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An evolutionary, data-driven approach for mechanism optimization: theory and application to ammonia combustion

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Abstract:	<p>In this work, we propose a novel data-driven approach for detailed kinetic mechanism optimization. The approach is based on a curve matching-based objective function and includes a methodology for the optimisation of pressure-dependent reactions via logarithmic interpolation (PLOG format). In order to highlight the advantages of the new formulation of the objective function, a comparison with L1 and L2 norm is performed. The selection of impactful reactions is carried out by introducing a Cumulative Impact Function (CIF), while an Evolutionary Algorithm (EA) is adopted to perform the optimization. The capabilities of the proposed methodology were demonstrated using a database of ~635 experimental datapoints on ammonia combustion, covering standard targets like ignition delay times, speciation and laminar flame speed. The optimization was carried out starting from a recently published mechanism, describing ammonia pyrolysis and oxidation, largely developed using first-principles calculation of rate constants. After the selection of the 24 most impactful reactions, the related 101 normalized Arrhenius parameters were simultaneously varied, within their uncertainty bounds. Their uncertainty bounds were taken from the literature, when available, or estimated according to the level of theory adopted for the determination of the rate constant. Hence, we also provide guidelines to estimate uncertainty for reaction rate constants derived from first principles calculations using well consolidated computational protocols as a reference. The optimized mechanism was found to improve the nominal one, showing a satisfactory agreement over the entire range of operating conditions. Moreover, the use of a 'curve matching' index was found to outperform the adoption of L1 and L2 norms. The comparison between the nominal mechanism and the one optimized via curve matching allowed a clear identification of different critical reaction pathways for different experimental targets. From this perspective, the methodology proposed herein can find further application as a useful design-of-experiments tool for an accurate evaluation of crucial kinetic constants, thus driving further mechanism improvement.</p>



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Bruxelles, October 13th 2020

Dear Editors,

Please find enclosed the manuscript:

"An evolutionary, data-driven approach for mechanism optimization: theory and application to ammonia combustion." by Andrea Bertolino, Magnus Fürst, Alessandro Stagni, Alessio Frassoldati, Matteo Pelucchi, Carlo Cavallotti, Tiziano Faravelli and Alessandro Parente, which we would like to submit for publication in Combustion and Flame.

The work aims at proposing and validating an approach developed for optimization of chemical kinetic mechanisms, using experimental data as targets.

The novelty of this paper is multiple, it lies first in the use of the Curve Matching (CM) index as objective function for the optimization, accounting for shape discrepancies between model predictions and experiments, rather than a point-wise measure of their difference. Secondly, an ad-hoc methodology to optimize the Arrhenius parameters of PLOG-based reactions was established. Lastly, an optimized mechanism for ammonia combustion was obtained, which was found to outperform the nominal one, as well as those obtained with point-wise formulations of the objective function (i.e. L1 and L2 norms), over a wide range of operating conditions involving more than ~635 experimental data points for pure ammonia combustion. For rates determined using first principle calculations, guidelines were established to estimate uncertainty ranges based on the level of theory adopted throughout the calculation protocols for electronic structures, potential energy surfaces and phenomenological reaction rate constants.

We confirm that this manuscript is based on original research. It has not been published elsewhere nor is under consideration by other journals.

We thank you in advance for your consideration.

Best regards,
Andrea Bertolino

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An evolutionary, data-driven approach for mechanism optimization: theory and application to ammonia combustion.

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Supplementary Material Folder SM available

SM contains:

- Detailed kinetic mechanisms developed in this study (/MECH sub-folder).
- Supplementary_Material.doc:
 - Uncertainty analysis. This section contains details about the employed methods for rate constants uncertainty estimation, performed on the basis of the accuracy of the level of theory adopted for the rate constant determination.
 - Penalties analysis. Here, a Monte Carlo approach was adopted to quantify the frequency of penalized kinetic rate samples retrieved by sampling from Arrhenius parameters bounded according to the approach presented in the main text.
 - Sensitivity analysis to estimated uncertainty factors. In this section, the insensitivity of optimization results to the absolute values of said uncertainty factors is demonstrated on a single test case.
 - Mechanism validation.
 - Details on reaction rates and related uncertainties.

Table of Contents

Abstract	3
Nomenclature	4
<i>Roman symbols</i>	4
<i>Acronyms</i>	5
<i>Subscripts</i>	6
1 Introduction	7
2 Methodology	12
2.1 <i>Optimization procedure</i>	12
2.2 <i>Optimization of reactions in PLOG formalism</i>	18
2.3 <i>Database</i>	20
2.3.1 <i>Numerical simulations</i>	21
2.4 <i>Impact-based reactions selection</i>	21
2.5 <i>Uncertainty estimation</i>	22
3 Results and Discussion	24
4 Conclusions	33
5 Acknowledgements	34
6 References	35
FIGURES	41

Abstract

In this work, we propose a novel data-driven approach for detailed kinetic mechanism optimization. The approach is based on a curve matching-based objective function and includes a methodology for the optimisation of pressure-dependent reactions via logarithmic interpolation (PLOG format). In order to highlight the advantages of the new formulation of the objective function, a comparison with L1 and L2 norm is performed. The selection of impactful reactions is carried out by introducing a Cumulative Impact Function (CIF), while an Evolutionary Algorithm (EA) is adopted to perform the optimization. The capabilities of the proposed methodology were demonstrated using a database of ~635 experimental datapoints on ammonia combustion, covering standard targets like ignition delay times, speciation and laminar flame speed. The optimization was carried out starting from a recently published mechanism, describing ammonia pyrolysis and oxidation, largely developed using first-principles calculation of rate constants. After the selection of the 24 most impactful reactions, the related 101 normalized Arrhenius parameters were simultaneously varied, within their uncertainty bounds. Their uncertainty bounds were taken from the literature, when available, or estimated according to the level of theory adopted for the determination of the rate constant. Hence, we also provide guidelines to estimate uncertainty for reaction rate constants derived from first principles calculations using well consolidated computational protocols as a reference. The optimized mechanism was found to improve the nominal one, showing a satisfactory agreement over the entire range of operating conditions. Moreover, the use of a ‘curve matching’ index was found to outperform the adoption of L1 and L2 norms. The comparison between the nominal mechanism and the one optimized via curve matching allowed a clear identification of different critical reaction pathways for different experimental targets. From this perspective, the methodology proposed herein can find further application as a useful design-of-experiments tool for an accurate evaluation of crucial kinetic constants, thus driving further mechanism improvement.

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Keywords

Optimization, detailed kinetics, ammonia, uncertainty quantification.

Nomenclature

Roman symbols

- A = pre-exponential factors [$s - \text{cm}^3 - \text{mol}$]
- E_a = activation energy [cal/mol]
- f_r = uncertainty factor for reaction r
- R = universal gas constant [cal/mol/K]
- d_j^0 = zero-order derivative dissimilarity index for the the j^{th} dataset
- d_j^1 = first-order derivative dissimilarity index for the the j^{th} dataset
- g = experimental data spline
- m = model evaluations spline
- p_c = cross-over rate
- p_m = mutation rate
- X = uniformly distributed random variable
- Y = optimisation target
- $I_{r,s}$ = impact coefficient of r^{th} reaction in s^{th} test case

1 $s_{r,s}$ = sensitivity coefficient of r^{th} reaction in s^{th} test case
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3 Greek symbols 4 5

6 κ = kinetic rate constant [$\text{cm}^3/\text{mol/s}$]
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9 α = $\ln(A)$ [-]
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12 β = temperature exponent [-]
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15 ε = activation temperature (E_a/R)
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20 Acronyms 21 22 23

24 GRI = Gas Research Institute
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27 B2B-DC = Bound to (2) Bound Data Collaboration
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30 EA = Evolutionary Algorithm
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33 GA = Genetic Algorithm
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36 MUM-PCE = Method of Uncertainty Minimization using Polynomial Chaos Expansion
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40 PLOG = Pressure LOGarithmic nterpolation
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43 CM = Curve Matching
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46 RCM = Rapid Compression Machine
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49 PFR = Plug Flow Reactor
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52 JSR = Jet Stirred Reactor
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55 FPF = Freely Propagating Flames
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58 TC = Test Case
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1 CSF = Cumulative Sensitivity Function

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3 CIF = Cumulative Impact Function

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6 PES = Potential Energy Surface

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10 **Subscripts**

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14 0 = nominal

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17 r = r^{th} reaction

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20 max = maximum value of the related variable

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23 min = minimum value of the related variable

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26 L_2 = dissimilarity index based on L_2 norm evaluation of given polynomials

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29 p = Pearson based measure of given polynomials

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32 m = mutation

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36 c = cross-over

1 Introduction

The development of detailed kinetic mechanisms for fuels combustion supports and facilitates the implementation of cleaner fuels and more efficient combustion technologies, in the perspective of a reduced environmental impact, a differentiation of energy sources and their wiser utilization [1]. From a chemical kinetics perspective, a combustion process involves a considerable amount of species connected by a complex network of reactions. The increase in computing capabilities and in the accuracy and availability of experimental data [2,3] pushes the development of kinetic models of increasing complexity in terms of number of species ($\sim 10^3$) and reactions ($\sim 10^4$) [1]. The rate constants of these reactions constitute the parameters of such models, together with thermodynamic and transport properties. These can be determined experimentally, theoretically or based on analogy with similar compounds for which kinetic subsets already exist [4]. The last decade was characterized by a more frequent adoption of theoretical methods (e.g. ab initio transition state theory-based master equation, AI-TST-ME) [5,6], for the determination of kinetic parameters and thermodynamic properties. Beyond the intrinsic advantages derived from the massive use of AI-TST-ME methods in terms of model predictive capabilities, the increasing popularity of such methods is justified by improved theoretical methods and algorithms currently available, and by the capability of measuring rate constants for elementary steps in a more accurate way, thus providing an immediate validation target for the theoretical results. In addition, automated computational protocols implementing the state-of-the-art AI-TST-ME methods [7–11] are reaching out to a much wider audience, thus paving the way to a more standardized approach to theoretical calculations within the combustion chemistry community. Nonetheless, adopting the best rate parameters does not necessarily lead to improved model performances when looking at a wide range of experimental targets [4,12]. This is due to multiple reasons: i) reference kinetic mechanisms within the combustion science and engineering community have a long and consolidated history, or, in machine learning terms, are “well-trained” models, iteratively validated over a wide range of experimental targets over decades of research activities

1 [12,13]. ii) Models that have been historically developed largely relying on analogy rules and on semi-
2 empirical, or at least less complex, thermochemical kinetics principles [14] are typically self-
3 consistent, even in terms of the very likely possibility of hiding error compensation phenomena. iii)
4 Every rate constant, including those from theoretical methods, is affected by an uncertainty [12,15,16].
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10 The implementation of theory-based development strategies is an iterative process that shows its
11 payback only in the mid-to-long-term perspective. In fact, due to the hierarchical nature of detailed
12 mechanisms and their development [17], implementing one single accurate rate parameter, or new rate
13 parameters for an entire reaction class, might strongly perturb the critical equilibrium between the
14 different modules of a kinetic model. This is particularly important if, while gradually introducing new
15 parameters from theoretical calculations, a well performing model is needed for applications of interest
16 to the end-user.
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27 Regarding theoretical determinations the uncertainty can be intuitively considered as decreasing with
28 an increasing detail in the level of theory [18]. In the past, uncertainty propagation methods were used
29 to quantify the level of uncertainty of phenomenological rate coefficients, in *n*-propyl radical
30 oxidation, obtained from theory [19]. In recent times, quantum chemistry calculations are said to have
31 reached a level of accuracy comparable to that of experimental measurements [5], promoting their
32 applicability in combustion mechanism development [20]. A multi-scale modelling approach was
33 proposed by Burke et al. [21,22], who optimized a set of uncertain theoretical kinetics parameters
34 directly relating their uncertainties to the combustion behaviour in terms of macroscopic targets
35 (ignition delay time, laminar flame speed, etc.). Shannon et al. [23] proposed the use of experimental
36 data and uncertainty quantification to constrain and optimize input parameters in the master equation
37 using MESMER [24].
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55 Essentially, each parameter of a kinetic model, expressed in any form, can be considered as a randomly
56 distributed variable within its uncertainty range [16]. This feature can be exploited in mathematical
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1 optimization if the model is required to accurately perform on small, as well as large, sets of
2 experimental targets.
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5 Optimization is a powerful tool for data-driven mechanism development, which can be used in
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7 combination with the solution of the so called “inverse problem”, consisting in obtaining a new set of
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9 constrained kinetic parameters, by minimizing or maximizing a chosen objective function using
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11 experimental data as targets.
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16 In the context of chemical mechanisms, *Solution Mapping* [25] was the first method applied to a large,
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18 complex system. This method faces the multi-modality of the problem through polynomial response
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20 surfaces, and it was applied for the development of the GRI-MECH [26]. This mechanism was trained
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22 on 77 well-documented and heterogeneous experimental targets describing the combustion of natural
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24 gas. Frenklach et al. [27] introduced the concept of *collaboration of data*, and demonstrated that a joint
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26 analysis on the entire data sample can increase the amount of extracted information and improve the
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28 results. Feeley et al. [28] showed that the technique of data collaboration can be used to rigorously
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30 assess the mutual consistency of experimental results and identify potential outliers, using a chemical
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32 kinetic model. The methodology, called Bound-to-Bound Data Collaboration (B2B-DC) has been
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34 successfully applied and refined in several other works [29–34]. The applicability of
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36 Evolutionary/Genetic Algorithms (EA/GA) to optimization problems involving detailed kinetics was
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38 broadly investigated by Elliott et al. [35]. EA/GA were found particularly suitable for searching
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40 objective-function spaces characterized by high dimensionality. Turányi et al. [36] proposed a sum-
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42 of-squared-error-based methodology, accounting for both direct and indirect measurements, and
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44 successfully applied it to H₂/O₂ [37], H₂/O₂/NO_x [38], H₂/CO mixtures [39], CH₂O and CH₃OH [40],
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46 and ethanol [41]. Najm et al. [42] applied forward Uncertainty Quantification (UQ) and Polynomial
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48 Chaos Expansion (PCE) to chemical kinetics. Sheen and Wang introduced the method of uncertainty
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50 minimization by polynomial chaos expansion (MUM-PCE) [43,44]. Cai and Pitsch [45] minimized
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52 the uncertainty in a *n*-pentane combustion mechanism by applying the MUM-PCE method to the
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1 optimization of rate rules. They also proposed a strategy to optimize pressure-dependent reactions,
2 formulated via logarithmic interpolation, i.e. PLOG standard [46]. PLOG expressions are indeed
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4 gradually substituting the previous formulation of pressure-dependent rate constants, as they yield a
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6 better fitting to experiments or calculations [5]. As this formalism uses accurate rates for discrete
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8 pressures, the parameters of each pressure value were considered independent from each other in [45].
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12 The optimization of relatively compact kinetic mechanisms, such as methane, hydrogen, and ammonia
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14 is particularly attractive, because of i) the large availability of high-fidelity data [4], ii) the current
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16 interest in e-fuels produced from renewable energy [47], and iii) their compact size allowing to
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18 benchmark the suitability of different optimization algorithms before their application to more
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20 complex networks. Among them, the combustion kinetics of ammonia (NH_3) is one of the most active
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22 research fields, due to the high potential of ammonia as a fuel, from both an economic and a technical
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24 perspective [48]. Indeed, ammonia is a carbon-free energy vector with high hydrogen content, which
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26 can be liquefied at pressures higher than 9.9 bar at ambient temperature. Historically ammonia has
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28 been used as NO reducing agent in both selective and non-selective catalytic reduction. The importance
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30 of ammonia is also related to other renewable energy sources: for example, it is a by-product of
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32 anaerobic digestion of municipal wastewater sludges [49], and it is found in trace amounts in biogas
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34 [50]. The combined use of NH_3 with conventional fuels like H_2 or CH_4 has also been studied in order
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36 to improve shortcomings related to its low reactivity [51,52]. Also, optimal operating conditions were
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38 found to minimize NO_x emissions [53]. Therefore, several mechanisms describing the oxidation of
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40 NH_3 and NH_3/H_2 fuel blends were developed [54–56]. Glarborg et al. [57] recently proposed a
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42 comprehensive nitrogen chemistry model, including ammonia itself. Anyway, uncertainties still persist
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44 in the characterization of ammonia chemistry for an accurate prediction of ignition, speciation, and
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46 laminar flame speed [57]. So far, optimization studies in chemical kinetics have been relying on
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48 objective functions based on the L1 and L2 norms of the difference between models predictions and
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50 corresponding experimental targets [35,58,59]. Recently, You et al. [31] minimized the L1-norm of
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1 the difference between the active variables values and the nominal ones, constrained on the feasible
2 set of combinations identified with B2B-DC [27]. The formulations in [31] not only improve the model
3 performance, but also minimize the number of parameters and the deviations of the new values from
4 the literature recommendations. Recently, Bernardi et al. [60] presented an innovative framework
5 based on Curve Matching (CM), consisting in a multi-faceted functional analysis of the profiles
6 obtained from both models and experiments. In this approach, they introduced a proper metric to
7 quantify the similarity between the curves representing experiments and simulations, rather than a
8 point-wise measure of the distance between them. Pelucchi et al. [61] revised and proposed such
9 framework as a further step towards an automatic model validation protocol.
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12 In this work, a novel methodology for the optimization of kinetic mechanisms is proposed, which
13 includes, for the first time, the possibility to optimize PLOG reactions by accounting for
14 interdependencies between rates at different pressures and using the CM index [61] as the objective
15 function. The effectiveness of such approach was verified by adopting a kinetic mechanism for
16 ammonia combustion as a case study [20]. This model was recently proposed and largely relies on
17 theoretical calculations of key reaction rate constants. As an added value, this work also presents
18 guidelines for attributing reasonable uncertainty factors for theoretical determinations performed with
19 different theory levels. On these bases, optimization was carried out using a non-gradient based, mono-
20 objective, Evolutionary Algorithm (EA) in OptiSMOKE++ [62], capable of handling all the
21 parameters as uniformly distributed random variable within their estimated bounds, simultaneously.
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24 The manuscript is organized as follows. Section 2 presents the proposed methodology. Section 3
25 describes the results, for pure ammonia on a wide range of experimental conditions covering ignition
26 delay times in Shock Tube (ST) and Rapid Compression Machines (RCM), Plug Flow (PFR) and Jet-
27 Stirred Reactor (JSR) speciation measurements and laminar burning speed in Freely Propagating
28 Flames (FPF). Finally, conclusions are presented in Section 4.
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2 Methodology

2.1 Optimization procedure

As in [18, 20], all the parameters of the selected rate constants expressed according to the modified Arrhenius expression ($k=A T^\beta \exp(-E_a/RT)$) undergo optimization, i.e. pre-exponential factors (A), temperature exponents (β), and activation energies (E_a). The logarithmic expression of the rate constant adopted in this work yields:

$$\kappa = \ln(k(T)) = \ln(A^*) + \beta \ln\left(\frac{T}{T_{ref}}\right) - \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right) = \alpha^* + \beta \ln\left(\frac{T}{T_{ref}}\right) - \varepsilon \left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \quad (1)$$

where, α^* , β , and ε are continuous random variables representing the Arrhenius parameters, usually assumed to be uniformly [59] or normally [63] distributed. In equation (1), A^* is a re-parametrized form of the pre-exponential factor at the reference temperature T_{ref} :

$$A^* = A T_{ref}^\beta \exp\left(-\frac{\varepsilon}{T_{ref}}\right), \quad (2)$$

The re-parametrization in equation (2) minimizes the high correlation between the parameters of the Arrhenius equation, and makes parameters estimation easier [64,65]. In this work, a reference temperature of 1000 K was adopted for all reactions.

The uncertainty of the rate coefficients is usually assumed as symmetric, and is reported in literature in terms of f_r factor [15], being defined as follows:

$$f_r = \frac{\kappa_{max} - \kappa_0}{\ln(10)} = \frac{\kappa_0 - \kappa_{min}}{\ln(10)}, \quad (3)$$

The problem of defining the constraints for the active parameters was dealt with in several studies. In the deterministic framework of B2B-DC [27][30], the feasible set is obtained by combining the initial bounds of both active variables and experimental data. In MUM-PCE [43], a statistical approach is

1 adopted, which assumes “a priori” distributions for both the model parameters and the measurements,
 2 and produces “a posteriori” distributions for both model parameters and predictions. These two
 3 approaches were recently compared, and they were found to give consistent results [32]. Nagy and
 4 Turányi [66,67] considered the dependence of f_r on temperature, and proposed a method to determine
 5 the covariance matrix and the multivariate normal distribution of the transformed Arrhenius
 6 parameters from prior information on the rate constant. In a later study, Nagy et al. [68] recommended
 7 the adoption of temperature-independent uncertainty and uniform distributions for Arrhenius
 8 parameters with little prior information. As we discuss later (see 2.5), the nominal mechanism in this
 9 study largely relies on ab-initio calculations. For this reason, the temperature dependence of f_r is not
 10 accounted for, and uniform distributions for all the active variables are employed.

11 As reported in equation (1), κ is a weighted sum of three random variables with joint uniform
 12 distribution, which results in a higher probability near κ_0 [68]. For the sake of simplicity, in the
 13 following we assume that for all temperatures the kinetic constant κ is a normally distributed random
 14 variable with mean value κ_0 , corresponding to $\kappa(p_0)$, and standard deviation σ_κ , with $\mathbf{p}_0 = [\alpha_0, \beta_0, \varepsilon_0]$.
 15 As in [43][59], we assume that f_r corresponds to the $2\sigma_\kappa$ of the distribution of κ , and we constrain it
 16 at 3σ . From equation (3), κ_{\max} and κ_{\min} can be obtained, i.e. the maximum and minimum linear
 17 constraints of κ in $T \in [T_{\min}, T_{\max}]$. As an element κ_i in κ can be retrieved by sampling from the
 18 distributions of the normalized Arrhenius parameters, f_r can also be propagated from κ to α , β , and ε
 19 to estimate their bounds. In the following, the hypothesis of mutual independence between parameters
 20 is used exclusively to achieve this goal. Given the equation:

$$10f_r = \frac{k_{\max}(T)}{k_0(T)} = \frac{k_0(T)}{k_{\min}(T)} = \exp[\Delta\alpha + \Delta\beta \ln T - \Delta\varepsilon T^{-1}], \quad (4)$$

and assuming that the maximum variation Δp_i of one parameter is determined by projecting the uncertainty of κ on the parameter itself (i.e. keeping constant the other two to their nominal values so that $\Delta p_i=0$), the following constraints can be retrieved:

$$\alpha_0 - \ln(10^{f_r}) \leq \alpha \leq \alpha_0 + \ln(10^{f_r}), \quad (5)$$

$$\beta_0 - \frac{f_r}{\log_{10}(T)} \leq \beta \leq \beta_0 + \frac{f_r}{\log_{10}(T)}, \quad (6)$$

$$\varepsilon_0 - f_r T \ln(10) \leq \varepsilon \leq \varepsilon_0 + f_r T \ln(10), \quad (7)$$

This operation results in 2 non-linear constraints for β and ε in $T \in [T_{\min}, T_{\max}]$. However, it can be shown that:

$$\lim_{T \rightarrow \infty} k(T) = \exp(\alpha) T^\beta, \quad (8)$$

$$\lim_{T \rightarrow 0} k(T) = \exp(-\varepsilon T^{-1}), \quad (9)$$

The limits (8) and (9) indicate that at high temperature, the term T^β controls the value of κ , while the contribution of εT^{-1} is progressively smaller. The opposite is true for low temperatures. Thus, the sensitivity of κ to β is maximum at T_{\max} . Conversely, the sensitivity of κ to ε is maximum at T_{\min} . By bounding β and ε in equations (6) and (7) at T_{\max} and T_{\min} , respectively, we ensure that $\kappa(\alpha_0, \beta_{\max}, \varepsilon_0, T)$, $\kappa(\alpha_0, \beta_{\min}, \varepsilon_0, T)$, $\kappa(\alpha_0, \beta_0, \varepsilon_{\max}, T)$, and $\kappa(\alpha_0, \beta_0, \varepsilon_{\min}, T)$ never violate the linear constraints on $\kappa(T)$, when $T \in [T_{\min}, T_{\max}]$. In this work, the minimum and maximum temperatures are 300 and 3000 K, respectively. Indeed, from the definition of f_r in equation (3), also $\kappa(\alpha_{\max}, \beta_0, \varepsilon_0, T)$, and $\kappa(\alpha_{\min}, \beta_0, \varepsilon_0, T)$ do not violate the mentioned constraints. The adoption of this methodology for the estimation of parameter boundaries has two main advantages. First, it reduces the probability of sampling a kinetic rate constant $\kappa(T)$, which violates the above mentioned linear constraints, with respect to previously proposed methods [69]. Further details about this feature are provided in the Supplementary Material (SM). Secondly, it also enables the optimization of PLOG-

1 based reactions. As an example, Figure 1 shows the projections of the parameters bounds on the kinetic
 2 constants of the reaction $\text{NH}_2+\text{NO}_2=\text{H}_2\text{NO}+\text{NO}$. Those resulting from varying only α overlap with the
 3 2σ of the distribution of κ . On the other hand, those resulting from the variation of β and ε only
 4 overlap with the 2σ of k only at T_{\max} and T_{\min} , respectively, while not exceeding them along $T \in [T_{\min},$
 5 $T_{\max}]$. The limit values of the corresponding κ distribution, i.e. $\kappa(\alpha_{\max}, \beta_{\max}, \varepsilon_{\min})$ and
 6 $\kappa(\alpha_{\min}, \beta_{\min}, \varepsilon_{\max})$, are also displayed. They include the entire space of κ and exceed it. In fact, since
 7 the parameters are correlated [66], not all the combinations of the three results are valid.
 8
 9

10 All the combinations, which result in values of κ belonging to the area between the limit values and
 11 the 3σ bounds of the distribution of κ , are excluded from the set of eligible parameter combinations.
 12 This is achieved by introducing a penalty function during the optimization: the associated objective
 13 function is equal to curve matching index of 0 (i.e. the maximum error in the CM methodology).
 14 Conversely, for each valid combination suggested by the adopted optimization algorithm, a
 15 corresponding set of simulations responses are obtained by performing model evaluations for the entire
 16 database. Subsequently, the CM indices:
 17
 18

$$19 \text{CM}_j = \frac{(d_{j,L_2}^0 + d_{j,L_2}^1 + d_{j,p}^0 + d_{j,p}^1)}{4} \in [0, 1], \quad (10)$$

20 are calculated, as a weighted sum of 4 dissimilarity indices, for each dataset j . A unitary CM value
 21 indicates a perfect matching between model evaluations and experiments. In particular, functional
 22 estimations of both experimental, $g(x)$, and model evaluations, $m(x)$ (and their derivatives $g'(x)$ and
 23 $m'(x)$) are obtained by interpolating smoothed splines, which result in satisfactory approximations of
 24 both data points and first derivatives [60,61]. Based on these estimations, the dissimilarity indices are
 25 computed as follows:
 26
 27

$$28 d_{j,L_2}^0 = \frac{1}{1 + \frac{\|m-g\|}{|D|}} \in [0, 1], \quad (11)$$

$$d_{j,L_2}^1 = \frac{1}{1 + \frac{\|m' - g'\|}{|D|}} \in [0, 1], \quad (12)$$

$$d_{j,p}^0 = 1 - \frac{1}{2} \left\| \frac{m}{\|m\|} - \frac{g}{\|g\|} \right\| \in [0, 1], \quad (13)$$

$$d_{j,p}^1 = 1 - \frac{1}{2} \left\| \frac{m'}{\|m'\|} - \frac{g'}{\|g'\|} \right\| \in [0, 1], \quad (14)$$

where $|D|$ is the intersection of the domain between g and m . For instance, if the abscissa values of g belong to $[500, 1500]$, and those of m belong to $[400, 1800]$, the value of $|D|$ would be 1000 (i.e. $|D| = 1500 - 500$). The $\|g\|$ is the L_2 -norm of the function g . All the dissimilarity indices are intrinsically constrained between 0 and 1, where 1 indicates maximum similarity, and 0 maximum dissimilarity. Individually, d_{j,L_2}^0 depends on the area enclosed by g and m , while d_{j,L_2}^1 evaluates the same quantity between their respective derivatives. Hence, the first generalizes a classical L_2 -norm, while the second extends it. On the other side, the Pearson dissimilarity measures $d_{j,p}^0$ and $d_{j,p}^1$ indicate perfect matching if g and m , and their derivatives, only differ by vertical translation. Further mathematical details and examples are given in [60,61]. In order to account for the uncertainty in the evaluation of (10), a bootstrapping procedure [70] on the experimental data is carried out. This procedure relies on the assumption that each data point is normally distributed within its experimental uncertainty. A sufficiently large set of possible experimental trends is generated taking random samples from the above-mentioned distributions. Figure 2 displays an example of the application of the bootstrap procedure for laminar flame speed data, where 7 gaussian distributions (i.e. one for each data point) were sampled 10 times to generate as many bootstrap variations.

A set of 50 bootstrap variations ($N_b=50$) for each data point was adopted after verifying the substantial independence of the final output on a further broadening of the set. Thus, the objective function in this work is defined as:

$$M = \frac{1}{DS} \sum_{i=1}^{DS} \left[1 - \frac{1}{N_b} \sum_{j=1}^{N_b} (CM_j) \right]_i, \quad (15)$$

Where, DS is the number of target datasets and N_b is the number of bootstrap variations. In order to discuss its advantages, the final index (eq. (15)) is compared to the modified versions of L1-norm and L2-norm:

$$L_1 = \frac{1}{DS} \sum_{i=1}^{DS} \frac{1}{E_i} \sum_{j=0}^{E_i} \left| \frac{Y_{i,j}^{exp} - Y_{i,j}^{sim}}{\sigma(Y_{i,j}^{exp})} \right|, \quad (16a)$$

$$L_2 = \frac{1}{DS} \sum_{i=1}^{DS} \frac{1}{E_i} \sum_{j=0}^{E_i} \frac{(Y_{i,j}^{exp} - Y_{i,j}^{sim})^2}{\sigma^2(Y_{i,j}^{exp})}, \quad (16b)$$

where E_i is the number of discrete experiments belonging to the i -th dataset. Y_{ij}^{exp} , Y_{ij}^{sim} and σ are the values of the j -th measurement, simulation, and experimental uncertainty in the i -th dataset, respectively.

As in Olm et al. [71], when the error on ignition delay times is evaluated, the following transformation is used, $Y_{ij}^{exp} = \ln(y_{ij}^{exp})$ and $Y_{ij}^{sim} = \ln(y_{ij}^{sim})$, where the y_{ij}^{exp} and y_{ij}^{sim} refers to the absolute experimental and simulated values, respectively. For other experimental targets, such as species concentrations and laminar flame speeds, the logarithmic transformation is not used. The same is done for the estimation of Curve Matching indices for ignition delay times.

In this work, the objective function minimization is performed by means of an Evolutionary Algorithm (EA) [72], whose solution is less dependent on the initial guess compared to other algorithms [35].

Indeed, in EA the initial guess is a set of sampled combinations of active parameters, i.e. the ‘population’. Initially, a population of 100 different combinations of parameters is sampled, evaluated and labelled with objective function values. Then, the algorithm starts the first iteration (a ‘generation’), where the elements of the current population (the ‘parents’) are ranked applying a linear scaling of probability based on the corresponding objective function values. In general, the best

1 performing parents undergo uniform crossover, where a couple of parents (or a ‘*chromosome*’) is
2 selected, and each parameter value can be swapped between the two with a probability equal to the
3 crossover rate p_c . This operation produces a new pair of elements (the ‘*off-springs*’), resulting from
4 the cross-over of as many *parents*. Subsequently, mutation is introduced. In particular, for each new
5 *off-spring*, every variable has the same probability to mutate, according to the mutation rate p_m . A non-
6 uniform mutation operator was adopted to assign a new parameter value by sampling from its
7 distribution. When mutation and cross-over are complete, a resulting population of 200 is obtained,
8 i.e. twice the size of the initial one. In this work, a replacement strategy, which selects the 50 best
9 individuals in 200 elements, and randomly selects other 50 from the remaining 150, was adopted. This
10 ensures the balance between global and local search. The adopted probability of cross-over ($p_c=0.65$)
11 and mutation ($p_m=0.5$) were suggested by Elliott et al. [35]. The new parent population undergoes the
12 same procedure iteratively until satisfactory accuracy is achieved. In the present work, Dakota [72]
13 and OpenSMOKE++ [73,74], are coupled in OptiSMOKE++ [62] to perform the optimization. The
14 first toolbox is specifically conceived to address engineering problems such as optimization,
15 calibration and uncertainty quantification. On the other hand, OpenSMOKE++ enables the simulation
16 of multiple experimental combustion facilities typically considered for kinetic model development and
17 validation.

2.2 Optimization of reactions in PLOG formalism

42 For those reactions exhibiting a “fall-off” behaviour, the rate $k(T,P)$ is usually determined from the
43 low and high-pressure limit constants, together with a blending function that smoothly connects the
44 limiting rates across the fall-off regime, using different possible formulations. Among these, the Troe
45 formulation [75,76] is the most widely used. An alternative formulation based on logarithmic
46 interpolations, expressed with the so-called PLOG, has been recently proposed [46], and is rapidly
47 growing in popularity because of the potentially superior accuracy, thus becoming the new standard

1 formalism. PLOG reactions are typically introduced in a kinetic mechanism using multiple Arrhenius
2 rate constants accounting for temperature dependence at constant pressures covering the entire range
3 of conditions from the low to the high-pressure limits. Then, a proper (i.e. logarithmic) interpolation
4 is adopted for the intermediate pressures. In this way, the combined effects of pressure (P) and
5 temperature (T) on the rate constant k is properly accounted for. As a result, the three Arrhenius
6 parameters for each pressure value cannot be optimized independently from each other, even within
7 their own uncertainty ranges, in order to keep the physical consistency in the whole pressure domain.
8 On the contrary, the same optimization performed using all the nominal pre-exponential factors,
9 temperature exponents and activation energies, i.e. treating reactions at different pressures as
10 independent from each other, would result in a non-monotonic behaviour with arguable physical
11 meaning. Additionally, since the number of reactions within the same PLOG is the result of a fitting
12 needed to describe complex $k(T, P)$ with a small acceptable error, the number of parameters to be
13 handled scales accordingly. This may result in an abrupt increase in the number of parameters for a
14 single reaction. For the first time in literature, we propose an approach to optimize the parameters at
15 all pressures simultaneously, based on what proposed for the parameters bounds in the previous
16 section, using only three, uniformly distributed random variables with an average value of 0, and
17 constrained in the following ranges:

$$18 \quad X_1 \in [-\ln(10^{f_r}), \ln(10^{f_r})], \quad (17)$$

$$19 \quad X_2 \in \left[-\frac{f_r}{\log_{10}(T_{max})}, +\frac{f_r}{\log_{10}(T_{max})} \right], \quad (18)$$

$$20 \quad X_3 \in [-f_r T_{min} \ln(10), +f_r T_{min} \ln(10)], \quad (19)$$

21 These variables are associated with α , β , and ϵ , at all pressures, respectively. The value of X_1 is
22 sampled from its distribution and added to all the α , at different pressures, i.e. each reaction rate is
23 changed by the same factor, and the same is done for β_0 and ϵ_0 , using X_2 and X_3 . As an example, Figure

3 displays results from the section 3 about the comparison between nominal and optimized rate for the decomposition reaction $\text{HNO}=\text{H}+\text{NO}$, to which we attributed an uncertainty factor f_r of 0.3. The reported pressure values for this reaction are 0.1,1,10,100 and 1000 bar. Figure 3 highlights the preserved consistency in the pressure dependent behaviour of the reaction rates.

2.3 Database

Figure 4 summarizes the features of each test case (TC) in the temperature, pressure and composition space. The experimental data considered in this work cover the entire space of operating conditions.

The database, consisting of 60 different datasets (with 635 experimental points) from different test cases, was divided in optimization and validation targets (i.e. 75% and 25%, respectively). For high-temperature conditions, the shock tube experiments from Mathieu and Petersen [55], and Shu et al. [77] cover ignition delay time in a wide range of composition ($\phi = 0.5$ to 2.0) and pressures (10 to 40 bar). Stagni et al. [20] reported data for ammonia oxidation at nearly atmospheric pressure for lean mixtures in two different systems, namely jet stirred and flow reactors. At low temperatures, He et al [78] and Pochet et al. [79] provided auto-ignition data at higher pressures, for lean, stoichiometric and rich mixtures in rapid compression machines. Wargadalam et al. [80] and Song et al. [81] published speciation data for very lean conditions, at pressures of 1, 30 and 100 bar, in flow reactors. Davidson et al. [82] investigated ammonia pyrolysis in a shock tube at extremely high temperatures ($T > 2500$ K). The laminar burning speed experiments by Lhuillier et al. [51] were only considered for validation. However, flame speed targets were included by using the data from Ronney [83]. The TCs from Rota [84] and Dagaut [85] in jet stirred reactors were excluded from the optimisation set, yet used for validation, as they cover a part of the operating conditions space which is already densely populated (see Figure 4).

2.3.1 Numerical simulations

In this work, the ignition delay time was calculated using the definition reported in the corresponding experimental paper. The constant volume assumption was used to simulate the shock tube data of Mathieu and Petersen [55], and Davidson [82]. In reproducing the data from Shu et al. [77], gas dynamic effects were accounted for using the methodology described in [86]. The RCM data were reproduced under the hypothesis of adiabatic core [87], and detailed volume profiles from He [78] and Pochet [79] were used to properly account for the compression stroke and heat exchange effects in each experiment. For the flow reactor experiments from Stagni et al. [20], measured, non-reactive temperature profiles were given as input to the simulations.

2.4 Impact-based reactions selection

Warnatz [88] suggested the joined use of sensitivity and uncertainty to identify key reactions in a detailed kinetic mechanism. This concept was also used in optimization of kinetic models for the first time by Frenklach et al. [25], who selected the active variables using a ranking based on the “impact factor”, i.e. considering the absolute values of sensitivity coefficients multiplied by their own uncertainty. Later on, this index was also referred to as “sensitivity-uncertainty index” [89] and “optimization potential” [45].

In this work, parameters selection is performed separately for each Test Case (TC), in order to retain all the important elementary steps. First, a local sensitivity analysis [73], was performed for each experimental point in TC. This produces a vector \mathbf{S} containing the average normalized sensitivity coefficient s_r (eq. (20)) for each reaction $r \in R$.

$$s_r = \frac{1}{D} \sum_{d=1}^D \left| \frac{A_r}{Y_{ref}} \frac{\partial Y_d}{\partial A_r} \right|, \quad (20)$$

1 where A_r is the pre-exponential factor of the reaction r , Y is the optimization target, Y_{ref} is a
2 normalizing factor, and D is the number of experiments for the test case. This vector is then sorted and
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4 elaborated in a cumulative sum, and the resulting one is referred to as *Cumulative Sensitivity Function*
5 (CSF). This methodology allows exploiting the properties of the cumulative sum, which enables the
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7 selection of reactions to be optimized with proper priority. In particular, a subset of sensitive reactions
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9 **Ss** can be retrieved by establishing a threshold corresponding to a defined fraction of the sum of the
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11 1st order sensitivity coefficients related to a specific **TC**. Subsequently, the test case related impact
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13 factor vector for each reaction r is evaluated with eq. (21):
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$$18 \quad I_{r,s} = s_{r,s} \cdot f_r, \quad (21)$$

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23 where each element of the sensitivity vector is multiplied with the corresponding uncertainty factor
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25 [15,16]. Figure 5 shows an example of Cumulative Impact Function (CIF) obtained by applying the
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27 cumulative sum for the test case from [81]. Here only 5 reactions, are responsible of 90% of the impact.
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29 The remaining set of 196 reactions retaining ~10% of the total impact are excluded in further
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31 investigations. All selected reactions at CSF and CIF level are reported in table S1 (SM).
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37 2.5 Uncertainty estimation

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41 Among the reactions included in this work 13 out of 43 rates come from experiments together with
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43 their uncertainty factors (see table S1 in SM). These reactions were selected by applying the procedure
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45 described in section 2.4 to each experiment inside the database (section 2.3). The remaining part
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47 involves phenomenological rate constants determined using first principle (*ab-initio*) calculations.
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49 Klippenstein et al. [18] declares that an uncertainty factor of 0.3 (see eq. (3)) can be obtained for for
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51 the rate constants of the reactions belonging to the families considered in the present work. In a more
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53 recent publication Cavallotti et al. [90] showed that the level of accuracy attainable using the *ab-initio*
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55 master equation approach can be a factor of 0.3 (see eq. (3)) or lower. The main factors contributing
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1 to uncertainty in a rate constant calculation derive from: 1) the level of theory used to determine the
2 energy of stationary points on the potential energy surface (PES); 2) the theoretical methods adopted
3 for the computation of the high pressure rate constant; 3) the level at which pressure effects and
4 reaction dynamics on a multi-well PES are described; 4) the treatment of anharmonicities, most
5 importantly the description of torsional motions, if active for a specific reaction; 5) the availability of
6 experimental rate constant data. The values from the protocols of Cavallotti et al. [90] and Klippenstein
7 et al. [18] are assumed as the lower uncertainty threshold in the present work, while the remaining
8 ones are assigned with a policy of inverse proportionality to the adopted level of theory. This threshold
9 corresponds to a f_r factor equal to 0.3 (see eq. (3)). The following penalty terms were used:

- 10 1) Concerning the level at which electronic structure calculations were performed, computational
11 protocols where energies are computed at the CCSD(T)/CBS or higher have no penalty term.
12 For CBSQB3 calculations a 0.2 factor is added to f_r , so that the uncertainty goes from 0.3 to
13 0.5. For DFT calculations, such as B3LYP, a factor of 0.3 is added, thus increasing the
14 uncertainty factor to 0.6.
- 15 2) High pressure rate constants can be determined using (in order of decreasing accuracy): i)
16 Variable Reaction Coordinate Transition State Theory (VRC-TST), ii) variational transition
17 state theory (VTST), or iii) conventional transition state theory (TST), where TST or VTST
18 are assumed to be suitable to study abstraction or addition reactions, while VRC-TST or VTST
19 are necessary to study barrierless processes such as recombination or bond dissociation
20 reactions (i.e. unimolecular initiations reactions). A penalty of 0.3 and 0.1 was assigned to TST
21 and VTST, respectively, in case of radical/radical recombination or decomposition reactions.
22 Otherwise, penalties of 0.1 and 0.05 were assigned.
- 23 3) Methods where the impact of pressure dependence and multi-well dynamics on the rate
24 constant are studied using the Master equation approach coupled with TST and ab initio
25 calculations (AI-TST-ME), are generally more accurate than methods with lower theoretical

1 detail, such as QRRK. The adopted penalty term is 0.4, so that for QRRK methods the
2 estimated rates are associated with an uncertainty factor ranging between 0.7 and 1. This value
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4 was adapted to 0.5 for Dean and Bozzelli [91], who also compared their rates with experimental
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6 data and adjusted their recommendations accordingly.
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10 4) Anharmonicities can have a quite relevant impact on rate constants if torsional motions are
11 present [92]. If no torsional motion treatment, such as the hindered rotor model, is used when
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13 torsional motions are active, a penalty term of 0.5 is added.
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17 More details regarding the uncertainty estimations in this work are provided in the Supplementary
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19 Material. In order to further support the general validity of the optimization method, a sensitivity
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21 analysis to the assigned uncertainty parameters was carried out by performing three different
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23 optimizations with a limited number of targets (see SM). The first, is carried out with uncertainty
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25 factors used in this work, the others by multiplying all of them by a factor of 0.5, and 2. Results are
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27 reported in the Supplementary Material showing that the majority of the resulting kinetic rate constants
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29 overlap with those obtained with the nominal values of f_r (eq. (3)), thus supporting the robustness of
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31 the methodology.
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39 3 Results and Discussion

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43 The model from Stagni et al. [20], hereafter reported as ‘nominal’, consists of 31 species and 210
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45 reactions. The proposed methodology for mechanisms optimization aims at improving the nominal
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47 one considering all target datasets and uncertain parameters, simultaneously. This represents a
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49 significant difference from previously suggested approaches, where a hierarchical and systematic
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51 procedure was adopted instead [41]. As already explained in section 2.3, the 60 datasets within the
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53 database were split into two parts, i.e. optimization and validation targets (45 and 15, respectively) to
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56 *a-posteriori* the the loss in predictability on the datasets, which were not used in the optimization. The
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1 evaluation of the impact of different objective functions on the optimized model performance is the
2 main purpose of this work. Using the same database, three detailed kinetic mechanisms were obtained
3 using CM (eq. (15)), L1-norm (eq. (16a)), and L2-norm (eq. (16b)). These are hereafter referred to as
4 CM-mech, L1-mech, and L2-mech, respectively. Specifically, CM-mech is available in the
5 Supplemental Material. The thermodynamic and transport properties (which were not involved in the
6 optimization) were taken from [20].

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15 The reactions to be optimized were selected using a cumulative sensitivity threshold (see 2.4) equal to
16 90%, applied for each test case, leading to a sensitive subset of 41 reactions. Then, a selected subset
17 of 24 most impactful reactions was obtained using the same threshold on the CIF (see 2.4) after the
18 estimation of reaction rates uncertainties (see section 2.5). More details about which reactions were
19 included in this sub-set are given in SM. It is also important to mention that 4 out of 24 reactions
20 (namely (R24, R111 and R112, and R143) are expressed with PLOG formalism. Indeed, R111 and
21 R112 are duplicate of the same reaction, as evaluated by Dean and Bozzelli [91].



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42 Overall, optimization was carried out considering 68 active variables. Nonetheless, only 56 out of 68
43 are directly linked to one single Arrhenius parameter, in pressure-independent reactions. Due to the
44 nature of the four pressure-dependent reactions (i.e. PLOG), the remaining 12 uncertain parameters
45 correspond to 45 Arrhenius parameters in the kinetic mechanism (see section 2.2). Subsequently, 101
46 kinetic parameters were optimized simultaneously.

1 Figure 6 shows a comparison between the optimized duplicate PLOG using the CM as objective
2 function, and the nominal reaction. The former falls within the 2σ uncertainty band and it is increased
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4 by the same factor, for all pressures.
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8 On average, the optimized rate deviates from the nominal value by +76.4% at the low-pressure limit
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10 and by +78.2% at the high-pressure limit, due to the sum of R111 and R112 at different pressures. The
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12 pre-exponential factors at three different pressures were optimized by multiplying them by a factor of
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14 ~ 1.567 and ~ 1.221 , for R111 and R112, respectively. Regarding other parameters, for R111 the
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16 temperature exponent is kept constant, while it increases for the R112 by a factor of 0.065. Inversely,
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18 a more significant change of -315.7 [cal/mol] in the energies of activation for R111, and no variation
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20 for the same parameter in R112, was observed.
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26 The agreement with the laminar flow reactor experiments from Stagni [20] is mostly affected by
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28 reactions (R24, R111, R112, and R143. Remarkable results are obtained, with all objective functions,
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30 for predictions of O_2 consumption, NH_3 conversion, H_2O and NO formation, as highlighted in Figure
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32 7. The major change occurs at 1523 K for NO , where also ammonia, oxygen, and water are
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34 significantly affected in shape. At this temperature, NH_3 consumption is delayed and NO volume
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36 fraction decreases by one order of magnitude (from ~ 1.3 to ~ 0.2 v/v %), resulting in a largely improved
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38 agreement with the experimental data for both CM-mech and L_2 -mech, while the L_1 -mech slightly
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40 underestimates the concentration of NO at this point. For temperatures between 1600 and 1800 K,
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42 none of the models can reliably reproduce the experimental observations. For the temperature ranges
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44 [1523,1600] and [1800,2000] K, the L_2 -mech shows the best agreement with the experiments. For NO
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46 formation, the CM index (see eq. (10)) increases from 0.849 to ~ 0.9 for all the optimized mechanism.
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48 The L_2 -norm for this dataset decreases from ~ 1560 to 172, 160 and 158 for CM-mech, L_1 -mech and
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50 L_2 -mech, respectively.
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2 In order to discuss this case further, sensitivity and rate of production analysis of both nominal and
3 CM-mech were performed at 1523 K to explain how modifying kinetic rate constants led to the
4 improvement discussed above. Figure 8a shows the main sensitive reactions for the formation of NO.
5 R26 is characterized by a negative sensitivity coefficient, which relatively increases after optimization.
6
7 This happens because the rate constant for this reaction increases by a factor of ~2, as shown in Figure
8 8b, and strongly impacts ammonia conversion, as well as NO formation. Existing direct measurements
9 for R26 [93,94] reported a lower rate with respect to the nominal mechanism. Therefore, model
10 optimization and measurements seem to recommend conflicting rate modification for this reaction.
11
12 However, recent advanced theoretical calculations [95] reported an increased rate for R26 with respect
13 to the nominal one, in agreement with the optimizer. In this context, a better characterization for this
14 reaction is recommended for future mechanism development. For instance, new experiments may be
15 carried out to confirm previous findings [95].
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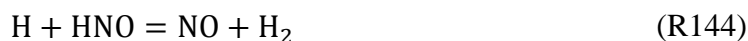
29 Globally, the rate of NH₃ consumption in the optimized mechanism decreases because of the
30 competition between R26 and R27.
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41 NH₂ is formed in a lower amount, since R27 is the dominant kinetic step for its formation. This
42 explains modified trend for ammonia in Figure 7. In spite of the ~27% increase in the combined kinetic
43 rate constant of R31 and R32 (see Figure 8c), HNO rate of production decreases due to the limited
44 availability of NH₂. It is clear that in L₂/L₁-mech the reduced production of HNO is enhanced by a
45 decrease in R31 and R32.
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2 As reported by Stagni et al. [20], HNO plays a key role in NO_x formation. This species dissociates
3 through R143, and undergoes H-abstraction in R144, forming nitrogen-oxide (NO).
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11 As shown in Figure 8a, R143 and R144 exhibit positive and negative sensitivity coefficients,
12 respectively. Therefore, the reduction of R143 by a factor of ~2 (see Figure 3) along with the increase
13 of R144 by a factor of ~2.5 (shown in Figure 8f) cause the pronounced NO reduction at 1523 K.
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20 Figure 8e shows a 6% increase in $k(T)$ for R76, which carries an enhanced negative sensitivity
21 coefficient in the optimized mechanism. Therefore, NO reduction is also due to its conversion to final
22 products through such reaction.
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31 Also, an average 7% increase in R39 (see Figure 8d), along with the abovementioned deviation of
32 R111/R112 from the nominal values, displayed in Figure 6, strengthen the following path
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1 i.e. high pressure [96], and was correlated to discrepancies between experimental data and predictions
2 using 1D laminar flames [97], for rich conditions. Since pure ammonia exhibits a very low laminar
3 burning speed, and the data from Lhuillier et al. [51] were not produced in microgravity conditions,
4 they were used only for the validation.
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10 Figure 9a displays the comparison between the nominal, and the optimized mechanisms on data from
11 Ronney [83]. The performance of CM-mech mostly falls within the experimental uncertainty and is
12 comparable to the nominal one. On the contrary, using the point-wise definitions of the objective
13 function, namely eq. (16a) and (16b), resulted in a loss in predictability. For the conditions in Figure
14 9a, the 4 most sensitive reactions (and their sensitivity coefficients) are $\text{H}+\text{O}_2=\text{O}+\text{OH}$ (0.804), R39
15 (0.196), $\text{NO}+\text{NH}_2=\text{OH}+\text{NNH}$ (0.151), and R31-R32 (-0.095). As shown in Figure 8c and Figure 8d,
16 R31-R32 decrease and R39 increases in both L_2/L_1 -mechanisms. Since these reactions show a negative
17 and a positive sensitivity coefficient, respectively, they determine an increase in reactivity for L_2/L_1 -
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32 In particular, R39 is pushed outside the 2σ of its distribution and approaches the upper bound at 3σ
33 for both L_2/L_1 -mech, resulting in a rate with lower probability than that of CM-mech.
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38 This reaction was found to be strongly impactful in the shock tube data from Davidson [82]. In Figure
39 9b, the L_2/L_1 -mech clearly outperform the nominal model, as well the CM-mech, for the formation of
40 NH_2 during the pyrolysis of ammonia at 2300 K and atmospheric pressure. Conversely, in the same
41 system and operating conditions, all of the models show satisfactory agreement for the experiment on
42 NH formation (see Figure 9c).
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51 Thus, to improve the predictions in Figure 9b and the NO formation in Figure 7 using the objective
52 functions in equations (16a) and (16b), the optimizer might force the kinetic parameters of R26 to less
53 probable values (see Figure 8c/d). The same does not happen CM-mech, where only 1 out of 24
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1 reactions exceeds the 2σ . The details about kinetic rate constants of the considered reactions in
2 optimization can be found in the supplementary material (SM).
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8 As already discussed in [57], reactions R74 and R75 are crucial for modelling extremely lean mixtures,
9 leading to formation of N_2O , and H_2NO . In the same study [57], R172 was defined as strongly
10 impactful for high O_2 excess and high pressures.
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26 In this work, the same three reactions were found to be strongly impactful for ignition delay time
27 predictions at high pressure in both shock tube [77] and rapid compression machine [78] experiments.
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31 Figure 10 shows examples from the 6 ignition delay time datasets from Shu et al. [77], at high pressure.
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34 For this test case, CM-mech has the highest similarity with experiments, in fact the average CM value
35 is 0.954, while the nominal one is 0.945. Even though L_1/L_2 -mech yield very good agreement with this
36 test case, their curve matching indices decreases to 0.927 and 0.931, respectively. At 20 bar and in rich
37 conditions, none of the mechanism is consistent with the experimental uncertainty at low temperatures.
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44 These results suggests that, only for these three points, measurement uncertainty might be higher than
45 20%.
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49 The reactions R74, R75 and R172 were also selected for the JSR data by Stagni [20], the RCM data
50 by Pochet [79], and the PFR data from Wargadalam [80], and Song [81]. In a similar temperature
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regime, ignition delay time measured at high pressures (20 and 40 bar) [78] give the most satisfying results in this work. In general, overall improvement can be appreciated in Figure 11.

Table 1 shows the overall objective function values for the optimized models and their deviations from those of the nominal mechanism. As expected, both L1-mech and L2-mech outperform the nominal mechanism in terms of L1 and L2-norms, but the first is characterized by lower a CM index (i.e. higher 1-CM), and the second shows little improvements. This indicates that using the objectives functions 16a/16b on large databases, may lead to a lower CM index (i.e. lower agreement with experimental data) with respect to the initial model. On the other hand, the CM-mech performs better than the nominal mechanism for all the measurements, not only in terms of CM index, which is expected, but also in terms of L₁/L₂-norm (even though its gain is much lower than that of the other two optimized mechanisms).

Mech. Label/Objective function	1-CM (% deviation)	L1-norm (% deviation)	L2-norm (% deviation)
Stagni	0.1919	3.77	176.35
CM-mech	0.1726 (-11.17%)	3.72 (-1.46%)	136.31 (-22.70%)
L1-mech	0.1962 (+1.76%)	2.71 (-31.51%)	58.94 (-66.58%)
L2-mech	0.1903 (-1.49%)	2.54 (-35.37%)	55.60 (-68.46%)

Table 1: Comparison between different error measures values of nominal and optimized mechanisms for the optimization subset.

Overall, the deviations of the objective function values between optimized and nominal mechanisms are smaller using CM with respect to the L₁/L₂-norm. Indeed, in equation (15), performance gains and losses for each curve contribute equally to the average value, which is always between 0 and 1. Additionally, it is very difficult, if not impossible, for any mechanism to show no similarity, or dissimilarity with experimental data, if a large set is considered. For this reason, the possible range of values for CM is even narrower than [0,1]. In general, a well-constructed and validated kinetic model,

as the one used in this work, is not expected to show outstanding global improvements in terms of curve matching. Yet, significant differences between the nominal model and the CM-mech were observed in this work when looking at single curves. To further support this, the CM index (see eq. (10)) was computed for the optimization target datasets inside the database (i.e. 44 out of 60), for all mechanisms (i.e. Stagni, CM/L1/L2-mech). Table 2 reports the number of *negatively/positively* impacted datasets in each optimized mechanism. The average, and maximum deviations from the nominal CM values are also reported. This deviation is the difference in percentage between the CM index of the nominal mechanism and of the optimized ones, and it was computed for each of the 44 optimization target datasets.

	Negative Impact			Positive Impact		
Adopted objective function	CM-mech	L1-mech	L2-mech	CM-mech	L1-mech	L2-mech
N° of datasets	12	26	23	32	18	21
Average CM deviation (%)	-1.42	-3.29	-3.21	+3.99	+3.29	+4.54
Maximum CM deviation (%)	-3.00	-8.75	-8.89	+14.39	+11.29	+18.35

Table 2: Performance comparisons between mechanisms on target datasets in optimization.

The CM-based optimization approach leads to a significantly larger number of improved datasets, with respect to point-wise based approaches. In fact, L1-mech shows reduced performances on a number of curves almost twice as big as the number of improved ones, and L2-mech behaves similarly. Additionally, both average and maximum negative deviations are significantly lower for the CM-mech compared to the others. For this reason, the latter approach can be considered as more conservative than the other two. Moreover, average and peak improvements in CM-mech are comparable to those of the L2-mech, which is the one leading to the biggest local improvement. All of this is graphically summarized in Figure 12, where the same information for the single dataset is delivered through a

1 parity plot. From Figure 12, it can be also concluded that the CM-mech yields the most homogeneous
2 and consistent improvement over the entire subset of optimization target datasets even in terms of L_1
3 and L_2 norms.
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7 Indeed, the absolute numerical values of relevant measures for combustion kinetic model validation
8 (i.e. laminar burning speed, main and intermediate species concentration, and ignition delay time)
9 range different order of magnitudes, namely from 10^{-6} to 10^2 . As a consequence, the point-wise
10 formulations of the objective function (i.e. eq. (16a-16b)) are characterized by very different absolute
11 values for each dataset, even when normalization is performed or the natural logarithm is adopted for
12 the ignition delay time, as suggested by Olm [71]. Therefore, in a mono-objective optimization study
13 targeting a wide set of experimental data, the optimizer focuses on those contributing more to the full
14 extent of the objective-function. CM prevents this issue, since it associates each curve with a score
15 between 0 and 1.
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31 4 Conclusions

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36 In this work, we proposed a novel data-driven approach for the optimisation of detailed kinetic
37 mechanisms. The employed optimization algorithm is the Evolutionary Algorithm (EA). For the first
38 time the objective function was based on a recently published curve matching algorithm that is capable
39 of quantitatively and qualitatively evaluate the agreement of kinetic models with experimental data,
40 characterizing it in terms of L_2 norm as well as on the first derivatives and shapes of the curves. Also,
41 a methodology to optimize the Arrhenius parameters of PLOG-based reactions was established. The
42 interdependencies between Arrhenius expressions at different pressures were accounted for by
43 handling three random variables for each PLOG, regardless of the number of discrete pressures
44 specified in the mechanism. To the authors knowledge, PLOG reactions were consistently optimized
45 for the first time within their entire temperature and pressure domain. An optimized mechanism for
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1 ammonia combustion was obtained, and it was found to outperform the initial one [20], as well as
2 those obtained with point-wise formulations of the objective function (i.e. L1 and L2 norms), over a
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4 wide range of operating conditions including more than ~635 experimental data points. Addressed
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6 features of ammonia combustion were conversion, oxidation, pyrolysis, ignition and laminar flame
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8 speed in several systems. Improvements driven by optimization on all the impactful reactions were
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10 constrained to their uncertainty bounds when experiments on single elementary steps were available.
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12 For rates determined using first principles calculations, guidelines were established to estimate
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14 uncertainty ranges based on the level of theory adopted throughout the calculation protocols for
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16 electronic structures, potential energy surfaces and phenomenological reaction rate constants. In this
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18 process, 41 reactions were involved and 24 were finally selected as the most impactful by introducing
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20 a Cumulative Sensitivity Function (CSF) and a Cumulative Impact Function (CIF) for each test case
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22 in the database. As a result, the approach involved all 101 kinetic parameters, which were addressed
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24 contemporarily by the optimizer during the optimum search. Finally, the comparison between nominal
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26 and optimized mechanisms was exploited to highlight crucial reaction pathways, in need of further
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28 characterization, demonstrating the applicability of the proposed methodology as a useful tool for a
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30 more accurate evaluation of crucial kinetic constants and for design of experiments.
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50 OPTimised kinetic Mechanisms for Advanced combustion technoLogies”. This project has received
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FIGURES

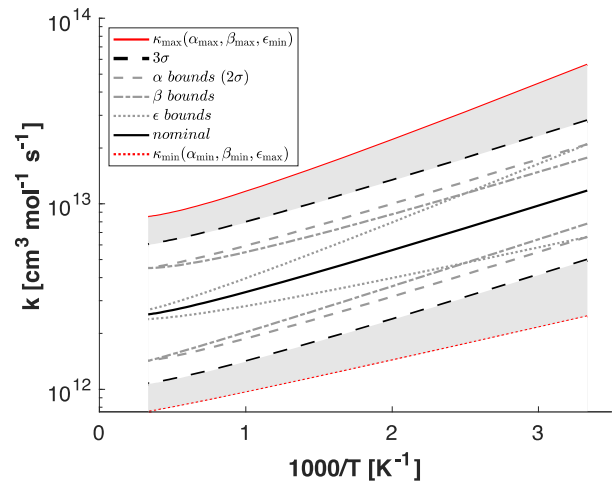


Figure 1: Projections of parameters bounds on the reaction rate constant k for the reaction $NH_2+NO_2=H_2NO+NO$ [98].

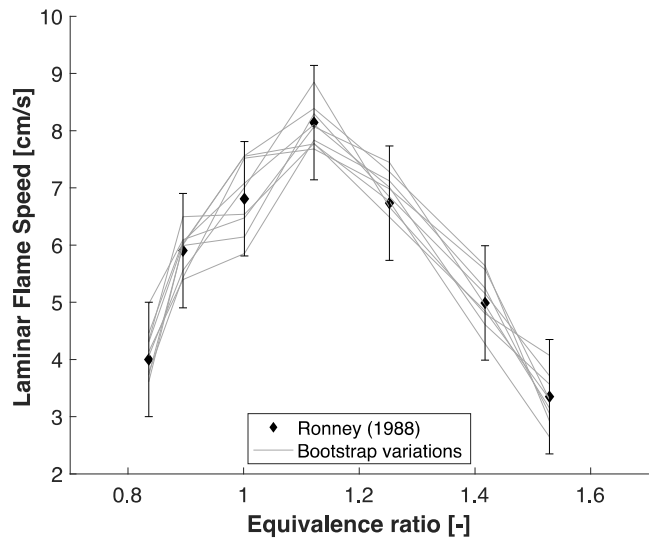


Figure 2: Example of bootstrap procedure with 10 variations. Experimental data from [83].

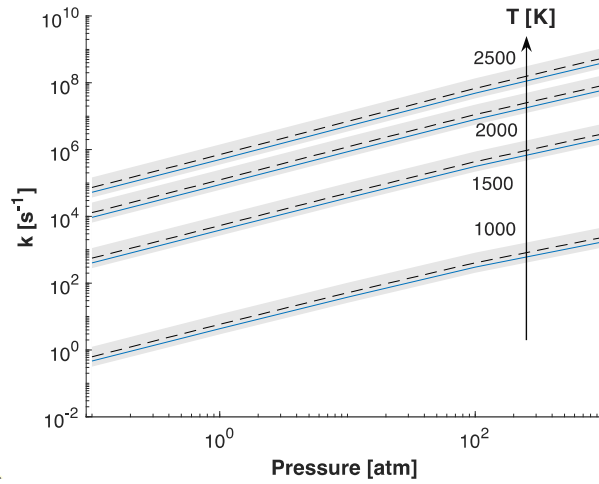


Figure 3: 3D behavior of a PLOG reaction. R143: $HNO=H+NO$ before (dashed line) and after optimization (continuous line).

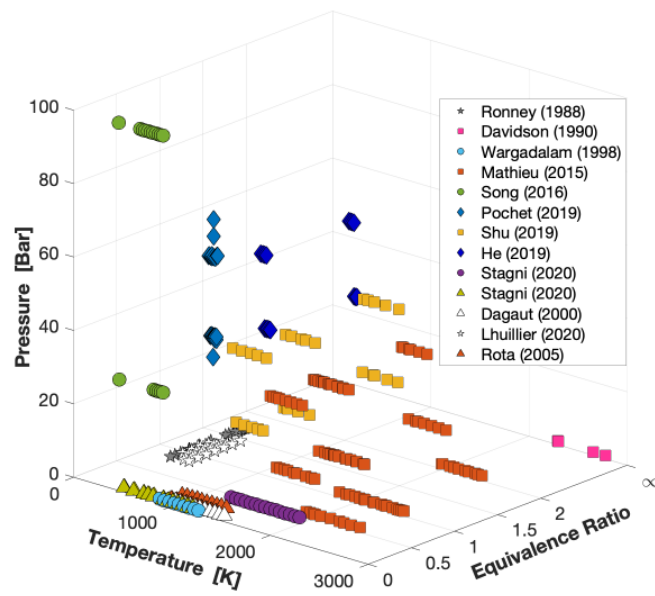


Figure 4: Collected data on Ammonia combustion in terms of operating conditions (temperature, pressure, and composition).

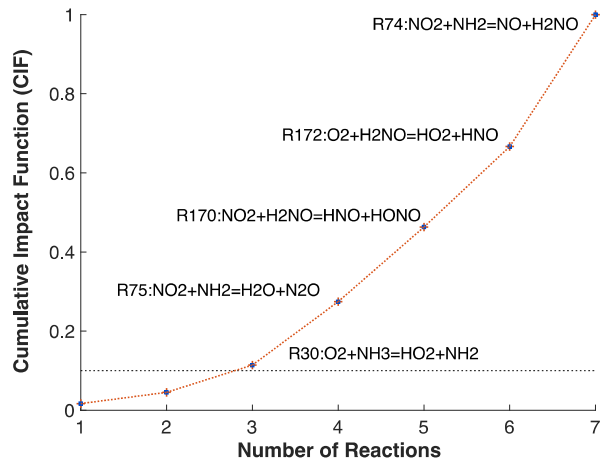


Figure 5: Example of reaction selection using the Cumulative Impact Function (CIF), (Test Case from Song [81]). The horizontal line represents the chosen threshold of 90% of the impact.

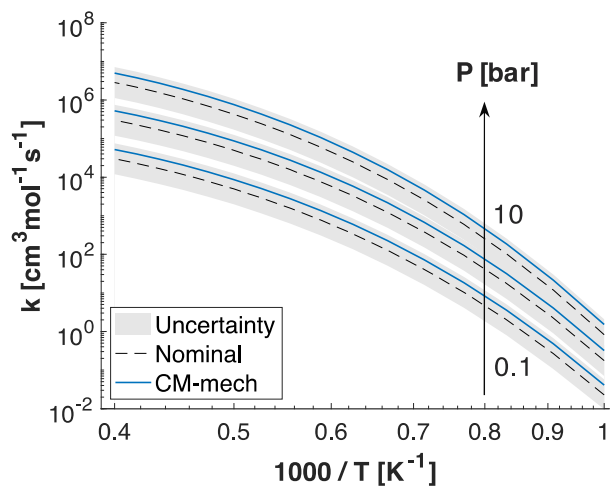


Figure 6: Sum of reaction rates constants for R111 and R112 at different pressures.

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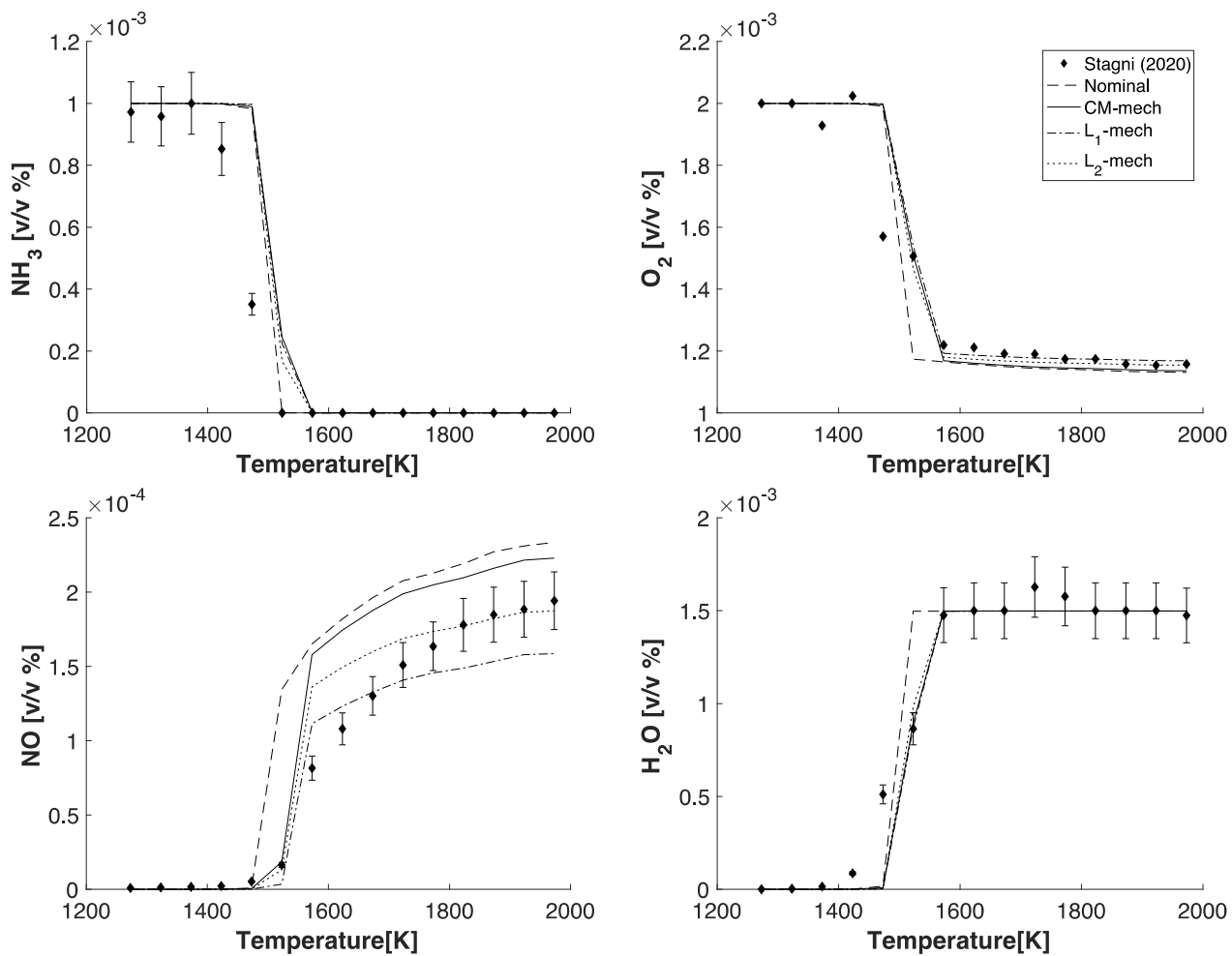
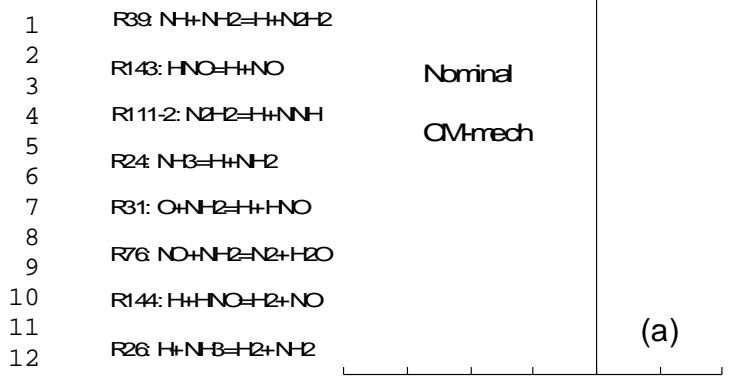


Figure 7: Comparison between speciation predictions with nominal and optimized mechanism for lean NH_3/O_2 mixture in a flow reactor, at 1.25 bar. Experimental data from [20].



Normalized sensitivity coeff.

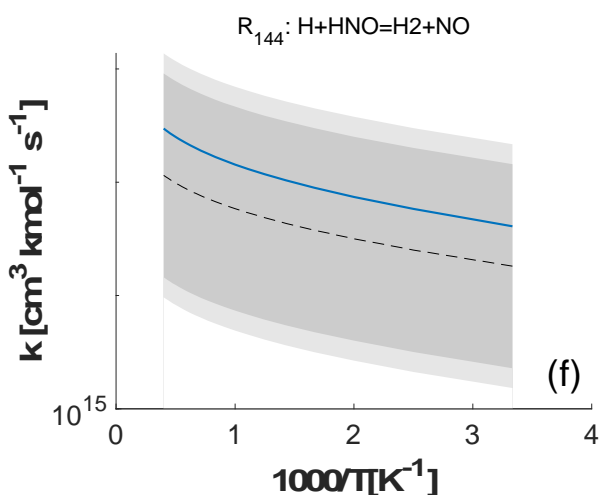
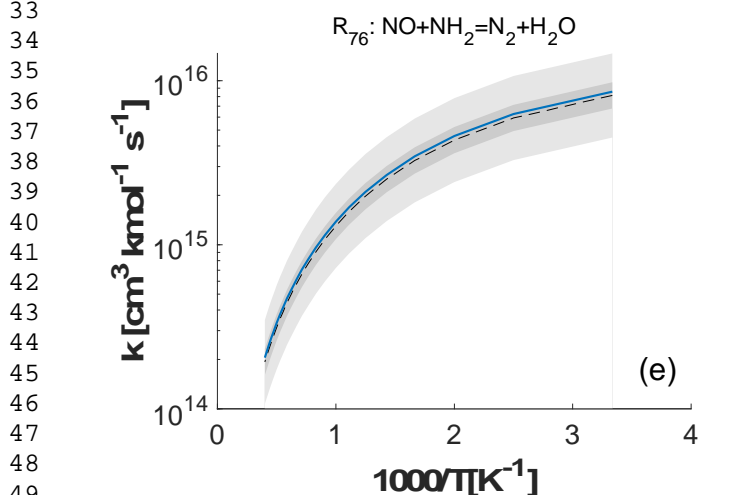
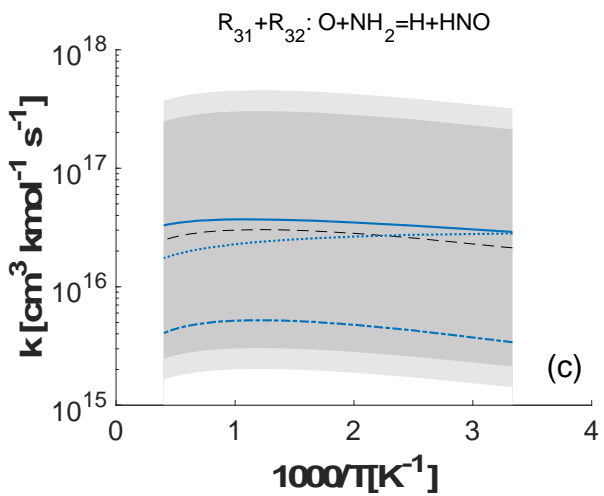
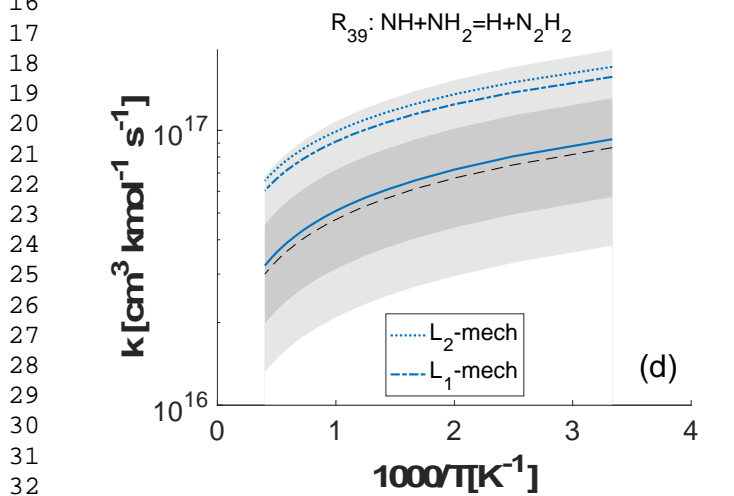
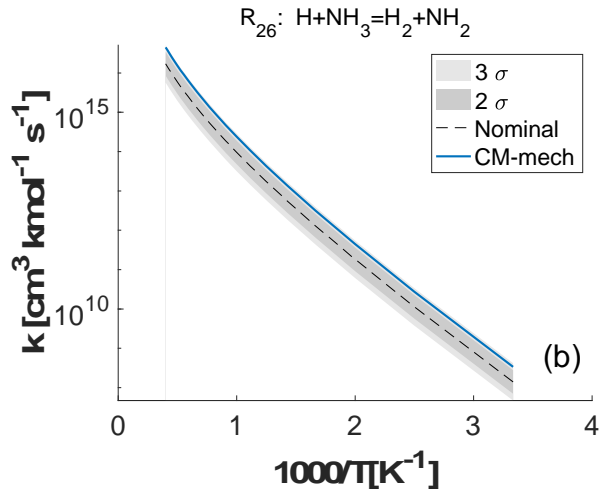


Figure 8: Sensitivity analysis (a) and kinetic rate constants (b-f) of key reactions for NO formation, comparison between nominal and optimized mechanisms. Test case: Stagni [20].

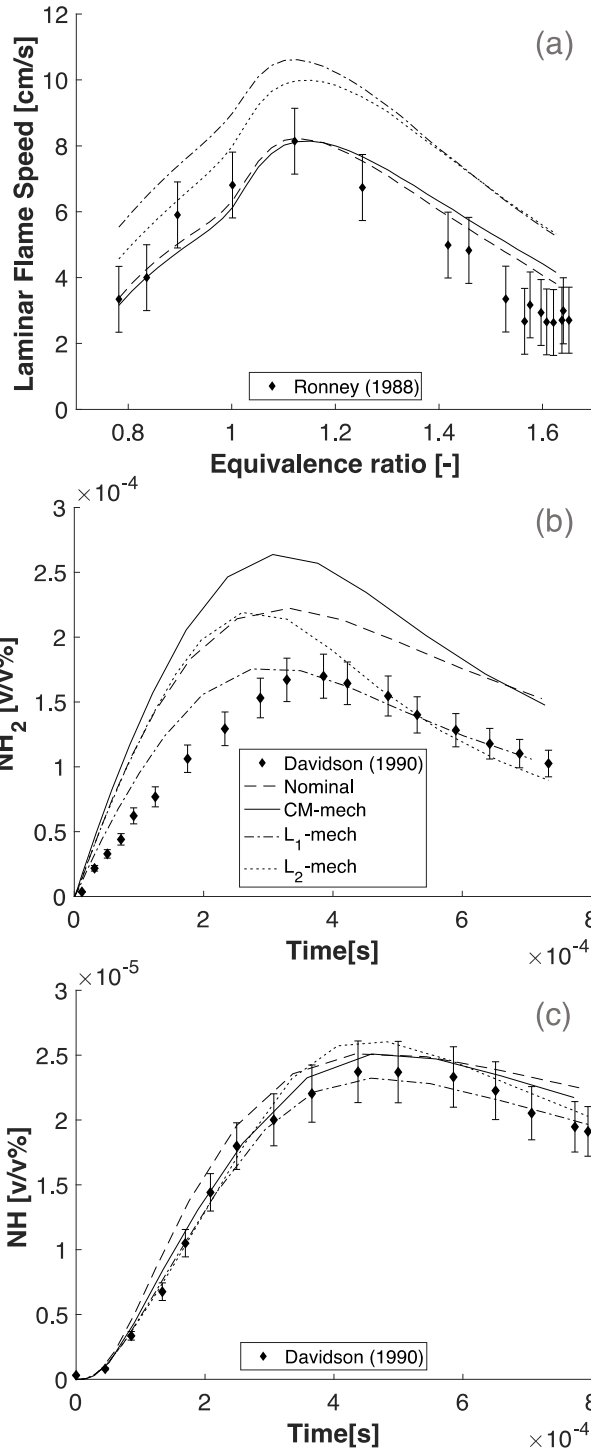


Figure 9: Comparison of nominal and optimized mechanisms. (a) Laminar flame speed of NH₃/air mixtures in microgravity conditions at 300 K; (b) Molar fraction of NH₂ in a shock tube at 1.028 atm and 2301 K. (c) Molar fraction of NH in a shock tube at 0.986 atm and 2294 K. Experimental data from [82,83].

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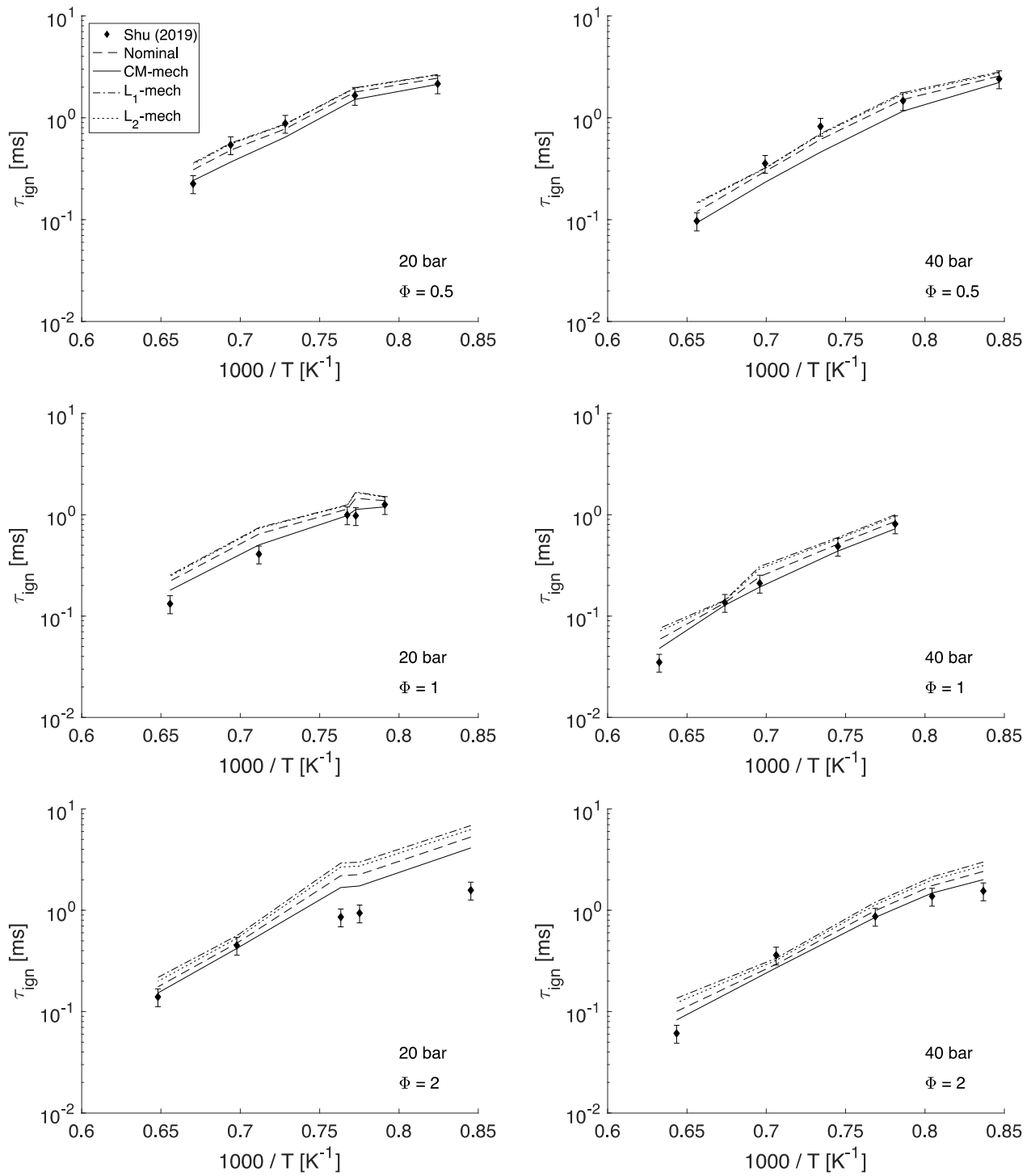


Figure 10: High pressure ignition delay time of NH₃/air mixtures in a shock tube for different equivalence ratios, namely 0.5, 1.0, and 2.0. Experimental data from [77].

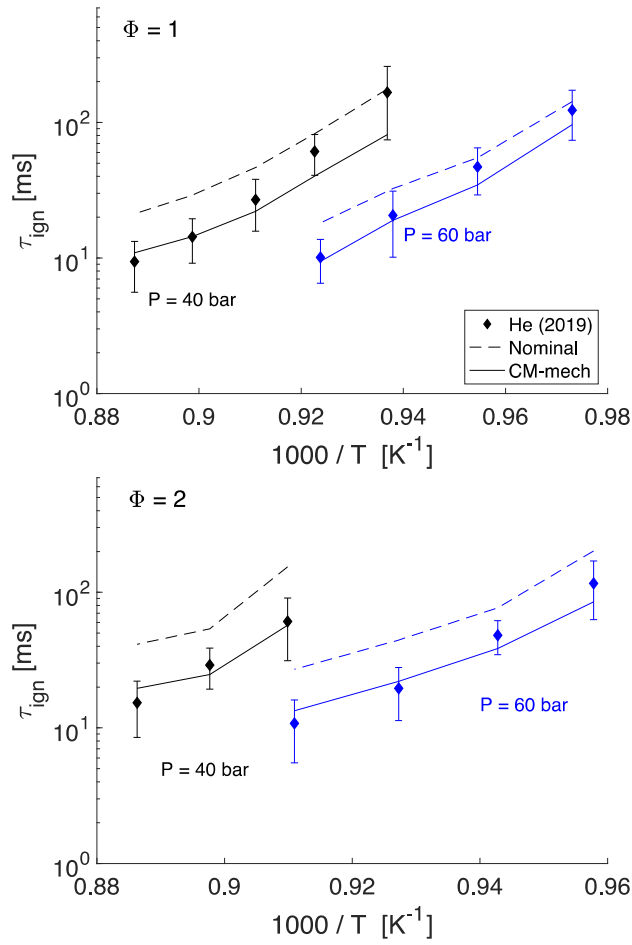


Figure 11: Comparison between nominal and optimized mechanism for NH_3 self-ignition at pressures between 40 and 60 bar in a Rapid compression machine. Experimental data from [78].

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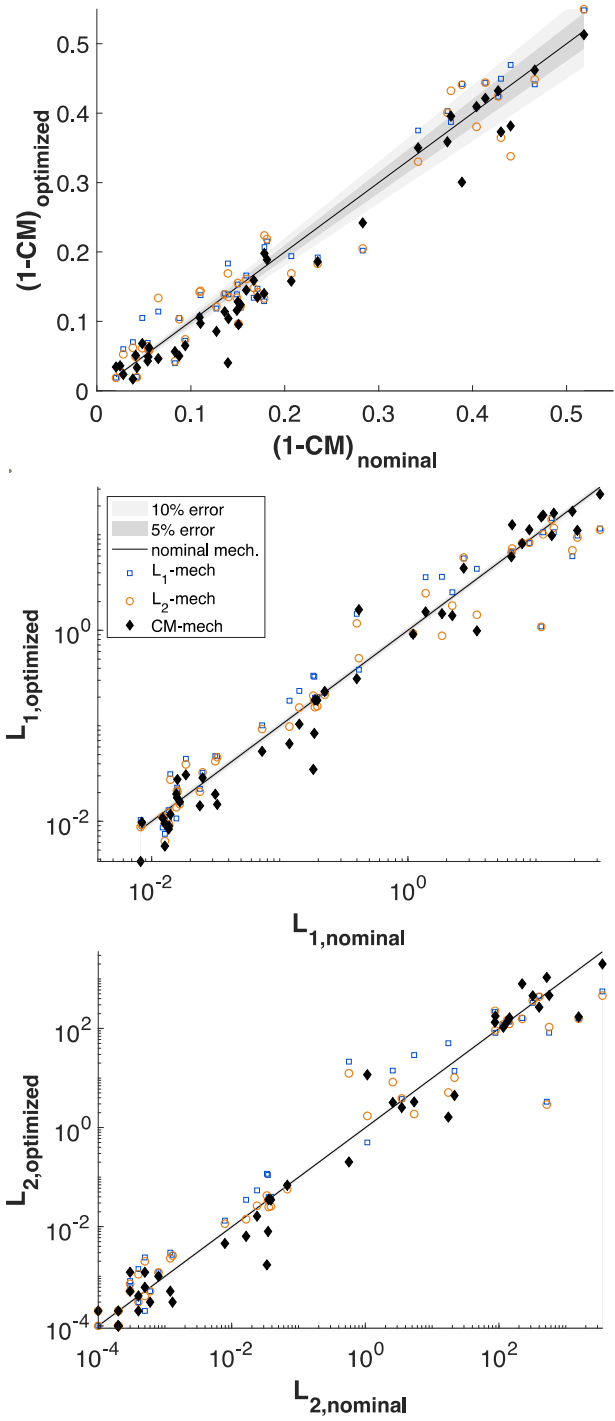


Figure 12: Parity plot: Comparison of curve matching indices between nominal [20] and optimized mechanisms in this work.

Figure 1: Projections of parameters bounds on

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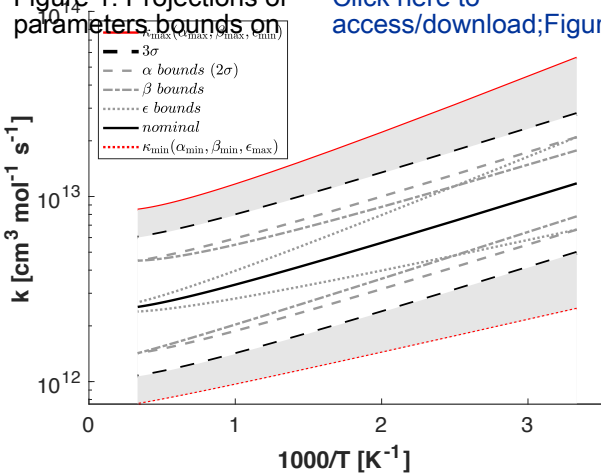


Figure 2: Example of bootstrap procedure with

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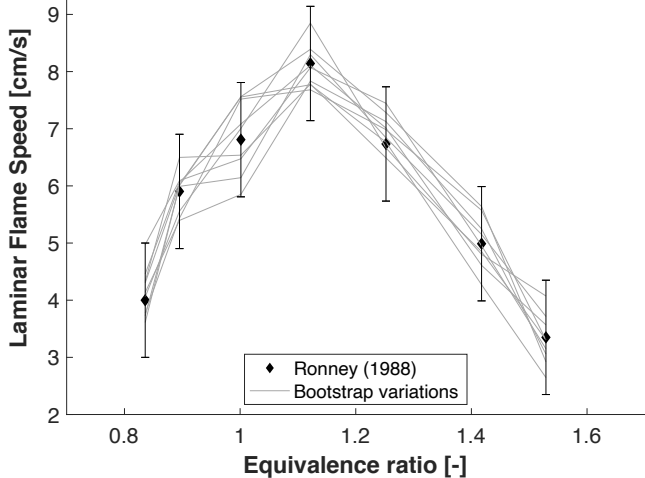


Figure 3: 3D behavior of a PLOG reaction. R143:

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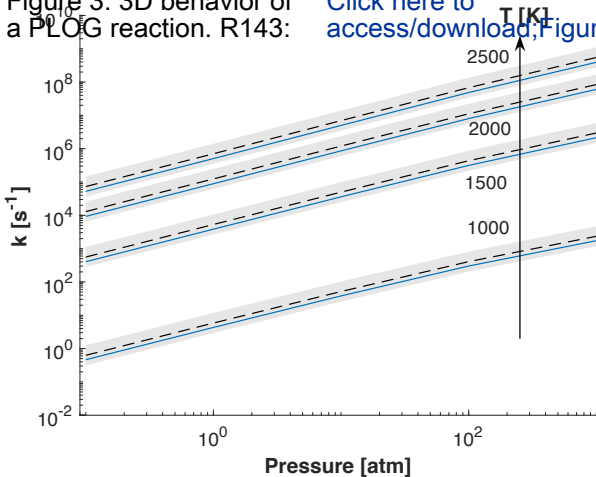


Figure 4: Collected data on Ammonia combustion

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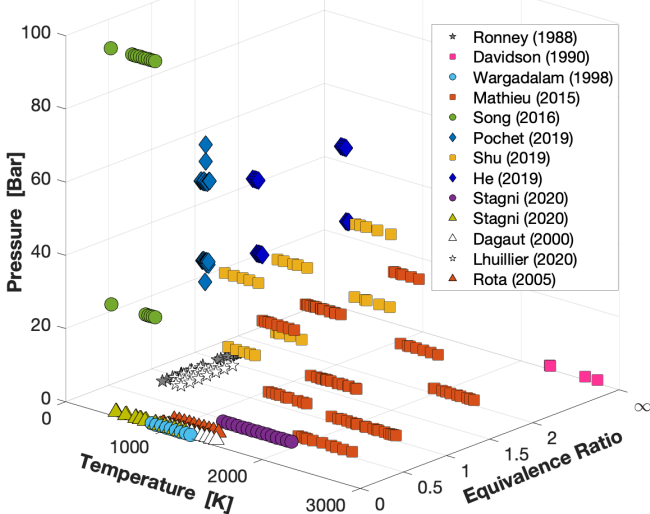


Figure 5: Example of reaction selection using

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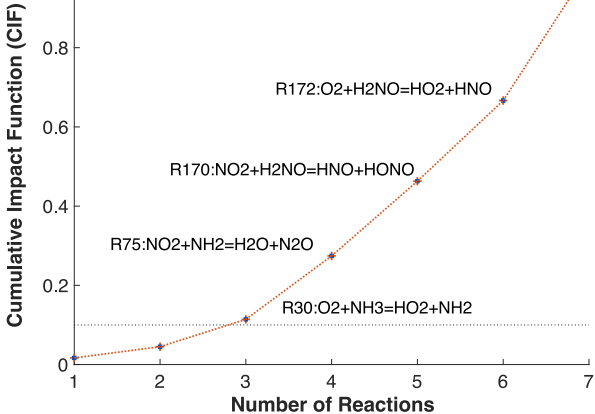


Figure 6: Sum of reaction rates constants for R111

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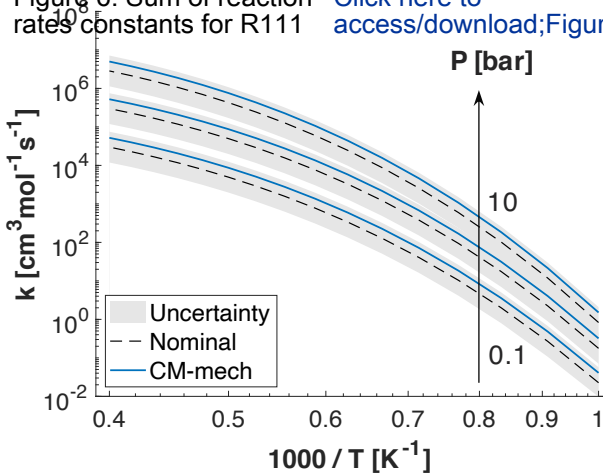
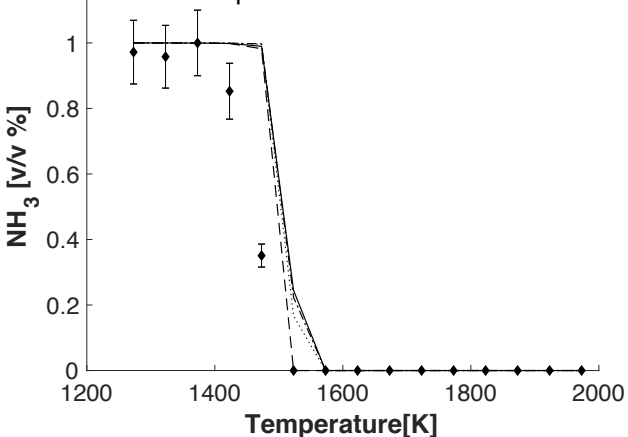


Figure 7. Comparison between speciation predictions with nominal and optimized mechanism for lean



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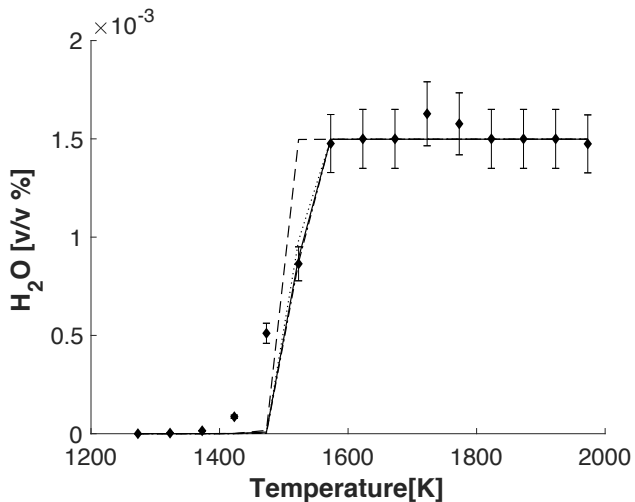
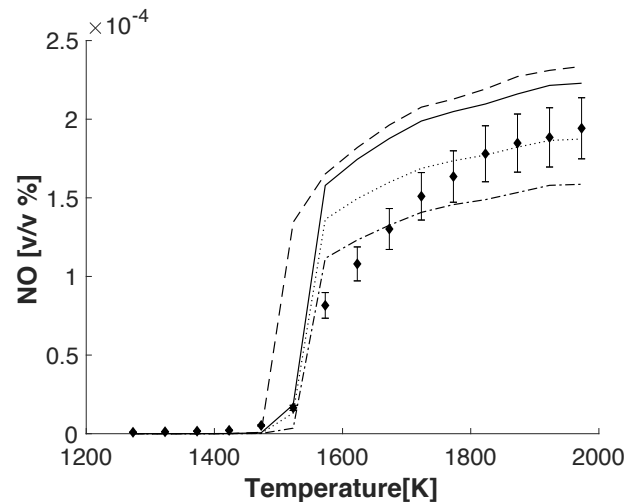
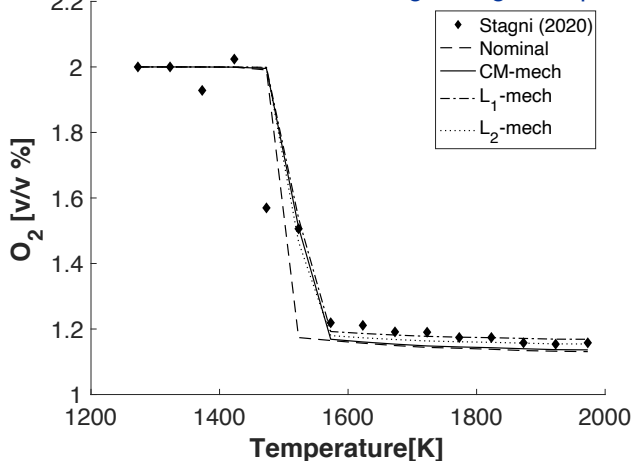
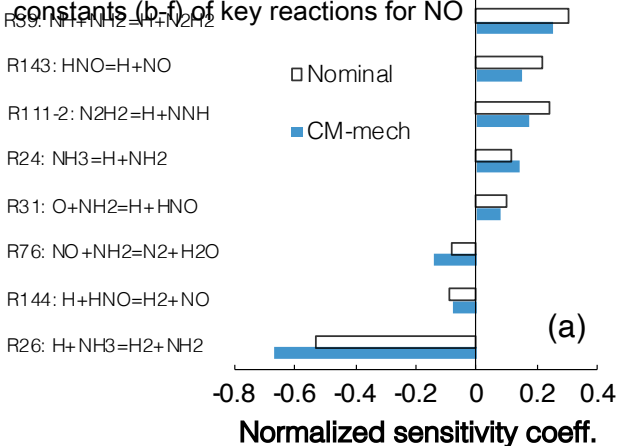
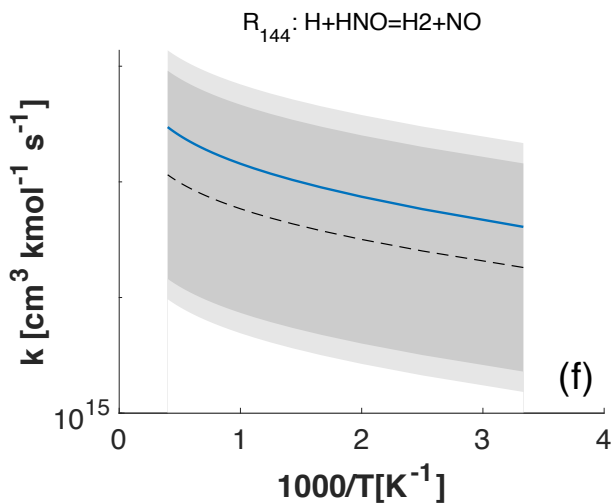
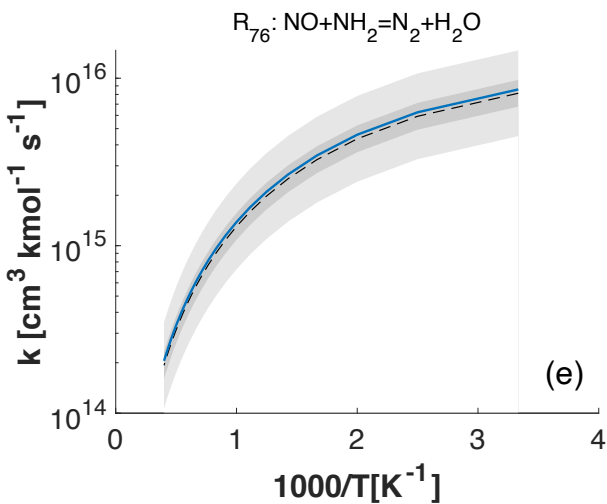
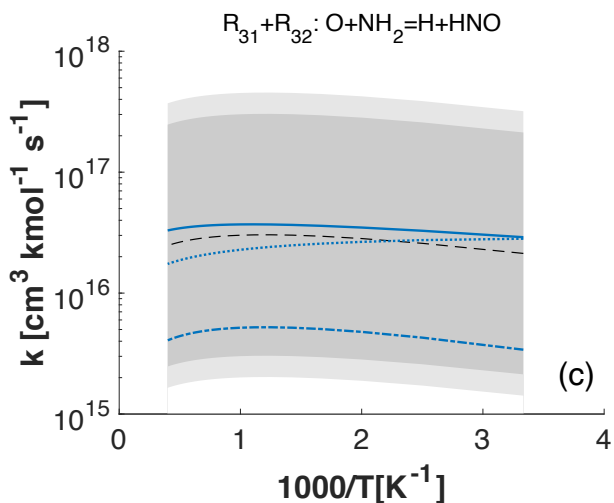
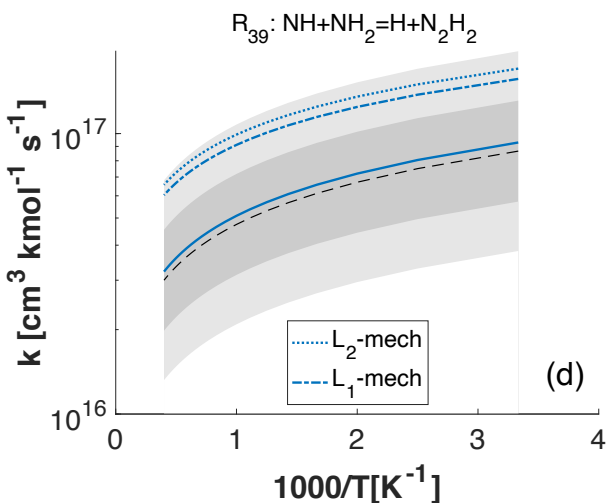
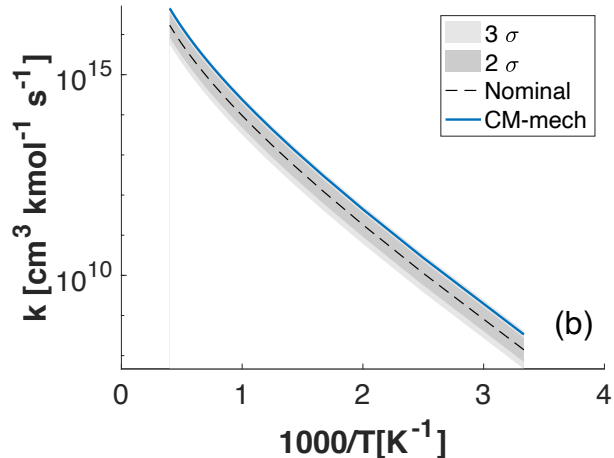


Figure 8: Sensitivity analysis (a) and kinetic rate constants (b-f) of key reactions for NO



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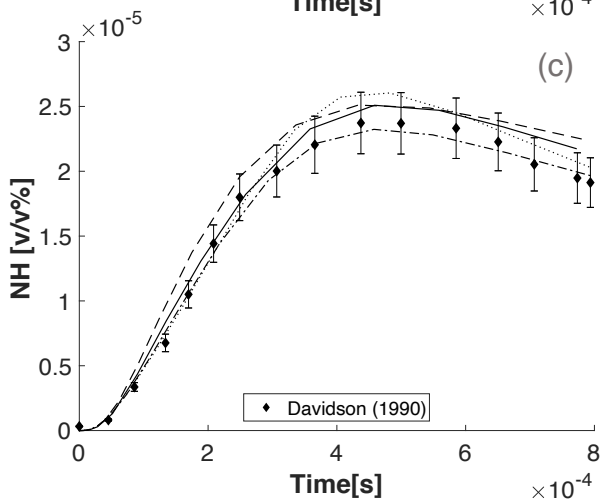
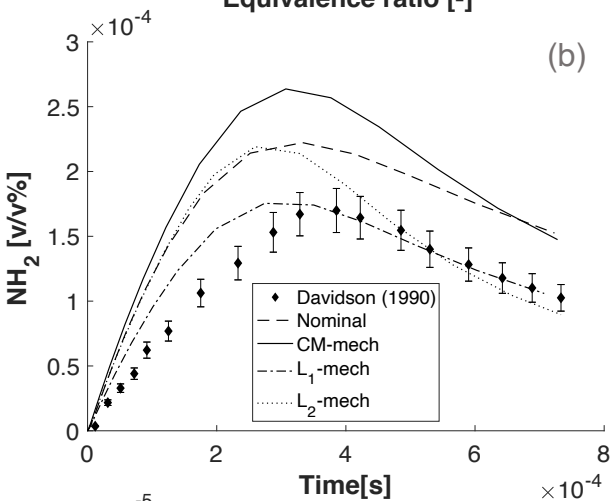
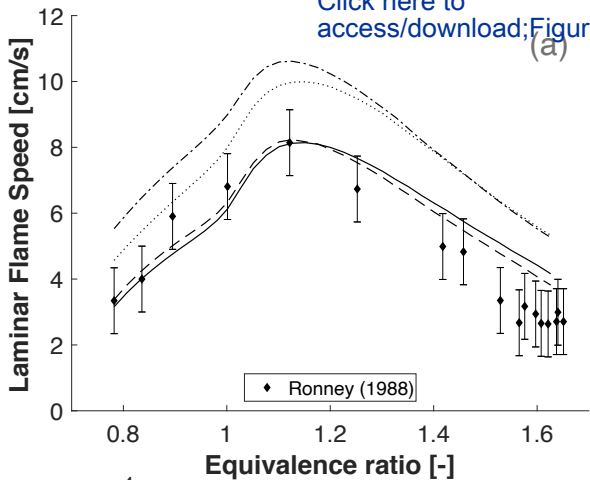


Figure 10: High pressure ignition delay time of NH₃/air mixtures in a shock tube for different

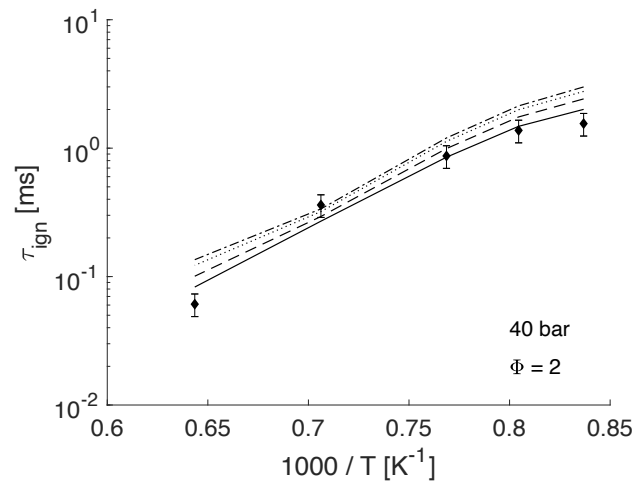
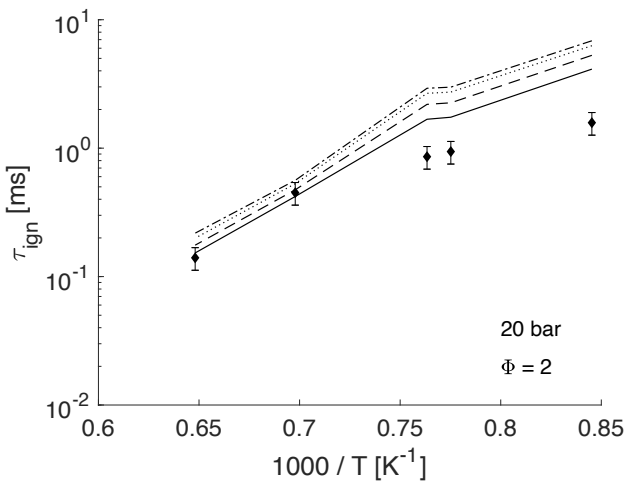
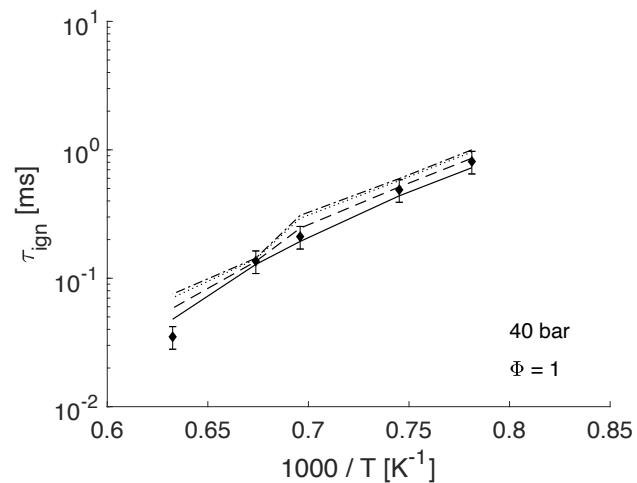
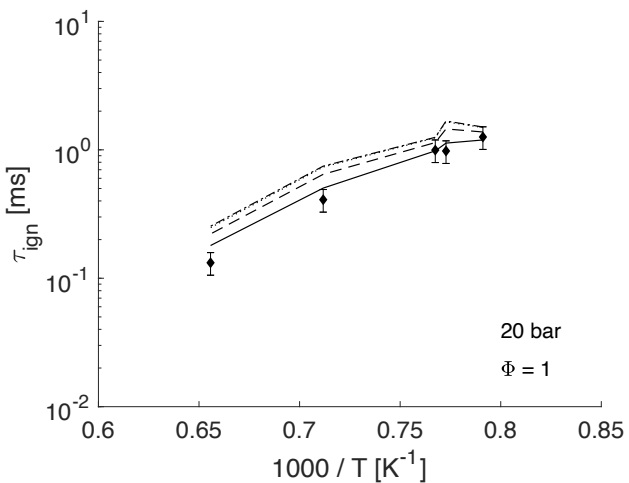
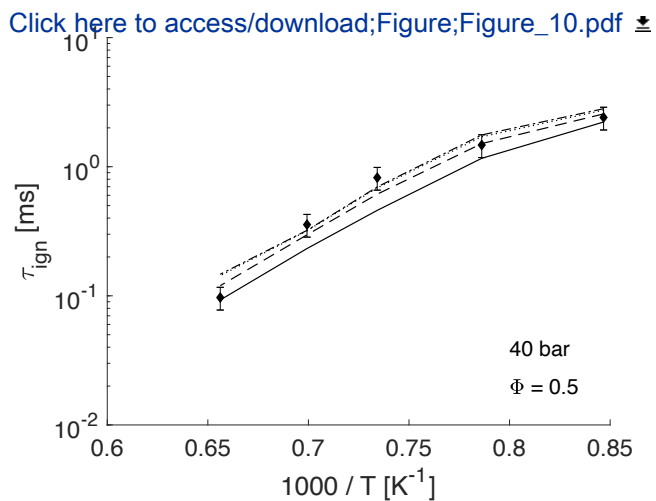
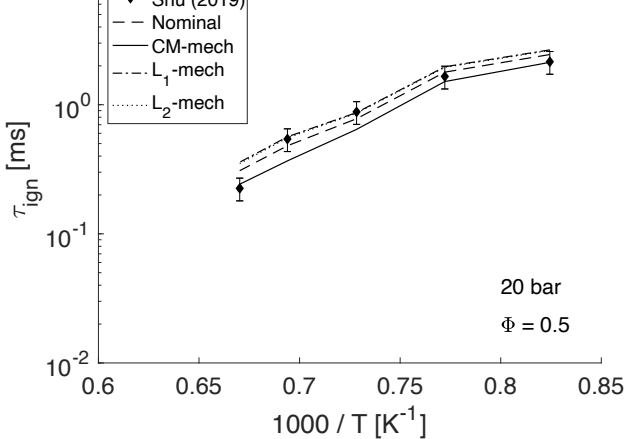


Figure 11: Comparison between nominal and

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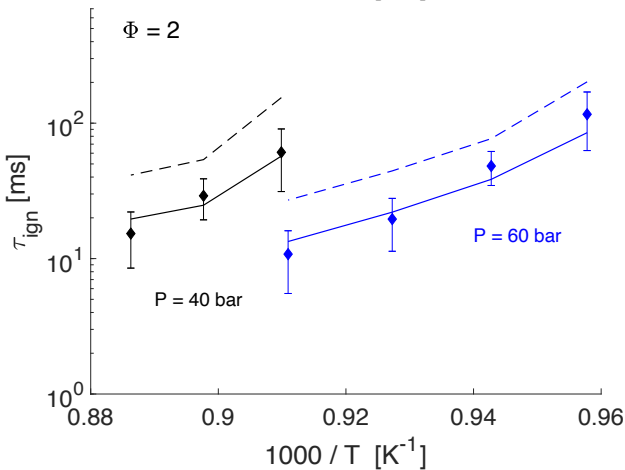
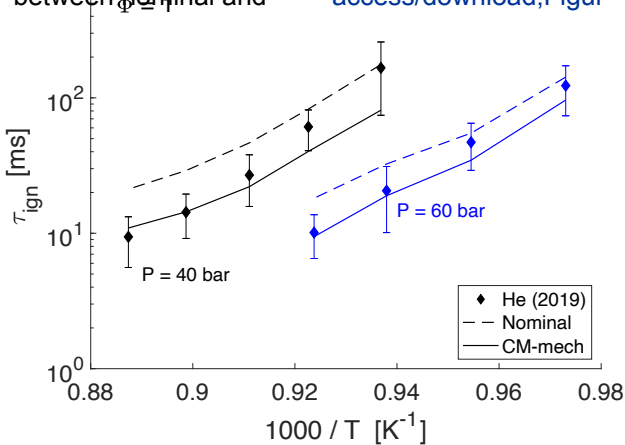
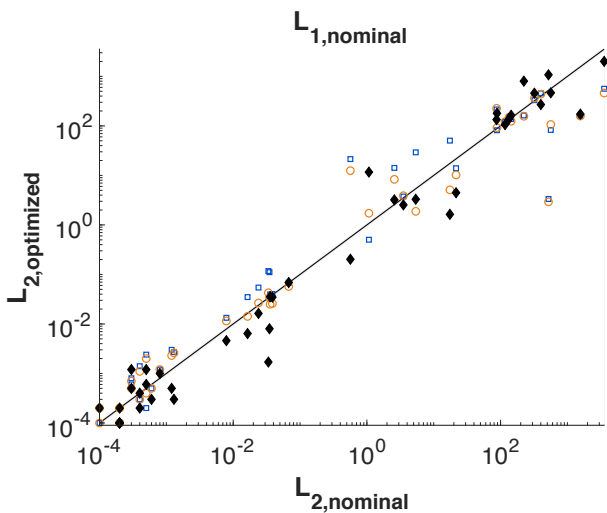
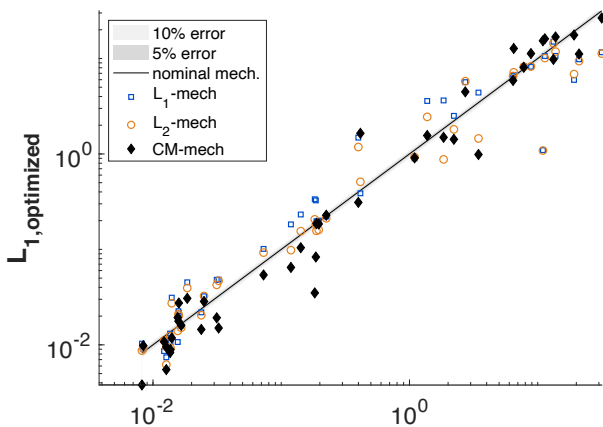
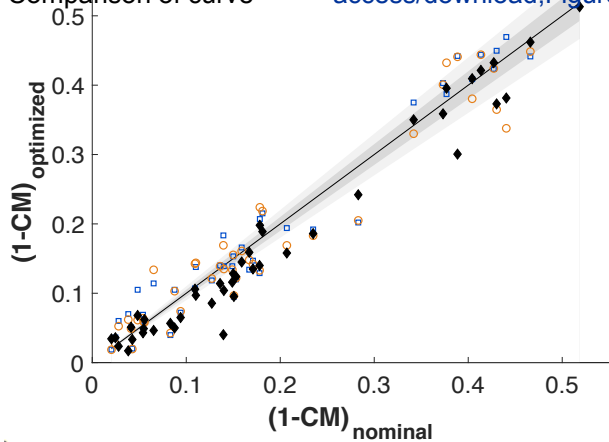



Figure 12: Parity plot:
Comparison of curve

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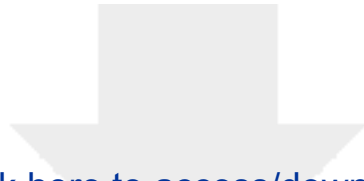




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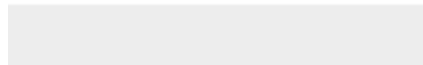
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