BAYESIAN UNCERTAINTY QUANTIFICATION
OF THE H + O$_2$ → OH + O REACTION RATE

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Abstract

We analyze the ignition delay in hydrogen-oxygen combustion, and the important chain branching reaction H + O$_2$ → OH + O that occurs behind the shock waves in shock-tube experiments. We apply a stochastic Bayesian approach (Beck *et al.,* 1998 and Cheung *et al.,* 2009) to quantify uncertainties in the theoretical model and experimental data. The approach involves a statistical inverse problem which has three "components" as input information: (a) the model, (b) a prior joint probability density function (PDF) of the uncertain parameters, and (c) the experimental data (Hong *et al.,* 2010). The solution of this statistical inverse problem is a posterior joint PDF of the uncertain parameters. We consider uncertainties in reaction rates, gas temperature, experimental errors and physical modeling errors, and also perform parametric studies to investigate how the form of the total uncertainty affects these uncertainties. More importantly, we introduce the idea of "irreducible" uncertainty when considering other uncertain parameters involved in the system. We compare our estimated reaction rate with other values obtained using the deterministic approach (Pirraglia *et al.,* 1989 and Masten *et al.,* 1990). Our results show that a small uncertainty in gas temperature (±3 K) introduces appreciable uncertainty in this reaction rate that can be as much as the reported uncertainty (Hong *et al.,* 2010).

1. Introduction

In this study, we utilize a stochastic system model based Bayesian approach to investigate the uncertainty in the reaction rate of H + O$_2$ → OH + O by using the well-calibrated experimental data recently acquired at the High Temperature Gasdynamics Laboratory at Stanford University (Hong *et al.,* 2010). The data describes the ignition of O$_2$/H$_2$/Ar mixtures behind reflected shock waves. We choose this reaction rate for our investigation because of the availability of well-calibrated experimental data as well as the significance of this reaction in combustion. Even though there are numerous studies conducted to estimate this reaction rate (Hong *et al.,* 2010, Pirraglia *et al.,* 1989, Masten *et al.,* 1990, and Yanga *et al.,* 1994), there is a large scatter of the coefficients in the Arrhenius form $k = 10^A T^m \exp\left(-\frac{\Theta}{T}\right)$, which we attribute to the difficulty of the experiments as well as to the drawback of using the conventional calibration procedure (least-squares curve fitting without considering uncertainties is typically used).

In addition, it is critical to understand the nature of each un-known parameter in the model, i.e., it is not always a good idea to directly specify these parameters. Instead, it is better to treat them as "incompletely known" and consider the effect of their uncertainties on the estimation of parameters of interest. Here, we call this "irreducible" uncertainty. For example, the uncertainties of other reaction rates from the literature can be categorized into this type of uncertainty. By doing so, we can include the knowledge of uncertainties associated with these reaction rates (for example, the comprehensive uncertainty data base for the hydrocarbon oxidation mechanism are available (Baulch *et al.,* 2005 and Manion *et al.*)) through our inverse problem as schematically showed in Fig. 1. There are many studies on how to properly propagate this type of uncertainty in a "forward" problem but few of them address this in the context of the inverse problem.

Our analysis in this paper is twofold. First, we investigate the effect of total uncertainty, i.e. the combination of modeling error and experimental uncertainty, on the estimation of the reaction rate. If there is no information about the uncertainty *a priori*, it is quite misleading to calibrate the
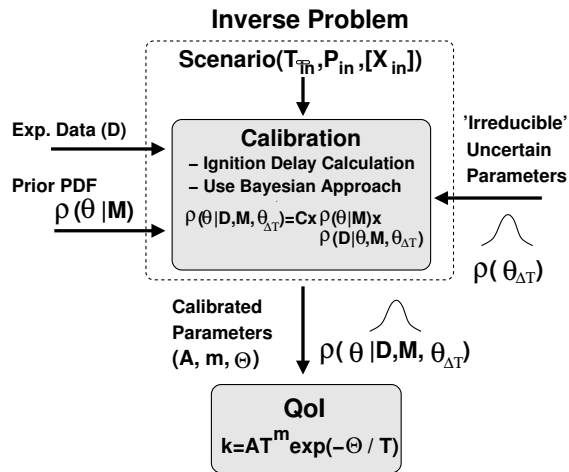
Figure 1: *Schematic of the proposed calibration procedure.*

Figure 2: *Experimental data (Hong et al., 2010) and an illustration of the effect of σ on the prediction of H_2O concentration.*

reaction rate against the data (e.g., by least-squares curve fitting). Fig. 2 shows the effect of the choice of standard deviation, σ, associated with the uncertainty. Due to the steep gradient of the [H_2O] concentration profile over the ignition period, a large value of σ has only a small effect on the ignition delay time. Second, we treat the uncertainty of the gas temperature as "irreducible" uncertainty and investigate its effect on the estimate of the reaction rate of $H + O_2 \rightarrow OH + O$. The pre-determined function of "irreducible" uncertainty is one of the input data. This modification requires an efficient sampling in high-dimensional spaces since we need to perform an additional integration when calculating these integrals. This is quite challenging numerically.

2. Stochastic Model based on Bayesian Approach

Let M designate a stochastic system model class (Beck *et al.,* 1998), that is, a set of predictive models. Each predictive model is specified by uncertain model parameters $\boldsymbol{\theta} \in \Omega \subset \mathbb{R}^d$, and has some prior relative plausibility in M, denoted by the prior probability density function (PDF) $p(\boldsymbol{\theta}|M)$. One can use data D to update the relative plausibility of each predictive model in M by computing the *posterior* PDF $p(\boldsymbol{\theta}|D,M)$ using Bayes' theorem

$$p(\boldsymbol{\theta}|D, M) = c^{-1}\, p(D|\boldsymbol{\theta}, M)\, p(\boldsymbol{\theta}|M), \qquad (1)$$

where c is a normalizing constant that makes the probability volume under the posterior PDF equal to unity, and $p(D|\boldsymbol{\theta}, M)$ is the *likelihood function*. The likelihood function expresses the probability of computing D based on the output of model $\boldsymbol{\theta}$ within M.

The experimental data (Table 1) used in this paper consists of $N_{exp} = 6$ experiments, each one with the same number N_d of data points. All data points are assumed to be statistically independent of each other. We denote by $D_{i,j}$ the jth data point of the ith experiment, and by $X_{i,j}$ the model output computed for the same scenario as $D_{i,j}$. We also consider an additive error: $D_{i,j} = X_{i,j} + r_{total}$. Following the Principle of Maximum Information Entropy, we choose
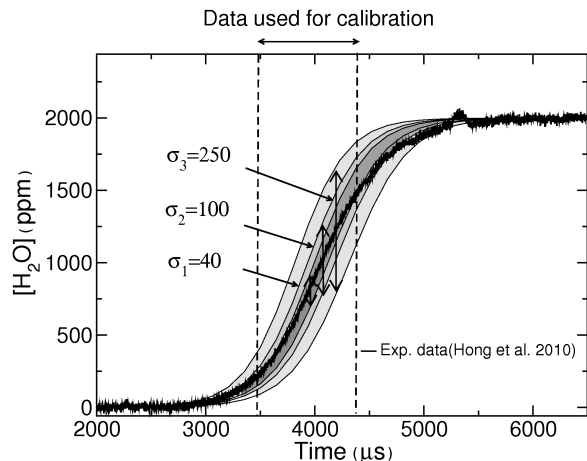
Table 1: *Experimental scenarios ($O_2/H_2/Ar$ mixture)*

Index	T_{in} K	P_{in} atm	[H_2] %	[O_2] %
1	1100	1.95	0.029	0.001
2	1197	1.84	0.029	0.001
3	1256	2.01	0.029	0.001
4	1317	1.91	0.009	0.001
5	1448	1.85	0.009	0.001
6	1472	1.83	0.009	0.001

the likelihood function

$$p(D|M,\boldsymbol{\theta}) = \frac{1}{\sqrt{2\pi(\sigma_{total}^2)^{N_y N_T}}}$$
$$\exp\left[-\frac{1}{2(\sigma_{total}^2)}\sum_{i=1}^{N_{exp}}\sum_{n=1}^{N_T}(D_n^{w_i} - X_n^{w_i}(x_n;\theta))^2\right] \qquad (2)$$

Here, σ_{total}^2 is the variance related to measurement errors and all the other types of errors related to the prediction of the quantity that is measured, including physical model inadequacies.

When we consider the "irreducible" uncertainty, the above expression needs to be modified. We assume that the uncertainty of T_{in} follows the Gaussian distribution denoted by $p(\mathbf{v}|M,\boldsymbol{\theta_v})$ where $\mathbf{v}$ is an uncertain vector storing the temperature and $\boldsymbol{\theta_v}$ and $\boldsymbol{\theta_v}$ is an uncertain model parameter vector associated with this distribution, such as $\sigma_{\Delta T}$. Then, the resultant likelihood function needs to be averaged as follows:

$$p^{'}(D|M,\boldsymbol{\theta},\boldsymbol{\theta_v}) = \int p(D|M,\boldsymbol{\theta},\mathbf{v})p(\mathbf{v}|M,\boldsymbol{\theta_v})d\mathbf{v} \quad (3)$$

This integration is not trivial. We compute it using a stochastic method recently developed in Cheung and Beck (2009).

3. Deterministic Model

We use the detailed chemical kinetic mechanism previously verified in Hong *et al.* (2010) and the updated version of GRI-Mech 3.0 (Smith *et al.,*) to model the ignition delay of $O_2/H_2/Ar$ mixtures behind reflected shock waves. This mechanism considers 35 elementary reactions and 13 species, O, H, N, H_2, H, O, O_2, OH, H_2O, HO_2, H_2O_2,
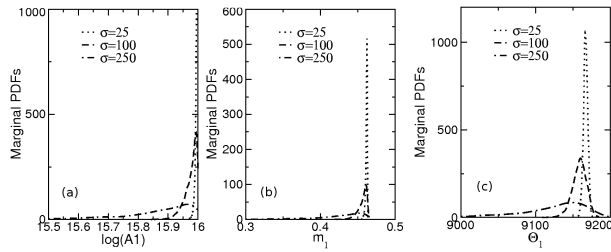
Figure 3: *Posterior PDFs of A_1, m_1, Θ_1, for different σ.*

N$_2$ and Argon. Assuming that the temperature is constant during the reaction behind the reflected shock waves, the chemical reaction system can be expressed using ordinary differential equations.

4. Description of Experimental data

Experimental data were recently collected at the High Temperature Gasdynamics Laboratory at Stanford University Hong *et al.* (2010). The data are composed of six profiles of the H$_2$O concentration history behind reflected shock waves over the temperature range 1100-1472 K. The detailed description of the shock tube is provided elsewhere (Hong *et al.*, 2010). Table 1 shows six experimental scenarios composed of the temperature, T_{in}, pressure, P_{in}, concentration of H$_2$ and O$_2$ prior to shock heating. There are 1000-7000 measurement points in each experimental record. However, in this study, we only use the data in the region where the H$_2$O concentration rapidly increases (i.e., when ignition occurs) because of our assumption that the total error (σ_{total}) is not a function of time. Hong *et al.*, (2010), reported an uncertainty ΔT_{exp} (± 10.2 K and ± 9.4 K for the low (1100 K) and high (1472 K) temperature measurements respectively) and an uncertainty of less than 1% in the gas composition.

5. Results

Figs. 3 (a)-(b) show the posterior PDF for three cases with the different values of σ, 25 (dotted line), 100 (dashed line), and 250 (dot-dash line). As the value of σ increases, the variance of each posterior PDF increases: i.e., the total uncertainty (sum of modeling and experimental uncertainty) propagates into these parameters. Indeed, when σ set to be 25, very narrow PDFs are obtained. Since the number of the data points (~ 3000) is very large compared with the number of parameters (=3), the data sufficiently inform these parameters. Posterior means of $log(A_1)$ and Θ_1 are much higher than reported values (Hong *et al.*, 2010, Pirraglia *et al.*, 1989, Masten *et al.*, 1990, and Yanga *et al.*, 1994). Note these two parameters are negatively correlated, and therefore, this result does not mean that the estimated reaction rate, k, differs much from published values. Fig. 4 (a) shows the estimated 95% CI of k for these three cases and experimental data (Hong *et al.*, 2010, Pirraglia *et al.*, 1989, and Masten *et al.*, 1990) and the reference data that is "deterministically" computed using the same data (Hong *et al.*, 2010). All 95% CIs are so close to each other that it is hard to recognize each of them separately. Considering the wide PDFs estimated by the case with $\sigma = 250$,
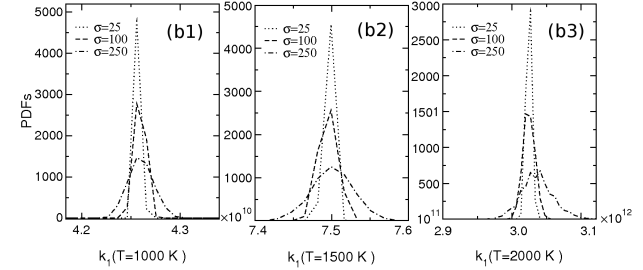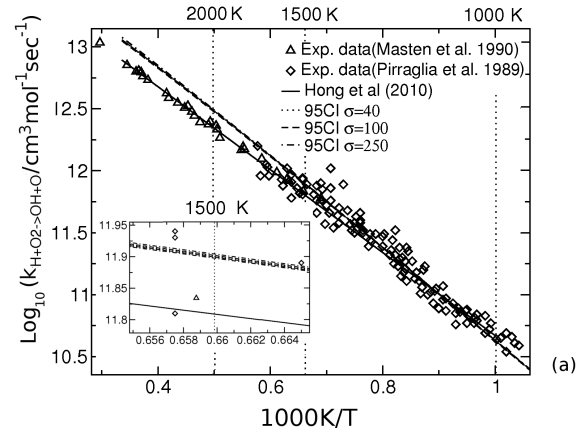

Figure 4: *(a) 95% CI for log(k) against 10^3/T 1/K with fixed sigma and experimental data (Hong; (b1-b3) k at three different temperatures.*

this result is surprising. Indeed, this implies that there are multiple combinations of three parameters to give the similar value of k: i.e., the three parameters are strongly correlated with each other. The computed k agrees well with the value reported by Hong *et al.* (2010) within the temperature range of the experimental data. However, they diverge in the high temperature region (~ 2000 K) where no experimental data is available. Figs. 4 (b1)-(b3) show the reaction rates at the three different temperatures (1000, 1500, and 2000 K). All cases show really small uncertainties (the largest uncertainty is at most $\pm 2.5\%$ for the case with $\sigma = 250$ at T=2000 K). This unrealistically underestimated uncertainty is attributed to the fact that we don't consider other uncertainties related to other reaction rates, gas composition, temperature, etc. Next, we consider the uncertainty of gas temperature and introduce it as "irreducible" uncertainty. The calibration parameters in this case are A_1, m_1, Θ_1 and σ. We consider two different values for the temperature uncertainty, $\Delta T = 3$ K and $\Delta T = 30$ K. (The authors are not aware of the definition of the reported uncertainty of gas temperature (~ 10 K). Therefore, we assume that $\Delta T_{exp} = 3\Delta T$ and $\Delta T_{exp} = \frac{1}{3}\Delta T$). Figs. 5 (a)-(d) show the posterior PDF of $log(A_1)$ (a), m_1 (b), Θ_1 (c) and σ(d). Except for σ, the three PDFs differ from each other for the two cases. It is interesting that the degree of temperature uncertainty significantly affects these posterior PDFs. The corresponding estimate of the reaction rate is shown in Figs. 6. Unlike the negligible uncertainty seen in Figs. 4, there is appreciable uncertainty especially in the low and high temperature regions for the case ΔT=30 K (See Figs 6 (b1)-(b3)). At T=1000 K and T=2000 K, the uncertainty

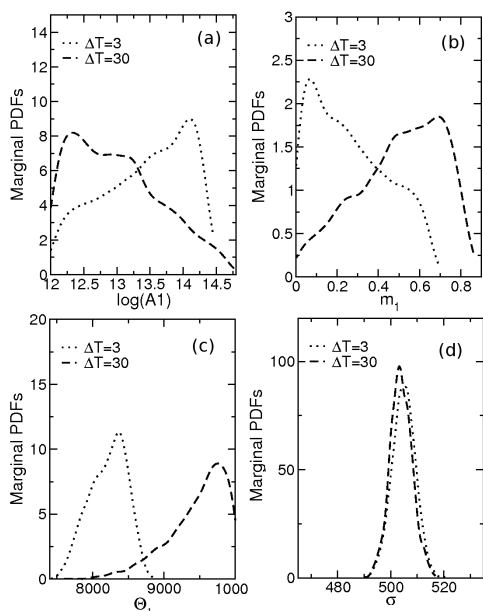Figure 5: *Marginal posterior PDFs of A_1, m_1, Θ_1, and σ, with "irreducible" uncertainty $\Delta T = 3$ K and $\Delta T = 30$ K in the temperature.*

of k is as much as $\pm 10\%$ for ΔT=3 K and $\pm 35\%$ for ΔT=30 K. At T=1500 K which is close to the experimental temperature, it becomes smaller ($\sim \pm 6\%$ for ΔT=3 K and $\sim \pm 15\%$ for ΔT=30 K). Considering that the reported uncertainty of gas temperature is ± 10 K, this introduces a $\pm 6 - 15\%$ uncertainty that is larger than the one computed "deterministically" by Hong *et al.* (2010).

6. Conclusions

In this paper we estimated, under uncertainty, the reaction rate of $H + O_2 \rightarrow OH + O$ using a Bayesian approach and experimental data recently obtained by Prof. Hanson's research group at Stanford University. We performed parametric studies of the total uncertainty and the uncertainty associated with gas temperature. An "irreducible" uncertainty was included in the calibration methodology. Our results show that the choice of the form of the total uncertainty does not have much effect on the estimated uncertainty of the reaction rate. However, a realistic "irreducible" uncertainty in the gas temperature introduces appreciable uncertainty in the rate. Since we do not include uncertainties from other reaction rates (currently fixed), the uncertainty of this reaction is expected to be larger than the reported value $\pm 4.6\%$ at 1500 K. We will consider uncertainties associated with other reaction rates as "irreducible" uncertainty in future studies.
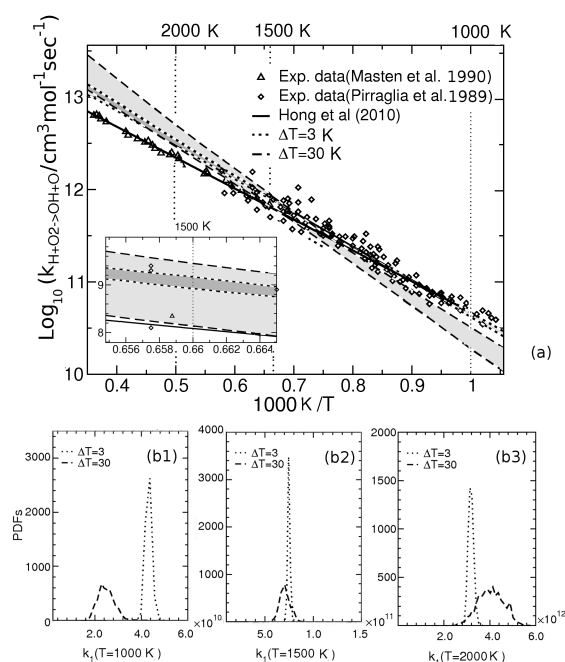
Acknowledgments

Figure 6: *(a) 95% CI for $\log(k)$ against $10^3/T$ considering "irreducible" uncertainty of T_{in} and experimental data; (b1-b3) k at the three different temperatures.*

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