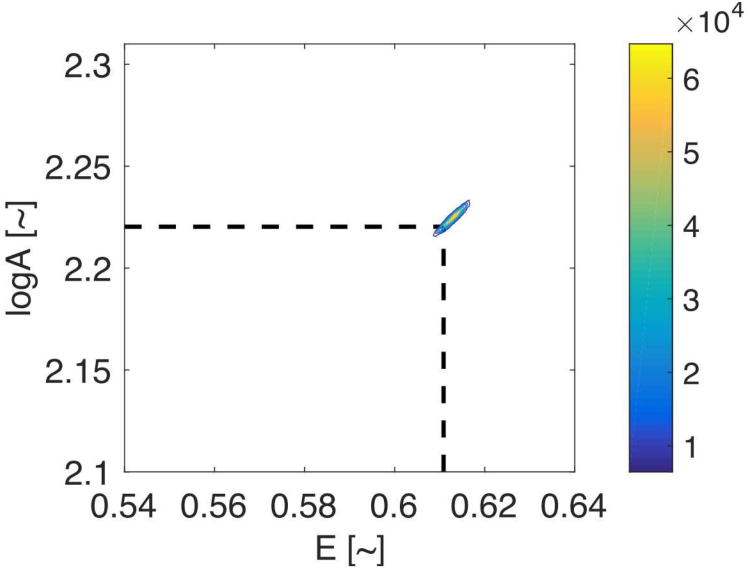




Bayesian inference: hierarchical model

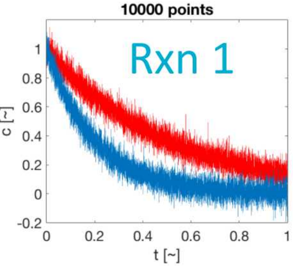
n=10000 $p(\mathrm{A, E, \sigma}|\mathrm{c_n}) \propto p(\mathrm{c_n}|\mathrm{A, E, \sigma})$

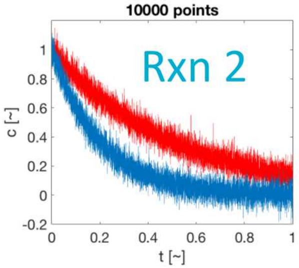


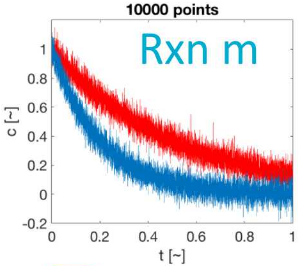


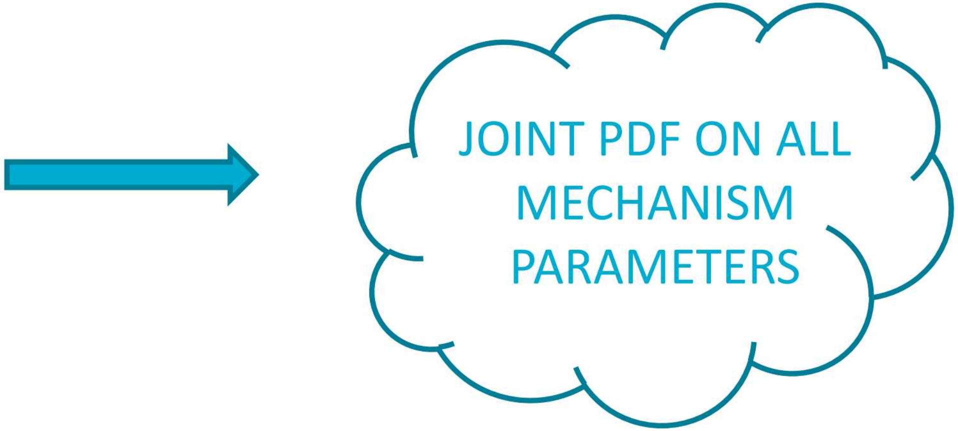
Bayesian inference: mechanism construction

n=10000 $p(A_1, \dots, Am, E_1, \dots, Em, \sigma_1, \dots, \sigma_m | c_n) \propto p(c_n | A_1, \dots, Am, E_1, \dots, Em, \sigma_1, \dots, \sigma_m | c_n)$

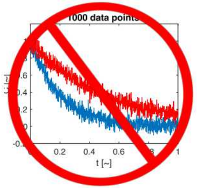








What if we don’t have data…?



Data is often unreported, missing, or lost forever

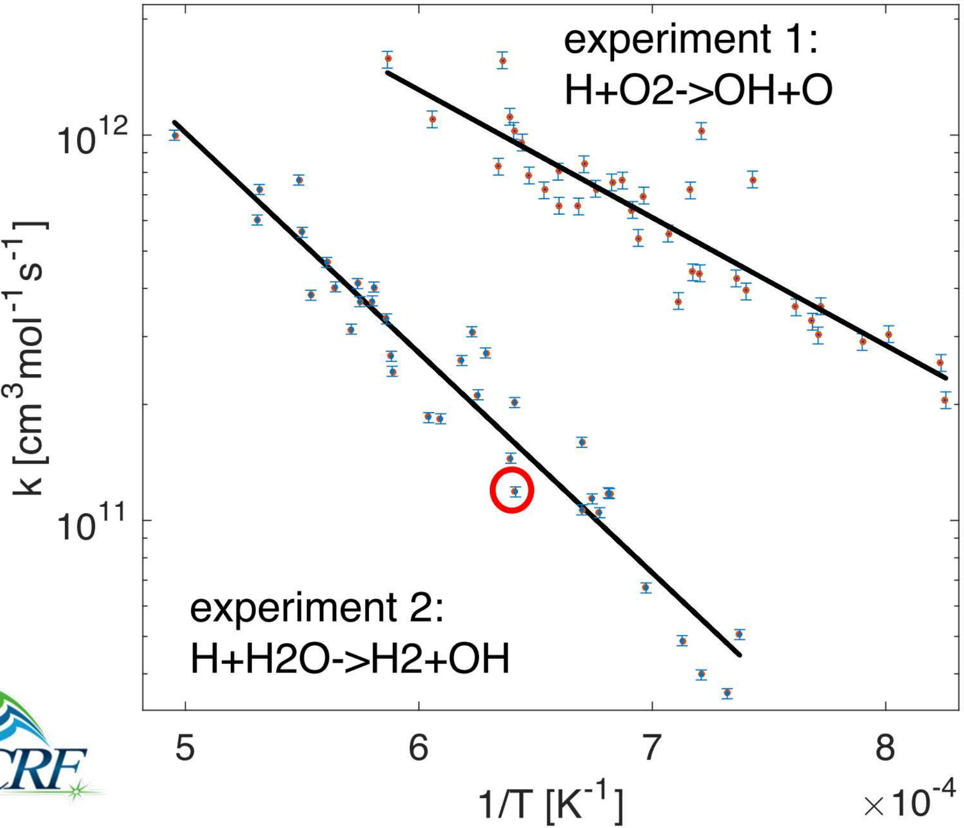
Experiments

- Pirraglia et al., J. Phys. Chem. (1989) shock tube study, $H+O_2$->OH+O

  signal: H atom decay
- Michael et al. J. Phys. Chem. (1988) shock tube study, $H+H_2O$->$OH+H_2$

  signal: H atom decay
- Results expresses as k(T) values with error bars

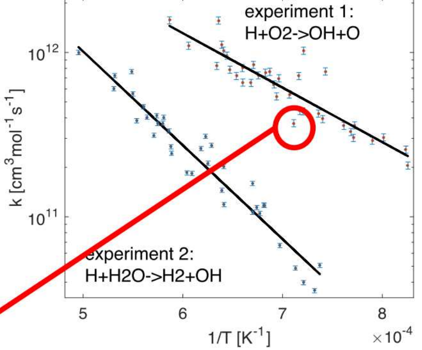
experiment results



In the absence of data: data inference

the reported k(T) values are summary statistics of the missing data,

interpret these statistics as **constraints** on a space of hypothetical data

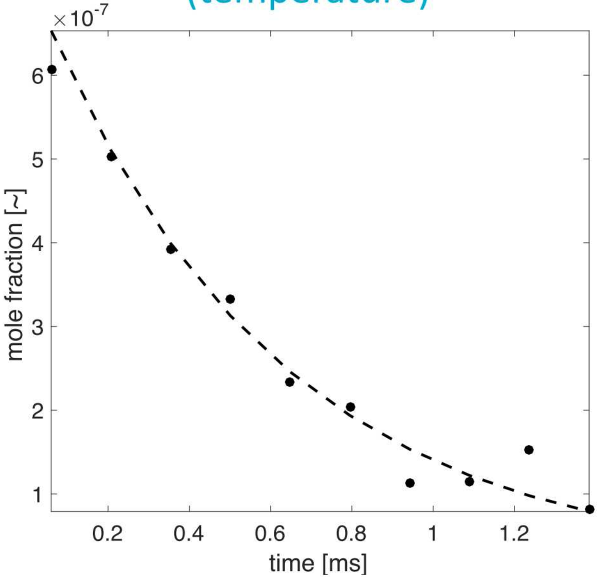


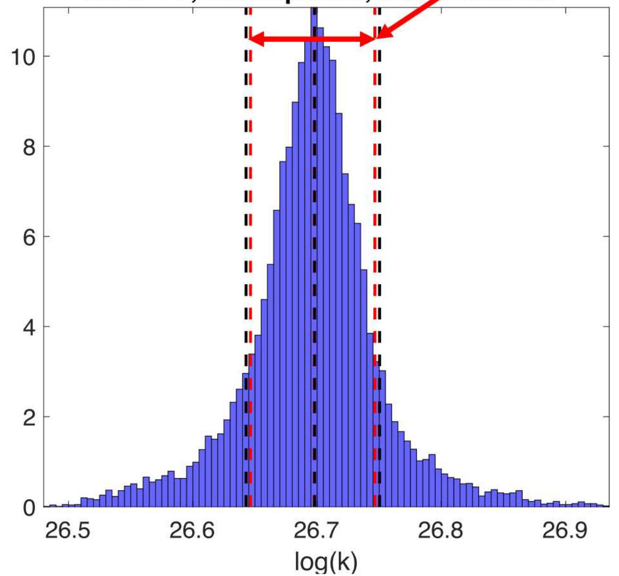
$$c(t) = f(k, t) + \sigma\varepsilon \qquad \varepsilon \sim N(0,1)$$

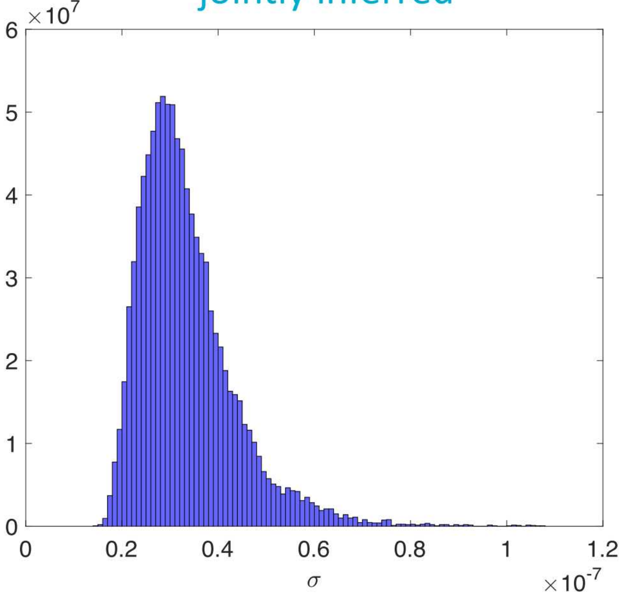
propose a hypothetical noisy data set for a specific experiment (temperature)

infer rate constant (at this temperature) compare to reported mean, error bars

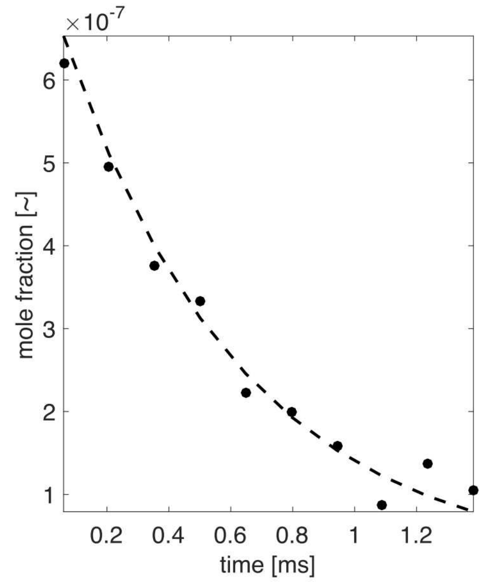
data noise model strength is jointly inferred



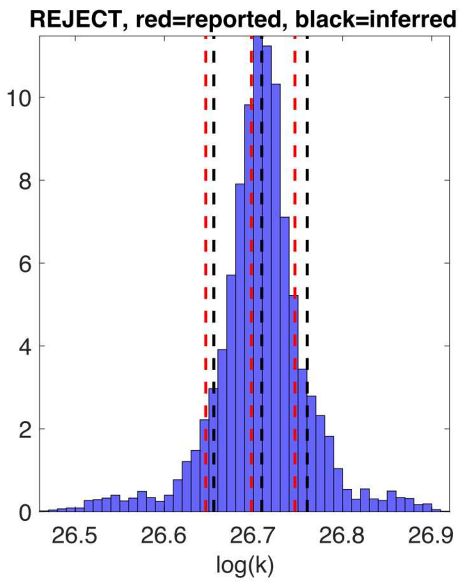




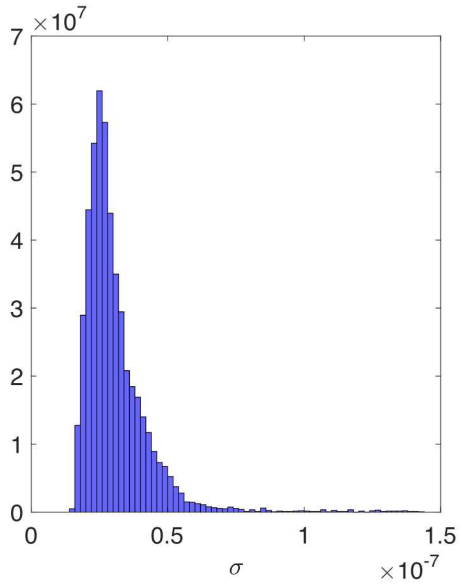
1



$\times 10^{-7}$
6
5
4
3
2
1
mole fraction [~]
0.2
0.4
0.6
0.8
1
1.2
time [ms]

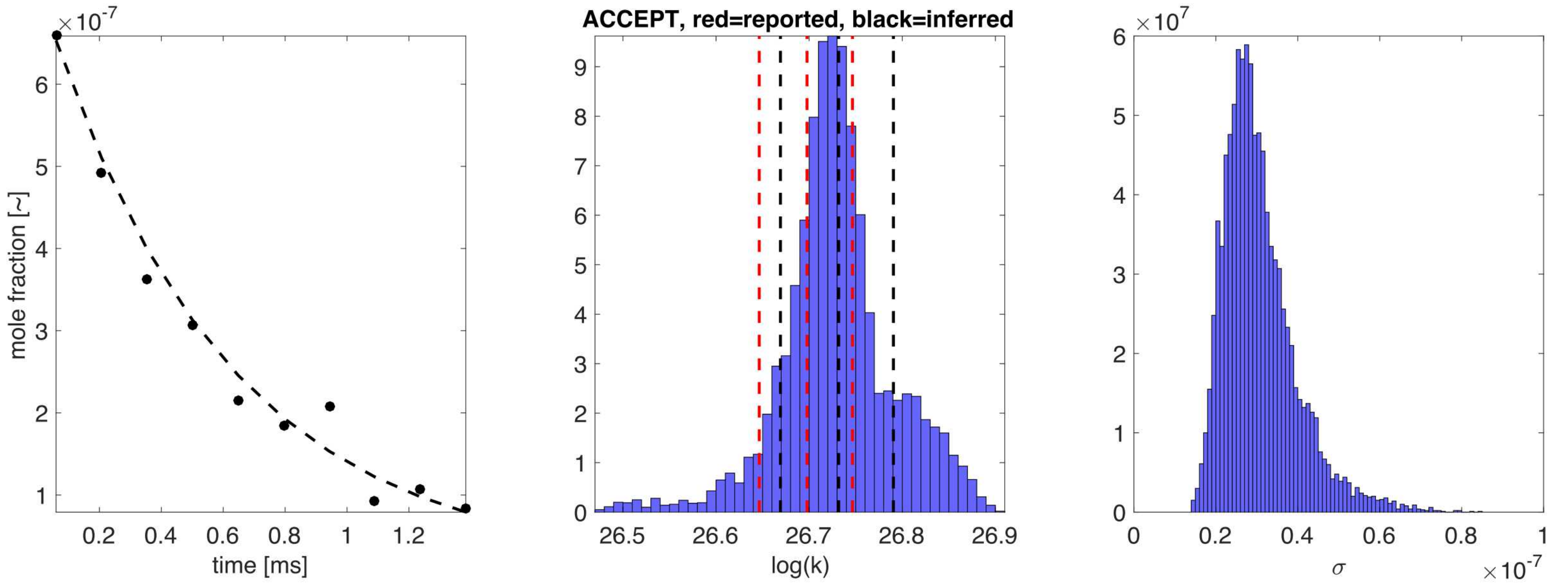


REJECT, red=reported, black=inferred
10
8
6
4
2
0
26.5
26.6
26.7
26.8
26.9
log(k)



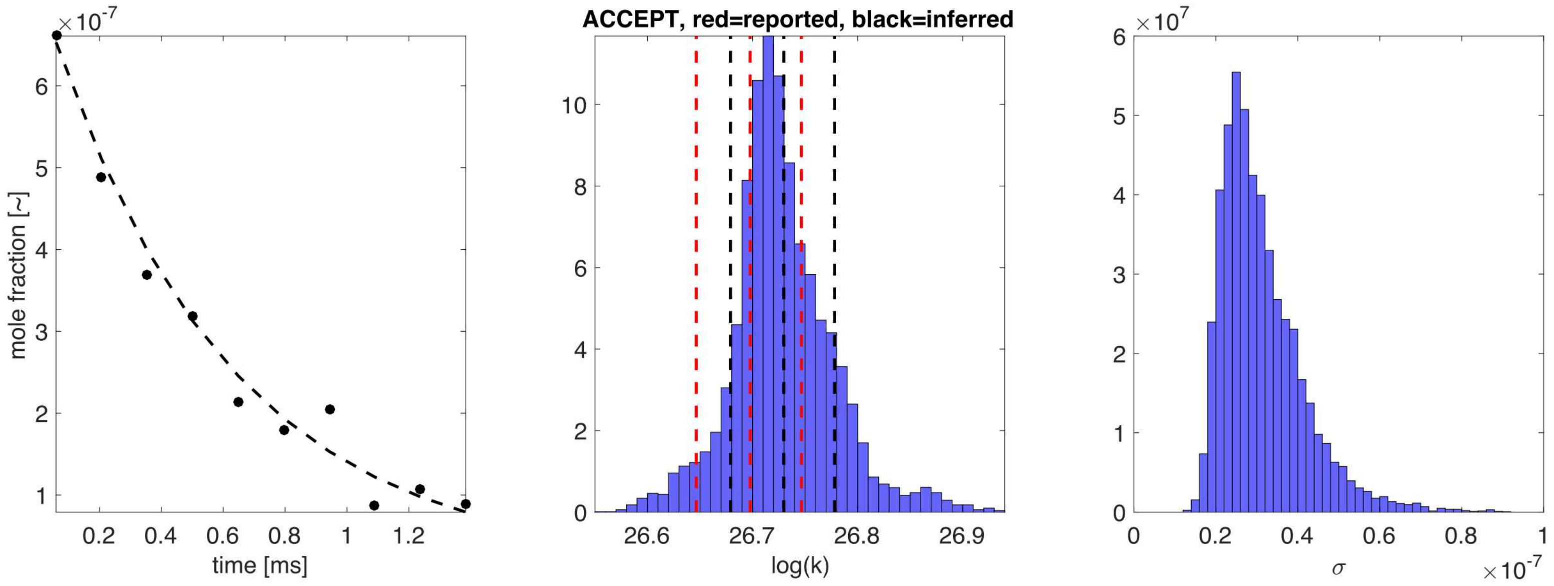
$\times 10^{7}$
7
6
5
4
3
2
1
0
0
0.5
1
1.5
σ
$\times 10^{-7}$

2



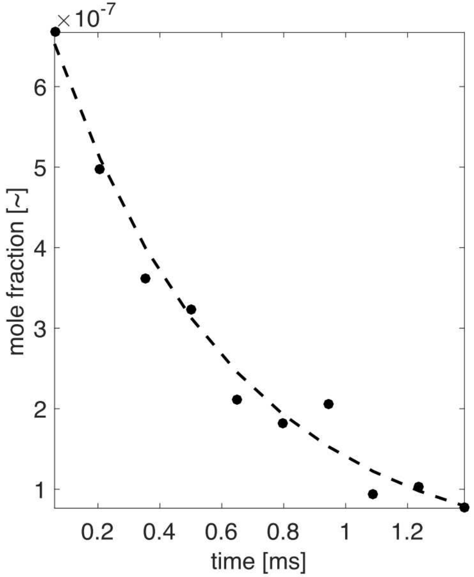
×10^-7
mole fraction [~]
time [ms]
ACCEPT, red=reported, black=inferred
log(k)
×10^7
σ
×10^-7

3

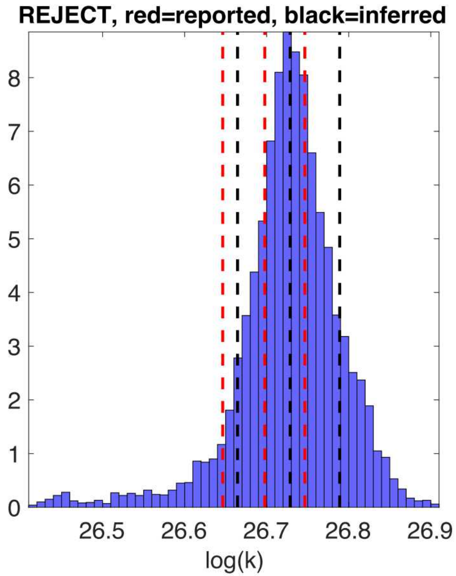


×10^-7
mole fraction [~]
time [ms]
0.2 0.4 0.6 0.8 1 1.2
1 2 3 4 5 6
ACCEPT, red=reported, black=inferred
log(k)
26.6 26.7 26.8 26.9
0 2 4 6 8 10
×10^7
σ
×10^-7
0 0.2 0.4 0.6 0.8 1
0 1 2 3 4 5 6

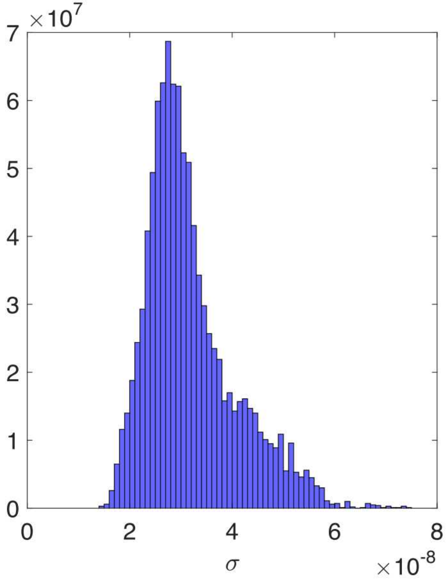
4



×10^-7
6
5
4
3
2
1
mole fraction [~]
0.2 0.4 0.6 0.8 1 1.2
time [ms]

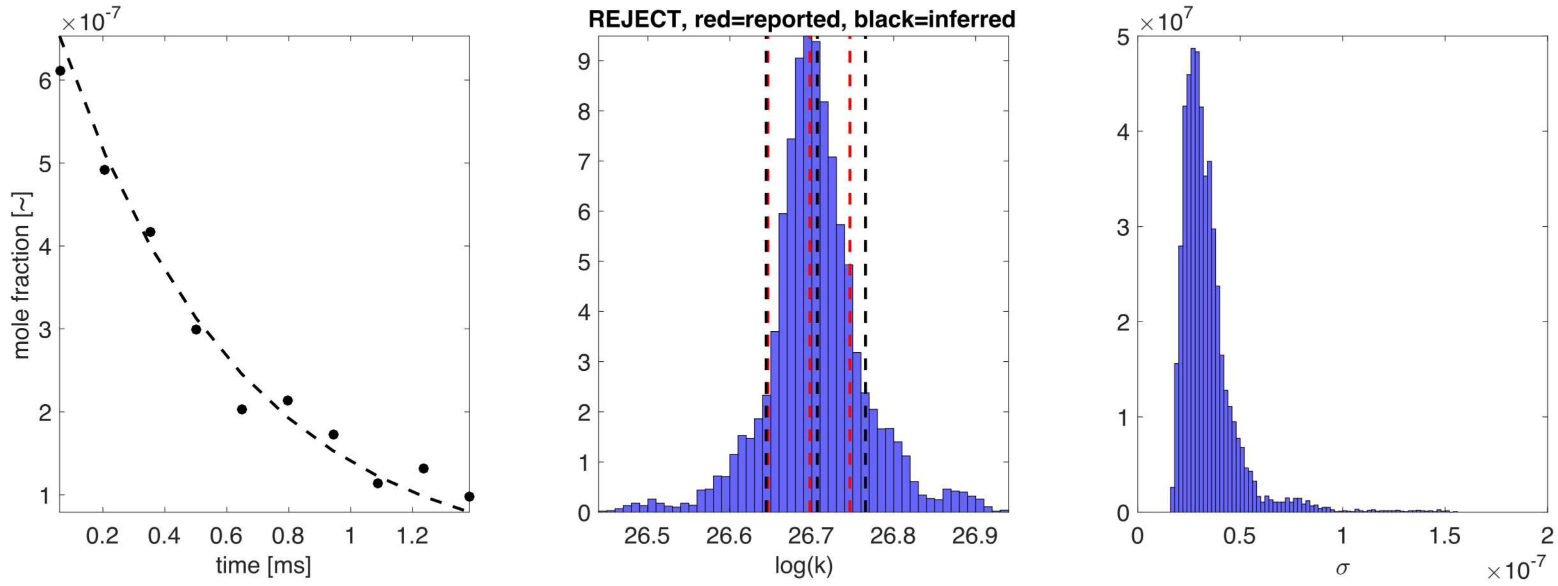


REJECT, red=reported, black=inferred
8
7
6
5
4
3
2
1
0
26.5 26.6 26.7 26.8 26.9
log(k)



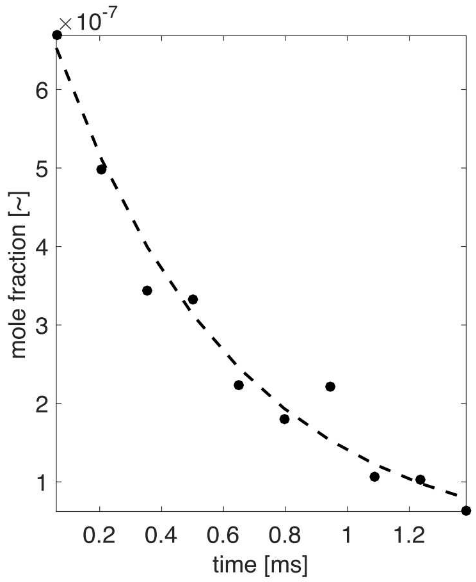
×10^7
7
6
5
4
3
2
1
0
0 2 4 6 8
σ
×10^-8

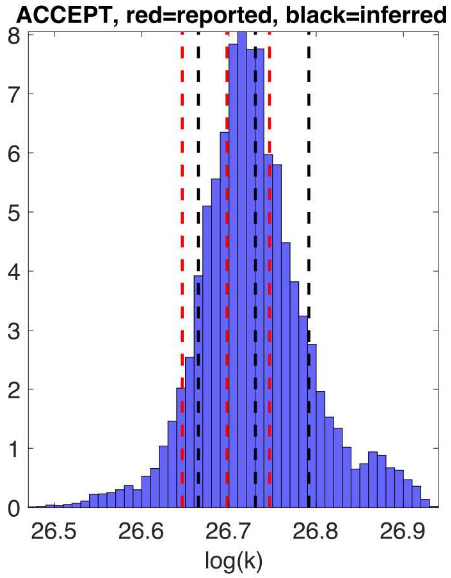
5

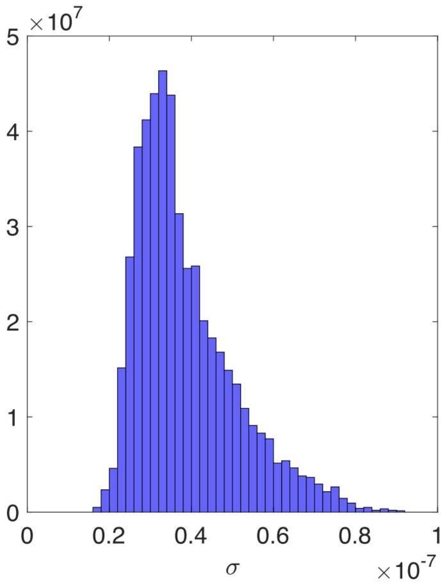


×10^-7
mole fraction [~]
time [ms]
REJECT, red=reported, black=inferred
log(k)
×10^7
σ
×10^-7

6

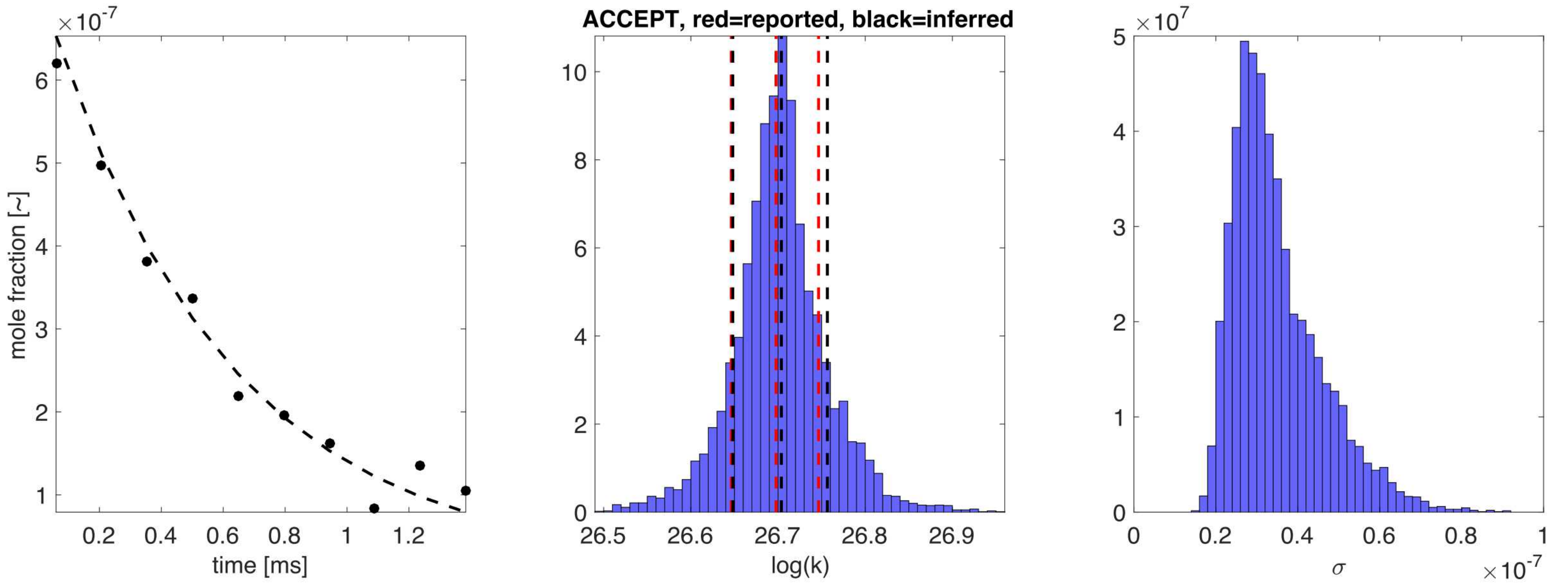

×10^-7
6
5
4
3
2
1
mole fraction [~]
0.2 0.4 0.6 0.8 1 1.2
time [ms]


ACCEPT, red=reported, black=inferred
8
7
6
5
4
3
2
1
0
26.5 26.6 26.7 26.8 26.9
log(k)


×10^7
5
4
3
2
1
0
0 0.2 0.4 0.6 0.8 1
σ
×10^-7

Building an ensemble of hypothetical consistent data

7



Bayesian framework

Bayesian inference (data space)

$$p\left(Data \middle| Constraints\right) = \frac{p(Constraints|Data)p(Data)}{p(Constraints)}$$

$$p\left(Constraints \middle| Data\right) := exp\left(-\delta\left(\frac{Statistics_{reported} - Statistics_{computed}}{Statistics_{reported}}^{2}\right)\right)$$

Bayesian inference (fitting model parameter space)

To compute the statistics of the proposed hypothetical data, perform an inner (inference) of model parameters:

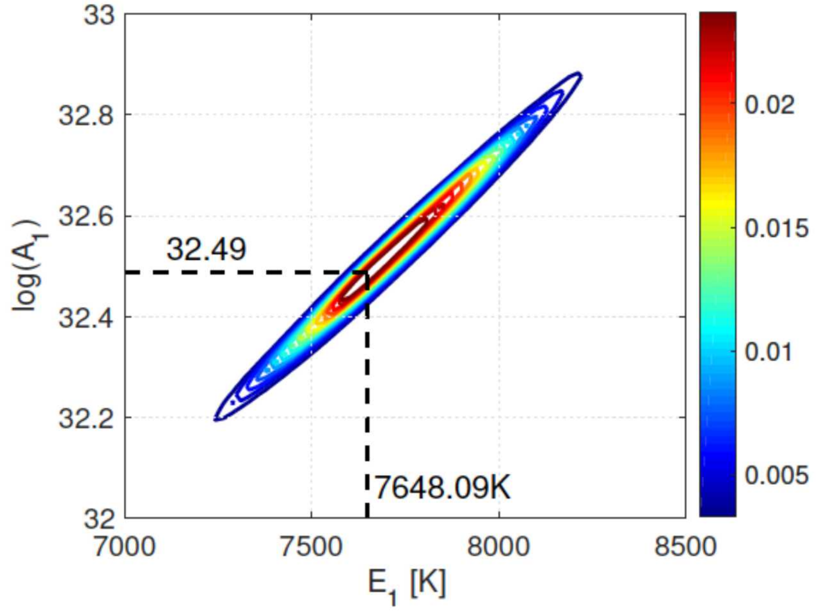
$$p\left(Parameters \middle| Data\right) = \frac{p(Data|Parameters)p(Parameters)}{p(Data)}$$

$$\Rightarrow Statistics_{computed} = f\left(p\left(Parameters \middle| Data\right)\right)$$

Consensus pooled parameter posterior (averaging)

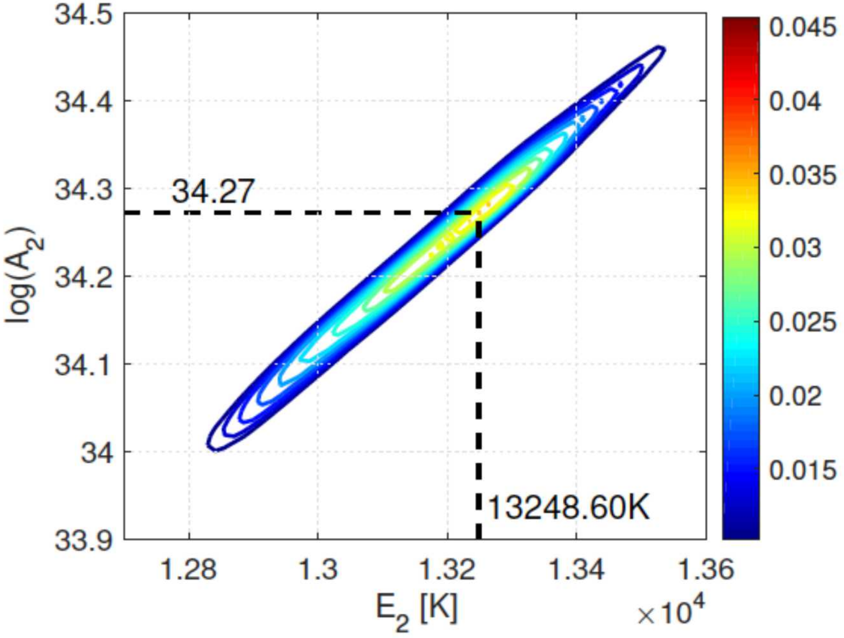
Experiment 1:

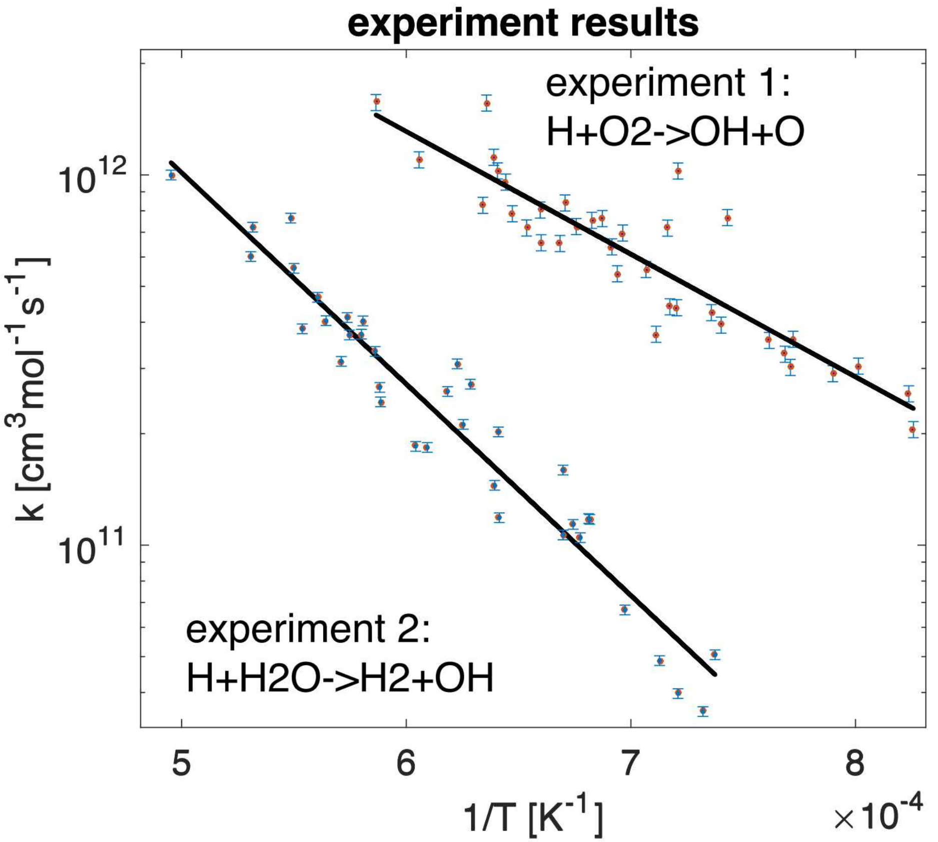
$H+O_2=OH+O$: $k_1= \mathbf{A_1}\exp(-\mathbf{E_1}/T)$

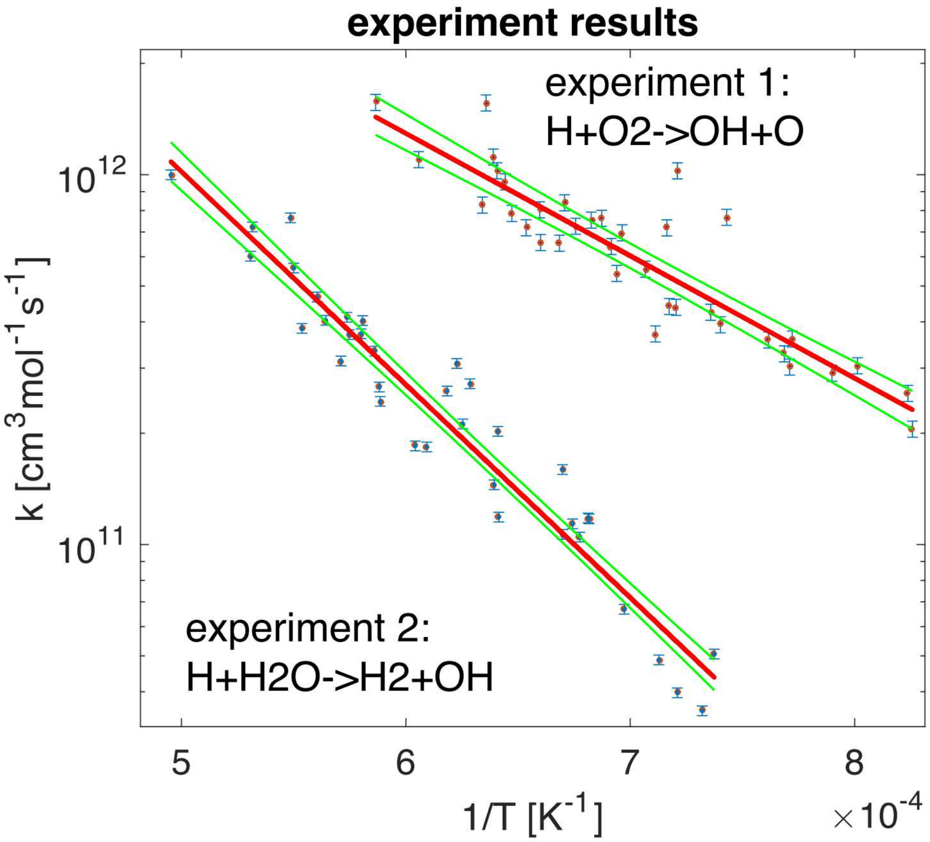


Experiment 2:

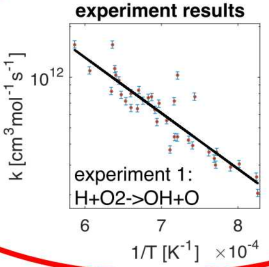
$H+H_2O=H_2+OH$: $k_2= \mathbf{A_2}\exp(-\mathbf{E_2}/T)$

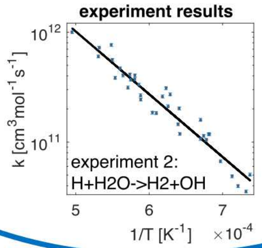



experiment results
experiment 1:
H+O2->OH+O
experiment 2:
H+H2O->H2+OH
10^{12}
10^{11}
k [$cm^3 mol^{-1} s^{-1}$]
5
6
7
8
1/T [K^{-1}]
$\times 10^{-4}$



Maximum likelihood k(T) values, and 99% confidence interval

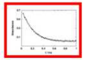
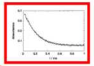
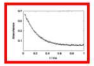
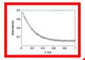




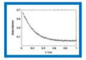
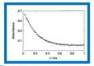
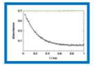
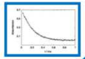
fitting chemical mechanism

fitting chemical mechanism

experiment 1 data

experiment 2 data

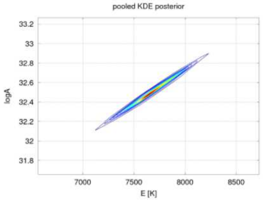





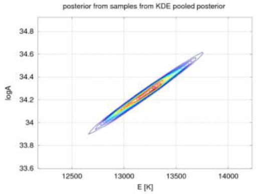
fitting chemical mechanism

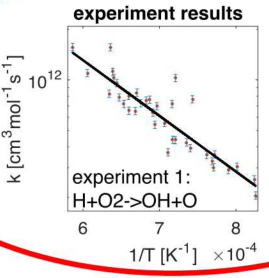
fitting chemical mechanism

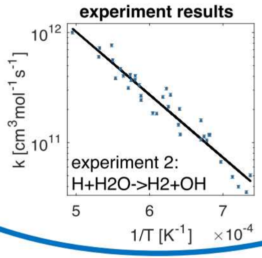
H+O_2->OH+O: k_1= $\mathbf{A_1}$exp(-$\mathbf{E_1}$/T)

H+H_2O->H_2+OH: k_2= $\mathbf{A_2}$exp(-$\mathbf{E_2}$/T)





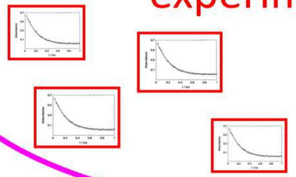


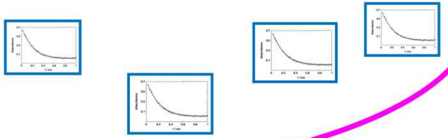


fitting chemical mechanism

fitting chemical mechanism

experiment 1 & experiment 2



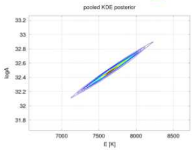


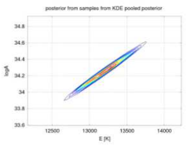
fitting chemical mechanism

```
ELEMENTS
O  H  AR  N
END
SPECIES
H2     H      O      O2     OH     H2O    HO2    H2O2
AR     N2
END
!THERMO
! Insert GRI-Mech thermodynamics here or use in default file
!END
REACTIONS
H+O2<=>O+OH                              3.550E+15   -0.410   16600.00
H2+OH<=>H2O+H                            2.160E+08    1.510    3430.00
H2O2(+M)<=>2OH(+M)                       2.950E+14    0.000   48400.00
     LOW  /  1.200E+17    0.000   45500.0/
O+H2<=>H+OH                              5.080E+04    2.670    6290.00
O+H2O<=>2OH                              2.970E+06    2.020   13400.00
H2+M<=>2H+M                              4.580E+19   -1.400  104380.00
H2/2.5/ H2O/12.0/
H2+AR<=>2H+AR                            5.840E+18   -1.100  104380.00
2O+M<=>O2+M                              6.160E+15   -0.500       0.00
H2/2.5/ H2O/12.0/
2O+AR<=>O2+AR                            1.890E+13    0.000   -1790.00
O+H+M<=>OH+M                             4.710E+18   -1.000       0.00
H2/2.5/ H2O/12.0/
H+OH+M<=>H2O+M                           3.800E+22   -2.000       0.00
H2/2.5/ H2O/12.0/ AR/0.38/
H+O2(+M)<=>HO2(+M)                       1.480E+12    0.600       0.00
     LOW  /  9.040E+19   -1.500  490.00/
     TROE/   0.50  1.0E+10  1.0E-10 /
HO2+H<=>H2+O2                            1.660E+13    0.000     820.00
HO2+H<=>2OH                              7.080E+13    0.000     300.00
HO2+O<=>OH+O2                            3.250E+13    0.000       0.00
HO2+OH<=>H2O+O2                          2.890E+13    0.000    -500.00
2HO2<=>O2+H2O2                           4.200E+14    0.000   11980.00
 DUPLICATE
2HO2<=>O2+H2O2                           1.300E+11    0.000   -1603.00
 DUPLICATE
H2O2+H<=>H2O+OH                          2.410E+13    0.000    3970.00
H2O2+H<=>H2+HO2                          4.820E+13    0.000    7950.00
H2O2+O<=>OH+HO2                          9.550E+06    2.000    3970.00
H2O2+OH<=>H2O+HO2                        1.000E+12    0.000       0.00
 DUPLICATE
H2O2+OH<=>H2O+HO2                        5.800E+14    0.000    9560.00
 DUPLICATE
END
```

$H+O_2$->$OH+O$: $k_1 = \mathbf{A_1}\exp(-\mathbf{E_1}/T)$

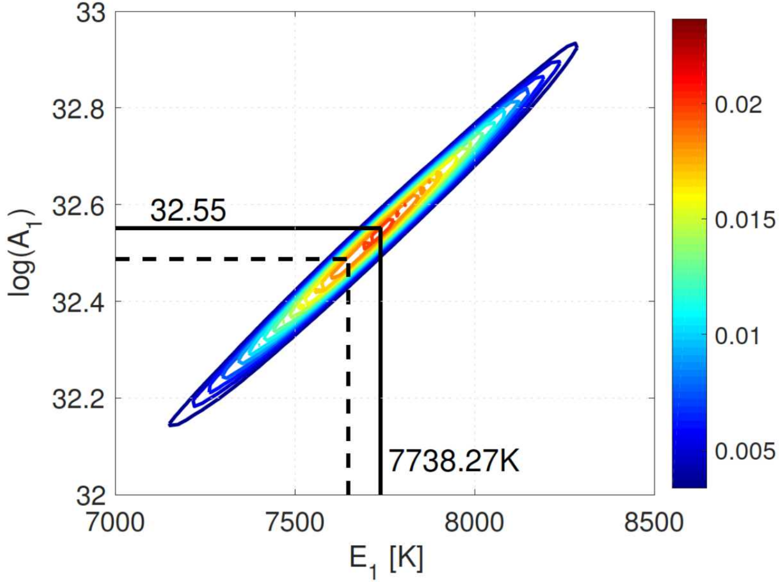
$H+H_2O$->H_2+OH: $k_2 = \mathbf{A_2}\exp(-\mathbf{E_2}/T)$



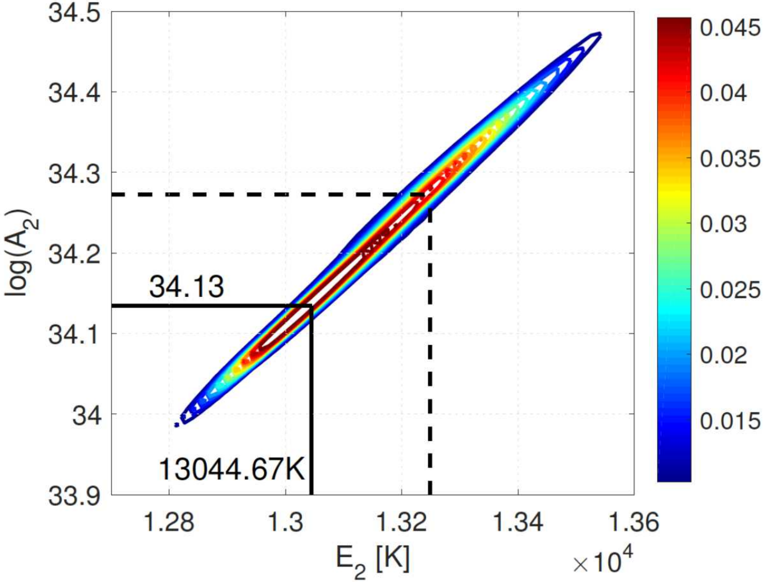


Joint Arrhenius parameter densities across reactions

$\log A_1$, E_1: $H+O_2 \rightarrow OH+O$

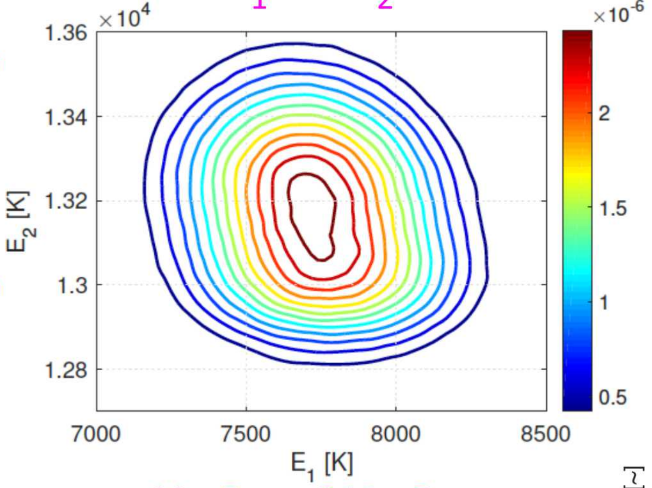


$\log A_2$, E_2: $H+H_2O \rightarrow OH+H_2$



Joint Arrhenius parameter densities across reactions

E_1 vs. E_2

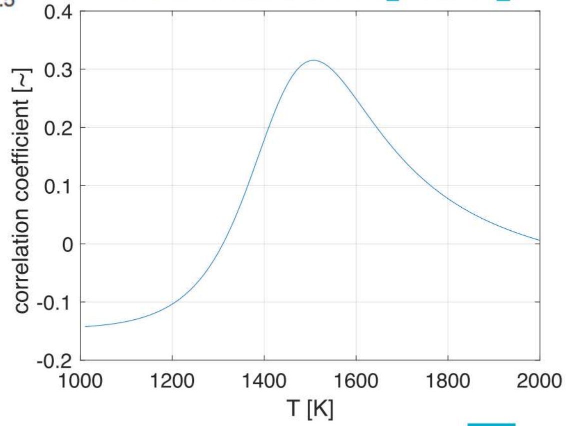


$H+H_2O\text{->}OH+H_2$

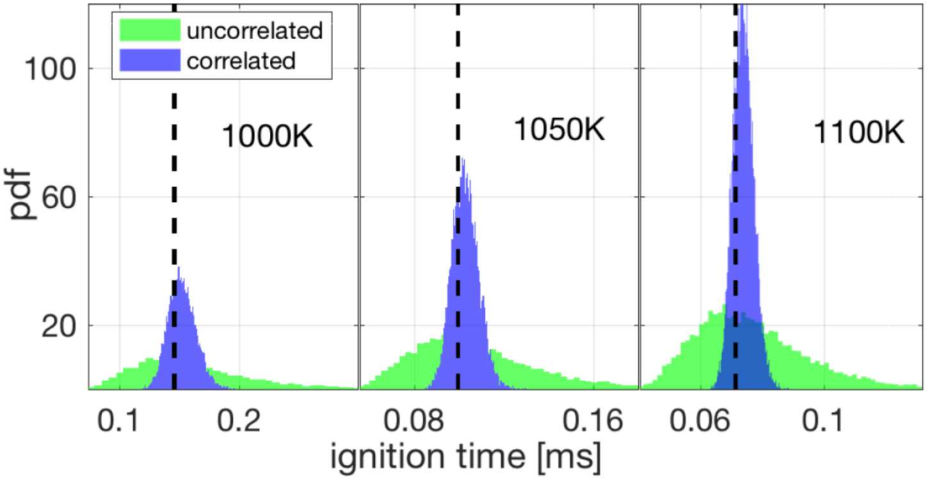
$H+O_2\text{->}OH+O$

Joint information on all the Arrhenius parameters across the 2 reactions

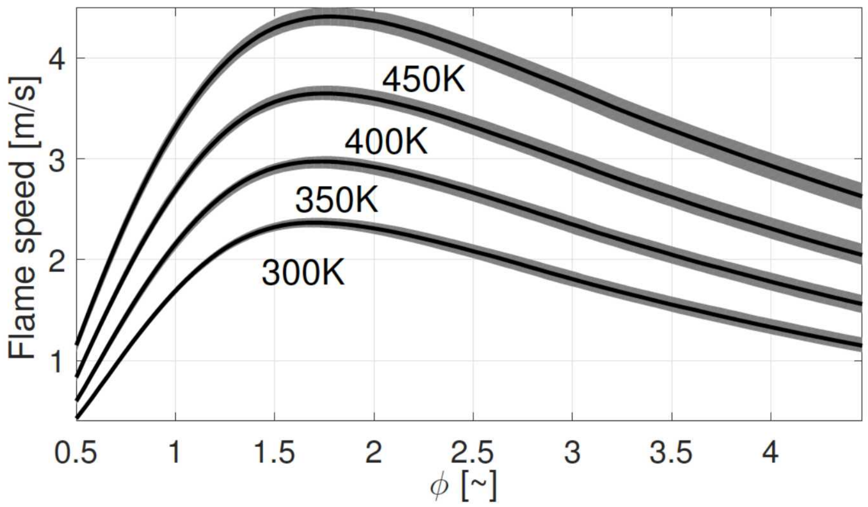
correlation coefficient k_1 vs k_2



Predictive simulations with uncertainty: correlation information (joint vs. marginal densities)



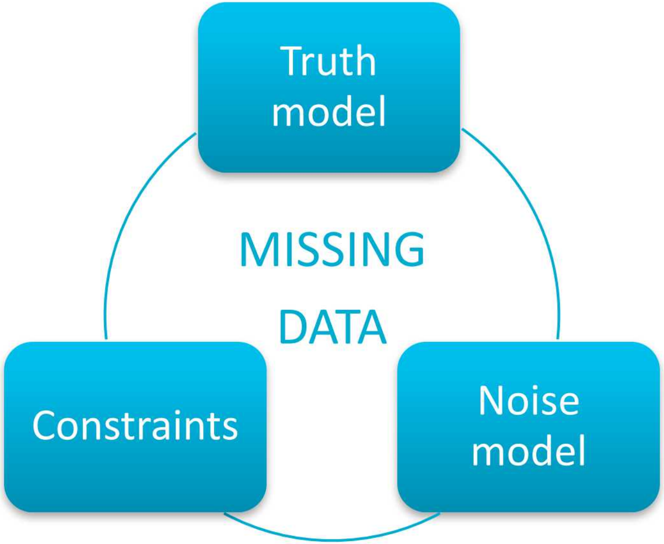
homogeneous ignition time



laminar flame speed

Summary

- Uncertainty quantification (UQ) enables us to pose and answer relevant questions about predictions
- With access to experimental data, we can build consistent chemical mechanism models with uncertainty measures
- When data is lost, we can infer data consistent with the available information
- With data we can cross-validate experiments, use UQ techniques to argue about appropriate model forms, model complexity, and determine what future experiments to perform to improve predictions
- There is no substitute for carefully collected experimental data



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