

UNIVERSITÉ D'ORLÉANS
ÉCOLE DOCTORALE: Énergie, Matériaux, Sciences de
la Terre et de l'Univers (ED 552)

ICARE-CNRS UPR3021

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Soutenance le : **11 Juin 2025**

pour obtenir le grade de : **Docteur de l'Université d'Orléans**

Discipline/ Spécialité : **Energétique**

**Role of radiative heat transfer in premixed ammonia
flames**

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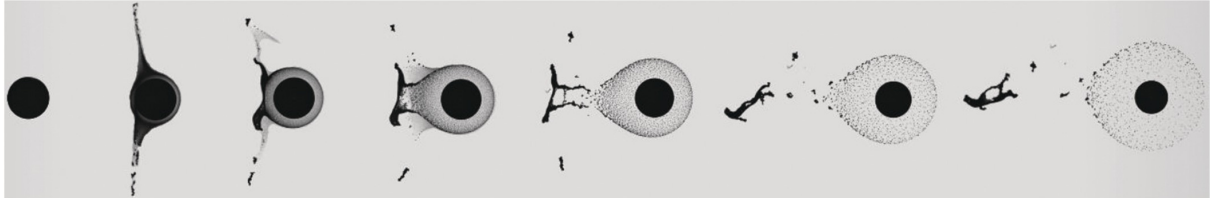
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A droplet's life in a nutshell.

This figure illustrates the formation of soot shell formation in microgravity of n-decane droplet. The droplet is released (first frame), the droplet is ignited (second frame), and the radiative extinction (last frame). (source: [\[1\]](#))

Acknowledgements

तत् त्वम् असि

This thesis would not have been possible without the support of both technical and bureaucratic nature by "GL, JLC & SZ." The professors' amazing mentoring made it possible to begin and proceed with this PhD. All three have been an enigma (whilst breaking the fundamental law of energy) to me as to how a person can be so cool and radiate energy and warmth simultaneously. Most importantly, I am deeply grateful for the perfect balance you have provided between academic freedom and guidance, allowing me to explore my "research interests" of that week. Most importantly, I would like to thank Guillaume and Jean-Louis from the bottom of my heart for converting me into a true believer in generating "neat figures" to convey the message and not the abomination that I used to create previously, and for providing all the necessary resources I need on an immediate basis. I would like to thank Stéphane for his on-the-hand approach to my progress and his Pulse meeting as a platform for me to ramble. It is because of you guys I can at least claim that I am a critical thinker (they tried their best to inculcate it, so let's not litigate the claim on my ability, at least for now). I sincerely thank Prof. Fabien Halter, Prof. Christian Chauveau (I am still a fan of the ILASS-2008 paper), and Prof. Guillaume Dayma for their expertise, from IT infrastructure to combustion rigs, and, importantly, for helping me to extrapolate my line of thinking to come to a logical conclusion. Thanks to all of the professors for critically questioning me, pointing out the fatal flaws in my results, and helping me learn and critically examine myself before reaching any conclusions.

I would like to sincerely thank the committee members—Prof. Céline Morin, Prof. Frédéric André, and Prof. Joachim Beeckmann—for kindly accepting to be part of my dissertation committee. I truly appreciate your willingness to review my work and the time you dedicated to doing so. Your contributions to the field have been a significant source of inspiration throughout my research, and I am especially grateful for the opportunity to benefit from your expertise. I want to use this opportunity to sincerely thank the Anonymous Reviewer 3 for his/her critical feedback, which helped to vastly improve the article on the spectral properties of ammonia by raising pertinent points about the mixing rules and cautioning about generalizing the claims.

I deeply and heartily thank Prof. Tomas Turanyi and Prof. Tim Lieuwen for democratizing their knowledge and resources on combustion sciences on the internet.

Sincere thanks to Christian Schwezener, Roman Glaznev, Prof. Joachim Beeckmann, and Prof. Heinz Pitsch from ITV for the access to FlameMaster and discussions on the FlameMaster, from the masters of combustion. The only two constants in this study were the constant support from my family (Appa, Amma, Atimber, Akka, Vishak, and Harish), without which this work wouldn't have progressed as it did. The second one is the constant support of my friends from NL on my mental sanity: Ing. Keerthana, Ir. Praveen, Ir. Aravind, Ir. Mano, Ir. Arvind (notice the absence of "a"), Ir. Manoj (aka BM), Ir. Karishma, Ir. Sid the Sai, Ir. Sai Saran, Ir. Naveen, and Ir. Vishnu. Special shout-out and thanks to Ing. Tulio Viola for baptizing me in the way of pasta and wine and making the stay in Orleans, a bit tolerable through our whining sessions. It is with immense gratitude that I would like to acknowledge Seif, the wizard of ammonia, for his expertise on the analytical methods of flame physics. Thanks to Prof. Augustin Guiband for introducing me to this topic and helping me get acquainted with radiation and the team's work (and who might have played a pivotal role in me getting this PhD). Special shout-out to then PhD leader Samuel JeanJean for showing me around, welcoming me to the group, even helping me out with the legal stuff, and most importantly, showing me a good "cave" to get some nice OH radicals. I would like to thank the un-yielding cluster "Leto" for its robust framework and stone-like support.

Finally, I would like to sincerely thank the doctoral school (the administrative staff) and then-director, Prof. Thierry Dudok de Wit, for his full support from the start to the end of the thesis. Can't really express the level of gratitude for his support in a mere 100-page document! Special thanks to Prof. Dunpin Hong, the Mobility Center, and Mr. Dylan Wrede for their support during my PhD.

"That which can be asserted without evidence, can be dismissed without evidence."

— **Christopher Hitchens**

Abstract

Ammonia (NH_3) can be a part of the conversation in decarbonizing the energy generation. It is easier to handle and is one of the most widely produced chemicals in the world, benefiting from decades of accumulated industry knowledge, which makes it an attractive option. Combustion of NH_3 has its own hurdles, such as (1) low burning velocity, (2) low flammability limits, and (3) poor performance of the detailed kinetic models. The former two can be mitigated by blending NH_3 with H_2 or in-situ cracking NH_3 . Poor performance of the kinetic models is a critical issue since detailed insights on the flame kinetics are required to select the operating regime to reduce NO_x emissions and develop digital twins to reduce the time in the R&D cycle of the combustors. Hence, a detailed comparison of numerical models against the experimental works is warranted to shed light on the performance of various kinetic models. NH_3 is also a radiatively participating species, hence leading possibly to radiative heat transfer between the fresh gases and hot water vapour (combustion products). Therefore, this also needs to be accounted for in the numerical models. The conventionally used optically thin approximation is not likely to be valid and necessitates finer radiation modelling. Spherically expanding flames (SEF) are a robust platform to investigate the premixed flame dynamics from sub-atmospheric to high-pressures (50 atm), both experimentally and numerically. The various experimental setups with special reference to the SEF are described in Chapter 2. SEF provides the burnt gas flame speed (S_b), Markstein length (L_b), and extrapolated laminar burning velocity S_L , a fundamental fuel property at the prescribed thermo-physical states. L_b controls the dissipation and amplification of the perturbations in a premixed flame, thereby controlling the operating regime of the combustors. In general, L_b and S_L control the global dynamics of the flame and are relatively insensitive (compared to other properties such as ignition time delay, speciation data, and so on) to the reaction rates.

To that end, various spectral databases with resolutions ranging from narrow band, Statistical Narrow Band Correlated k-distribution (SNBCK) to full spectrum models, such as WSGG (Weighted Sum of Grey Gases) and RC-FSK (Rank Correlated Full Spectrum k-distribution), were developed in Chapter 3. The spectral models were tested in decoupled computations for a set of pressures and flame configurations (planar and spherical) against the detailed line-by-line (LBL) model. Special attention was paid to capturing the re-absorption of the emitted thermal radiation in the fresh gases. The SNBCK25, a wide-band model with varying resolution across the spectrum, was selected on account of the model's accuracy and the computational cost. The applicability of SNBCK25 was also tested for CH_4 - NH_3 -air mixtures, which represents highly inter-coupled system, schematically CH_4 and NH_3 absorbing thermal radiation in the fresh gases, while H_2O , CO_2 , and CO emitting thermal radiation in the burnt section.

The developed spectral models were solved with the discrete ordinate method (DOM) along with SNBCK25 for both SEF and planar, freely propagating premixed flames in the open-source solver, FlameMaster [2]. The SEF isobaric and isochoric flames, together with planar ones were simulated for a set of conditions and equivalence ratios, as described in Chapter 4. Comparisons against the experimental measurements were conducted when available. In the initial stages of the flame propagation, DOM/SNBCK25 were close to the OTM model, and as the flame expanded, the effects of re-absorption became crucial. The effects of radiation were quantified using the burnt flame speed, extrapolation routine of Kelly and Law [3]. As expected, the role of re-absorption increases with pressure and molar content of NH_3 . Notably, the non-monotonic behaviour of L_b was attributed to the Zeldovich number (Ze), which was observed for the lean and stoichiometric flames. The re-absorption hastens the transition of the non-monotonic behaviour. A sensitivity analysis in CANtera [4] was conducted to highlight the chemical pathways that lead to the non-monotonic behaviour of Ze with respect to pressure. The

contributions of the various physical processes were computed for $\phi = 0.7$ to understand radiation's effects on the local flame dynamics. It was observed that the direct effect of re-absorption was minimal. The effects of Fourier conduction terms are more pronounced in DOM/SNBCK25 due to the change in temperature near the flame front and the reduction in the flame thickness, both stemming from the re-absorption of radiated energy. In addition, the inability of OTM to capture the flame dynamics was noted in several cases with special reference to the rich NH_3 -air flames at high pressure. The effects of molar content of NH_3 on the DOM/SNBCK25 was assessed against the adiabatic models (ADI), highlighting the direct role of partial pressures of NH_3 on the radiative processes. The effects of domain size on the flame structure of NH_3 -air flames were demonstrated for DOM/SNBCK25, implying the need for finer methods to include the spatial information of the thermal radiative transfer in the flamelets. Finally, the mass-burning flux of NH_3 -air flames at $\phi = 1.0$ was computed to highlight the increase in mass-burning rate with pressure. Although S_L reduces with pressure, this is particularly interesting since NO and NH_3 slip reduce with pressure, the latter being critical in rich- NH_3 flames. The study results are briefly summarised in Chapter 5 and highlight the future scope of the study of radiative heat transfer among participating species with special reference to NH_3 .

Keywords: spherically expanding premixed flames, ammonia, radiative re-absorption, Markstein length

Abstract

L'ammoniac (NH_3) peut faire partie de la conversation sur la décarbonation de la production d'énergie. Il est plus facile à manipuler et constitue l'un des produits chimiques les plus largement produits dans le monde, bénéficiant de décennies de connaissances industrielles accumulées, ce qui en fait une option attrayante. La combustion de NH_3 présente ses propres obstacles, tels que 1) un faible taux de combustion, 2) de faibles limites d'inflammabilité et 3) de mauvaises performances des modèles cinétiques détaillés. Les deux premiers peuvent être atténués en mélangeant le NH_3 avec du H_2 ou en effectuant un craquage in situ du NH_3 . La faible performance des modèles cinétiques est un problème critique, car des informations détaillées sur la cinétique de la flamme sont nécessaires pour sélectionner le régime de fonctionnement afin de réduire les émissions de NO_x et développer des jumeaux numériques pour réduire le temps dans le cycle de RD des chambres de combustion. Par conséquent, une comparaison détaillée des modèles numériques avec les travaux expérimentaux est justifiée pour faire la lumière sur la performance de divers modèles cinétiques.

Le NH_3 participe également au rayonnement, conduisant ainsi à un transfert de chaleur radiatif entre les gaz frais et la vapeur d'eau chaude (produits de combustion). Par conséquent, cela doit également être pris en compte dans les modèles numériques. L'approximation optiquement mince conventionnellement utilisée n'est pas valide et nécessite une meilleure modélisation du rayonnement. Les flammes sphériques en expansion (SEF) sont une plateforme robuste pour étudier la dynamique des flammes de la pression sub-atmosphérique aux hautes pressions (50 atm), à la fois expérimentalement et numériquement. Les différents dispositifs expérimentaux, avec une référence particulière aux SEF, sont décrits dans le chapitre 2. Les SEF fournissent la vitesse de flamme des gaz brûlés (S_b), la longueur de Markstein (L_b), et la vitesse de combustion laminaire extrapolée S_L , une propriété fondamentale du combustible dans les états thermo-physiques prescrits. Le L_b contrôle la dissipation et l'amplification des perturbations dans une flamme, contrôlant ainsi le régime de fonctionnement des chambres de combustion. En général, le L_b et le S_L contrôlent la dynamique globale de la flamme et sont relativement insensibles (par rapport à d'autres propriétés telles que le délai d'allumage, les données de spéciation, etc.) aux taux de réaction.

À cette fin, diverses bases de données spectrales avec des résolutions allant de la bande étroite aux modèles de spectre complet, tels que WSGG et RC-FSK, ont été développées dans le chapitre 3. Les modèles spectraux ont été testés dans un cas découplé pour un ensemble de pressions et de configurations de flamme (plane et sphérique) par rapport au modèle détaillé ligne par ligne (LBL). Une attention particulière a été accordée à la capture de la réabsorption du rayonnement thermique émis dans les gaz frais. Le SNBCK25, un modèle à large bande avec une résolution variable à travers le spectre, a été sélectionné en raison de la précision du modèle et du coût computationnel. L'applicabilité de SNBCK25 a également été testée pour les mélanges CH_4 - NH_3 -air, qui représentent un système hautement couplé, CH_4 et NH_3 absorbant dans les gaz frais et H_2O , CO_2 , et CO émettant un rayonnement thermique dans la section brûlée.

Les modèles spectraux développés ont été résolus avec la méthode des ordonnées discrètes (DOM) ainsi qu'avec SNBCK25 pour les flammes SEF et les flammes planes se propageant librement dans le solveur open-source, FlameMaster [2]. Les flammes SEF isobares, isochores, et planes ont été simulées pour un ensemble de conditions et de rapports d'équivalence sont décrits dans le chapitre 4. Des comparaisons

avec les mesures expérimentales

ont été effectuées lorsqu'elles étaient disponibles. Dans les stades initiaux de la propagation de la flamme, DOM/SNBCK25 étaient proches du modèle OTM, et à mesure que la flamme se dilatait, les effets de la réabsorption devenaient cruciaux. Les effets du rayonnement ont été quantifiés en utilisant la vitesse de flamme brûlée, la routine d'extrapolation de Kelly et Law [3]. Comme prévu, le rôle de la réabsorption augmente avec la pression et la teneur molaire en NH_3 . Notamment, le comportement non monotone du L_b a été attribué au nombre de Zeldovich (Ze), qui a été observé pour les flammes pauvres et stœchiométriques. La réabsorption accélère la transition du comportement non monotone. Une analyse de sensibilité dans CANTERA [4] a été menée pour mettre en évidence les voies chimiques qui conduisent au comportement non monotone du Ze par rapport à la pression. Les contributions des différents processus physiques ont été calculées pour $\phi = 0.7$ afin de comprendre les effets du rayonnement sur la dynamique locale de la flamme. Il a été observé que l'effet direct de la réabsorption était minime. Les effets des termes de conduction de Fourier sont plus prononcés dans DOM/SNBCK25 en raison du changement de température près du front de flamme et de la réduction de l'épaisseur de la flamme, les deux découlant de la réabsorption de l'énergie rayonnée. De plus, l'incapacité d'OTM à capturer la dynamique de la flamme a été notée dans plusieurs cas, avec une référence particulière aux flammes riches NH_3 -air à haute pression. Les effets de la teneur molaire en NH_3 sur DOM/SNBCK25 ont été évalués par rapport aux modèles adiabatiques (ADI), mettant en évidence le rôle direct des pressions partielles de NH_3 sur les processus radiatifs. Les effets de la taille du domaine sur la structure de la flamme des flammes NH_3 -air ont été démontrés pour DOM/SNBCK25, impliquant la nécessité de meilleures méthodes pour inclure l'information spatiale du transfert radiatif thermique dans les flammes. Enfin, le flux de combustion massique des flammes NH_3 -air à $\phi = 1.0$ a été calculé pour mettre en évidence l'augmentation du taux de combustion massique avec la pression. Bien que le S_L diminue avec la pression, ceci est particulièrement intéressant car le glissement de NO et de NH_3 diminue avec la pression, ce dernier étant critique dans les flammes riches en NH_3 .

Les résultats de l'étude sont brièvement résumés dans le chapitre 5 et mettent en évidence la portée future de l'étude du transfert de chaleur radiatif entre les espèces participantes, avec une référence particulière au NH_3 .

Mots-clefs: Ammoniac, réabsorption, flammes à expansion sphérique, longueur de Markstein

Résumé

Le chapitre 1 décrit la trajectoire actuelle des émissions de gaz à effet de serre et la nécessité de recourir à des carburants décarbonés pour soutenir l'activité humaine. Dans cette optique, les défis liés à la production de NH_3 sont abordés, notamment la réduction du carbone incorporé et des émissions de carbone associées à la production d'ammoniac. Cette section introductive se conclut par la présentation de concepts intéressants sur la production de H_2 , tels que la pyrolyse du méthane et la combustion de l'aluminium. Ensuite, la structure de flamme prémélangée et non prémélangée est examinée, ainsi que la distinction entre ces configurations de flamme, notamment en termes d'épaisseur de flamme et de vitesse de combustion laminaire. Après cette description de la structure de la flamme, la modélisation mathématique régissant les processus fluidiques et cinétiques sont exposés à travers la conservation de la masse, des espèces, de la quantité de mouvement et de l'énergie. Enfin, l'équation du transfert radiatif et les modèles utilisés pour calculer le transfert thermique d'origine radiative sont décrits pour une configuration plane. Finalement, l'équation du transfert radiatif pour une configuration monodimensionnelle de symétrie sphérique est également présentée.

Dans le chapitre 2, les divers concepts liés à la vitesse de flamme prémélangée sont discutés, et l'énumération des avantages et des inconvénients constitue l'objectif principal de ce chapitre. La vitesse de combustion laminaire pour une flamme plane se propageant librement est définie, et l'absence d'un équivalent expérimental strictement plan est soulignée. Ensuite, différentes définitions de la vitesse de flamme sont introduites, en commençant par la vitesse de déplacement de la flamme, qui est la vitesse absolue du front de flamme dans le référentiel du laboratoire. La vitesse de flamme des gaz non brûlés est distinguée de la vitesse de combustion laminaire (LBV). Enfin, la vitesse de consommation de la flamme est définie comme étant la vitesse des gaz non brûlés d'un point de vue cinétique. Cette vitesse de consommation est calculée à partir des taux de réaction intégrés ; elle est assez robuste numériquement, mais sa validation expérimentale n'est pas exacte et nécessite des approximations.

Concernant les techniques expérimentales, quatre dispositifs expérimentaux couramment utilisés sont décrits, à savoir:

- le brûleur Bunsen;
- la méthode du flux de chaleur;
- la flamme de stagnation;
- les bombes sphériques.

Le brûleur Bunsen est l'un des dispositifs expérimentaux les plus largement utilisés, malgré les approximations nécessaires pour y mesurer la vitesse de combustion laminaire. En particulier, il ne permet pas de capturer le rayon de courbure à la pointe du cône, ce qui oblige à utiliser des approximations via la méthode du cône de flamme (supposant un très faible angle de cône) ou la méthode de la surface de flamme, qui déduit la LBV à partir de la vitesse d'entrée et de l'aire du cône (front de flamme). Cela entraîne des imprécisions dans la détermination de la LBV à haute pression. La section suivante explore les effets de la richesse (*equivalence ratio*), de la teneur en H_2 et du nombre de Reynolds. Avec une augmentation de la richesse, on observe une intensification du rayonnement orange dans le spectre visible attribué à NH_2 .

Ensuite, le brûleur à flux de chaleur est décrit. Ce dispositif permet de mesurer les pertes de chaleur à l'aide de thermocouples sur une plage de vitesse d'entrée. Cela permet d'extrapoler la vitesse de combustion laminaire en déterminant la vitesse à laquelle la perte de chaleur est nulle. Comme la flamme

préchauffe les gaz frais, les effets du rayonnement sont minimes. Cependant, son principal inconvénient est sa limitation à des pressions relativement basses (inférieures à 5 atm).

Les deux derniers dispositifs expérimentaux, la flamme de stagnation et les bombes sphériques, sont largement utilisés en raison des diagnostics précis qu'ils permettent de mettre en place. La flamme de stagnation est un élément central des configurations expérimentales, ayant joué un rôle-clé dans le développement des premières théories sur l'étirement des flammes. Dans pareil cas, la flamme peut être configurée en écoulement contre-courant double ou en flamme unique selon les débits d'oxydant et de carburant. Des traceurs sont injectés dans le champ d'écoulement afin de mesurer leur vitesse à un point de référence, généralement juste avant le front de flamme. Ces mesures sont répétées pour différentes vitesses d'entrée afin d'obtenir la vitesse de flamme en fonction du taux de déformation. Malgré les avancées qu'elle a permises, cette configuration présente un inconvénient majeur : l'augmentation du nombre de Reynolds à haute pression affecte le comportement des traceurs.

Les bombes sphériques sont très simples dans leur conception et permettent d'atteindre des pressions allant jusqu'à 60 atm de manière fiable. Dans cette configuration, le mélange de combustible est introduit dans une chambre sphérique et enflammé par une paire d'électrodes en son centre. Une caméra à haute vitesse capture alors l'évolution de la flamme, permettant de déterminer la vitesse de flamme. Selon le régime de fonctionnement, les bombes sphériques peuvent être classées en :

- bombes à pression constante;
- bombes à volume constant.

Dans le cas d'une bombe à pression constante, la LBV est obtenue par extrapolation de la vitesse de déplacement de la flamme en fonction de l'étirement. Pour une flamme isochore au sein d'une bombe à volume constant, les premières phases de combustion sont écartées en raison de la montée en pression, et la LBV est directement calculée à partir de la vitesse de déplacement de la flamme et des variations de pression, sans extrapolation. Comme discuté précédemment, les flammes sphériques sont sensibles à l'étirement de la flamme, qui peut être atténué ou amplifié selon le nombre de Lewis du mélange. L'étirement de la flamme est défini comme la variation temporelle relative de la surface lagrangienne de la flamme. Dans une configuration 1D, il peut être décrit par une relation simple, tandis que pour des problèmes de dimension supérieure, il doit être calculé à partir des termes de courbure et de taux de déformation. Il est essentiel de noter que les flammes sphériques sont affectées à la fois par le transfert thermique radiatif et par des instabilités intrinsèques.

Les effets du rayonnement sont particulièrement significatifs, car les mesures expérimentales tiennent toujours compte des processus radiatifs, alors que ces derniers sont généralement négligés dans les modèles numériques. L'importance du rayonnement est démontrée par le fait que les limites de flammabilité prédictives du CH_4 se sont avérées correspondre aux mesures expérimentales après l'inclusion du transfert thermique radiatif dans une flamme sphérique, comme l'ont documenté Sibulkin et Frendi [5]. Ju et al. [6] ont également mis en évidence l'impact de la ré-absorption radiative sur les flammes planes se propageant librement. Ces auteurs ont observé que la LBV obtenue via le modèle DOM (*Discrete Ordinates Method*), associé au modèle de propriétés radiatives SNB (*Statistical Narrow Band*), était plus élevée que dans un modèle adiabatique en raison de la ré-absorption du rayonnement thermique émis, ce qui entraîne une température plus élevée des gaz frais à proximité du front de flamme. Ils ont également mis en évidence l'existence de limites d'inflammabilité indépendantes de l'extension du domaine, en raison du déséquilibre entre les gaz frais et les gaz brûlés. Conventionnellement, la ré-absorption radiative est faible pour des combustibles comme l'hydrogène et le méthane. C'est pourquoi un groupe de recherche à Princeton a développé une corrélation [7] permettant de calculer la vitesse de combustion laminaire adiabatique à partir des mesures expérimentales, afin de comparer ces valeurs avec les prédictions numériques correspondantes.

Les flammes sphériques sont également sujettes aux instabilités intrinsèques, notamment à haute pression. Ces instabilités sont contrôlées par le nombre de Lewis critique et le rapport de densité à l'interface qu'est le front de flamme, et le rayonnement influence ces paramètres. Enfin, dans ce chapitre, les équations de conservation exploitées par l'outil numérique FlameMaster ainsi que l'équation du transfert radiatif dans sa version sphérique sont discutées.

Comme nous l'avons vu précédemment, l'ammoniac pourrait faire partie de la solution au problème de la décarbonation. Cela nécessite une évaluation détaillée des propriétés fondamentales et des voies cinétiques dans l'oxydation des flammes d'ammoniac. Comme l'ammoniac participe au rayonnement, une attention particulière doit être accordée au transfert de chaleur radiatif des flammes ammoniac-air. Dans le chapitre 3, les modèles spectraux pour les flammes NH_3 -air ont été développés à partir d'un modèle ligne par ligne (LBL) bien résolu de différentes résolutions spectrales, tels que les modèles à bande étroite (SNB), ce jusqu'aux modèles globaux tels que RCFSK (*Rank Correlated Full Spectrum k-distribution*), WSGG (*Weighted Sum of Gray Gases*), et Multi-scale RCFSK. Les modèles développés ont été testés en référence au LBL pour une configuration de calculs radiatifs découplés au sein d'une flamme prémélangée et non-prémélangée, ce à différentes pressions. Les modèles SNB capturent les propriétés de la bande en utilisant les moments du premier ordre et du second ordre basés sur le travail d'André et de Vaillon [8]. Les modèles SNB développés ont été testés par rapport au LBL via la transmissivité et l'émissivité. Comme prévu, les performances des modèles SNB se sont révélées fort appréciables pour prédire les quantités sus-mentionnées. Les modèles SNB ne peuvent cependant pas être utilisés dans tous les solveurs radiatifs. SNB ne peut être utilisé qu'en conjonction avec les méthodes de traçage de rayons. En conséquence, SNBCK (*Statistical Narrow Band Correlated k-distribution*) a été développé à partir de SNB, exploitant le fait que le coefficient d'absorption est atteint plusieurs fois au cours d'un intervalle. Le coefficient d'absorption est donc ré-ordonné à l'aide d'une fonction de probabilité cumulative. Il convient de noter que la relation entre la probabilité cumulative et le coefficient d'absorption est une expression analytique basée sur une hypothèse. Bien que SNBCK ait donné de très bons résultats, le modèle ne peut pas être utilisé dans des calculs entièrement couplés en raison de la charge de calcul. Les modèles globaux, tels que la distribution k du spectre complet corrélé par rang (RCFSK), la distribution k du spectre complet corrélé par rang à plusieurs échelles (MSRCFSK) et la somme pondérée des gaz gris (WSGG) modélisent, eux, les propriétés radiatives sur l'ensemble du spectre au lieu d'une bande étroite (25 cm^{-1}). Le développement de la base de données RCFSK est similaire à celui de SNBCK, le ré-ordonnement étant effectué sur le spectre au lieu d'une bande étroite. La variation de la fonction de Planck est également prise en compte car elle est significative sur le spectre. L'intégration spectrale de l'équation du transfert radiatif (RTE) nécessite une attention particulière car la fonction de Planck varie à travers le spectre, ce qui conduit à des termes de Leibnitz. Ce problème peut être atténué en calculant le coefficient d'absorption et les poids du corps noir sur la base des états de référence ou en invoquant une hypothèse co-monotone et en spécifiant la température de Planck. Cette dernière solution permet de réduire le nombre d'évaluations et d'éliminer la spécification des états de référence. Dans MSRCFSK, les non-inhomogénéités associées à diverses espèces à différentes températures sont atténuées en divisant le problème en deux échelles ; la première échelle est résolue à une température de Planck proche de la température de cette espèce et de la même manière pour la deuxième échelle. Cela permet de réduire considérablement les erreurs associées à la température de Planck dans un système RCFSK. WSGG est un modèle intéressant en raison de ses faibles coûts de calcul. Avec WSGG, le comportement des gaz non-gris est approché de telle sorte que deux gaz gris ou plus peuvent décrire le comportement intégré de l'espèce. WSGG est obtenu en ajustant les émissivités du corps noir à partir du modèle LBL.

En examinant les différents modèles spectraux pour une flamme prémélangée par rapport au modèle LBL, le modèle SNBCK a obtenu les meilleurs résultats, suivi du MSRCFSK, du RCFSK et du WSGG. Le gain de précision entre RCFSK et MSRCFSK est minime. Ceci est principalement dû à la nature séparée d'une flamme prémélangée. Dans une flamme prémélangée, les espèces sont séparées avec H_2O chaud dans une section et NH_3 froid dans l'autre section. Par conséquent, MSRCFSK et RCFSK ne parviennent pas à capturer ce phénomène avec précision. Les performances étaient similaires à différentes pressions et configurations de flamme (plane ou sphérique). Les performances de MSRCFSK étant relativement moins bonnes que celles de SNBCK, un modèle à large bande basé sur le SNBCK a été développé et baptisé SNBCK25. SNBCK25 a une résolution variable sur l'ensemble du spectre, ce qui mène à 25 bandes au lieu de 398 bandes (dans SNBCK). Il a été résolu avec quatre points de Gauss. Par conséquent, le nombre total d'évaluations pour un seul point est de 100 au lieu de 4000. SNBCK25 a donné d'assez bons résultats pour tous les cas de test.

Les modèles spectraux développés ont ensuite été testés pour une configuration non-prémélang-

ée, car cette configuration conduit à l'évaluation des règles de mélange en raison de la potentielle présence simultanée de carburant et de produits. Les performances étaient similaires à celles des flammes prémélangées. Enfin, l'applicabilité de SNBCK25 a été testée pour des flammes $\text{CH}_4\text{-NH}_3\text{-air}$ car cela représente un cas épineux de combustibles participant radiativement CH_4 et NH_3 dans une partie du domaine et de CO_2 , CO et H_2O chauds dans l'autre partie du domaine. Les performances de SNBCK25 sont bonnes comparées à celles du LBL.

Le chapitre 4 décrit les effets du rayonnement sur la propagation de la flamme dans une simulation où la résolution de la RTE est couplée à celle de l'équation de conservation de l'énergie. Une brève description des travaux expérimentaux récents sur les flammes sphériques, à la fois isobares et isochores, est présentée. L'objectif principal des flammes isobares est l'évaluation de la pertinence de la correction dite *Optically Thin Model* (OTM) développée par l'équipe de Princeton pour rendre compte des pertes de chaleur radiatives. Les corrections OTM permettent d'évaluer la vitesse de flamme laminaire équivalente à partir des expériences et, par conséquent, de la comparer aux modèles numériques adiabatiques. Les corrections OTM ne tiennent compte que des pertes de chaleur radiatives. Elles ne sont pas applicables en présence d'un agent absorbant puissant dans les gaz frais, comme le gaz naturel synthétique, la recirculation des gaz d'échappement, les flammes diluées à la vapeur, etc. Des travaux récents se sont concentrés sur l'applicabilité de la correction OTM pour les flammes d'ammoniac-air en raison de leur faible vitesse de flamme. L'équipe de RWTH Aachen a validé cette correction pour des flammes d'ammoniac ultra-lentes en micro-gravité.

Les flammes isochores constituent un outil intéressant pour évaluer la vitesse de combustion laminaire (à l'aide de LBV) sur une gamme de pressions (et de températures) en une seule expérience. Le fait que l'émission radiative soit prise en compte (en présence d'un accès optique) en fait un outil encore plus pertinent. Les effets du rayonnement dans une chambre isochore ont été testés par l'équipe d'ICARE-CNRS pour des flammes $\text{CH}_4\text{-air}$ à très haute pression (aux pressions de fonctionnement des moteurs de fusée à propergol liquide). Les caractéristiques générales des flammes $\text{NH}_3\text{-air}$ ont également été décrites, avec un accent particulier sur la température adiabatique maximale et les émissions de NO via des calculs d'équilibre à diverses pressions. L'objectif principal était de déterminer les effets de la pression et de la richesse sur la fraction molaire de NO. Les calculs d'équilibre sont une bonne méthode pour illustrer ces effets, mais une prudence est requise, car les prédictions de NO basées sur l'équilibre sont inférieures en raison de l'hypothèse d'équilibre. Les prédictions de NO dépendent fortement du temps de résidence, et dans les expériences ainsi que dans les simulations 1D, ce dernier est limité par la taille du domaine.

Les détails de la modélisation sont alors décrits, notamment le nombre de directions discrètes pour le rayonnement et le nombre total de points de grille pour les flammes 1D sphériques en expansion. Les modèles de diffusion moyenne des mélanges et la thermo-diffusion ont été utilisés pour toutes les simulations. Dans ce chapitre, DOM et DOM/SNBCK font référence à l'équation du transfert radiatif (RTE) avec DOM, les propriétés spectrales étant fournies par SNBCK25. Le modèle cinétique de Zhu 2024 a été principalement utilisé et validé en le comparant à trois modèles cinétiques de pointe avec les mesures expérimentales de l'ITV en micropesanteur. Cela est particulièrement important, car à gravité terrestre, la flottabilité affecte fortement la flamme. Le modèle Zhu 2024 s'est révélé supérieur aux autres modèles cinétiques. Aux premiers stades de la propagation de la flamme, les simulations DOM étaient plus proches des simulations OTM, mettant en évidence le rôle de l'émission radiative. Cependant, avec l'augmentation du rayon de la flamme, les imulations DOM tendaient vers les simulations ADI, soulignant les effets marqués de la ré-absorption radiative.

Enfin, les flammes $\text{NH}_3\text{-air}$ ont été étudiées à diverses pressions (1 à 50 atm) pour des mélanges pauvres ($\phi=0.7$), stoechiométriques ($\phi=1.0$) et riches ($\phi=1.3$). L'accent a été mis sur le cas pauvre en raison de comportements intéressants des flammes $\text{NH}_3\text{-air}$.

Le chapitre 4 s'est conclu en mettant en évidence les limitations de l'étude.

Dans le chapitre 5, les conclusions de cette étude ont été mises en avant, ainsi que les perspectives futures de recherche. Parmi ces dernières, on peut citer les ambitions liées à:

- une meilleure formulation du nombre de Zeldovich (Ze) applicable aux conditions stoechiométriques ■

- l'inclusion des termes de ré-absorption dans la procédure d'extrapolation.

Contents

1	Introduction	1
1.1	Context	1
1.2	Physics of flames	4
1.3	Modelling of flames	6
1.4	Radiative heat transfer	8
1.5	Objective of this work	11
2	Spherically expanding flames	13
2.1	Introduction	13
2.2	Configurations of interest	14
2.2.1	The canonical configuration of the planar freely propagating flame	14
2.2.2	Flame speed evaluation	14
2.2.3	Associated experimental techniques	15
2.3	Introduction to stretched flames	19
2.3.1	Background	19
2.3.2	Post-processing extraction	20
2.3.3	Isochoric flame propagation	20
2.4	Some potential effects on the dynamics of expanding premixed flame	21
2.4.1	Effects of radiation	21
2.4.2	Effects of intrinsic flame instabilities	22
2.5	Governing equations and subsequent numerical simulation	23
3	Spectral models of radiative properties for species met in NH₃-air flames	27
3.1	Introduction	28
3.2	Spectroscopic databases and line-by-line model	30
3.2.1	Background	30
3.2.2	Spectroscopic databases	30
3.2.3	Line-by-line model	31
3.3	Statistical narrow band	32
3.3.1	SNB parameters	33
3.3.2	Narrow band (NB) correlated-k and k-g distribution	33
3.4	Global models	36
3.4.1	RCFSK	36
3.4.2	Multi-scale RCFSK	37
3.4.3	WSGG model	38
3.4.4	Assessment of WSGG	38
3.5	Verification of DOM	39
3.6	Reduced SNBCK	39
3.7	Application to radiative heat transfer in flames	40
3.7.1	Premixed flames	40
3.7.2	Non-premixed flames	42
3.7.3	Applicability of reduced SNBCK to other species	44
3.8	Line of sight for premixed flames	44
3.9	Conclusions on the spectral modelling	45
3.10	Spectral models' implementation in RTE resolution	45

4	Effects of radiation on the characteristics of NH₃ flames	47
4.1	Introduction	47
4.2	Literature review	48
4.2.1	Isobaric flames	48
4.2.2	Isochoric flames	49
4.2.3	Kinetic mechanisms	49
4.2.4	General characteristics of NH ₃ -air combustion	50
4.3	Computational details	51
4.4	Isobaric flame propagation	52
4.4.1	Experimental validation	52
4.4.2	Effects of pressure on the propagation of NH ₃ - air flames	53
4.4.3	Effects of pressure on the propagation of NH ₃ /H ₂ - air flames	65
4.5	Isochoric flame propagation of NH ₃ -air	69
4.6	Discussion on planar freely propagating flames	71
5	Conclusion and perspectives	75
5.1	Conclusion	75
5.2	Perspectives	76
	Bibliography	76

1 Introduction

What doesn't kill you makes you stronger (in Earth). Anything can kill you in space but fire and soot will seal the deal

Contents

1.1	Context	1
1.2	Physics of flames	4
1.3	Modelling of flames	6
1.4	Radiative heat transfer	8
1.5	Objective of this work	11

The introductory chapter highlights the potential implications of the unabated use of fossil fuels and the need for low-carbon energy sources. It then discusses possible alternatives to carbonaceous fuels. Within the context of the ongoing modelling refinement of combustion processes, we briefly outline the current state of knowledge on the structure of the flames and the associated mathematical models, focusing more specifically on radiative heat transfer, where the objectives of this work stand.

1.1 Context

Energy production is the primary anthropogenic source of greenhouse emissions, accounting for three-fourths of emissions [9]. Globally, primary energy consumption from low-carbon sources (renewables and nuclear) has seen a tepid increase from 14.5% in 2000 to 18.5% in 2023 [9], with oil, coal, and gas being the predominant sources of the energy mix. According to the Paris Agreement, it is essential for humanity to limit CO₂ emissions. To keep global warming below 1.5 °C, we can only emit an additional 250 billion tonnes of CO₂. However, in 2022 alone, 41 billion tonnes were already released. The under-performance of the policies against pledges can be inferred from Fig. 1.1, underscoring the need for the valorization of low-carbon energy sources.

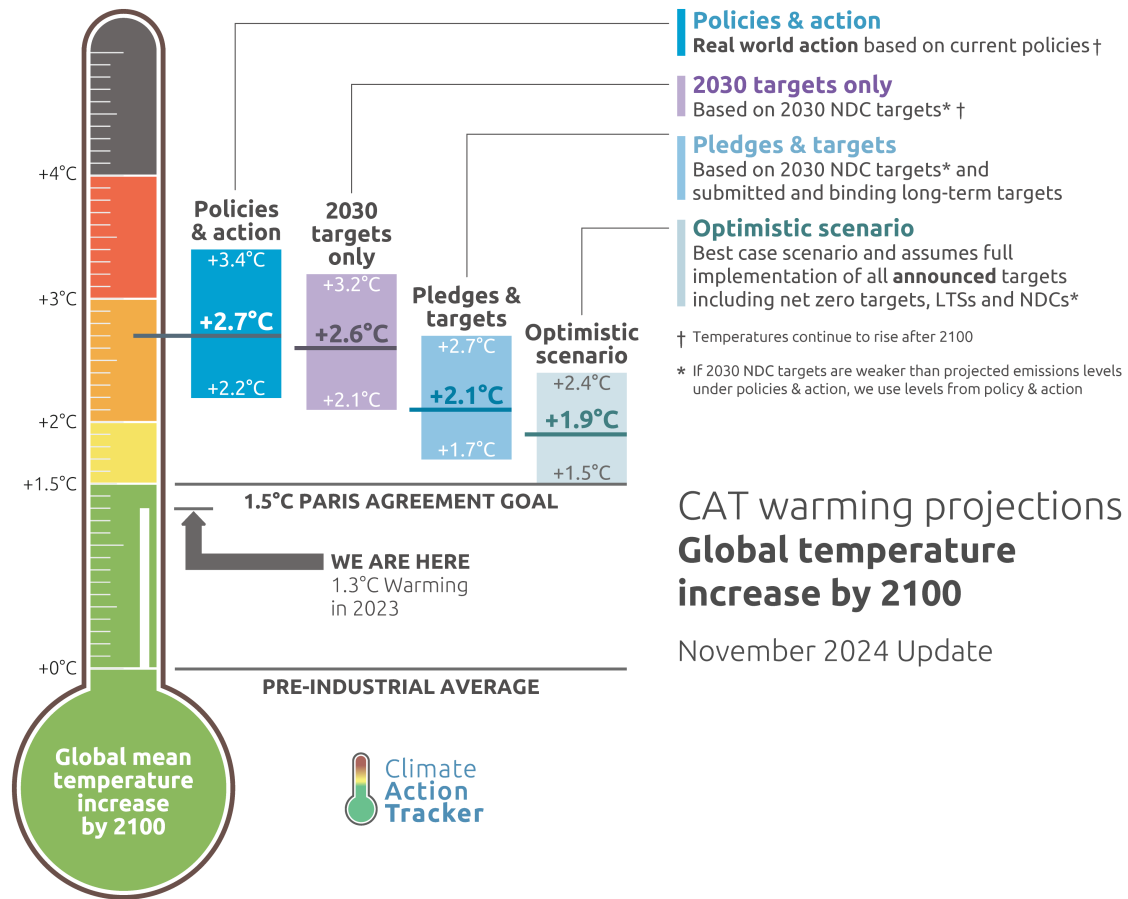
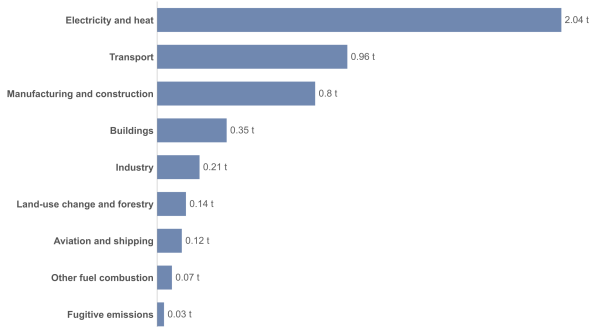


Figure 1.1: Illustration of various scenarios on the global median warming estimates (source: [10])

In the context of carbon footprint reduction, ammonia (NH_3) and hydrogen (H_2) are particularly important to the discussion on decarbonization since a significant portion (93.8% according to Ref. [11]) of the greenhouse gases come from the use of fossil fuels (coal, oil, and gas). Figure 1.2 illustrates the breakdown of the CO_2 emissions and the breakdown of electricity production from various sources. It is seen that coal, gas, and oil form the major part of the energy mix [12]. NH_3 and H_2 mixtures can be used as fuel for ground-based applications with relative ease for various sectors in Fig. 1.2. The advantages of NH_3 and H_2 mixtures include:

- the potential to scale. Since ammonia is the second most produced chemical [13], the industry could have a proclivity to transition into an energy sector partially powered by ammonia.
- the smooth upgrade of the combustors infrastructure. As a matter of fact, blending NH_3 and H_2 should help to increase the low laminar flame speed (LFS) exhibited by NH_3 while reducing the LFS of H_2 , so that a regular combustor burning fossil fuels can be operated in the regimes postulated in its manufacturing phase.

Per capita CO₂ emissions by sector, World, 2021

Data source: Climate Watch (2024); Population based on various sources (2024)
OurWorldinData.org/co2-and-greenhouse-gas-emissions | CC BY

Electricity production by source, World

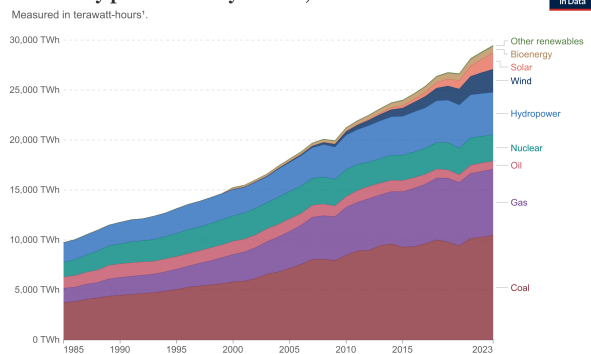


Figure 1.2: Illustration of per capita CO₂ emissions and breakdown of energy source for the production of electricity in the World (source: [12])

In addition to the above challenges, ammonia and its related species are radiatively active species. As an illustration, N₂O is a greenhouse gas with a potential 265 times higher than that of CO₂ [14] while H₂ also produces NO_x through atmospheric reactions which might further sustain issues from chronic lung diseases to acid rain [15]. For this reason, the design of combustion devices fueled by ammonia and ammonia/hydrogen requires an accurate assessment of the performances in terms of both the local heat release rate and the associated environmental costs. Among the challenges to be faced, the role of radiative heat transfer in both premixed and non-premixed flames remains in itself an important issue [16, 17]. Still, there is limited work on thermal radiation related to ammonia flames.

The production of NH₃ also remains a major challenge in and of itself since the agriculture sector is already trying to decarbonize the production of NH₃. NH₃ is predominately produced by the Haber-Bosch process at high temperature and high pressure, resulting in emissions of 2.16 kg CO₂ per kg of NH₃ [18]. In addition, one of the main sources of CO₂ is the steam methane reforming (SMR), i.e., conversion of CH₄ to H₂, resulting in 9-10 tonnes of CO₂ for one tonne of H₂ produced [18].

Recently, the production of NH₃ from excess renewable energy has been gaining attention as a means of energy storage, particularly in the production of H₂ from surplus renewable energy. However, the large-scale implementation is not practical due to the water requirements for this process. Hence, the production of NH₃ and H₂ also needs to be revisited using more efficient methods, such as methane pyrolysis in a metal bath, a process investigated by a group at d'Alembert (Sorbonne University) [19], or by the combustion of aluminum currently studied at ICARE-CNRS [20].

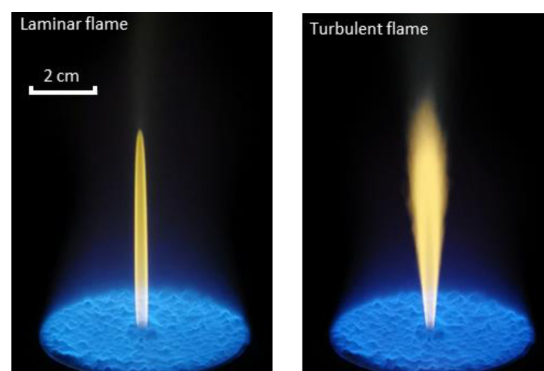


Figure 1.3: Illustration of a laminar and turbulent NH₃-air flames (orange region) stabilized by a piloted CH₄-air flame (blue region) (source: [21])

Finally, NH₃-air flames at laminar and turbulent conditions are illustrated in Fig. 1.3. The NH₃-air flame was stabilized here with a pilot CH₄-air flame. The frames are taken from the study of Fan et al. [21]. The main focus of the study was the characterization of NH and NO radicals to further refine the knowledge of the flame structure at laminar and turbulent conditions. The structure and modelling of flames are described in the subsequent sections.

1.2 Physics of flames

Oxygen, fuel, and heat are the three controlling parameters of a flame, which can be defined as the region of exothermic reaction. Flames can broadly be classified into premixed and non-premixed configurations based on the controlling process of the reactions. In premixed flames, fuel and oxidizer are locally mixed, and a hot spot initiates the exothermic reaction. Hence, these flames are more prone to severe incidents. This section discusses the basics of premixed and non-premixed flames' structure.

Premixed flames have a unique flame structure that is usually split into the three following regions:

- The preheat zone: Upstream to the flame, the reactants are heated by conduction and radiation from the flame. While the former mode of heat transfer is quite properly modeled in conventional flame configurations, the latter is subject to the spectral nature of the reactants and is usually poorly modeled. The pre-heating region is illustrated by the shaded area beneath the temperature profile in Fig. 1.4. A magnified view of the preheat zone and reaction zone from Fig. 1.4 is presented in Fig. 1.5, along with the profiles of key radicals that participate in the exothermic reactions are highlighted. These species can be utilized in experimental diagnostics as a flame marker.
- The reaction zone: This region is characterized by intense rates of reactions that are globally exothermic. This typically leads to a high local temperature and significant amounts of H, O, OH, and NH radicals [22]. The reaction zone is described by the region encapsulated by the heat release rate (HRR) curve in Fig. 1.4. The species presented in the Fig. 1.5 are the potential candidates for flame markers in the experimental measurements of NH₃ flames.
- The post-combustion zone: In this region of the field, the burnt products are present at high temperatures. These act as an energy source, potentially via thermal radiation, which further leads to the reduction in temperature as illustrated in Fig. 1.4.

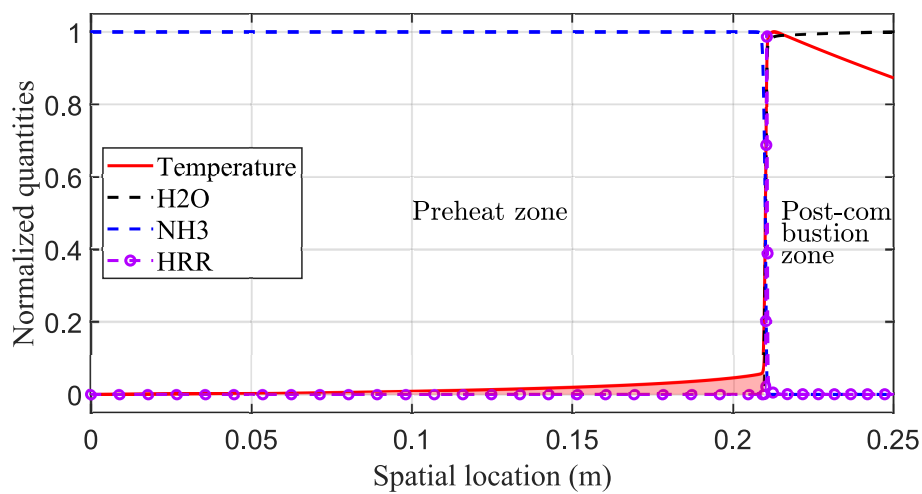


Figure 1.4: Characteristic fields within a non-adiabatic, premixed, planar, stoichiometric NH₃-air flame at 2 atm. The shaded region highlights the preheating zone, while the reaction zone is enclosed within the HRR curve. A close-up of this region of high gradient is presented in Fig. 1.5. Any quantity ξ , shown, i.e. temperature T , mass fraction Y_i of species i or the heat release rate HRR, is normalized as $(\xi - \xi_{\min}) / (\xi_{\max} - \xi_{\min})$.

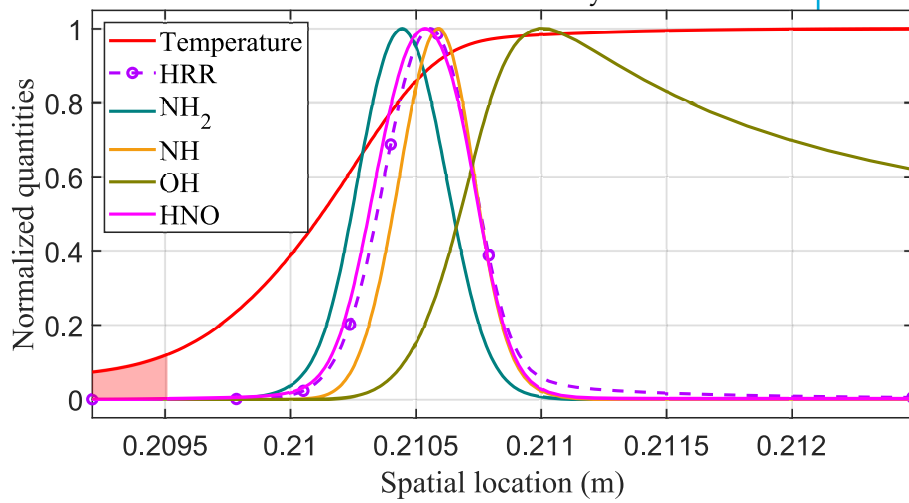


Figure 1.5: Close-up view within the region of high gradient of the fields displayed in Fig. 1.4. For clarity, note that only a portion of the preheating zone is highlighted via shading.

In contrast, non-premixed flames burn the fuel and the oxidizer as they are introduced separately to the reaction region where they are mixed (the diffusion process is the rate-determining step due to the low time scale of chemical reactions compared to the diffusion) (as seen in Fig. 1.6). This process generally results in a safer combustion environment due to the reduced risk of pre-ignition. However, it often leads to inefficiencies, such as incomplete combustion or higher emissions, because the mixing processes are more sophisticated than in premixed flames. A non-premixed flame is characterized by a reaction layer, producing burnt products and heat, both of which diffuse to the oxidizer-rich and fuel-rich regions. Since diffusion plays a limiting role in the transport of the reactants, it is also termed a diffusion flame in the literature.

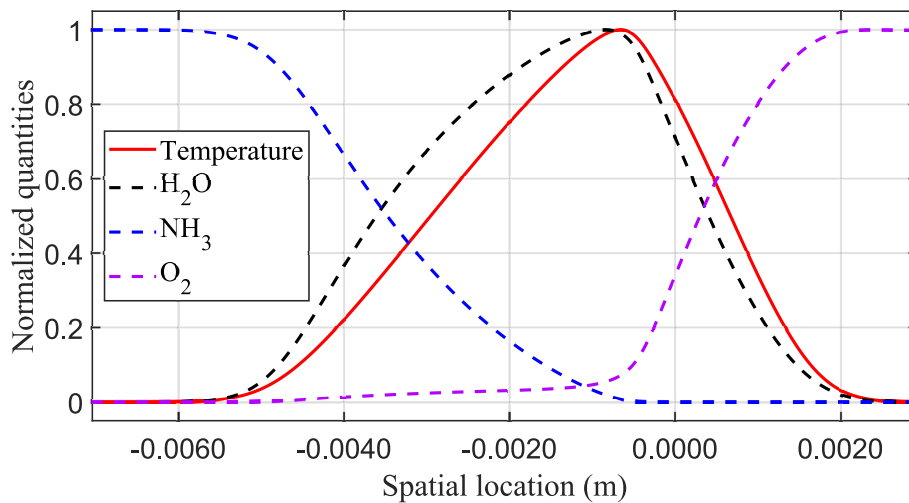


Figure 1.6: Illustration of computed fields within a 1D non-premixed strained flame (50 s^{-1}) NH_3 -air flame at $T = 373 \text{ K}$ and 1 atm without any radiation model. Any quantity ξ shown, i.e. temperature T or mass fraction Y_i of species i , is normalized as $(\xi - \xi_{\min}) / (\xi_{\max} - \xi_{\min})$.

In addition to the difference in the flame structure, a premixed flame has a few distinct characteristics. The major ones are:

- the laminar flame speed;
- the flame thickness.

Laminar flame speed

In a premixed flame, the flame can propagate through the unburnt mixture upon ignition. Laminar flame speed is then defined as the speed of the flame front with respect to the unburnt mixture. It is a fundamental property of the fuel for a given thermo-physical state. Laminar flame speed is also referred

to as laminar burning velocity (S_L , LBV) in the literature. Unlike premixed flames, non-premixed flames do not propagate, and the flame is developed near the surface of stoichiometry.

Flame thickness

Flame thickness can be defined by the temperature gradient or the Full width at half maximum (FWHM) of the reaction layer's heat release rate (HRR). In this work, flame thickness is computed via the HRR. The flame thickness of a diffusion flame is not unique since it depends on the flame's strain rate applied to the fuel and oxidizer; the flame thickness will change depending on the strain rate. Since an unstrained steady flame is impossible for non-premixed flames [23].

1.3 Modelling of flames

The mathematical equations can describe the underplay of various physical processes, albeit with some reasonable approximations. The regular system of governing equations for a low-Mach reacting system is given by:

- the conservation of mass and species;
- the conservation of momentum;
- the conservation of energy.

Chapter 2 describes the numerical model utilized in this work, while the general outline of the equations is given below.

Conservation of mass

The conservation of mass governs the mass balance for the fluid system via the empirical assumption that mass can neither be created nor destroyed. The conservation of mass in its integral formulation is given by:

$$\frac{\partial}{\partial t} \int_V \rho dV + \int_S \rho \mathbf{v} \cdot \mathbf{n} ds = 0 \quad (1.1)$$

In the above equation, ρ and $\mathbf{v}$ correspond to the material density and the velocity vector, respectively. We can obtain the local formulation of the conservation of mass through the Gauss divergence theorem for the advection terms, leading to:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (1.2)$$

Conservation of species

The conservation of species takes an overarching role in modelling the combustion systems. It describes chemical species' advection, diffusion, and generation (described by the kinetic mechanism) during combustion. The conservation of species is characterized by the transport of a scalar quantity (usually mass fraction Y_i or mole fraction X_i , here i denoting the species index). Its initial integral expression can be readily formulated for species i , species density ρ_i as follows:

$$\int_V \frac{\partial \rho_i}{\partial t} dV + \int_V \nabla \cdot \rho_i \mathbf{v} dV = \int_V W_i \hat{\omega}_i dV - \int_V \nabla \cdot \rho_i \mathbf{V}_i dV \quad (1.3)$$

Here, $\hat{\omega}_i$, W_i , and $\mathbf{V}_i$ correspond to the molar reaction rate, the molar mass, and the diffusion velocity of the species i , respectively. The L.H.S. describes the material derivative, while the R.H.S. describes the species production and diffusion, respectively. The equations can then be also be formulated locally:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v} + \rho_i \mathbf{V}_i) = W_i \hat{\omega}_i \quad (1.4)$$

The diffusion velocity of species i , $\mathbf{V}_i$, has to satisfy the following constraint at all the spatial locations:

$$\sum_{i=1}^{N_s} X_i \mathbf{V}_i = 0 \quad (1.5)$$

The exact $\mathbf{V}_i$ can be obtained implicitly from the Stefan-Maxwell (MS) equations, which leads to a relatively very high computational overhead to compute the diffusion velocities for all the species present in the system (N_s) across the spatial location. The MS system for the mass diffusion and the thermal diffusion is given by:

$$\nabla X_i = \sum_{j=1}^{N_s} \frac{X_i X_j}{D_{ij}} (\mathbf{V}_i - \mathbf{V}_j) + \sum_{j=1}^{N_s} \frac{X_i X_j}{\rho D_{ij}} \left(\frac{D_j^T}{Y_j} - \frac{D_i^T}{Y_i} \right) \left(\frac{\nabla T}{T} \right) \quad (1.6)$$

The numerical overload can be mitigated by invoking Fick's law or Hirschfelder-Curtis approximation (Mixture-averaged diffusion coefficient). In the former, the $\mathbf{V}_k$ is obtained directly from the binary diffusion coefficients and is exact only for systems involving two species or all the species have the same diffusion coefficient. For a mixture-averaged assumption, the diffusion velocity can be written as:

$$X_i \mathbf{V}_i = -\mathcal{D}_{i,m} \nabla X_i \quad (1.7)$$

In Eq.(1.7), the diffusion coefficient $\mathcal{D}_{i,m}$ does not correspond to the binary diffusion coefficient but to the mixture-averaged diffusion coefficient.

$$\mathcal{D}_{i,m} = \frac{1 - X_i}{\sum_{j \neq i}^{N_s} X_j / D_{i,j}} \quad (1.8)$$

This leads to molar diffusion velocity,

$$\mathbf{V}_i = -\frac{1}{X_i} \mathcal{D}_{i,m} \nabla X_i \quad (1.9)$$

Special correction terms needs to included to enforce the conservation of mass ($\sum_{i=1}^{N_s} Y_i \mathbf{V}_i = 0$) due to inclusion of $\mathcal{D}_{i,m}$ and hence an additional correction term $\mathbf{V}_{\text{corr}}$ is added to the diffusion flux, such that:

$$\mathbf{V}_{\text{corr}} = -\sum_{i=1}^{N_s} X_i \mathbf{V}_i \quad (1.10)$$

Eq.(1.10) is only a function of the spatial location.

Conservation of momentum

The conservation of momentum can be written as [24]:

$$\frac{\partial}{\partial t} \int_V \rho \mathbf{v} dV + \int_S \rho \mathbf{v} \mathbf{v} \cdot \mathbf{n} dS = \int_S \mathbf{T} \cdot \mathbf{n} dS \quad (1.11)$$

In the above equation, gravity is neglected. Here, ρ , $\mathbf{v}$, $\mathbf{T}$ correspond to material density, velocity vector, and stress tensor. Stress tensor consists of both shear and normal stresses and is given by:

$$\mathbf{T} = -\left(p + \frac{2}{3} \mu \nabla \cdot \mathbf{v}\right) \mathbf{I} + 2 \mu \mathbf{D} \quad (1.12)$$

Here, $\mathbf{D}$ is the strain tensor and is given as $\frac{1}{2}[\nabla \mathbf{v} + (\nabla \mathbf{v})^T]$.

The Eqn. (1.11) can then be manipulated to express a local formulation that relates the material derivative

of momentum ρv_i along axis i and the various forces acting on the control volume:

$$\frac{\partial \rho v_i}{\partial t} + \nabla \cdot (\rho v_i \mathbf{v}) = \nabla \cdot \tau_{ij} - \nabla p \cdot \mathbf{I}_i \quad (1.13)$$

$\mathbf{I}_i$ is the unit vector in the direction of the coordinate x_i and τ_{ij} is the deviatoric stress tensor [25] which is equivalent to Eqn. (1.12) without the pressure terms. The above equation can also be written in terms of the material derivative of $\mathbf{v}$ termed as a non-conservative form of conservation of momentum.

Conservation of energy

The conservation of energy relates the material derivative of total energy against the heat generation and heat flux across the control volume. The final equation for the conservation of energy e per unit mass in terms of specific internal energy as opposed to the total energy (internal energy + kinetic) can be given as:

$$\begin{aligned} \frac{\partial}{\partial t} \int_V \rho e dV + \int_S \rho e \mathbf{v} \cdot \mathbf{n} dS = \int_V \rho S dV - \int_S (\mathbf{q} + \mathbf{q}_{\text{rad}}) \cdot \mathbf{n} dS - \int_V \tau : (\nabla \mathbf{v}) dV \\ - \int_V p(\nabla \cdot \mathbf{v}) dV \end{aligned} \quad (1.14)$$

Here, S corresponds to the heat source, $\mathbf{q}$ is the vector of heat flow density attributed to Fourier heat conduction and enthalpy diffusion, while $\mathbf{q}_{\text{rad}}$ is the one that refers to the radiative heat flux. The third and fourth term on the R.H.S. corresponds to the viscous work and pressure work done by the system. Assuming the viscous effects to be negligible and invoking the relation introducing the enthalpy per unit mass h , i.e. $e = h - \frac{p}{\rho}$, the governing equation can be locally formulated as follows:

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho h \mathbf{v}) = \rho S - \left(\frac{\partial p}{\partial t} + \mathbf{v} \cdot \nabla p \right) - \nabla \cdot (\mathbf{q} + \mathbf{q}_{\text{rad}}) \quad (1.15)$$

1.4 Radiative heat transfer

Radiative heat transfer is typically identified as one of the three modes of heat transfer, along with conduction and convection. It is particularly important in combustion studies and the atmospheric sciences, considering the radiative forcing throughout the atmosphere on Earth. Unlike heat conduction, radiative heat transfer is a non-local phenomenon, and it is crucial to account for radiation's directional and spectral nature. Analysis of radiative heat flux involves the study of radiant energy dE_η in the wavenumber interval $(\eta, \eta + d\eta)$ across an element of area dA in the direction of the element of the solid angle $d\omega$ is given as,

$$dE_\eta = I_\eta \cos\theta d\eta dA d\omega dt \quad (1.16)$$

Here, θ is the angle between the normal of the area element, $d\omega$ is the the solid angle, and I_η is the spectral intensity, i.e., intensity at the wavenumber. The radiant energy can be computed by computing the spectral intensity, accounting for the absorption and emission of a pencil of radiation (see Fig. 1.7).

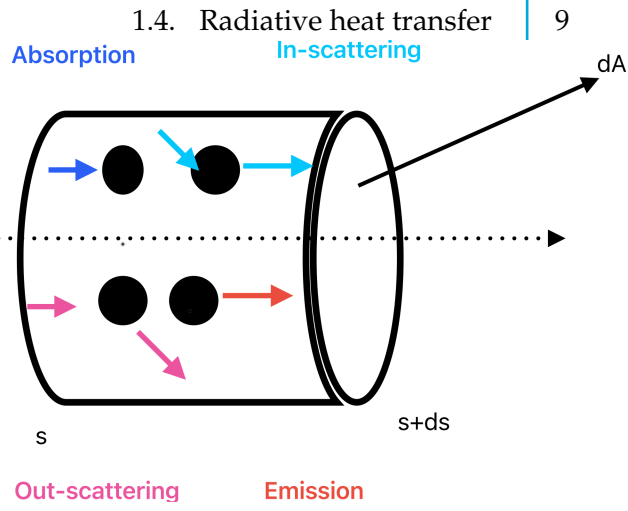


Figure 1.7: Pencil of rays for radiative balance, the arrow's color represents different radiative processes. The filled circles illustrates the radiatively participating molecules.

In the presence of scattering¹, the radiative transfer equation (RTE) for a steady-state at thermodynamic equilibrium, scattering and absorbing media along the direction $\hat{s}$ is given as:

$$\frac{dI_\eta}{ds} = \hat{s} \cdot \nabla I_\eta = \kappa_\eta I_{b\eta} - \kappa_\eta I_\eta - \sigma_\eta I_\eta(\hat{s}) + \frac{\sigma_\eta}{4\pi} \int_{4\pi} I_\eta \Phi_\eta(\hat{s}_i, \hat{s}) d\Omega_i \quad (1.17)$$

Here, $\hat{s}$ is the direction of the incident radiation, κ_η the absorption coefficient at wavenumber η , $I_{b\eta}$ the Planck function, that depends on temperature T and η , and $I_\eta(\hat{s})$ the intensity at wavenumber η towards the direction $\hat{s}$. The first and second terms on the R.H.S. characterize the local emission via the emission coefficient and the absorption of the incident radiation, respectively. At local thermodynamic equilibrium, the emission coefficient is given as the product of the absorption coefficient and the Planck function [26]. The third and fourth terms on the R.H.S. denote the out and in scattering, respectively. Φ denotes the scattering phase function and describes the redistribution of the radiation due to scattering. It is important to note that κ_η is not a smooth function. It can be very erratic throughout the spectrum considered, and hence, special attention has to be paid to the computation of the total intensity, which is the accumulation of I_η throughout the spectrum.

The governing equation that governs radiative heat transfer (for a single-ray, steady-state, planar configuration, and non-scattering media) is then given for a medium where scattering is neglected by:

$$\frac{dI_\eta}{ds} = \kappa_\eta I_{b\eta} - \kappa_\eta I_\eta \quad (1.18)$$

As stated previously, radiation is an omnidirectional process occurring over infinite solid angles between 0 and 4π , and we need an assumption to close Eq.(1.18). Eq.(1.18) can then be solved analytically for only very limited, idealized conditions [26].

Subsequently, the discrete ordinate method (DOM) can be used to close the directional discretization using Gaussian quadrature formula as developed by Chandrasekhar [27]. Much of the earlier work on DOM was done at Los Alamos National Laboratory by Lathrop and Carlson [28] for neutron transport in nuclear reactors. Assuming that the net radiative heat flux can be approximated to weighted sum of discrete intensities, as illustrated in Fig. 1.8. μ_i and w_i being the directional cosines of the ray i and the weight of the direction i , respectively, the DOM strategy leads to the discrete RTE for a 1-D non-scattering medium [26]:

$$\mu_i \frac{dI_{\eta,i}}{dx} = \kappa_\eta I_{b,\eta} - \kappa_\eta I_{\eta,i} \quad (1.19)$$

Once Eqs. (1.19) are solved for $I_{\eta,i}$, the total intensity in the direction i can be evaluated as the summation

¹that can be significant, for instance in the presence of agglomerated soot

of the spectral intensity over small intervals $\Delta\eta_j$:

$$I_i = \int_0^\infty I_\eta d\eta \approx \sum_j I_{\Delta\eta_j,i} \Delta\eta_j \quad (1.20)$$

Then the vector of radiative heat flux density can be computed as follows:

$$\mathbf{q} = \sum_{i=1}^N w_i I_i \hat{\mathbf{s}}_i \quad \text{with} \quad \hat{\mathbf{s}}_i = \mu_i \hat{\mathbf{i}} \quad (1.21)$$

The radiative heat flux converges to a value with an increase in the number of discrete directions. The only condition for selecting the discrete ordinates directions is that the zeroth, first, and second moments of the direction cosines must satisfy their respective conditions. For instance, for a N discrete directions [26].

$$\int_{4\pi} d\Omega = \sum_{i=1}^N w_i = 4\pi \quad (1.22)$$

$$\int_{4\pi} \mathbf{s} d\Omega = \sum_{i=1}^N w_i \mathbf{s}_i = 0 \quad (1.23)$$

$$\int_{4\pi} \mathbf{s} \mathbf{s} d\Omega = \sum_{i=1}^N w_i \mathbf{s}_i \mathbf{s}_i = \frac{4\pi\delta}{3} \quad (1.24)$$

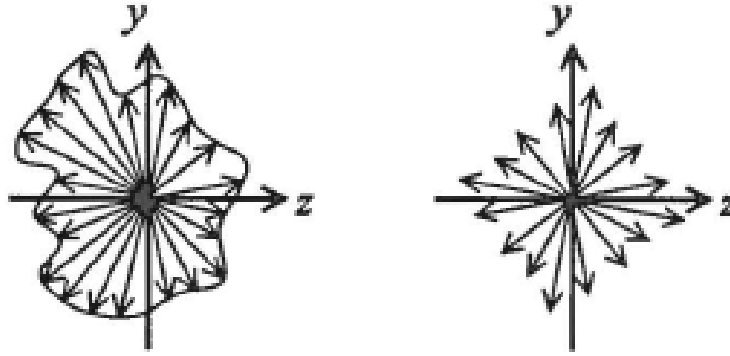


Figure 1.8: Left: Illustration of actual radiative intensity over all the directions, described by the continuous curve; Right: Illustration of radiation in discrete directions by the directions prescribed by the arrow. (source: [29])

It is worth mentioning now that the RTE for a 1D spherically symmetric configuration is slightly special since with an increase in radial location, the local directional cosine also changes [26]:

$$\frac{dI}{ds} = \mu \frac{\partial I}{\partial r} + \frac{1 - \mu^2}{r} \frac{\partial I}{\partial \mu} \quad (1.25)$$

Hence, the RTE using DOM for a 1D spherically symmetric configuration is given as follows:

$$\mu_i \frac{\partial I_{\eta,i}}{\partial r} + \frac{1 - \mu_i^2}{r} \frac{\partial I_{\eta,i}}{\partial \mu_i} = \kappa_\eta I_{b,\eta} - \kappa_\eta I_{\eta,i} \quad (1.26)$$

The spherical RTE is distinct compared to the planar RTE, specifically due to the inter-coupling of intensities of different directions through the second term on the L.H.S.

More generally, the RTE is a first-order equation, so it needs one boundary condition. It is set to the emission term at the starting point of the radiation's propagation.

It is worth reminding that the application of the radiative transport equation is inconsequential for species that are majorly radiatively transparent ($\kappa_\eta \sim 0 \text{ cm}^{-1}$) between the wavenumbers of 50 cm^{-1} to 10000 cm^{-1} . Thus, a few species that are radiatively participating are of interest to the combustion community.

These are H_2O , NH_3 , CO_2 , CO , CH_4 , and so on. Chapter 3 deals with the spectral models that are utilized in this study in a more elaborate manner.

Among others, the fire safety community has paid significant attention to radiation in non-premixed flames of terrestrial [30–32] and spacecraft applications [33, 34]. In the latter, the absence of buoyancy enhances the effects of radiative transfer. It is important to note that scattering might become significant in the presence of soot, leading to interdependencies of intensities across various directions.

On the other hand, premixed flames have steadily garnered significant interest [6, 17, 35], over the years for their role in flammability limits for slow-burning flames (diluted hydrogen and hydrocarbon flames).

1.5 Objective of this work

The main objective of this work is to assess the role of radiative heat transfer on the quantitative and qualitative behaviour of NH_3 and NH_3/H_2 spherically expanding premixed flames using sophisticated RTE solvers along with detailed kinetics. Once these are included in a numerical tool that enables fine simulations of the configuration studied, the results will be contrasted with those obtained with more usual adiabatic and optically thin models (OTM). Chapters 4 and 5 will be dedicated to these ultimate objectives. The various radiation models will be especially assessed, illustrating their influence on the stretched flame displacement speed, the laminar burning velocity, and the Markstein length.

2 Spherically expanding flames

A spark negelected has often raised a
conflagration

Quintus Curtis Rufus

Contents

2.1	Introduction	13
2.2	Configurations of interest	14
2.2.1	The canonical configuration of the planar freely propagating flame . .	14
2.2.2	Flame speed evaluation	14
2.2.3	Associated experimental techniques	15
2.3	Introduction to stretched flames	19
2.3.1	Background	19
2.3.2	Post-processing extraction	20
2.3.3	Isochoric flame propagation	20
2.4	Some potential effects on the dynamics of expanding premixed flame	21
2.4.1	Effects of radiation	21
2.4.2	Effects of intrinsic flame instabilities	22
2.5	Governing equations and subsequent numerical simulation	23

This chapter is devoted to spherically expanding premixed flames (SEF), highlighting the major characteristics of flame speed and various processes affecting SEF.

2.1 Introduction

Laminar flame speed (S_l) is a fundamental quantity characterizing the properties of the combustible mixture. It also plays an important role in the potential stabilization of premixed flames. Laminar flame speed, also termed as the laminar burning velocity, can be defined with no ambiguity for planar freely propagating flames. But for unsteady flames, it becomes a local property subject to a level of discretion. For planar freely propagating flames, the laminar burning velocity, is defined as the speed at which the unburnt gas propagates towards the flame front within the frame attached to this front.

2.2 Configurations of interest

In this section are briefly outlined the configurations that allow the laminar flame speed and its evolution with the operational conditions to be extracted, from the more canonical one to the one we intend to further model.

2.2.1 The canonical configuration of the planar freely propagating flame

In an idealized case, the laminar flame speed S_L for a planar flame is the eigenvalue of the configuration shown in Fig. 1.4. Within the frame attached to the flame front, S_L can then be obtained from the steady-state of the 1D equations, further described in Section 2.5. The existence of the solution was shown by the pioneering work by Smooke et al. [36].

In a numerical approach, such as that elaborated for the numerical tool FlameMaster that we will extend in the following chapters, the theoretical domain, infinitely long, is approximated by a finite domain of length L , such that the temperature and mass fraction derivatives tend to zero at both ends. Because the mass flow rate is an unknown of the problem (and the very reason why it is investigated), the associated boundary condition at the inlet needs to be released. As a result, an additional internal condition is imposed. Usually, the flame's location is then anchored based on the temperature profile. The mathematical implementation was duly proved and extended by Smooke et al. [36].

In practice, a parameter called flame thickness multiplier (the default value being 1), along with flame thickness, is utilized to set the upstream (fresh gas) and downstream (burnt gas) parts, respectively. It is worth noticing that the flame thickness parameter is pertinent in non-adiabatic flames with re-absorption since the magnitude of re-absorption by the fuel depends on the upstream length, as documented by Ju et al. [6]. A detailed description of the FlameMaster's numerical models can be found in the doctoral work of Hesse [37].

Although planar freely propagating flames have a precise meaning, finding an experimental counterpart coupled with the need for high-pressure measurements is difficult. Hence, scientists utilize other flame configurations, such as Bunsen burners, heat flux burners, stagnation flames, or spherical bombs, for the experimental assessment of flame properties.

2.2.2 Flame speed evaluation

As discussed above, there is a certain level of discretion in defining the laminar burning velocity from experimental measurements. As a result, there are different definitions of flame speeds. Among these, the more documented ones are:

- the flame displacement speed
- the unburnt gas flame speed
- the flame consumption speed

Ideally, as the effects of stretch due to unsteady motion and curvature reduce, the flame consumption speed and the laminar burning velocity converge to a single value, as evidenced in a planar freely propagating flame.

Flame displacement speed

Flame displacement speed is defined as the propagation speed of an isotherm or a consistent location (such as peak heat release rate) relative to the flow field. This can potentially lead to scenarios (shown in Fig. 2.1) with a negative displacement field for the flames with the convective flux directed against the burnt products while the diffusive flux supplies the reactants to the flame [38, 39]. The negative flame displacement speeds are usually encountered in high flame stretch cases.

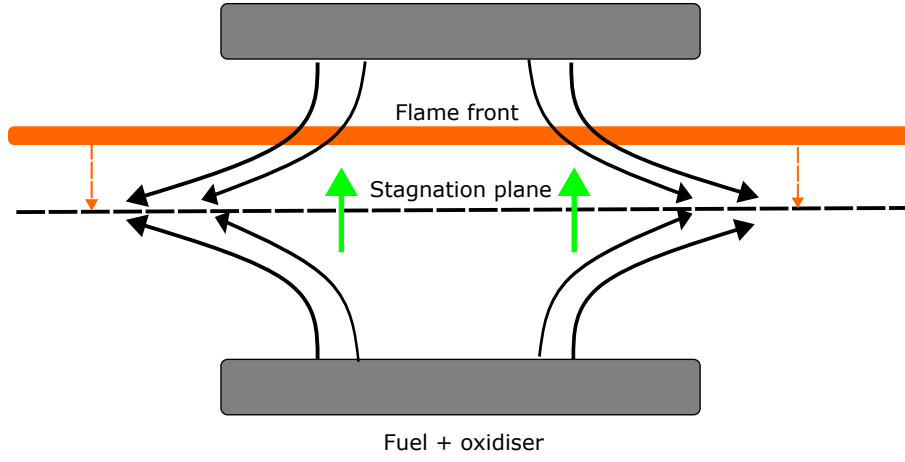


Figure 2.1: Pictorial illustration of a negative flame displacement speed. The orange dashed lines represent the direction of flame propagation, and the green solid lines represent the diffusion from the fresh gases to the flame front. A higher linewidth is used to highlight the critical role of diffusion in these flames. Regenerated from the work of Lieuwen [39]

The flame displacement speed can be assumed to be the burnt gas flame speed, assuming that the magnitude of the inward velocity is low.

$$S_{b,\kappa} \approx \frac{dR_f}{dt} \quad (2.1)$$

The subscript κ in the L.H.S. highlights the stretched nature of the flame displacement speed.

Unburnt gas flame speed

The unburnt gas flame speed can also be termed as a stretched laminar burning velocity. It can be computed as the product of the density ratio and the flame displacement speed.

$$S_{u,\kappa} = \frac{\rho_b}{\rho_u} S_{b,\kappa} \quad (2.2)$$

Here, ρ and $S_{b,\kappa}$ refer to the density and the stretched burnt gas flame speed. The subscripts u and b denote burnt and unburnt, respectively.

Flame consumption speed

Flame consumption speed is defined from a kinetics perspective. It is the integrated reaction rates of the fuel across the flame front. The advantage of this formulation is the distinct, exact nature of the definition. In contrast, we do not have information about the flame radius since we have computed the flame consumption speed from the integrated reaction rates. The definition of flame location requires further assumptions, and equivalent experimental measurements are not feasible. As the stretch reduces, the flame consumption speed and the unburnt gas flame speed converge to a single value.

2.2.3 Associated experimental techniques

As explained before, various experimental flame configurations allow the laminar burning velocity to be extracted and compared against the value provided by the canonical configuration. Konnov et al., [40] have recently detailed the advantages and disadvantages of various experimental reference configurations. In this work, the trade-offs in the selection of the experimental setup are briefly elucidated for:

- the Bunsen burner;
- the heat flux method;
- the stagnation flame;

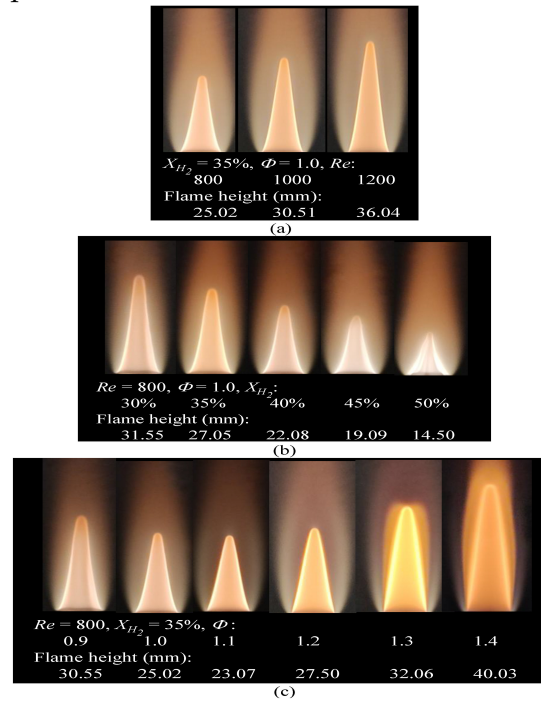


Figure 2.2: Experimental visualizations of blended fuel / air premixed flames established over a Bunsen burner. The blended fuel is a mixture of NH_3 and H_2 , defined by the molar fraction X_{H_2} . The flame height evolution is shown as influenced by: (a) the flow rate (characterized by the Reynolds number Re); (b) the blending (characterized by X_{H_2}); (c) the equivalence ratio Φ . The figure has been taken from the experimental work by Zhen et al., [41]

- the spherical bombs.

Bunsen burner

A Bunsen burner is a widely used experimental setup to determine the laminar burning velocity. The flame in a Bunsen burner is aerodynamically stabilized when the inlet velocity equals the stretched laminar burning velocity. Here, the flame stretched due to the curvature of the flame surface. The stretch flame speed can be determined using either the conical flame angle or the flame area method.

In the former, the angle between the flame surface and the central line is measured using Schlieren or chemiluminescence, which enables the computation of the stretched flame speed, as the center-line velocity is a known quantity. It deals with a certain level of approximation since the flame over the Bunsen burner is not a perfect cone (see Fig. 2.2) due to the effects of stretch attributed to curvature.

In the latter, the stretched laminar burning velocity is given by the ratio of the volumetric flow rate and the surface area of the cone. This method is also subject to uncertainties due to the inability to acquire the surface area of the fresh gases, which is approximated to the surface area of the flame front (via chemiluminescence/PIV or from other experimental diagnostics). Depending on the Lewis number, a Bunsen burner can lead to an open tip (local blow-off) or super-adiabatic temperature, leading to a pronounced flame tip [42].

From Fig. 2.2, we can observe that the Reynolds number Re is not a critical factor other than controlling the flame height via the flow velocity through the nozzle. Meanwhile, as the hydrogen fraction X_{H_2} increases, the laminar burning velocity also increases, leading to a reduction in flame height, which is consistent with the works in the literature [43]. As for the effects of the equivalence ratio Φ , the flame is more intense at $\Phi = 1.1$, leading to a sharp visible front in Fig. 2.2c, whereas for rich mixtures, the flame is more intense orange stemming from the radiation emitted by NH_2^* and H_2O^* in the visible spectrum.

Heat flux method

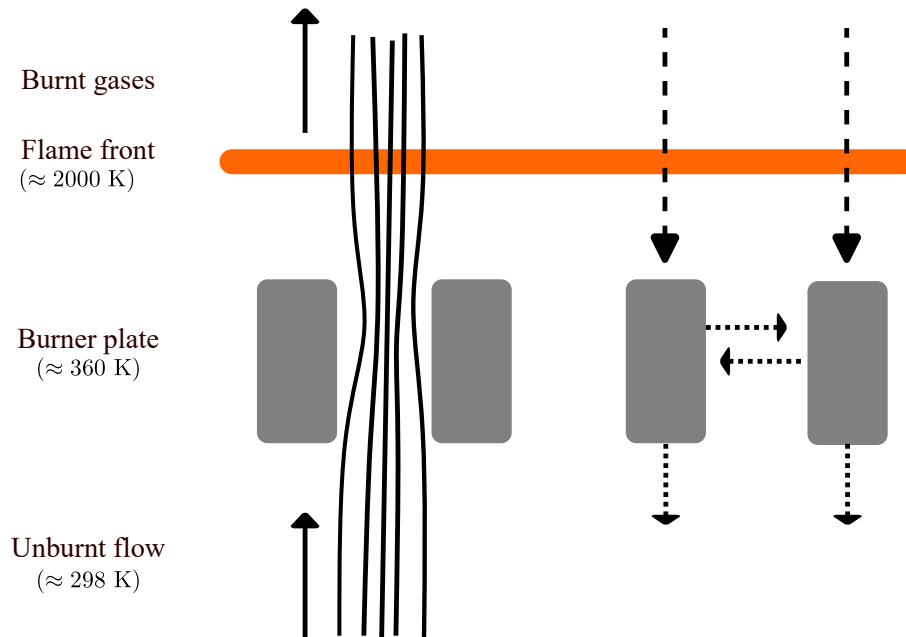


Figure 2.3: Schematic representation of the burner needed for the heat flux method. The orange solid line denotes the flame front stabilized by heat loss to the burner plate and the black solid lines are the streamlines. The direction of the streamlines is represented by solid arrows, while the dashed arrow denotes the direction of heat transfer. This figure has been regenerated based on the work by Goswami et al. [44]

The heat flux method [44, 45] is a modified version of the burner-stabilized flames by Botha and Spalding. In the original configuration, the authors intended to measure the heat loss during the stabilization for various burner inlet velocities. In doing so, they measured the laminar burning velocity by minimizing heat loss. However, the methodology led to flame stabilization issues near the inlet velocity corresponding to the laminar burning velocity. The group of de Goey at TU/e significantly improved the method by placing perforated, preheated burner plates (as seen in Fig. 2.3), thereby accounting for the heat loss to the plate from the flame. The width of the burner plate is selected such that the temperature distribution reaches a one-dimensional distribution, dependent on the radius [46]. Once the flame is stabilized, the radial distribution of the temperature in the burner is measured by thermocouples on the burner plate, allowing for the determination of the heat loss constant for a specified inlet velocity. The laminar burning velocity is the velocity at zero heat loss, a condition which is determined using extrapolation. The methodology is shown to be quite robust at atmospheric pressure. Notable disadvantages include the need for a low nozzle diameter for fuels exhibiting high laminar burning velocity (such as H_2) due to flashback concerns and stabilization issues for high-pressure applications (typically $P \geq 5$ atm).

Stagnation flame

This arrangement enables a classical approach for the determination of laminar burning velocity and was extensively used by various groups across the globe, such as Seshadri [47, 48], Law [49], and many others. Depending on the setup, a twin or single stagnation flame can be obtained (see Fig. 2.4). In a twin-stagnation flame, the reactants are supplied from both sides, leading to a twin flame where the effects of heat loss are minimized, and the flame stabilization is primarily aerodynamic in nature by varying the inlet velocity of the flame. The hydrodynamic stretch can be determined from the velocity gradient, and hence velocity controls the hydrodynamic stretch. In stagnation methods, velocity acquisition is achieved through non-intrusive methods, such as Laser Doppler Anemometry (LDA) or Particle Imaging Velocimetry (PIV), using tracers. In these experiments, it is crucial to maintain a low separation distance to jet diameter, ensuring alignment with the one-dimensional assumption. One of the main limiting factors of stagnation flames is an increase in Reynolds number for high-pressure applications.

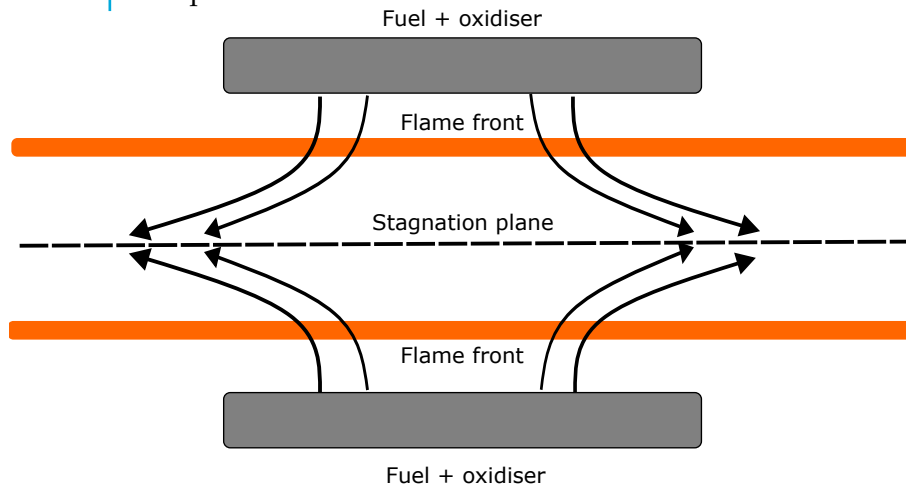


Figure 2.4: Schematic representation of a twin stagnation flame

Spherical bombs

Spherical bombs are one of the most robust and versatile experimental configurations. It has been used by the community since the 1930s [50]. In this setup, the combustible mixture stored in a sphere is ignited at the center by an electrode in a quiescent condition. The versatility of this configuration can be inferred by the fact that the mixture can be ignited in a soap bubble to a steel-enclosed sphere. The subsequent spherical flames are then affected by two main processes:

- Radiative heat transfer, including radiative emission (heat losses mainly in the hot region) and potential radiative re-absorption of the aforementioned radiative energy by the fresh gases;
- Intrinsic flame instabilities.

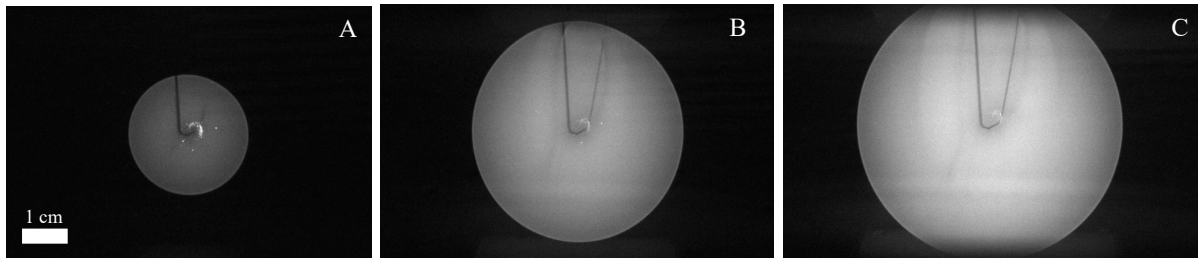


Figure 2.5: Set of frames capturing the expanding flame burning mixture of $\text{NH}_3/\text{H}_2/\text{air}$ mixture (initial conditions: $\phi=0.8$, $P=1$ atm; $T=300$ K). The time from the ignition is: (A) 7.35 ms; (B) 15.9 ms; and (C) 20 ms. Source: private communication from Ir. Victor Cheoux-Damas, ICARE.

Depending on the desired quantity, we can target two regimes of flame propagation:

- the isobaric regime;
- the isochoric regime.

Figure 2.5 shows the flame propagation obtained via high-speed camera (25000 fps) for $\text{NH}_3\text{-H}_2\text{-air}$ flames. These images can be post-processed depending on the operating regimes (isobaric and isochoric), what will be discussed below.

In the isobaric regime, the pressure rise is nearly equal to 1% of the initial pressure. This regime is particularly useful for investigating the effects of stretch on the flame displacement speed. In this configuration, we acquire the flame radius using a high-speed camera, leading to the computation of the flame displacement speed. The stretched burnt gas flame speed (or flame displacement speed) is extrapolated to obtain the unstretched burnt gas speed, leading to the unstretched laminar burning velocity after accounting for the density ratio. Conventionally, the isobaric propagation is limited to $0.5 \times R_0$, with R_0 being the chamber radius.

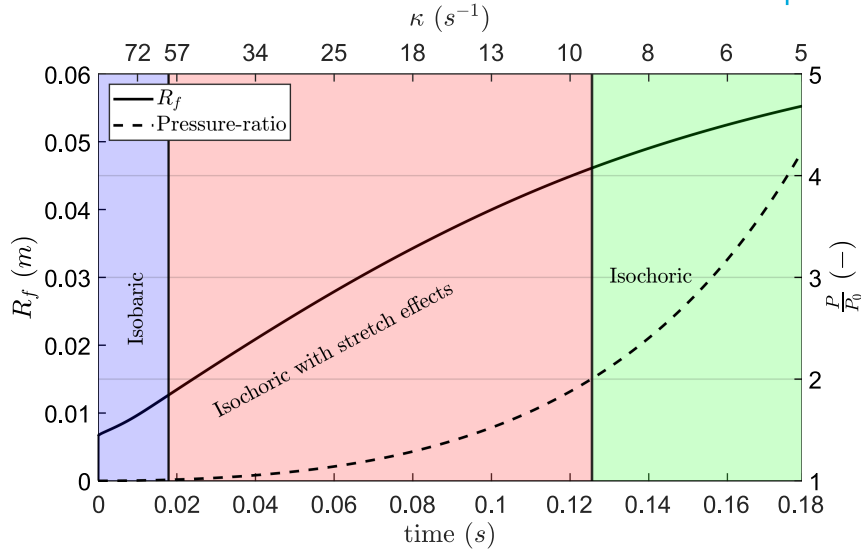


Figure 2.6: Illustration of a spherically expanding flame's isobaric and isochoric regimes throughout the time history of flame radius. In this instance, the pressure rise defining the isobaric regime is set to 1%, and the isochoric region has relatively low flame stretch. The exact criteria are subjective and can vary among various groups.

Figure 2.6 illustrates the flame radius and pressure ratio over the flame propagation time. The flame propagation is divided into three regimes, i.e. (1) the isobaric one (the region with minimal pressure rise), (2) the isochoric flame propagation along with stretch effects, and (3) the isochoric flame with minimal stretch effects. R_f , P , κ , and P_0 correspond to the flame radius, instantaneous pressure, flame stretch, and initial pressure, respectively. In this instance, Fig. 2.6 was generated from a numerical simulation for an initial pressure of 5 atm and an initial temperature of 300 K at stoichiometric conditions for NH_3 -air flames.

In the isochoric regime, pressure increases considerably. For instance, the end pressure can be 5 times the initial one. Due to isentropic compression, the unburnt temperature also increases as the pressure increases. Above $P/P_0 > 2$ [51] (the green region in Fig. 2.6), the stretch effects can usually be neglected at this stage of flame propagation, and a certain level of care needs to be ensured that flame propagation is not affected by the heat losses to the chamber wall.

The pressure trace from the sensor is here the primary experimental output required for this regime, and in the absence of flame radius data (i.e. absence of optical access), we can obtain the laminar burning velocity, albeit subject to certain assumptions for the flame radius.

In the spherical bombs setup, we can isolate the flame process and remove any hydrodynamic flow effects (although the flame will be subject to hydrodynamic and thermo-diffusive instability). Hence, spherical bombs have been used to measure the laminar burning velocity of H_2 up to 60 atm and are a primary source for the database of laminar burning velocity sustained by various groups across the globe.

2.3 Introduction to stretched flames

2.3.1 Background

Flame stretch κ , as introduced among others by Williams [52], is given by a seemingly innocuous equation:

$$\kappa = \frac{1}{A} \frac{dA}{dt} \quad (2.3)$$

where A is the flame surface that evolves with time t . Thus, the stretch appears as the normalized rate in s^{-1} at which the flame surface spreads over.

In the general case of a multidimensional problem, the change in the flame area - or flame stretch - can be expressed as follows [53]:

$$\kappa = \nabla_t \cdot \mathbf{V}_f + (\mathbf{V}_f \cdot \mathbf{n})(\nabla \cdot \mathbf{n}) \quad (2.4)$$

where $\mathbf{V}_f$ is the instantaneous velocity of the flame surface, $\mathbf{n}$ the unit vector normal to the local flame surface pointing in the direction of the propagation, ∇ the first spatial derivative (or gradient) operator, and ∇_t this operator restricted to the components encompassed within the plane whose normal is $\mathbf{n}$. Then, assuming the tangential velocity of the flame surface is equal to the tangential component of the flow velocity, the stretch is expressed as follows:

$$\kappa = \nabla_t \cdot \mathbf{v}_{s,t} + (\mathbf{V}_f \cdot \mathbf{n})(\nabla \cdot \mathbf{n}) \quad (2.5)$$

Eq.(2.5) thus shows that the stretch appears as the accumulation of two contributions. The first one in the LHS is a strain due to the non-uniformity of the flow velocity. The second one is a combination of the effects of the unsteady motion of the flame surface (when $\mathbf{V}_f \neq \mathbf{0}$) and its curvature (when $\nabla \cdot \mathbf{n} \neq 0$). The above relation can be applied to a 1-D spherically symmetric expanding flame. This readily leads to the following expression:

$$\kappa = \frac{2}{R_f} \frac{dR_f}{dt} \quad (2.6)$$

where R_f is the flame radius.

2.3.2 Post-processing extraction

The strategy that enables the evaluation of the stretch time history along the expansion of a spherical premixed flame is governed by the regime that the flame is experiencing.

Isobaric flame propagation

The post-processing of the experimental and numerical flames requires computing the flame displacement speed as a function of flame stretch. The effects of radiative cooling (inducing flow towards the chamber's center) throughout the burned gas can be neglected without loss of accuracy, at least for NH_3 -air flames. Determining the unstretched flame speed from the stretched flame speed requires a nonlinear extrapolation, subject to some uncertainties and approximations. The extrapolation relations are obtained from the slowly varying flame (SVF) formulation with small heat loss $\mathcal{O}(\frac{1}{\beta})$ [54], where β is the Zeldovich number (also denoted as Ze in the literature). The coordinate system and variables are scaled such that $x < 0$ and $x > 0$ denote the domains of burnt and fresh gases, respectively. In the formulation of the SVF, the radiative reabsorption is ignored. In this work, the extrapolation routine of Kelly and Law [3] is utilized. The non-linear extrapolation of Kelly and Law [3] is given by:

$$\left(\frac{S_b}{S_{b,0}}\right)^2 \ln\left(\frac{S_b}{S_{b,0}}\right)^2 = -\frac{2 L_b \kappa}{S_{b,0}} \quad (2.7)$$

The subscript 0 indicates the extrapolated quantity. S_b and L_b correspond to the burnt flame speed and the Markstein length, respectively. In this work, the flame front located at a radial distance R_f is defined as the location of the peak heat release rate, and the burnt flame speed is calculated from the temporal derivative of R_f . The LBV (S_l) can be obtained from the density ratio ($\frac{\rho_b}{\rho_u}$) and the extrapolated burnt gas flame speed. The subscript 0 denotes an extrapolated quantity.

$$S_l = \frac{\rho_b}{\rho_u} S_{b,0} \quad (2.8)$$

2.3.3 Isochoric flame propagation

The post-processing of isochoric flame propagation differs from the isobaric case, as the flame displacement speed ($\frac{dR_f}{dt}$) spans over different thermodynamic pressures. To compute the laminar burning velocity, we invoke the isentropic compression model together with the assumption that the flame stretch is minimal after the pressure ratio of 2:

$$\frac{dP}{P} = -\gamma_u \frac{dV}{V} \quad (2.9)$$

V is the volume of the concentric sphere between the flame radius R_f and vessel radius R_0 , and γ_u is the ratio of the specific heat capacity of the unburnt gaseous mixture. To compute the volume change, the velocity of the unburnt gas at the flame front is used, i.e., $\frac{dR_f}{dt} - S_l$ from [55], leading to:

$$\frac{dP}{P} = \frac{3\gamma_u R_f^2 (dR_f - S_l \times dt)}{R_0^3 - R_f^3} \quad (2.10)$$

After re-arrangement, we get:

$$S_l = \frac{dR_f}{dt} - \frac{R_0^3 - R_f^3}{3\gamma_u P R_f^2} \frac{dP}{dt} \quad (2.11)$$

In the absence of optical access (as in the case of the steel enclosure over the spherical bomb due to safety concerns), some approximations are made to compute the radius from the pressure rise in the chamber via the burnt mass fraction. This approximation involves the radiative heat loss. The approximation for the burnt mass fraction x is given as follows[56]:

$$x = \frac{P - P_0 \times f(P)}{P_{\text{final}} - P_0 \times f(P)} \quad (2.12)$$

$$f(P) = \frac{\gamma_b - 1}{\gamma_u - 1} + \frac{\gamma_b - \gamma_u}{\gamma_u - 1} \left(\frac{P}{P_0} \right)^{(\gamma_u - 1)/\gamma_u} \quad (2.13)$$

The fraction x is very sensitive to the specific heat ratio of the burnt gas, γ_b , and consequently to the burnt gas temperature. As a result, this requires terms to account for the heat loss, such as (see Faghieh and Chen [56] for an extended review of the usual corrections),

$$\gamma_{b, \text{shift}} = \frac{\gamma_b + 8}{8} \quad (2.14)$$

The need for this kind of empirical correction might be partially released provided that fine modelling of heat losses, such as the radiative ones, is assessed.

2.4 Some potential effects on the dynamics of expanding premixed flame

2.4.1 Effects of radiation

Radiation has been one of the critical factors that needs to be accounted for in the spherically expanding flames. H_2O and CO_2 are the main source of thermal radiation in combustors.

As a result, radiation plays a crucial role in the numerical determination of the lean flammability results of spherically expanding flames. This has been illustrated for CH_4 - O_2 - N_2 flame by Sibulkin and Frendi [5] against the experiments conducted by Ronney in microgravity [57]. The adiabatic models were not able to capture decently the flammability limits observed in the experiments.

The work by Ju et al. [6] also demonstrated the effects of pre-heating by radiative re-absorption for planar CH_4 flames and the existence of unique (domain-independent) flammability limits.

Furthermore, Chen et al. [17] illustrated the effects of over-prediction of heat loss by the versatile still rough optically thin method (OTM) as compared to the adiabatic (ADI) models, highlighting especially the effects of pressure on the level of radiative re-absorption. These authors utilized the discrete ordinate method (DOM) in conjunction with fitted statistical narrow band-correlated k-distribution (F-SNBCK). They observed that DOM+F-SNBCK was over-predicting the laminar burning velocity S_l , and with increased pressure, the discrepancy reduced. Most importantly, they studied the effects of flame radius on the Boltzmann number, i.e. the ratio of convective transfer to radiative transfer, and found that the Boltzmann number increased with flame radius. In contrast, with the OTM model, it decreased with

flame radius.

Additionally, Zheng Chen [58, 59] conducted a series of studies on the effects of radiation on the flame dynamics for (1) ultra-lean methane/air flames to highlight the coupling of the radiative processes and chemistry and (2) large-scale flames. In the former configuration, the authors noted that radiation plays a pronounced role near the flammability limits and, hence, plays a pivotal role in the validation of the kinetic mechanism. In the latter configuration, the authors observed that for near-stoichiometric flames, the role of radiation is minimal for flames of a radius smaller than 4 cm. For large-scale adiabatic flames, the flame displacement speed is nearly constant. In addition, the discrepancy between DOM+ F-SNBCK and OTM is increasing with the flame radius, and the flame speed predicted with the use of OTM is drastically reduced due to radiative emission.

It is finally worth mentioning that the work by Yu et al. [7] is an important study as it developed corrections accounting for radiative heat transfer. It is mainly targeted towards the experimental setup, such that the experimental measurements (which involve radiation) are corrected to yield the adiabatic results. These results can then be compared against the 1-D planar adiabatic simulations. The authors highlight that the work only accounts for radiative emission and is not valid for fuels diluted with radiatively participating species, such as steam diluted H_2 , exhaust gas recirculation, etc.

2.4.2 Effects of intrinsic flame instabilities

As a spherical premixed flame is expanding, intrinsic flame instabilities can be triggered. These instabilities can be broadly classified into three types based on the underplay of physical mechanisms involved, i.e.:

- thermo-acoustic instabilities;
- thermo-diffusive instabilities;
- hydrodynamic instabilities.

Thermo-acoustic instabilities

Thermo-acoustic instabilities are an important phenomenon that needs to be accounted for in high-pressure combustion systems. As suggested by the term itself, it is due to the coupling between the acoustic waves stemming from the pressure waves and the heat-release rate. It was so severe that Vostok 1 had a 50% chance of exploding due to the thermo-acoustic instability [60]. It remains challenging for high-pressure applications such as liquid rocket engines and rotating detonation engines.

Thermo-diffusive instabilities

Thermo-diffusive (TD) and hydrodynamic instabilities are closely coupled phenomena, where the preferential diffusion between heat transfer and mass transfer (the preferential diffusion is characterized by the Lewis number of the mixture, Le) and the density ratio tend to destabilize the local flame propagation. It leads to segmented flames, with the size of the structures determined by the critical processes. As the flame propagates, in the initial stages, the diffusive process stabilizes the flames, whereas as the flame expands, hydrodynamic instabilities dominate the process, and in between, the flames are affected by a combination of them. Depending on the Lewis number, the thermo-diffusive instability can be categorized into:

1. Cellular structures for $Le < Le_{crit1}$
2. Pulsating instability for $Le > Le_{crit2}$

Le_{crit1} and Le_{crit2} are the respective critical Lewis numbers, with the former being close to 1, and can be given as:

$$Le_{crit1} = 1 - \frac{Pr B_3 + B_1}{Ze B_2} \quad (2.15)$$

In Eq. (2.15), Pr , B_1 , B_2 , and B_3 represent the Prandtl number, coefficients of thermal conduction, mass diffusion, and viscosity, respectively and these are function of the density ratio. Le_{crit1} can be also approximated to $Le_{crit1} = 1 - \frac{2}{Ze}$ [61] for conditions of weak thermal expansion. The above assumption is not completely valid, but the results do provide insight into the global flame dynamics.

Le_{crit2} is usually large such that, $Le > \frac{10.928}{Ze} + 1$, where Ze is the Zeldovich number. Hence, it is not usually observed in the experiments [62, 63].

The formation of cellular structures is primarily due to discrepancies between heat diffusion and species near the flame front. The stretch further aggravates this Le number effect along with the differential diffusion. The thermo-diffusional instability has been the target of the community due to its self-acceleration nature, and depending on the Markstein length (L_b), in the extremes, the flame can be either dissipated due to excessive stretch or local blow-off due to flame augmentation from the mass diffusivity. Le_{crit1} is pivotal in the determination of the sign of the Markstein length L_b . If a Lewis number of the mixture is below Le_{crit1} , L_b is negative, and the flame is thermo-diffusively unstable, and vice-versa for the Lewis number above Le_{crit1} . The Markstein length L_b can be viewed as the slope of the flame displacement speed over the stretch. The exact formulation of L_b for a linear model is then:

$$S_b = S_{b,0} - L_b \kappa \quad (2.16)$$

This leads to:

$$L_b = -\frac{dS_b}{d\kappa} \quad (2.17)$$

Figure 2.7 illustrates the effects of the Markstein length L_b on the dissipation/amplification of perturbations of a flame front between two consecutive time steps (t_1 & t_2). First, S_b over κ is shown on the left of the figure. The figure in the center illustrates the dissipation of the perturbation via deceleration in the crests and acceleration in the troughs, which can be inferred from the plot of S_b over κ . Conversely, the perturbations' amplification scenario is shown on the right of the figure.

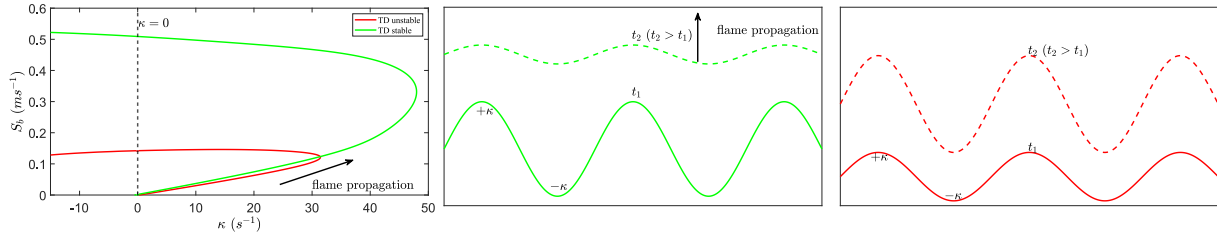


Figure 2.7: Left: Illustration of the evolution of the burnt gas flame speed S_b over stretch κ for thermo-diffusively stable (green solid line) and unstable (red solid line) flames; Center: Illustration of the damping of the fluctuations along the stable flame front stemming from positive L_b ; Right: Illustration of the amplification of thermo-diffusive instability due to self-acceleration of the flame stemming from negative L_b . The initial increase in stretch in the left is the ignition-affected regime.

Hydrodynamic instabilities

Hydrodynamic instabilities are also known as the Darrieus-Landau instability, named after Georges Darrieus from Toulon, France, and Lev Landau from the USSR. Hydrodynamic instability is due to the gas expansion in the burnt section following the heat release, and hence, any small perturbations in the unburnt gas tend to affect the burnt gas disproportionately. This instability leads to flames with larger cell sizes, similar to segmentation in a football [61].

It is worth mentioning that Matalon [61] has pedagogically discussed the hydrodynamic and thermo-diffusive instabilities of the flames discussed here.

2.5 Governing equations and subsequent numerical simulation

To assess the magnitude of the above potential effects, the modeling and the subsequent numerical simulation are of high importance, given the computational resources that are available today. Consequently,

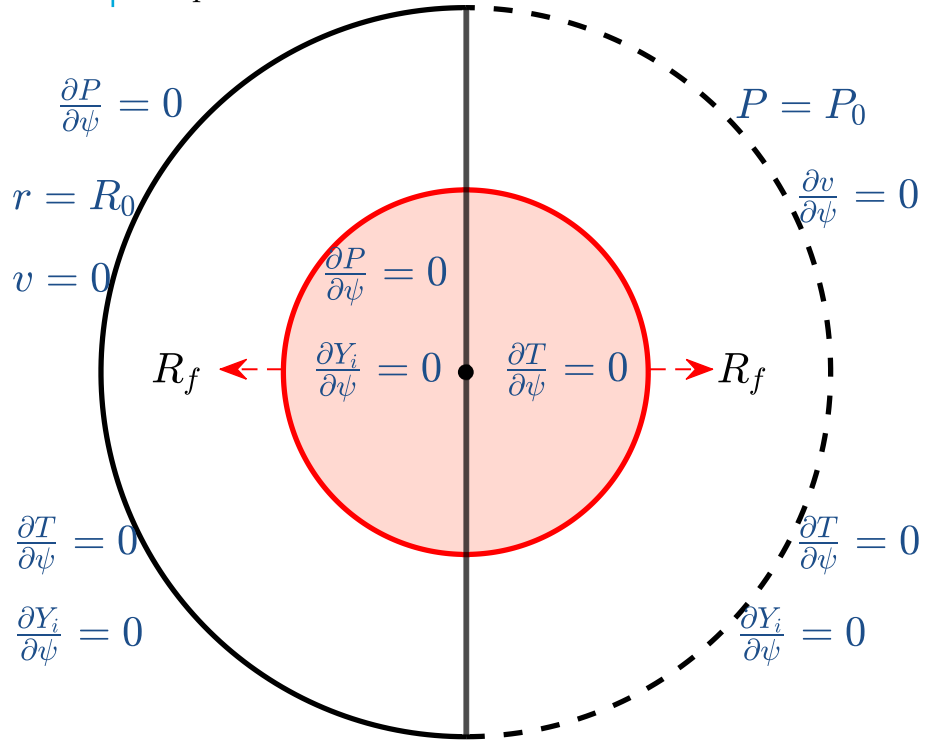


Figure 2.8: Schematic of spherically expanding flames for the isochoric configuration (left half of the circle) and the isobaric one (right half of the circle). The shaded regions illustrate the burnt gas region, and the red solid line denotes the flame front of radius R_f . The boundary conditions for the origin ($r=0$) are given inside the red circle. Those at the other domain's end ($r = R_0$) stand outside the black circle.

this section describes the governing equations that drive the propagation of a premixed flame. More specifically, these equations are further derived in the configuration of 1-D spherical symmetric flames, as used among other numerical tools by FlameMaster [2].

FlameMaster is an open-source finite difference solver that can simulate a range of flames from planar premixed flames to counterflow premixed ones. FlameMaster employs a Lagrangian coordinate transformation to eliminate the advective terms. The mathematical implementation is inspired by the work of Maas and Warnatz [64].

The spherically expanding flames using isochoric and isobaric numerical configurations are illustrated in Fig. 2.8.

Continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (2.18)$$

Species

$$\frac{\partial \rho w_i}{\partial t} + \nabla \cdot (\rho \mathbf{v} w_i) + \nabla \cdot \mathbf{j}_i = \dot{\omega}_i M_i \quad (2.19)$$

Momentum

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla P - \nabla \cdot \boldsymbol{\tau} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \mathbf{0} \quad (2.20)$$

Energy

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho \mathbf{v} h) - \left(\frac{\partial P}{\partial t} + \mathbf{v} \cdot \nabla P \right) + \nabla \cdot \mathbf{j}_q + \boldsymbol{\tau} : \nabla \otimes \mathbf{v} = \dot{q} - \nabla \cdot \mathbf{q}_{\text{rad}} \quad (2.21)$$

Here ρ , $\mathbf{v}$, w_i , M_i , $\dot{\omega}_i$, $\mathbf{j}_i$, $\mathbf{j}_q$, $\boldsymbol{\tau}$, and h denote the material density, the velocity vector, the mass fraction of species i , molar mass of the species i , the molar production rate of the species i , the diffusion flux of species i , the heat flux vector, the stress tensor, and the enthalpy per unit mass of the mixture respectively. $\dot{q}$ and $\mathbf{q}_{\text{rad}}$ denote the heat source (ignition energy or exothermic reactions) and the radiative heat flux vector.

Now, we convert the equations into Lagrangian formulation, using the following relation [37, 64, 65]:

$$\psi = \int_0^r \rho r^2 dr \quad (2.22)$$

The relation between the Lagrangian coordinate (ψ) and radial coordinate (r) is given by $\frac{\partial r}{\partial \psi} - \frac{1}{\rho r^2} = 0$. The system of equations is further simplified by ignoring the momentum equation via the assumption of uniform pressure ($\nabla P = 0$), that can still be unsteady ($\frac{dP}{dt} \neq 0$). The unsteady pressure terms are significant for the isochoric flame configuration. As for isobaric flames, the domain expands/contracts to maintain the isobaric nature of the flame [37].

Including the Lagrangian formulation, the conservation equations become [37, 64],

Mass

$$\frac{\partial \rho}{\partial t} + \rho^2 \frac{\partial}{\partial \psi} (\mathbf{v} r^2) = 0 \quad (2.23)$$

Species

$$\frac{\partial w_i}{\partial t} + \frac{\partial}{\partial \psi} (\rho r^2 w_i \mathbf{V}_i) - \frac{\dot{w}_i M_i}{\rho} = 0 \quad (2.24)$$

Equation of state

$$P - \frac{\rho R T}{M} = 0 \quad (2.25)$$

Energy in terms of temperature

$$\begin{aligned} \frac{\partial T}{\partial t} - \frac{1}{\rho c_p} \frac{\partial P}{\partial t} - \frac{1}{c_p} \frac{\partial}{\partial \psi} \left(\rho r^4 \lambda \frac{\partial T}{\partial \psi} \right) + \frac{r^2}{c_p} \sum_{i=1}^{n_s} \rho w_i \mathbf{V}_i c_{p,i} \frac{\partial T}{\partial \psi} \\ + \frac{r^2}{\rho c_p} \sum_{i=1}^{n_s} \dot{w}_i h_i M_i = -\frac{1}{\rho c_p} (\nabla \cdot \mathbf{q}_{rad}) + \frac{\dot{q}}{\rho c_p} \end{aligned} \quad (2.26)$$

Here,

$$\mathbf{V}_i = \mathbf{V}_{d,i} + \mathbf{V}_{t,i} + \mathbf{V}_c \quad (2.27)$$

with

$$\mathbf{V}_{d,i} = -\frac{1}{w_i} \mathcal{D}_{i,m} \nabla w_i \quad (2.28)$$

As before, $\mathbf{V}_i$ represents the diffusion velocity of the species i for the diffusion flux, which is the sum of the ordinary diffusion velocity of species i ($\mathbf{V}_{d,i}$), the thermal diffusion velocity of species i ($\mathbf{V}_{t,i}$), and the correction velocity at that spatial location ($\mathbf{V}_c$). The $\mathbf{V}_{d,i}$ is given by the Curtis-Hirschfelder approximation. The finite difference method is used for the spatial derivatives for the above system of equations, while the method of lines (MOL) is used for the temporal derivatives. The temporal derivatives are solved implicitly using a varying-order backward differentiation formula (BDF) using the CVODE solver.

The thermal conductivity (λ) and diffusion coefficients ($\mathcal{D}_{i,m}$) were computed from the ideal gas law. The effects of real gas were not significant for evaluating the thermophysical properties (ρ , c_p , h_i , and so on), even at high-pressure cases such as 50 atm. The mixture's thermal conductivity and diffusion coefficient are evaluated using Mathur and the mixture-averaged formula, respectively [66].

As stated previously, the RTE - solved to compute $\nabla \cdot \mathbf{q}_{rad}$ in the energy equation above - in a spherically symmetric configuration between $[0, R_0]$ is,

$$\mu_i \frac{\partial I_{\eta,i}}{\partial r} + \frac{1 - \mu_i^2}{r} \frac{\partial I_{\eta,i}}{\partial \mu_i} = \kappa_{\eta} I_{b,\eta} - \kappa_{\eta} I_{\eta,i} \quad (2.29)$$

where μ_i and r are the directional cosine of direction i and the radial distance. The RTE needs two boundary conditions for the two directions of propagation. For the inward propagation ($\mu < 0$), the boundary condition is the blackbody emission term at the location $r = R_0$. The perfectly reflecting boundary condition at the origin is used for the outward propagation ($\mu > 0$). The spectral database

for $\text{NH}_3\text{-H}_2\text{O}$ is developed from high-resolution spectral databases for varying spectral resolution. The developed spectral models were tested for some decoupled test cases in Chapter 3.

3 Spectral models of radiative properties for species met in NH₃-air flames

What fire does not destroy, it hardens

Oscar Wilde

Contents

3.1	Introduction	28
3.2	Spectroscopic databases and line-by-line model	30
3.2.1	Background	30
3.2.2	Spectroscopic databases	30
3.2.3	Line-by-line model	31
3.3	Statistical narrow band	32
3.3.1	SNB parameters	33
3.3.2	Narrow band (NB) correlated-k and k-g distribution	33
3.4	Global models	36
3.4.1	RCFSK	36
3.4.2	Multi-scale RCFSK	37
3.4.3	WSGG model	38
3.4.4	Assessment of WSGG	38
3.5	Verification of DOM	39
3.6	Reduced SNBCK	39
3.7	Application to radiative heat transfer in flames	40
3.7.1	Premixed flames	40
3.7.2	Non-premixed flames	42
3.7.3	Applicability of reduced SNBCK to other species	44
3.8	Line of sight for premixed flames	44
3.9	Conclusions on the spectral modelling	45
3.10	Spectral models' implementation in RTE resolution	45

This chapter inspired the article “Performances of approximate radiative property models for conditions met in ammonia combustion,” which appeared in the International Journal of Thermal Sciences, Volume 213, July 2025.

3.1 Introduction

Radiative heat transfer is a complex phenomenon, especially due to its spectral and directional dependencies. As a result, specific attention is to be paid to capture these spectral and directional features when radiative heat fluxes are to be evaluated. To a large extent, the modelling level is affected by the selection of:

1. a spectral model that describes the radiative properties of the species over different spectral intervals [16, 26].
2. a radiative transfer equation (RTE) solver, such as the discrete ordinate method (DOM) [26, 67], discrete transfer method (DTM) [68], ray tracing [69], or the Monte Carlo method [70], that has to capture the potential anisotropy of radiation.

Various levels of spectral models are available in the literature. Starting from the elementary contributions, the Line-By-Line (LBL) model describes the absorption lines over wavenumber with a typical spectral resolution of $0.005 - 0.01 \text{ cm}^{-1}$, leading to around $2 \times 10^6 - 10^6$ RTEs to be solved for wavenumber ranging from 50 cm^{-1} to $10,000 \text{ cm}^{-1}$. LBL solutions are usually used as a reference to benchmark other models. Narrow band (NB) models evaluate the radiative properties over a set of spectral intervals with a typical width around 25 cm^{-1} . Over each interval, the Planck function (also referred to as the spectral blackbody intensity in the literature [71]) remains nearly constant. The statistical narrow band (SNB) model, which utilizes statistical arguments to describe the average transmissivity [8], shows high accuracy but cannot be used with all radiative solvers since transmissivity is the primary output of SNB, whereas the absorption coefficient is the primary input of most of the RTE solvers. To overcome this difficulty, models based on the k-g distribution concept can be used to compute the spectrally averaged radiative intensity [16]. Narrow band correlated k-distribution models rely on the concept of re-ordering the absorption coefficient into a narrow band (i.e., over an interval of nearly constant Planck function) such that each absorption coefficient is solved only once. It is accurate but computationally expensive since the RTE has to be solved for every narrow band. Full-spectrum k-distribution (FSK) relaxes the assumption of constant Planck function by accounting for its variation. It is computationally efficient, but its performance needs to be examined since it relies on the concept of correlated / scaled / comonotonic k-distribution to solve the full spectrum [26].

In the present work, rank correlated (comonotonic) full-spectrum k-distribution [72] is used to resolve the non-constant Planck function which leads to Leibnitz terms [73]. When facing an extremely non-uniform path, multi-scale full-spectrum k-distribution [71, 74], which solves for 2 or more scales taking into account the overlap between the scales, may be preferred. The weighted sum of grey gases (WSGG) [75, 76] is also a full spectrum model where the total integrated behaviour is described by 2 or more grey gases. It is worth highlighting here that the performances of the overall modelling highly depend on the combination of the RTE solver and the spectral models used as input in the RTE.

While locally exhibiting extremely non-uniform fields, the premixed flame structure can be represented by a two-layer system with, on one side, the cold fuel-oxidizer mixture and, on the other side, the hot combustion products. In this configuration, the thermal radiative transfer is characterized by a net emission from the relatively hot products and a net absorption by the relatively cool reactants. Still, the magnitude of the latter contribution highly depends on the spectral nature of the reactants. Using profiles of temperature and species mole fractions provided by the numerical simulation of a canonical laminar 1D premixed flame at atmospheric pressure, Fig. 3.1(A) illustrates the radiative pre-heating effect that might occur within a NH_3 -air premixed flame. To obtain the evolution of the local radiative balance $\nabla \cdot q_{\text{rad}}$ throughout the flame, the evaluations of the local radiative properties, i.e. the local spectral absorption coefficient κ_η and the local emission term $\kappa_\eta I_{b\eta}$, are needed. As a result, Fig. 3.1(B) and 3.1(C) show $\kappa_\eta I_{b\eta}$ (right y-axis) as a function of wavenumber, η , for a hot product, i.e. H_2O at 2000 K, 1 atm and

mole-fraction of 0.2. In addition, Fig. 3.1(B) and 3.1(C) display κ_η (left y-axis) as a function of η for a cold fuel at 300 K, 1 atm, and mole-fraction of 0.2, i.e. (B) NH_3 , and (C) CH_4 . The discrepancy of the spectral overlap between the burnt product and the cold fuel may then lead to significant modification of the radiative transfer effect on the flame's structure. It is worth noting here that the spectral overlaps shown in Fig. 3.1 are purely illustrative. These are obtained from the post-processing of the fields provided by numerical simulations that did not include any radiative modelling.

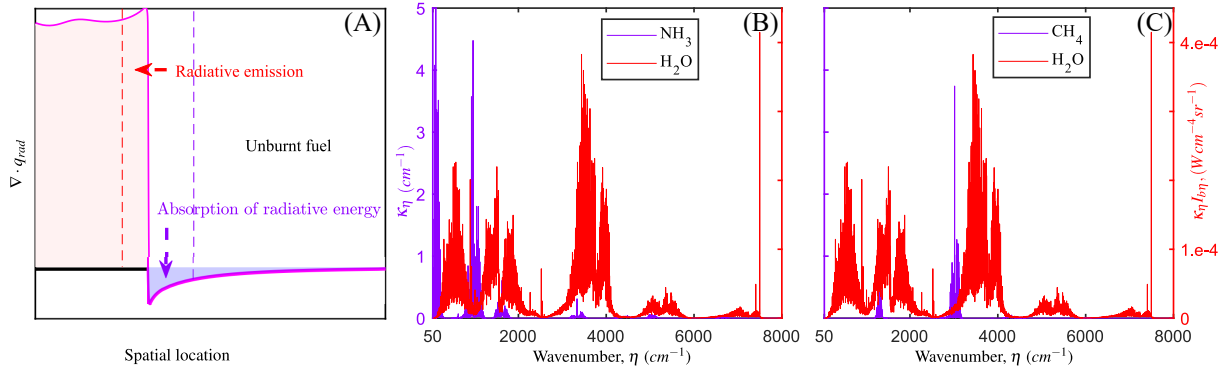


Figure 3.1: (A) Illustration of the computed divergence of the radiative heat flux throughout a canonical laminar unstretched 1D premixed flame at atmospheric pressure; (B) Spectral overlap between the spectral absorption coefficient κ_η (left y-axis) of cold NH_3 (300 K, 1 atm, mole fraction of 0.2) and the spectral radiative intensity $\kappa_\eta I_{b\eta}$ (right y-axis) of hot H_2O (2000 K, 1 atm, mole fraction of 0.2); (C) Spectral overlap for the equivalent configuration as NH_3 is substituted by CH_4 . The dashed lines in (A) indicate the locations where the conditions selected for the hot and cold species, respectively, might be observed in the canonical flame.

Ju et al. [6] reported one of the first numerical studies on the effects of radiative re-absorption on premixed flame structure. These authors simulated unstretched planar laminar premixed $\text{CH}_4/\text{O}_2/\text{N}_2$ flames seeded with CO_2 by using the PREMIX code and the SNB model. They observed that the absorption of radiation by the fuel increases the laminar burning velocity and leads to a higher flammability range. Later on, noticeable works assessed the effect of radiative re-absorption for spherically expanding premixed flames. Among them, Chen et al. [17] also reported a significant additional preheating of the unburnt gases due to radiative heat transfer for $\text{CH}_4/\text{O}_2/\text{He}$ flames seeded with CO_2 . Investigating H_2/air flames seeded with H_2O , Zenou and Vicquelin [35] noticed that radiative absorption increases the temperature of the unburnt gases and lead to a 500% increase in flame speed for very slow flames.

In contrast, few works addressed radiative heat transfer effects for pure NH_3 and its blends. Zheng et al. [77] studied the impact of radiative re-absorption on the flame speed of NH_3/H_2 mixtures. They used PREMIX to simulate planar freely propagating flames. The spectral properties of H_2O and NH_3 were modelled using the EM2C SNB database [78] and HITRAN 2016 [79], respectively, whereas the ray tracing method was considered as the RTE solver. These authors observed that considering the radiative re-absorption increased the laminar flame speed and led to a finer agreement with the experiments. They also investigated the effects of radiation on the flame structure, leading to the conclusion that considering radiation increased the flame temperature and NO peak mole fraction. The authors finally assessed the effects of pressure on the laminar flame speed and the sensitivity to the key reactions. Zheng et al. [80] later studied the effects of radiation on the ignition of 1D spherically symmetric $\text{NH}_3/\text{H}_2/\text{H}_2\text{O}/\text{N}_2$ mixture at equivalence ratio of $\phi = 1.2$ with different levels of H_2O . Thermal radiative transfer was solved with ray tracing and a SNB model based on HITRAN 2016. These authors assessed the effects of radiation on the flame thickness, heat release rate, and the minimum ignition energy. They noted that simulations with the SNB model predicted higher and lower minimum ignition energy for flame propagation compared to those run with the adiabatic assumption and the optically thin approximation (OTM), respectively. Zheng et al. [81] also investigated the role of radiation in $\text{NH}_3/\text{CH}_4/\text{air}$ freely propagating flames using PREMIX and the SNB model coupled to ray tracing. They showed that radiation re-absorption increased the burning velocity for all the equivalence ratios in the range 0.6-1.5 and that this enhancement behavior displayed a nonlinear trend, first reducing and then increasing with ϕ . The preheat-induced chemical effect was found to be the dominant factor when $\phi \in [0.6, 1.2]$, whereas the direct radiation effect prevails for $\phi \in [1.2, 1.5]$.

Previous works on NH_3 premixed flames have used the SNB model to compute spectral properties, coupled with ray tracing as the RTE solver. The extension of ray tracing to 2-D and 3-D computations will come up at a significant computational cost; hence, dedicated k-distribution models are needed for ammonia-air flames. As a result, the main objective of the present part is to investigate the performance of k-g distribution and WSGG models. To this end, various spectral models for ammonia-air flames for decoupled flame fields are selected. Four flame fields are considered:

- Flame fields corresponding to NH_3 -air spherically expanding premixed flames at 5 atm and 20 atm [82].
- Flame fields corresponding to NH_3 -air planar freely propagating premixed flames at 5 atm and 20 atm.
- Flame fields corresponding to NH_3/CH_4 -air spherically expanding premixed flames at 5 atm and 20 atm [83].
- A synthetic non-premixed flame field at different heights above the burner and for a set of pressure levels.

3.2 Spectroscopic databases and line-by-line model

3.2.1 Background

The spectral RTE for an emitting-absorbing non-scattering medium is expressed as follows [26]:

$$\frac{dI_\eta}{ds} = \kappa_\eta(\phi) [I_{b\eta}(T) - I_\eta] \quad (3.1)$$

where I_η , κ_η , and $I_{b\eta}$ are the local spectral radiative intensity, the local spectral absorption coefficient, and the blackbody intensity at wavenumber η , respectively. ϕ is a set of thermophysical properties affecting the absorption coefficient of the gaseous species, i.e. the pressure, p , the molar fraction, x , and the temperature, T .

The spectrally-integrated radiative intensity, I , and the divergence of the radiative flux, $\nabla \cdot \mathbf{q}_{\text{rad}}$, can then be computed using the following formulations:

$$I = \int_0^{+\infty} I_\eta d\eta \quad (3.2)$$

$$\nabla \cdot \mathbf{q}_{\text{rad}} = 4\pi x p \kappa_p I_b(T) - \int_0^{+\infty} \kappa_\eta \left(\int_{4\pi} I_\eta d\Omega \right) d\eta \quad (3.3)$$

with κ_p the pressure-based Planck-mean absorption coefficient, defined as [26]:

$$\kappa_p(T) = \frac{1}{I_b(T)} \int_0^{+\infty} \frac{\kappa_\eta(\phi)}{x p} I_{b\eta}(T) d\eta \quad (3.4)$$

3.2.2 Spectroscopic databases

The absorption coefficients as a function of pressure, temperature, mole fraction, and wavenumber were taken from the high-resolution spectroscopic databases. HITRAN 2020 [84] was considered for NH_3 , HITEMP 2020 [85] for CH_4 , HITEMP 2019 [86] for NO , N_2O , NO_2 , and HITEMP 2010 [87] for H_2O , CO_2 , and CO . It is worth mentioning that spectra for hot ammonia were improved in HITRAN 2020 as compared to HITRAN 2016 [79] with the inclusion of a new hot line list, CoYuTe, designed for temperature up to 1500 K [84, 88].

Figure 3.2 shows the absorption coefficients (averaged over 1.0 cm^{-1} for legibility whilst preserving the line details) of NH_3 at 300 K and 700 K and a partial pressure of 0.1 atm. Due to its pyramidal structure, NH_3 has 6 vibrational degrees of freedom with double degeneracies [89]. The four fundamental vibrational band centers of NH_3 are around 932.5 cm^{-1} to 968 cm^{-1} (symmetric bend), 1626.1 cm^{-1} (asymmetric bend), 3336.2 cm^{-1} (symmetric stretch), and 3443.6 cm^{-1} (asymmetric stretch) in

decreasing order of band area at standard temperature and pressure [90, 91]. Two significant developments in HITRAN 2020 compared to HITRAN 2016 are the addition of vibrational lines lists between 2400 to 5500 cm^{-1} and 7400 to 8600 cm^{-1} . Hot bands are a critical factor of consideration for spectra at high-temperature applications. These fundamental transitions are due to the transition to a higher state from the existing vibrationally excited state stemming from the Boltzmann distribution, which is insignificant at low temperatures. The significance of hot bands is illustrated in Fig. 3.2 by highlighting three spectral windows [92–94], ranging from 300 to 600 cm^{-1} , from 1200 to 1300 cm^{-1} , and from 3600 to 3845 cm^{-1} . Note that these spectral windows are not exhaustive.

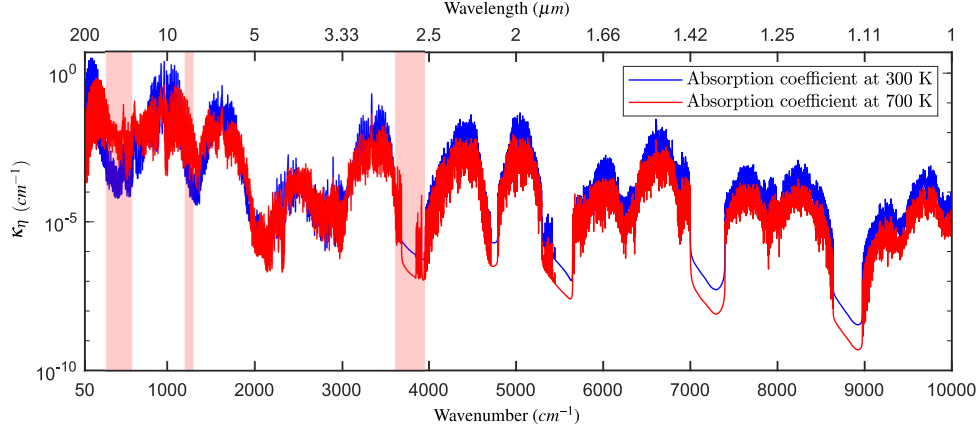


Figure 3.2: Absorption coefficient of NH_3 at 300 K and 700 K at 1 atm and partial pressure of 0.1 atm with the hot bands located within the shaded regions.

3.2.3 Line-by-line model

The line-by-line (LBL) model provides the reference high-resolution spectra of the absorption coefficient. κ_η is computed from the line intensities, as follows [26]:

$$\kappa_\eta(x, p, T) = N_{\text{abs}}(x) \sum_{i=1}^{N_{\text{line}}} S_i(T) F_i(\eta, \eta_i, p, T) \quad (3.5)$$

where N_{abs} is the molecule number density of the absorbing species under consideration. S_i , F_i , η_i , and N_{line} are the line intensity, the line shape profile, the wavenumber at the center of the line of the i^{th} transition line, and total number of lines contributing to the transition at that wavenumber, respectively. For a medium composed of a mixture of participating gases, the total spectral absorption coefficient of LBL is computed by linear superimposition of the absorption coefficient of the different gases. Every single contribution of radiative transition is taken from the aforementioned high-resolution spectroscopic databases. More specifically, they provide, for each listed transition line, the line center η_i , the line intensity at a reference temperature $T_{\text{ref}} = 296$ K, referred to as $S_i(T_{\text{ref}})$, and the lowest level energy for transition, E_l . The line intensity $S_i(T)$ at any temperature T is then obtained by scaling the reference line intensity with the internal partition function of the molecule, Q [95]:

$$S_i(T) = S_i(T_{\text{ref}}) \frac{Q(T_{\text{ref}})}{Q(T)} \exp \left[-\frac{E_l}{kT} + \frac{E_l}{kT_{\text{ref}}} \right] \frac{1 - \exp \left(-\frac{hc\eta_i}{k_B T} \right)}{1 - \exp \left(-\frac{hc\eta_i}{k_B T_{\text{ref}}} \right)} \quad (3.6)$$

h , k_B , and c correspond here to the Planck constant, Boltzmann constant, and the speed of light in vacuum, respectively. In this work, the absorption coefficients are computed for the ranges of thermophysical states given in Tab. 3.1 by using the open-source routine, Radis [96]. The following modeling assumptions were considered:

- For all the molecules, a Voigt profile accounting for both Doppler and collisional line broadening is considered.
- A wavenumber resolution of 0.01 cm^{-1} is applied, leading to the solution of about 10^6 RTE to cover the spectral range under consideration.

- Only lines with an intensity higher than $S_{\text{cut}} = 10^{-40}$ cm/molecule have been considered.
- For NH_3 , NO , NO_2 , N_2O , CO_2 , CO , and CH_4 a line wing-cut off of $\delta\eta_{\text{cut}} = 500 \text{ cm}^{-1}$ is used. For H_2O , the progressive line wing cutoff optimized in Ref. [97] was adopted, leading to $\delta\eta_{\text{cut}} = 500 \text{ cm}^{-1}$ for $T < 2100 \text{ K}$ and $\delta\eta_{\text{cut}} = 200 \text{ cm}^{-1}$ for $T \geq 2100 \text{ K}$.

Parameter	Range	Sampling rate
Temperature	300 K- 3000 K	Every 100 K
Pressure	1 atm - 15 atm 15 atm - 50 atm	Every 1 atm Every 5 atm
Mole fraction	10^{-6}	10^{-6}
	0.01-0.05	Every 0.01
	0.1-0.5	Every 0.1
	0.8-1.0	[0.8,1.0]

Table 3.1: Thermodynamic states of LBL database

The mean transmissivity $\tau_{\Delta\eta}$ over a narrow band of width $\Delta\eta$ and the total emissivity ϵ were computed from the LBL data as:

$$\tau_{\Delta\eta}(\phi, l) = \frac{1}{\Delta\eta} \int_{\Delta\eta} \exp(-\kappa_{\eta}(\phi) l) d\eta \quad (3.7)$$

$$\epsilon(\phi, l) = \frac{1}{I_b(T)} \int_0^{+\infty} [1 - \exp(-\kappa_{\eta}(\phi) l)] I_{b\eta}(T) d\eta \quad (3.8)$$

In the above expressions, l is the length of a uniform path.

Pressure-based Planck-mean absorption coefficients were computed from the LBL database. They are shown in Fig.3.3. Note that HITEMP NO_2 database contains line data for wavenumber up to 4775 cm^{-1} and $T \leq 1000 \text{ K}$. The temperature limitation stems from the partition function [95].

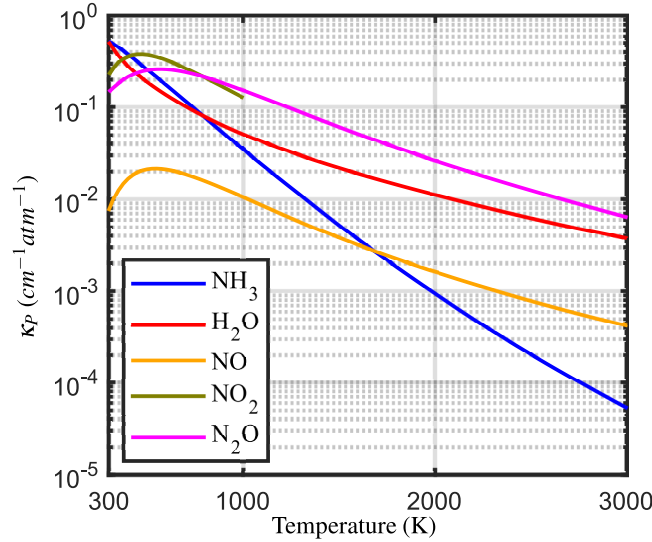


Figure 3.3: Evolution with temperature of the pressure-based Planck mean absorption coefficients for NH_3 , H_2O , NO , NO_2 , and N_2O .

3.3 Statistical narrow band parameters and narrow band k-g distribution databases

NB data were generated with a spectral resolution of $\Delta\eta = 25 \text{ cm}^{-1}$, over which the Planck function and the radiative properties of particles and walls can be assumed to be essentially constant. This leads to

$n_{NB} = 398$ narrow bands to cover the spectral range $50\text{-}10,000\text{ cm}^{-1}$. The statistical narrow band (SNB) is the starting point for the development of k-g distribution based spectral models considered in this study.

3.3.1 SNB parameters

The SNB model for Lorentz lines based on Malkmus' distribution of line strengths is recognized as the most suitable SNB model for hot radiating gases [98]. In this model, the mean transmissivity, averaged over a NB of width $\Delta\eta$, of a uniform path of length l , at total pressure p , and with a mole fraction x of the absorbing species is given by [26]:

$$\tau_{\Delta\eta}(l) = \exp \left[-\frac{\bar{\beta}}{\pi} \left(\sqrt{1 + \frac{2\pi x p l \bar{k}}{\bar{\beta}}} - 1 \right) \right] \quad (3.9)$$

$$\bar{k} = \frac{1}{\Delta\eta} \sum_{i=1}^{n_{NB}} S_i \quad (3.10)$$

$$\bar{\beta} = \frac{2\pi\bar{\gamma}}{\bar{\delta}} \quad (3.11)$$

$\bar{k}$ and $\bar{\beta}$ are the SNB parameters. $\bar{k}$ represents the pressure-based absorption coefficient where N is the total number of spectral lines whose center is within $\Delta\eta$. $\bar{\beta}$ represents the ratio between the mean line half width, γ , and the mean line spacing, δ . In the present study, the SNB parameters are determined from the procedure proposed by André and Vaillon [8]. These authors demonstrated that these parameters can be related to the first and second moments of the absorption coefficient distribution:

$$\bar{k} = \frac{\langle k^1 \rangle}{x p}, \quad \bar{\beta} = \frac{\pi (x p \bar{k})^2}{\langle k^2 \rangle - (x p \bar{k})^2} \quad (3.12)$$

with the m^{th} moment of the absorption coefficient distribution being computed as [8]:

$$\langle k^m \rangle = \frac{1}{\Delta\eta} \int_{\Delta\eta} \kappa_{\eta}^m d\eta \quad (3.13)$$

A database of SNB parameters denoted as SNB hereafter has been generated for each participating gas. The SNB parameters are stored in this database for the $n_{NB} = 398$ narrow bands and the thermo-physical conditions provided in Tab.3.1. The accuracy of this database is illustrated in Figs. 3.4 and 3.5 that shows the transmissivity as a function of the wavenumber at $T = 500\text{ K}$, $x = 0.1$, and $l = 100\text{ cm}$ for different levels of pressure ranging from 1 to 50 atm and the total emissivity as a function of the temperature for $x = 0.1$, different values of l and two levels of total pressure, i.e., 1 and 20 atm. The total emissivity for the SNB is computed as:

$$\epsilon(l) = \frac{1}{I_b(T)} \sum_i^{n_{NB}} (1 - \tau_{\Delta\eta}(l)) I_{b\eta}(T) \Delta\eta \quad (3.14)$$

3.3.2 Narrow band (NB) correlated-k and k-g distribution

Background

k distribution based models assume that the spectral absorption coefficient is a random variable. At the NB resolution, the probability Pr of encountering inside an NB a value of κ_{η} lower than a prescribed value k is introduced [16]:

$$g^{NB}(\phi, k) = \text{Pr}(\kappa_{\eta} < k) = \frac{1}{\Delta\eta} \int_{\Delta\eta} H(k - \kappa_{\eta}(\phi)) d\eta \quad (3.15)$$

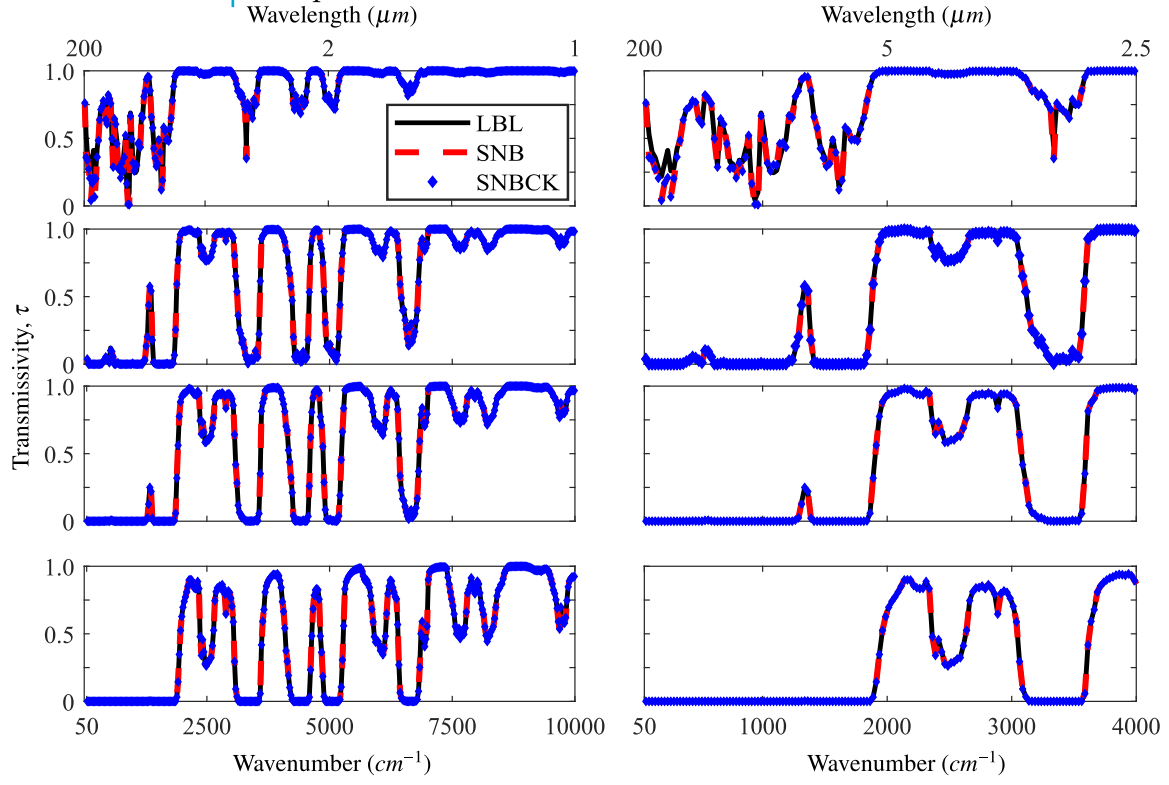


Figure 3.4: NH_3 transmissivity as a function of the wavenumber at 500 K, $x = 0.1$, and $l = 100$ cm. From top to bottom, the pressure p is set to 1, 10, 20, and 50 atm. The diagrams on the left side are relative to the spectral range $50\text{--}10,000\text{ cm}^{-1}$, whereas the diagrams on the right side focus on the spectral interval $50\text{--}4,000\text{ cm}^{-1}$.

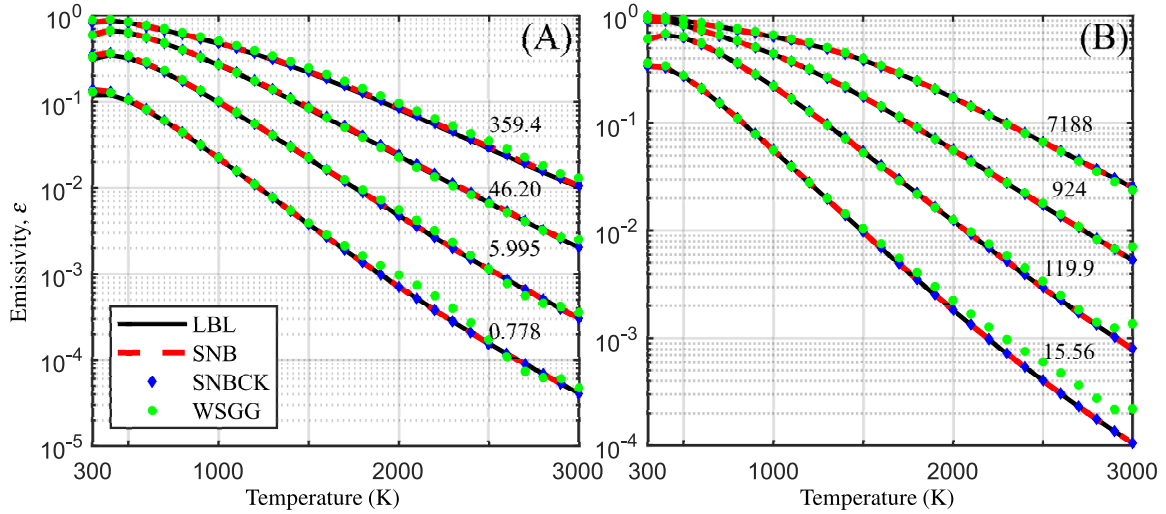


Figure 3.5: (A) Total emissivity of NH_3 (mole fraction $x = 0.1$) as a function of temperature for $p = 1$ atm; (B) Total emissivity of NH_3 (mole fraction $x = 0.1$) as a function of temperature for $p = 20$ atm. For each curve, the specific value of $x \cdot l$ is indicated in atm.cm.

where $\phi = \{x, p, T\}$ and H is the Heaviside function. The mean value over the NB of any function of κ_η (including the emissivity, transmissivity, or the radiative intensity $I_{\Delta\eta}$) can be expressed as the expectancy of this function with respect to the probability measure [16]:

$$I_{\Delta\eta} = \frac{1}{\Delta\eta} \int_{\Delta\eta} I_\eta d\eta = \int_0^{+\infty} I(k) dg(k) = \int_0^1 I_g[k(g)] dg \quad (3.16)$$

where $k(g)$ is the inverse of Eq.(3.15) and a smooth monotonically increasing function of g . A consequence is that $I_{\Delta\eta}$ can be obtained with high accuracy by integrating the last expression of Eq.(3.16) with a quadrature scheme with few points (typically of the order of $N_g = 10$):

$$I_{\Delta\eta} \approx \sum_{i=1}^{N_g} I_g [k(g_i)] w_i \quad (3.17)$$

where g_i and w_i are the points and weights of the quadrature scheme, respectively. The corresponding NB RTE can be expressed as [26]:

$$\frac{dI_g}{ds} = k(\phi, g) [I_{b,\eta}(T) - I_g] \quad (3.18)$$

Single species NB k-g distribution database

For each radiating gaseous species, a database of NB k-g distributions, g^{NB} , was generated for the $n_{NB} = 398$ narrow bands and the thermophysical states summarized in Tab. 3.1. These k-g distributions were stored over $N_g = 128$ values of g corresponding to a 128-point Gauss quadrature scheme. The corresponding k values were obtained by using the SNB parameters derived in Section 3.3.1 through the inversion of the Malkmus SNB-based cumulative density function [99]:

$$g^{NB}(k) = \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{a}{\sqrt{k}} - b\sqrt{k} \right) \right] + \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{a}{\sqrt{k}} + b\sqrt{k} \right) \right] \exp(\pi B) \quad (3.19)$$

where $a = \sqrt{\frac{x p \beta \bar{k}}{2}}$, $b = \sqrt{\frac{\beta}{2 x p \bar{k}}}$, and $B = 2 \beta / \pi^2$. This inversion was performed through a Newton-Raphson iteration method [99]. The accuracy of this SNBCK database is illustrated in Figs. 3.4 and 3.5, with the SNBCK-based transmissivity being computed as:

$$\tau_{\Delta\eta}(l) = \int_0^1 \exp(-k(g)l) dg \approx \sum_{i=1}^{N_g} \exp(-k(g_i)l) w_i \quad (3.20)$$

Radiative calculations using the single species narrow band database are performed as follows. At each computational grid node and for each NB, the following procedure is used to determine the absorption coefficient:

- Step I. For each species, the NB k-g distribution for each NB and each of the 128 Gauss points is interpolated from the database with linear interpolations on p , x , and spline interpolations on T [100].
- Step II. For each NB, a mixed NB k_m - g_m distribution is then obtained by using the mixing scheme of Modest and Riazzi [100]:

$$\begin{aligned} g^{NB}(k_m, \phi) &= \int_0^1 \int_0^1 H [k_m - k_{H_2O}(g_1) - k_{NH_3}(g_2)] dg_1 dg_2 \\ &\approx \sum_{i=1}^{N_g} \sum_{j=1}^{N_g} w_i w_j H [k_m - k_{H_2O}(g_i) - k_{NH_3}(g_j)] \end{aligned} \quad (3.21)$$

w_i and g_i refer to the weights and nodes of the 128-point Gauss-Legendre scheme.

- Step III. For each N_g , the absorption coefficients at the 10 Gauss points were used to solve the NB RTE. The k_m - g_m distribution was obtained using a linear interpolation.

Optimized database for NB calculations

An optimized NB database was generated from the single species NB database described above in order to improve the computational efficiency. In this database, mixed k-g distributions are stored for reduced sets of lumped NBs and quadrature points for the thermophysical states in Tab. 3.1. It was generated by using the following procedure:

1. Mixed NB k-g distributions are generated for each of the $n_{NB} = 398$ NBs and thermophysical properties in Tab. 3.1 by performing the steps I and II described in Section 3.3.2.
2. The lumping strategy, prescribed in Ref. [101], is applied to reduce the number of NBs from $n_{NB,h} = 398$ to $n_{NB,l} = 25$:

$$g_i^{NB_l}(k) = \sum_{j=1}^{n_{NB,i}} \frac{\Delta\eta_{h,j}}{\Delta\eta_{l,i}} g_j^{NB_h}(k) \quad (3.22)$$

h and l denote the high spectral resolution and the low one, respectively. i and j refer to the i^{th} and j^{th} narrow band in low and high spectral resolution, respectively, with corresponding band widths of $\Delta\eta_{l,i}$ and $\Delta\eta_{h,j}$. $n_{NB,i}$ represents the number of high-resolution NBs included in the i^{th} low-resolution NB. The following splitting scheme was adopted:

- 1 NB of 250 cm^{-1} between 50 and 300 cm^{-1} .
 - 19 NBs of 300 cm^{-1} between 300 and $6,000 \text{ cm}^{-1}$.
 - 5 NBs of 800 cm^{-1} between $6,000$ and $10,000 \text{ cm}^{-1}$.
3. For each lumped narrow band and each thermophysical state in Tab. 3.1, the absorption coefficients of $\text{H}_2\text{O-NH}_3$ mixtures of known mole fractions are stored in the database for the 4-Gauss points that are used to solve the NB RTE.

At each computational grid node and for each NB and quadrature point, the absorption coefficient required to solve the NB RTE (Eq. (3.18)) is extracted from the database by using linear interpolations on p , x_{NH_3} , $x_{\text{H}_2\text{O}}$, and a spline interpolation on T . This method will be referred to as SNBCK25 hereafter and the gain in computational cost is discussed in Section 3.6.

3.4 Global models

The global models include full-spectrum k-distribution based (FSK) models [102] and WSGG [103]. The RTE for these models can be written in a generic form as follows [102, 104]:

$$\frac{dI_i}{ds} = k_i [\alpha_i(T) I_b(T) - I_i], \quad i = 1, N_g \quad (3.23)$$

N_g and α_i are the number of quadrature points and the stretching function for the FSK models or the number of grey gases and the weight factor for the non-grey WSGG, respectively.

3.4.1 RCFSK

Full-Spectrum k-distribution models rely on the FS k-g distribution defined as [26, 102]:

$$g^{\text{FS}}(k, \phi, T_p) = \frac{1}{I_b(T_p)} \int_0^{+\infty} H(k - \kappa_\eta(\phi)) I_{b\eta}(T_p) d\eta \quad (3.24)$$

T_p is the Planck temperature. The Rank-Correlated Full-Spectrum k-distribution (RCFSK) scheme, proposed by Solovjov et al. [105], is used to determine k_i and α_i at the quadrature point g_i of quadrature scheme:

$$g^{\text{FS}}(k_i, \phi, T_p) = g_i \quad (3.25)$$

$$\alpha_i(T) = \frac{g(k_i, \phi, T) - g(k_{i-1}, \phi, T_p)}{g_i - g_{i-1}} \quad (3.26)$$

The RCFSK preserves the total emission and does not require any specification of a reference state [105]. A consequence is that T_p can be fixed at a prescribed value, 650 K is chosen here based on a parametric study for the spherically RTE at various T_p (see comments in Section 3.7.1).

The FS database is then generated from the single-species NB databases described in Section 3.3.2 by using the procedure proposed by Modest and Riazzi [100]. Mixed FS k-g distributions are generated for mixtures of NH_3 and H_2O and the RCFSK parameters, k_i and a_i , are stored for 10 values of g corresponding to a 10-point Gauss-Legendre quadrature scheme and the thermophysical states summarized in Tab.3.1. The Planck temperature T_p was set to 650 K. For each specific values of $\phi = \{x_{\text{NH}_3}, x_{\text{H}_2\text{O}}, T\}$, FS k-g distributions were assembled from the following procedure [100]:

1. Mixed NB k-g distributions are generated for each of the $n_{\text{NB}} = 398$ NBs and thermophysical properties in Tab. 3.1 by performing the steps I and II described in Section 3.3.2.
2. The full spectrum distribution function is then assembled as follows:

$$g(k_m, \phi, T_p) = \frac{1}{I_b(T_p)} \sum_{j \in \text{all NB}} I_{b, \eta j}(T_p) \Delta \eta g_j^{\text{NB}}(k_m, \phi) \quad (3.27)$$

Once this function is known, it can be used to calculate the RCFSK parameters, i.e., absorption coefficients of the gas mixture at any local state, k_i , and the stretching function, a_i , from their definitions given by Eqs.(3.25-3.26).

NH_3 -air premixed flame involves a two-layer system with on one side the radiation emitted by H_2O that is absorbed by cold NH_3 in the other side (see Section 3.7.1). The spectrum of NH_3 and H_2O can be assumed to be statistically independent, and the double summation approach appears to be a natural way to address the problem:

$$\frac{dI_{i,j}}{ds} = (k_i + k_j) [a_i(T) \times a_j(T) I_b(T) - I_i], \quad i, j = 1, N_g \quad (3.28)$$

where the indices i and j refer to H_2O and NH_3 , respectively. This formulation will be referred to as RCFSK-DI hereafter.

3.4.2 Multi-scale RCFSK

k-distribution based models, such as FSK and spectral line weighted-sum-of-gray-gases (SLW) models, deal with non-uniform media by assuming that the spectra in different thermophysical states are related by a functional (correlated or scaled, [102]) or statistical (comonotonic, [72]) relationship. This modelling strategy provides accurate prediction as long as moderate gradients of temperature and species concentrations are encountered. It can be no longer satisfied when radiation emitted at high temperature by a species (here combustion products) is absorbed by another species at an ambient - or a relatively low-temperature (here fuel) as encountered in the NH_3 flame spread scenario [71, 74]. In order to address this issue, Modest and co-workers [71, 74] proposed the multi-scale FSK. The multi-scale approach consists of separating the contributions of the M different radiatively participating species, called scales, to the absorption coefficient. Two scales are considered for NH_3 combustion applications in this work: scale 1 corresponds to H_2O and scale 2 to NH_3 , respectively. The spectral RTE is then transformed into two component RTEs, one for each scale, and the reordering of the absorption coefficient is applied to each scale, leading to two FS RTEs:

$$\frac{dI_{\text{H}_2\text{O}}}{ds} = k_{\text{H}_2\text{O}}^*(g_0) a_{\text{H}_2\text{O}}(g_0) I_b(T) - \lambda_{\text{H}_2\text{O}}(g_0) I_{\text{H}_2\text{O}, g_0} \quad (3.29)$$

$$\frac{dI_{\text{NH}_3}}{ds} = k_{\text{NH}_3}^*(g_0) a_{\text{NH}_3}(g_0) I_b(T) - \lambda_{\text{NH}_3}(g_0) I_{\text{NH}_3, g_0} \quad (3.30)$$

The overlap parameter (λ) is computed by assuming the intensity emitted by a homogeneous slab bounded by cold walls is predicted exactly [71, 74]. The RCFSK scheme [105] is applied to determine k^* and a [106].

In a similar manner as for the RCSFK, k^* , a , and λ are stored in a database at the 10 quadrature points used to solve the RTE and for the thermodynamic states summarized in Tab.3.1.

3.4.3 WSGG model

WSGG is based on the idea that a finite number of grey gases (in this work, N_g is set to 4) can describe the integrated behaviour of the spectrum. To that end, we utilize total emissivity from LBL (Eq. (3.8)) to compute the grey gas absorption coefficient and the fraction of blackbody energy of grey gases. The blackbody energy is represented by a 5th order polynomial with $T_{ref} = 1000$ K. The WSGG formulation used in this work is as follows:

$$\epsilon_{WSGG} = \sum_{i=0}^{NG=4} a_i(T_r) [1 - \exp(-\kappa_i \times p l)] \quad (3.31)$$

$$a_i = \sum_{k=1}^9 b_{i,k}(T_r)^{k-4} \quad \text{with} \quad T_r = \frac{T}{T_{ref}} \quad (3.32)$$

where κ_i is the absorption coefficient related to the i^{th} grey gas. For each pressure level in Tab.3.1, the WSGG coefficients were computed using the `lsqcurvefit` function in MATLAB R2023b and are given in the supplementary materials of Raman et al., [107]. To account for the self-broadening of the radiatively participating species, the optimization procedure is carried out for a range of path length (1 cm to 1000 cm) and mole fraction (0.01,0.05,0.1,0.2,0.5,0.8,1.0), similar to the work of Cassol et al. [108].

During the optimization the following constraints were set:

- The absorption coefficients κ_j of j^{th} grey gas cannot be negative.
- The blackbody weights a_j of j^{th} grey gas can only vary between 0 and 1.

Consistent with the works in the literature, 0th grey gas is set to be the transparent window leading to $\sum_{i=0}^{NG} a_i = 1$.

The developed WSGG model is valid for partial pressure length ranging from 1 atm cm to 1000 atm cm and for temperature between 300 K to 3000 K. The multiplication scheme, that relies on the assumption of uncorrelated absorption coefficients among the gas species, is used as mixing scheme [30, 31, 109]. WSGG has been traditionally applied for emission dominated regions as reported by Refs. [76, 110]. Hence, its performances are expected to be weaker in the low-temperature regions (absorption-dominated regions). Assessment of the WSGG model for a classical benchmark configuration involving sinusoidal profiles of temperature and NH_3 and H_2O mole fractions is provided below.

3.4.4 Assessment of WSGG

The WSGG model developed in this study was assessed using a synthetic flame field from the literature. Specifically, the flame field is similar to the test case-4 with a domain size of 100 cm from the work of Sadeghi et al. [76]. The WSGG was tested against the LBL. The decoupled computations were done at 5 atm to check the performance of the models in a configuration similar to a non-premixed flame. From Fig. 3.6, it can be seen that the WSGG model resulted in a peak relative error of 13% and a mean absolute relative error of 5.5%. To model the directional nature of the radiation, DOM was used with 12 directions.

$$\begin{aligned} T(x) &= 400 + 1000 \sin^2(\pi x) \\ X_{\text{NH}_3}(x) &= 0.03 \sin^2(\pi x) \\ X_{\text{H}_2\text{O}}(x) &= 0.12 \sin^2(2\pi x) \\ &\quad x \text{ is in meter} \end{aligned}$$

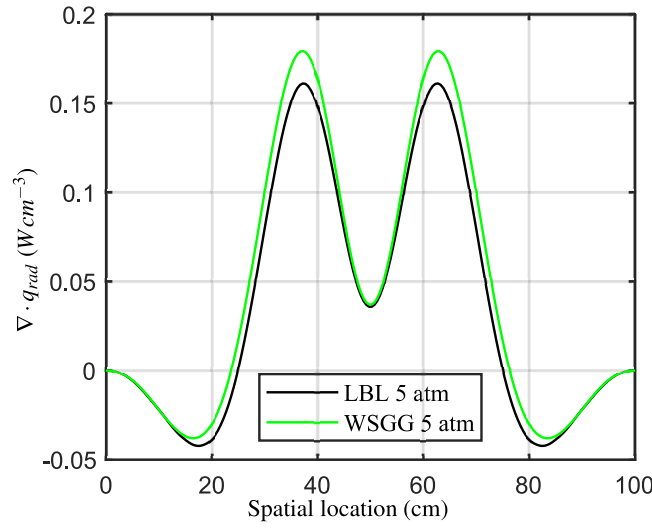


Figure 3.6: Verification of the WSGG model at 5 bar

3.5 Verification of DOM

The DOM model utilized in this work was tested against the following planar and spherical configuration studies, as illustrated in Fig. 3.7.

- The planar configuration is tested against the work of Chu et al., [111]
- spherical RTE against the results of Chen et al. [17]

The planar and spherical configurations are of pure H_2O at a uniform temperature of 1000 K.

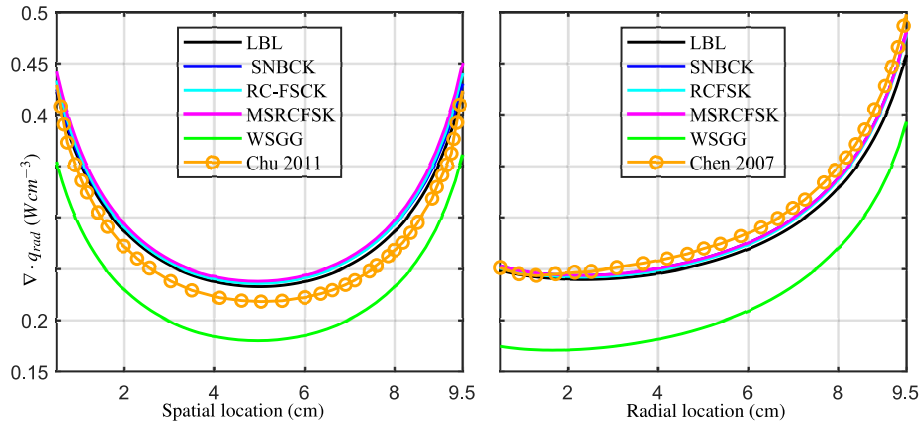


Figure 3.7: Verification of the directional model using various spectral models against the reference works

3.6 Reduced SNBCK

SNBCK is not desirable for a fully coupled simulations due to high computational overload. Hence, reducing the number of bands and gauss points heuristically would be desirable. In this work, an optimized NB model with 25 bands and 4 gauss points were utilized. The gain in computational efficiency can be inferred from the number of iterations required to execute a decoupled simulation for spherical configuration at 5 atm, 20 atm, and 50 atm, respectively, from Fig. 3.8.

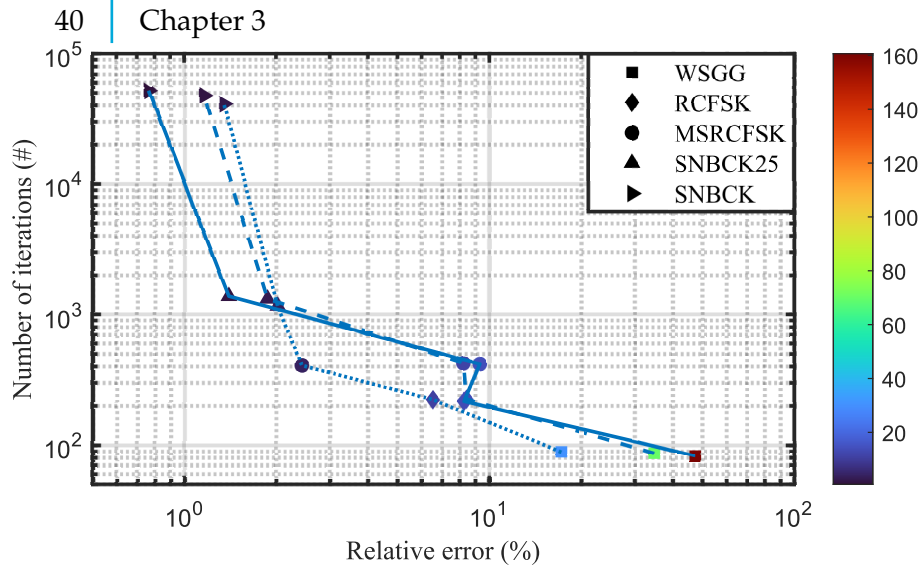


Figure 3.8: Performance of various spectral models for premixed flames vis-à-vis the number of iterations against the mean of the absolute of relative error at 5 atm (dotted lines), 20 atm (dashed lines), and 50 atm (solid lines) respectively, the symbols are colored with respect to the MARE in the transition region (flame-front)

3.7 Application to radiative heat transfer in flames

In this section, we will illustrate the performances of the above-described spectral models against the LBL for various flame fields, such as spherically symmetric premixed flames, planar freely propagating premixed flames, and non-premixed flames.

3.7.1 Premixed flames

The laminar planar and spherical premixed flames investigated in this study have a 1D structure characterized by a very thin reaction zone ($O(\text{mm})$) separating the fresh cold unburnt gases, composed of fuel and oxidizer (air), and the burnt hot gases, composed of the combustion products. The premixed flame structure can be represented by a two-layer system, with the cold fuel-oxidizer mixture on one side and the hot combustion products on the other. This configuration has been investigated by the radiative heat transfer community as it explores an extreme case for the correlated k-distribution based models based on which the absorption spectra at the two layers are almost statistically independent [105, 112]. It should also be pointed out that for the NH_3 -air premixed flames, only one radiating species is present in significant amount on each side of the reaction zone, i.e., NH_3 in the cold layer and H_2O in the hot layer. Thus, no mixing scheme is necessary. Finally, pressure positively influences re-absorption within the fuel layer, emphasizing its importance for engineering applications.

To assess the performances of the spectral models for NH_3 -air premixed flames, the flame conditions of Kanoshima et al. [82], i.e. an equivalence ratio of 0.8 and an initial temperature of the fresh gas of 500 K, were adopted. Two flame configurations, i.e., planar and spherical, and 2 pressure levels, i.e., 5 and 20 atm, were considered.

The flames were simulated with FlameMaster [2] using an isobaric model and the chemical mechanism of Shrestha [113]. For the spherical flame, the spherical domain of 10 cm was discretized with 10^4 grid points. As for the planar flame, the spherical flame field is solved using the planar radiative transfer equation. Figure 3.9 shows the profiles of temperature and species mole fractions obtained at $t = 30$ ms after ignition. These profiles are then used for the subsequent decoupled radiative calculations. Figure 3.10 (left) shows the divergence of radiative heat flux over the radial profile with and without the minor burnt products. The figure on the right shows the relative error incurred by neglecting the minor species. The effects of minor burnt products are not significant, as seen in Fig. 3.10, at least assuming low concentration of NO , NO_2 , and N_2O on comparison with the other major species such as NH_3 and H_2O

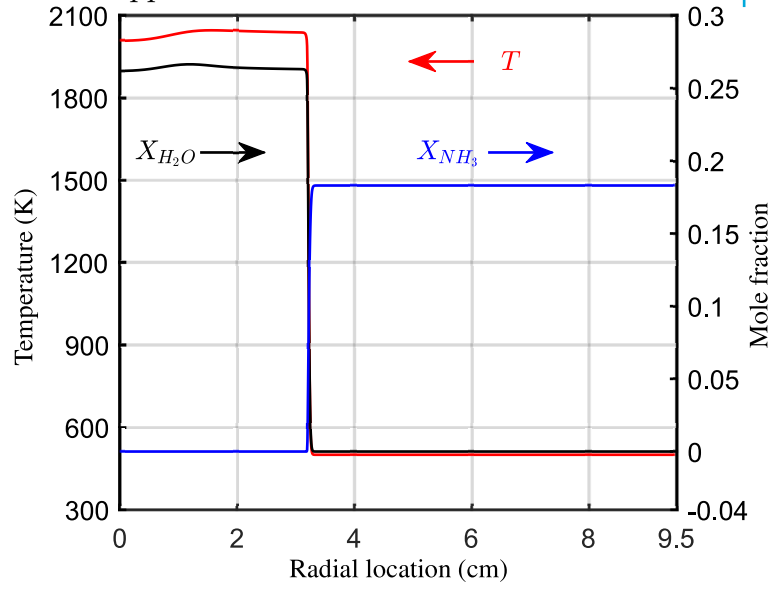


Figure 3.9: Flame field utilized for NH_3 -air premixed flames at 5 and 20 atm. The horizontal axis is the radial distance from the center for the spherical flame or the streamwise coordinate originated from the input boundary condition for the planar flame.

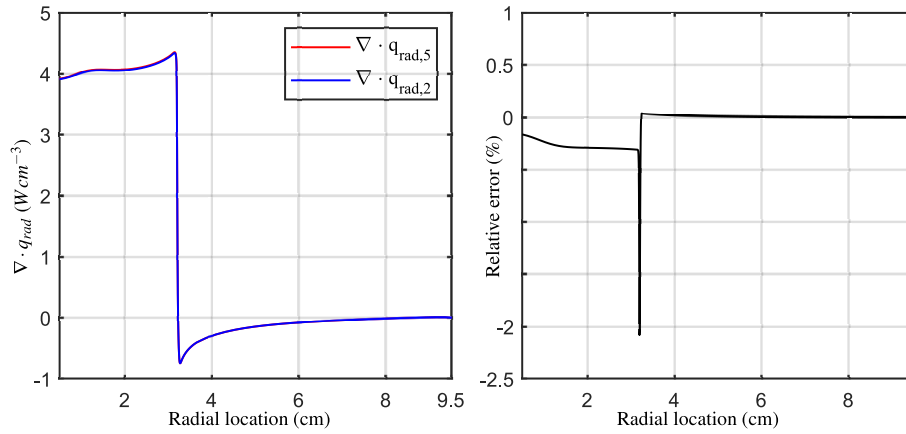


Figure 3.10: Estimation of the effects of the minor species for a premixed NH_3 / air flame. $\nabla \cdot q_{\text{rad},5}$ refers to divergence which includes all the 5 species (NH_3 , H_2O , NO , NO_2 , and N_2O) while $\nabla \cdot q_{\text{rad},2}$ includes contributions of NH_3 and H_2O . The calculations were computed for a spherical configuration at 5 atm

The discrete ordinates method (DOM) [26, 67] was used to solve the RTE. Its implementation was validated in both planar and spherical configurations by comparison with literature results involving pure H_2O [17, 111] (see Section 3.5). For premixed flames, the RTE was solved with 12 discrete directions, as increasing the angular resolution was not found to result in noticeable differences. It was also observed that the contributions of NO , NO_2 , and N_2O did not significantly contribute to the divergence of radiative heat flux due to their low concentrations (see Fig. 3.10). Consequently, these species were ignored in the simulations reported in this section. The performances are gauged by the relative error and the mean of the absolute relative error (MARE) over all the grid points.

$$\text{Relative error} = \frac{\phi_{\text{Model}} - \phi_{\text{LBL}}}{\max(\phi_{\text{LBL}})} \times 100 \quad (3.33)$$

Figure 3.11 shows the predictions of the divergence of the radiative flux and the corresponding relative errors. For both pressure levels and both spherical and planar configurations, the SNBCK and SNBCK25 are in good agreement with the LBL solutions.

Consistent with the conclusions drawn in previous studies [31, 32], the Planck temperature, T_p , was not found to significantly affect the prediction of the RCFSK. The best agreement was found for $T_p = 650$ K, leading to a relative error of 6.5%. Considering $T_p = 2000$ K was found to result in a slightly higher relative error of 7.31 %. More specifically, it can be observed that the RCFSK performs well in the hot

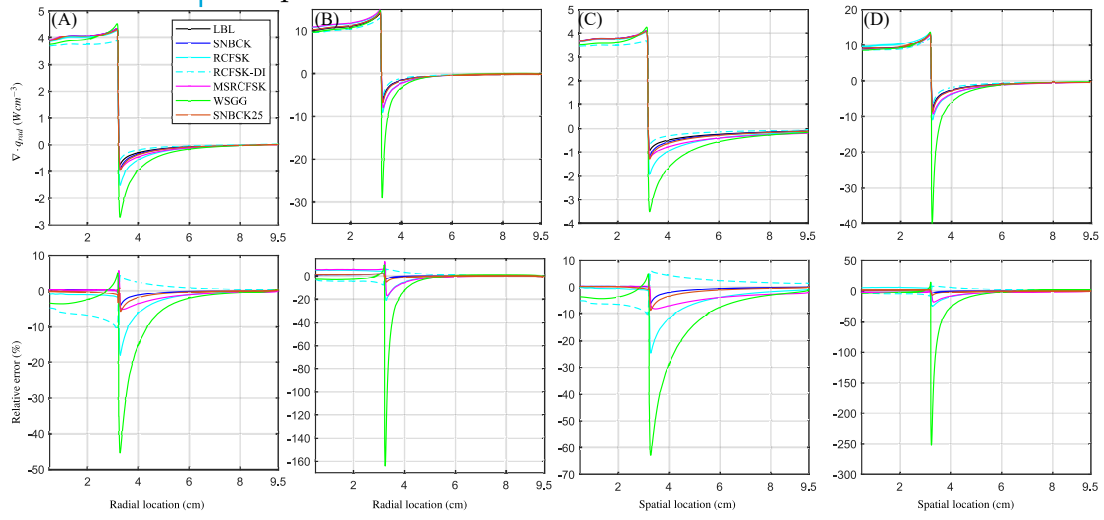


Figure 3.11: Top row: Divergence of the radiative heat flux for: (A) spherical configuration at 5 atm; (B) spherical configuration at 20 atm; (C) planar configuration at 5 atm; (D) planar configuration at 20 atm. Bottom row: Relative error (see Eq.(3.33)) on the divergence of the radiative heat flux throughout the flame considered just above.

burnt gases but overpredicts the absorption in the cold NH_3 layer. Similar discrepancies were reported for the RCFSK in two-layer configurations in previous works [105]. The RCFSK-DI significantly improves the predictions in the cold NH_3 layer and underestimates the absorption. However, the discrepancies are still higher than for the SNBCK25.

The MSRCFSK, which was specifically designed to handle highly heterogeneous configurations where the radiation emitted by a species is reabsorbed by another species [71], also significantly improves the RCFSK in the cold layer, especially at 5 atm, but the corresponding discrepancies also remain higher than for the SNBCK25. It is interesting to note that the MSRCFSK is, on the whole, more accurate than the RCFSK-DI at 5 atm but less accurate at 20 atm. As discussed previously, the two-layer system is very challenging for correlated-k models, and these results indicate that the SNBCK25 is a good compromise between accuracy and computational efficiency (see Appendix 3.6) in this configuration.

The WSGG model's performance was relatively bad within the context of premixed flames with relative error in the flame front ranging from around 45% to 160% in the spherical configuration with pressure adversely affecting the performance of the model. This poor performance is attributed to the peculiar configuration of premixed flames rather than to the present WSGG formulation. This is supported by radiative simulations made in a 1D configuration involving sinusoidal profiles of x_{NH_3} , x_{H_2O} , and T , representative of the benchmarks usually used to assess radiative property models in the literature (see Refs. [108, 114] as illustrations). The results, reported in the Appendix, show that WSGG predicts the divergence of radiative flux with maximum and relative errors of 13 % and 5.5 % as compared to LBL, which is consistent with the expected errors for the WSGG in this configuration. The results of line-of-sight calculations for the premixed flames are provided in Section 3.8 after the line-of-sight of non-premixed flames.

3.7.2 Non-premixed flames

In this section, the performances of the spectral models in non-premixed configurations are assessed by decoupled radiative simulations along a line-of-sight for synthetic flame fields (see Fig. 3.12) corresponding to the centerline of non-buoyant turbulent jet diffusion flames burning into still air. The radiative transfer equation along these line-of-sights was solved from a location in the far field toward the nozzle. The performances in non-premixed configurations are important in assessing the mixing rules since, at some locations, both the products and the fuel may be found in significant amounts. The profiles of NH_3 and H_2O mole fractions, together with that of temperature, were generated by combining the analytical solution proposed in Ref. [115] with the Burke-Schumann flame structure. The axial evolution of the

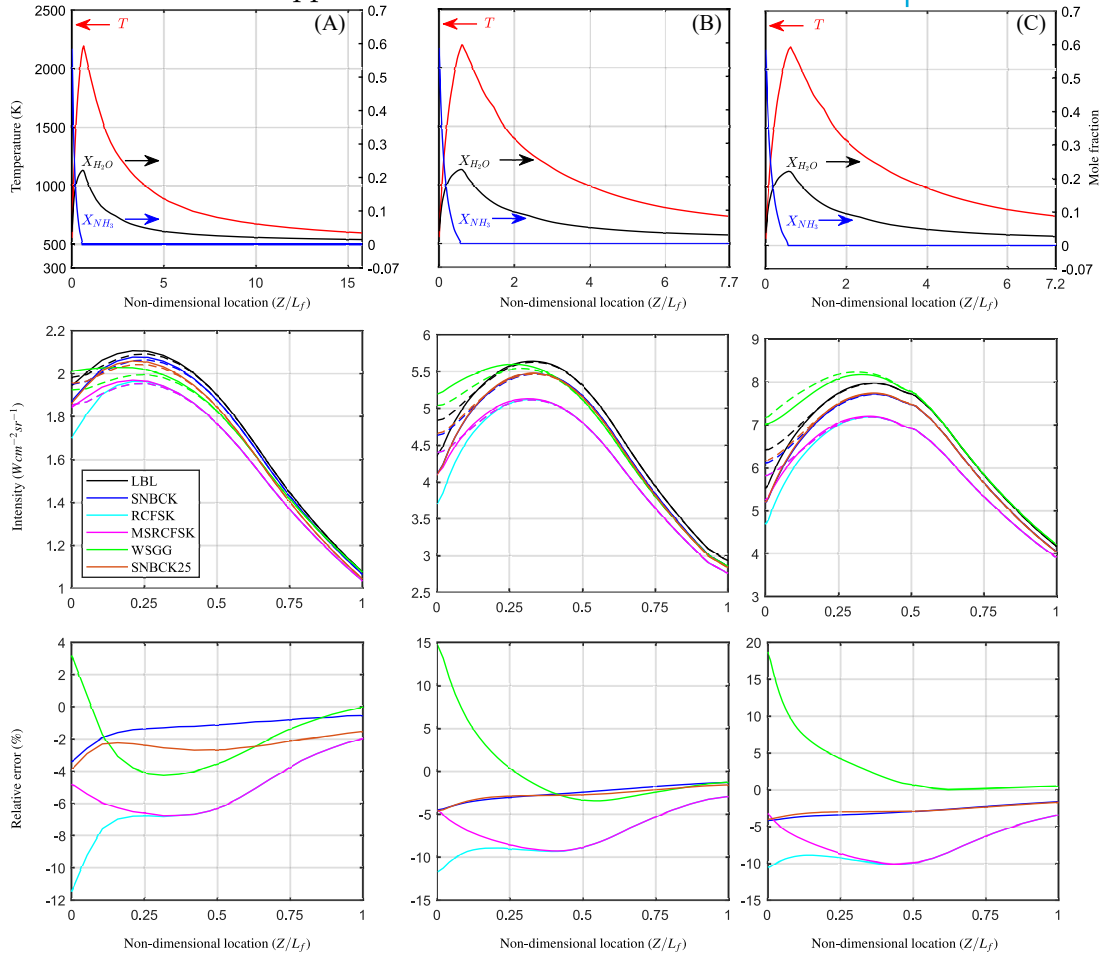


Figure 3.12: Top row: Flame fields utilized for the radiative computations in non-premixed flames referred to as flame-1, flame-2, and flame-3 (from the left to the right); Middle row: Radiative intensity over a line-of-sight starting from the far field towards the nozzle ($Z/L_f = 0$); Bottom row: Relative error profiles of the various spectral models considered. The solid lines correspond to the contributions by NH_3 and H_2O , while the dashed ones represent the contribution by only H_2O .

mixture fraction is given by [115]:

$$\bar{z} = \frac{2.19 (1 + 2\sigma_z) d}{z + z_0} \left(\frac{\rho_F}{\rho_{st}} \right)^{1/2} \quad (3.34)$$

$$z_0 = 6.56 d \left(\frac{\rho_F}{\rho_{st}} \right)^{1/2} \quad (3.35)$$

$$\frac{L_f + z_0}{d} = \frac{5.3}{\bar{z}_{st}} \left(\frac{\rho_F}{\rho_{st}} \right)^{1/2} \quad (3.36)$$

where $\sigma_z = 0.71$ and ρ , d , L_f , and z are the density, the nozzle diameter, the flame height, and the axial coordinate, respectively. The indices F and st refer to the fuel inlet and the stoichiometry, respectively. Three synthetic line-of-sights, referred to as flame-1, flame-2, and flame-3, hereafter, corresponding to $L_f = 38$, 193, and 387 cm, respectively, were generated. To illustrate the effects of pressure, one of the flames was simulated at 5 atm (see Fig. 3.13) while the other ones were done at 1 atm. The flame field is illustrated as a function of non-dimensional location with respect to the flame length, i.e., 38 cm, 193 cm, and 387 cm for flame-1, flame-2, and flame-3, respectively.

In Figs. 3.12 and 3.13, the dashed lines represent the intensity stemming from hot H_2O and the solid lines from both H_2O and NH_3 to highlight the importance of the fuel re-absorption. For the RCFSK, the H_2O case perfectly overlaps with the MSRCFSK's H_2O case. Finally, except for flame-3, the WSGG model does not reproduce this behaviour. The intensity profile and relative error for the 5 atm case are given below. The intensity profiles for 1 atm and 5 atm are presented here only up to the non-dimensional length of 1 to emphasize the fuel-rich region and its effects. The performances of the models in the non-premixed

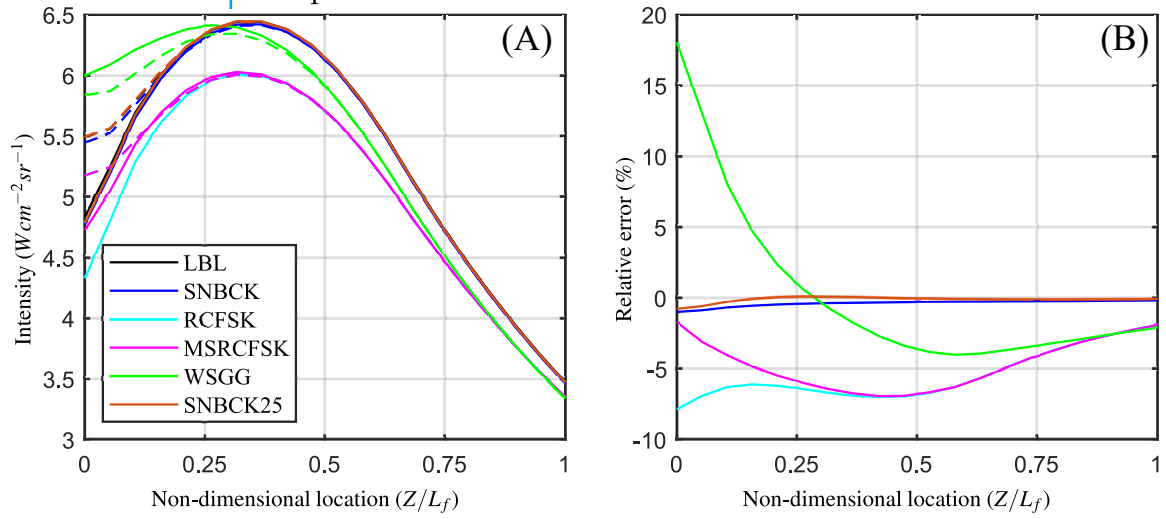


Figure 3.13: (A) Radiative intensity from the far field towards the nozzle ($Z/L_f = 0$) for flame-1 at 5 atm; (B) Relative error for flame-1 at 5 atm. Consistent with Fig.3.12, the intensity in the region of interest is shown. Solid lines correspond to the contributions by both NH_3 and H_2O , and the dashed ones to the contribution by H_2O .

configuration are similar to those in the premixed configuration, with both SNBCK and SNBCK25 being close to the reference LBL model, followed by MSRCFSK, RCFSK, and WSGG, respectively.

3.7.3 Applicability of reduced SNBCK to other species

The objective of this section is to further assess the performances of the SNBCK25 for a more complex spherical premixed flame configuration resulting from the combustion of a 50% CH_4 / 50% NH_3 -air fresh mixture at an equivalence ratio $\phi = 1.0$ and two pressure levels, i.e. 5 and 20 atm at 300 K. The 5 atm case corresponds to the experimental conditions of Shu et al. [83]. For these flames, the radiative contributions are due to CO_2 , H_2O , and CO for the hot mixture and to CH_4 and NH_3 for the cold mixture. Similar to the previous section, the flow field used to perform the decoupled radiative simulations has been obtained from a numerical simulation. The flame field is displayed in Fig.3.14(A). Figs.3.14 (B) and (C) show the computed divergence of the radiative flux by the SNBCK25 and the LBL, as well as the corresponding relative error of SNBCK (RE-SNBCK). The agreement is still good, considering the very challenging configuration for correlated-k models with peak relative error within 10 % of the LBL solutions.

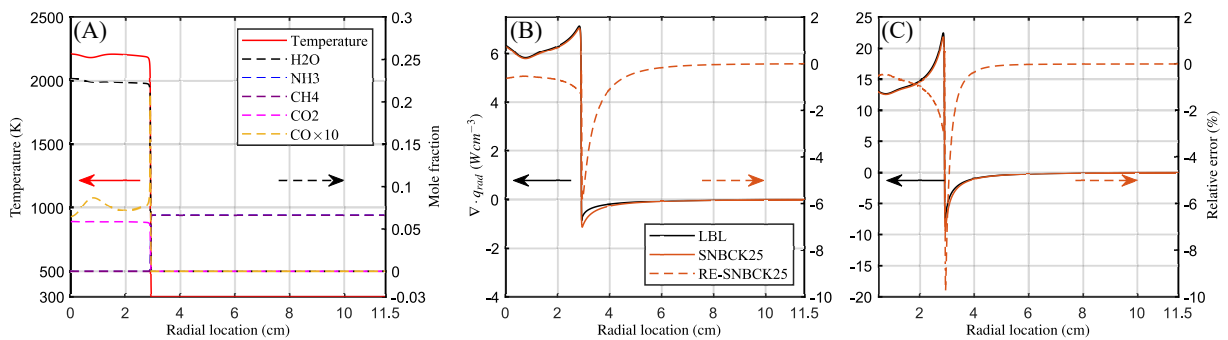


Figure 3.14: (A) Flame field utilized for a decoupled radiative computation in 50% CH_4 / 50% NH_3 -air premixed spherical flames at $\phi = 1$. Divergence of the radiative heat flux (left y-axis) and local relative error (right y-axis) of SNBCK25 as compared to LBL for mixtures at: (B) 5 atm; (C) 20 atm.

3.8 Line of sight for premixed flames

The line of sight calculations are performed for the premixed configuration investigated in this work using LBL, SNBCK, RCFSK, MSRCFSK, WSGG, and SNBCK25 models at 5 and 20 atm, respectively. In Fig. 3.15, solid lines represent the intensity from the hot burnt gas region to the cold fuel side, and the dashed lines represent the intensity from the cold fuel region to the hot burnt products.

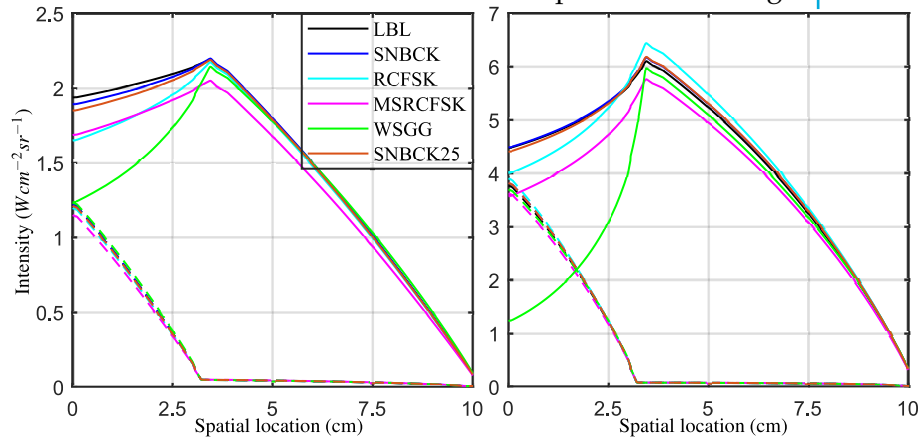


Figure 3.15: Performance of various spectral models for premixed flames at 5 atm (left) and 20 atm (right) respectively

3.9 Conclusions on the spectral modelling

In this chapter, various spectral models were benchmarked with emphasis on the capacity of k-distribution models, i.e. SNBCK, RCFSK, and MSRCFSK, to accurately capture the radiative re-absorption by the relatively cold ammonia. The spectral models were tested using the discrete ordinate method for premixed flames and the line-of-sight method for non-premixed flames. For premixed flames, both planar and spherical configurations were considered. The conclusions drawn are as follows:

- Radiative re-absorption is relatively significant for ammonia as compared to other fuels due to its absorption coefficient and its overlap with hot H_2O vapour which is the source of thermal radiation in practical combustors.
- The performances of the k-distribution spectral models were assessed, showing that the statistical narrow band correlated k-distribution (SNBCK) leads to predictions that are the closest to the ones provided by the line-by-line (LBL). While multi-scale rank correlated full spectrum k-distribution's (MSRCFSK) overall performances are close to those of SNBCK at lower computational cost, it is not accurate enough within the very flame front. The performances of the optimized SNBCK, called SNBCK25, were also better than those of MSRCFSK, although associated with an additional computational cost.
- For instance, for NH_3/air premixed spherical flames at 5 atm, a mean absolute relative error (MARE) of 1.3% is obtained for SNBCK, while RCFSK with "Modest and Riazzi" mixing scheme, the RCFSK with the double integration, MSRCFSK, WSGG, and SNBCK25 lead to MAREs of 6.5%, 4.58%, 2.4%, 17.2%, and 2.0%, respectively.
- Due to its relatively lower computational cost, the WSGG model was also investigated, leading to the conclusion that it is not accurate in absorption-dominated regions, as reported in previous studies [76, 110].

3.10 Spectral models' implementation in RTE resolution

During the present works, a spherical configuration of the Discrete Ordinates Method has been implemented to FlameMaster. Due to the associated computational cost, the parallel computing release of FlameMaster has been complemented.

Our DOM routine computes the radiative source ($-\nabla \cdot \mathbf{q}_{\text{rad}}$) once for every iteration by the master thread. The code is parallelized based on the narrow bands, solving each narrow band and Gauss point separately using the available threads.

Though future studies need to investigate the optimal sub-cycling level for the spherical flames of respective fuels, the resulting code delivered the expected simulations at acceptable wall times. As an illustration, the simulation for the propagation of the NH_3/air flame shown by the orange solid line in Fig. 4.2 spent 383553 seconds of wall-time.

4 Effects of radiation on the characteristics of NH₃ flames

O! for a muse of fire, that would ascend
the brightest heaven of invention

William Shakespeare

Contents

4.1	Introduction	47
4.2	Literature review	48
4.2.1	Isobaric flames	48
4.2.2	Isochoric flames	49
4.2.3	Kinetic mechanisms	49
4.2.4	General characteristics of NH ₃ -air combustion	50
4.3	Computational details	51
4.4	Isobaric flame propagation	52
4.4.1	Experimental validation	52
4.4.2	Effects of pressure on the propagation of NH ₃ - air flames	53
4.4.3	Effects of pressure on the propagation of NH ₃ /H ₂ - air flames	65
4.5	Isochoric flame propagation of NH ₃ -air	69
4.6	Discussion on planar freely propagating flames	71

4.1 Introduction

This section deals with the effects of radiation on the characteristics of the NH₃ flames, both for isobaric spherically expanding flames and planar flames vis-à-vis laminar burning velocity and Markstein length (L_b) for the former and laminar burning velocity (S_L) for the latter, respectively. The numerical and theoretical models are tested against each other (via the adiabatic quantities such as flame thickness, Lewis number, and so on). The effects of pressure on the theoretical models via the kinetic mechanism are also investigated. The role of NH₃ is particularly examined for lean spherical blended (NH₃/H₂) flames for a range of pressures. Finally, the effects of radiation are also illustrated for isochoric spherically

4.2 Literature review

4.2.1 Isobaric flames

Spherically expanding flames are a robust platform for investigating the fundamental properties of fuels over a wide range of pressures. Significant attention has been paid to capturing the flame dynamics of ammonia-air flames in spherically expanding flames (SEF) configuration. In this section, recent observations from the literature on the effects of radiation on SEF are presented. Ju et al. [7] conducted a detailed investigation of the effects of radiation on spherically expanding flames from an emission perspective and formulated a correction scheme that accounts for the radiative losses for several fuels of increasing carbon content from H_2 to nC_8H_{18} . In their study, the maximum initial pressure and temperature were limited to 12 atm and 450 K. Based on the numerical simulations of these flames, they postulated a reduction factor, R , to quantify the departure of both OTM and SNB from the ADI model. The discrepancy between OTM and SNB was minimal, with the lowest R -value near the stoichiometric region. The minimal discrepancy between OTM and SNB was due to the weakly absorbing nature of the fuels selected for the study. They observed a correlation between R and adiabatic LBV (Laminar burning velocity, the relative velocity of the front with respect to the fresh gases, $S_{l,ADI}$) and fitted it into an expression. The authors emphasized that the fitted expression is only valid for flames without dilutions. If $\text{CO}_2/\text{H}_2\text{O}$ are added, the fresh gases will absorb the radiated energy leading to higher preheating, hence the developed correlation would be invalid. The correlation is given as [7]:

$$S_{l,RCFS}^0 = S_{l,Exp}^0 + 0.82S_{l,RCFS}^0 \left(\frac{S_{l,Exp}^0}{S_0} \right)^{-1.14} \left(\frac{T_u}{T_0} \right) \left(\frac{P_u}{P_0} \right)^{-0.3} \quad (4.1)$$

Here, S_0 , T_0 , and P_0 are constants, set to 1 cm/s, 298 K and 1 atm, respectively. $S_{l,RCFS}$ corresponds to radiation corrected flame speed and is equivalent to $S_{l,ADI}$. $S_{l,Exp}$ corresponds to the experimental measurements that have both radiative emission and radiative reabsorption; the latter's magnitude would be minimal for the chosen fuels in the study by Yu et al. [7]. The numerical equivalent $S_{l,Exp}^0$ would be the S_l predicted by DOM/SNBCK. Terms with subscript u correspond to the unburnt/ initial quantities.

The work by Faghih et al. [116] investigated the accuracy of Eq. (4.1) for NH_3 -based fuels. As Eq. (4.1) was developed primarily for $S_{l,ADI} > 10$ cm/s higher than ammonia flame speed $S_l < 8$ cm/s, they observed 15 % errors in predicting the reduction factor. Consequently, they postulated a new relation to account for the radiative losses for spherical flames of $S_l < 9$ cm/s.

Mei et al. [117] studied the LBV of partially cracked ammonia at various cracking ratios and pressures in a constant-volume cylindrical chamber and tested the results against the planar results. They improved their kinetic mechanism based on their experimental data. The experimental setup has a chamber with an inner diameter of 15 cm. In comparison, only data between 1 cm and 2.3 cm were used for the extrapolation routine to determine the laminar burning velocity (S_l) and the Markstein length (L_b). The authors investigated the effects of pressure on the flame propagation at various equivalence ratios but placed a special emphasis on 40% cracking since the LBV at 1 atm, 40% cracked ammonia at $\phi = 1.1$ was close to the LBV of methane. Glaznev et al. [118] conducted an experimental and numerical study on the validity of the OTM corrections proposed by Faghih et al. [116] and Yu et al. [7] for flames with LBV < 4 cm/s. They canceled the effects of buoyancy through microgravity experiments. They determined the S_l for isobaric flames ($P \leq 3$ bar) with OTM corrections and tested it against the isochoric measurements ($P < 9.3$ bar). The performance of the OTM corrections of Yu et al. [7] for isobaric flames yielded good agreement against the isochoric measurements. It is particularly important since LBV in an isochoric chamber is obtained without considering burnt gas emissions (briefed in Sec. 4.2.2). They evaluated the performance of various kinetic models (Han et al., [119], Mei et al. [117], and KAUST 2023 [120]) with and without OTM corrections, emphasizing the role of these corrections on the mechanism's predictions. Hayakawa et al. [121] reported experiments on spherically expanding flames at high pressures up to 2 MPa with optical visualization up to a flame radius of 3.5 cm. They observed severe

buoyancy and mitigated its effects on the analysis by considering only the downward flame propagation. Due to the intrinsic instabilities of lean flame configuration, they limited the high-pressure tests to the rich mixtures.

4.2.2 Isochoric flames

Halter et al. [51] developed an optical access constant volume combustion chamber. The optical access accurately determines R_f without any approximations based on the pressure and burnt gas section. The latter requires further approximations to account for radiative heat loss. Hence, the optical access constant volume chamber results in an exact computation of LBV. The equation from Chapter 2 is repeated:

$$S_l = \frac{dR_f}{dt} - \frac{R_0^3 - R_f^3}{3\gamma_u R_f^2 P} \frac{dP}{dt} \quad (4.2)$$

Here, R_0 , R_f , γ_u , and P denote the chamber radius, instantaneous flame radius, specific heat ratio of the unburnt gas, and instantaneous pressure, respectively. In the absence of optical access, certain assumptions regarding the flame location via the pressure trace (pressure values from the sensors) are made. These assumptions are made via the burnt gas fraction, x ($x = \frac{m_b}{m}$, where m is the total mass, and m_b is the mass of the burnt gas section), which is affected by the radiative emission. The authors tested the validity of various radiation models for CH_4 flames in an optical access combustion chamber. They proved that the effects of radiation in the presence of optical access are minimal, and approximations involving burnt gas fraction from the work of Omari et al. [122] and Faghih et al. [56] are redundant. The recent work of Mornettas et al. [123] separately confirmed the negligible impact of radiation for isochoric configuration for CH_4 at high pressures.

4.2.3 Kinetic mechanisms

Due to the promising potential of NH_3 in the pursuit of decarbonization and the scope of improvements in describing the kinetics of ammonia, there are numerous kinetic mechanisms developed to describe the fundamental properties such as LBV, ignition delay timing (IDT), and speciation data such as NO_x , NH_2 , and so on. Alnasif et al. [124] and Girhe et al. [125] are notable works that evaluated the performance of these mechanisms. In the former, the authors examined a range of NH_3 oxidation mechanisms in the literature. They computed the discrepancy between various mechanisms for blended NH_3 at different ϕ values against experimental data. They note that only few mechanisms predict the LBV at stoichiometry within 20% of the experiments, including Mei 2021 [117], Gotama 2022 [126], KAUST 2021 [127], and Arunthanayothin et al. [128].

Girhe et al. [125] rigorously investigated the performance of 16 mechanisms of the literature based on both the absolute error and the trends of the predictions, thereby quantifying the similarity between the data. The authors utilized experimental data from the literature across various regimes, including a jet-stirred reactor (JSR), a shock tube (ST), a flow reactor, spherical bombs, and heat flux burners. They scored each mechanism on the physical process at play, from pyrolysis to LBV predictions. They observed that the following mechanisms had the best performance: Zhu 2024 [129], KAUST 2023 [120], KAUST 2021 [127], and Stagni 2023 [130] (note, Stagni 2023 can be regarded as the updated version of Arunthanayothin et al. [128]). The main difference between KAUST 2021 and KAUST 2023 is the inclusion of the carbonaceous reactions in the latter, such that it is applicable for a mixture of ammonia and carbonaceous fuels.

In this work, the Zhu 2024 [129] mechanism is primarily used. The selection was based on its performance against the experiments by comparison with other mechanisms, namely, Stagni 2023 [130] and Gotama 2022 [126] (described in Sec. 4.4.1). The details of these mechanisms are summarized in Tab. 4.1. In the description of the experimental conditions used in the development of the mechanism in the comments section, the experimental setup is not discriminated, i.e., for instance, 0.8 atm of pressure can be in a shock tube while 100 atm can be in a flow reactor.

Mechanism	No. of species	No. of Rxns	Comments
Zhu 2024 [129]	39	306	298 - 2000 K and 0.8 - 100 atm
Stagni 2023 [130]	31	203	298 - 2800 K and 0.026 - 98.69 atm
Gotama 2022 [126]	32	165	Based on GRI-Mech 3.0 [131] with additional reactions for NH ₃

Table 4.1: Chemical kinetic mechanisms for NH₃

4.2.4 General characteristics of NH₃-air combustion

As discussed previously, NH₃ could be a part of a multi-pronged solution (Refs. [132, 133]) to the carbon-neutral/negative society due to the ease of handling and transportation, at least for the ground-based applications, which are usually classified as hard-to-abate sectors. Ammonia flames are characterized by low-burning velocity, and the heat released by the combustion of ammonia is relatively lower due to the high energy requirements to break the covalent bond between the N-H atoms [132].

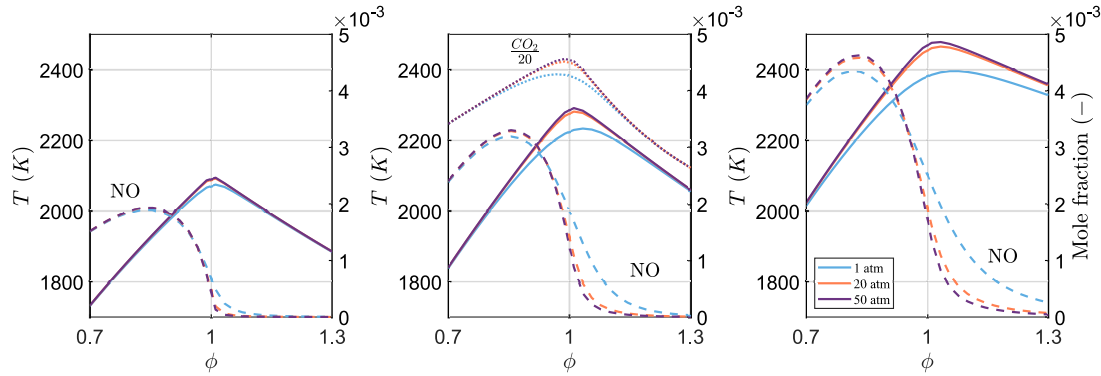


Figure 4.1: Maximum adiabatic temperature (left y-axis, solid lines) and mole fraction of major pollutants (right y-axis, dashed lines) (NO and CO₂ when applicable) at equilibrium conditions for NH₃ (left), CH₄ (middle), and H₂ (right) with air as an oxidizer, for three pressures (1 atm, 20 atm, and 50 atm) and at T = 300 K

The general characteristics of various fuels such as NH₃, CH₄, and H₂, such as adiabatic temperature, the equilibrium mole fraction of the fuel, and NO are provided in Fig. 4.1 for a range of equivalence ratios and a set of pressures (1 atm, 20 atm, and 50 atm). The equilibrium models in CANTERA [4] calculate the adiabatic temperature for the respective fuels at the required equivalence ratios; the model captures the ideal heat release by neglecting flow effects typically encountered in 1-D or multidimensional models. The adiabatic temperature and pollutant mole fraction are plotted in Fig. 4.1 for the above-mentioned fuels across the equivalence ratio and a set of pressures (1, 20, and 50 atm). Special attention must be paid to the NO mole-fraction as it heavily depends on the flame's residence time and, in turn, on the combustors' dimensions. Hence, NO emissions are prone to being underestimated for NH₃ flames by the equilibrium calculations. The work by Kobayashi et al. [132] indicated that NO reduces with pressure. The increased pressure reduces NO emissions through OH third-body reactions. Although NH₃ consumption remains largely unchanged, pressure also suppresses NH production, further lowering NO. Therefore, high-pressure conditions are advantageous for NH₃-based combustors.

Lean NH₃ flames

NO is primarily formed due to the oxidation of NH_i through HNO [132]. The formation of NO is favored by the presence of O/H radicals, and hence NO peaks in the lean side of the stoichiometry. The effects of equivalence ratio, ϕ , and pressure on the NO production can be seen in Fig. 4.1. Notably, pressure increases the equilibrium mole-fractions of NO in NH₃-air (albeit minimally) in the lean conditions.

Rich NH₃ flames

The amount of NO is significantly lower than the lean mixtures, and it is formed mainly by the reaction of NNH with O [132]. In addition to that, NO is also formed in the rich flames from the extended Zeldovich mechanism. However, due to the lower availability of O₂, ammonia slip (unburnt/unreacted ammonia emissions) is a critical issue that can only be identified in spatial configurations, such as 1-D flames, and not in equilibrium calculations (see Fig. 4.1). From the design perspective, rich flames are interesting since:

- low NO_x in the rich conditions
- H₂ is produced in the burnt gas section from NH₃, which can be used as a part of staged combustion, thereby improving combustion efficiency, reducing the ammonia slip, and potentially increasing the residence time, further reducing the NO_x values.

4.3 Computational details

To model the spherically expanding flames, an open-source solver, FlameMaster [2], is utilized. 5×10^3 grid points are used such that at least 15 grid points resolve the region of the heat release. A grid sensitivity analysis was performed with 15×10^3 , showing that the coarser grid with 5×10^3 grid points is sufficient to capture the flame dynamics adequately. Hence, it is used hereafter for the numerical models. The flame front is described as the location of the maximum heat release rate. It was observed that the flame dynamics in the weakly stretched region are independent of this criterion, i.e., the behaviour of the flame described by an isotherm and heat release rate is the same.

Zhu kinetic mechanism is used for the numerical model (mechanism validation is discussed in Section 4.4.1). Consistent with the literature [125], Zhu 2024 [129] and KAUST 2021 [127] show very good agreement with the experimental measurements. The flame is simulated for a physical propagation time of 120 ms. The flame is initiated by placing a planar flame on the burnt side defined by the input file (here $R_{\text{ignition}} = 0.7$ cm). A single ignition radius has been chosen to mitigate the effects due to different ignition radii. A special attention has been placed on evaluating the effects of pressure on the flame dynamics. The comparison between various pressures is executed via

- the dimensional stretch vs. dimensional flame speed ($\frac{dR_f}{dt}$) to evaluate the effects of radiation and pressure on the burnt flame speed.
- Extrapolated Markstein length, L_b and the laminar burning velocity, S_L

In addition, predictions of the simulations are examined against the experimental measurements when available. The effects of three radiation models —namely, adiabatic (ADI), which neglects radiation; optically thin (OTM), which neglects reabsorption; and DOM/SNBCK — are compared. The SNBCK in this chapter refers to the SNBCK25 in the previous chapter, which was optimized to maintain a reasonable computational cost of 100 RTE evaluations at one grid point and one direction instead of 3980 RTE evaluations in SNBCK. The RTE for the DOM/SNBCK was solved for eight discrete directions. The optimization was performed such that higher band resolution is used in a relatively high absorption coefficient region. In cases where a single simulation is compared using different radiation models, colors are used for distinction. The extrapolation is done only for the results within the observation window (1 cm to 3 cm). This observation window, used for experimental measurements, ensures that the pressure increase doesn't affect flame propagation due to compression effects. The end radius of 3 cm is consistent with experiments, as most experimental setups involve a chamber with a radius of 6 cm, and the analysis is performed on half of the chamber radius to maintain the isobaric property of the flames. It is important to note that the selection of the extrapolation window is quite arbitrary and requires a certain level of discretion. All the simulations were performed using the mixture-averaged diffusion model along with thermo-diffusion. As for the OTM, the Planck mean absorption coefficients were based on HITRAN-2020 for NH₃ and HITEMP-2010 for H₂O, as described in the previous chapter.

4.4 Isobaric flame propagation

4.4.1 Experimental validation

This section compares the numerical predictions with the experimental measurements. Additionally, we test the performance of various kinetic mechanisms for one test case (Case 1). The two experimental works that are utilized in validating the numerical model are:

- Case 1: The microgravity experiments of Roman Glaznev, ITV (private communication) for NH_3 -air at $\phi = 0.7$, $T = 373$ K, and $P = 3$ atm.
- Case 2: The high-pressure isobaric flame of Hayakawa et al. [121] for NH_3 -air at $\phi = 1.1$ at $T = 500$ K, and $P = 2$ MPa.

The extrapolated quantities, namely L_b and S_b , are tested against the experimental measurements for both cases in the literature.

Case 1

Three different mechanisms were utilized to model Case 1, namely, Zhu 2024 [129], Gotama 2022 [126], and Stagni 2023 [130]. Figure 4.2 shows the evolution of numerical and experimental flame displacement speed over stretch for lean ($\phi = 0.7$) NH_3 -air flame at 373 K and 3 atm. The solid, dashed, and dotted lines represent the DOM/SNBCK, adiabatic (ADI), and optically thin (OTM) models. From Fig. 4.2, it can be observed that, for all the mechanisms, the DOM/SNBCK and OTM are in close agreement in the early stages of the flame propagation, and at higher flame radius DOM/SNBCK and OTM starts to deviate, highlighting the pronounced effects of reabsorption in the fresh gases. It can be observed that DOM/SNBCK has a lower than ADI but higher flame speed than OTM, primarily due to the heat losses in OTM, which weaken the flame speed. Although the OTM of the Zhu model predicts the closest agreement with the experiments, the slope of the curve is different compared to the experimental measurements. These discrepancies in the slope are improved by considering the DOM/SNBCK with the Zhu 2024 mechanism. Zhu 2024 is used hereafter for all the numerical simulations due to its better predictions. L_b with the Zhu 2024 [129] within the observation window of 2 cm (from the experimental dataset) for ADI, OTM, and DOM/SNBCK are -0.0542, -0.1790, and -0.1026 cm, respectively. The L_b values did not change significantly with the increase in the observation window to 3 cm.

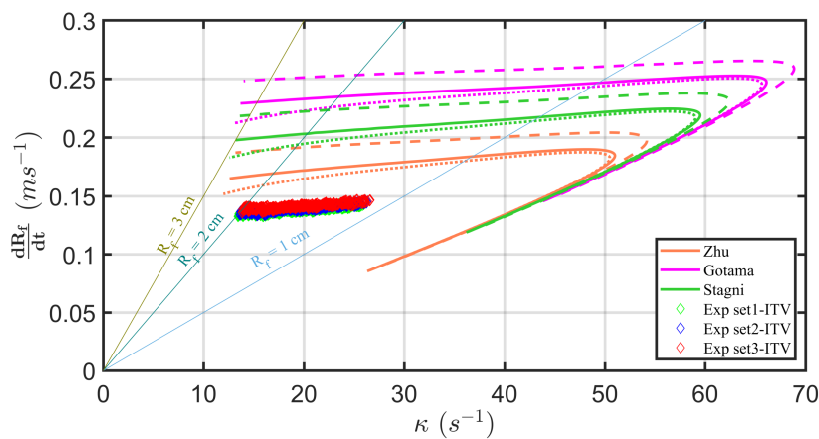


Figure 4.2: Illustration of the stretch vs flame speed for NH_3 - air flame at $\phi = 0.7$, $T = 373$ K, and $P = 3$ atm for a set of kinetic mechanisms against the experimental work of Glaznev ([118]); the solid lines represent DOM/SNBCK, dashed lines represent adiabatic (ADI) model and the dotted lines represent optically thin model (OTM).

Case 2

This case is particularly interesting for elucidating the effects of radiation on NH_3 -air flames, given the high pressure, which enhances reabsorption as observed in Chapter 3. The data set used in this study

represents a quasi-steady regime for $\phi = 1.1$ at 500 K and 2 MPa, before the onset of the buoyancy-driven flame regime, as indicated by the authors. The flame displacement speed over flame stretch is plotted in Fig. 4.3 for a rich NH_3 -air flame at 2 MPa. It can be observed that DOM/SNBCK and OTM are initially close to each other. As the flame propagates, the flame displacement speed from DOM/SNBCK exceeds (as seen in the inset in the southeast corner of Fig. 4.3) the flame displacement speed from ADI due to the reabsorption of emitted thermal radiation. Hayakawa et al. [121] reports an experimental L_b of 0.023 cm for an observation window of 1.35 cm. The numerically computed L_b for ADI, OTM, and DOM/SNBCK are 0.0403, 0.0294, and 0.0438 cm, respectively. From Fig. 4.3, we can observe that OTM predicts a negative L_b when the observation window has been extended to 3 cm, which is quite unlikely due to the Lewis number of the mixture ($Le \geq 1$). L_b when the entire 3 cm is accounted with ADI, OTM, and DOM/SNBCK are 0.0235, -0.0117, and 0.0302 cm, respectively. As for the flame displacement speeds, the DOM/SNBCK overpredicts it by 20 % (similar deviation for the ADI model as well). Although the deviation between the OTM and experimental measurements is lower (17.5%), its significance is diminished by the variations in the L_b .

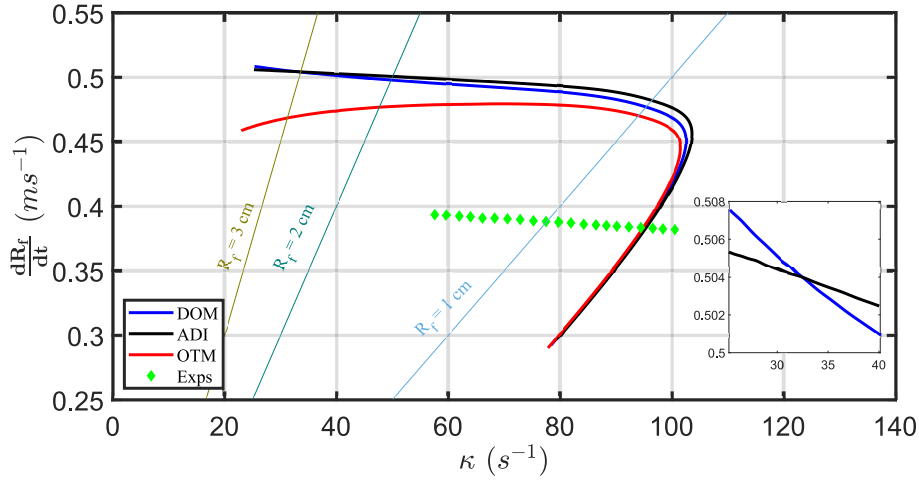


Figure 4.3: Stretch vs flame speed for NH_3 - air flame at $\phi = 1.1$, $T = 500$ K, and $P = 20$ MPa for various radiation models against the experimental work of Hayakawa et al. [121]

Conclusion

From the above figures, we can observe that the Zhu 2024 mechanism [129] is able to predict the laminar burning velocity with good accuracy compared to the other mechanisms. As for the comparisons between the radiation models on $\frac{dR_f}{dt}$, the discrepancy with OTM is lower against the experiments. It can be clearly observed that the predictions of L_b by DOM/SNBCK are much closer to the experiments than OTM, especially for the full observation window (3 cm) under study.

4.4.2 Effects of pressure on the propagation of NH_3 - air flames

In this section, we will investigate the effects of pressure on the dynamics of NH_3 -air flames at lean, stoichiometric, and rich conditions. The conditions are summarized in Tab. 4.2. The cases with pressure 20 atm and above are particularly interesting from a radiation perspective since it was observed in Chapter 3, that the magnitude of the divergence of radiative heat flux at the burnt gas and fresh gases are close to each other,

$$\frac{\max(|\nabla \cdot Q_{\text{fresh,rad}}|)}{\max(|\nabla \cdot Q_{\text{burnt,rad}}|)} \approx 1 \quad (4.3)$$

The maximum of the respective values in Eq. (4.3) is close to the flame front on either side. This highlights the better transfer of energy and the importance of reabsorption. The extrapolated LBV and L_b are presented for all the cases, while the analytical computation is provided for the lean cases to examine the consistency of the numerical and theoretical models.

Parameter	Value
ϕ	0.7, 1.0 & 1.3
Temperature	373 K
Pressure	1, 2, 3, 5, 7, 10, 20, 30, 40 & 50 atm

Table 4.2: Conditions studied for the effects of pressure on NH_3 - air flames

Lean flames

The lean NH_3 -air flames ($\phi = 0.7$) were simulated (see Tab. 4.2), and the temperature and divergence of radiative heat flux are provided in Fig. 4.4 for three pressures at different flame radius (for 1 atm, $R_f = 3$ cm, for 20 atm, $R_f = 1.54$ cm, and, for 50 atm, $R_f = 1.36$ cm).

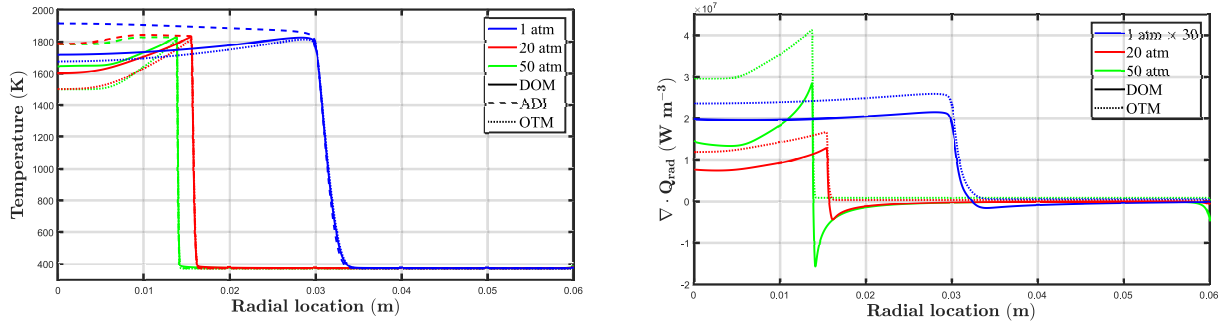


Figure 4.4: Temperature profile (left) and divergence of radiative heat flux (right) for NH_3 -air at $\phi = 0.7$ for a set of pressures (1 atm, 20 atm, and 50 atm). Please note that $\nabla \cdot Q_{rad}$ for 1 atm is scaled up by 30 for ease of visualization, and $\nabla \cdot Q_{rad}$ for the ADI model is zero.

Figure 4.4, illustrates the temperature profile on the left and the divergence of radiative heat flux on the right. It can be seen from Fig. 4.4 that the ADI model predicts higher temperature than DOM/SNBCK in the burnt side as it neglects the radiative loss. On the other hand, the OTM predicts lower temperatures than DOM/SNBCK due to excessive radiative heat loss, and this underprediction is enhanced while increasing the pressure. The OTM also predicts a radiative heat loss in the fuel side (although very low), while the DOM/SNBCK captures the effects of radiative reabsorption in the entire flame field.

The local minima of $\nabla \cdot Q_{rad}$ predicted by the DOM/SNBCK model in the burnt products side especially for pressures of 50 atm (see Fig. 4.4 (right)) can be related to the profile of the hot H_2O (Fig. 4.5 (left)). The reduction of NO mass fraction while increasing pressure can also be seen in Fig. 4.5 (right). The radiation model affects the mass fraction of NO through temperature owing to the Zeldovich mechanism of NO production. NO is higher and lower for DOM/SNBCK than for ADI and OTM due to higher and lower temperatures. The comparison between DOM/SNBCK and OTM highlights the crucial role of radiative reabsorption on NO production. Furthermore, NO mole fraction decreases with pressure in the case of 1D spherically expanding flames, whereas it increases in equilibrium calculations.

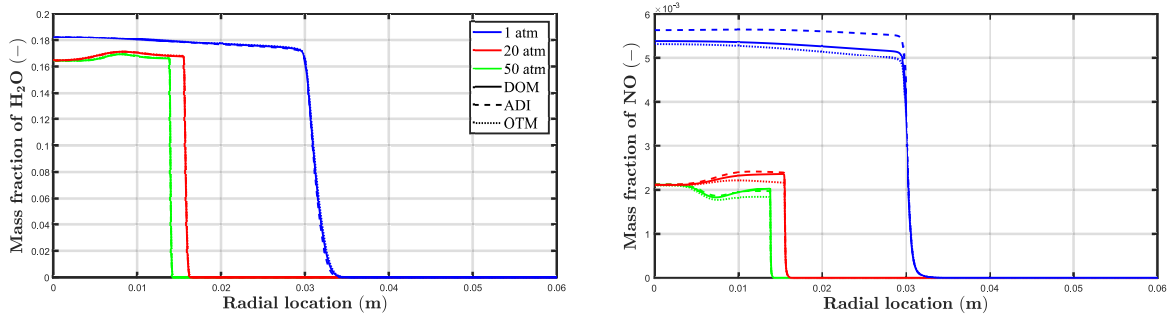


Figure 4.5: Species profiles of H_2O (left) and NO (right) of NH_3 -air at $\phi = 0.7$ for a set of pressures (1 atm, 20 atm, and 50 atm).

Figure 4.6 shows the flame displacement speed vs. flame stretch for a wide range of pressure from 1 atm to 50 atm. For both OTM and DOM/SNBCK models, the flame displacement speed can be approximated

to the burnt gas flame speed (S_b), i.e. the flame speed with respect to burnt gas, as inclusion of the burnt gas velocity did not change the qualitative behavior and the change is minimal, as compared to the flame displacement speed. However, there are cases reported in the literature where this approximation is no longer valid [134]. As the flame propagates initially, the flame speed of DOM/SNBCK is closer to the OTM than ADI, highlighting the importance of emission. As the flame further propagates, the deviation between ADI and DOM/SNBCK decreases, and this deviation is totally dependent on the pressure. The extrapolated laminar burning velocities (S_l) and the Markstein length (L_b) were obtained from the numerical predictions and are plotted in Fig. 4.7 by using the non-linear extrapolation method of Kelly and Law [3]. The deviation between ADI and DOM/SNBCK is interesting from the pressure of 20 atm and above; the change in the L_b at these conditions can be observed from Figs. 4.6 and 4.7. On the other hand, the analytical L_b for the adiabatic system is computed from the work of Bechtold and Matalon [135], similar to Refs. [136, 137], where Le_{eff} is the effective Lewis number of the flames from the deficient species, δ the flame thickness of the adiabatic 1D flame, and Ze (β) the Zeldovich number:

$$\frac{L_b}{\delta} = \gamma_1 + \frac{1}{2}\beta (Le_{eff} - 1) \gamma_2 - (\sigma - 1) \frac{\gamma_1}{\sigma} \quad (4.4)$$

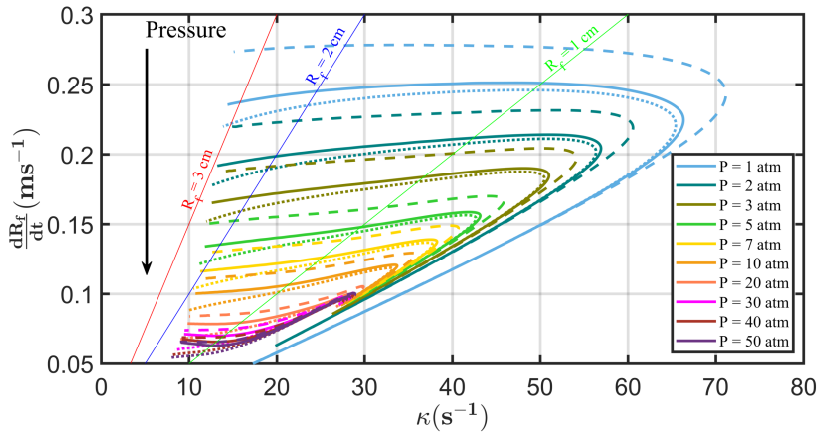


Figure 4.6: Flame speed vs flame stretch for NH_3 - air at $\phi = 0.7$ and $T = 373$ K for a range of pressures; Consistent with the previous figures, solid, dashed, and dotted lines represent DOM/SNBCK, ADI, and OTM, respectively.

Assuming that the thermal conductivity scales with $T^{0.5}$, $\lambda \propto T^{0.5}$, the constants γ_1 and γ_2 becomes:

$$\gamma_1 = \frac{2\sigma}{\sqrt{\sigma} + 1} \quad (4.5)$$

$$\gamma_2 = \frac{4}{\sigma - 1} \left[\sqrt{\sigma} - 1 - \ln \frac{1}{2} (\sqrt{\sigma} + 1) \right] \quad (4.6)$$

Where, $\sigma = \frac{\rho_u}{\rho_b}$. L_b is computed for $\phi = 0.7$ due to this validity of the analytical formulation [136]. The Zeldovich number (β , also denoted as Ze in the literature) is given by:

$$\beta = \frac{E_A}{R} \frac{T_{adi} - T_{initial}}{T_{adi}^2} \quad (4.7)$$

E_A is the activation energy of the multistep kinetic mechanism and is obtained by [49]:

$$\frac{E_A}{R} = -2 \left. \frac{\partial \ln(m_0)}{\partial (1/T_{adi})} \right|_p \quad (4.8)$$

The m_0 is the mass burning flux, and the $\left. \frac{\partial m_0}{\partial (1/T_{adi})} \right|_p$ can be obtained by changing the initial temperature or by changing the inert gas composition at constant pressure [138].

Figure 4.6 shows that the curves dR_f/dt vs. κ predicted by the DOM/SNBCK model exhibit a non-

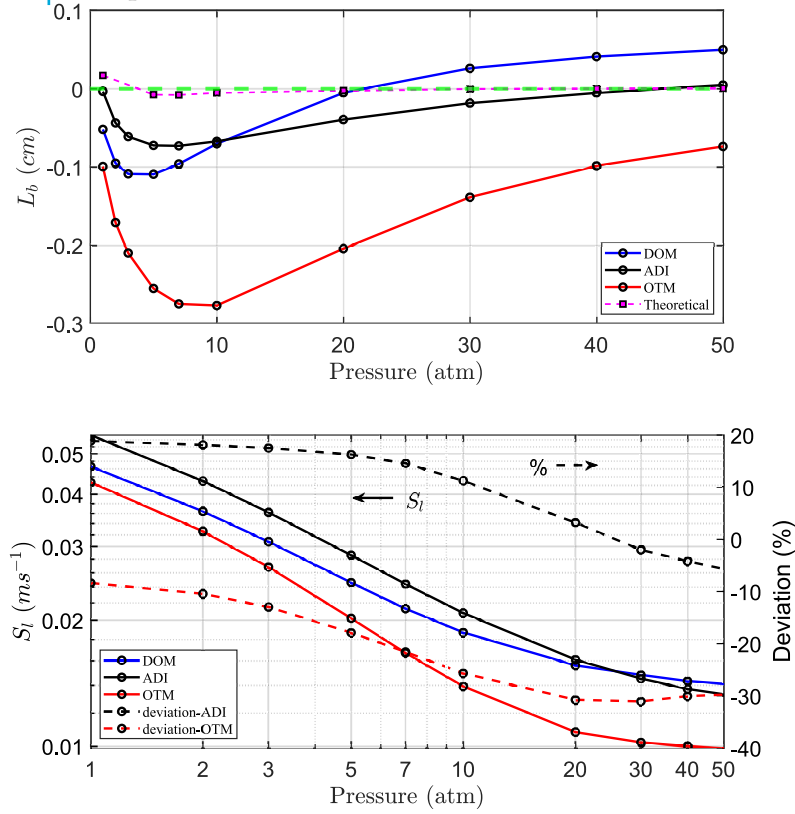


Figure 4.7: Top: extrapolated Markstein length (L_b) of NH_3 -air at $\phi = 0.7$ and $T = 373$ K for a range of pressures; Bottom: Extrapolated laminar burning velocity. The green dashed lines represent the transition from a positive L_b to a negative L_b configuration.

monotonic behavior as the pressure increases: for $P < 20$ atm, dR_f/dt decreases as κ is reduced whereas an opposite trend is observed for $P > 20$ atm. The evolution of the Markstein length L_b , with the pressure is reported in Fig. 4.7, where the behavior depicted previously is observed with $L_b < 0$ for $P < 20$ atm and $L_b > 0$ for $P > 20$ atm. The figure clearly highlights the role of the radiation model on the prediction of L_b . The OTM predicts a negative value of L_b over the entire range of pressure. These discrepancies have a great impact on the prediction of the stability of the system, as a negative Markstein length is associated with the onset of thermodiffusive instabilities [39, 139]. On the other hand, the ADI model captures the transition between a negative and a positive L_b , but the transition pressure is significantly over-predicted at $P \approx 40$ atm. The analytical expression (Eq. 4.4) has been obtained by neglecting radiation and, consistently, is in closer agreement with the prediction of the ADI model. It should be pointed out that analytical curve reported in Fig. 4.7 has been obtained by using an effective Lewis number, Le_{eff} , of 0.90 based on the fuel and that using $Le_{eff} = 0.93$ recommended by [135] does not capture the non-monotonic behavior exhibited by L_b with P , predicting a monotonic decrease throughout the pressure range. The change in the direction of the Markstein length with pressure can be attributed to the changes in the Zeldovich number. The variation of the Ze with pressure for NH_3 and NH_3 - H_2 flames is presented in Fig. 4.23. Recent works [138, 140] have also observed the non-monotonic variation of the Zeldovich number with pressure for NH_3 - H_2 and H_2 flames, respectively. A sensitivity analysis is carried out to highlight the sensitivity of Ze to individual reactions as a function of the pressure. This sensitivity analysis was done by scaling up the reaction rates of individual reactions by 50% [141]. The results are reported in Fig. 4.8. The sensitivity coefficients show that at higher pressures (above 10 atm), most of the pathways tend to reduce the Ze number. This explains the non-monotonic behavior of Ze with pressure, observed in Fig. 4.23 for pure NH_3 and $\phi = 0.7$, and, in turn, that of L_b .

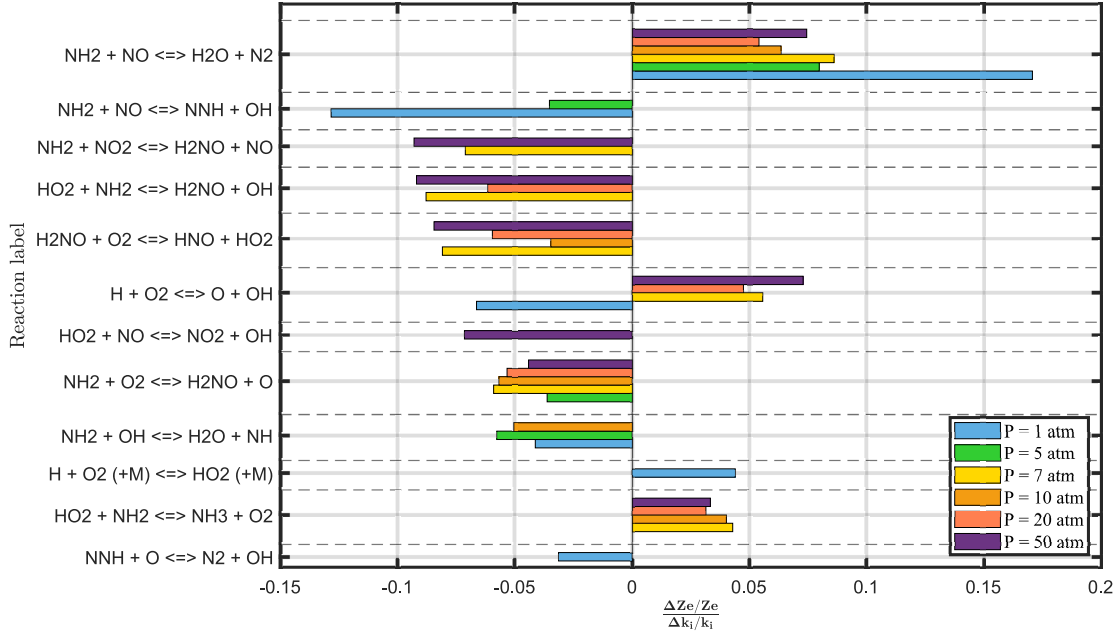


Figure 4.8: Normalized sensitivity coefficients of NH_3 -air at $\phi = 0.7$ for a set of pressures for the adiabatic case. k_i refers to the reaction rate of that specific reaction, i.

Figure 4.7 also quantifies the effect of pressure and the radiation model on the extrapolated laminar burning velocity. Simulation performed with the DOM/SNBCK model shows that the LBV decreases as the pressure increases. The radiation model significantly affects the predictions. The ADI overpredicts the LBV by more than 7% up to a pressure of 7 atm. Beyond this value, it is interesting to note that the departure between the LBV predicted by the DOM/SNBCK and the ADI models reduces and that the two curves intersect for a pressure of about 25 atm. On the other hand, the OTM model underpredicts the LBV by more than 10 %, with this error increasing with the pressure to reach about 30 % at 30 atm.

In order to further analyze the effects of pressure and radiation model on the flame spread mechanism, the different contributions (enthalpy diffusion, conductive, and the heat release rate) to the energy conservation equation are computed for an equivalence ratio of 0.7, for different pressures of 1 atm, 20 atm, and 50 atm and with the different radiation models (DOM/SNBCK, ADI, and OTM). The flame profiles chosen for the calculation of the contributions are those reported in Figs. 4.4 and 4.5. The three pressures are selected as they represent the different regions in the evolution of L_b from negative for $P < 20$ atm, approximately equal to 0 for $P = 20$, and positive for $P > 20$ atm (see Fig. 4.7). The energy equation for an isobaric flame spherically expanding flame in Lagrangian coordinates (described in Chapter 2 and also in [37, 64]) is given by:

$$\frac{\partial T}{\partial t} = \frac{1}{c_p} \frac{\partial}{\partial \psi} \left(\rho r^4 \lambda \frac{\partial T}{\partial \psi} \right) - \frac{r^4}{c_p} \sum_{i=1}^{n_s} \rho w_i V_i c_{p,i} \frac{\partial T}{\partial \psi} - \frac{1}{\rho c_p} \sum_{i=1}^{n_s} \dot{\omega}_i h_i M_i - \frac{\nabla \cdot \mathbf{q}_{\text{rad}}}{\rho c_p} \quad (4.9)$$

The first term on the right hand side corresponds to Fourier conduction, the second term to enthalpy diffusion and thermo-diffusion (the latter is accounted for in the diffusion velocity, V_i), the third term to the heat release rate (HRR), and finally, the fourth term to the divergence of the radiative heat flux. The enthalpy diffusion, thermo-diffusion, and Fourier conduction are grouped together and referred to as diffusion terms hereafter. The term on the left-hand side is termed as a temporal term. The temporal, HRR, radiative, and diffusion terms are plotted in Fig. 4.9A, B, C, and D, respectively. The conductive and the diffusion terms are slightly noisy at the 1 atm case.

Radiation Model	1 atm ($R_f = 3$ cm)	20 atm ($R_f = 1.54$ cm)	50 atm ($R_f = 1.35$ cm)
DOM/SNBCK	0.2375	0.0786	0.0649
ADI	0.2752	0.0842	0.0657
OTM	0.2220	0.0660	0.0543

Table 4.3: Flame displacement speeds (in m s^{-1}) at their respective flame radius from Fig. 4.9.

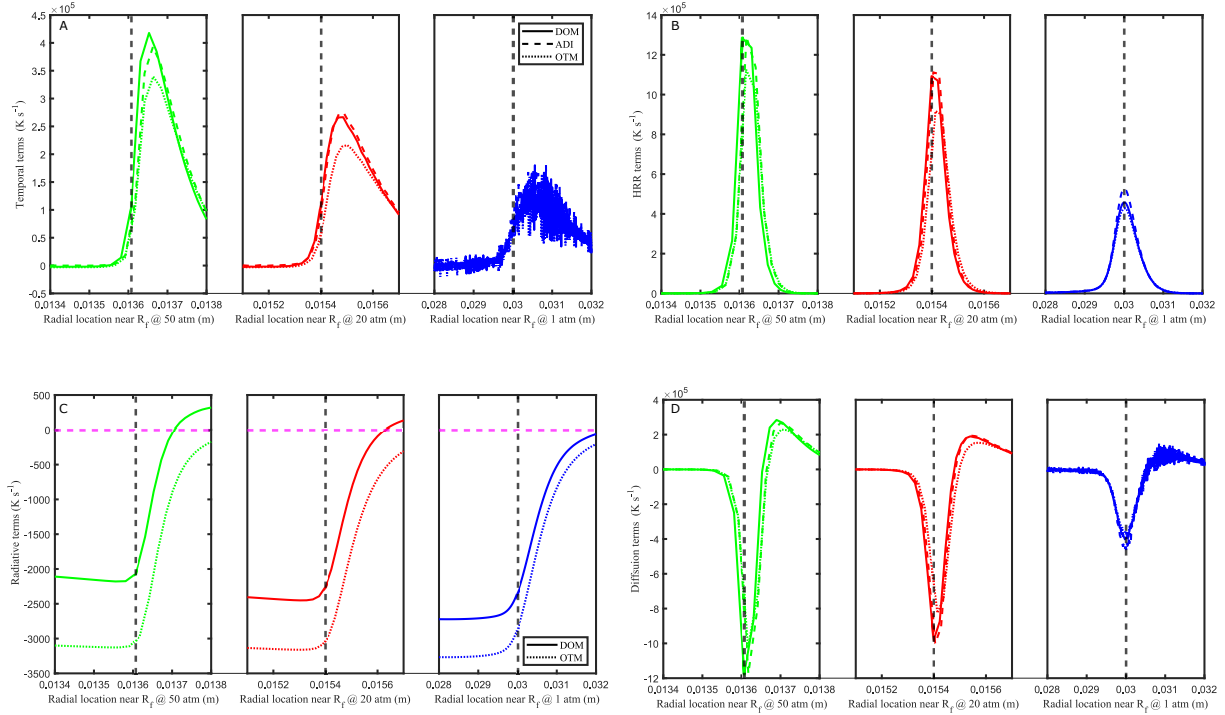


Figure 4.9: Top-left: Net contribution from all the respective physical processes; Top-right: HRR terms; Bottom-left: Radiative terms, the magenta dashed lines highlight the transition from heat loss to heat gain due to re-absorption, the OTM models are always below the red dashed line; Bottom-right: Diffusion terms that account for the Fourier conduction and enthalpy flux. The pressure values are given in the x-label. These calculations correspond to NH_3 -air at $\phi = 0.7$ and 373 K, and the black dashed lines highlight the flame radius (see Fig. 4.4)

The effects of pressure on DOM/SNBCK are discussed below. As expected, increasing the pressure enhances the peak of HRR, reduces the flame thickness, and increases reabsorption, leading to lower radiative loss in the burned region and higher preheating on the fuel side. These processes contribute to enhancing the flame speed.

The effects of the radiation models on the different contributions are similar, regardless of the pressure, although they are enhanced with the pressure. It appears clearly in Fig. 4.9 C that the contribution of radiation ahead of the flame front is negligible compared to the other contributions and, more specifically, to the diffusion term that drives the spread rate. The effects of radiative reabsorption on the flame speed is then related to indirect mechanisms: first, reabsorption of radiation increases the temperature in the flame front. This contributes to enhancing the HRR, as observed in Fig. 4.9B, by comparing the solutions obtained by DOM/SNBCK and OTM. This produces a thinner flame front, which, added to the higher temperature, tends to increase the diffusion of heat ahead of the flame front as observed in Fig. 4.9 D, inducing a higher spread rate.

The different contributions are spatially-integrated using the trapezoidal method in MATLAB R2023b, and each term is scaled by integrated temporal terms. The consistency of the integrated value was verified using different numerical methods. The effects of pressure on the different contributions are compared in Fig. 4.10. It appears that the normalized total contributions are not very sensitive to pressure, with a slight reduction in HRR and radiative term with an increase in pressure. The latter can be explained by an increase in reabsorption. The effects of the radiation model are analyzed in Fig. 4.11 for a pressure of 50 atm. The total normalized HRR is significantly affected by the radiation model with $\text{ADI} < \text{DOM/SNBCK} < \text{OTM}$. It also appears clearly that the OTM significantly overpredicts the overall

radiative loss. Although the diffusion term is higher at the flame front for DOM/SNBCK compared to OTM, as discussed previously, its overall contribution is higher for OTM.

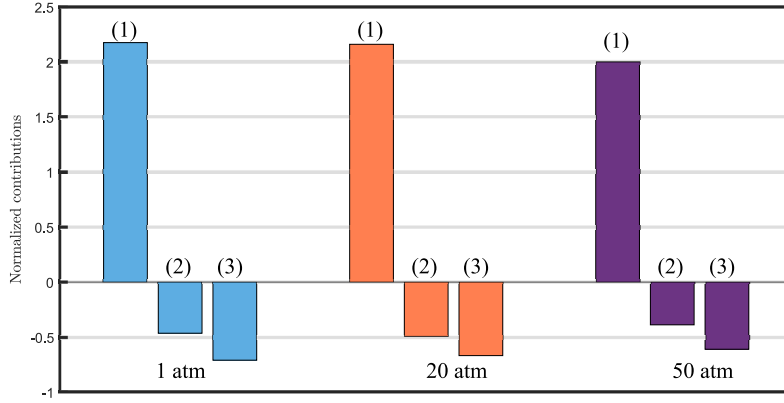


Figure 4.10: Normalized contributions of various processes using DOM/SNBCK at three different pressures for NH_3 -air at $\phi = 0.7$ and 373 K, (1), (2), and (3) corresponds to the HRR, radiation and diffusion terms (see Eqn.4.9) respectively.

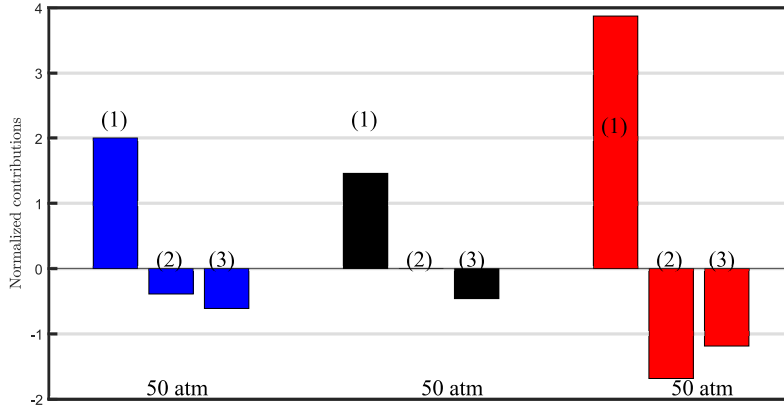


Figure 4.11: Normalized contributions of various processes using DOM/SNBCK (blue), ADI (black), and OTM (red) at 50 atm for NH_3 -air at $\phi = 0.7$ and 373 K, (1), (2), and (3) corresponds to the HRR, radiation and diffusion terms (see Eqn.4.9) respectively. Note that (2) for the ADI model is zero.

The Tab. 4.3, summarizes the flame displacement speeds at their respective time steps corresponding to temperature and contributions profile. From Fig. 4.6, at high pressures (20 atm and 50 atm), we can observe that although DOM/SNBCK's flame displacement speed is lower than the ADI, the DOM/SNBCK's behaviour is different compared to the ADI. Specifically, unlike ADI, these pressures represent the case where flame displacement speed increases with radius for DOM/SNBCK.

Stoichiometric flames

Stoichiometric NH_3 -air flames are also interesting in understanding the effects of radiative reabsorption on the flame characteristics due to higher emission from the burnt part. In addition, they also allow experimental verification of the radiative process on flame physics due to their high LBV (compared to the lean cases), which can be inferred from the relative abundance of high-pressure experimental data on stoichiometric and rich NH_3 -air flames in the literature [82, 117, 121, 142]. Consistent with the previous section, profiles of temperature, divergence of radiative heat flux, and species profiles of NH_3 , H_2O , and NO are plotted in Figs. 4.12 and 4.13 at $R_f = 3$ cm for 1 atm, $R_f = 2.70$ cm for 20 atm, and $R_f = 2.4$ cm for 50 atm.

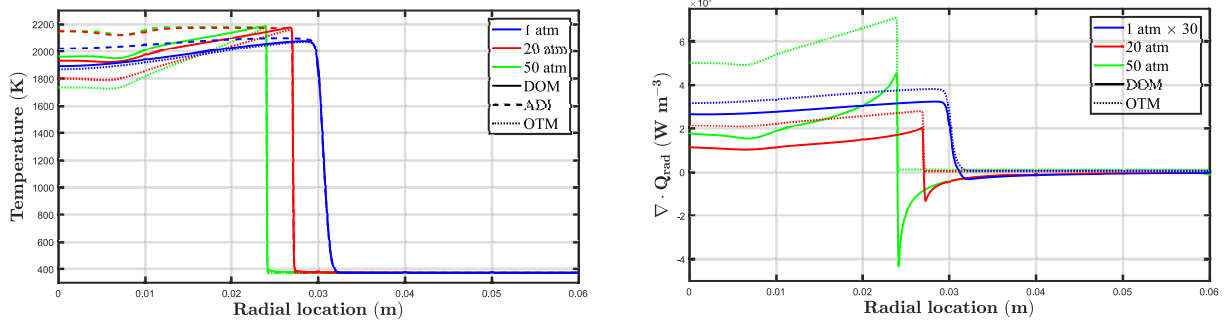


Figure 4.12: Temperature profile (left) and divergence of radiative heat flux (right) for NH_3 -air at $\phi = 1.0$ for a set of pressures (1 atm, 20 atm, and 50 atm). Please note that $\nabla \cdot Q_{\text{rad}}$ for 1 atm is scaled up by 30 for ease of visualization, and $\nabla \cdot Q_{\text{rad}}$ for the ADI model is zero.

Figure 4.12 illustrates the temperature (left) and divergence of radiative heat flux (right) profile for the stoichiometric case for three different pressures. Similar to the lean cases, the $\nabla \cdot Q_{\text{rad}}$ for 1 atm is scaled up by 30. Also, from the temperature profiles at 50 atm, it can be observed (by zooming in) that the temperature in the flame front predicted by DOM/SNBCK is higher (marginally by 11 K) than the temperature predicted by ADI, highlighting the role of radiative reabsorption. The reabsorption by the fresh gases leads to higher fresh gas temperatures and, consequently, a higher flame temperature in the flame front. At 1 atm, the ratio of the radiative source terms (Eq. (4.3)) between the fresh gas and the burnt products is around 0.1, and OTM over-predicts the $\nabla \cdot Q_{\text{rad}}$ by 17%. At 50 atm, the ratio is around 0.98, and the OTM overpredicts the divergence of radiative heat flux by 50%, highlighting the importance of radiation and OTM's inability to capture the physics with the required level of accuracy.

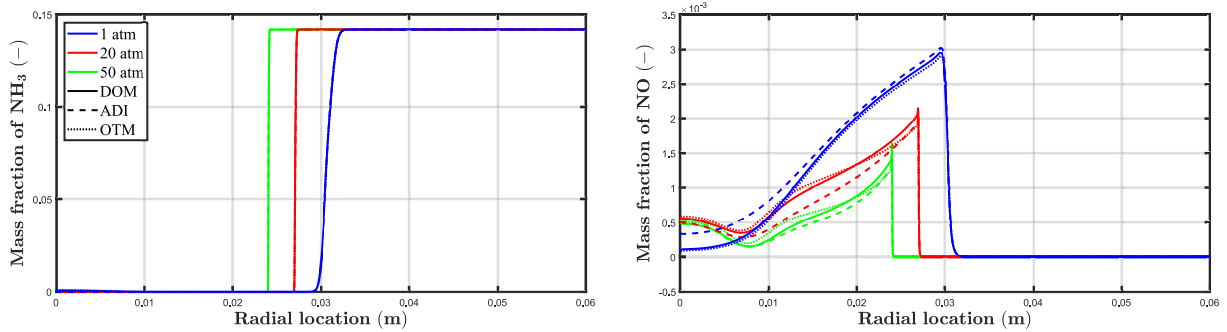


Figure 4.13: Species profile of NH_3 (left) and NO (right) of NH_3 -air at $\phi = 1.0$ for a set of pressures (1 atm, 20 atm, and 50 atm). Note that due to perfect agreement between various radiation models on the mass fraction of NH_3 , it is overlapping one with the other.

Figure 4.13 illustrates the NH_3 (left) and NO (right) profiles at three different pressures (1 atm, 20 atm, and 50 atm). The mass fraction profiles of NH_3 are provided to compare and contrast the unburnt ammonia (ammonia slip) in the burnt part of rich flames ($\phi = 1.3$) in the upcoming section. From Fig. 4.13(left), it can be seen that the NH_3 mass fraction profiles are almost insensitive to both pressures and radiation models. Most interestingly, we can observe from Fig. 4.13(right) that NO predictions are slightly non-linear with respect to the magnitude of temperature at higher pressures (20 atm and 50 atm). By convention, NO increases with temperature via the Zeldovich mechanism of NO production (usually above 1800 K). The magnitude of temperature varies (in increasing order) from OTM, DOM/SNBCK, and ADI in the burnt section. OTM predicts higher NO compared to DOM/SNBCK and ADI, highlighting the effects of radiative heat transfer on the intermediates via the temperature. This further requires a detailed investigation of the kinetic pathways with various radiation models for a range of kinetic mechanisms.

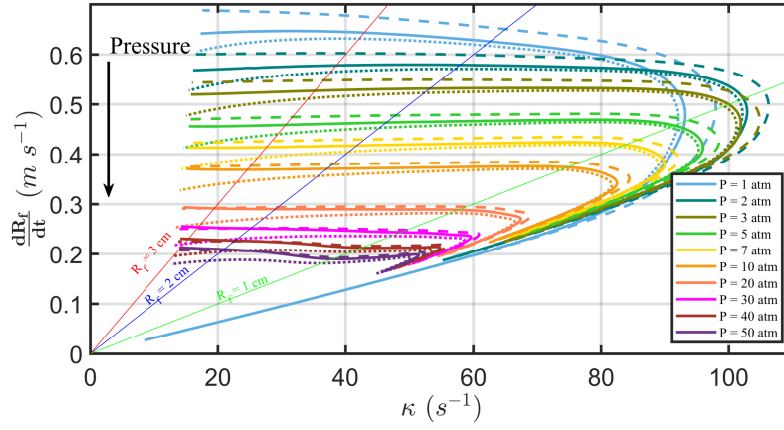


Figure 4.14: Flame displacement speed vs flame stretch for NH_3 -air at $\phi = 1.0$ and $T = 373$ K for a range of pressures; In the above figure, consistent with the previous figures, solid, dashed, and dotted lines represent DOM/SNBCK, ADI, and OTM, respectively.

Figure 4.14 illustrates the flame displacement speed ($\frac{dR_f}{dt}$) over the stretch (κ) for a set of pressures and radiation models. Interestingly, in Fig. 4.14, there is a change in the trend even for 1 atm for DOM/SNBCK and OTM. However, this occurs after 3 cm, which brings into question the universality of L_b and extrapolated S_L , and the source of this non-linearity at 1 atm needs to be further investigated. The flame's thermo-diffusional stability can be assessed from the extrapolated quantities L_b and S_L (shown in Fig. 4.15) from the extrapolation routine from the flame displacement speed and flame stretch. Consistent with the previous results, we observe a non-monotonic behavior on the L_b , although the inflection point occurs at a higher pressure for the radiation models. It can be seen (Fig. 4.15) that initially, for DOM/SNBCK and ADI NH_3 flames, the pressure range of 1 atm to 3 atm is thermo-diffusively stable, although L_b decreases with increasing pressure. As the pressure is further increased, the L_b becomes negative, denoting a thermo-diffusively unstable flame configuration, and it reaches an inflection point. With further increase in pressure, the flame becomes relatively more thermo-diffusively stable than at the inflection point. The inflection point is 7, 10, and 20 atm for DOM/SNBCK, ADI, and OTM, respectively. These observations are in qualitative agreement with the experimental observations, although experimental uncertainty needs to be critically examined due to the low absolute values of the flame speeds. In the bottom of the Fig. 4.15, we can observe the effects of radiation (via pressure) on the extrapolation of S_L . More interestingly, after 20 atm, DOM/SNBCK predicts a higher S_L than ADI due to the reabsorption of radiated energy, and for the lean case, this occurred at a higher pressure (≥ 30 atm), illustrating the effects of partial pressures and pressure effects on the absorption coefficients. On the other hand, the discrepancies between the OTM and DOM/SNBCK increases continuously with pressure from 5% at 1 atm to 20% at 50 atm.

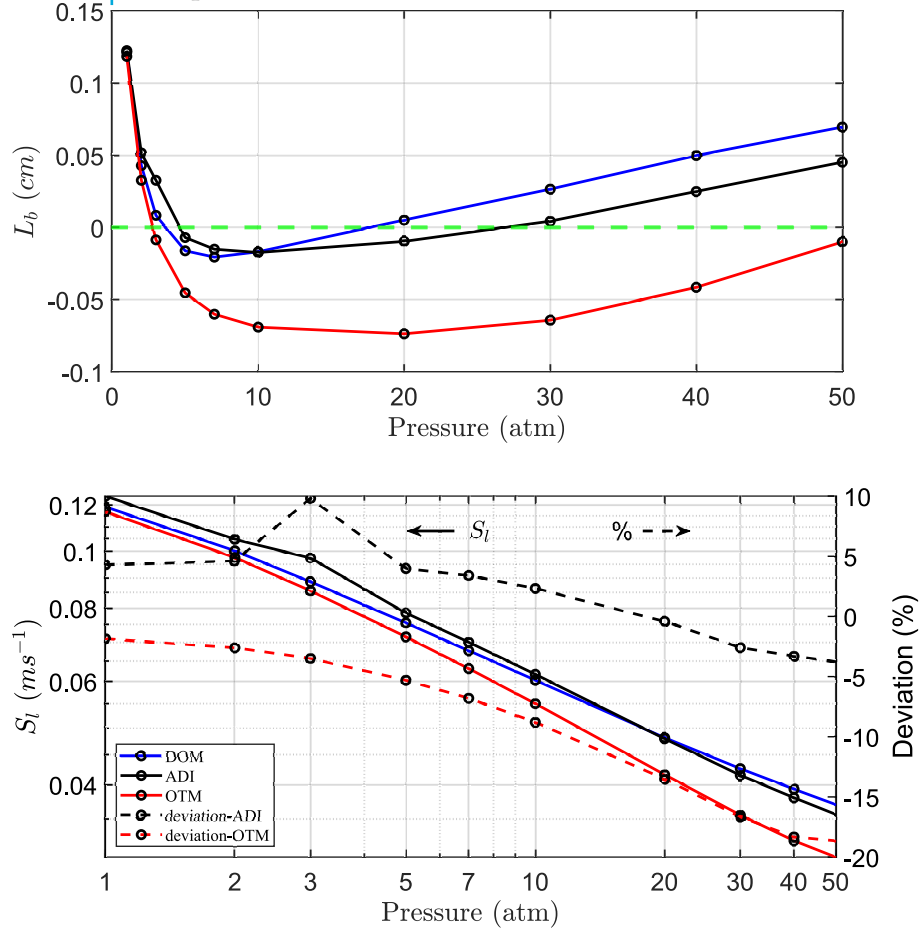


Figure 4.15: Top: extrapolated Markstein length (L_b) of NH_3 -air at $\phi = 1.0$ and $T = 373$ K for a range of pressures; Bottom: Extrapolated laminar burning velocity. The green dashed lines represent the transition from a positive L_b to a negative L_b configuration.

Rich flames

Rich NH_3 -air flames form an important facet of the investigation of radiative processes due to the relative abundance of NH_3 and its impact on the radiative reabsorption ahead of the flame front. The unburnt ammonia after combustion is termed as ammonia slip. Since ammonia is classified as a pollutant, slip of rich ammonia flames is an important phenomenon that needs to be addressed. Consistent with the previous section, profiles of temperature, divergence of radiative heat flux, and species profiles of NH_3 and NO are plotted at $R_f = 3$ cm for 1 atm, $R_f = 2.70$ cm for 20 atm, and $R_f = 2.4$ cm for 50 atm for ease of visualization. Like the previous cases, the DOM/SNBCK computed a higher temperature in the flame front than ADI (8 K for 20 and 10 K for 50 atm). As expected, in this rich case, the ratio of $\nabla \cdot Q_{\text{rad}}$ (Eq. (4.3)) is higher than the burnt section, but the integrated $\nabla \cdot Q_{\text{rad}}$ in the burnt section is always higher than the fresh gases (see Fig. 4.16). The ratio between the fresh gases and the burnt section is around 1.086 at 50 atm, and the ratio is 0.9318 even at 1 atm, highlighting the role of re-absorption for rich NH_3 -air flames in the flame front.

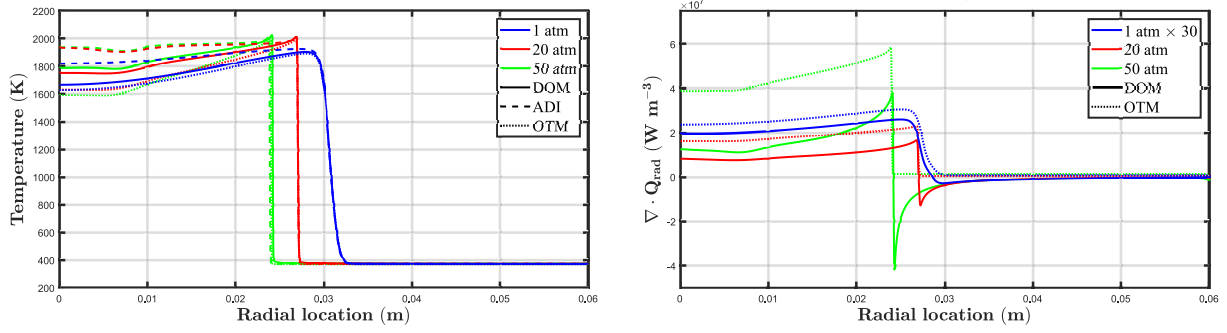


Figure 4.16: Temperature profile (left) and divergence of radiative heat flux (right) for NH_3 -air at $\phi = 1.3$ for a set of pressures (1 atm, 20 atm, and 50 atm). Please note that $\nabla \cdot Q_{\text{rad}}$ for 1 atm is scaled up by 30 for ease of visualization, and $\nabla \cdot Q_{\text{rad}}$ for the ADI model is zero.

The effects of ammonia slip can be illustrated with the mass fraction profile of NH_3 , left in Fig. 4.17. We can see that non-minimal NH_3 exists in the burnt part of the flame, which is also a concern due to NH_3 environmental impacts. It can be observed that with an increase in pressure, the mass-fraction of unburnt ammonia reduces. However, caution needs to be exercised, as the partial pressures of NH_3 in the burnt gas may be higher due to the high operating pressure. As for the NO predictions, it can be seen that with pressure, the NO reduces both in the flame front and the burnt gas, but the magnitude of reduction in the burnt gas was seen in other stoichiometric conditions (Figs. 4.5 and 4.13). The deviations between various radiation models are low, and importantly, in the burnt gas section, it tends to be 2e-5 or 20 ppm (within the EU limit of 24 ppm for medium-sized burners, [143]). The behaviour of the NO predictions conforms to the temperature dependence, i.e., in the burnt gas, ADI predicts the highest, and OTM predicts the lowest.

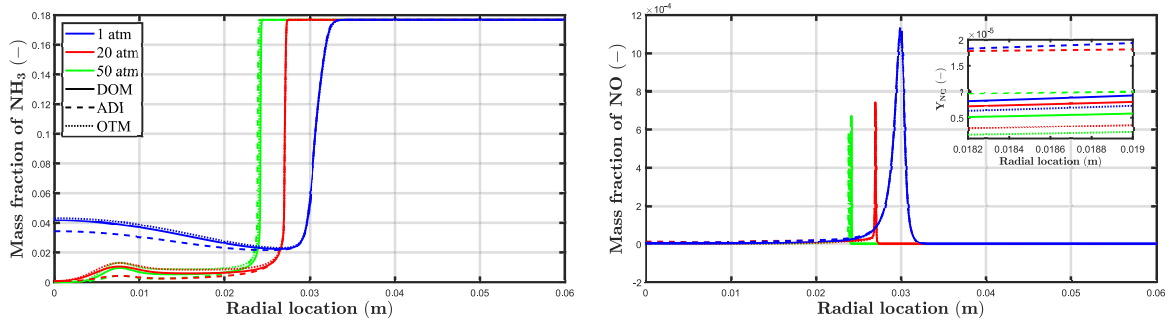


Figure 4.17: Species profile of NH_3 (left) and NO (right) of NH_3 -air at $\phi = 1.3$ for a set of pressures (1 atm, 20 atm, and 50 atm). The inset in the NO profile (right) shows the zoomed part of the burnt gases.

Figure 4.18 describes the flame displacement speed, $\text{FDS} \left(\frac{dR_f}{dt} \right)$ over stretch (κ) for a set of pressures. In Fig. 4.18, the flame displacement speed of DOM/SNBCK is higher compared to ADI, even in the observation window (1 cm to 3 cm) for the pressures above 20 atm, illustrating the effects of reabsorption for the rich cases. The effects of reabsorption in the extrapolation routine will be discussed below.

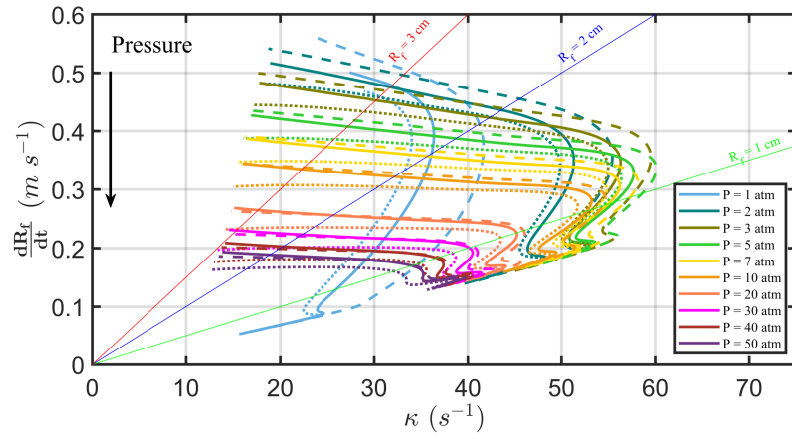


Figure 4.18: Flame displacement speed vs flame stretch for NH_3 - air at $\phi = 1.3$ and $T = 373$ K for a range of pressures; In the above figure, consistent with the previous figures, solid, dashed, and dotted lines represent DOM/SNBCK, ADI, and OTM, respectively.

Also, from the S_l plot, we can observe that from 10 atm, S_l of DOM/SNBCK is higher than ADI, whereas the FDS were higher in magnitude from 20 atm in Fig. 4.18. We can see that for $\phi = 1.3$, the deviation between the ADI and DOM/SNBCK becomes nearly stagnant. OTM has nearly the same level of deviation between $\phi = 1.0$ & 1.3.

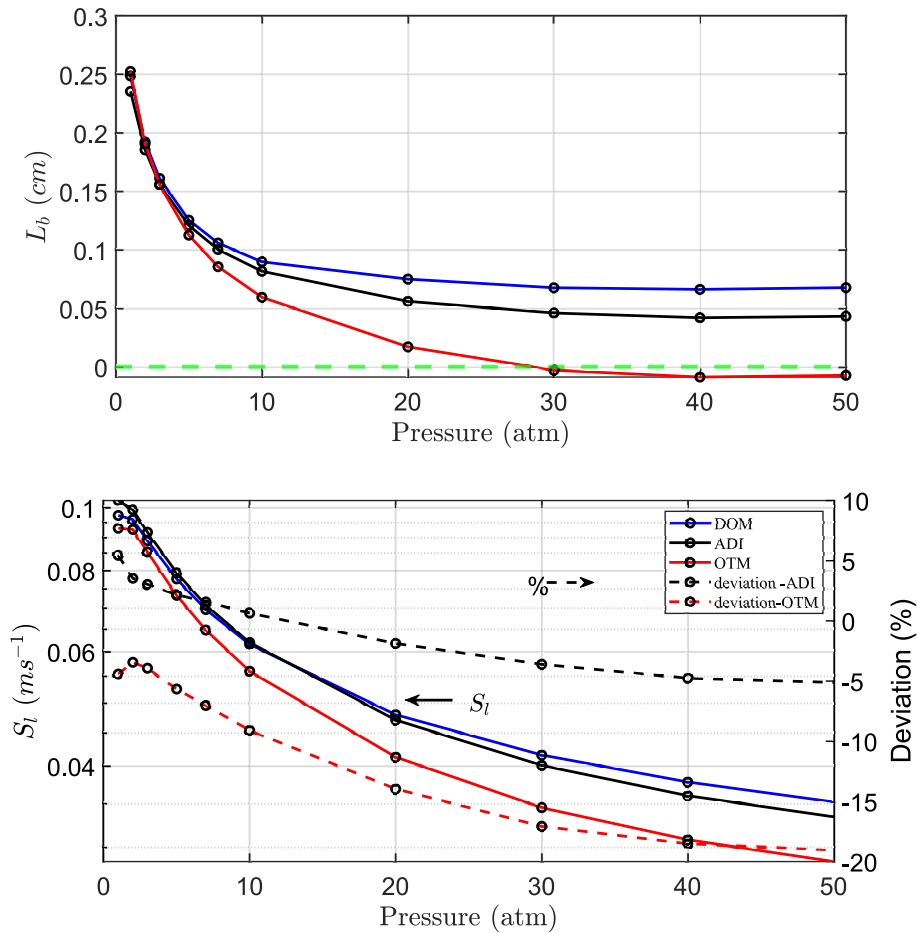


Figure 4.19: Top: Respective extrapolated Markstein length (L_b) of NH_3 - air at $\phi = 1.3$ and $T = 373$ K for a range of pressures; Bottom: Extrapolated laminar burning velocity. The green dashed lines represent the transition from a positive L_b to a negative L_b configuration.

4.4.3 Effects of pressure on the propagation of NH₃/H₂- air flames

Case	Parameter	Value
Case 4: Cracked NH ₃ -air	ϕ	1.0
	Temperature	300 K
	Pressure	1, 2, 3, 5, 10, 20, 30 & 50 atm
	cracking ratio (γ)	40% (0.12068)
Case 5: Blended NH ₃ -H ₂ -air	ϕ	0.8
	Temperature	373 K
	Pressure	1, 5, 10 & 40 atm
	H ₂ ratio (X)	0(0.1830), 5 (0.1762), 15 (0.1621) & 30 (0.1395) %

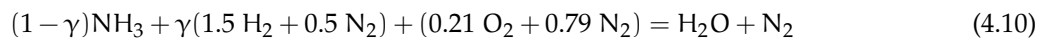
Table 4.4: Conditions studied for Case 4 and Case 5, the values within the parenthesis in the cracking ratio and H₂ ratio indicate the mole-fraction of NH₃

This subsection analyzes the effects of hydrogen addition on radiative heat transfer and flame propagation. This is particularly important since the H₂ is considered the prime candidate to increase the LBV of NH₃ mixtures. Two cases were considered for this work,

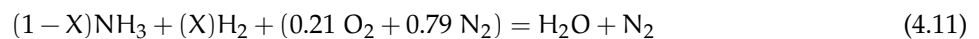
- Case 4: Ammonia (cracked up-to 40 %) similar to experimental work of Bowen et al. [117] at an equivalence ratio of $\phi = 1.0$ and an initial temperature $T = 300$ K.
- Case 5: Blended mixtures of NH₃ and H₂ in air at an $\phi = 0.8$ and $T = 373$ K.

Cracked ammonia is an interesting option since the on-board ammonia is cracked into N₂ and H₂, eliminating the need for dual-feed systems to the combustion chamber. As previously reported by Mei et al. [117], ammonia starts to crack at 473 K, and the percentage of cracking can be improved by recirculating the heat of the exhaust gases. To simulate cracked ammonia and blended ammonia, we set the mole fractions of NH₃, H₂, O₂, and N₂ according to the reaction equation, Eqs. (4.10-4.11). Case 4 is simulated at various pressures from 1 atm to 50 atm to evaluate the effects of reabsorption on the flame propagation; the full set of conditions simulated are in Tab. 4.4.

The reaction equation for the cracked ammonia case is given as,



Case 5 is simulated for select values of H₂ ratios from 0% to 30% for select values of pressures as shown in Tab. 4.4. The reaction equation for the blended ammonia is given as:



Finally, evaluation of the Zeldovich number is performed for the conditions mentioned in Case 5, $\phi = 0.8$ for various H₂ content.

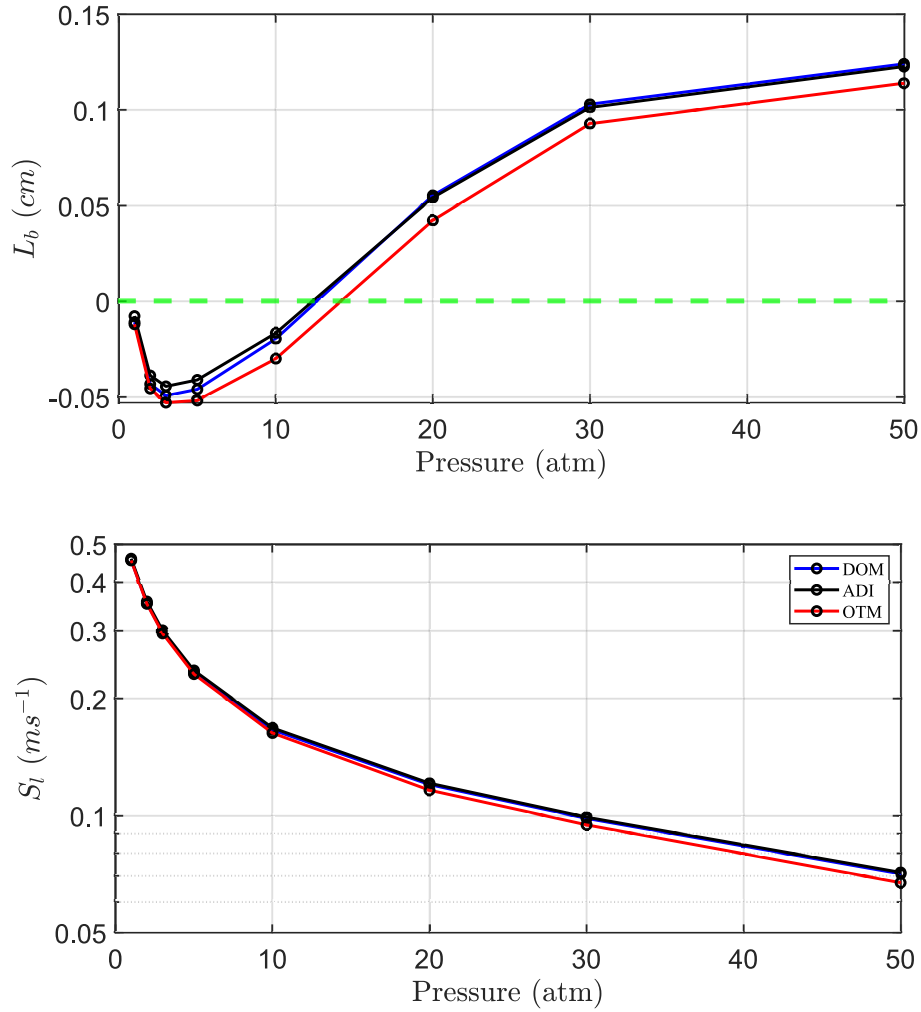
Case 4: Effects of pressure on the flame propagation of cracked ammonia

Figure 4.20: Top: Extrapolated Markstein length (L_b) of 40 % cracked NH_3 flame at $\phi = 1.0$ and $T = 300$ K for a range of pressures; Bottom: Extrapolated laminar burning velocity. The green dashed lines represent the transition from positive L_b to negative $L_b < 0$ configuration.

Figure 4.20 shows the evolution of L_b and S_l over pressures for the cracked ammonia- air case. First, we can observe that the effects of radiation are minimal across the pressures to the extent that the non-monotonic behavior occurs at the same pressure. The second interesting observation is that the pressure at which non-monotonic behavior occurs is 5 atm, earlier than previously observed for NH_3 -air at $\phi = 1.0$. These results are consistent with the results of Lehmann et al., [138], where the authors identified the source of the non-monotonicity for the H_2 and NH_3 blended flames to be the interaction between NH_2 and HO_2 radicals. Hence, the addition of H_2 promotes the non-monotonic behaviour to occur at lower pressure.

The effects of reabsorption can be observed to be minimal both from the L_b and S_l from the Fig. 4.20. The effects of reabsorption are minimal due to the lower molar concentration of NH_3 in the fuel, and OTM performs significantly better both on L_b (top) and S_l (bottom) than the previous cases due to the high temperature at the flame front (leading to minimal effects of heat loss on the flame) associated with the cracked ammonia flames. Comparisons against experimental data are avoided against the experimental works due to the uncertainty in the reported LBV from the work of Mei et al., [117].

Case 5: Effects of H_2 content on the flame propagation

H_2 ratio plays a pivotal role in the thermo-diffusional stability of blended mixtures via the Markstein length (L_b) as previously investigated in Refs. [137, 138]. In the work by Zitouni et al. [137], the authors observed that the L_b of pure H_2 -air flame was higher than blended NH_3 - H_2 mixtures with a

non-monotonic behavior.

Hence, pure H₂-air might be relatively more stable than NH₃-H₂-air flames. It was postulated in Ref. [138] that this might be due to the pronounced effects of certain chain branching reactions in the blended mixtures at high pressures. This regime is particularly interesting due to the relatively high concentration of NH₃, which also acts as a radiative absorber of emitted thermal radiation. The flame speed is plotted as a function of the flame stretch for the 40 atm case and different H₂ content in Fig. 4.21. It can be observed that with the increase in H₂ content, there is a qualitative agreement between ADI and DOM/SNBCK, highlighting the reduced effects of reabsorption. However, OTM is under-predicting the $\frac{dR_f}{dt}$ for all the H₂ contents. The L_b and S_l were obtained from the extrapolation routine of Kelly and Law [3]. From the L_b plot, we can observe that 15% H₂ is relatively more unstable than 30% H₂, underscoring the non-linear and highly coupled processes underplay in flame structure. The previous works [137, 138] note a minimum L_b between 30% to 40% of H₂ from experiments and linear stability analysis, respectively. Consistent with previous results, the OTM always under-predicts the L_b across all the pressures and all the H₂ contents. It can also be observed in Fig. 4.22 that, at a given pressure, an increase in H₂ content reduces the discrepancy between the DOM/SNBCK and the ADI.

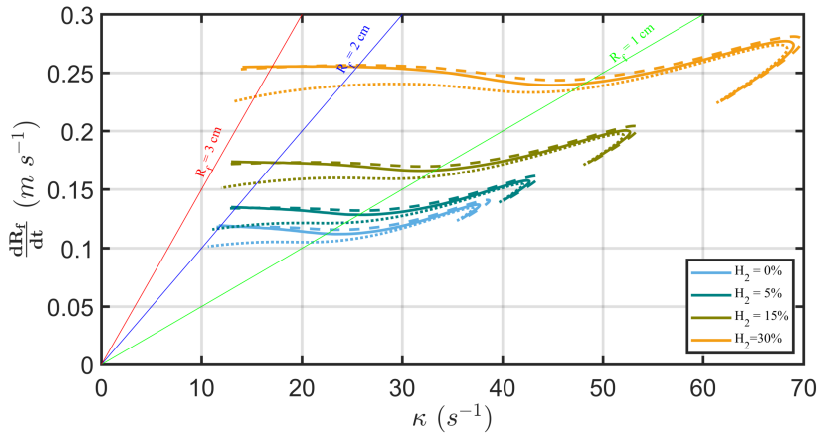


Figure 4.21: Flame displacement speed vs. flame stretch for NH₃-H₂-air at $\phi = 0.8$, $P = 40$ atm and $T = 373$ K for a range of H₂ content; In the above figure, consistent with the previous figures, solid, dashed, and dotted lines represent DOM, ADI, and OTM, respectively.

At high pressures (40 atm), the effects of H₂ content are minimal in the computation of L_b for the respective radiation models, specifically DOM/SNBCK and ADI. Finally, the ADI model is relatively more stable than DOM/SNBCK at 1 atm, whereas at 40 atm, DOM/SNBCK is more stable than ADI (consistent with lean case NH₃-air results).

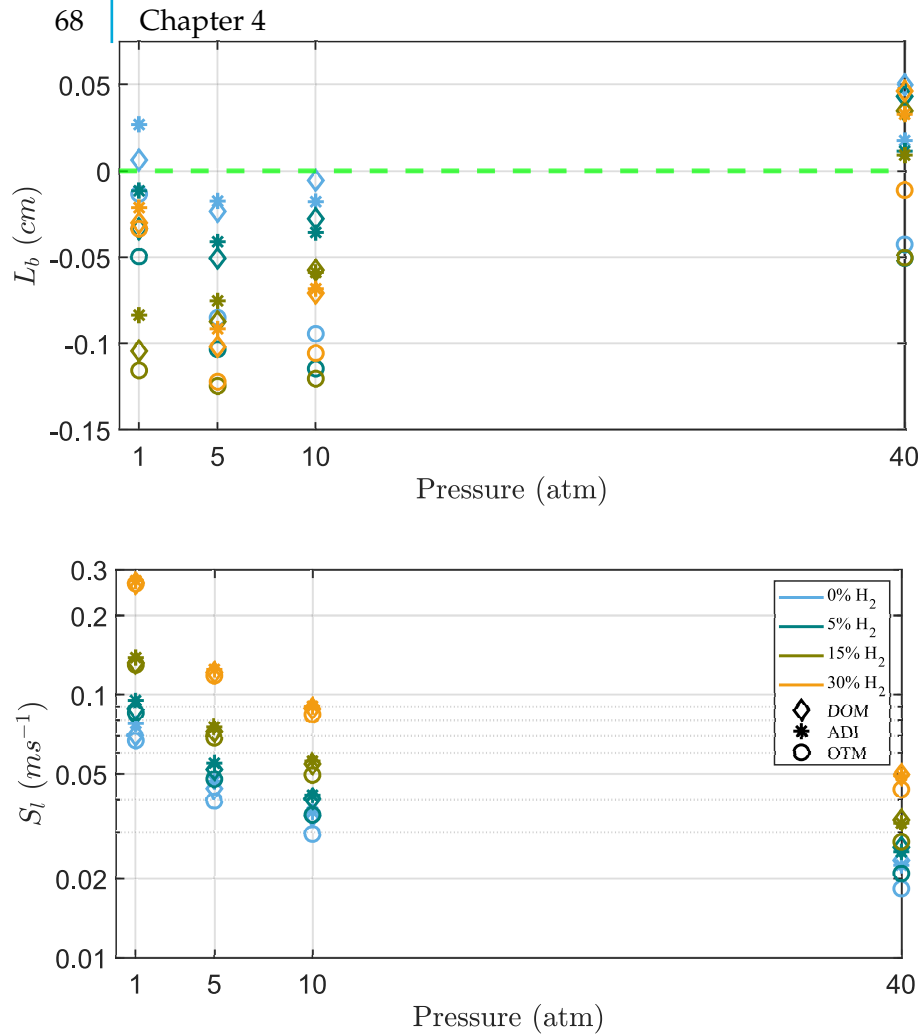


Figure 4.22: Top: Extrapolated Markstein length (L_b) of NH_3 - H_2 - air at $\phi = 0.8$, and $T = 373$ K for a range of H_2 content and pressures, the symbols denote the radiation model and the color denotes H_2 content; Bottom: Extrapolated laminar burning velocity. The green dashed lines represent the transition from positive L_b to negative $L_b < 0$ configuration.

As for the effects of pressure and H_2 content on the S_L , a similar trend is observed; it can be seen that the discrepancy between DOM/SNBCK, ADI, and OTM decreases with an increase in H_2 . Although at 40 atm, irrespective of the H_2 , the discrepancy between OTM and DOM/SNBCK is not minimal. As observed before, at 1 atm, the deviation on S_L between OTM and DOM/SNBCK is very minimal across the H_2 content; this is not the case for L_b as seen earlier. As the pressure is increased and H_2 content is increased, leading to higher deviations between DOM/SNBCK and OTM. Overall, the performance of OTM is worse in the predictions of L_b and slightly better in the case of S_L (especially at high H_2 content).

Figure 4.23 illustrates the variation of Ze with pressure for various H_2 content for a fixed equivalence ratio (ϕ). We can also observe the variation of non-monotonic behaviour with the ϕ (from $\phi = 0.7$ to $\phi = 0.8$). Specifically, the location of non-monotonic behavior occurs at a higher pressure for a relatively rich flame, and its magnitude is also reduced. Note that the local fluctuations in Fig. 4.23 are the artifact of the computation of Ze , specifically on the method of changing the T_{adi} in Eq. (4.8).

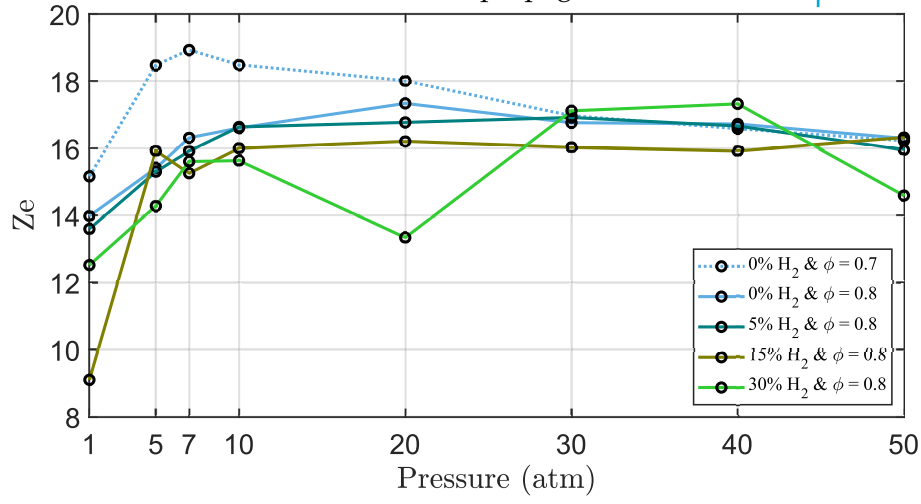


Figure 4.23: Variation of Z_e with pressure for a range of H_2 content in NH_3 flame for $\phi = 0.8$ at $T = 373$ K. Pure NH_3 at $\phi = 0.7$ is also presented to evaluate the variation of Z_e with the ϕ

4.5 Isochoric flame propagation of NH_3 -air

Isochoric flame propagation is a very robust and useful experimental setup since we can evaluate the laminar burning velocity over a range of pressures in a single run. In an isochoric test case, we capture the flame radius and the pressure trace and compute the laminar burning velocity S_L directly using an isentropic compression assumption (described in Sec. 2.3.3).

As described previously, the isochoric setup accounts for the radiative emission in the presence of an optical access. All spherical bombs are isochoric in nature, but the presence of optical access and pressure sensors distinguishes them from the isobaric setup.

In an isobaric setup, only the initial stages (after the dissipation of ignition energy) of the flame propagation data are used. Since, in the initial stages, pressure rise is minimal, it is considered isobaric, and the flame speed is extrapolated from $\frac{dR_f}{dt}$ and κ . As for isochoric, we obtain the S_L from $\frac{dR_f}{dt}$ and $\frac{dP}{dt}$ provided $\frac{P}{P_0} > 2$. In this particular configuration, we investigate

- the dynamic effects of pressure on flame propagation via the reabsorption of the radiated energy.
- the effects of reabsorption on the flame propagation, as discussed above, the effects of emission are accounted for by the optical access of the experimental setup.

Parameter	Value
ϕ	0.8, 1.0 & 1.2
Initial temperature	300 K
Initial pressure	5 atm
Chamber radius	6 cm

Table 4.5: Conditions studied for Case 6

The S_L is computed by

$$S_L = \frac{dR_f}{dt} - \frac{R_0^3 - R_f^3}{3\gamma_u R_f^2 P} \frac{dP}{dt} \quad (4.12)$$

The isochoric simulations were done for three equivalence ratios for NH_3 -air at $\phi = 0.8, 1$, and 1.2 at an initial temperature and pressure of 300 K and 5 atm, respectively. Zhu 2024 [129] kinetic mechanism was used to model the species production rates. The flames were simulated for a propagation time of 180 ms. The maximum end pressure for some of these cases was 21 atm, which is very interesting from a

radiation point of view. The laminar burning velocity is not presented for $\phi = 0.8$ in the upcoming sections due to the relatively low flame radius at the end of the simulation ($t = 180$ ms), leading to $\frac{P}{P_0} < 2$. Instead, the stretched unburnt flame speed over instantaneous pressure is presented in Fig. 4.24. Stretched unburnt flame speed has been calculated using the same equation, Eq. (4.12), but with the caution that the value is stretched and does not represent laminar burning velocity. It should be pointed out that the laminar burning velocity is the limit of $S_{u,\kappa}$ as the κ tends toward zero.

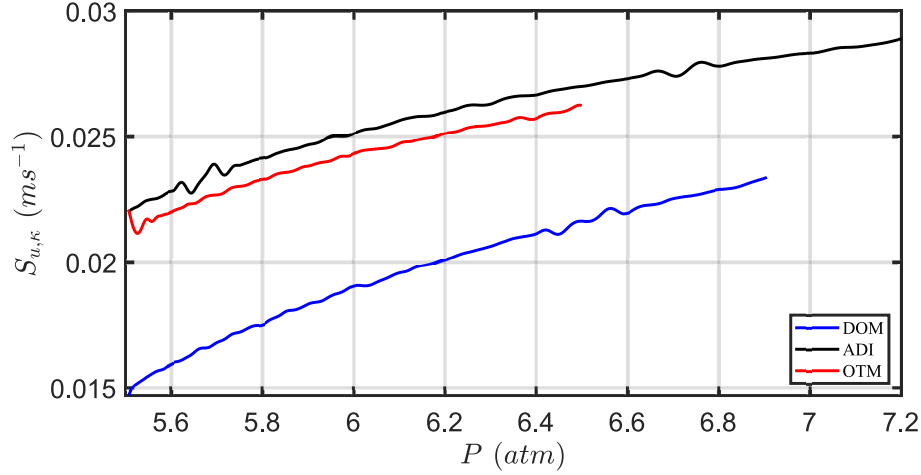


Figure 4.24: Stretched unburnt gas flame speed of NH_3 - air at $\phi = 0.8$ for the different radiation models, DOM/SNBCK (blue solid lines), ADI (black solid lines), and OTM (red solid lines) for an initial pressure of 5 atm

The stretched unburnt gas flame speed (denoted as $S_{u,\kappa}$, u and κ denoting the unburnt and stretch, respectively) is presented in Fig. 4.24. It can be seen that the prediction by DOM/SNBCK is lower than that of OTM. This phenomenon holds true for the other two equivalence ratios as well (Fig. 4.25). This is essentially from the formula used in the computation of $S_{u,\kappa}$ since $S_{u,\kappa}$ is the difference between the flame displacement speed (FDS, $\frac{dR_f}{dt}$) and the pressure evolution terms coefficients of $\frac{dP}{dt}$ (see Eq. (4.12)). The lower magnitude of $S_{u,\kappa}$ for DOM/SNBCK over OTM over pressure will be discussed below as it has been observed for all the ϕ .

Figure 4.25 illustrates the variation of laminar burning velocity S_l over pressure for the stoichiometric and the rich case. It can be seen that the data has been post-processed after a pressure ratio above 2. Consistent with the previous result, initially, DOM/SNBCK is lower than OTM, although after a certain pressure, it becomes higher than OTM and ADI. The contributions from each term of the Eq. (4.12) are plotted in Fig. 4.26. Initially, with an increase in pressure, FDS reduces but after a certain pressure, slope of reduction is lower, leading to a higher S_l and change in trend as seen in Fig. 4.25 and would have been seen had the lean flame ($\phi = 0.8$) reached 5 cm.

In conclusion, FDS is always higher for DOM/SNBCK. Still, due to the formulation of S_l with $\frac{dR_f}{dt}$ and $\frac{dP}{dt}$ along with assumptions involving isentropic compression, we observe S_l by DOM/SNBCK lower than OTM.

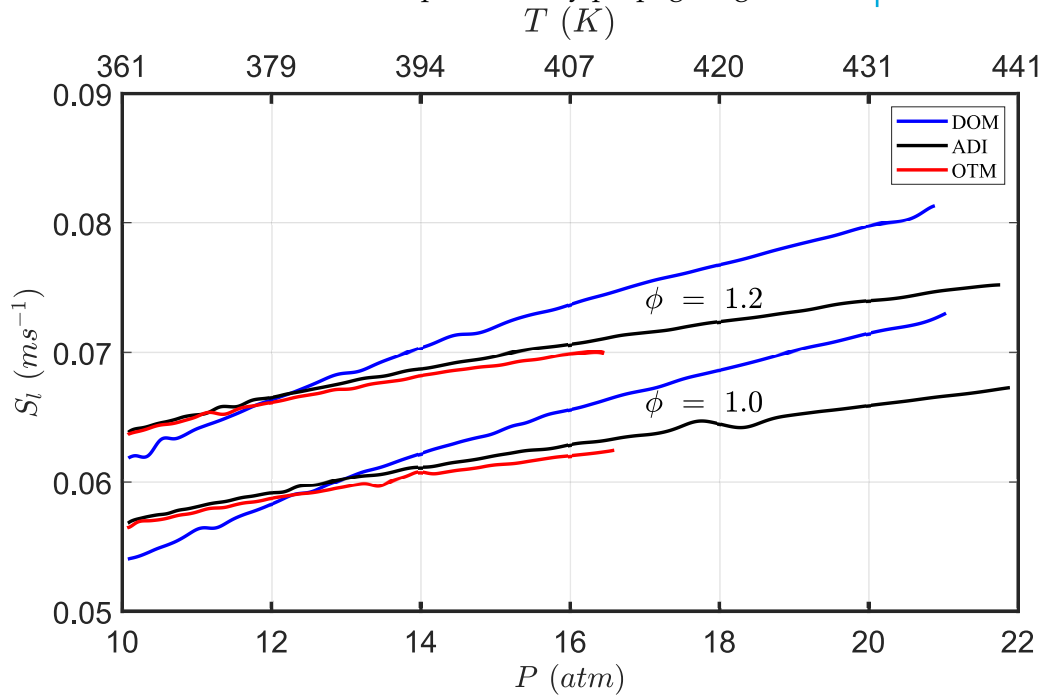


Figure 4.25: LBV of NH_3 - air for $\phi = 1.0$ and $\phi = 1.2$ for various radiation models, DOM/SNBCK (blue solid lines), ADI (black solid lines), and OTM (red solid lines) for an initial pressure of 5 atm.

Interestingly, it can be discerned that the discrepancy between the ADI and OTM models is lower since the formulation implicitly accounts for radiative emission. The discrepancy between DOM/SNBCK and ADI is approximately $< 10\%$, although it is expected to increase with increasing pressure. This highlights the overall capacity of isochoric models to capture the effects of radiative emission, as previously explored by Halter and his team [51, 123]. Additionally, the effects of radiation on the temperature at the end of the domain (resulting from isentropic compression) are not significant, as they are driven by the pressure rise. However, reabsorption does affect the temperature near the flame field due to the reabsorption of radiated energy.

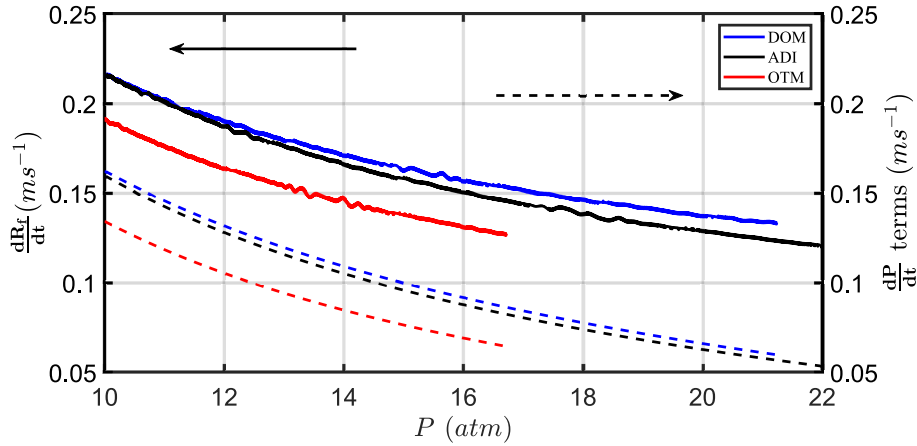


Figure 4.26: Various contributions for the LBV of isochoric model for NH_3 -air at $\phi = 1.0$. Solid lines represent the flame displacement speed contribution, and the dashed lines represent $\frac{dP}{dt}$ terms.

4.6 Discussion on planar freely propagating flames

Planar, freely propagating flames present a unique opportunity to compare and contrast the effects of radiation via the optical path length of the flames without the effects of stretch. The effects of radiation have been investigated in the context of planar flames in the literature by Ju et al. [6]. The above-mentioned study by Ju et al. [6] demonstrated the existence of domain-independent flammability limits via numerical simulations and bridged the gap between experimental works and numerical models. It is

particularly pertinent since the discrepancy of the spectral overlap between the hot products and cold reactants means that the upstream fresh gases cannot absorb all the radiated energy, leading to net heat loss in the flame and the existence of flammability limits.

In FlameMaster, the domain size is controlled by a parameter (briefly described in Chapter 2) called flame thickness multiplier (FLM, default value is 1), a unique value for fresh and burnt gases, respectively. In the fresh gases, the domain is set as $L_1 = 4 \times \text{FLM}_1 \times \delta_T$, where δ_T is the flame thickness defined by the temperature gradient while in the burnt gases it is determined by $L_2 = \text{FLM}_2 \times \delta_T$. In this work, we also tested the effects of the domain size (both the fresh and burnt section) on the S_l for NH_3 -air flame at $\phi = 1.0$, $P = 10$ atm, and $T = 300$ K via the flame thickness parameter. It is worth noting that when the FLM of fresh gases was varied, the burnt section was kept constant at a FLM of 50. Once the FLM of fresh gases was obtained (it was 200), that particular value was fixed, and the burnt section was varied from 50 to 2500. The convergence in the burnt gas section was slower, and a full convergence would be expected for a higher domain size.

From Fig. 4.27, it can be observed that the LBV (S_l) converges much earlier for the fresh gases region (left) while the convergence in the burnt gas region is slow, although the subsequent increase is from FLM of 2000 to 2500 is 0.78%. Due to computational time requirements, the simulation was stopped when the increase in S_l reached 0.78%, compared to an initial increase of 13% for the burnt region.

Figure 4.27 highlights the need for special care in capturing the dynamics of radiative processes in the flamelet modelling of premixed and non-premixed flames [144]. Specifically, to account for the spatial dimensions of the problem since the effects of radiation depend on the domain size. The aforementioned study highlighted the improvement in performance achieved by using scaled variables for methane-air diffusion flames compared to run-time radiative heat transfer calculations.

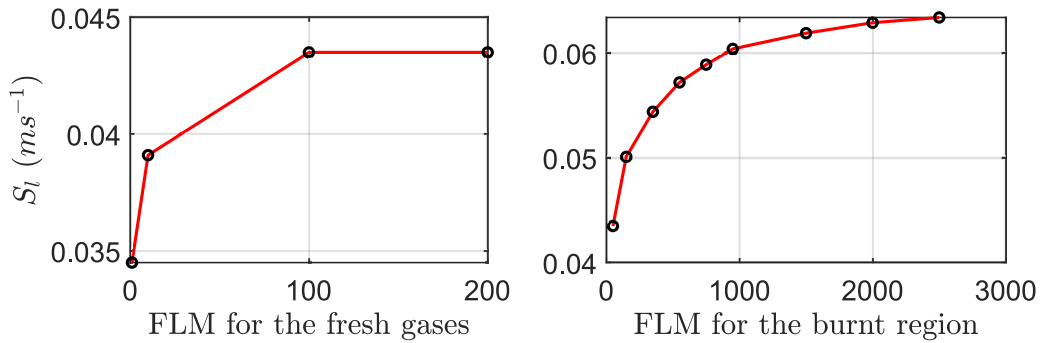


Figure 4.27: Illustration of the LBV for NH_3 - air flame at $\phi = 1.0$, $T = 300$ K, and $P = 10$ atm for a range of flame thickness parameters for the fresh gases (left) and burnt products (right)

The converged FLM values were utilized to determine the effects of extrapolation by comparing the planar S_l against the extrapolated S_l from spherically expanding flames. Figure 4.28 plots the planar S_l for ADI and DOM/SNBCK against the S_l from the spherically expanding flames. It can be observed that planar DOM/SNBCK is consistently higher than spherical DOM/SNBCK due to the influence of domain size. For DOM/SNBCK, the discrepancy in S_l , from SEF to planar varied from 45% to 15%, decreasing with an increase in pressure. As for ADI, the discrepancy between the extrapolated S_l and the planar value was constant at around 25%.

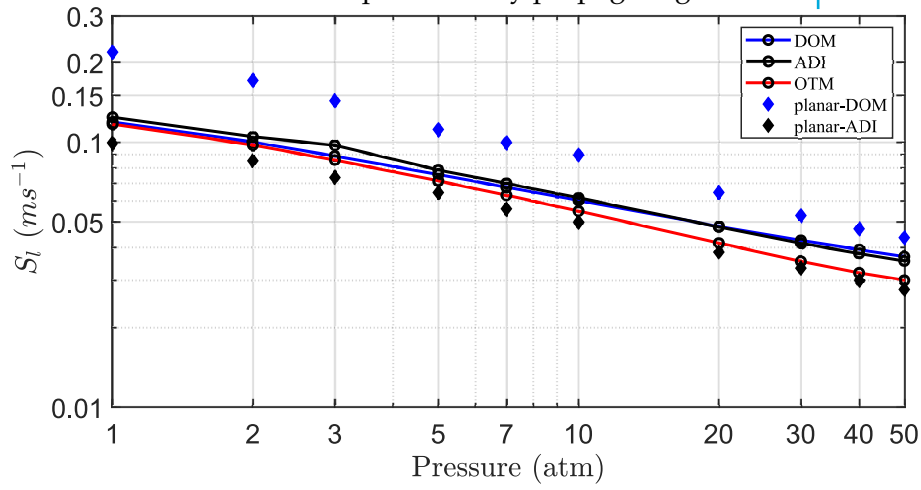


Figure 4.28: Extrapolated S_L (lines with circles from a SEF) and S_L from planar (diamond symbols) for NH_3 - air at $\phi = 1.0$ and $T = 373$ K for a range of pressures

The comparison between the planar and extrapolated S_L (from SEF) highlights the effects of radiation and extrapolation for a slow and radiatively participating flame such as NH_3 . There is a slight but consistent discrepancy between the planar LBV and the extrapolated LBV for ADI and DOM/SNBCK.

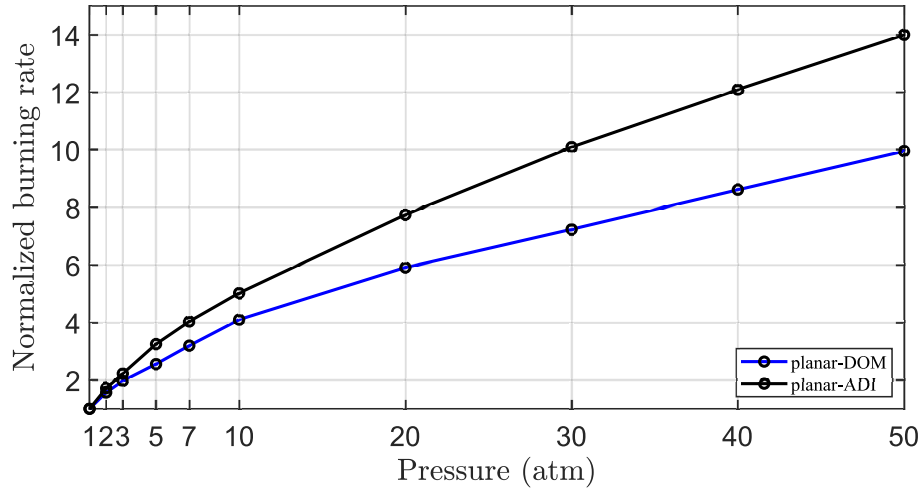


Figure 4.29: Normalized mass burning rate for NH_3 - air at $\phi = 1.0$ and $T = 373$ K for a range of pressures; normalized with their respective values at 1 atm

Figure 4.29 shows the normalized mass burning rate $\left(\frac{\rho_u S_L}{\rho_u S_{L1 \text{ atm}}}\right)$ for DOM/SNBCK and ADI at a stoichiometric case. The mass burning rates were normalized by their respective values at 1 atm. Finally, it is significant to note that although the LBV of NH_3 - air flames reduces with an increase in pressure, the mass burning flux increases (see Fig. 4.29). Literature ([140, 145]) reports an increase in mass burning rate with pressure. Also, Mousavi and Lipatnikov [140] report the non-monotonic behavior of mass-burning flux along with the non-monotonic behavior of Ze, emphasizing the coupled nature of mass-burning flux rate with Ze (Ze was obtained by the derivative of mass-burning flux w.r.t the inverse of adiabatic flame temperature). In this work, the mass burning flux of NH_3 increases. At the same time, the Ze of the flame decreases, highlighting the reduced dependency of the flame temperature on the mass burning flux and the increased role of the kinetics on the mass burning flux as the pressure increases.

Finally, it is important to note that the qualitative behaviour of the flame dynamics can be different due to the kinetic mechanisms employed, although in this work, the behaviour of KAUST 2021 and Zhu 2024 was similar for the spherically expanding flames. The choice of mechanism and the evaluation method of Ze and perturbation in the sensitivity analysis (as outlined by Turanyi [141]) might affect the sensitivity coefficients, as observed by Lehmann et al. [138] for Ze.

Hence, from this chapter and the previous we can infer that we need a critical examination of the following,

- Special mixing rules that can be applied for premixed and non-premixed flames
- Turbulent radiative interactions (TRI) of NH_3 and $\text{NH}_3\text{-H}_2$ flames since the practical applications are always turbulent.
- To evaluate the effects of Ze formulations on the analytical formulations of thermo-diffusional stability.
- A physically consistent extrapolation routine to capture the effects of reabsorption since the previous models have neglected or considered only radiative emission.
- Detailed analysis on the extrapolation window on the extrapolated values L_b and S_L , especially the correlation between the onset of non-linear behaviour (see Fig. 4.14) and the flame structure.

5 Conclusion and perspectives

I admit I'm getting a little gray, but
radiation will do that to you

Captain James T. Kirk

Contents

5.1	Conclusion	75
5.2	Perspectives	76

5.1 Conclusion

In these works, the effects of radiation on premixed NH_3 -air flames were examined for a range of pressure and fuel contents, accounting for re-absorption in the fuel layer and emitted radiation in the burnt gas. This is particularly important since NH_3 can absorb thermal radiation at a significant level, and the reaction kinetics discrepancies are well documented. Radiation cannot be mitigated in the experimental setup; hence, it must be accounted for in the numerical models.

Thus, the effects of radiation were studied within the context of spherically expanding premixed flames, which provide a robust method to evaluate the laminar burning velocity S_L in both isobaric and isochoric configurations. To that end, spectral models for NH_3 - H_2O were developed for varying spectral resolution from narrow band (25 cm^{-1}) to global models (entire spectrum) from the detailed Line-by-Line (LBL) data of HITRAN 2020 [84]. Finally, a wide band model called SNBCK25 was selected as a compromise between the accuracy and the computational overload.

The developed spectral models were coupled to the open-source solver FlameMaster [2] for planar, isobaric spherically expanding flames, and isochoric spherically expanding flames. The radiation models were utilized to critically examine the effects of radiation on the flame dynamics.

The following fuel mixtures in isobaric flames were simulated for pressures from 1 atm to 50 atm:

- NH_3 -air at lean, stoichiometric and rich flames;
- cracked NH_3 -air flames;
- blended NH_3 - H_2 -air flames.

In addition, the consistency of the isochoric flames was also investigated for NH_3 -air flames. The flame displacement speed $\left(\frac{dR_f}{dt}\right)$ was obtained by defining the location of the peak heat release rate as the flame radius R_f . The extrapolation routine of Kelly and Law [3] were utilized to compute the laminar burning velocity S_L and the Markstein length L_b . Contributions of various physical processes were computed from the solution file to gain insights on the local processes of the flame dynamics. It was observed that the direct effect of radiation was second-order. In contrast, the radiation affects the flame thickness and the temperature profile, leading to enhanced Fourier conduction terms and higher flame spread.

It was seen that NH_3 -air flames exhibited non-monotonic behaviour for Zeldovich number Ze and L_b for all the radiation models. H_2 -air flames also exhibits a similar behaviour, albeit at much lower equivalence ratios ($\phi < 0.8$). It was seen that re-absorption aids in the occurrence of non-monotonic behaviour earlier than the adiabatic model. The inability of the optically thin model (OTM) to predict L_b of the rich flames was also noted due to extensive heat loss.

The sensitivity of the chemical kinetics on Ze was also performed for an adiabatic model. The sensitivity analysis of adiabatic models conforms to the numerical results, which show that high-pressure kinetic pathways tend to reduce Ze , making the flame more intense. The effects of low Ze result in intense flame since the reaction zone thickness is relatively higher than the flame's thermal thickness. The contributions of various terms were computed to shed light on the flame dynamics with different radiation models. For the Discrete Ordinates Method (DOM), it was noted that the direct contribution to the energy equation via $\nabla \cdot q_{rad}$ was relatively minimal compared to the Fourier conductive flux due to a reduction in flame thickness and increased temperature in the flame front.

The effects of NH_3 mole-fraction were also assessed via L_b and S_L in NH_3 - H_2 -air flames. The discrepancy between the ADI and DOM models is reduced as the NH_3 content reduces. More importantly, as the flame temperature increased, the discrepancy between OTM and DOM models was also minimal. Finally, the effects of domain size on the radiative heat transfer for planar flames were studied by independently changing the size of the fresh and burnt gases' domains. This is particularly important since the effects of dimensions might affect the thermal radiation effects, and a finer model that accounts for the domain dependency for the thermal radiation is warranted. This would drastically reduce computational overload. Since flamelets account for the detailed chemistry, including the radiation consistently, would be a natural selection choice.

5.2 Perspectives

Future works should also include developing a finer Ze formulation that can be utilized in stoichiometric conditions, more appropriate analytical formulations for L_b that account for radiative re-absorption, and an efficient extrapolation routine that accounts for radiative re-absorption based in the outline of the work by Ronney and Sivashinsky [57]. This would be a crucial step since radiation is usually ignored or only the emission is considered.

Finer mixing rules for spectral models based on deep learning could be insightful to unravel the mixing rules for the absorption spectrum, as done for the thermo-physical properties. Based on the single species' absorption coefficient, the mixture's absorption coefficient from LBL, and the single species' absorption coefficient from narrow band to wide band would be a worthwhile endeavor.

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Raghavendran RAMAN

Rôle du transfert de chaleur radiatif dans les flammes d'ammoniac prémélangées

L'ammoniac peut faire partie du débat sur la décarbonisation de la production d'énergie. Il est plus facile à manipuler et c'est l'un des produits chimiques les plus largement produits dans le monde, bénéficiant de décennies de connaissances industrielles accumulées, ce qui en fait une option attrayante. NH_3 participe également au rayonnement, entraînant ainsi un transfert de chaleur radiatif entre les gaz frais et la vapeur d'eau chaude. Il faut donc en tenir compte dans les modèles numériques. L'approximation conventionnelle de l'épaisseur optique n'est pas valable et nécessite une meilleure modélisation du rayonnement. L'objectif de cette thèse est d'étudier numériquement les effets du rayonnement. Ce travail a utilisé un modèle optimisé à bande étroite en conjonction avec la méthode des ordonnées discrètes (DOM) pour les flammes SEF et les flammes planes se propageant librement dans le solveur open-source, FlameMaster. Dans les premières étapes de la propagation de la flamme, DOM/SNBCK25 étaient proches du modèle OTM, et au fur et à mesure que la flamme s'étendait, les effets de la réabsorption devenaient cruciaux. En outre, l'incapacité de l'OTM à capturer la dynamique de la flamme a été notée dans plusieurs cas, avec une référence particulière aux flammes d'air NH_3 riches en haute pression.

Mots clés : Ammoniac, réabsorption, flammes à expansion sphérique, longueur de Markstein

Role of radiative heat transfer in premixed ammonia flames

Ammonia can be part of the conversation about decarbonizing energy production. It is easier to handle and is one of the most widely produced chemicals in the world, benefiting from decades of accumulated industrial knowledge, making it an attractive option. NH_3 also participates in radiation, thus leading to radiative heat transfer between fresh gases and hot water vapor. Therefore, this must also be taken into account in numerical models. The conventionally used optically thin approximation is invalid and requires better radiation modeling. The objective of the thesis is to investigate the effects of radiation numerically. This work used an optimized narrow band model in conjunction with the discrete ordinate method (DOM) for spherically expanding flames and freely propagating plane flames in the open-source solver, FlameMaster. In the initial stages of SEF, DOM/SNBCK25 were close to the OTM model, and as the flame expanded, the effects of reabsorption became crucial. Furthermore, the inability of OTM to capture flame dynamics was noted in several cases, with particular reference to high-pressure rich NH_3 -air flames.

Keywords: spherically expanding premixed flames, ammonia, radiative re-absorption, Markstein length