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High-pressure Chemistry, Transport and Flame Dynamics in LRE Combustion Instability

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High-pressure Chemistry, Transport and Flame Dynamics in LRE Combustion Instability

Final Report for the Period 2019 06 15 to 2021 06 14

Submitted by Chung K. Law, Princeton University

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Abstract

The subject program investigate the chemistry, transport, and dynamics of combustion processes in the high-pressure, near-critical and supercritical environment of liquid-propellant rockets. Studies were performed on the following components. (1) Determination and development of detailed and reduced-order reaction mechanisms in $\text{H}_2\text{-O}_2$ systems. (2) Development of radiation heat transfer models in high-density fluids to allow for reabsorption and pressure broadening. (3) Modeling of flame structure and propagation in high-pressure fluids. (4) Preliminary experimental study on near-critical, high-pressure flames. A total of three papers on these topics were published in leading journals.

Project 1: High-Pressure $\text{H}_2\text{+O}_2$ Reaction Mechanisms

Combustion in a variety of internal combustion engines including gas turbines and rockets occur at elevated pressures which could be close to or exceed the thermodynamic critical state of the mixture. At such states the properties of supercritical fluids could substantially deviate from those of ideal gases, and as such real-fluid models of equation of state, thermodynamics, and thermal and mass diffusion need to be considered. In addition to these supercritical thermal and transport properties, another essential block in the modeling of supercritical combustion is the chemical kinetics at elevated pressures. In particular, due to the increasing importance of radical-radical recombination reactions at these pressures, the uncertainty in the kinetic models is much larger as compared with that at the normal pressure, such that chemical kinetics could contribute to the largest uncertainty in combustion modelling at high-pressure conditions.

For hydrogen/oxygen combustion, the most important pair of elementary reactions are

(R1): $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ and (R2): $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$, which are also essential for the foundational hydrocarbon fuel chemistry, with R1 acting as the chain-branching reaction and R2 the chain-termination reaction at intermediate pressures. However, with increasing pressure R2 could

become the dominant reaction in producing the HO₂ radical to propagate the chain reaction. In terms of the rate coefficients, while R1 has been extensively examined by numerous experimental and theoretical studies, the rate of R2 has been much less studied and has larger uncertainties, especially at elevated pressures and high temperatures such as those in the range of 10-100 bar and 800-1500K where R2 plays an important role in flame propagation.

In this work, we have systematically investigated the literature experimental data of the R2 rate at elevated pressures. The evaluation involved the collateral re-evaluation of various associated reaction including for example updates of the NO_x mechanism with NO₂+HO₂ estimated by high-level *ab initio* quantum chemistry calculation on potential energy surfaces and kinetic calculations of the rate in the temperature range of 500-1500K. Simulation with the new mechanism shows that the rates of the lower pressure experiments are barely affected but the rates of the higher pressure experiments can be increased by 10-50%, which resolves most of the disagreement between the experiments and the model rates. A new Troe formula of R2 with argon as bath gas covering the temperature range of 300-2000K and pressure range 1-150 bar was proposed with ~20% uncertainty for all available experimental data. We also proposed a Troe formula of R2 with N₂ as the bath gas with less experimental constraint. The new rate of R2 would provide increased confidence on high pressure combustion simulation in which R2 plays a critical role.

This work is reported in: “Reevaluation of the reaction rate of $H + O_2 (+ M) = HO_2 (+ M)$ at elevated pressures,” by Xueliang Yang, Wenkai Liang, Ting Tan and Chung K. Law, *Combustion and Flame*, Vol. 217, pp. 103-112 (2020).

Project 2: High-Pressure Radiation Heat Transfer

In addition to heat conduction, radiation is a major mode of heat transfer in combustion systems, with heat loss through emission and heat gain through reabsorption. These in turn would affect the flame temperature, the temperature-sensitive reaction rates, the extent of thermal conduction, and the global flame phenomena such as the flame propagation rate and the thresholds of extinction, flashback and blowoff. Important as it is, systematic analytical and computational studies of radiation-affected phenomena have been challenged by the immensely complex species-dependent integro-differential equations governing its transport, leading to simplifying efforts at various levels of accuracy and the possible obscuring of certain controlling physics.

In the present study, we first applied a band-lumping formulation, developed in heat transfer studies, to the problem of flame propagation, and subsequently demonstrated that there is an optimum number of bands, 9 in the present investigation, that is both physically accurate and computationally facilitating. Because of the generality of the formulation, the potential utility of the 9-band lumping formulation in the simulation of combustion phenomena is suggested. We then used this computationally efficient formulation to study the impact of radiation emission and reabsorption on the structure and propagation of the prototypical freely propagating planar premixed flame, especially in the practically important high-pressure environments, recognizing that the comprehensiveness and accuracy of previous worthwhile studies have been challenged by the high demand of the computation cost.

Mechanistically, our study found that the burning flux is promoted by the upstream radiation reabsorption and with increasing CO₂ concentration. Furthermore, with increasing pressure, radiation reabsorption first increases and then reduces the burning flux because of the corresponding increases of the reabsorption efficiency and the optical thickness, respectively. The blockage of radiation emission from the burnt mixture due to the increased optical thickness is dominant with the addition of the stronger radiative species CO₂ at higher pressures.

This work is reported in: “On band lumping, radiation reabsorption, and high-pressure effects in laminar flame propagation,” by Shu Zheng, Ran Sui, Wenkai Liang, Huaichun Zhou and Chung K. Law, *Combustion and Flame*, Vol. 221, pp. 86-93 (2020).

Project 3: High-Pressure Flame Propagation

This work was initiated with the support of our previous program. In that earlier study the propagation of hydrogen/air and methane/air flames at supercritical conditions were simulated for the planar flame configuration. Descriptions of real-gas Equation of State (EoS), thermodynamics, and transport, together with high-pressure chemistry, were incorporated into the numerical simulations at progressively more complete levels of implementation.

For the laminar flame speed of hydrogen/air mixtures, it was found that it is increased due to the non-ideal equation of state, which is mainly caused by the density modification of the initial mixture. Including the thermodynamic description would reduce the laminar flame speed because of the decreased adiabatic flame temperature through the real-fluid model. Furthermore, the enthalpy format of the energy equation leads to lower laminar flame speed compared with the temperature format of the energy equation.

This is because the mixing rule at supercritical state further reduces the mixture enthalpy, hence decreases the flame temperature. Transport models, however, are found to have minimal effect on the laminar flame speed even at very high pressures. For the methane/air flames, the effect of the EoS is much weaker than the hydrogen/air flames, and is mainly due to the higher critical points of methane/air mixtures. Furthermore, use of the recently-developed high-pressure kinetics mechanism leads to substantially reduced flame speed at supercritical states; the reason is kinetic in nature in terms of revised rate parameters instead of the different flame temperatures resulting from different supercritical thermodynamic descriptions.

This work was reported at the 37th International Combustion Symposium held in 2018 and published in: “Laminar flame propagation in supercritical hydrogen/air and methane/air mixtures,” by Wenkai Liang, Weiyu Li and Chung K. Law, *Proceedings of the Combustion Institute*, Vol. 37, pp. 1733-1739 (2019).

The above investigation has been continued in the present program to investigate the roles of using the Van der Waals and the Redlich-Kwong equations of state for the fluid properties on the propagation and structure of the planar adiabatic/radiative flame in supercritical fluids. It is demonstrated that the effective molecular volume and attractive force terms in these non-ideal equations of state show opposite effects on the density modification, especially in the upstream unburned region. Furthermore, the non-ideal effect is found to strongly couple with radiative downstream emission and upstream reabsorption, whose respective weakening and strengthening effects can substantially affect the state of radiation-induced quenching. The theory is useful for the description of high-pressure flames as both the non-ideal state and radiation become more pronounced under such conditions.

This work is reported in: “Theory of supercritical flames with real-fluid equation of state,” by Wenkai Liang and Chung K. Law, *Combustion Theory and Modeling*, 2021, DOI: [10.1080/13647830.2021.1919319](https://doi.org/10.1080/13647830.2021.1919319).

Project 4: Preliminary Experimental Study on High-Pressure Flames

Notwithstanding the disruption caused by the coronavirus pandemic in the lockdown of university laboratories, we have designed and started manufacturing a high-pressure chamber to conduct the studies on flame dynamics at near-supercritical conditions. The designed chamber has the following features:

1. The chamber is designed for an operational pressure of 20 atm and a surge pressure of 100 atmosphere. The flame used will be a helium-diluted methane or HC flame, whose supercritical pressure would be lower than 20 atm.
2. The fuel-oxidizer mixture that will be used will be cooled to a temperature close to 100 K to ensure that the reactant mixture is close to its critical point. A heat exchanger suspended in a liquid nitrogen bath will be used for cooling the reactant mixtures.
3. The combustion chamber will have optical access through a quartz circular window of radius 5 cm. This ensures that we can perform flow characterization and flame imaging.
4. The burner configuration inside the chamber could be varied. Preliminary experiments will be performed using a strained flame in a stagnation flow configuration. This configuration ensures easy stabilization of the flame.
5. The burner configuration could also be varied to that of a Bunsen flame. Here, the super-cooled gas of say 100K is issued from a Bunsen tube and ignited inside the pressurized chamber forming a Bunsen flame cone over the tube. To the leading order, the flame speed of the mixture is simply given by the angle of the Bunsen cone, which can be readily determined. Consequently, the laminar flame speeds and fluxes can be determined as functions of the mixture equivalence ratio, which can then be compared with the calculated values to interrogate the accuracy of the chemical and radiation models.

This experiment is mainly for studying steadily burning premixed flames operating close to the critical condition for the premixed combustible mixture. The specific objectives are:

1. To measure the flame speeds and in turn the reaction rates for reactant mixture close to critical conditions.
2. To study the corresponding effects of strain, pressure, and temperature on the flame response.

Publications (Appended)

“Reevaluation of the reaction rate of $\text{H} + \text{O}_2 (+ \text{M}) = \text{HO}_2 (+ \text{M})$ at elevated pressures,” by Xueliang Yang, Wenkai Liang, Ting Tan and Chung K. Law, *Combustion and Flame*, Vol. 217, pp. 103-112 (2020). **(Appendix A)**

“On band lumping, radiation reabsorption, and high-pressure effects in laminar flame propagation,” by Shu Zheng, Ran Sui, Wenkai Liang, Huaichun Zhou and Chung K. Law, *Combustion and Flame*, Vol. 221, pp. 86-93 (2020). **(Appendix B)**

“Theory of supercritical flames with real-fluid equation of state,” by Wenkai Liang and Chung K. Law, *Combustion Theory and Modeling*, 2021, <https://doi.org/10.1080/13647830.2021.1919319>. **(Appendix C)**



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Reevaluation of the reaction rate of $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$ at elevated pressures

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ABSTRACT

The rate coefficients for $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$ at high-pressure conditions were re-evaluated using the reported experimental shock tube data of Davidson et al. (1996), Bates et al. (2001), Shao et al. (2019) and Choudhary et al. (2019), and based on an updated mechanism of Hong et al. (2011). The major updates of the Hong et al. Mechanism compared to the originally used GRI-Mech in the works of Davidson et al. (1996) and Bates et al. (2001) were the interfering reactions of $\text{H} + \text{O}_2$, $\text{H} + \text{HO}_2$ and $\text{OH} + \text{HO}_2$ as well as NO_x -related reactions. After applying the updates of the elementary reaction kinetics, the revised rates of $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$ for Davidson et al. (1996) and Bates et al. (2001) showed improved agreement with each other, and consequently led to a more reliable Troe formula of $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$ with $\text{M} = \text{Ar}$ and N_2 covering the pressure range of 1–150 bar and temperature range of 300–1800 K. The new Troe formula is expected to facilitate kinetic model development and high-pressure combustion studies.

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1. Introduction

Combustion at elevated pressures is practically important for improved thermodynamic and fuel efficiency in a variety of internal combustion engines, such as the aircraft engines at ~30 atm, diesel engines ~60 atm and rocket engines > 100 at [1]. However, at such high pressures the combustion processes could occur close to or even above the thermodynamic critical state of the mixture. As demonstrated previously [2] at such states the properties of supercritical fluids could substantially deviate from those of ideal gasses, such that real-fluid models of equation of state (EoS), thermodynamics, and thermal and mass diffusion need to be considered.

In addition to these supercritical thermal and transport properties, another essential block in the modeling of supercritical combustion is the chemical kinetics at elevated pressures. In particular, due to the increasing importance of radical-radical recombination reactions at these pressures, the uncertainty in the kinetic models is much larger as compared with that at the normal pressure, such that chemical kinetics could contribute to the largest uncertainty in combustion modeling at high-pressure conditions. This concern

has been noted and investigated, for example for the $\text{OH} + \text{CO}$ reactions in supercritical CO_2 environments [3].

For hydrogen combustion, the most important pair of elementary reactions are:



which are also essential for the foundational hydrocarbon fuel chemistry, with R1 acting as the chain-branching reaction and R2 the chain-termination reaction at the second limit. Furthermore, with increasing pressure R2 could become the dominant reaction in producing the HO_2 radical to propagate the chain reaction. In terms of the rate coefficients, R1 has been extensively examined by numerous experimental and theoretical studies [4,5], with the most recent efforts being the shock tube experiments of [5,6] by using tunable diode laser absorption measurements of H_2O , OH and CO . The results showed excellent agreements with previous data and further refined the uncertainty of R1 down to ~7% in the temperature range of 1000–3000 K along with other available experiments.

However, compared with R1, the rate of R2 has been much less studied and has larger uncertainties, especially at elevated pressures and high temperatures such as those in the range of 10–100 bar and 800–1500 K where R2 plays an important role

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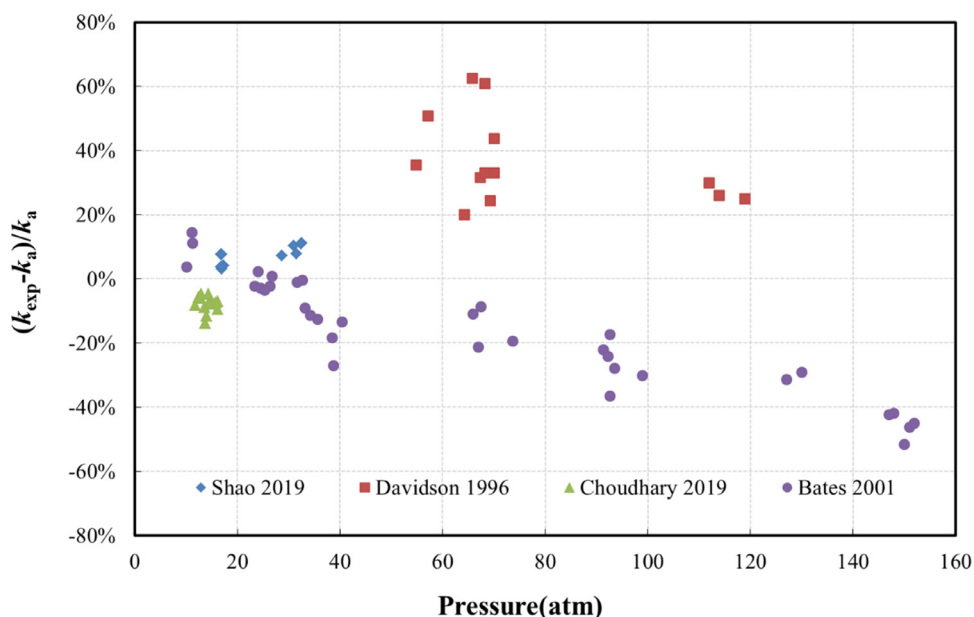


Fig. 1. Deviation of experimental rate of $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$ for $\text{M}=\text{Ar}$ from four most recent measurement comparing to Eq. (a) at each pressure.

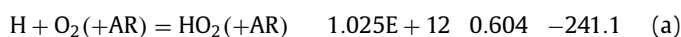
in flame propagation. It is thus of interest to note that independent measurements often claimed uncertainties of ~30% and different studies within similar temperature and pressure ranges often disagree with each other by 30% or even more. Specifically, for the shock tube measurements at elevated pressures, Davidson et al. [7] measured this rate at ~60 atm and ~120 atm between 1260 K and 1380 K through the OH absorption profiles and reported uncertainty of 30–40%. Furthermore, Bates et al. [8] extracted the rate of R2 by measuring the NO_2 laser absorption signals, using NO addition in the $\text{H}_2\text{--O}_2$ system in the temperature range of 1050 to 1300 K and pressure range of 7 to 150 bar, and reported uncertainty of 20–35%. The rates of these two studies also differ from each other significantly, with the former being roughly twice those of the latter in the corresponding temperature and pressure ranges. Recently, two more studies revisited the reaction at lower pressures, with Shao et al. [9] using ignition delay to derive the reaction rate from 16 to 30 atm and around ~1200 K, while Choudhary et al. [10] measured the rate by monitoring the OH radical time history at ~15 atm and from 1500 to 2050 K. These two low pressure rates have uncertainty down to ~10%, and agree reasonably well with other available data.

Based on these considerations, the present work focuses on the re-evaluation of the aforementioned shock tube experiments based on the best current knowledge of chemistry and possible experimental assumptions that may contribute to the measurements' errors/uncertainties. In particular, considering the most recent important experimental rate revisions of $\text{H}_2\text{--O}_2$ model were mostly from Hong et al. works, we used the mechanism developed by Hong et al. in 2011 [11] with updates of the $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$ (R3) and $\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$ (R4) reactions [12] as the base mechanism (denoted as Hong et al. Mech hereafter) to reevaluate the rate and the uncertainty associated with each measurement. New rate of R2 in the Troe formula with much constrained uncertainty will be proposed using least square fitting after completing the rate evaluation.

2. Results and discussion

We start the data consistency analysis by fitting all previous measurements of R2 into a Troe formula shown below in the

Chemkin Format as Eq. (a). The experiment data used for this fitting are provided as Supplement S1.



$$\text{LOW}/1.720\text{E} \quad + 19 - 1.277 \quad 203.9/$$

$$\text{TROE}/0.454 \quad 1.0\text{E} - 10 \quad 1.0\text{E} + 30 \quad 1.0\text{E} + 30/$$

The high pressure limit rate is taken from uc-MRCI results of a recent high level *ab initio* and kinetics calculation on the $\text{H} + \text{O}_2 = \text{HO}_2$ [13]. The low pressure limit rate and fall-off parameters are determined by the least square fitting of experimental data assuming the broadening factor F_c is not sensitive to temperature [14]. Figure 1 plots the deviations from the four shock tube data sets by comparing the experimental rate values with Eq. (a). It is obvious that the agreement between the experiments and Eq. (a) is quite good when the pressure is lower than 30 bar. The deviation becomes much larger when the experimental pressure is higher than the supercritical pressure (~35 bar), with the Davidson data being respectively much higher and the Bates data progressively lower than Eq. (a). Such an observation shows the importance to examine the possible causes of the large deviation of the experimental R2 rates at high pressures for the sake of accurate modeling of hydrogen combustion at elevated pressures.

2.1. Re-evaluation of data from Davidson et al. (1996)

We start by analyzing the data reported by Davidson et al. [7] In the experiment, the OH time history profile was measured by laser absorption spectroscopy at 306.5 nm and GRI-Mech 1.2 [15] was used to simulate the experimental profile to extract R2 by matching the OH profile. It was [7] suggested that the entire OH time history could be greatly affected by small amount of hydrogenous impurities of the gas mixture but the effect on the peak OH concentration was barely detectable, and therefore the measured OH peak concentration was a better experimental target for the kinetics determination.

In the experiments, the OH peak concentration has the largest sensitivity to the R1/R2 pair. However, other side reactions such as $\text{H} + \text{HO}_2 = \text{OH} + \text{OH}$ (R5) and $\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$ (R6) also have

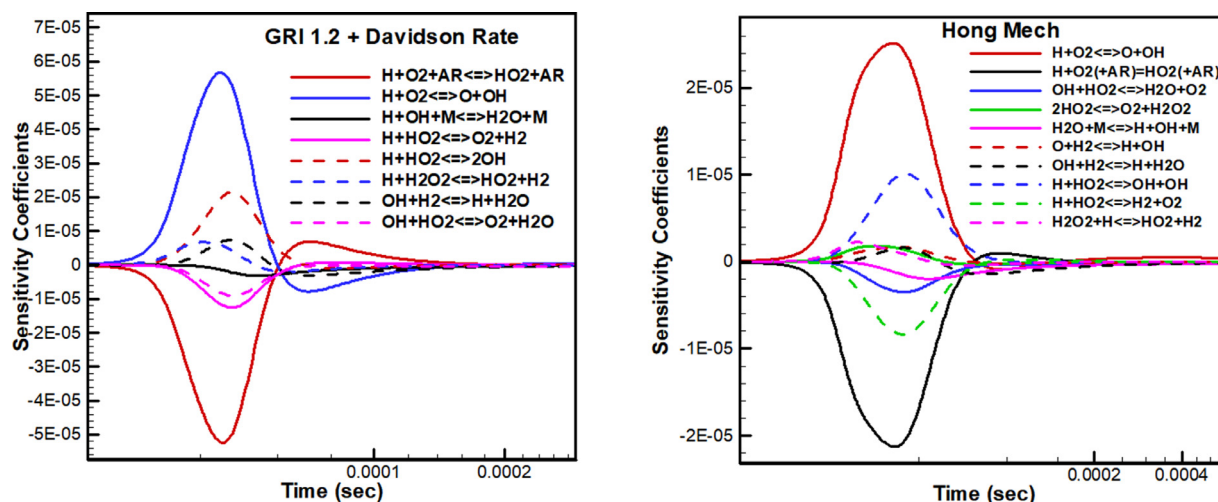


Fig. 2. Sensitivity analysis of OH concentration for Davidson data at 112 atm and 1376 K based on GRI-Mech 1.2 and Hong et al. Mech.

Table 1

Comparison of evaluated rate by the Hong et al. Mech and the original Davidson determination with Ar as bath gas. $k_{2,0}$ unit ($\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$); $k_{2,1}$ unit ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$).

T (K)	P (atm)	Davidson- $k_{2,0}$	GRI-Mech-PreA	Davidson- $k_{2,1}$	Hong-AR-PreA	Hong-AR- $k_{2,1}$
1326	64.3	1.50E + 15	4.72E + 17	8.86E + 11	9.23E + 18	8.97E + 11
1366	69.3	1.50E + 15	4.84E + 17	9.27E + 11	1.03E + 19	1.01E + 12
1260	57.2	2.00E + 15	6.04E + 17	1.11E + 12	9.58E + 18	9.24E + 11
1262	54.8	1.80E + 15	5.45E + 17	9.53E + 11	9.21E + 18	8.50E + 11
1279	67.4	1.70E + 15	5.20E + 17	1.09E + 12	8.47E + 18	9.32E + 11
1290	70.1	1.70E + 15	5.24E + 17	1.13E + 12	8.58E + 18	9.64E + 11
1291	68.3	1.70E + 15	5.24E + 17	1.10E + 12	8.70E + 18	9.36E + 11
1315	70.1	1.80E + 15	5.63E + 17	1.17E + 12	9.50E + 18	1.02E + 12
1327	68.2	2.00E + 15	6.30E + 17	1.25E + 12	1.06E + 19	1.03E + 12
1344	65.8	2.00E + 15	6.36E + 17	1.19E + 12	1.13E + 19	1.09E + 12
1316	118.9	1.50E + 15	4.69E + 17	1.65E + 12	7.63E + 18	1.38E + 12
1332	113.9	1.50E + 15	4.74E + 17	1.56E + 12	7.52E + 18	1.27E + 12
1376	112.0	1.50E + 15	4.86E + 17	1.49E + 12	8.08E + 18	1.25E + 12

substantial contributions, as shown in Fig. 2 by sensitivity analysis using either GRI-Mech 1.2 or the Hong et al. Mech for the experiments at 1376 K and 112 atm. Clearly, both mechanisms show similar sensitivity coefficients on each reaction and the Hong et al. Mech should be able to provide more accurate determination of R2 with more accurate knowledge of R1, R3, R4, R5, and R6. Given the uncertainty of 7%, ~30%, 60%, 20%, 30% for each aforementioned reaction rates, R2 can be determined with an uncertainty of ~15% using the Hong et al. Mech.

We note that R1 used in the Hong et al. Mech is ~15% smaller than that of GRI-Mech 1.2 and R2 may be reduced ~15% to reconcile the effect of R1. As shown in Fig. 2, other side reactions could also play important roles in the OH generation and consumption. It is not appropriate to single out any of them to discuss the effects. Instead, it is better to treat the mechanism as a whole to perform the simulation. In the process of re-evaluating the reaction rate of R2, we create the OH profile using GRI-Mech 1.2 and the Davidson rate as the first step. Then we tune the pre-exponential factor of the low-pressure limit rate of R2 to match the OH peak produced in the first step. Table 1 summarizes the experimental conditions, the Davidson rates and the evaluated rate using the Hong et al. Mech. The first order rate $k_{2,1}$ of the Hong et al. Mech is 15–20% lower than the Davidson determination for the same condition except for the first two experiments where the concentrations of H_2 and O_2 are much smaller. The values of $k_{2,1}$ are around $9.60\text{E} + 11 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$ for ~65 bar and $1.30\text{E} + 12 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$ for ~114 bar, displaying substantial falloff behavior and demonstrating that it is not in the low-pressure limit any more.

As mentioned earlier, the first order rate of R2 derived with the Hong et al. Mech has about 15% uncertainty without considering the experimental fitting procedure. However, given the large noise of the experimental OH signal, the value of the OH peak is highly sensitive to the selection of the signal baselines. Figure 3 shows three different simulation lines by changing the baseline and rate of R2 against the experimental OH time history profile. Due to the noisy profile, all three lines arguably have similar fitting quality to the experiment. It is seen that the original Davidson fit (black line) represents the lower limit of the OH peak value, while the Hong et al. Mech fitting with shifting the baseline by 4 ppm has upper limit of the OH peak value. Nevertheless, the baseline change results in 10–15% reduction of R2. Fitting uncertainty may become smaller as the experimental OH peak increases.

We have also re-analyzed the R2 with N_2 as bath gas around 52 bar reported by Davidson et al. in the same paper as demonstrated in Table 2. With the rate of R2 in Argon obtained in Table 1, the pre-exponential factor of the low-pressure limit rate in the Troe formula of N_2 was changed to match the experimental OH peak. The obtained first order rates of R2 with N_2 are ~10% smaller than the determination of Davidson et al., which is consistent with the re-evaluated data of the Argon experiments.

2.2. Reevaluation of data from Bates et al. (2001)

We proceed to analyze the data reported by Bates et al. [8] in which a small amount of NO was added to the hydrogen-oxygen mixture and the rate of R2 was extracted by monitoring the absorption of NO_2 at elevated temperatures and pressures. Due to the

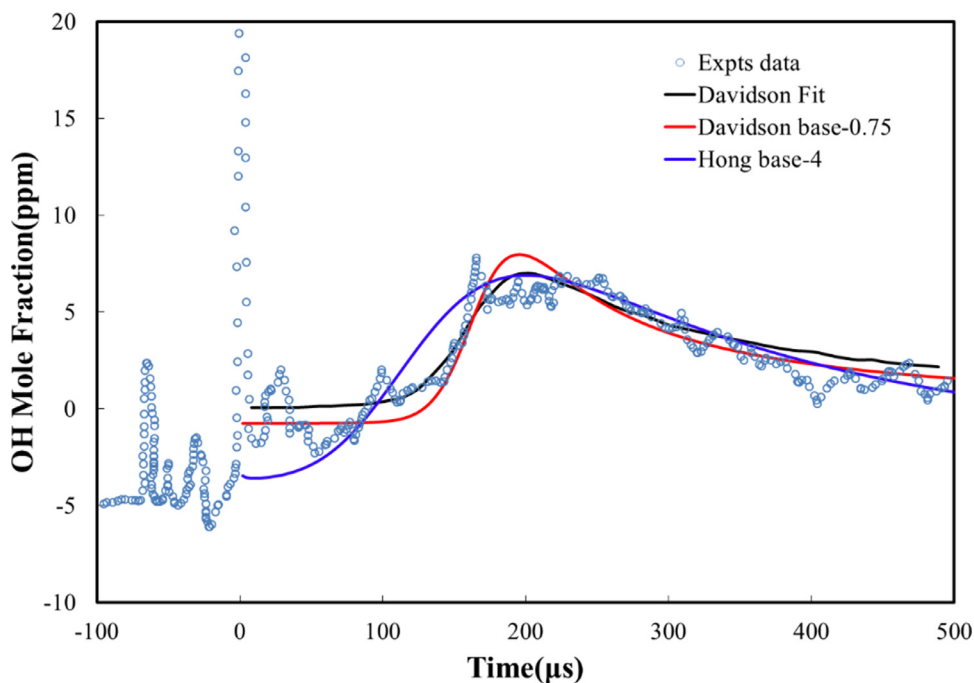


Fig. 3. Three different fittings using GRI-Mech 1.2 and the Hong et al. Mech with variation of baseline against experimental data at 1326 K and 64.3 atm. — Fitting using GRI-Mech 1.2 with original Davidson R2; — Fitting using GRI-Mech 1.2 by reducing 20% of the original Davidson R2 and lower baseline by 0.75 ppm; — Fitting using the Hong et al. Mech with baseline lower by 4 ppm and $8.30\text{E} + 18$ as Hong_AR_PreA, a reduction of $\sim 10\%$ from the value in Table 1.

Table 2

Comparison of evaluated rate of R2 using the Hong et al. Mech with the original Davidson rate with N_2 as bath gas. $k_{2,0}$ unit ($\text{cm}^6 \text{mol}^{-2} \text{s}^{-1}$); $k_{2,1}$ unit ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$).

T (K)	P (atm)	Davidson_ $k_{2,0}$	Davidson_ $k_{2,1}$	Hong_AR_PreA	Hong_ N_2 _PreA	Hong_ N_2 _ $k_{2,1}$
1278	48.6	$2.50\text{E} + 15$	$1.16\text{E} + 12$	$8.47\text{E} + 18$	$2.64\text{E} + 19$	$1.04\text{E} + 12$
1289	54.5	$2.50\text{E} + 15$	$1.29\text{E} + 12$	$8.58\text{E} + 18$	$2.55\text{E} + 19$	$1.10\text{E} + 12$
1298	55.6	$2.50\text{E} + 15$	$1.31\text{E} + 12$	$8.90\text{E} + 18$	$2.60\text{E} + 19$	$1.13\text{E} + 12$
1304	48.8	$2.70\text{E} + 15$	$1.23\text{E} + 12$	$9.30\text{E} + 18$	$2.92\text{E} + 19$	$1.10\text{E} + 12$
1323	50.8	$2.70\text{E} + 15$	$1.26\text{E} + 12$	$1.02\text{E} + 19$	$2.99\text{E} + 19$	$1.13\text{E} + 12$
1328	52.7	$2.70\text{E} + 15$	$1.31\text{E} + 12$	$1.06\text{E} + 19$	$3.10\text{E} + 19$	$1.21\text{E} + 12$
1347	55.7	$2.50\text{E} + 15$	$1.26\text{E} + 12$	$1.13\text{E} + 19$	$3.05\text{E} + 19$	$1.21\text{E} + 12$
1350	57.2	$2.70\text{E} + 15$	$1.39\text{E} + 12$	$1.13\text{E} + 19$	$3.20\text{E} + 19$	$1.30\text{E} + 12$
1375	52.7	$2.50\text{E} + 15$	$1.17\text{E} + 12$	$1.20\text{E} + 19$	$3.61\text{E} + 19$	$1.01\text{E} + 12$

competition of R2 with $\text{NO} + \text{OH} = \text{NO}_2 + \text{H}$ (R7), the formation of NO_2 will reach a plateau after a certain time, which can be analytically expressed as

$$[\text{NO}_2]_{\text{plateau}} = k_2[\text{O}_2][\text{M}]/k_7$$

With well determined reaction rate of R7 and other secondary reactions such as R1 and $\text{NO} + \text{HO}_2 = \text{NO}_2 + \text{OH}$, the rate coefficient of R2 can be extracted by adjusting R2 to match the plateau NO_2 concentration derived from the absorption signal. However, the analytical expression is only approximately accurate under certain conditions. The obtained R2 are significantly smaller than both the fitted Troe formula values in Ref. [8] (see Fig. 6) and the values in current paper (see Fig. 1) when pressure increases, which indicates that some important interference reactions at higher pressures either have substantial uncertainties or are missing in the mechanism, or there is some experimental uncertainty in deriving the concentration of NO_2 .

2.2.1. Critical reaction rate assessment and update

To restrain the uncertainties of the model used in the simulation, we construct the model based on the revised Hong et al. Mechanism discussed earlier and the NO_x mechanism from Glarborg et al. [16] in which NO_x -related reaction rates have been updated recently. A careful examination of the R7 rate shows that the rate expression in Glarborg's NO_x mechanism cited from Ko

and Fontijn [17] can reproduce the rates recently measured by Haas and Dryer [18] in high pressure flow reactor at 750–900 K and Su et al.'s [19] shock tube experiment between 1000 and 2000 K and theoretical calculations within 10%. The rate expression of $\text{NO}_2 + \text{OH} = \text{NO} + \text{HO}_2$ reactions in Glarborg's NO_x mechanism cited from Howard's [20] lower temperature measurement agrees very well with Michael and co-workers [21] and Troe's [22] high temperature shock tube experiment. We updated $\text{NO}_2 + \text{O} = \text{NO} + \text{O}_2$ rate noting that a very recent experimental measurement [23] produced a more accurate rate which is $\sim 30\%$ higher than that of the Glarborg mechanism in the temperature range of Bates et al.

The $\text{NO}_2 + \text{HO}_2 = \text{HONO} + \text{O}_2$ or $\text{HNO}_2 + \text{O}_2$ reactions are other possible sources that consume NO_2 at high pressures. Rasmussen et al. [24] reported the theoretical rates of the two reactions obtained at the level of CBS-QB3 and transition state theory (TST), where the rates in Glarborg mechanism came from. Zhang et al. [25] computed the reaction rates from 240 K to 425 K, and found that the triplet reaction channels were favorable over single potential energy surface. However, reaction rates at higher temperatures are not reported. The two presented theoretical results differed orders of magnitude at the low temperature range. Consequently, we performed a high-level *ab initio* calculation on the triplet potential energy surface with the Gaussian 09 package [26]. The

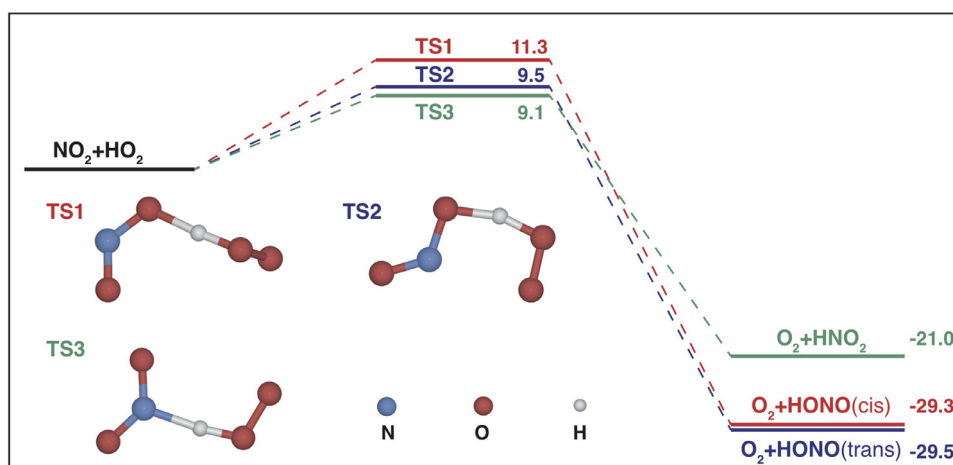


Fig. 4. The potential energy surface (in kcal/mol) for the three reaction channels of $\text{NO}_2 + \text{HO}_2$, forming $\text{O}_2 + \text{HONO}(\text{cis})$, $\text{O}_2 + \text{HONO}(\text{trans})$, and $\text{O}_2 + \text{HNO}_2$, with the corresponding TSs denoted as TS1, TS2 and TS3, respectively. Structures of the three TSs are also shown.

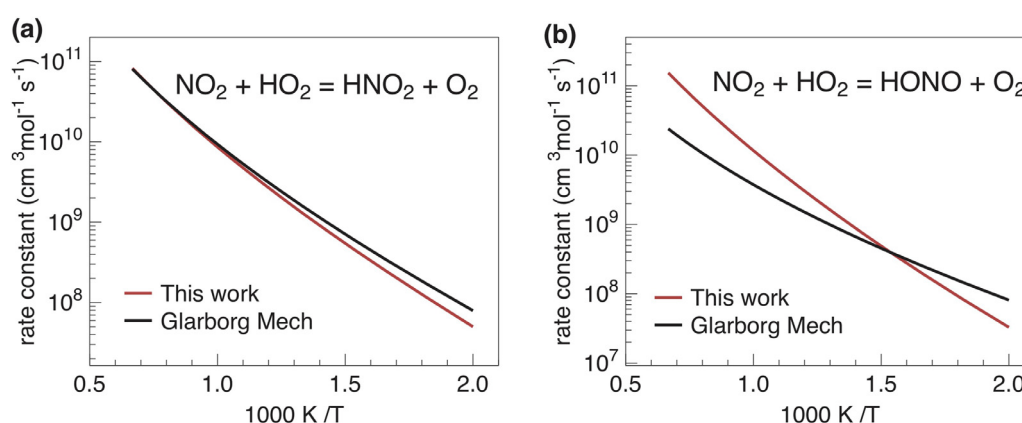


Fig. 5. Comparison of rate constants (predicted this work in red) for $\text{NO}_2 + \text{HO}_2$ reaction and the rates used in Glarborg mechanism. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

equilibrium structures and vibrational frequencies of all stationary points are obtained at B3LYP/aug-cc-pVTZ level. The zero point energies (ZPEs) are obtained within the harmonic approximation and scaled by a factor of 0.968 to account for anharmonicity. The single point energies for all the critical points are then refined using the high-level correlated wavefunction method, CCSD(T), with basis sets aug-cc-pVXZ ($X = T, Q$). The energies are then extrapolated to complete the basis set (CBS) with the two-point extrapolation scheme [27] given by

$$E(l_{\max}) = E_{\infty} + \frac{B}{(l_{\max} + 1)^4}$$

The predicted relative energies to the reactant $\text{NO}_2 + \text{HO}_2$ are depicted in Fig. 4 without including the pre-reactive complexes discussed by Zhang et al. The corresponding transition states of the three reaction channels producing $\text{O}_2 + \text{HONO}(\text{cis})$, $\text{O}_2 + \text{HONO}(\text{trans})$, and $\text{O}_2 + \text{HNO}_2$ are denoted as TS1, TS2, TS3 respectively. The barrier heights of the three reaction channels are predicted to be 11.3 kcal/mol, 9.5 kcal/mol, and 9.1 kcal/mol, indicating that all the three channels could contribute to the consumption of NO_2 at high temperatures. It is noted that the T1 diagnostics (>0.04) of TS1 (0.041) and TS2 (0.044), shows moderate multireference effects and hence introduces slightly higher uncertainties to the obtained energies.

The rates of these three reaction channels from 500 to 1500 K are calculated based on transition state theory (TST) using Variflex [28]. The ideal gas, rigid rotor, and harmonic oscillator approxima-

Table 3

Comparison of modified Arrhenius ($k = AT^n \exp(-\frac{E_a}{RT})$) parameters for $\text{NO}_2 + \text{HO}_2$ reactions, obtained by TST within the 1D separable-hindered-rotor approximation and with energies obtained at the CCSD(T)/CBS limit.

Reaction	$A(\text{cm}^3 \text{mol}^{-1} \text{s}^{-1})$	n	E_a (cal/mol)
$\text{NO}_2 + \text{HO}_2 \rightarrow \text{O}_2 + \text{HNO}_2$	6.85E + 01	3.130	5918.6
$\text{NO}_2 + \text{HO}_2 \rightarrow \text{O}_2 + \text{HONO}$	5.84E + 01	3.305	7399.7

tions are applied for translational, rotational, and vibrational partition functions, respectively. The torsional modes are treated as internal rotors within the one-dimensional separable-hindered-rotor approximation. The asymmetric Eckart tunneling correction is applied to the final rate constants. Based on TST, the uncertainty of the rate at 1500 K is estimated as ~30% assuming the uncertainty of barrier height being 1 kcal/mol. Given the accuracy of the theoretical method and the relatively high T1 diagnostic, all the reaction barriers are lowered by 1 kcal/mol in computing the rates. The predicted modified Arrhenius ($k = AT^n \exp(-\frac{E_a}{RT})$) parameters for the reactions are summarized in Table 3, where the $\text{O}_2 + \text{HONO}$ reaction is the sum of both cis- and trans-HONO channels. As shown in Fig. 5, the current predictions show overall higher energy barrier and larger temperature dependence than the corresponding rate in the Glarborg mechanism. The predicted rate of the HNO_2 channel agrees well with the Glarborg rate. However, the HONO channel rate is significantly larger than the corresponding Glarborg rate at higher temperatures but contrary in the lower temperature range. The subsequent dissociation or transformation rates of

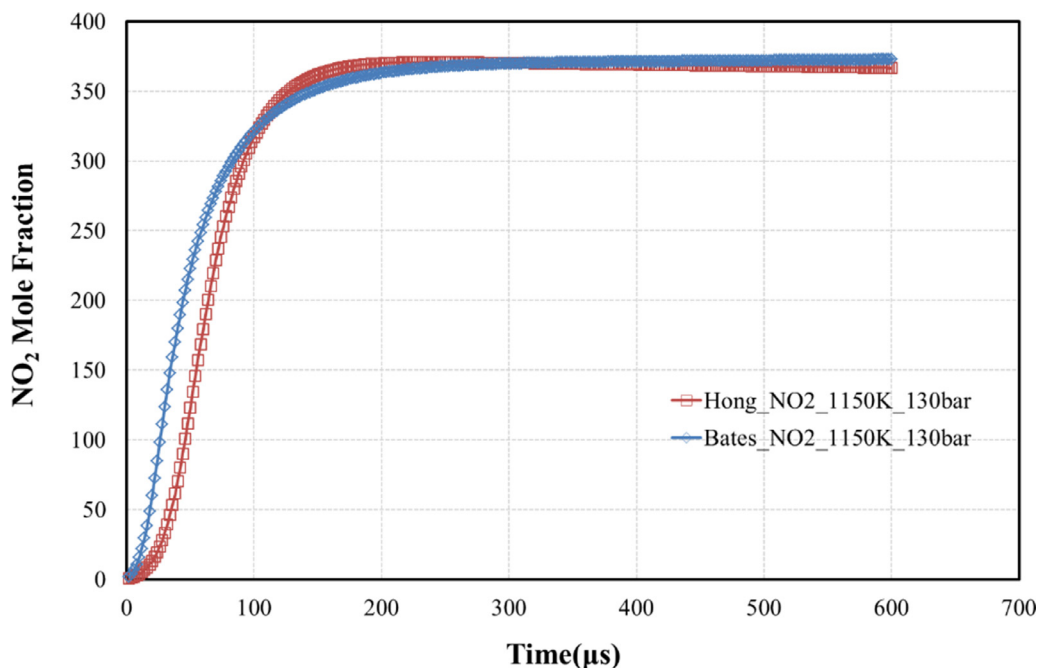


Fig. 6. NO₂ time history profile simulated using GRI-Mech 2.11 with Bates rate and Hong et al. Mech plus updated NO_x mechanism for experiments at 1150 K and 130 bar.

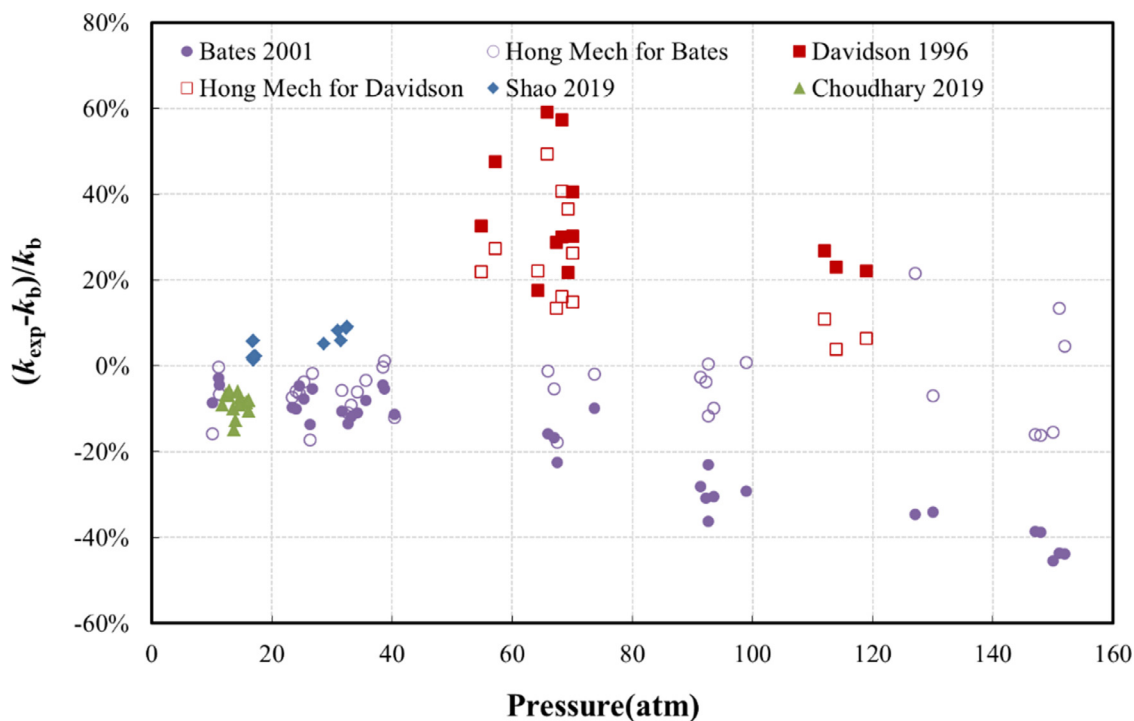


Fig. 7. The rates of $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$ of Bates and Davidson experimental data along with Shao and Choudhary data for $\text{M} = \text{Ar}$ compared against the Troe formula in Eq. (b) at each pressure.

HNO_2 are also updated using the very recent calculations of Chen et al. [29] where the $\text{HNO}_2 = \text{OH} + \text{NO}$ reaction was missing in the mechanism and the $\text{HONO} = \text{HNO}_2$ rate was five to six orders smaller than that in the Glarborg mechanism.

2.2.2. Uncertainty analysis of the experiments

The temperature uncertainty is assumed to be 1% and as such is not expected to contribute much to the R2 rate determination. The most significant uncertainty of the experiments is expected to come from the absorption cross section of NO₂, which

was used to derive the NO₂ concentration in the R2 determination. In Ref. [8] it is indicated that no measurable pressure dependence has been found for elevated temperatures for NO₂ at 472.7 nm, while Ref. [30] states that, at higher pressures, the absorption cross-section is reduced slightly with pressure up to 75 atm and the absorption cross section is temperature independent at 472.7 nm $\sim (3.0 \pm 0.2) \times 10^{-19} \text{ cm}^2/\text{mole}$. All other measurements of absorption cross section of the same wavelength at low temperature reported the absorption cross section of around $\sim 3.2 \times 10^{-19} \text{ cm}^2/\text{mole}$, showing strong support to the results of

Table 4

Comparison of the first order rates of the Hong et al. Mech with Bates data for the same experimental condition. The mole fraction of H₂, O₂, Ar and NO are varied to assure NO₂ plateau appears no later than 400 μ s. The unit for rate is cm³ mol⁻¹ s⁻¹.

T (K)	P (atm)	Bates_k _{2,1}	H ₂	O ₂	Ar	NO	Hong_k _{2,1}
1019	10.1	2.04E + 11	0.004900	0.0588	0.935890	0.000410	1.88E + 11
1045	26.4	4.58E + 11	0.004900	0.0588	0.935890	0.000410	4.38E + 11
1075	11.3	2.12E + 11	0.002450	0.0588	0.937930	0.000820	2.08E + 11
1078	24.1	4.11E + 11	0.004900	0.0588	0.935480	0.000820	4.29E + 11
1097	31.7	5.10E + 11	0.004900	0.0588	0.935480	0.000820	5.38E + 11
1106	67.5	8.80E + 11	0.004900	0.0588	0.936095	0.000205	9.31E + 11
1115	32.7	4.92E + 11	0.004900	0.0588	0.935890	0.000410	5.06E + 11
1115	66.0	9.21E + 11	0.002450	0.0588	0.938545	0.000205	1.08E + 12
1125	127.0	1.27E + 12	0.002450	0.0588	0.938545	0.000205	2.36E + 12
1134	33.2	4.91E + 11	0.002450	0.0588	0.937930	0.000820	5.06E + 11
1139	23.4	3.58E + 11	0.002450	0.0588	0.937930	0.000820	3.67E + 11
1145	91.4	1.00E + 12	0.002450	0.0588	0.938545	0.000205	1.36E + 12
1147	24.6	3.91E + 11	0.002450	0.0588	0.938340	0.000410	3.83E + 11
1147	99.0	1.06E + 12	0.002450	0.0588	0.938545	0.000205	1.51E + 12
1148	92.2	9.70E + 11	0.002450	0.0588	0.938545	0.000205	1.35E + 12
1149	92.6	8.96E + 11	0.002450	0.0588	0.938545	0.000205	1.24E + 12
1150	130	1.26E + 12	0.004900	0.0588	0.935890	0.000410	1.77E + 12
1156	11.2	1.84E + 11	0.002450	0.0588	0.937930	0.000820	1.89E + 11
1182	151.0	1.16E + 12	0.002450	0.0588	0.938545	0.000205	2.34E + 12
1186	26.8	3.92E + 11	0.002450	0.0588	0.937930	0.000820	4.08E + 11
1188	25.3	3.61E + 11	0.002450	0.0588	0.937930	0.000820	3.77E + 11
1191	152.0	1.15E + 12	0.002450	0.0588	0.938545	0.000205	2.14E + 12
1202	93.5	9.02E + 11	0.002450	0.0588	0.938545	0.000205	1.17E + 12
1203	67.0	7.95E + 11	0.002450	0.0588	0.938545	0.000205	9.02E + 11
1208	92.6	9.82E + 11	0.002450	0.0588	0.938545	0.000205	1.28E + 12
1213	150.0	1.06E + 12	0.002450	0.0588	0.938545	0.000205	1.65E + 12
1215	35.7	4.77E + 11	0.002450	0.0588	0.937930	0.000820	5.01E + 11
1216	34.2	4.42E + 11	0.002450	0.0588	0.937930	0.000820	4.67E + 11
1227	73.7	9.03E + 11	0.002450	0.0588	0.938545	0.000205	9.82E + 11
1235	40.4	5.00E + 11	0.002450	0.0588	0.938340	0.000410	4.96E + 11
1245	148.0	1.13E + 12	0.002450	0.0588	0.938545	0.000205	1.54E + 12
1264	38.5	4.90E + 11	0.002450	0.0294	0.967740	0.000410	5.12E + 11
1264	147.0	1.09E + 12	0.001225	0.0588	0.939770	0.000205	1.49E + 12
1317	38.7	4.48E + 11	0.001225	0.0294	0.968965	0.000410	4.79E + 11

Table 5

Comparison of the first order rates of the Hong et al. Mech with Bates data for the same experimental condition. The mole fraction of H₂ is varied to assure NO₂ plateau appears no later than 400 μ s. The unit of the rate is cm³ mol⁻¹ s⁻¹.

T (K)	P (atm)	Bates_k _{2,1}	H ₂	O ₂	Ar	NO	N ₂	Hong_k _{2,1}
1119	8.1	2.20E + 11	0.001225	0.0588	0.27859	0.00082	0.66	2.18E + 11
1136	7.3	1.91E + 11	0.001225	0.0588	0.27859	0.00082	0.66	1.90E + 11
1192	21.7	4.89E + 11	0.004900	0.0588	0.27859	0.00082	0.66	5.27E + 11
1180	20.9	4.85E + 11	0.004900	0.0588	0.27859	0.00082	0.66	5.19E + 11
1222	22.6	4.79E + 11	0.004900	0.0588	0.27859	0.00082	0.66	5.26E + 11
1189	31.3	7.22E + 11	0.004900	0.0588	0.27859	0.00082	0.66	7.72E + 11
1200	33	7.46E + 11	0.004900	0.0588	0.27859	0.00082	0.66	7.96E + 11
1195	32.7	7.65E + 11	0.004900	0.0588	0.27859	0.00082	0.66	8.18E + 11

Ref. [30]. Consequently, we consider the absorption cross section of NO₂ at 472.7 nm has no obvious temperature and pressure dependence, but note nevertheless that the uncertainty can be as much as 3% over the experimental measurement.

2.2.3. Fitting procedure and evaluated rate of R2

Similar to reanalyzing Davidson data, we first generated the NO₂ profile using GRI-Mech 2.1 [31] with the update of R2 to Bates rate and OH + HO₂ = H₂O + O₂ (R3) from Hipper et al.'s measurements as Bates et al. did as step 1. The mole fraction of each species in the mixture concentrations were varied to produce NO₂ plateau between 400 and 600 μ s as Bates et al. indicated (step 1). We then performed the simulations using the Hong et al. Mech (plus updated NO_x rates discussed in Section 2.2.1) to match the NO₂ plateau and ensure that the maximum NO₂ concentration does not deviate from the values in step 1 by 1 ppm. Figure 6 shows the simulations of the NO₂ time history profile at

1150 K and 130 bar using GRI-Mech 2.11 with the Bates rate and the Hong et al. Mech plus updated NO_x mechanism. It is clear that the NO₂ mole fraction of the two simulations differ quite substantially at early stage, but matches well after 300 μ s where only a few reactions determine the height of the plateau.

The first order rates of R2 with the Hong et al. Mech as derived are listed in Table 4 along with the original Bates data. It is seen that there is very little difference between each other at lower pressures. However, the Hong et al. Mech rates start to be ~10% higher than the corresponding Bates value at 60 bar and >50% at 130–150 bar. We also found that the height of the NO₂ plateau is sensitive to R2/R7 at lower pressures as discussed by Bates et al. and consequently the uncertainty of R2 derived below 60 atm can be estimated as less than ~15%. However, many HO₂ generation and consumption reactions can affect the NO₂ concentration at higher pressures, and therefore the NO₂ plateau is less sensitive to the changes of R2; consequently the R2 value derived from

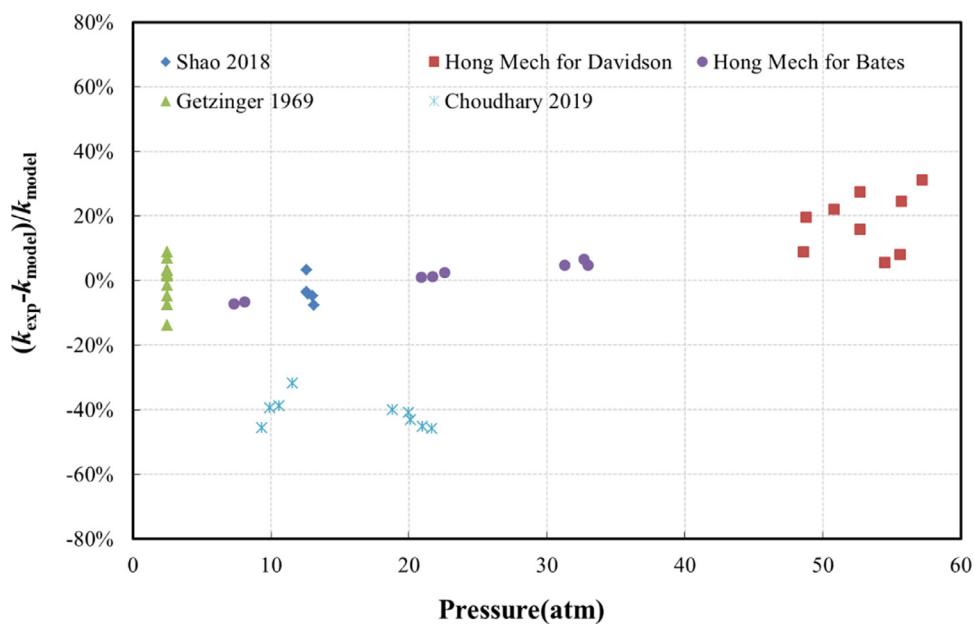


Fig. 8. Comparison of the Troe formula in Eq. (c) with the reevaluated Bates and Davidson experimental rates, Shao rate, Getzinger rate [32] and Choudhary rate of $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$ for $\text{M} = \text{N}_2$ at each pressure.

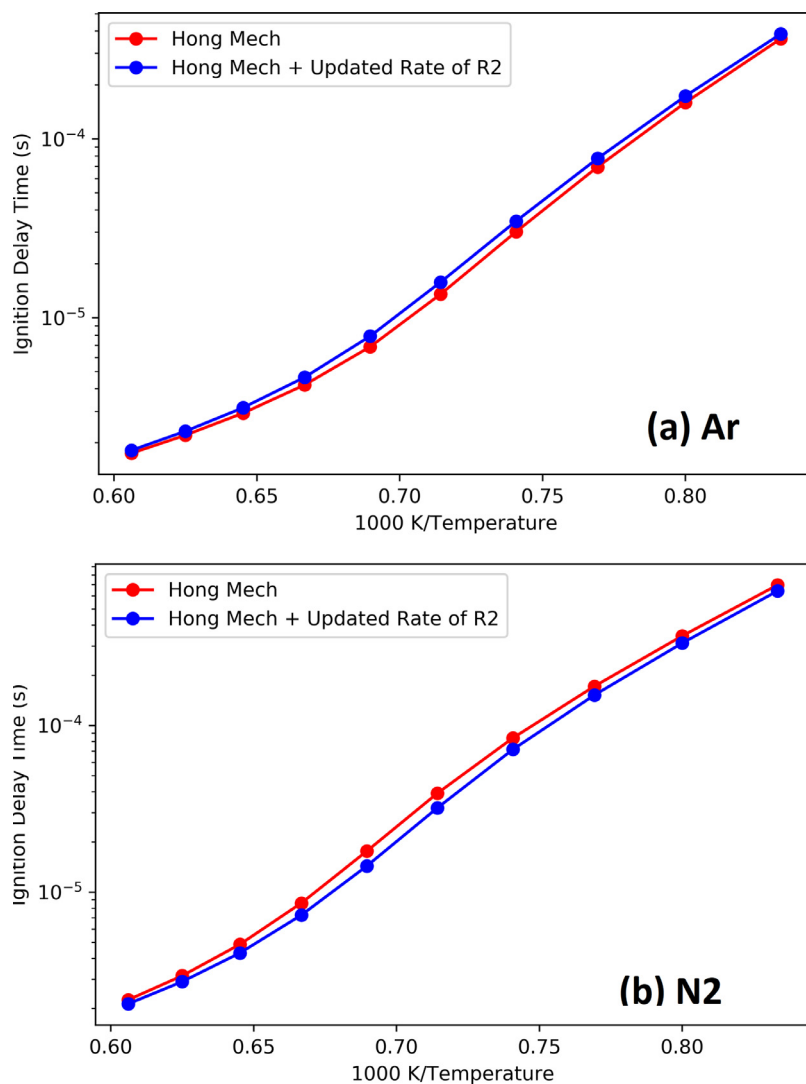


Fig. 9. Comparison of the ignition delay times with and without the updated rate coefficients of R2 for (a) Ar diluted and (b) N_2 diluted mixtures at 100 atm.

higher pressure experiments and are expected to have larger uncertainties by as much as ~30%.

Similarly, rates of R2 with the N₂ experiments of Bates et al. were re-evaluated with the Hong et al. Mech with updated NO_x mechanism. For mixtures with dilutions of both Ar and N₂, the single expression mixing rule of the third body has been used in our re-evaluations. Table 5 shows comparison of the first order rates of R2 with the Hong et al. Mech against the original Bates rate. A few upward corrections of the first order rate are clearly observed for the same experimental condition for the pressure range of 7–33 bar, which is consistent with our evaluation of the experiments with Argon at similar pressures.

3. New Troe formula with tighter uncertainty

With the updated rates for Davidson et al. and Bates et al. experiments using the Hong et al. Mech, a least square fitting of all the available experimental results using the Troe formula for R2 with Argon as bath gas result in the following Eq. (b):

$$\text{H} + \text{O}_2(+\text{Ar}) = \text{HO}_2(+\text{Ar}) \quad 1.025\text{E} + 12 \quad 0.604 \quad -241.1 \quad (\text{b})$$

$$\text{LOW}/2.220\text{E} + 19 \quad -1.309 \quad 278.2/$$

$$\text{TROE}/0.481 \quad 1.0\text{E} - 10 \quad 1.0\text{E} + 30 \quad 1.0\text{E} + 30/$$

The deviations of the first order rate of the four major high temperature and high pressure from Eq. (b) are plotted as Fig. 7. The original Davidson and Bates data are also plotted for comparison and much improved agreement with the new Troe formula is noted. It is clear that most of the updated experimental data agree with Eq. (b) within 20%. We note that the updated rates for Davidson's experiments still differ substantially from the new Troe formula, although we believe that a potential 10–15% reduction in uncertainty of the rate is possible with improved OH signal-to-noise ratio using current start-of-the-art shock tube technique and the OH absorption spectroscopy technique. The agreement between Eq. (b) and other low temperature and/or low pressure experimental data are also well within 20% (not shown in Fig. 7).

An accurate Troe formula for $\text{H} + \text{O}_2 + \text{N}_2 = \text{HO}_2 + \text{N}_2$ reaction requires additional considerations. Specifically, the highest pressure of N₂ experiments is only up to ~50 bar reported by Davidson et al. comparing to 150 bar using Argon as bath gas, of which accuracy is limited by the OH signal-to-noise ratio. Secondly, the most recent measurement by Choudhary et al. reported low pressure limit rate of R2 with N₂ is even lower than that with Ar at similar conditions, which is contrary to the common knowledge that the collisional efficiency of N₂ is larger than Argon and therefore the low-pressure limit is generally 1.5 times larger than Argon. With these considerations, the Troe formula of N₂ is obtained without Choudhary et al.'s N₂ data as Eq. (c) in the following:

$$\text{H} + \text{O}_2(+\text{N}_2) = \text{HO}_2(+\text{N}_2) \quad 1.025\text{E} + 12 \quad 0.604 \quad -241.1 \quad (\text{c})$$

$$\text{LOW}/2.720\text{E} + 19 \quad -1.290 \quad 0/$$

$$\text{TROE}/0.458 \quad 1.0\text{E} - 10 \quad 1.0\text{E} + 30 \quad 1.0\text{E} + 30/$$

The deviation for the experimental data with the Troe formula at corresponding temperature and pressure are shown in Fig. 8. Comparing Eq. (b) and Eq. (c), the relative collisional efficiency of N₂ to Argon is 1.6 around 1000 K, which is in excellent agreement with most experimental measurements. We however suggest further experimental examinations on Davidson and Choudhary conditions which are critical for rate evaluation.

To test the effects of updating the rate coefficients of R2 at elevated pressures, the ignition delay times as the global targets have been simulated. The mixture consists of 2% H₂, 1% O₂ and 97% diluent (Ar or N₂), and the pressure is 100 atm. The results, demonstrated in Fig. 9, show that both the rates of $\text{H} + \text{O}_2 (+\text{Ar})$ and $\text{H} + \text{O}_2 (+\text{N}_2)$ strongly affect the ignition delay time predictions, especially at the intermediate to low temperature regions where the HO₂ kinetics plays an essential role of the ignition processes.

4. Conclusions

In this work, we have systematically investigated the literature experimental data of the $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$ rate at elevated pressures. With updated Hong et al. Mech, we found that the rates from the experiments of Davidson et al. can be lowered by ~15%, which is mainly due to the reduction of R1 and the more accurate understanding of the associated important reactions R3, R4, R5 and R6. The re-evaluation of the Bates et al. experiments involves updates of the NO_x mechanism with NO₂ + HO₂ being estimated by high-level *ab initio* quantum chemistry calculation on potential energy surfaces and kinetic calculations of the rate in the temperature range of 500–1500 K. Simulation with the new mechanism shows that the rates of the lower pressure experiments are barely affected but those of the higher pressure experiments can be increased by 10–50%, which eliminates most of the disagreement between the experiments and the model rates. A new Troe formula of R2 with Argon as the bath gas covering the temperature range of 300–2000 K and pressure range 1–150 bar was proposed with ~20% uncertainty for all available experimental data. We also propose a Troe formula of R2 with N₂ as bath gas with less experimental constraint. The new rate of R2 would provide increased confidence on high pressure combustion simulation in which R2 plays a critical role.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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Reference

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On band lumping, radiation reabsorption, and high-pressure effects in laminar flame propagation

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ABSTRACT

Effects of radiation reabsorption on the burning flux of freely propagating laminar premixed flames at atmospheric and elevated pressures were numerically investigated for $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ mixtures. Models with SNBCK 9 bands and 7 bands based on the spectral band lumping for H_2O , CO_2 , CO and CH_4 were developed to improve the computational efficiency. It is found that the burning flux is promoted by the upstream radiation reabsorption and with increasing CO_2 concentration. Furthermore, with increasing pressure, radiation reabsorption first increases and then reduces the burning flux because of the corresponding increases of the reabsorption efficiency and the optical thickness, respectively. The blockage of radiation emission from the burnt mixture due to the increased optical thickness is dominant with the addition of the stronger radiative species CO_2 at higher pressures. Extensive computation further demonstrates that, compared with the benchmark case of 367 bands, the SNBCK 9 bands lumping retains good accuracy while substantially facilitates the computational efficiency.

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1. Introduction

In addition to heat conduction, radiation is a major mode of heat transfer in combustion systems, with heat loss through emission and heat gain through reabsorption. These in turn would affect the flame temperature, the temperature-sensitive reaction rates, the extent of thermal conduction, and the global flame phenomena such as the flame propagation rate and the thresholds of extinction, flashback and blowoff [1,2]. Important as it is, systematic analytical and computational studies of radiation-affected phenomena have been challenged by the immensely complex species-dependent integro-differential equations governing its transport, leading to simplifying efforts at various levels of accuracy and the possible obscuring of certain controlling physics.

There are two objectives of the present study. First, we shall apply a band-lumping formulation, developed in heat transfer studies, to the problem of flame propagation, and demonstrate that there is an optimum number of bands, 9 in the present investigation, that is both physically accurate and computationally facilitating. Because of the generality of the formulation, the potential utility of the 9-band lumping formulation in the simulation of combustion phenomena is suggested. The second objective is to

use this computationally efficient formulation to study the impact of radiation emission and reabsorption on the structure and propagation of the prototypical freely propagating planar premixed flame, especially in the practically important high-pressure environments, recognizing that the comprehensiveness and accuracy of previous worthwhile studies [2,3] have been challenged by the high demand of the computation cost.

To briefly substantiate the above statements, it is noted that in terms of the various useful radiation models that have been either adopted or developed in flame simulations, Buckmaster and Ronney [4] first used a gray gas model to study the radiation effect on the dynamics of flame balls, while Ju et al. [5] proposed improved Planck mean absorption coefficients for H_2O , CO_2 and CO to investigate the radiative heat loss on flame bifurcation in counterflow flames, and examined the accuracy of Tien's data [6]. Since the gas absorption coefficient used in optically thin models only considers the temperature dependence and ignores radiation reabsorption, Ju et al. [7] studied radiation reabsorption in the planar methane flame by considering the spectral dependence based on the statistical narrow-band (SNB) model, while Chen et al. [2] proposed a fitted statistical narrow-band correlated- k (FSNB-CK) model to calculate the radiative reabsorption in CH_4/air flames [8], as well as large-scale spherical flames [9] by solving the radiative transfer equation (RTE) using the discrete ordinate method (DOM) [10].

Recognizing the high computational cost for both SNB and FSNB-CK models, for example there are a total of 367 bands

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needed to be solved for the RTE when the bandwidth is 25 cm^{-1} for wave numbers from 150 cm^{-1} to 9300 cm^{-1} , Liu et al. [3] proposed a band lumping strategy to formulate a wideband CK model based on SNBCK. Thus instead of solving the RTE multiple times for each narrow band in the wideband, radiative transfer over the wideband is calculated by lumping several successive narrow bands into a single wideband. The reduction in the computation cost is however expected to be accompanied by reduced accuracy since the Planck blackbody function cannot be considered as constant with the wide bandwidth.

Considering the competing roles of computational accuracy and cost, we aim to assess the effects of spectral band numbers on these two computational parameters: clearly substantial loss in accuracy would not justify the reduction in the cost as the band number is reduced to a certain level. Here we note that Liu et al. [3] has demonstrated that an 18 band lumping incurred practically no loss in the radiation parameters. Consequently we aim to assess to what level of further reduction in the band number and the associated cost, as well as for multicomponent combustion systems, such accuracy can be largely maintained. We shall demonstrate in due course that the SNBCK 9 band lumping seems to exhibit an optimal range of accuracy-vs-cost.

Furthermore, in order to also gain further understanding on the role of radiation on laminar flame propagation, we shall extend the worthwhile work of Refs. [2,7] in assessing the influence of radiation reabsorption, especially in preheating the upstream region as it directly elevates the temperature of the reaction zone and hence Arrhenius facilitates the reaction rates. The role of elevated pressure, which has not been adequately studied, is of particular interest because of its direct influence on the optical thickness, which increases with increasing pressure and hence reduces the extent of reabsorption, and as such counteracts the opposing effect due to the correspondingly increased absorptivity.

2. The SNBCK model and numerical method

For an isothermal and uniform medium with path-length L , mole fraction of the radiant gas X and pressure P , the narrow band averaged transmissivity in the SNB model can be expressed as [11]:

$$\bar{\tau}_\eta(L) = \exp \left[-\frac{\pi B}{2} \left(\sqrt{1 + \frac{4SL}{\pi B}} - 1 \right) \right] \quad (1)$$

where, $B = 2\bar{\beta}_\eta/\pi^2$, $S = \bar{\kappa}_\eta XP$ and $\bar{\beta}_\eta = 2\pi\bar{\gamma}_\eta/\bar{\delta}_\eta$. The mean narrow-band parameters $\bar{\gamma}_\eta$, $\bar{\delta}_\eta$ and $\bar{\kappa}_\eta$ can be calculated according to Young's band model [12].

The line parameters used in this paper are based on the HITRAN 2016 database [13]. The temperature range is from 300 to 2900 K, and the corresponding spectral range is from 150 to 9300 cm^{-1} . The gas averaged transmissivity in Eq. (1) can be expressed as the absorption coefficient distribution function $f(k)$ in the SNBCK model based on the inverse Laplace transformation [14]:

$$f(k) = \frac{1}{2} k^{-3/2} (BS)^{1/2} \exp \left[\frac{\pi B}{4} \left(2 - \frac{S}{k} - \frac{k}{S} \right) \right] \quad (2)$$

The cumulative distribution function $g(k)$ is introduced for the non-isothermal inhomogeneous media calculation and is defined as $g(k) = \int_0^k f(k') dk'$. Substituting it into Eq. (2) yields:

$$g(k) = \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{a}{\sqrt{k}} - b\sqrt{k} \right) \right] + \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{a}{\sqrt{k}} + b\sqrt{k} \right) \right] e^{\pi B} \quad (3)$$

where $a = \sqrt{\pi BS}/2$, $b = \sqrt{\pi B/S}/2$ and $\operatorname{erf}(x)$ is the error function specified by $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$.

Based on the band lumping strategy, the cumulative distribution function of a wide band formed from N narrow bands is obtained by averaging $g_i(k)$ for the N narrow bands. Inversion of $g(k)$ yields the gas absorption coefficients at the wideband, which can be performed efficiently by using a Newton–Raphson iteration method described by Lacis and Oinas [15] and Liu et al. [16]. The g -values for the mixture are calculated by Ref. [17].

The benchmark results are obtained for the bandwidth of 25 cm^{-1} , which corresponds to 367 bands used in the spectral range from 150 to 9300 cm^{-1} . Since Liu et al. [3,18] have already validated the high accuracy for radiative heat transfer cases using a reduced number of bands, to 18 bands where the bandwidth is 500 cm^{-1} , we shall study herein the accuracy and efficiency of 9 bands with bandwidth 1000 cm^{-1} and 7 bands with bandwidth 1200 cm^{-1} .

The radiative transfer equation (RTE) [19] can be solved in the rectangular coordinate using the DOM method [20]. The T_4 [21] angular quadrature set with 128 directions in the entire 4π solid angle were used in the DOM.

Once the radiative intensity field is obtained, the net radiative flux can be calculated as

$$\dot{q}_r = \sum_{i=1}^{N\text{-band}} \sum_{j=1}^{N\text{-gauss}} w_j k_{i,j} \left(\sum_{m=1}^M I_{i,j,m} - 4\pi I_{bi,j}(T) \right) \Delta \eta \quad (4)$$

where $N\text{-gauss}$ is the Gauss points, and w_j the corresponding weight factor. The absorption coefficient $k_{i,j} = XPk$, where X is the mole fraction and P the pressure, and k can be obtained by inverting Eq. (3) at a given quadrature point g_j . The four-point Gauss–Lobatto quadrature was adopted in this work.

To validate the radiation model in this study, the radiative source from a one-dimensional layer bounded by a black emitting wall at 300 K and atmospheric pressure was investigated. The parallel-plane space was divided into 20 uniform volumes and the thickness of the medium was 0.1 m, 1 m and 5 m, respectively. The 1D parallel-plane layer was filled with H_2O , CO_2 , CO and CH_4 , respectively. The radiative power distributions calculated by the SNBCK 367 bands, 9 bands, 7 bands and HITEMP 2010 are shown in Fig. 1. The results for H_2O , shown in Fig. 1(a), are in addition compared with the FSNB-CK calculations in Ref. [2], which shows that the SNBCK 367 bands can well reproduce the FSNB-CK results. Consequently, results calculated by the SNBCK 367 bands are used as the benchmark for the flame cases. The results calculated by HITEMP 2010 [22] are used as the benchmark for the 1-D layer cases. As shown in Fig. 2(a), the averaged relative error of radiative power is 9.52% for H_2O , while that calculated by the SNBCK 7 bands is larger than that by the SNBCK 9 bands. In terms of the CPU time, the SNBCK 367 bands model (34.6 s) is about 10.9 times slower compared to the 9 bands model (3.12 s), while the 9 bands model only needs 13% more CPU time than the 7 bands model (2.76 s). Considering its higher computational accuracy (see the average relative errors in Fig. 2), the 9 bands model clearly outperforms the 7 bands model. Consequently, recognizing the relatively larger inaccuracy of the 7 band model, in the following we will not specifically discuss results based on it, although the quantitative results are still included in the figures. The coefficients for the SNBCK 9 bands model are provided as supplementary material.

3. Effects of radiation reabsorption

Planar flames of $\text{CH}_4/\text{O}_2/\text{N}_2/\text{Ar}/\text{CO}_2$ mixtures, with $\text{O}_2/(\text{O}_2+\text{N}_2+\text{Ar}+\text{CO}_2)=21\%$, were calculated using the PREMIX code [23]. The reaction rates and transport properties were evaluated by the CHEMKIN and TRANSPORT packages, respectively. The detailed methane reaction mechanism GRI Mech 3.0 was employed [24]. To quantify the radiation effects, five radiation models, i.e.

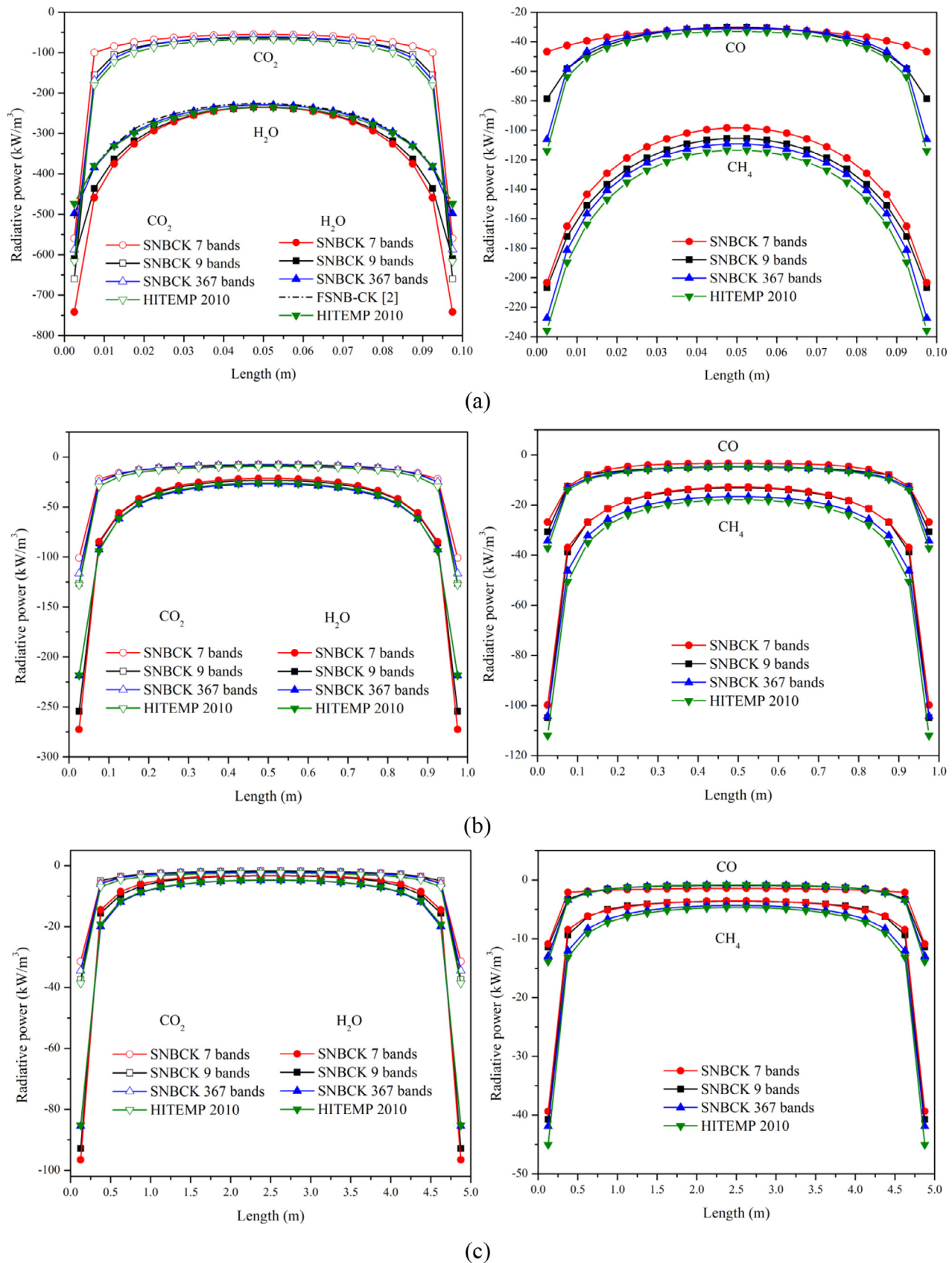


Fig. 1. Distributions of radiative power from a 1-D layer in a parallel-plane space at 1000 K, filled with H_2O , CO_2 , CO and CH_4 for (a) $L = 0.1$ m, (b) $L = 1$ m and (c) $L = 5$ m.

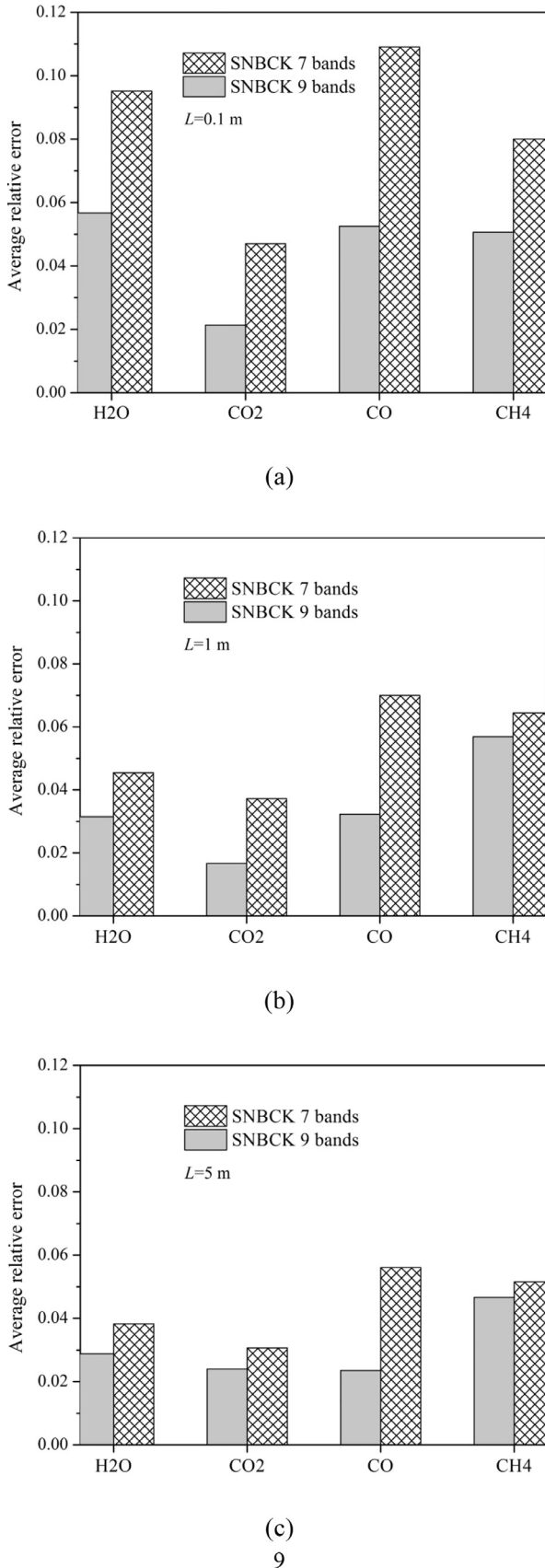


Fig. 2. Average relative error of radiative power for H₂O, CO₂, CO and CH₄ of the SNBCK 9 bands and 7 bands models at (a) $L = 0.1$ m, (b) $L = 1$ m and (c) $L = 5$ m.

ADI (adiabatic), OTM (optically thin model), SNBCK 367 bands, SNBCK 9 bands and SNBCK 7 bands, were applied in the simulations and compared. To assess the effects of different spectral band numbers on the radiation reabsorption, different amounts of CO₂, which is a strong absorber, were added in the unburned gas and partially substituted N₂. Furthermore, Ar dilution was used together with CO₂ dilution in the mixture to maintain the same mixture specific heat capacity. Consequently, the thermal effect of adding CO₂ is balanced with the Ar dilution and the pure effect of radiative heat loss is separated out.

The burning fluxes with different CO₂ percentages calculated by the five different radiation models for CH₄/O₂/N₂/Ar/CO₂ flames ($\phi = 1.0$) are shown in Fig. 3(a), demonstrating their different capabilities. First, the burning flux decreases with increasing CO₂ content due to the reduction of the flame temperature (from 2230 to 2150 K). Second, the burning fluxes of all the SNBCK models are higher than those of the ADI/OTM models. This is due to their inclusion of radiation reabsorption by the upstream unburned mixture as radiation reabsorption is only caused by CH₄ in the absence of CO₂. Third, the differences in the burning flux of the SNBCK 9 bands and the SNBCK 367 bands decrease progressively with increasing amount of CO₂. This is due to two reasons: first, the relative error of the radiative power calculated by the SNBCK 9 bands for CH₄ is larger than that for CO₂ (see Fig. 2); second, CO₂ has stronger absorption than CH₄ and hence the radiation reabsorption effect is dominated by the increased amount of CO₂ in the gas mixture. Specifically, with 3% CO₂, the relative increments of the burning flux calculated by the SNBCK 367 bands and 9 bands are 8.06% and 6.97%, respectively. However, when CO₂ addition is increased to 20%, the relative increments of the burning flux computed by the two SNBCK models are 18.6% and 18.3%, respectively. This indicates that the accuracy of the burning flux prediction becomes similar with increasing CO₂ percentage for the two models. As for the computational efficiency, the CPU times for solving RTE are: 1254.79 s for 367 bands and 109.88 s for 9 bands. Consequently, considering both the computational accuracy and efficiency, the SNBCK 9 bands model shows better performance than the 367 bands model. We have also calculated the burning fluxes by the full-spectrum correlated-k-distribution (FSCK) method [25] based on HITEMP 2010. As shown in Fig. 3(a), the FSCK-HITEMP predictions are in very good agreement with the SNBCK 367 bands predictions.

Figure 3(b) shows effects of different SNBCK models on the burning flux caused by the inclusion of radiation reabsorption of all species. Reabsorption can be assessed by comparing the system dimension to the Planck mean absorption length (L_p) of the burnt gas, defined as $L_p^{-1} = \int_0^\infty k(u)G(u)du$, and the optical thickness can be calculated by $\tau = L/L_p$ [7]. It is seen that the effect of radiation reabsorption becomes more important for CH₄/O₂/N₂/Ar/CO₂ mixtures with increased amount of CO₂, and is caused by the following two opposing trends. On one hand, this is due to the increased absorption coefficient with more CO₂, and thus more radiation reabsorption from upstream. On the other hand, the thermal radiation energy emitted by the products is blocked by the optical thickness τ of the burnt gas mixture, for which the maximum τ is only 0.053 in this case.

To understand the detailed structure of the radiation-affected flame, Fig. 4 shows how radiation reabsorption affects the burning flux, temperature and radiative heat loss distribution, calculated by ADI, OTM, SNBCK 367 bands, SNBCK 9 bands and SNBCK 7 bands, with 10% CO₂. With the reabsorption as demonstrated by using the SNBCK models, radiative heat loss is negative in the unburned region because radiation emitted from the high temperature downstream region is partially reabsorbed by the lower temperature gas. This leads to preheating the unburned mixture, such that the maximum temperature in the reaction zone ex-

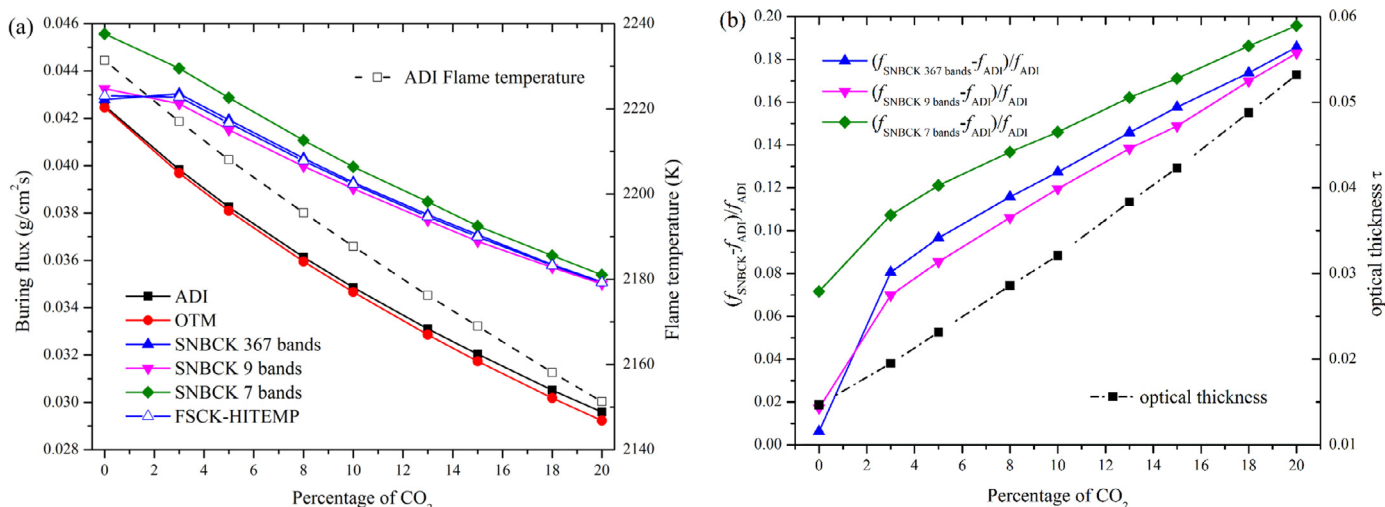


Fig. 3. (a) Burning flux as a function of CO₂ percentage calculated by different radiation models for a planar CH₄/O₂/N₂/Ar/CO₂ flames ($\phi=1.0$); (b) Radiation reabsorption effects on the burning flux calculated by different SNBCK models and optical thickness as a function of CO₂ percentage.

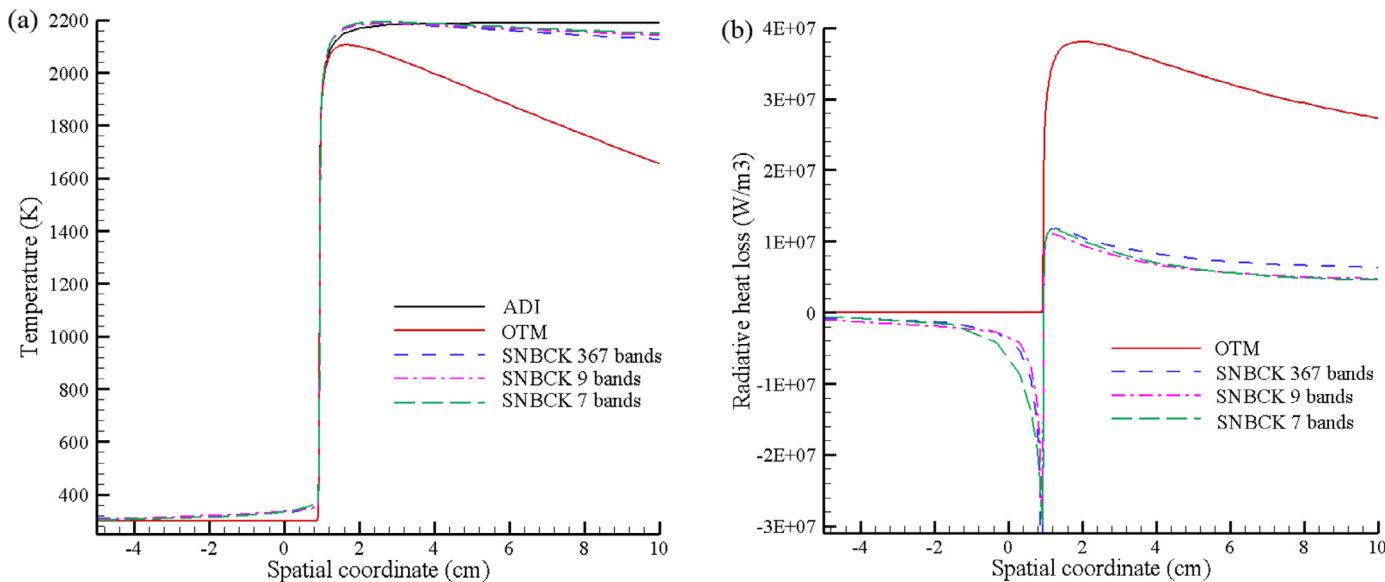


Fig. 4. Distributions of (a) temperature and (b) radiative heat loss in planar CH₄/O₂/N₂/Ar/CO₂ ($\phi=1.0$, CO₂/(O₂+N₂+Ar+CO₂)=10%) flames.

ceeds the adiabatic flame temperature. This effect would further enhance the temperature-sensitive chain branching reactions such as $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ in the reaction zone. In addition, preheating in the diffusion zone would facilitate the chain initiation reactions such as the H-abstraction reaction for methane, which also has a high activation energy due to the strong C–H bond in methane. Such radiation emission-reabsorption effect provides an additional mechanism for heat re-distribution in the flame to heat conduction from the major downstream heat release $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ reaction.

4. Effects of pressure

We next examine the effects of pressure variation on the radiation reabsorption for the burning flux of CH₄/air flames. Fig. 5(a) shows the burning flux at pressures up to 25 atm calculated by different radiation models (ADI, OTM, SNBCK 367 bands, SNBCK 9 bands and SNBCK 7 bands) for CH₄/air flames ($\phi=1.0$). Here we recognize that while the burning flux is expected to increase with pressure even without radiation heat transfer according to $f^0 \sim P^{n/2}$

[26], where n is the global reaction order, it could further increase due to upstream reabsorption and hence increase in the upstream temperature. Figure 5(b) shows the effects of different SNBCK models on the predicted burning flux and optical thickness as a function of pressure. It is found that the effects of radiation reabsorption first increase slowly with increasing pressure, but then decrease beyond 23 atm. This non-monotonic behavior is due to the fact that although the absorption coefficient of CH₄ increases with increasing pressure according to Eq. (4), the optical thickness however would increase from 0.016 to 0.35, which is six times larger than that in Fig. 3(b). At sufficiently high pressures, the optical thickness of the burnt mixture is so large that much of the thermal radiation energy is blocked and cannot reach the upstream unburned mixture. Consequently, the effect of radiation reabsorption is the result of the competition between these two effects.

The CPU times for solving RTE of CH₄/air ($\phi=1.0$) flames are: 1655.26 s for SNBCK 367 bands and 156.34 s for SNBCK 9 bands. For $P = 25$ atm, the relative increments of f are 4.53% (367 bands) and 5.26% (9 bands). This indicates that as a compromise for the much lower computational cost (10 times faster than the SNBCK

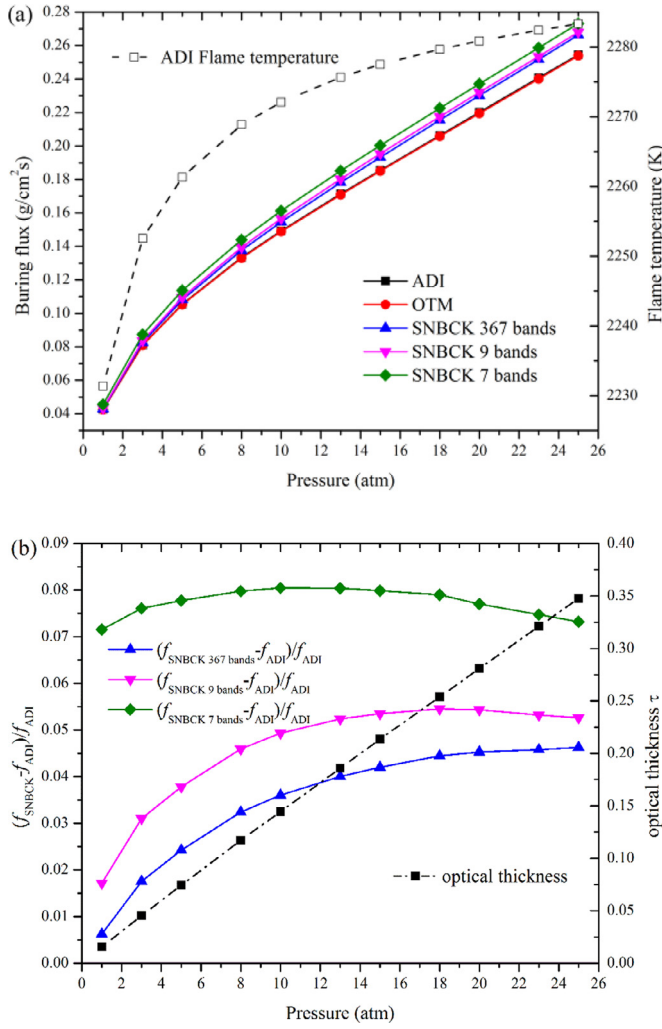


Fig. 5. (a) Burning flux of planar CH_4/air flames ($\phi=1.0$) as a function of pressure calculated by the different radiation models; (b) Radiation reabsorption effects on the burning flux calculated by different SNBCK models and optical thickness as a function of pressure.

367 bands), SNBCK 9 bands incurs a reduction in accuracy by only 16.1% as compared to SNBCK 367 bands. Consequently, the SNBCK 9 bands can be considered to be quite satisfactory in predicting the planar CH_4/air flames at elevated pressures.

In diesel engines, at excessive exhaust gas recirculation (EGR) conditions, radiation reabsorption of CO_2 reduces the radiation heat loss and even increases the flame speed through increasing the temperature of the unburned gas. To investigate this effect, we have added 3% CO_2 in the CH_4/air flames to mimic the EGR intake port in a modern diesel passenger car [27] to study the radiation reabsorption effects in planar $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ flames at elevated pressures.

Figure 6(a) shows the burning fluxes at elevated pressures up to 25 atm calculated by using the different radiation models for $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ flames ($\phi = 1.0$, $\text{CO}_2/(\text{O}_2+\text{N}_2+\text{CO}_2)=3\%$). Compared to the CH_4/air flames, the increase of the burning fluxes in the $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ flames are more obvious when considering radiation reabsorption since the radiative property of CO_2 is stronger than that of CH_4 . Figure 6(b) shows that the maximum radiation reabsorption effect calculated by the SNBCK 367 bands is 12.6% for the $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ flame while it is only 4.63% for the corresponding CH_4/air flame. Moreover, the effect of radiation reabsorption decreases at pressures above 13 atm, which is earlier than that in

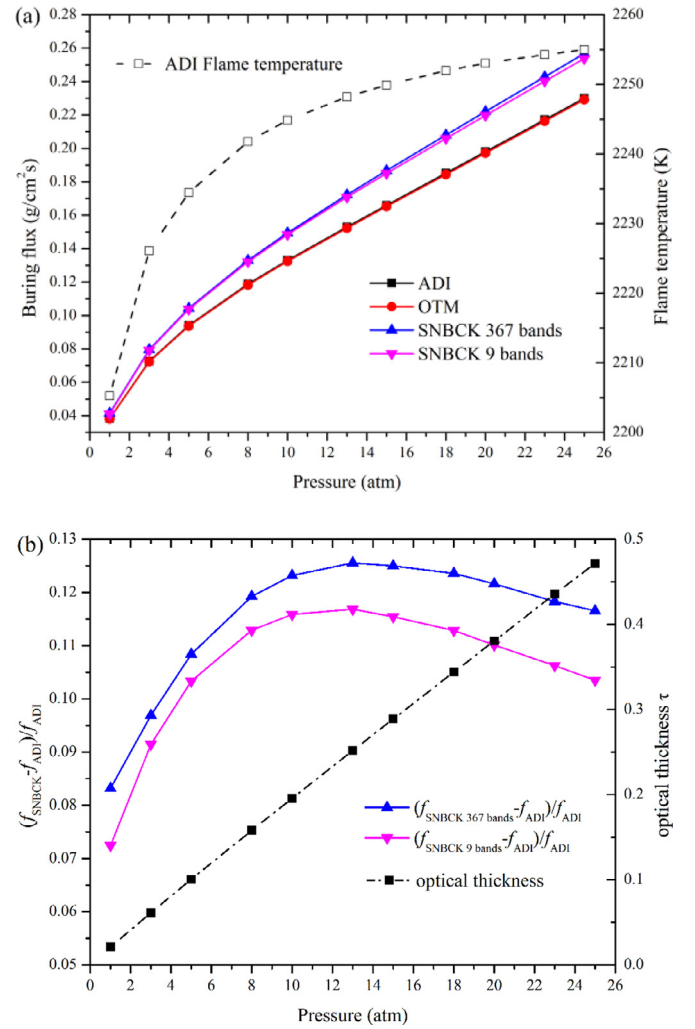


Fig. 6. (a) Burning flux $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ flames ($\phi = 1.0$, $\text{CO}_2/(\text{O}_2+\text{N}_2+\text{CO}_2) = 3\%$) as a function of pressure calculated by the different radiation models; (b) Radiation reabsorption effects on the burning flux calculated by different SNBCK models and optical thickness as a function of pressure.

the CH_4/air flame. The maximum τ is 0.47 larger than that of the CH_4/air flames. These results therefore demonstrate that the optical thickness becomes thicker with the addition of the stronger radiative species CO_2 , hence leading to stronger blockage for radiation emission from the burnt gas.

The predicted average radiation reabsorption effects are 11.47% and 10.85% for the SNBCK 367 and 9 bands, respectively, with their corresponding CPU times of solving RTE being 1303.38 s and 120.81 s. This again demonstrates that the SNBCK 9 bands model not only maintains adequate accuracy but is also more computational efficient.

To illustrate how radiation reabsorption affects temperature at different pressures, Fig. 7 shows the temperature distributions calculated by SNBCK 367 bands for the $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ flames at $P = 1, 13$ and 25 atm. It is seen that the flame temperature increases with increasing pressure and temperature in the upstream due to radiation reabsorption. However, the increment of temperature in the upstream at $P = 13$ atm is larger than that at $P = 1$ and 25 atm, as shown in the enlarged inset in Fig. 7. This is why the maximum radiation reabsorption effect on the burning flux occurs at $P = 13$ atm for the $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ flames.

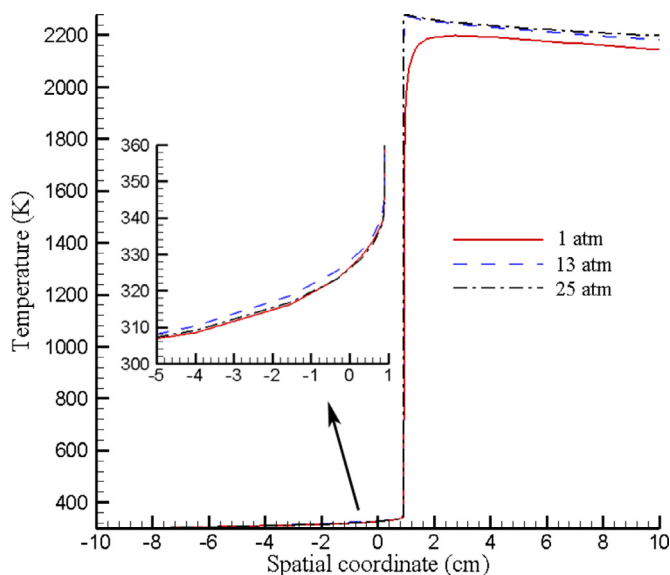


Fig. 7. Distributions of temperature calculated by the SNBCK 367 bands for planar $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$ flames ($\phi = 1.0$, $\text{CO}_2/(\text{O}_2 + \text{N}_2 + \text{CO}_2) = 3\%$) at $P = 1, 13$ and 25 atm.

5. Conclusions

Effects of radiation reabsorption on the burning flux of methane flames at elevated pressures are investigated using SNBCK models. To facilitate the computational efficiency, an SNBCK 9 bands model for H_2O , CO_2 , CO and CH_4 is employed and validated for the computation of planar flames with radiation.

Results demonstrate that radiation reabsorption increases the burning flux, which is further increased with CO_2 addition. As such, radiation reabsorption should be included in the quantitative analyses of flame structure and temperature, burning intensity and propagation rate, and other associated reaction and flame propagation quantities. Due to the competition between the absorption coefficient and optical thickness, the radiation reabsorption effect first increases and then decreases with increasing pressure. The addition of stronger radiative species such as CO_2 enhances blockage of the burnt mixture radiation emission effect at higher pressures. The 9 bands lumping appears to be an optimum number in terms of accuracy and computation cost, at least for the present problem studied. The potential of extending the concept of lumping, from the present procedure based on uniform lumping to one that depends on the structure of the radiation spectrum, merits further study.

Comparing results of the OTM without those allowing for reabsorption, Fig. 4 shows substantial downstream temperature reduction and hence heat loss without reabsorption. While effects of upstream reabsorption has been found to dominate over those of downstream reabsorption in the present study, there are two situations for which downstream heat loss and reabsorption are expected to be important and require further study. The first is for near-limit situations of radiation-induced extinction and flammability limit, for which simplified analysis [28] has shown that effects of upstream and downstream heat loss have equal influence on the extinction boundary; the latter through the increase in the (negative) temperature gradient in the downstream region next to the reaction zone and consequently the temperature in the reaction zone. The second is the effect of the temperature and hence density change in the downstream region due to the combined effects of radiation emission and reabsorption. This effect has been shown to substantially reduce the flame propagation rate for spherical flame propagation with closed flame surface

[1], although the separate effects due to emission and reabsorption needs to be clearly identified.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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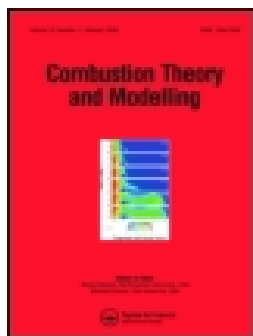
Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2020.07.042.

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Theory of supercritical flames with real-fluid equations of state[†]

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We report a theoretical analysis of the propagation and structure of the planar adiabatic/radiative flame in supercritical fluids, employing the Van der Waals and the Redlich-Kwong equations of state to describe the fluid properties. It is demonstrated that the effective molecular volume and attractive force terms in these non-ideal equations of state show opposite effects on the density modification, especially in the upstream unburned region. Furthermore, the non-ideal effect is found to strongly couple with radiative emission and reabsorption, whose respective weakening and strengthening effect can substantially affect the state of radiation-induced quenching. The theory is useful for the description of high-pressure flames as both the non-ideal state and radiation become more pronounced under such conditions.

Keywords: supercritical fluids; equation of state; flame theory

1. Introduction

Recognising that higher efficiency and lower emissions of certain pollutants can be achieved at elevated pressures, and that internal combustion engines [1], including gas turbines and rocket engines [2], all operate at elevated pressures, it is of both fundamental and practical interest to investigate the flame response under such conditions. Specifically, an important aspect of high-pressure flame dynamics is the existence of the supercritical state [3], in that when the (local) state of the mixture is near/beyond its critical pressure and temperature, substantial real-fluid effects, which are fundamentally different from the conventional ideal gas or liquid properties, will emerge. For example, phase transition between liquid and gas disappears, with the continuous transition occurring in the phase diagram. Near the critical points, small changes in pressure and temperature could result in large variations in density and other properties.

In terms of recent investigations on supercritical combustion, Yang [3] extensively reviewed studies on droplet vaporisation and burning at the supercritical state. Ribert et al. [4] and Huo et al. [5] computationally investigated the canonical counterflow hydrogen/oxygen diffusion flames with supercritical fluid properties. Liang et al. [6] analysed the various factors that could affect the structure and propagation of laminar premixed flames at supercritical states, including the equation of state (EoS), thermodynamics, transport properties and chemical kinetics. It was found that the EoS could substantially influence the

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[†] Dedicated to Professor Moshe Matalon on the occasion of his 70th birthday, in celebration of the many beautiful theories that he has advanced in combustion and fluid science.

flame propagation speed through modification of the local density. Moreover, it is important to use the non-ideal thermodynamic formulations as well as the physically correct form of energy equation for the accurate modelling of the laminar flame speed and adiabatic flame temperature.

We next note that experiments at such high-pressure conditions are difficult to conduct, that previous studies were mostly computational, and that theoretical analysis has been limited even though it is reasonable to expect that leading-order responses of such sensitive phenomena could be largely captured through appropriate analysis. Furthermore, theoretical analysis of flames could benefit from such high-pressure conditions in that, when the pressure increases, the flame becomes thinner and thus approaches either the reaction-sheet or even the flame-sheet limit, which can be treated as discontinuities. Indeed, theoretical analyses of various flame configurations and phenomena on the disparate flames scales flourished during the late 1970s to the 1980s [7–13], such as the analysis of Matalon and Matkowsky [7] by modelling the flame structure as a layer of reaction-dominated zone inside another layer of transport-dominated zone; the work of Frankel and Sivashinsky [8,9] on the effects of thermal expansion ratio and Lewis number on the propagation and extinction of stretched expanding spherical flame, and the study of Clavin and co-authors [10–12] on the instability of premixed flames for the roles of hydrodynamics and molecular non-equidiffusion. Furthermore, the role of heat loss such as through radiation has progressively gained attention in flame theory [12,13], with the recent theoretical analyses of Chen [14,15] demonstrating the importance of radiative heat loss on flame propagation and extinction, and a computational study by Zheng et al. [16] showing that radiative emission and reabsorption are essentially coupled through heat exchange and redistribution within the flame, and as such should be considered synergistically.

In view of the valuable contributions of the above studies, it is nevertheless also recognised that most of them adopted either the ideal gas or even the constant density assumption, and that supercritical fluid properties such as the real-fluid EoS have not been adequately considered in the development of flame theories. Consequently, as a beginning step, the current work aims to address the issue of the supercritical state by incorporating the real-fluid EoS into the flame theory. In particular, we shall investigate the effects of real-fluid EoS in two canonical planar laminar premixed flames, namely the reference, backbone, adiabatic flame and the nonadiabatic, radiative flame. The former defines one of the most important parameters in laminar flame propagation, namely the laminar flame speed [17]; while the latter addresses the issue of non-adiabaticity with the attendant flammability limits [17] of the combustible mixture. Two extensively studied real-fluid EoS will be adopted and compared with the ideal gas EoS, for the adiabatic and radiative flames, identifying the corresponding real-fluid effects.

2. Equations of state

Since the current work aims to investigate the effects of non-ideal EoS, the ideal gas EoS will be used as the reference to quantify the extent of real-fluid effect in the flame structure and propagation. The ideal gas EoS is given by:

$$PV_m = RT \quad (1)$$

where P is the pressure, V_m the molar volume, R the universal gas constant and T the temperature. Consequently, for the ideal gas EoS, the compressibility factor $Z = PV_m/RT$ is unity, while Z can be larger/smaller than unity when non-ideal EoS is considered.

For the non-ideal EoS, perhaps the most extensively considered is the Van der Waals EoS, which accounts for effects of molecular volume and attraction, and is expressed as:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (2)$$

where the constant a is the attraction parameter and b the repulsion parameter or the effective molecular volume. Subsequently, an improved relation which accounts for the temperature dependence of the attraction term was proposed, as the Redlich-Kwong EoS [18]:

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m + b)} \quad (3)$$

The critical point of either EoS is defined by the condition $(\partial P/\partial V_m)_T = 0$ and $(\partial^2 P/\partial V_m^2)_T = 0$. The RK EoS has been widely used in studying the supercritical combustion problems, recognising nevertheless latter modifications of it [19] showed adequate performances.

Then, the two parameters in the EoS can be expressed by the critical temperature T_c and critical pressure P_c as

$$a = \frac{27(RT_c)^2}{64P_c} \quad b = \frac{RT_c}{8P_c} \quad (4)$$

for the Van der Waals EoS, and

$$a \approx 0.42748 \frac{R^2 T_c^{5/2}}{P_c} \quad b \approx 0.08664 \frac{RT_c}{P_c} \quad (5)$$

for the Redlich-Kwong EoS. Based on Equations (4) and (5), two dimensionless reference parameters A and B can be defined as $A = aP_{ref}/(RT_{ref})^2$, $B = bP_{ref}/(RT_{ref})$ for the Van der Waals EoS and $A = aP_{ref}/(R^2 T_{ref}^{5/2})$, $B = bP_{ref}/(RT_{ref})$ for the Redlich-Kwong EoS, respectively, where T_{ref} and P_{ref} are the reference temperature and pressure, respectively. The constant A and B have been used in the following analysis for simplicity. Based on these definitions of A and B , taking the Van der Waals EoS as example, we can see that the ratio satisfied the relation $B/A \propto T_{ref}$. Hence, large B and small A corresponds to high-temperature conditions, and the opposite corresponds to low-temperature conditions. It is also noted that in this work we focus on the non-ideal EoS effect, which contributes greatly to the overall prediction of the laminar flame speed as demonstrated previously in computations [6]. Hence, the non-ideality of other properties such as the transport properties are not considered.

For simplicity in the following discussions, the ideal gas EoS, Van der Waals EoS and Redlich-Kwong EoS will be designated as I-EoS, V-EoS and RK-EoS, respectively. Furthermore, for better assessment of these non-ideal EoS with real combustion situations, the critical and reference temperatures and pressures for some major combustion species based on the two non-ideal EoS are listed in Table 1. The two reference parameters are fixed as $A = 0.1$ and $B = 0.1$, which are also the values mostly used in the following analyses. We selected the values of these two parameters based on order-of-magnitude evaluation

Table 1. Critical and reference temperatures and pressures for some representative species with the reference parameters $A = 0.1$ and $B = 0.1$.

Species	Critical point		V-EoS		RK-EoS	
	T_c/K	P_c/atm	T_{ref}/K	P_{ref}/atm	T_{ref}/K	P_{ref}/atm
Oxygen	154.6	49.8	521.8	168.1	448.1	144.3
Nitrogen	126.2	33.5	425.9	113.1	365.7	97.1
Hydrogen	33.2	12.8	112.0	43.2	96.2	37.1
Methane	190.8	45.8	643.9	154.6	553.0	123.7
Ammonia	405.5	111.3	1368.6	375.6	1175.2	322.6

of the real supercritical combustion applications for which the pressure is normally above 100 atm.

These values provide some sense as at which temperature and pressure conditions the non-ideal EoS for the major combustion species need to be considered. Specifically, for the main components of air, oxygen and nitrogen, substantial non-ideal EoS effects can be expected at temperatures slightly above room temperature and pressures around 100-150 atm. Since air is mostly used as the oxidiser, the amount of air is much larger than that of the fuel. Then, the critical and characteristic temperatures and pressures are determined by the air properties. Hence, it is expected that the non-ideal EoS is essential for these listed conditions for oxygen and nitrogen. The properties of three fuels (hydrogen, methane and ammonia) are also listed in Table 1. For hydrogen, the required pressure is comparatively low (below 50 atm), while the temperature requires the cryogenic condition around 100 K. For methane, the condition is close to those of oxygen and nitrogen. However, for ammonia to exhibit substantial non-ideal EoS effects, the temperature has to reach more than 1000 K, which is typical in the preheat zone of a flame, and the pressure needs to approach more than 300 atm. Furthermore, it is also noted that the values from V-EoS are close to those from RK-EoS, hence demonstrating consistency of the two non-ideal EoS.

3. Theoretical analysis

We shall now incorporate these EoS into the theoretical analysis of the one-dimensional adiabatic and radiative planar flames.

For the planar flame, we assume zero-Mach-number flow, one-dimensional propagation, and one-step Arrhenius reaction. Thus, the dimensionless form of the governing equations [17] of continuity, species and energy equations can be expressed as:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} = 0 \quad (6)$$

$$\rho \frac{\partial Y}{\partial t} + \rho u \frac{\partial Y}{\partial x} = \frac{1}{Le} \frac{\partial^2 Y}{\partial x^2} - w \quad (7)$$

$$\rho \frac{\partial T}{\partial t} + \rho u \frac{\partial T}{\partial x} = \frac{\partial^2 T}{\partial x^2} - H + w \quad (8)$$

where ρ, Y, T are the (dimensionless) density, reactant mass fraction, and temperature scaled by the unburned density, unburned reactant mass fraction, and temperature change from the unburned temperature to the adiabatic temperature. Furthermore, the parameters

A and B will be used for the non-ideal EoS. u, x, t are non-dimensionalized by the laminar flame speed S_L , flame thickness δ , and characteristic time scale δ/S_L . Le is the Lewis number and H, w are the dimensionless heat loss term and reaction term, respectively. Following previous theories [8,15], the reaction front, which we shall call the flame front according to convention, is assumed as a discontinuity with velocity S_f , for which the flame structure satisfies the quasi-steady state assumption. By using the coordinate $\eta = x - x_f$, where x_f is the flame location, the governing equations is transformed as:

$$\frac{df}{d\eta} = 0 \quad (9)$$

$$-f \frac{dY}{d\eta} = \frac{1}{Le} \frac{d^2 Y}{d\eta^2} - w \quad (10)$$

$$-f \frac{dT}{d\eta} = \frac{d^2 T}{d\eta^2} - H + w \quad (11)$$

where $f = \rho(S_f - u)$ is the constant burning flux defined by the boundary conditions. By using this transformed coordinate, it is seen that the burning flux is a *conserved quantity* embedding the density variation within it, implying that the non-ideal EoS is implicitly incorporated in the analysis and does not need to be separately specified. With the reaction term assuming a delta function at the flame (that is the reaction zone) surface [17], it has the form

$$w = \left(\frac{T_f}{T_{ad}} \right)^{n+1} \exp \left(\frac{\beta}{2} \left(1 - \frac{T_{ad}}{T_f} \right) \right) \delta(\eta),$$

where n is the reaction order, T_{ad} and T_f are the dimensionless adiabatic flame temperature and flame temperature, respectively, and $\beta = T_a/T_{ad} \gg 1$, for which T_a is the dimensionless activation energy. The assumptions underlying the current theoretical analysis is the constant properties including the flame properties such as Lewis number and the non-ideal EoS properties such as the parameters A and B . These assumptions have been widely used and validated in previous theoretical analysis [7–13] showing good predictability for the flame speeds as well as the flame structures. It is noted that some efforts were made to incorporate property variations, the modifications only led to quantitative changes and did not qualitatively affect the results.

3.1. Planar adiabatic flames

For the adiabatic case in the doubly infinite domain, the heat loss term $H = 0$, and the boundary conditions are

$$\eta \rightarrow -\infty : T = T_{ad} = T_u + 1, Y = 0, u = 0 \quad (12)$$

$$\eta \rightarrow +\infty : T = T_u, Y = 1, \frac{du}{d\eta} = 0 \quad (13)$$

Thus, Equations (9–11) can be readily solved, for which the key steps are shown in the Appendix. This yields the solution:

$$T = T_{ad} = T_u + 1, Y = 0,$$

$$\rho = \frac{Z_u T_u}{Z_{ad} T_{ad}}, u = 0 \quad \text{for } \eta < 0 \quad (14)$$

$$T = T_u + \exp(-\eta), Y = 1 - \exp(-Le\eta),$$

$$\rho = \frac{Z_u T_u}{ZT}, u = \frac{Z_{ad} T_{ad} - ZT}{Z_u T_u} \quad \text{for } \eta > 0 \quad (15)$$

Here, Z is the compressibility obtained from the different EoS and the burning flux $f = 1$. Based on this solution, we obtain the flame structure profiles shown below, with Le and T_u set as 1 and 0.2, respectively.

The temperature, mass fraction, compressibility, density and velocity profiles from different EoS are shown in Figure 1. For this solution, the two parameters in the non-ideal EoS have been set as $A = 0.1$ and $B = 0.1$. It is seen from Figure 1(a) that temperature reaches the adiabatic value at the downstream burned regime and the reactants are totally consumed. Figure 1(b) shows that by definition the compressibility, Z , is always unity for the I-EoS. However, for both the V-EoS and RK-EoS, Z on the unburned side is mostly less than unity. Then, it crosses the unity at a location slightly in front of the reaction surface and becomes larger than unity on the burned side. Furthermore, Z deviates more from unity for the RK-EoS than the V-EoS, which is due to the fact that the RK-EoS considers the temperature dependence of the attraction force term. Such behaviour of the compressibility further leads to crossing of the density profiles from the V-EoS and RK-EoS as compared with that from I-EoS, as demonstrated in Figure 1(c). It indicates that the non-ideal EoS enhances the density gradient in the preheat zone and hence results in a larger compression ratio, which is different from the temperature ratio across the flame. Because of this augmented density variation, stronger thermal-expansion induced flow is observed in Figure 1(d). Also, although both the V-EoS and RK-EoS show substantial differences from the I-EoS, deviation between the two non-ideal EoS is not large. Nevertheless, the RK-EoS shows greater influence on the compressibility and induced flow compared with the V-EoS. Since the RK-EoS normally has better performance in predicting experimental values [18,19], this result indicates that the supercritical effect could be more accurately captured by the RK-EoS. Such findings suggest that when the system condition is close to the critical point, non-ideal EoS has to be applied in order to accurately capture the density and velocity variations in the preheat zone.

Next, we examine effects of the parameters A and B in the non-ideal EoS. First, Figure 2 demonstrates the case with $A = 0.01$ and $B = 0.1$, for which the parameter B dominates, corresponding to high-pressure and high-temperature situations. As observed in Figure 2(a), the compressibility for this case is always larger than unity for the two non-ideal EoS, with its effect pronounced in the low-temperature region. Physically, since B represents the effective volume occupancy by the molecules, such an effect increases the molar volume compared with the ideal gas case, and hence leads to $Z > 1$. It is more noticeable at the upstream unburned region, where the temperature is lower and the molecules are more aggregated. This compressibility behaviour leads to the trend opposite to the previous case, namely the density gradients from the non-ideal EoS are smaller than those of the I-EoS (see Figure 2(b)), and the reduced expansion ratio results in decreased flow induced by thermal expansion compared to the ideal case (see Figure 2(c)). Furthermore, results from V-EoS and RK-EoS are very close to each other. This is reasonable as when A is reduced to zero, the two non-ideal EoS degenerate to the same form.

We next study the case of $A = 0.1$ and $B = 0.05$ in Figure 3. Contrary to the previous case, this is the condition in which A dominates, corresponding to high-pressure and

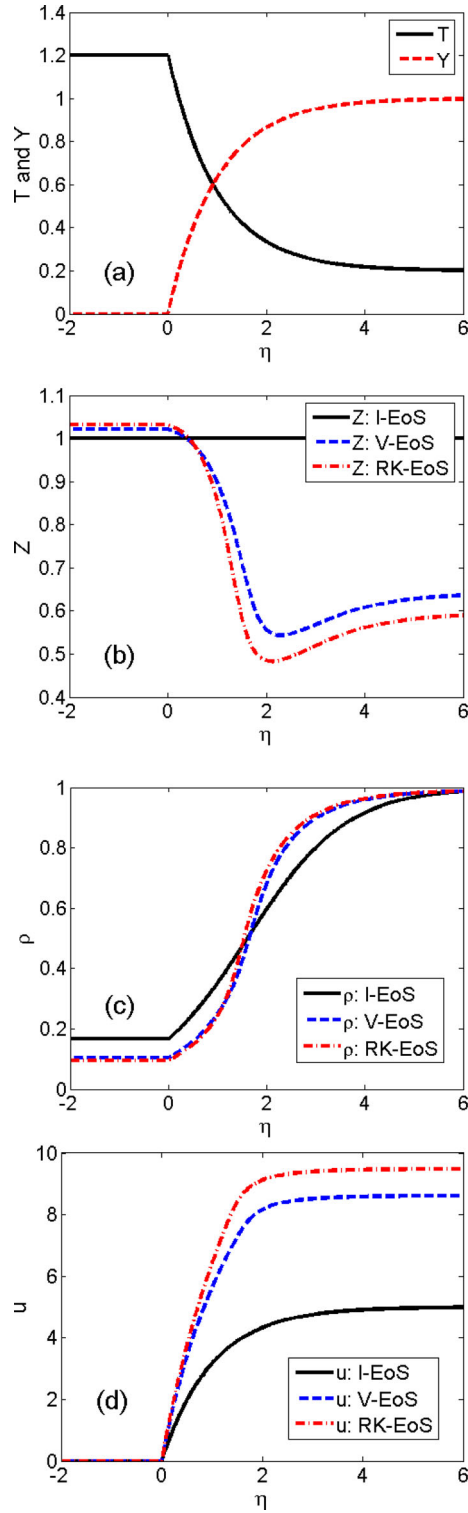


Figure 1. Theoretical solution for (a) temperature and mass fraction, (b) compressibility, (c) density and (d) velocity for different EoS with $A = 0.1$ and $B = 0.1$.

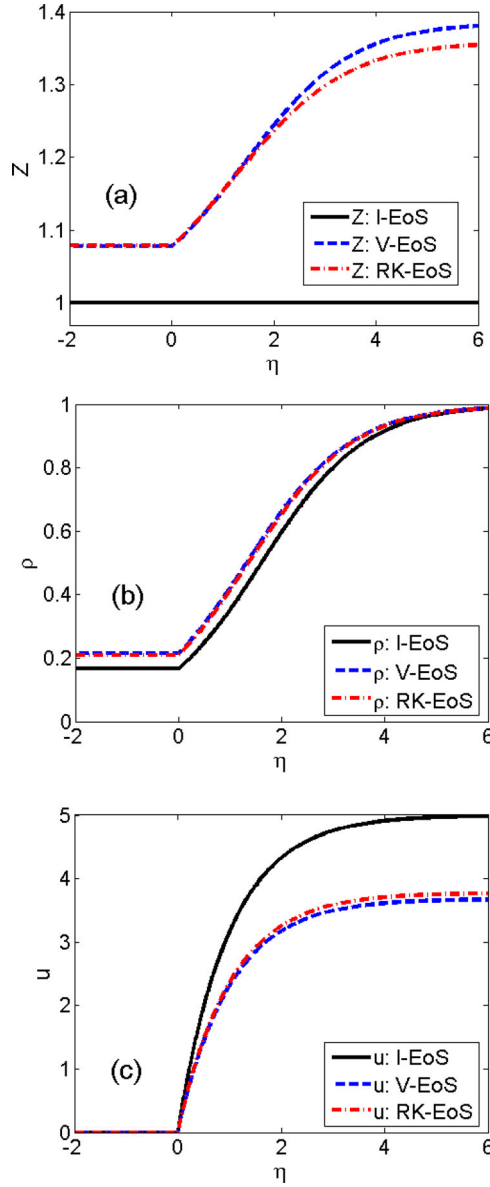


Figure 2. Theoretical solution for (a) compressibility, (b) density and (c) velocity for different EoS with $A = 0.01$ and $B = 0.1$.

low-temperature situations. Figure 3(a) shows that Z is always less than unity when the non-ideal EoS is used, which is opposite to the results in the previous case where Z is always larger than unity. This is due to the competing effects of A and B , in that the former reduces compressibility through the attraction force between molecules, while the latter increases compressibility through the molecular volume. Also, in this case Z exhibits a strong gradient similar to a discontinuity in front of the reaction sheet around $\eta = 1$.

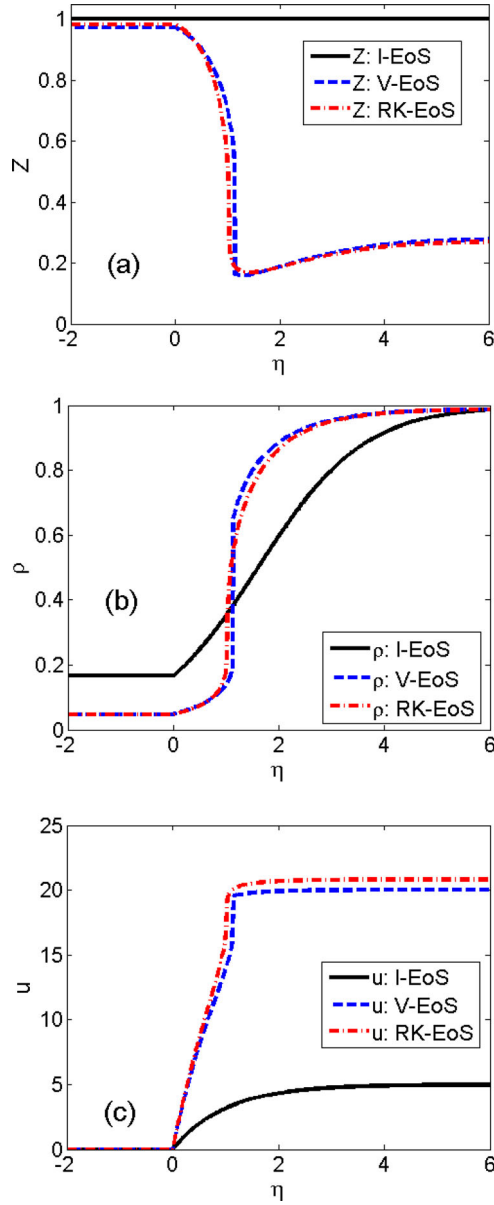


Figure 3. Theoretical solution for (a) compressibility, (b) density and (c) velocity for different EoS with $A = 0.1$ and $B = 0.05$.

This behaviour then induces the large density gradient of phase change or phase-change-like phenomena as shown in Figure 3(b). Such steep gradient has also been reported in a previous computational study for cryogenic conditions [4], and could impose difficulties in numerical solutions. Then, due to the strong density gradient, the thermal-expansion induced velocity is also much larger for the non-ideal case compared to the ideal case, as demonstrated in Figure 3(c).

The current findings in the planar adiabatic flame show that the non-ideal EoS could substantially modify the density and hence the velocity profiles of the flame. However, for the planar adiabatic flame, since the total enthalpy is conserved, the temperature will always reach the adiabatic flame temperature and the eigenvalue of propagation, namely the burning flux, is also conserved with $f = 1$. The flame velocity itself, of course, can be strongly modified by the non-ideal EoS depending on whether the compressibility is larger/smaller than unity.

3.2. Planar radiative flames

Next, we study the situation when heat exchange through radiation is taken into account. Since radiation is a long-range heat transfer mechanism, it is sensitive to the domain size. Recognising that practical situations involve only confined spaces with finite domain sizes, we shall analyse the flame in a finite domain with downstream radiative emission and upstream radiative reabsorption. Hence, for the linearised radiation heat transfer term, the downstream burned heat emission term is $H = h_b(T - T_u)$, for $\eta < 0$; and the upstream unburned heat reabsorption term is $H = -h_u(T - T_u)$, for $\eta > 0$, where h_b and h_u are the downstream radiation loss coefficient and upstream radiation reabsorption coefficient, respectively. The boundary conditions are specified as

$$\eta = -x_f : \frac{dT}{d\eta} = 0, \frac{dY}{d\eta} = 0, u = 0 \quad (16)$$

$$\eta = L - x_f : T = T_u, Y = 1 \quad (17)$$

Then, Equations (9–11) can be solved, for which the key steps are demonstrated in the Appendix, yielding the explicit solution:

$$T = T_u + (T_f - T_u) \frac{\lambda_{b2} \exp(\lambda_{b1}\eta) - \lambda_{b1} \Delta_b \exp(\lambda_{b2}\eta)}{\lambda_{b2} - \lambda_{b1} \Delta_b}, Y = 0, \quad (18)$$

$$\rho = \frac{Z_u T_u}{ZT}, u = \frac{Z_b T_b - ZT}{Z_u T_u} f \quad \text{for } \eta < 0$$

$$T = T_u + (T_f - T_u) \frac{\exp(\lambda_{u2}\eta) - \Delta_u \exp(\lambda_{u1}\eta)}{1 - \Delta_u}, Y = 1 - \exp(-Lef\eta), \quad (19)$$

$$\rho = \frac{Z_u T_u}{ZT}, u = \frac{Z_b T_b - ZT}{Z_u T_u} f \quad \text{for } \eta > 0$$

where $\lambda_{b1,2} = \left(-f \pm \sqrt{f^2 + 4h_b} \right) / 2$ and $\Delta_b = \exp[(\lambda_{b2} - \lambda_{b1})x_f]$ for the burned side; and $\lambda_{u1,2} = \left(-f \pm \sqrt{f^2 - 4h_u} \right) / 2$ and $\Delta_u = \exp[(\lambda_{u2} - \lambda_{u1})(L - x_f)]$ for the unburned side. Also, Z_b, T_b denote the state at the left burned boundary and Z_u, T_u the state at the right unburned boundary. Then based on the jump condition, the flame temperature and burning flux for this non-adiabatic case can be determined as

$$(T_f - T_u) \left[\frac{\lambda_{b1} \lambda_{b2} (1 - \Delta_b)}{\lambda_{b2} - \lambda_{b1} \Delta_b} - \frac{\lambda_{u2} - \lambda_{u1} \Delta_u}{1 - \Delta_u} \right] = f = \left(\frac{T_f}{T_{ad}} \right)^{n+1} \exp \left(\frac{\beta}{2} \left(1 - \frac{T_{ad}}{T_f} \right) \right) \quad (20)$$

From this formula, the relationship of the flame position x_f , the flame temperature T_f and the burning flux f can be determined. The condition where no solution exists indicates the

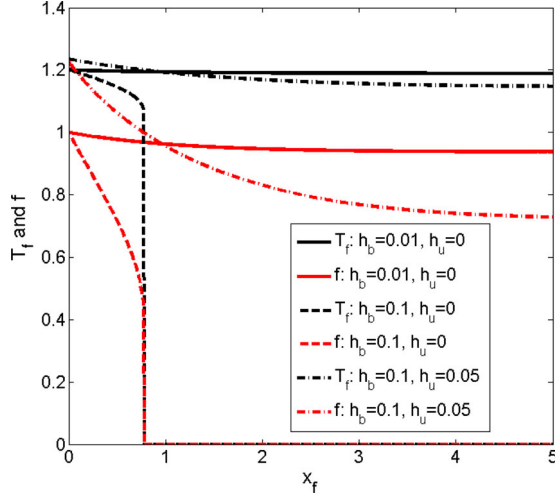


Figure 4. Flame temperature and burning flux change as functions of flame location with different radiation parameters.

extinction state of the flame, due to radiation. Such flame dynamic behaviour with different radiation parameters are plotted in Figure 4. The L, β, Le and T_u are set as 100, 10, 1 and 0.2 respectively. The reaction order is assumed to be unity.

In Figure 4, it is observed that, when the downstream radiative loss is $h_b = 0.01$ and the upstream reabsorption is zero, both the flame temperature and burning flux decrease at the early stage of the flame propagation. The flame then reaches almost steady propagation with the flame temperature and burning flux both lower than their respective adiabatic values (see the solid lines in Figure 4). Then, if the downstream radiative loss is further increased to $h_b = 0.1$, the flame shows the initial stage of decaying propagation and sudden extinction at finite values of the flame temperature and burning flux (see the dashed lines in Figure 4), which is consistent with the classical radiative flame theory [17]. However, for this extinction case with $h_b = 0.1$, if we include the radiation reabsorption term, say by increasing h_u from 0 to 0.05, the extinguishing flame can be rescued from extinction by the upstream preheating effect (see the dash-dotted lines in Figure 4). When both radiative emission and reabsorption are considered, the flame initially propagates at the super-adiabatic condition, and as the burned region becomes larger, it decays to the sub-adiabatic condition. This finding indicates that preheating through reabsorption is an important mechanism when considering extinction of radiative flames.

Since radiation heat exchange also leads to density variation and induces flows, we now examine the temperature, mass fraction, compressibility, density and velocity profiles with different EoS, and investigate the coupling of non-ideal EoS with radiative heat exchange.

Figure 5 shows results of the radiative flame with only radiative emission, without reabsorption, with $h_b = 0.05$, $h_u = 0$. Figure 5(a) shows the temperature and species profiles, which demonstrate that although the species profile is not significantly modified by radiative heat loss, the temperature profile illustrates radiation-induced cooling downstream of the flame. Also, the flame temperature at the reaction front $\eta = 0$ is smaller than the adiabatic value of $T_{ad} = T_u + 1 = 1.2$. Then, for different EoS, the compressibility from ideal and non-ideal conditions are plotted in Figure 5(b). It is seen that compared with the

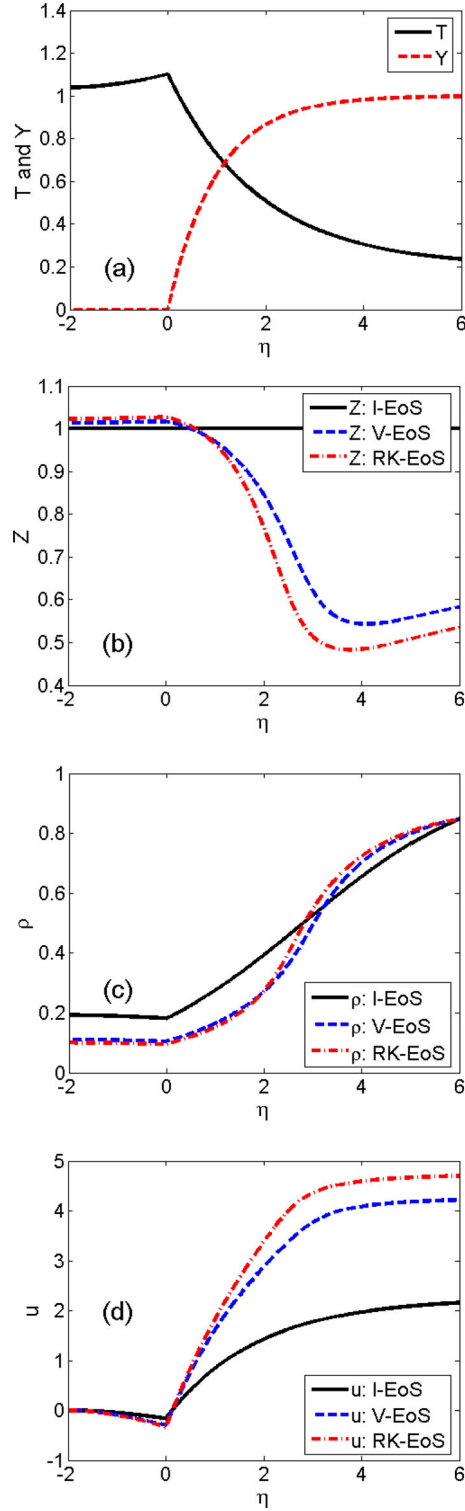


Figure 5. Theoretical solution for (a) temperature and mass fraction, (b) compressibility, (c) density and (d) velocity for different EoS with $h_b = 0.05$, $h_u = 0$, $A = 0.1$ and $B = 0.1$.

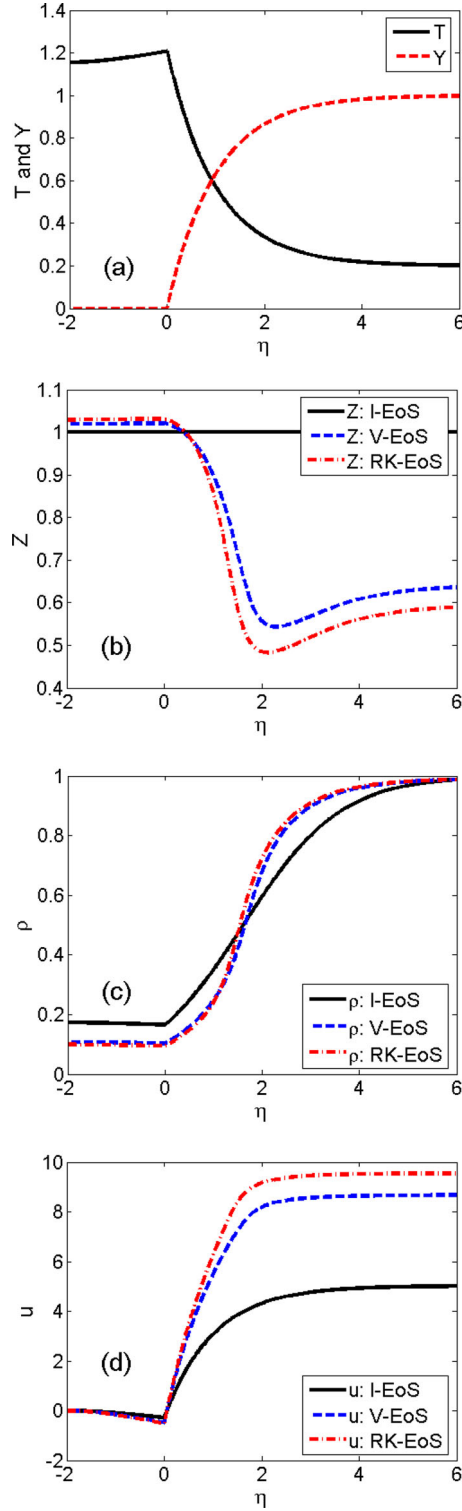


Figure 6. Theoretical solution for (a) temperature and mass fraction, (b) compressibility, (c) density and (d) velocity for different EoS with $h_b = 0.05$, $h_u = 0.05$, $A = 0.1$ and $B = 0.1$.

adiabatic case in Figure 1(b), the compressibility at the upstream unburned region is minimally affected by radiation. However, for the downstream burned region, as the radiative loss brings down the temperature, compressibility is also reduced after reaching the flame front. Since the upstream unburned region is where non-ideal effect is strong and this pre-heat zone is almost not affected by radiative loss, the density modification demonstrated in Figure 5(c) is similar to that observed in Figure 1(c). A difference is that the density crossing between ideal and non-ideal cases occurs further upstream in the radiative case. For the radiation loss, it both leads to decreased flame temperature and the induced flow. The current analysis can quantify both effects. We next further examine the effect of radiation-induced flow. As both the radiative cooling and thermal expansion could induce flow in the radiative situation, the non-ideal EoS affects both types of flows. As demonstrated in the velocity profile of Figure 5(d), the negative radiation cooling induced flow near the flame front is amplified by the non-ideal EoS compared with the ideal case, which is caused by the stronger density variation using non-ideal EoS, though the radiative induced flow is not significantly affected by the selection of non-ideal EoS. However, for the thermal expansion induced flow, the RK-EoS exhibits a stronger effect of thermal expansion as compared with the V-EoS.

Then, in Figure 6, we include radiative reabsorption in the unburned regime, for which the radiative parameters are $h_b = 0.05$ and $h_u = 0.05$. The temperature profile in Figure 6(a) shows that the flame is actually super-adiabatic although the temperature drops after reaching the maximum at the flame front. This indicates that the effect of reabsorption could potentially enhance the burning intensity and accelerate the flame. Then, because of the increased temperature, the compressibility is also increased near the flame front as seen in Figure 6(b). Such an effect further leads to the increased density ratio as seen in Figure 6(c), as well as the increased thermal-expansion induced flow and reduced radiation-induced flow as seen in Figure 6(d). Furthermore, due to the reabsorption pre-heating, the radiation-induced flow is much weaker compared with the previous case and the velocities resulted from radiative cooling based on ideal and non-ideal EoS are similar, indicating that the non-ideal EoS effect is weakened due to the competition between radiative loss and reabsorption.

These findings show that both radiation emission and reabsorption are essential heat exchange process for the flame propagation, which are further coupled with the non-ideal effects. When the system pressure increases, effects of both radiative emission/reabsorption heat exchange and non-ideal EoS are enhanced, implying that these two physical processes have to be simultaneously considered in understanding the flame structure and propagation.

4. Conclusions

In summary, this work has derived the theoretical solutions for planar flames with/without radiation, considering both the ideal and non-ideal EoS. Two non-ideal EoS, namely V-EoS and RK-EoS, are adopted and compared with the ideal gas EoS. In the mass conserved coordinate, the temperature, species, density and velocity profiles can be derived based on the infinitely thin reaction sheet, which is relevant for the high-pressure, supercritical flames, as the flame thickness decreases with increasing pressures.

For the planar adiabatic flame, it is demonstrated that the burning flux and flame temperature are not affected by the non-ideal EoS, while the density and velocity are strongly

affected by it when they are separated out from the burning flux. In the limit of high pressures and high temperatures, the effective molecular volume effect dominates and this leads to larger-than-unity compressibility. The two non-ideal EoS show similar performance in this limit. However, in the limit of high pressure and low temperature, the attractive force dominates and results in very steep density gradient within the preheat zone, leading to strong expansion induced flow. The density and velocity profiles at this limit is sensitive to the selection of the non-ideal EoS. The RK-EoS shows stronger effects in density and velocity variations compared with the V-EoS, as it considers the temperature-dependence of the attraction force.

For the radiative planar flames, both the downstream radiative emission and upstream radiative reabsorption are considered. The radiation effect is coupled with the non-ideal EoS effect. Both the radiation-induced flow and the thermal-expansion induced flow are amplified by the non-ideal EoS, for which the radiative induced flow is not sensitive to the selection of non-ideal EoS, but the thermal expansion induced flow is sensitive to the choice of non-ideal EoS. If only the downstream radiative loss is considered, the non-ideal EoS substantially amplifies the radiation induced flow near the reaction front and further downstream. However, if reabsorption is considered, such effect is weakened due to the competing effects of radiative emission and reabsorption.

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Appendix

For the adiabatic case, external to the reaction zone we can assume the reaction term is zero. Hence the governing equations are:

$$-f \frac{dY}{d\eta} = \frac{1}{Le} \frac{d^2 Y}{d\eta^2} \quad (\text{A1})$$

$$-f \frac{dT}{d\eta} = \frac{d^2 T}{d\eta^2} \quad (\text{A2})$$

For these two linear equations, the general forms of solutions are:

$$Y = C_1 \exp(\lambda_1 \eta) + C_2 \exp(\lambda_2 \eta) \quad (\text{A3})$$

$$T = C_3 \exp(\lambda_3 \eta) + C_4 \exp(\lambda_4 \eta) \quad (\text{A4})$$

Substituting the general forms into the governing equations (A1) and (A2), we can get the eigenvalues of the solution:

$$\lambda_1 = 0 \quad \lambda_2 = -Le f \quad (\text{A5})$$

$$\lambda_3 = 0 \quad \lambda_4 = -f \quad (\text{A6})$$

Then, by using the condition that $f = 1$ and the boundary conditions (12) and (13), we can readily obtain the solutions (14) and (15).

For the non-adiabatic case, external to the reaction zone we again assume the reaction term is zero. Hence the governing equations are:

$$-f \frac{dY}{d\eta} = \frac{1}{Le} \frac{d^2 Y}{d\eta^2} \quad (\text{A7})$$

$$-f \frac{dT}{d\eta} = \frac{d^2 T}{d\eta^2} - H \quad (\text{A8})$$

Here, the radiation term H corresponds to the downstream burned heat emission term $H = h_b(T - T_u)$, for $\eta < 0$ or the upstream unburned heat reabsorption term $H = -h_u(T - T_u)$, for $\eta > 0$. For simplicity of the presentation, here we use the more general form of $H = h(T - T_u)$. For these two linear equations, the general forms of solutions are:

$$Y = C_1 \exp(\lambda_1 \eta) + C_2 \exp(\lambda_2 \eta) \quad (\text{A9})$$

$$T = C_3 \exp(\lambda_3 \eta) + C_4 \exp(\lambda_4 \eta) + T_u \quad (\text{A10})$$

Substituting them into the governing equations (A7) and (A8), we obtain the eigenvalues of the solution:

$$\lambda_1 = 0 \quad \lambda_2 = -Lef \quad (\text{A11})$$

$$\lambda_{3,4} = \left(-f \pm \sqrt{f^2 + 4h} \right) / 2 \quad (\text{A12})$$

Then, by using the boundary conditions (16) and (17), we readily derive the solutions (18) and (19).