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Assessment of OH* as a flame marker
in premixed H₂ - air flames

 valuation du radical OH* comme marqueur de flamme dans les flammes pr m lang es hydrog ne-air

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Abstract

Hydrogen combustion holds a key role in low-carbon energy systems. Chemiluminescence from excited OH^* radicals is widely used as a qualitative marker of heat release. However, their interpretation across different hydrogen flame configurations remains elusive because OH^* signals are highly sensitive to local equivalence ratio, pressure, temperature, and flow dynamics. In this study, we evaluate the significance of OH^* chemiluminescence as a marker for flame front characterization. Particular attention is given to its reliability under varying combustion conditions. This study aims to clarify the diagnostic value of OH^* for flame visualization.

Firstly, we investigate OH^* chemiluminescence in laminar premixed hydrogen–air flames using a spherically expanding flame configuration in a constant-volume chamber. Experiments are performed over a wide range of equivalence ratios, initial pressures, and temperatures. The flame front and the burnt gas regions are extracted from these spatially resolved chemiluminescence measurements. Detailed one-dimensional numerical simulations using sub-mechanisms of Kathrotia and JIHT are conducted to complement the experimental observations. The results reveal that OH^* intensity is highly sensitive to equivalence ratio, pressure, and temperature, with distinct formation mechanisms dominating at different regions of the flame. In the flame front region, the OH^* mole fraction is governed by both mass diffusion and chemical production. Whereas in the burnt gas zone, it is predominantly influenced by chemical production. The performance of both sub-mechanisms was also evaluated by comparing them with experimental results, and Kathrotia appears to be a better fit. The spatial variation between the flame front and the burnt gas reveals a stronger signal in the burnt gases at higher pressures and temperatures, raising important questions about the reliability of OH^* as a consistent marker for identifying the reaction zone across all conditions.

To extend the applicability of the findings to practical burner-stabilized flames, the study was extended to a Bunsen burner configuration, where steady, axisymmetric premixed hydrogen flames were investigated. Spatially and spectrally resolved OH^* chemiluminescence measurements were acquired to characterize flame structure, and the influence of equivalence ratio on emission intensity was evaluated. The Bunsen burner configuration provides a supplementary platform to assess the robustness of OH^* as a combustion diagnostic under steady-state conditions. The OH^* signal was primarily localized at the flame

front, while contributions from the burnt gases were negligible compared to the earlier spherical flame case, indicating that OH^* chemiluminescence remains effective under specific flame geometries and thermodynamic conditions. Complementary spectroscopic measurements of OH^* were performed in addition to chemiluminescence measurements, and OH mole fractions and temperatures were determined through spectral modelling. The measured profiles were compared with 1D simulations, showing good agreement for the mole fraction profiles, whereas the retrieved rotational temperatures were higher than the gas temperatures because of non-equilibrium effects.

This study presents a comprehensive assessment of OH^* chemiluminescence in hydrogen combustion, providing new insight into its behaviour. By integrating spherically expanding and burner-stabilized flames, it establishes the suitability of OH^* for flame marking, bridging fundamental flame studies with practical diagnostic tools.

Keywords: OH^* chemiluminescence, hydrogen, spherically expanding flames, Bunsen burner, thermal excitation, high-resolution spectroscopy.

Résumé

La combustion de l'hydrogène joue un rôle clé dans les systèmes énergétiques décarbonés. La chimiluminescence issue des radicaux excités OH^* est largement utilisée comme marqueur qualitatif du dégagement de chaleur. Cependant, leur interprétation à travers différentes configurations de flammes d'hydrogène demeure évasive, car les signaux OH^* sont hautement sensibles à la richesse locale, à la pression, à la température et à la dynamique de l'écoulement. Dans cette étude, nous évaluons la pertinence de la chimiluminescence de OH^* en tant que marqueur pour la caractérisation du front de flamme. Une attention particulière est portée à sa fiabilité sous diverses conditions de combustion. Cette étude vise à clarifier l'intérêt comme diagnostic de l'émission de OH^* pour la visualisation des flammes.

Tout d'abord, nous étudions la chimiluminescence d' OH^* dans des flammes laminaires de prémélange hydrogène-air en utilisant une configuration de flamme à expansion sphérique dans une enceinte à volume constant. Les expériences sont menées sur une large gamme de richesses, de pressions initiales et de températures. Le front de flamme et les zones de gaz brûlés sont extraits de ces mesures de chimiluminescence résolues spatialement. Des simulations numériques unidimensionnelles détaillées, utilisant les sous-mécanismes de Kathrotia et du JIHT, sont effectuées pour compléter les observations expérimentales. Les résultats révèlent que l'intensité d' OH^* est extrêmement sensible à la richesse, à la pression et à la température, avec des mécanismes de formation distincts prédominants dans différentes régions de la flamme. Dans la région du front de flamme, la fraction molaire d' OH^* est régie à la fois par la diffusion de masse et la production chimique, tandis que dans la zone des gaz brûlés, elle est principalement influencée par la production chimique. La performance des deux sous-mécanismes a également été évaluée en les comparant aux résultats expérimentaux, et le modèle de Kathrotia semble offrir une meilleure correspondance. La variation spatiale entre le front de flamme et les gaz brûlés révèle un signal plus intense dans les gaz brûlés à des pressions et températures plus élevées, soulevant des questions importantes sur la fiabilité d' OH^* en tant que marqueur cohérent pour identifier la zone de réaction dans toutes les conditions.

Afin d'étendre l'applicabilité des résultats aux flammes stabilisées sur brûleur, l'étude a été élargie à une configuration de brûleur type Bunsen, où des flammes de prémélange hydrogène-air stationnaires et axisymétriques ont été examinées. Des mesures de

chimiluminescence d' OH^* résolues spatialement et spectralement ont été acquises pour caractériser la structure de la flamme, et l'influence de la richesse sur l'intensité d'émission a été évaluée. La configuration du brûleur type Bunsen constitue une plateforme supplémentaire pour évaluer la robustesse d' OH^* en tant que diagnostic de combustion en régime permanent. Le signal d' OH^* était principalement localisé au niveau du front de flamme, tandis que les contributions des gaz brûlés étaient négligeables par rapport au cas précédent de la flamme sphérique, indiquant que la chimiluminescence d' OH^* reste efficace sous certaines géométries de flamme et conditions thermodynamiques. En complément des mesures de chimiluminescence, des mesures spectroscopiques d' OH^* ont été réalisées, et les fractions molaires ainsi que les températures d' OH ont été déterminées par modélisation spectrale. Les profils mesurés ont été comparés à des simulations 1D, montrant un bon accord pour les profils de fraction molaire, tandis que les températures de rotation extraites étaient supérieures aux températures du gaz en raison d'effets de non-équilibre.

Cette étude présente une évaluation complète de la chimiluminescence d' OH^* dans la combustion de l'hydrogène, apportant un nouvel éclairage sur son comportement. En intégrant des flammes à expansion sphérique et des flammes stabilisées sur brûleur, elle établit la pertinence d' OH^* pour le marquage du front de flamme, faisant ainsi le lien entre les études fondamentales sur les flammes et les outils de diagnostic pratiques.

Mots-clefs: Chimiluminescence du radical OH^* , Hydrogène, Flammes à expansion sphérique, brûleur type Bunsen, Excitation thermique, Spectroscopie à haute résolution.

Résumé synthétique

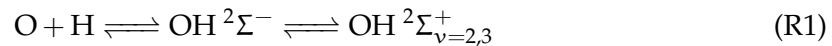
L'objectif principal de ce travail est d'évaluer le rôle de OH^* comme marqueur de la flamme dans des flammes prémélangées H_2 - air. Pour évaluer cela, nous avons d'abord étudié OH^* dans des flammes à expansion sphérique, ce qui nous a permis de mesurer l'influence de pression et de température sur l'évolution de OH^* . La caractérisation de OH^* est effectuée séparément au niveau du front de flamme et dans les zones de gaz brûlés à l'aide de la chimiluminescence. De plus, les observations expérimentales ont été complétées par des simulations numériques 1D à l'aide de FlameMaster, et les performances de différents mécanismes cinétiques ont été évaluées. Les analyses de sensibilité et de taux de production fournissent des informations sur la cinétique chimique de OH^* .

L'étude a été étendue à une autre configuration de flamme, un brûleur type Bunsen, où des mesures de OH^* ont été effectuées à la pression atmosphérique et à la température ambiante. Des mesures de chimiluminescence et de spectroscopie à haute résolution ont été réalisées afin d'étudier la structure de la flamme et de quantifier les radicaux OH fondamentaux. De plus, NO^* et d'autres espèces importantes ont été analysés à travers la flamme. Une étude exploratoire sur l'émission bleue a également été menée afin d'évaluer son rôle dans la signature spectrale de la flamme.

Le chapitre 1 offre une brève description des différents sous-mécanismes OH^* . Le chapitre 2 fournit une analyse approfondie de OH^* dans une flamme en expansion sphérique, tandis que le chapitre 3 évalue différents radicaux excités dans une flamme conique. Le chapitre 4 résume l'étude et conclut avec quelques perspectives importantes.

Le chapitre introductif 1 décrit le rôle de l'hydrogène dans la transition énergétique vers une économie à faibles émissions de carbone et présente certaines propriétés fondamentales de l'hydrogène. Dans le contexte de l'amélioration des processus de combustion, nous exposons brièvement l'état actuel des connaissances sur la structure des flammes H_2 -air et les marqueurs de flamme associés. Nous concentrons plus particulièrement sur la capacité d'un marqueur de flamme couramment utilisé, OH^* , à représenter le taux de dégagement de chaleur. Un résumé détaillé des sous-mécanismes de OH^* est également fourni.

L'une des premières études sur OH* remonte à 1958, lorsque Charton et Gaydon [1] ont présenté les spectres d'excitation de OH dans les flammes d'hydrogène. Ils ont proposé que la réaction de préassociation R4 puisse entraîner une augmentation des bandes OH à $v' = 2$ et 3, en raison d'une population excessive d'O et de H.



À la suite de leur étude, Kaskan [2] a proposé R2 qui conduirait à la formation d'OH*.



Plusieurs autres auteurs ont travaillé à l'amélioration des constantes de vitesse de R1 et certaines études ont écarté R2.

Kathrotia et al. [3] ont proposé l'un des sous-mécanismes OH* les plus validés utilisés dans la communauté pour la chimie de l'oxydation de l'hydrogène. Nous avons également pris en compte le sous-mécanisme développé par Skrebkov et al.[4] pour nos études, car il est récent et hautement optimisé. Les capacités de prédiction de ces derniers sont testées plus en détail au chapitre 2.

Le chapitre 2 vise à fournir une compréhension approfondie de la chimiluminescence OH* en tant qu'outil de diagnostic dans la combustion, en mettant l'accent sur l'influence des richesses, de pression et de température. Il examine de manière systématique comment ces paramètres influencent la formation, la distribution spatiale et l'intensité d'émission de OH* dans les flammes d'hydrogène. En reliant la chimiluminescence OH* aux principales voies de réaction et aux zones de dégagement de chaleur, ce chapitre fournit des informations essentielles sur la structure des flammes et la dynamique de la combustion, qui sont indispensables pour améliorer la précision du diagnostic dans les environnements de combustion pratiques.

Les objectifs de ce chapitre sont triples :

- Étude expérimentale et numérique du comportement de la chimiluminescence OH* dans des flammes d'hydrogène sous différentes conditions de mélange, pressions et températures.
- Étudier la capacité prédictive de différents sous-mécanismes.
- Utiliser des simulations numériques et une analyse cinétique détaillée pour explorer la relation entre l'émission OH* et les caractéristiques de la flamme.

Une flamme à expansion sphérique est examinée dans une chambre à volume constant OPTIPRIME [5], à l'aide d'une imagerie à haute vitesse permettant de capturer l'évolution spatiale et temporelle de l'émission OH*. Des mesures de chimiluminescence OH* ont été réalisées pour divers mélanges hydrogène-air, en prenant en compte des variations des rapports d'équivalence, des pressions d'admission et des températures. Les mélanges ont été testés dans des conditions pauvres, stœchiométriques et riches à $\phi = 0,8, 1,0$ et $1,2$, respectivement. Les pressions initiales ont été étudiées à $0,5, 0,75$ et $1,0$ bar. Les expériences ont été réalisées à une température initiale de 295 K pour toutes les richesses, tandis que des tests supplémentaires à haute température à 303 K et 353 K ont été effectués pour $\phi = 1,2$. Les images déconvoluées dans le champ visuel ont ensuite été obtenues à l'aide de l'inversion d'Abel. L'analyse des images de la flamme indique que l'intensité OH* est répartie dans toute la flamme, au niveau du front de flamme où se produit le dégagement de chaleur, et qu'une rémanence est observée dans les gaz postcombustion. La distribution du signal OH* observée dans les expériences est donc divisée en ces deux zones, et la caractérisation des émissions est effectuée séparément.

Une simulation numérique 1D a été réalisée à l'aide de FlameMaster [6] dans des conditions similaires à celles des expériences, puis comparée aux résultats expérimentaux. Les intensités de chimiluminescence ont été calculées à l'aide de l'équation décrite par Kojima et al. [7]. Les effets de différents modèles de rayonnement, tels que les méthodes adiabatiques, optiquement minces et à coordonnées discrètes, ont été évalués en comparant les profils d'OH* et de température, ce qui a conduit à des différences minimales. Le modèle de rayonnement optiquement mince a été pris en compte tout au long des simulations en raison de son coût de calcul réduit. Les performances des différents modèles de transport ont été évaluées en comparant les profils d'OH*. Les simulations sont réalisées avec une approximation du nombre de Lewis constant, suivie de modèles de transport à moyenne mixte et à plusieurs composants, ce qui conduit à des profils OH* similaires. Le modèle à moyenne mixte est finalement choisi à nouveau en raison de son coût de calcul. La diffusion de Soret s'avère importante dans la combustion de l'hydrogène, c'est pourquoi elle est prise en compte. Les effets du mécanisme de base sur la production de radicaux fondamentaux, qui auront un impact sur OH*, sont estimés à l'aide de différents schémas cinétiques. Les profils sont presque identiques, ce qui signifie que le choix du mécanisme de base n'affecterait pas la formation d'OH*. Enfin, les effets du sous-mécanisme sur l'évolution de OH* ont été testés en effectuant des simulations avec Kathrotia et al. [8], Konnov [9] et Sharipov et al. [10]. Konnov a obtenu des résultats très élevés au front de flamme par rapport aux deux autres ; il a donc été écarté. Les mécanismes de Kathrotia et Sharipov ont été utilisés et leurs performances ont été testées par rapport aux expériences.

Les résultats de la simulation ont été comparés aux expériences. À une pression et une température plus basses, l'intensité de la chimiluminescence (nommée CLI par la suite), au front de flamme était plus élevée que celle des gaz brûlés. Avec l'augmentation de la pression et de la température, l'intensité des gaz brûlés augmentait et contribuait de

manière significative à l'émission globale. Les effets de la richesse, de la pression et des températures sur l'intensité de la chimiluminescence ont été évalués plus en détail.

Quelle que soit la richesse, les résultats de simulation des deux sous-mécanismes sous-estiment le CLI dans la zone des gaz brûlés par rapport aux expériences. Mais en ce qui concerne les rapports d'intensité, Kathrotia semble offrir de meilleures performances et une bonne correspondance, c'est pourquoi ce mécanisme est utilisé pour la comparaison avec les expériences. En raison de la compression isentropique, la pression et la température changent, contribuant ainsi à l'évolution de OH*.

Les études ont ensuite été étendues aux configurations isobares et isochores, où un signal de OH* significatif a été détecté dans la zone de gaz brûlés dans le cas isochore en raison d'un gradient de température marqué. Cela met en évidence l'importance de la température dans l'excitation thermique de OH*.

Les contributions des différents termes, la diffusion et le taux de production ont été évalués à travers le front de flamme et dans les zones de gaz brûlés. Au niveau du front de flamme, la diffusion massique et la production chimique ont toutes deux une incidence significative sur les distributions d'OH*, tandis que dans la zone des gaz brûlés, celles-ci sont principalement régies par les termes de production.

OH* au niveau du front de flamme est principalement formé par excitation chimique par R1, tandis que dans les gaz brûlés, il est formé par excitation thermique par réaction inverse R3. La définition des températures seuils pour l'excitation thermique dépend du mécanisme utilisé. D'après l'analyse des taux de production dans Kathrotia et JIHT, les réactions responsables de OH* sont différentes au niveau du front de flamme, ce qui met en évidence les différences mécanistiques. Il est formé par Kathrotia R1 et par R2 JIHT. Dans la zone des gaz brûlés, il est formé par R3



La corrélation l'évolution de OH* avec la richesse, la pression et la température a été déterminée en effectuant des simulations numériques en régime permanent à l'aide des sous-mécanismes Kathrotia et JIHT. Les richesses ont été variées de 0,6 à 3, à des pressions de 1, 5, 10 et 20 et à des températures de 300, 500 et 700 K. L'intensité de la chimiluminescence suit une courbe non monotone en forme de cloche lorsque la richesse varie dans les deux régions. Le CLI augmente en fonction la richesse, atteint un pic à 1,1, puis décroît. Le front de flamme présente une fenêtre CLI plus large sur la richesse par rapport aux gaz brûlés. Au niveau du front de flamme, le CLI augmente avec l'augmentation de la pression, tandis qu'au niveau des gaz brûlés, l'intensité diminue, probablement en raison de l'extinction.

La température semble avoir un effet positif marqué. Le CLI augmente de manière linéaire dans les deux zones lorsque la température augmente. Un modèle a été développé afin de prédire la chimiluminescence à partir de la richesse, des pressions et des températures.

La chimiluminescence OH^* a été utilisée dans la littérature pour indiquer le taux de dégagement de chaleur des flammes d'hydrogène. La relation entre la chimiluminescence locale et le taux de dégagement de chaleur local a été évaluée. CLI est décalé spatialement par rapport au HRR et atteint son maximum en aval du HRR. L'évolution radiale des deux a été interprétée pour différentes richesses et aucune corrélation forte n'a été obtenue.

Voici quelques-unes des principales conclusions tirées de ce chapitre :

- Des émissions d' OH^* sont observées dans la zone des gaz brûlés, révélant une activité radicalaire persistante au-delà du front de flamme, ce qui met en évidence une chimie post-flamme unique caractéristique des flammes d'hydrogène. Cela nous amène à reconsidérer son utilisation comme indicateur de flamme dans certaines conditions.
- Contrairement aux flammes planes en régime permanent, les flammes transitoires tiennent compte de l'historique de la température et des espèces, soulignant le rôle de la température dans la chimiluminescence OH^* dans la zone de postcombustion.
- Les capacités prédictives des sous-mécanismes montrent une précision limitée dans la zone des gaz brûlés par rapport aux données expérimentales, bien que le sous-mécanisme de Kathrotia fournisse une meilleure concordance pour le rapport d'intensité.
- Différents mécanismes régissent les formations d' OH^* dans des régions spécifiques de la flamme. La diffusion de masse et la production chimique contribuent toutes deux aux fractions molaires d' OH^* près du front de flamme, tandis que la production chimique prédomine dans la zone des gaz brûlés.
- Les intensités d' OH^* dépendent fortement de la richesse, de la pression et de la température. Les intensités augmentent avec la pression et la température pour tous les mélanges à la fois au niveau du front de flamme et dans la zone des gaz brûlés, avec une augmentation relative plus importante dans les gaz brûlés.
- Une faible corrélation est observée entre le taux de dégagement de chaleur et la chimiluminescence au niveau du front de flamme, ce qui souligne les difficultés liées à l'utilisation de OH^* comme marqueur de flamme.

Le chapitre 3 vise à étudier la structure de la flamme et à élucider les effets du transport sur la distribution des radicaux dans une flamme prémélangée canonique H_2 -air sur une plage de richesse allant de $\phi = 0,6$ à $1,4$. La spectroscopie d'émission optique à haute résolution combinée à l'imagerie bidimensionnelle de la chimiluminescence a été utilisée pour étudier les caractéristiques spectrales et spatiales des radicaux. La cartographie des

espèces à travers le front de flamme fournit des informations sur la chimie et la dynamique des réactions dans la zone de réaction. Les fractions molaires d'OH et les températures de H₂O ont été déterminées quantitativement par modélisation spectroscopique. Les variations spatiales et spectrales de l'émission bleue des flammes d'hydrogène ont été caractérisées dans tout le domaine de la flamme. L'analyse des gaz d'échappement a révélé la présence de CO. Dans l'ensemble, cette étude fournit des informations sur la distribution spatiale des espèces réactives, la structure de la flamme et les caractéristiques des émissions, offrant une compréhension plus approfondie de la chimie des flammes d'hydrogène.

L'objectif général est d'établir une compréhension mécanistique de la manière dont la diffusivité élevée de l'hydrogène influence la structure de la flamme et la réactivité chimique. Dans ce contexte, l'influence de la richesse sur la structure de la flamme et les caractéristiques d'émission est étudiée à la fois spatialement et spectralement.

Les trois principaux objectifs de ce travail sont les suivants :

- Évaluer la structure de la flamme à travers la caractérisation des émissions pour différentes richesses.
- Quantifier la distribution spatiale de la température et des fractions molaires des espèces à l'aide de mesures spectrales.
- Étudier les caractéristiques de l'émission de flamme bleue dans les flammes laminaires prémélangées à l'aide de mesures spatiales et spectrales, et examiner son potentiel en tant que marqueur de flamme.

Les essais ont été réalisés sur un brûleur type Bunsen stabilisé aérodynamiquement, équipé d'une buse circulaire de 7 mm de diamètre. Un mélange prémélangé d'hydrogène et d'air a été introduit dans le bec, et les effets de la variation de la composition du mélange air-combustible ont été étudiés de manière systématique en maintenant un rapport constant entre la vitesse d'écoulement global et la vitesse de la flamme laminaire pour toutes les richesses. Les expériences ont été réalisées à pression atmosphérique (1 atm) et à température ambiante (295 K), sur une plage de richesses allant de $\phi = 0,6$ à 1,4.

Les émissions de chimiluminescence provenant de divers radicaux ont été capturées à l'aide d'une caméra PI-MAX 4 intensifiée, d'un objectif Cerco d'une longueur focale de 105 mm et, grâce à l'ajout d'adaptateurs, la longueur focale effective a été étendue à 180 mm, améliorant ainsi la résolution spatiale à 17 $\mu\text{m}/\text{pixel}$. Un ensemble de huit filtres optiques à bande étroite a été utilisé pour capturer les signaux de chimiluminescence des radicaux, en se concentrant principalement sur les espèces OH* et NO*, entre autres, afin d'analyser l'émission bleue. Les images visibles de la flamme ont été enregistrées à l'aide d'une caméra Nikon Z8, équipée d'un capteur CMOS plein format de 45,7 mégapixels. La résolution spatiale était de 19 $\mu\text{m}/\text{pixel}$. Les données spectrales ont été enregistrées à

l'aide d'un spectromètre à haute résolution de la marque Princeton Instruments, modèle IsoPlane SCT-320. Le système optique se compose d'une lentille convexe de 25 mm de diamètre, placée à 40 mm du centre de la flamme. La lumière a ensuite été collimatée à l'aide d'une lentille de 5 mm de diamètre, puis couplée à une fibre optique de 1 mm de diamètre et de 2 m de long, ainsi qu'à une fente de spectromètre de 25 μm de largeur. L'imagerie a été réalisée à l'aide d'une caméra ProEM EMCCD haute résolution avec rétroéclairage. Des réseaux de diffraction avec des densités de rainures de 3600 g/mm, 1200 g/mm et 300 g/mm, correspondant à des résolutions spectrales de 0,01 nm, 0,035 nm et 0,15 nm, ont été utilisés. La zone d'intégration était de 5 mm² et 10 images au total ont été capturées, avec un temps d'intégration ajusté pour chaque radical afin d'optimiser l'intensité du signal. L'analyse des gaz d'émission ciblant le CO a été réalisée à l'aide de l'analyseur de gaz de combustion KIGAZ 500, équipé d'un capteur électrochimique de CO. Les mesures ont été effectuées dans le panache, à une distance de 50 mm de la flamme et à une température de 500 K.

La chimiluminescence à haute résolution des radicaux a permis d'obtenir une cartographie détaillée des espèces présentes dans le front de flamme. Au total, 100 images instantanées ont été capturées et moyennées dans le temps. L'intensité intégrée dans la ligne de visée a été déconvoluée en une distribution radiale bidimensionnelle à l'aide d'un code MATLAB interne utilisant la méthode BASEX (Basis Set Expansion). Un algorithme de détection des contours a été appliqué pour identifier le front de flamme. L'intensité maximale, présentée plus loin dans nos résultats, a ensuite été évaluée dans la direction normale au front de flamme et analysée en fonction de la hauteur le long de l'axe central du brûleur. Les principaux intermédiaires réactifs dans les flammes d'air et d'hydrogène, à savoir OH* centré à 310 nm et NO* entre 245 et 270 nm, ont été étudiés en détail en examinant leurs distributions spatiales. L'émission bleue a également été étudiée à l'aide d'une imagerie à large bande dans la gamme de longueurs d'onde de 220 à 900 nm, ainsi que par des mesures à des longueurs d'onde sélectionnées. Ces observations complémentaires ont permis d'établir une corrélation entre les caractéristiques d'émission à large bande et leurs contributions sous-jacentes.

En examinant les distributions d'intensité des intermédiaires réactifs près de la base de la flamme, on observe une augmentation prononcée de l'intensité de l'émission, le pic d'émission apparaissant à environ 2 mm au-dessus du bord du brûleur, ce qui correspond à la région de chimiluminescence locale maximale. Ce pic varie en fonction du radical et sera décrit en détail. Au-delà de ce point, les intensités ont tendance à diminuer. La diminution d'intensité est plus prononcée pour un mélange pauvre et cesse presque lorsque l'on s'approche d'un mélange riche. Pour $\phi = 0,8$, OH*, NO* et la bande large ont tendance à présenter des profils similaires et sont relativement sensibles par rapport aux autres espèces. H₂O, supposé être à 632 nm, présente la variation la plus faible. Avec l'augmentation de la richesse, la séparation entre OH*, NO* et la bande large augmente le long de la flamme. Pour mieux comprendre l'évolution des espèces le long du contour

de la flamme, le déplacement spatial des émissions des espèces est analysé afin d'élucider la dynamique de la zone de réaction. Pour toutes les richesses, les autres espèces ont tendance à apparaître en aval du front OH^* avec un ΔX positif, tandis que la bande large visible semble se trouver en amont du front OH^* .

OH^* et NO^* ont été examinés plus en détail en caractérisant la distribution des émissions au sein du front de flamme et dans la zone de postcombustion. Les effets de richesse du mélange et de la vitesse ont été étudiés. Après avoir évalué les distributions d'intensité de divers radicaux à la base de la flamme, on observe une forte augmentation de l'intensité à mesure que le mélange s'enrichit. En revanche, l'augmentation est moins importante dans des conditions de mélange pauvre. Ce comportement peut être attribué à des pertes par extinction accrues près du bord du brûleur dans les flammes riches. Toutes espèces confondues, les intensités maximales sont observées systématiquement à environ 2-3 mm du bord du brûleur, ce qui correspond à l'emplacement de la chimiluminescence locale la plus élevée. Au-delà de l'emplacement du pic, à mesure que l'on remonte le long de la flamme, les intensités radicalaires diminuent progressivement. La décroissance de l'intensité est plus prononcée pour les mélanges pauvres que pour les mélanges riches, ce qui indique une plus grande sensibilité des flammes pauvres aux variations des conditions locales du mélange, entraînant des gradients réactifs accrus.

La caractérisation de la zone d'émission à travers le front de flamme et la zone des gaz brûlés est également effectuée pour OH^* et NO^* . Les intensités moyennes du front de flamme et de la zone des gaz brûlés augmentent lorsque l'on passe d'un mélange pauvre à un mélange stœchiométrique, atteignent un pic à $\phi = 1,1$ et diminuent en dessous de ce point. Une branche de diffusion secondaire se forme pour les mélanges plus riches, en plus du cône prémélangé. À une richesse de 1,4, les contributions dans les gaz brûlés sont plus élevées pour NO^* que pour OH^* , ce qui indique une sensibilité plus élevée.

En complément des mesures par chimiluminescence, des mesures spectroscopiques ont été effectuées à l'aide d'un spectromètre à faible résolution, en prenant des mesures ponctuelles à trois distances axiales et à plusieurs positions radiales à travers la flamme. Des résultats similaires ont été obtenus. Les pics d'intensité sont situés près de la base de la flamme et diminuent progressivement avec la hauteur.

Pour résoudre le problème des émissions, une imagerie spectroscopique à haute résolution a été réalisée pour OH^* , NO^* , l'émission bleue et $\text{H}_2\text{O} \cdot$ dans le but principal de quantifier les fractions molaires d'OH. La modélisation spectrale a été réalisée à l'aide d'une optimisation dans laquelle un ajustement a été effectué entre les données expérimentales et les simulations. La température de rotation et les fractions molaires ont été obtenues. En raison du déséquilibre, les températures de rotation obtenues pour OH^* étaient plus élevées, c'est pourquoi H_2O a été utilisé comme traceur d'équilibre pour les mesures de température.

Bien que les flammes de H_2 soient théoriquement non lumineuses, l'émission bleue visible est généralement observée. Une imagerie visible et des mesures spectroscopiques ont été réalisées afin d'analyser cette émission. L'analyse RVB des images de la flamme montre que le canal bleu est le principal contributeur au front de la flamme, ce qui suggère que les émissions observées précédemment dans la chimiluminescence à large bande sont principalement dues au signal du canal bleu. Les données spectroscopiques ont été recueillies à l'aide d'un réseau de diffraction de 300 rainures/mm et ont révélé un continuum à large bande avec des pics distincts à des longueurs d'onde de 384,65, 392,71, 396,65, 402,18, 407,55 et 409,27 nm.

Les émissions de radicaux H_2 , H , O_2 , O , OH et H_2O_2 contribuent très probablement aux émissions bleues lorsqu'elles sont combinées. Des traces de CO ont également été détectées dans l'analyse des gaz d'échappement, ce qui indique que la combustion de l'hydrogène n'est pas totalement neutre en carbone. La caractérisation des émissions bleues a également été effectuée sur le front de flamme et sur les gaz brûlés, puis comparée à OH^* . Les émissions bleues sont très intenses dans les gaz brûlés, ce qui nous permet d'exclure leur utilisation comme marqueurs de flamme.

Ce chapitre conclut que la structure de la flamme et le comportement d'émission variaient fortement en fonction de la richesse, avec des changements morphologiques et une chimiluminescence radicalaire clairement observables entre les conditions pauvres et riches. La diffusion préférentielle, l'étirement et la courbure ont considérablement influencé la distribution des radicaux dans la zone de réaction. L'analyse spectroscopique a été utilisée pour quantifier les fractions molaires de OH et les températures des gaz à partir des émissions de H_2O , ce qui a permis de caractériser avec précision les concentrations des espèces et les champs de température. L'émission de flamme bleue provenait de la chimiluminescence de multiples espèces combinées, du rayonnement thermique.

Le chapitre 4 présente une vue d'ensemble de la thèse et résume ses principales conclusions. Il expose les implications de ces résultats pour notre compréhension de la chimiluminescence de OH^* . Enfin, il présente les perspectives et les orientations pour les recherches futures.

De manière générale, cette étude conclut que la chimiluminescence OH^* présente une variation spatiale prononcée entre les différentes zones de la flamme. L'excitation chimique domine à l'avant de la flamme, tandis que l'excitation thermique se produit principalement dans la zone des gaz brûlés. Cette distinction est cruciale pour interpréter OH^* comme un diagnostic de flamme. Dans les configurations à flamme libre, telles que celles des becs Bunsen, l'émission de OH^* reste un marqueur de flamme fiable. Cependant, dans les configurations fermées, son applicabilité doit être soigneusement évaluée dans différentes conditions de fonctionnement. L'analyse montre également que l'émission d' OH^* est fortement influencée par la composition du mélange, la pression et la température. Même dans des conditions très pauvres ou très riches, OH^* continue à servir de marqueur de

flamme efficace ; cependant, à des pressions élevées, la contribution de la zone des gaz brûlés est considérablement réduite. À des températures des gaz brûlés plus basses, OH^* conserve son utilité en tant que diagnostic, à condition que les mécanismes d'excitation soient correctement pris en compte. L'évaluation de la précision prédictive des sous-mécanismes de OH^* semble être plus efficace lorsqu'on utilise Kathrotia.

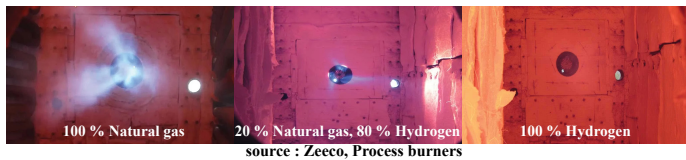
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1 Introduction



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The introductory chapter begins with an overview of the thesis. The role of hydrogen in the low-carbon energy transition, along with some fundamental properties of hydrogen, is discussed. We briefly outline the structure of the H₂-air flames and the associated flame markers, focusing more specifically on the ability of flame markers and one commonly used flame marker, OH*, to ascertain the heat release rate. A detailed summary of OH* sub-mechanisms based on the current state of knowledge is provided at the end of the chapter.

1.1 Thesis outline

The principal objective of this work is to assess the role of OH* in flame marking in a premixed H₂ - air flames. To evaluate this, OH* was first studied in spherically expanding flames, where the effects of equivalence ratios, pressure and temperature on OH* evolution were determined. The OH* characterization is done across the flame front and in the burnt gas zones separately using chemiluminescence. Further, the experimental observations

were complemented by 1D numerical simulations using FlameMaster, and the performance of different kinetic mechanisms was assessed. Sensitivity and rate-of-production analyses provided some insight into the chemical kinetics of OH*.

The study was extended to another flame configuration, a Bunsen burner, where OH* measurements were performed at atmospheric pressure and ambient temperature. High-resolution chemiluminescence and spectroscopic measurements were conducted to investigate the flame structure and to quantify ground OH radicals. Additionally, NO* and other important species were analysed across the flame. An exploratory study on blue emission was also done to evaluate its role in flame marking.

Chapter 1 presents an overview of OH* sub-mechanisms. Chapter 2 provides a detailed analysis of OH* in a spherically expanding flame, while in Chapter 3 the evaluation of OH* along with various excited radicals is done in a conical flame. Chapter 4 summarizes the study, concluding with some important findings and perspectives.

1.2 Hydrogen readiness today

The global transition to sustainable energy is often seen through the lens of the energy trilemma, which highlights the challenge of balancing energy reliability, affordability, and environmental protection. Reliable energy means having a steady supply that can withstand disruptions such as political conflicts or adverse weather. Affordable energy means keeping prices fair for households and businesses, without causing financial hardship. Protecting the environment entails reducing greenhouse gas emissions and other pollutants to mitigate climate change. Improving one aspect of the trilemma can sometimes make others more difficult to achieve. For example, rapidly deploying clean energy technologies to benefit the environment often requires substantial initial investment, which can increase costs and reduce reliability during the transition. On the other hand, merely seeking to keep costs low can mean prolonging the use of fossil fuels, which is harmful to the environment in the long run [1], [2]. Because of this, today's energy plans seek balanced solutions, such as integrating diverse renewable energy sources, using energy when it is most needed, and developing new clean fuels, like hydrogen, that can scale to meet demand.

Low-emission hydrogen is likely to play a key role in energy systems that aim to reduce greenhouse gas emissions. However, to compete in the race, we need to increase production, and there are several ways to do so, either through steam methane reforming, anaerobic digestion or through electrolysis [3], [4], [5]. Fig. 1.1 demonstrates different production pathways in the hydrogen spectrum, as shown in various colours [6]. Currently, the production costs of hydrogen are high [7]. If countries pursue ambitious goals, such as achieving net-zero emissions, the cost of producing low-emission hydrogen could fall

significantly over the next decade. By 2030, producing hydrogen from renewable electricity may cost approximately half as much as it does today, making it more competitive with hydrogen produced from fossil fuels. The projected cost of hydrogen produced by renewable energy is between 2 and 9 USD/kg by 2030. If countries maintain current policies, cost reductions will be much smaller, underscoring the need for robust policy support and large-scale projects. At the same time, producing hydrogen from natural gas with carbon capture and storage is expected to become cheaper, particularly as natural gas prices stabilize in some regions [8].

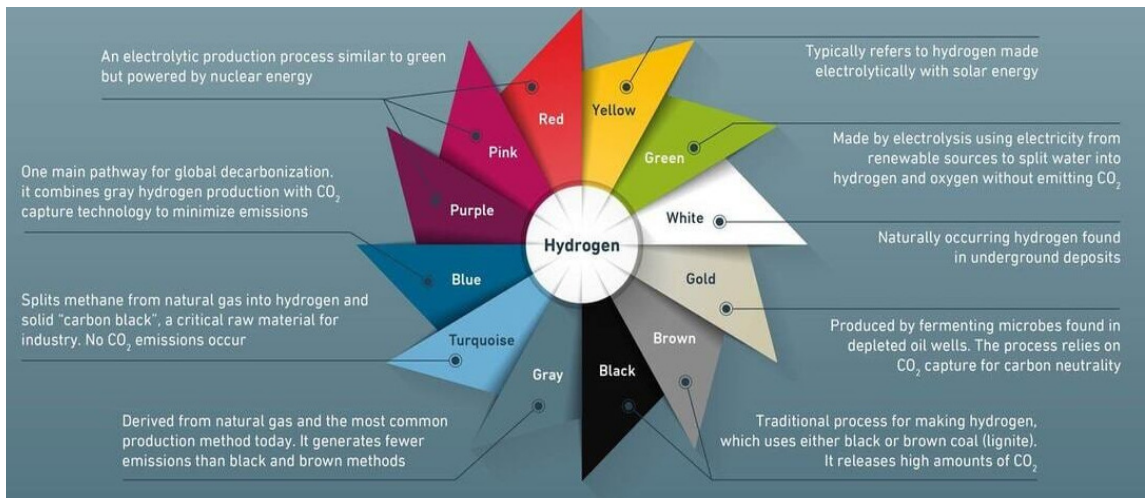


Figure 1.1: Illustration image of hydrogen production methods (source: [6])

According to the recent report by the European Clean Hydrogen Alliance [9], Europe currently has a large gas network valued at about €260 billion, with around 200,000 km of main pipelines and almost 2 million km of distribution pipelines. Together, these supply more than 40% of the energy used by households and businesses. Hydrogen can be added to this system by mixing it with natural gas or biomethane, up to 30% by volume, or by using only hydrogen. Lower mixing levels, typically up to 20%, are compatible with current appliances and help gradually bring hydrogen into the energy market. When using mostly pure hydrogen, specialized systems to monitor gas quality are usually not needed, since the fuel is expected to remain fairly consistent. However, in real situations, so-called "pure" hydrogen often has small amounts of impurities, with hydrogen levels usually around 98%. These impurities may lead to variations in the Wobbe Index, thereby affecting combustion behaviour and performance.

Apart from production or transportation issues, the main challenge of hydrogen infrastructure is its combustion. Some of the challenges in hydrogen combustion are high NO_x emissions due to high adiabatic flame temperatures [10], [11], the risk of potent flashback due to high laminar flame speed, a wide flammability range, and a small quenching distance [12], [13]. Fig. 1.2 image illustrates a transition from natural gas to hydrogen, where the flashback phenomenon is occurring [14].

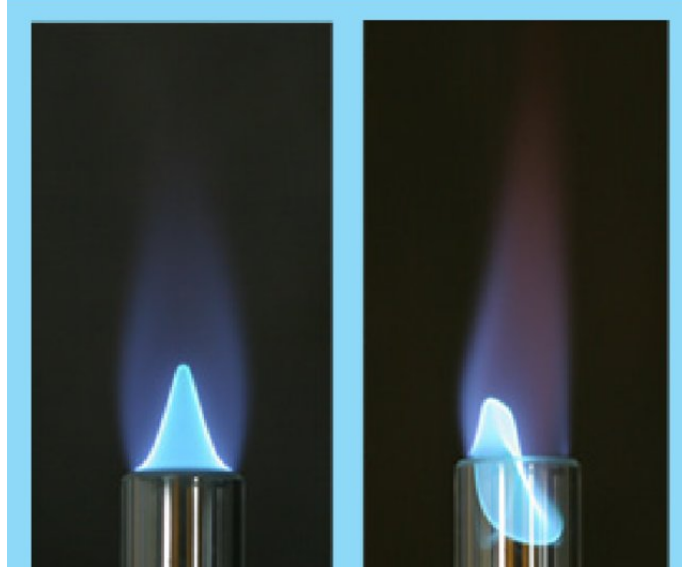


Figure 1.2: Illustration image of flame flashback, left (Natural gas), right (Hydrogen) (source: [14])

Fuels with similar Wobbe Index values are considered interchangeable, as they deliver comparable thermal power to a combustion device operating at fixed nozzle geometry. Consequently, variations in the Wobbe Index caused by changes in fuel composition or impurities can lead to deviations in flame stability, heat release, and emission characteristics [15], [16]. Therefore, it's important to understand the fundamental properties of hydrogen, which are crucial for evaluating safe operational limits.

1.3 Fundamental flame properties of hydrogen

Hydrogen's flame properties stand out sharply from those of hydrocarbons like methane, driven by its unique physical chemistry that shapes everything from laboratory burners to real-world safety.

The physical and chemical properties of hydrogen are compared and contrasted against methane and ammonia [17], [18]. Hydrogen is a very light molecule and is highly diffusive, with wide flammability limits that extend from ultra-lean mixtures at $\phi = 0.1$ to super-rich mixtures at $\phi = 7.1$, making it an attractive candidate for a wide range of combustion applications. Hydrogen has a higher heating value and a higher laminar burning velocity, thereby improving combustion efficiency but increasing the risk of flashback. Adiabatic flame temperatures of hydrogen are slightly higher than those of methane, whereas autoignition temperatures are slightly lower than those of methane. The stoichiometric air-to-fuel ratio is lowest for hydrogen owing to its carbon-free composition, highest for methane due to its greater oxygen requirement for complete oxidation, and intermediate for ammonia as a result of its hydrogen content and the presence of inert nitrogen. Tab. 1.1 represents the physical and chemical properties of hydrogen, methane and ammonia, respectively.

Property	Hydrogen	Methane	Ammonia
Molecular weight (g/mol)	2.016	16.043	17
Density (kg/m ³)	0.08	0.65	0.73
Mass diffusivity in air (cm ² /s)	0.61	0.16	0.228
Flammability limits (ϕ)	0.1 – 7.1	0.5 - 1.7	0.63 - 1.4
Lower heating value (MJ/kg)	120	50	18.6
Boiling temperature at 1 atm (°C)	-253	-161	-33.4
Maximum laminar burning velocity (cm/s)	291	37	7
Adiabatic flame temperature (°C)	2110	1950	1800
Minimum autoignition temperature (°C)	520	630	650
Stoichiometric air-to-fuel ratio (kmol/kmol)	2.387	9.547	6.046

Table 1.1: Comparison of the properties of hydrogen, methane and ammonia.

Liquification of hydrogen requires very low temperatures, and therefore, storage at room temperature requires high pressures. The volumetric energy density of hydrogen is lower than that of methane or ammonia, as shown in Fig. 1.3, hence, hydrogen requires higher costs for storage and transportation.

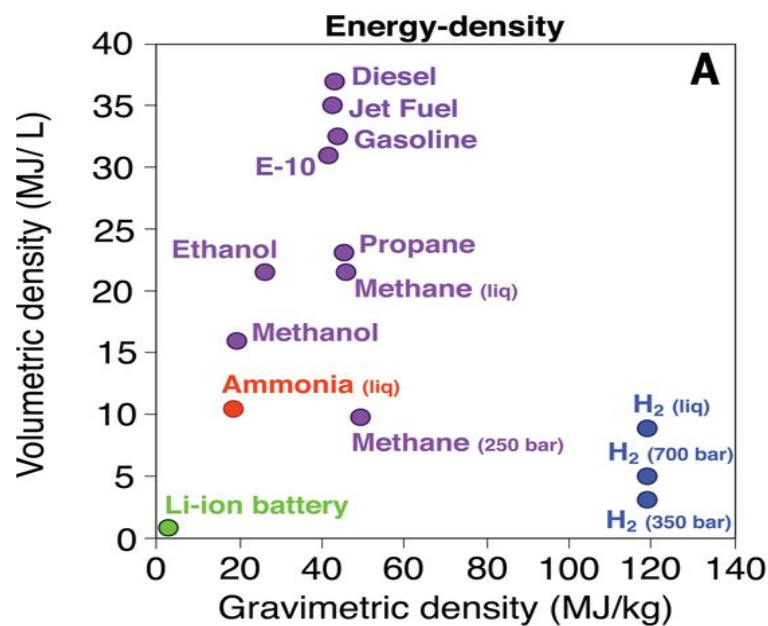


Figure 1.3: Volumetric energy density of fuels (source: [19])

1.4 Flame structure and emission characteristics

Understanding the flame structure is vital in combustion research, as it enables the identification of key reaction zones, such as the preheat, reaction, and burnt gas regions, and clarifies their respective roles in flame stabilization and propagation. It provides

detailed descriptions of the spatial distributions of heat-release rate profiles, temperature, and species profiles, and offers insights into chemical reactions and transport processes across the flame front. Therefore, the study of flame structure serves as a cornerstone for verifying chemical kinetic models.

A one-dimensional premixed stoichiometric planar H_2 - air flame at 1 atm and 295 K is plotted in the Fig. 1.4 and depicts different flame zones. A detailed chemical kinetic mechanism by Zhang et al. [20], which includes the OH^* sub-mechanism developed by Katrothia et al. [21], is used in our simulations.

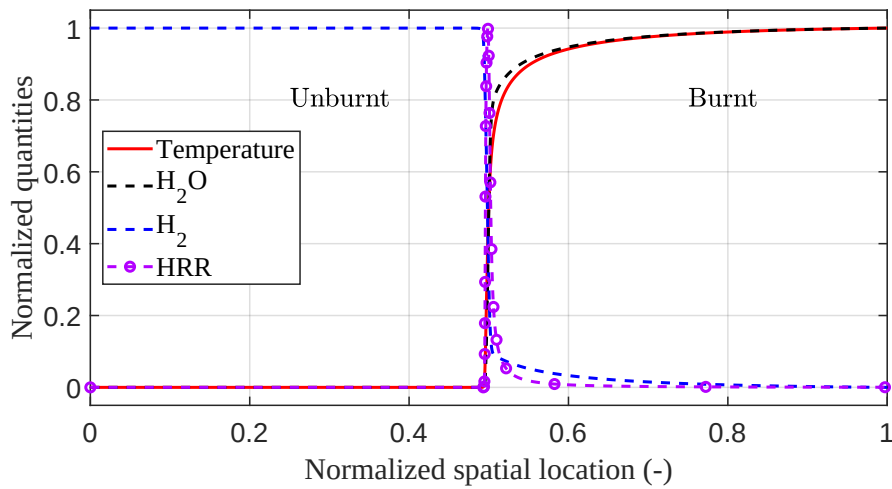


Figure 1.4: Characteristic fields for a premixed, planar, stoichiometric H_2 -air flame at 1 atm. A close-up of this region of high gradient is presented in Fig. 1.5. Any quantity ξ shown, i.e., temperature T , mole fraction X_i of species i or the heat release rate HRR, is normalized as $(\xi - \xi_{\min}) / (\xi_{\max} - \xi_{\min})$.

- The unburnt zone: The unburnt region lies upstream of the flame and is characterized by preheating of the reactants via conductive and radiative heat transfer. While conductive heat transfer is significant across all flame configurations, the radiative heat transfer is negligible for flames with high burning intensity and radiatively nearly transparent species in the infrared region, such as H_2 -air flames. 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 exothermic reactions. These species can be utilized in experimental diagnostics as a potential flame marker.
- The reaction zone: Within this zone, chemical reactions proceed most vigorously, leading to significant net heat release. This typically leads to a high local temperature and significant amounts of H , OH , H_2O_2 , and HO_2 radicals [22]. The reaction zone is described by the region enveloped by the heat release rate (HRR) curve in Fig. 1.4. The heat release rate of individual reactions results in the net HRR. The species presented in the Fig. 1.5 are the potential candidates for flame markers in the experimental measurements of H_2 flames. Note that there is a significant numerical noise in the mole fraction of the NO^* . This can be due to the relatively lower

magnitude of the mole fraction of NO^* , 10^{-16} , compared to 10^{-10} for OH^* .

- The burnt gas zone: This region occurs downstream of the flame front and consists of fully reacted combustion products at high temperatures. In this region, chemical reactions are largely completed, and the gas composition approaches equilibrium. The elevated temperatures and extended residence times promote the formation of thermal NO_x through temperature-sensitive mechanisms. Consequently, a significant portion of the total NO_x produced during combustion originates in the burnt gas zone.

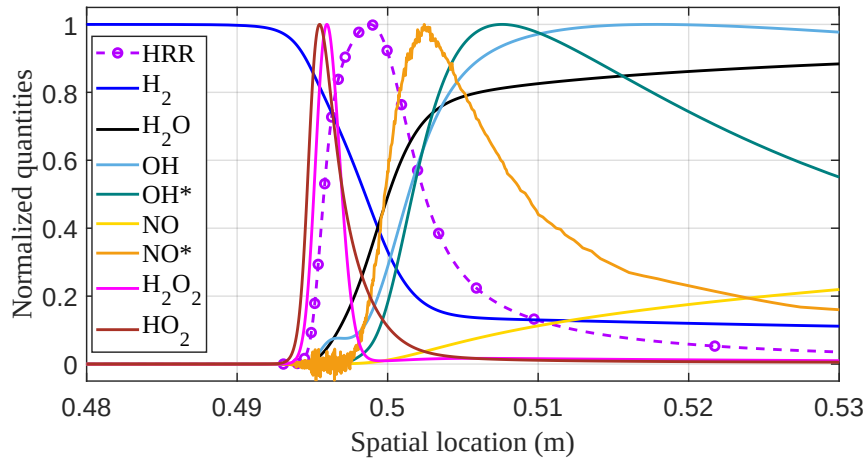


Figure 1.5: Magnified view of a premixed, planar, stoichiometric H_2 -air flame at 1 atm for key species, both ground and excited states.

1.5 Heat release rate and chemical markers

As seen previously, heat release rate is a fundamental flame property that characterizes the reaction zone and marks any instabilities, and is of high importance in both laminar and turbulent flames. But direct measurement of it is herculian task, as it depends on many parameters

$$\dot{Q} = \sum_{\alpha=1}^N \dot{\omega}_{\alpha} h_{f,\alpha}^0 \quad (1.1)$$

here, N = number of species, $h_{f,\alpha}^0$ = standard enthalpy of formation of species α and $\dot{\omega}$ = reaction rate [23]. Hence, relying on chemiluminescence or other diagnostics is ideal for qualitatively correlating it with HRR. Since chemiluminescence is relatively simple, we have primarily used it in our studies. Many studies in the literature have linked the heat release rate or local equivalence ratios to chemiluminescence [24], [25], [26].

Gazi et al. [26] investigated the use of chemical markers to interpret the heat-release rate, studying methane flames and attempting to extend the correlation to other hydrocarbons. It was a numerical assessment using the detailed kinetic mechanism of NTU A [27], where

species, elementary reaction and HRR were computed for 24 burner stabilized laminar premixed flames. The HRR correlation proposed in the literature was first validated with methane flame, where it showed a good correlation for methyl, formaldehyde and formyl radical pathways, while extending it to other fuels, one needs to account for major carbon formation pathways. They emphasized the fact that correlation should be based on a complete understanding of kinetics.

Hardalupas et al. [28] showed that local HRR can be estimated from measurements of local chemiluminescence. They investigated OH^* , CH^* , C_2^* and CO_2^* in a premixed counterflow flame when using natural gas for mixtures with ϕ ranging from 0.7 to 1.3 and strain rates from 800 - 400 s^{-1} . Chemiluminescence was measured using Ocean Optics, coupled with Cassegrain optics. From their analysis, OH^* , CH^* and CO_2^* were reliable indicators of HRR, whilst C_2^* was not. They also tried to relate the heat release rate to the equivalence ratio by computing intensity ratios, which eliminate the effects of pressure and temperature. They observed that OH^*/CH^* decreased monotonically in both lean and stoichiometric mixtures and was independent of strain rate. C_2^*/OH^* and C_2^*/CH^* had a non-monotonic dependence on ϕ and were dependent on strain. Hence, they concluded that OH^*/CH^* can be used to assess local equivalence ratio instead of the latter.

Samaniego et al. [29] demonstrated that integrated HRR can be obtained through integrated chemiluminescence. They performed a numerical study of CO_2^* chemiluminescence in laminar and turbulent premixed methane and propane flames. In a laminar and weakly turbulent configuration, the local flame chemiluminescence per unit area ($\mathcal{J}_x$) is equal to that of a one-dimensional unstrained laminar flame ($\mathcal{J}_{x,0}$), while the total flame chemiluminescence ($\mathcal{J}_{\text{tot}}$) equals the local flame chemiluminescence integrated over the total flame surface area (Σ).

$$\mathcal{J}_x = \mathcal{J}_{x,0} \quad (1.2)$$

$$\mathcal{J}_{\text{tot}} = \mathcal{J}_{x,0} \Sigma \quad (1.3)$$

In a turbulent flame, the heat release rate ($\dot{Q}$) can be estimated from emission intensity ($\mathcal{J}$) by integration along the normal to the flame front.

$$\mathcal{J} = \int_{-\infty}^{+\infty} I \, dx \quad (1.4)$$

$$\dot{Q} = \int_{-\infty}^{+\infty} \dot{Q} \, dx \quad (1.5)$$

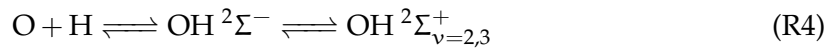
The effects of equivalence ratio, dilution, and strain were investigated, and the integrated intensity and HRR varied monotonically with each. The equivalence ratio and dilution had a positive effect, as they reflect temperature, whereas strain showed a negative effect due to reactant leakage or reduced species residence time in the reaction zone.

Numerous extensive chemiluminescence studies have been carried out in the past, and some of the extensively studied chemical species are CH* [26], [28], [30], HCO* [26], CO₂* [28], [29], [30], OH* [28], [21], [31] and C₂* [28] for hydrocarbons and hydrogen. Ammonia has garnered significant interest in recent days in the combustion community, and some investigations on NH* [32], NH₂* [33], [34], [35] have been carried out. Although present in small quantities, excited nitrogen-containing species such as NO* [36], [37], NO₂* [35], [38] [39] and N₂O* [40] are of concern due to their contribution to harmful NO_x emissions, and relatively few studies have addressed their formation. As the present study focuses on hydrogen flames, the analysis begins with an examination of OH*, which is widely used as a flame marker in hydrogen and hydrocarbon flames. We have conducted some exploratory studies of NO* and blue emission and interpreted their role in flame marking, and characterized their emission.

1.6 Brief history of OH* sub-mechanisms

A short review of some of the most important OH* sub-mechanisms, from the earliest to date, is provided in this section, describing key formation and quenching pathways along with their reaction rates, and offering insight into OH* kinetics based on data from hydrogen flames and shock tube measurements.

One of the earliest studies of OH* dates back to 1958, when Charton and Gaydon [41] presented the excitation spectra of OH in hydrogen flames. They measured the rotational and vibrational intensities of OH bands in H₂/O₂/N₂ flames using a Raman spectrograph with a Meker and a Slot burner at low and high temperatures, respectively. Extending on their previous study of hydrogen flames, The preassociation reaction R4 may cause the enhancement of OH bands at $v' = 2$ and 3, due to excess population of O and H.



They also observed an anomaly in f_1 spin bands were stronger in hydrogen flames, unlike hydrocarbon flames. They noted that OH (0,0) was strong at base and decayed rapidly, whereas higher vibrational bands decayed less rapidly.

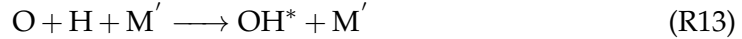
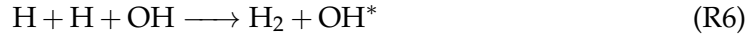
They described OH* is mainly formed by three body collision reaction through R5



R5 reaction is a likely source of OH* excitation, as it releases about 101 kcal, in comparison to the preassociation reaction R4, which requires 108.5 and 116 kcal at $v' = 2$ and 3, respectively.

Kaskan [42] measured OH* emissions using a photomultiplier tube along with OH concentration measured through absorption in H₂/O₂/N₂ flames using a flat porous burner.

They measured OH* emission at the (0,0), (1,0), (2,1), and (3,2) vibrational levels at various distances from the burner. It was demonstrated that OH* emission was due to non-thermal excitation and varied as the cube of the ground-state OH radical. It arises from the recombination of radicals such as H, O, and O₂ at excess equilibrium conditions and results in the formation of OH* at temperatures of 1500 K via underlying reactions.



where M and M' are collisional partners, and $h\nu$ = photon energy.

The recombination of O and H at $v = 0$ results in R13. The R7 is the best fit for all the vibrational bands, and is most likely the reaction that results in OH* formation. R8 is suitable for (2,1) and (1,0) bands and offers quantitative measurements of H, when O and temperature are known a priori. Temperature could be measured by determining the rotational temperature of ground OH, whilst O concentration could be determined by adding NO. Emission is through R11, accompanied by which quenching mainly occurs through R12. At $v = 0$, the reverse of other reactions is highly unlikely due to endothermicity, but at higher quenching levels ($v = 3$), reverse reactions may become important and also result in quenching.

Studies of Kaskan [42] were limited to lower temperatures, where chemical excitation is an important mode of OH* excitation, whereas at higher temperatures thermal excitation becomes an important pathway. Studies by Hidaka et al. [43] demonstrated OH* intensity variations over a wider temperature range (1200 - 3200 K) and determined the OH* formation reaction and its rate constant. Experiments were performed in a shock tube using H₂/O₂ mixtures in highly diluted Ar environments, and OH* emissions were recorded with a photomultiplier tube. They reported that OH* is mainly formed through a three-body collision reaction, as shown in R4, which was previously seen by several authors like Charton and Gaydon [41], and also in the same period by Koike and Moriga. [44].



They described that the reverse of R14 results in thermal excitation which becomes dominant above 2500 K and is purely through it above 3000 K. They demonstrated H₂O and Ar to be principal quenchers and determined their quenching rates using the kinetic theory of gases. They determined the rate expression by fitting the OH* maximum intensity from their experiments and obtained $k = 1.2 \times 10^{13} \exp\left(\frac{-6940 \text{ cal}}{RT}\right) \text{ cm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ for the R5.

Smith et al. [45] further worked on the rate constants of reactions R5 and R7 proposed by Kaskan. They measured absolute OH concentrations in low-pressure H₂ - air flames in the McKenna burner. They measured OH temperature by LIF, chemiluminescence intensities by ICCD at 310 nm, and absolute concentration after Abel inversion. They used the PREMIX code and GRI-Mech 3.0 [46] for the 1D simulations. They remodelled the rate constants of Kaskan and proposed new rate constants of $k(1) = 5.45(2.3) \times 10^{12} \text{ cm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ and $k(2) = 1.45(0.6) \times 10^{15} \text{ cm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ with uncertainties around 40%. They modelled contributions of k(1) and k(2) to be 1/4 and 3/4, where R5 is dominant at low pressures, while R7 is dominant at high pressures. They further compared the Abel-inverted intensity profiles with R5 and R7, which were unable to capture the OH* intensities in the burnt gas region, but a combination of both provided a better match with the experiments.

Hall and Petersen [47] proposed an OH* model at high temperatures and atmospheric pressures. They proposed an optimized kinetic model to predict OH* by developing a fitting routine for the OH* formation rate at 1490 K. Experiments were performed in a shock tube for H₂/O₂/Ar mixtures, and OH* emission was collected through a photomultiplier tube. Modelling was performed using the shock and Senkin routines in Chemkin, and the GRI-Mech 3.0 [46] mechanism was employed. As previously described in the literature, R5 along with R7 is considered to be the main formation pathway. Quenching in their case was a highly diluted Ar environment, which was through R15 and R16, whereas generally it is via R14.



First, a fitting routine was performed to find the function dependence of peak [OH*] on temperature for the R5. The curves were compared to obtain a relationship between k and E. The best fit converges to E of 10 kcal/mol, and the value of this is higher than previous results by Hidaka et al. [43] or Koike and Moriga. [44] due to dual peak. Further dilution had no effect and rate constant of R5 can be best described by $k = 3.1 \times 10^{14} \exp\left(\frac{-10000 \text{ cal}}{RT}\right) \text{ cm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$. For the R7 the rate constants of Smith et al. [45] was used and is given by $k = 1.45 \times 10^{15} \text{ cm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$. The quenching rate constants were taken from the literature, and it was found that uncertainties for H₂O are

larger than those for Ar due to delayed H₂O production.

Kathrotia et al. [21] further proposed a new OH* sub-mechanism by developing the rate constant of R5. They measured the temporal variation of OH* in a shock tube using a photomultiplier tube at 1 bar and temperatures ranging from 1400 to 3300 K. The measured OH* intensities were converted to concentration using a calibration factor. Above 2800 K OH* is generally due to thermal excitation through R14, which allowed to calibrate the measured peak intensities at 3000 K. This calibration factor was then used to describe the chemiluminescence intensity throughout the temperature range. Intensities were further converted to concentration using this calibration factor. A 0D model is performed at constant volume and temperature, along with one-dimensional modelling of burner-stabilized simulations using the Warnatz [48] base mechanism. Quenching rate constants are taken from literature, H₂O from Tamura et al. [49], and for Ar from Paul et al. [50]. The rate constant for R11 is taken as $k = 1.45 \times 10^6 \text{ mol}^{-1} \cdot \text{s}^{-1}$. The measured OH* concentrations are compared against predicted OH* concentrations for R5 and are also compared and contrasted against the literature, where Hidaka et al. [43] underpredicted and Hall and Petersen [47] and Smith et al. [45] overpredicted. A sensitivity analysis further revealed that R17 is the most sensitive reaction affecting OH* formation. H, O and OH are most influential to OH* formation. Uncertainties in H, O predictions would affect the predictions of the rate constant. Further comparisons were also made using the GRI-Mech 3.0 [46] mechanism for other OH* reactions, where some differences of R17 were observed along with different rate coefficients involving HO₂ and H₂O₂ leading to slight differences in OH* predictions.



A complete OH* sub-mechanism is provided in Chapter 2. The rate constant proposed for R5 is $k(1) = 1.5(0.4) \times 10^{13} \exp\left(\frac{-25 \text{ kJ / mol}}{RT}\right) \text{ cm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$.

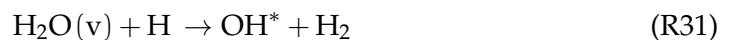
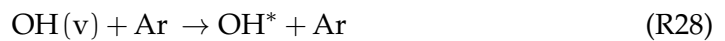
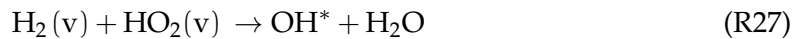
Konnov [51] further proposed a new sub-mechanism for OH* that retains some existing reactions and discards others. The proposed new sub-mechanism was modelled using Chemkin Pro for a perfectly jet-stirred reactor and a closed homogeneous reactor model while PREMIX was used for burning velocity and flame structure. He used Alekseev's mechanism [52] as the base mechanism. No changes were made with respect to the rate coefficient of R5 and the ones of Kathrotia et al. [21] were retained. Many reactions like R7, R18, R19 were found to be irrelevant and hence ignored.



Quenching rate constants were taken from the literature from those of Tamura et al. [49] and Paul et al. [50], and most of the reactions in the literature only considered non-reactive quenching. Konnov proposed some reactive quenching reactions, including O₂, H₂ and H₂O.



Skrebkov et al. [53] proposed vibrational non equilibrium excitation of OH* (²Σ⁺) for a H₂/O₂/Ar mixtures for temperatures less than 1500 K and P ≤ 2 atm for the shocktube experimental data. In the literature, OH* reactions were treated as chemical equilibria, but when vibrational relaxation times are of the same order of magnitude as, or greater than, chemical time scales, one needs to account for vibrational non-equilibrium. The height of the activation energy is the main criterion for the excitation of reagents, and in vibrationally non-equilibrium conditions, this energy barrier is overcome due to reagent excitation. The typical termolecular reactions for OH* formation R5 can be ignored in such scenarios. In the hydrogen oxidation chemistry, vibrational non-equilibrium of HO₂ is the most important one, along with this vibrational non-equilibrium of H₂, O₂, OH, O*, H₂O were also considered, in the case of OH*, it could be neglected due to low concentration and high rates of vibrational relaxation. Several OH* formation and quenching reactions were proposed considering this vibrational non-equilibrium.



Mulvihill and Petersen [54] proposed a set of OH* chemiluminescence reactions for the first time in NO₂ and N₂O systems. The experiments were carried out in a shock tube, and OH* emission was measured by a photomultiplier tube over a temperature range of 1535-2003 K. Modelling was performed in a closed, homogeneous reactor using Zhang et al.'s [20] base mechanism. The rate constant was determined based on best fit with experimental data. R36 was proposed as new OH* formation reaction, while rate constants for R37 was taken from Hidaka et al. [43] and R5 taken by Kathrotia et al. [21] and were also included as OH* formation reactions. Quenching rate constants for all the important species were taken from Tamura et al. [49], and quenching reactions including Ar, NO, NO₂, N₂O were also fitted with literature data. Since quenching data for NO₂ are unavailable, it was assumed to be the same as for N₂O.



They emphasized the relaxation criteria for the relationship between exothermicity and chemiluminescence intensity.

Sharipov et al. [55] further proposed an optimized OH* sub-mechanism in 2024. They developed a kinetic model and validated it against a representative dataset of OH* in a shock tube. They reviewed and revised some reactions reported in the literature and further validated them using theoretical calculations. For some of the sensitive OH* reactions, a global optimization was performed. A partially optimized submodel was tested against various sub-mechanisms. The optimization targets were the characteristic times of OH* = t , the absolute OH* peak mole fractions = $y_{\text{OH}^*}(\text{T}, \text{p})$, and the relative OH* peak concentrations = $\frac{y_{\text{OH}^*}^{\text{peak}}(\text{T}, \text{p})}{y_{\text{OH}^*}^{\text{peak}}(\text{T}_0, \text{p}_0)}$. The base mechanism by Varga et al. [56], along with the NOX reaction chemistry of CRECK [57], was chosen for modelling. R5 in all the previous studies was found to be a temperature-dependent, along with the NOX reaction chemistry of CRECK, reaction. A new bi-variate temperature-pressure dependence of this was found using a PLOG double-Arrhenius fit. For R7 early studies indicated high rate constants $k = 10^{15} - 10^{16} \text{ cm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ due to pressure dependency which later was modified and known to have 10 times lower rate constant in comparison with R5 and used to be generally neglected. The rate constants of this were reassessed, and a maximum $k = 10^{15} \text{ cm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$ was found up to temperatures of 3000 K, although at higher temperatures it traces back to its original magnitude. The detailed sub-mechanism is provided in Chapter 2. The performances of different sub-mechanisms and the error contribution of each optimized parameter to reproduce the experimental dataset are summarized in the Fig. 1.6 below. The error percentage of their study was lowest, followed

by Mulvihill and Petersen [54] and Konnov [51].

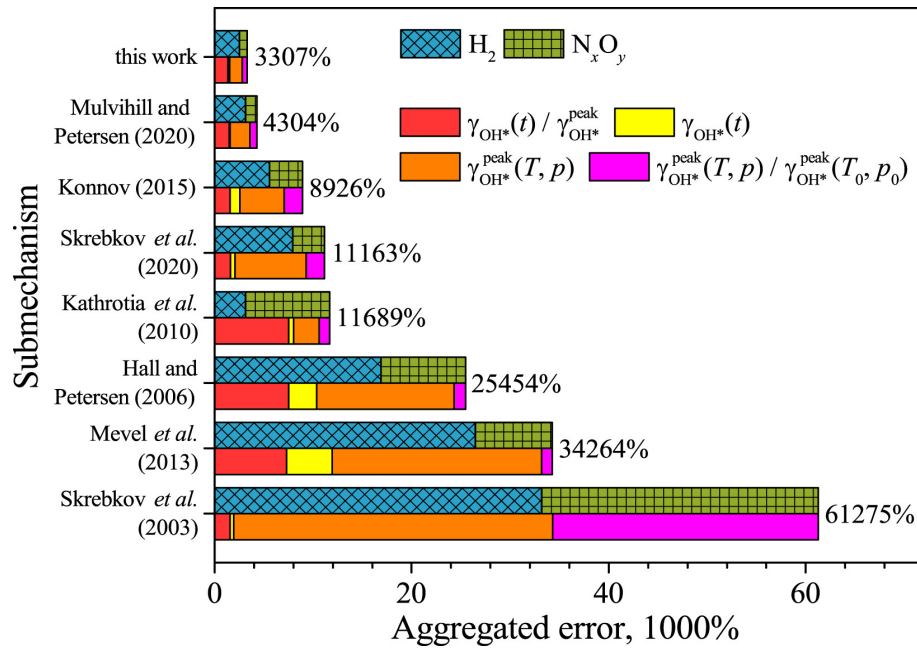


Figure 1.6: Contributions of error percentage across various optimization parameters for different sub-mechanisms (source: [55]).

For our study, we have compared the OH* sub-mechanism by Kathrotia et al. [21] as it is extensively used in hydrogen flames, Sharipov et al. [55] as it is the latest OH* sub-mechanism to date, along with Konnov [51] as it is withing top three performers as seen previously in Fig. 1.6 and all these will be further discussed in Chapter2.

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2 Spherically Expanding Flames: Dynamic chemiluminescence characterization of OH*



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This chapter aims to provide a comprehensive understanding of OH* chemiluminescence as a diagnostic tool in combustion, focusing on the effects of equivalence ratios, pressure, and temperature on OH*. It systematically examines how these parameters affect the formation, spatial distribution, and emission intensity of OH* in hydrogen flames. By linking OH* chemiluminescence to key reaction pathways and heat-release zones, the chapter provides critical insights into flame structure and combustion dynamics that are essential for improving diagnostic accuracy in practical combustion environments.

2.1 Introduction to Spherically expanding flames

The laminar flame can be regarded consisting of 4 regions,

1. An upstream preheat zone, where the fresh gases receive energy from the flame front.
2. A thin reaction layer, where exothermic reactions take place.
3. The flame front, the region with the highest temperature.
4. The burnt gas region, where the products lose heat due to conduction and radiation towards the downstream and upstream (fresh gases).

2.1.1 Laminar flame properties

Laminar flames provide experimentalists with opportunities to investigate flame structure and properties in detail. It accounts for both spatial and temporal fluctuations, which would require significant interpretation in an otherwise turbulent configuration. Research on the flame properties of non-carbon-based fuels has received renewed interest due to the growing awareness of climate action, as discussed in the previous chapter. A few

fundamental properties of laminar flames are critical for understanding the operation of such fuels in both laminar and turbulent configurations.

- Laminar burning velocity (S_l)
- Flame thickness (δ)
- Zeldovich number (Ze)
- Lewis number (Le)
- Markstein length (L_b)

Laminar burning velocity

The laminar burning velocity (S_l or LBV) is the characteristic velocity of the fresh gases towards the flame front. S_l is directly proportional to the reactivity of the fuel-air mixture and it is defined in a stretch-free configuration. The stretch refers to the elongation or contraction of the flame front and is usually assumed to be a thin flame front, which is a reasonable assumption for H_2 -air flames. S_l can be measured in various configurations, such as Bunsen burners, closed spherical vessels, heat-flux burners, and counterflow burners. Post-processing is required to extrapolate the effects of flame stretch. Spherically expanding flames provide a robust experimental configuration that allows for the evaluation of flame properties from sub-atmospheric to very high pressures (around 60 atm, in the literature). Other configurations are affected by the increase in Reynolds number (due to increased pressure), while heat-flux burners are typically limited to about 5 atm in the literature [1]. In the Bunsen burner, characterizing the flame stretch at the flame tip is difficult, and extrapolating stretched flame speeds to obtain the laminar burning velocity is an arduous task. In addition to the ease of experimental measurements, spherically expanding flames have a numerical counterpart, enabling validation of chemical kinetic mechanisms against experimental data. Conventionally, the S_l decreases with pressure, although the mass burning flux (density of fresh gases $\times S_l$) increases.

If the inlet velocity of the fuel-air mixture is significantly higher than the laminar burning velocity, flame blow off may occur. If the inlet velocity is too low, flashback may occur. The latter is a particular concern for fuels with a high burning propensity. Hence, the computation of S_l is critical for the pursuit of fuel-flexible burners to enable the seamless adoption of non-carbonaceous fuels.

Laminar flame thickness

Laminar flame thickness is also an important property of the flames that needs to be evaluated. Since it also determines the impact of eddies on the disruption of the reaction layer and the subsequent characteristics of the flame. The flame stretch and the laminar flame thickness can be used to define a non-dimensional number, Karvolitz number (Ka),

from the spherical flame perspective.

$$Ka = \frac{\kappa \delta}{S_l} \quad (2.1)$$

The laminar flame thickness can be evaluated for the spherical flames from the full width at half maxima (FWHM) of the thickness of the broadband emission or chemiluminescence intensity from a specific species at a certain wavelength. The impact of the evaluation of flame thickness in H_2 -air could be minimal, but it could provide invaluable insight in the case of thick flames such as NH_3 -air flames.

Zeldovich number

Zeldovich number (Ze or β) qualitatively describes the ratio of the length of the reaction layer to the length of the thermal flame thickness. A high value of Ze indicates a very small region of intense heat release rate and is often used in analytical approaches. Although it doesn't have an exact analytical equation, it can be obtained from certain assumptions [2] for a planar flame configuration. Conventionally, it increases with pressure, highlighting a reduction in the region of heat release. The Ze can be computed via Egolfopoulos and Law [2]:

$$\beta = \frac{E_A}{R} \approx -2 \frac{\partial \ln(m_0)}{\partial (1/T_{adi})} \Big|_p \quad (2.2)$$

E_A is the activation energy of the multistep kinetic mechanism and R is the gas constant. β is obtained by derivative of the mass burning rate (m_0) and T_{adi} refers to the adiabatic flame temperature.

Markstein length

The Markstein length characterizes the impact of the flame disturbances on the burning intensity. In case of a negative L_b , it is termed as a thermo-diffusively unstable configuration, as the onset of any disturbances will amplify with time and eventually lead to stretch-induced extinction. Whereas, in the case of positive L_b , the disturbances will decay with time, but in the presence of negative stretch (flame thickening), it will also lead to extinction due to incomplete combustion. This behaviour needs to be accounted for, since in combustors the flame field is turbulent and we need to avoid extinction from either regime. Markstein length also decreases with pressure, highlighting the increased propensity of the flames to thermo-diffusive instabilities. Markstein length also has its non-dimensional counterpart, Markstein number, $Ma = \frac{L_b}{\delta}$. It is the ratio of Markstein length to the laminar flame thickness. The analytical L_b for the adiabatic system can be computed from the work of Bechtold and Matalon [3], similar to Refs. [4, 5], where Le_{eff} is the effective Lewis number of the flames (from the deficient species/weighted average, [3]), δ the flame thickness of the adiabatic 1D flame, and Ze is the Zeldovich number (β),

(γ_1) is thermal expansion coefficient, and (σ) is density ratio :

$$\frac{L_b}{\delta} = \gamma_1 + \frac{1}{2}\beta (Le_{eff} - 1) \gamma_2 - (\sigma - 1) \frac{\gamma_1}{\sigma} \quad (2.3)$$

Lewis number

The Lewis number describes the flame's enthalpy loss from the flame front to the fresh gases and the mass diffusion from the fresh gases to the flame front. As for the diffusivity, the diffusion of the deficient reactant to the mixture is considered. The Lewis number determines the stability of the flames via heat loss/chemical gain for stretched flames and will be discussed below.

$$Le = \frac{\lambda}{\rho D_{d,m} c_p} \quad (2.4)$$

In the above equation, λ , ρ , and c_p correspond to the mixture's thermal conductivity, density, and heat capacity, respectively. $D_{d,m}$ corresponds to the diffusion coefficient of the deficient species in the mixture.

2.1.2 Theoretical framework of spherical flames

As previously mentioned, the spherical flames are subjected to flame stretch due to curvature, which promotes the unequal diffusion of Lewis numbers. Hence, the impact of stretch is not significant for a flame with a near-unity Lewis number for the fuel-air mixture (for instance, CH_4 -air flames). The flame stretch can be computed via

$$\kappa = \frac{1}{A} \frac{dA}{dt} \quad (2.5)$$

where A is the instantaneous flame surface area with time t . The computation becomes arduous for multi-dimensional flames. In the case of spherically expanding flames, the flame stretch can be computed via the above equation (Eq. 2.5). It becomes,

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

where R_f is the flame location and $\frac{dR_f}{dt}$ corresponds to the flame displacement speed. The relationship between the flame displacement speed and flame stretch can be used to compute the burnt gas flame speed (via non-linear equation Kelley and Law [6], Eq. 2.7) and the laminar burning velocity.

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

In the above equation, S_b , $S_{b,0}$, and L_b correspond to the stretched burnt gas flame speed, extrapolated burnt gas flame speed, and burnt Markstein length. The laminar burning velocity can be computed via ($S_{b,0} = \sigma S_{b,0}$) where σ is the density ratio between burnt

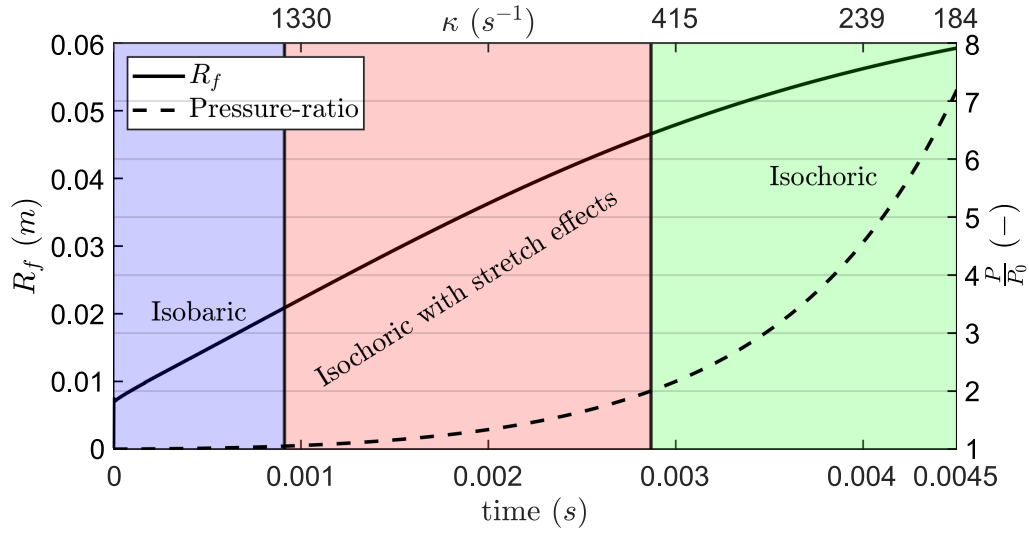


Figure 2.1: Illustration of the isobaric and isochoric regimes of a spherically expanding H_2 flame throughout the flame propagation. In this instance, the pressure rise defining the isobaric regime is set to 1%, and the isochoric region has relatively low flame stretch. The exact criteria are subjective and can vary among various groups.

gas to the fresh gas mixture.

2.1.3 Flame configurations

The spherically expanding flames can be operated in two regions of interest:

- Isobaric flame propagation
- Isochoric flame propagation

In the isobaric regime, the pressure increment is below 1% of the initial pressure. This regime is particularly useful for investigating the effects of stretch on the flame displacement speed and description of the flame stability via flame stretch. In this regime, the flame radius is captured using a high-speed scientific CMOS camera, leading to the flame displacement speed from the flame radius history. The flame displacement speed can be extrapolated to obtain the unstretched burnt gas speed. The unstretched burnt gas speed, along with the density ratio, up to can be used to obtain the unstretched laminar burning velocity. Conventionally, the isobaric propagation can be extended up to $0.33 \times R_0$, with R_0 being the inner chamber radius of the vessel.

Fig. 2.1 illustrates the evolution of the flame radius and pressure ratio over the flame propagation time. The flame propagation is divided into three regimes, i.e. (1) the isobaric regime (the region with minimal increase in pressure), (2) the isochoric regime 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. 2.1 was generated from a numerical simulation for an initial pressure of 1 atm and an initial temperature of 300 K at stoichiometric conditions for H_2 -air flames using spherically expanding flames in FlameMaster [7] (the numerical

aspects will be discussed in the upcoming sections).

In the isochoric regime, pressure increases considerably. For instance, the end pressure can be $8 \times P_0$. Due to isentropic compression, the unburnt temperature also increases with increasing pressure. Above $P/P_0 > 2$ [8] (the green region in Fig. 2.1), 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 [8].

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

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 of laminar burning velocity by various groups.

2.1.4 Flame instabilities

Flame instabilities pose a critical challenge for experimentally evaluating H_2 flame properties (due to the very low Lewis number of H_2 species). Since instabilities might affect local flame propagation, thereby affecting the accuracy of experimental acquisition. The flame instabilities can be broadly classified into,

- Intrinsic flame instabilities
- Intrinsic thermoacoustic instabilities

Intrinsic flame instabilities

Instabilities arise from the flame's natural propensity develop instabilities. The intrinsic flame instabilities can be classified into,

- Hydrodynamic instabilities
- Thermo-diffusive instabilities

The hydrodynamic instabilities stem from the sudden variation in the densities from the burnt gas to the fresh gases, thereby any fluctuations are further amplified due to the lower density in the burnt gas. It is also termed as Darrieus-Landau instability and leads to large segmentation of the flames [9]. It is always present in the system, although an increase in pressure promotes the onset of the hydrodynamic instabilities [10]. The hydrodynamic instabilities are unstable at all the wavenumbers, which leads to the conclusion that a stable laminar flame is not possible experimentally by Darrieus and Landau [11]. This paradox between numerical predictions and experimental observations

was later identified due to the interplay of hydrodynamic and thermo-diffusive instabilities.

Thermo-diffusive instabilities are caused by the variation of the Lewis number and differential diffusion leading to a mismatch in the enthalpy loss from the flame front to the fresh gases compared to the chemical gain in the flame front from the fresh gases [12]. It is controlled by the Markstein length L_b , which highlights the propensity of the flame subjected to thermo-diffusive instability. $L_b > 0$, denotes a thermo-diffusively stable flame whereas $L_b < 0$ denotes a thermo-diffusively unstable flame. Depending on the operating Lewis number, the flame can be further subjected to different thermo-diffusive instabilities. For $Le < Le_{critical1}$, the flames will be subjected to cellular structures leading to local acceleration of the flame front, thereby making the experimental acquisition of the flame displacement speed unreliable. This is particularly pertinent for lean H_2 -air flames, and it can be mitigated by adding dilutents such as He, Ar, and so on. The critical Lewis number also increases with the operating pressure, thereby leading to widening of the unstable regime with pressure.

For $Le > Le_{critical2}$, the different type of instability arises called pulsating instability. It arises due to the $Le > 1$ at very rich conditions [13]. This results in faster enthalpy loss from the flame front to the fresh gases while the O_2 diffusion (deficient reactant) is slower, thereby weakening the flame (reducing the flame temperature). During this process, the reaction layer receives higher energy, leading (via enthalpy loss) to an increase in the reaction rate and strengthening the flame (increasing the flame temperature). Since this process occurs in very rich conditions, it is not generally seen in the experiments.

Intrinsic thermoacoustic instabilities

Intrinsic thermoacoustic instabilities in flames are an important challenge that must be addressed in a lean flame configuration. It is also referred to as combustion instability in the literature. They are due to the coupling of the acoustic waves (reflected from the boundaries) and the heat release rate, which can lead to significant structural damage due to the positive feedback loop of such a configuration [12]. It was observed in the last decade that there were cases of thermo-acoustic instability even in the absence of acoustic waves [14]. OH^* has received particular attention from the combustion instability community [15, 16, 17, 18] to identify the flame's characteristics due to the perturbations. Hence, the performance of OH^* as a flame marker has significant implications in studying the flame dynamics leading to both passive and active controls of combustion instability.

2.1.5 Literature review

In this subsection, a few significant works on the topic of chemiluminescence of OH^*/CH^* are presented. Although there are a plethora of works in the literature on chemiluminescence, only a few works have investigated the impact of thermal excitation of chemiluminescence and chemiluminescence in spherically expanding flames.

Yoo et al., [19] investigated chemiluminescence of OH* and CH* species in a spherical diffusion flame under terrestrial gravity at sub-atmospheric pressures. They utilized spherical diffusion flames of H₂ and H₂ - CH₄ flames. The latter are affected by buoyancy, and hence this configuration was chosen to mitigate the effects of buoyancy since the flames are primarily driven by diffusion. The primary objective of their work was to assess the role of two reactions (refer to R38 and R39) in H₂ and H₂ - CH₄ flames.



It is particularly important since (R39) is the most important reaction in hydrogen flames, whereas in CH₄ flames, it is not significant. They complemented the experimental study with numerical simulations of spherical diffusion flames using a variant of PREMIX to handle the transient diffusion flames in a 1-D spherical symmetric configuration, along with radiative absorption and emission using a statistical narrow band model. The OH* band at 310 nm and CH* at 410 nm, respectively, were used for the study. The 2-D images were postprocessed and then deconvoluted to obtain the radial chemiluminescence profiles. As for the excitation mechanisms for OH* in H₂ flames, the excitation primary pathway was R39 while the de-excitation pathway was a third-body reaction with OH* and photon emission (radiative lifetime), respectively. As for the H₂ - CH₄ flames, OH* was formed via R38 while CH* was formed via R40



They observed very good agreement between the experimental OH*, numerical OH* and numerical heat release rate for H₂ flames and the agreement improved with an increase in pressure. In H₂ - CH₄, they observed significant discrepancies between the OH* from experiments and numerical simulations in the absence of R39 and also in the magnitude of CH*. While accounting for the R39, they observe a double peak (of OH*) both in experiments and simulations and this double peak merged as the amount of CH₄ in H₂ - CH₄ was increased. The correct interpretation of the double peak is crucial since, in the absence of spatial resolution in experiments or reactions in the kinetics, it might be misconstrued as a relatively thick flame signalling weak energy release.

De Leo et al. [20] investigated the effects of strain rate on the chemiluminescence in counterflow oxy-methane diffusion flames due to paucity of data in such a configuration. They utilized both a spectrometer and a camera to obtain the resolved signatures in both spectral and spatial space. The OH* spectra were captured between 300 and 320 nm, while the CH* spectra were acquired between 420 and 440 nm. The optical system's sensitivity was quantified for every measurement using a tungsten lamp. They observed a very good qualitative agreement between experiments and the simulations (OPPDIF), and

the excited profiles aligned with the ground profile due to the predominance of thermal excitation of the ground radicals. They highlighted that such an agreement wouldn't be possible in the case of purely chemical excitation. The authors highlighted the better suitability of CH^* due to its relative invariance to the operating parameters (O_2 content) while OH^* was strongly affected by the operating parameters. The OH^* concentration varied by a factor of 400, whereas CH^* changed by only 1.6 times. The authors observed that chemical excitation was the main pathway for CH^* formation, while for OH^* , it was a chemical pathway until oxygen content of 35%, whereas above 35%, thermal excitation seems to be the dominant pathway. The authors also highlighted the direct role of OH concentration, as an increase in O_2 would also be a point of consideration. They tested the role of various reaction pathways for OH^* and CH^* and concluded that thermal luminescence (thermal excitation of the ground state radicals) is the major pathway after 35% of O_2 , and it wasn't observed in CH_4 -air flames due to relatively low temperature.

Fiala and Sattelmayer [21] numerically examined the proportionality of heat release rate to the OH^* radiation in liquid rocket engine conditions. The main goal of the work was to assess chemiluminescence OH^* , so that the heat release rate could be extracted and hence combustion instabilities can be examined in detail. They utilised non-premixed counterflow flamelets for pressures from 1 to 100 bar. The laminar flames are subjected to a strain rate at low levels (equilibrium condition) to stretch-induced extinction. They computed the threshold temperature when the thermal excitation exceeded the chemical excitation, which occurred at 2700 K at 1 bar, whereas it occurred at around 2600 K at 20 bar, and at 50 atm, the thermal excitation exceeded the chemical excitation at all temperatures. They also observed that OH^* peaks in the location where temperature is maximum and also OH radicals are present, which is typically in the middle of the flame front, while the maximum heat release rate typically occurs upstream of the flame front. Fiala and Sattelmayer [22] later tested the performance of chemiluminescence for high-temperature flames (> 2700 K) using two main levels of chemiluminescence modelling,

1. a kinetic mechanism which assumes the OH^* chemiluminescence is proportional to the concentration of OH^*
2. a detailed spectral model that accounts for both OH emission and absorption using a high-resolution spectral database, HITRAN-2008

They highlighted the applicability of spectral models for OH^* because thermal excitation is more significant than chemical excitation, and ray tracing was used to solve the radiative transfer equation. They observed that the chemical mechanism over-predicted the OH^* radiance, whereas spectral modelling with self-absorption provided the best agreement with simulations. Hence, the authors concluded that a detailed description of radiative heat transfer, along with absorption and emission, is critical for flames with high optical density for OH^* formation.

Turner et al. [23] investigated the chemiluminescence characteristics of CH_4 -air flames

in an isobaric regime of flame radius up to 6.5 cm. They utilized CH^* and OH^* at 434 nm and 315 nm, respectively. This study improves on the previous measurements of chemiluminescence by capturing the evolution of chemiluminescence in a spherically expanding flame. It could provide invaluable insights into the heat release rate markers of the experiments against the kinetic mechanisms. The main objective of the work was to capture the evolution of the flame thickness of the flame front and test it against the numerical counterpart. They performed numerical simulations using PREMIX with the AramcoMech2.0 kinetic mechanism due to the latter's robust performance. The raw chemiluminescence images were post-processed to remove artefacts due to the duration of the gate width and centered. The processed image was deconvoluted using the inverse Abel transform (Hansen and Law method) to remove the information from the 3-D volume. They observed a limitation from an experimental acquisition due to the requirements of high resolution for capturing the flame and the limited field of view of the flame stemming from the resolution requirements. They noted the increase in the flame thickness with a decrease in flame stretch (or an increase in flame radius). They obtained the laminar flame thickness via linear extrapolation of the instantaneous flame thickness.

Turner et al., [24] utilized high-speed, species-specific chemiluminescence imaging (OH^* at 315 nm, CH^* at 434 nm, broadband) for simultaneous measurements of laminar flame speed, thickness, and Markstein length in spherically expanding CH_4 -air and $\text{CH}_4/\text{C}_2\text{H}_6$ -air flames at atmospheric pressure and room temperature, thereby extending the flame physics significantly. The above-mentioned closed spherical vessel was used, which had a relatively huge isobaric region of around 6 cm. The post-processed the raw images using an edge detection (Canny edge detection) and circle-fit method using in-house codes. They illustrated the independence of the laminar burning velocity and the burnt Markstein length on the experimental evaluation of the species' chemiluminescence (OH^* , CH^* or broadband), hence instilling confidence in the captured data. The same team at TAMU, [25], has demonstrated the efficacy of chemiluminescence as a diagnostic for NH_3 flames at oxygen-enriched conditions at various temperatures and oxidizer ratios. They utilized chemiluminescence of NH_2^* . They mitigated the low-burning velocity of ammonia by increasing the O_2 content, and they observed that the flame thickness was relatively constant across the flame propagation time, highlighting the negligible impact of stretch on a thick flame such as NH_3 . They observed excellent agreement between experimental measurements and simulations at certain mixture conditions, highlighting the need to further improve the kinetic models. They have further extended the calculation of flame thickness of methane-and propane-air mixtures [26].

Schiavone et al. [27] examined the performance of OH^* as the flame marker for H_2 -air flames using Kathrotia [28] and Konnov [29] sub-mechanism. They also investigated the impact of the fuel in H_2 - and CH_4 -air and the performance of the OH^* for counterflow diffusion flames in CANTERA [30] for a multi-component diffusion model along with Soret diffusion. They observed that for planar H_2 - and H_2 - CH_4 -air flames, the

location of the peak OH* and the heat release rate are displaced by a distance δ_{peak} and this is less than 10% δ_L (laminar flame thickness) for the blended flames while for H₂-air flames, it is around 50% of δ_L . They further extended the analysis for counterflow-diffusion flame and observed that the correlation between OH* and heat release rate weakens as the strain rate was increased. Schiavone et al. [31] recently investigated the variation of the δ_{peak} for various canonical configurations such as 1 D planar, 1 D strained flames, and 2 D stretched flames with two-sub mechanisms Kathrotia [28] and JIHT by Sharipov et al. [32] for a range of conditions between 300 K to 900 K, pressures up to 20 atm, and for equivalence ratios between 0.3 to 3.0. They further illustrated the growing discrepancies between OH* and the heat-release rate in 2 D cylindrically expanding flames, thereby highlighting the need for a better flame marker for H₂ flames.

2.2 Motivation and objectives

The chemiluminescence of OH* provides essential insights into the flame structure, heat-release rates, and local reaction conditions. Although OH* chemiluminescence has been extensively studied in atmospheric pressure flames, its behaviour and effectiveness as a diagnostic tool under high-pressure, high-temperature conditions, which are common in real-world combustion systems, have not been thoroughly investigated.

The motivation for this study stems from the increasing importance of high-pressure combustion systems in modern applications, including rotating detonation engines, gas turbines, rocket engines, and advanced internal combustion engines. As these systems operate at higher pressures and temperatures to improve efficiency and performance, there is a pressing need to extend our understanding of combustion diagnostics in these challenging conditions. OH* chemiluminescence, with its potential for providing real-time, spatially resolved information about the reaction zone, presents an attractive option for monitoring and characterizing such systems. However, interpreting OH* chemiluminescence signals at elevated pressures and temperatures is not straightforward. Several factors complicate the analysis: The chemical kinetics governing the formation and quenching of OH* may change significantly under these conditions. The relationship between OH* emission and key combustion parameters, such as the heat-release rate and equivalence ratio, may deviate from established correlations. The influence of pressure and temperature on spectral characteristics and signal intensity remains incomplete. This work investigates OH* chemiluminescence in laminar premixed hydrogen flames under high-pressure, high-temperature conditions. A spherically expanding flame is studied in a constant-volume chamber with the application of high-speed chemiluminescence to identify OH* radicals. By combining experimental observations, numerical simulations, and detailed kinetic analysis, we aim to elucidate the complex relationships between OH* emission, flame properties, and operating conditions in these environments.

The objectives of this chapter are threefold:

- Experimental and numerical investigation of the behaviour of OH* chemiluminescence in hydrogen flames under varying mixture conditions, pressures and temperatures.
- Investigate the predictive capability of different sub-mechanisms.
- Use numerical simulations and detailed kinetic analysis to explore the relationship between OH* emission and flame characteristics.

2.3 Experimental setup: The OPTIPRIME

The experiments described in this section were conducted using the OPTIPRIME [33] facility at ICARE-CNRS, Orléans, France. OPTIPRIME is a state-of-the-art, constant-volume spherical combustion chamber designed to enable comprehensive and precise studies of flame propagation phenomena. Its design combines advanced optical accessibility with precise control of thermodynamic and mixture conditions. Fig. 2.2 represents the experimental rig.

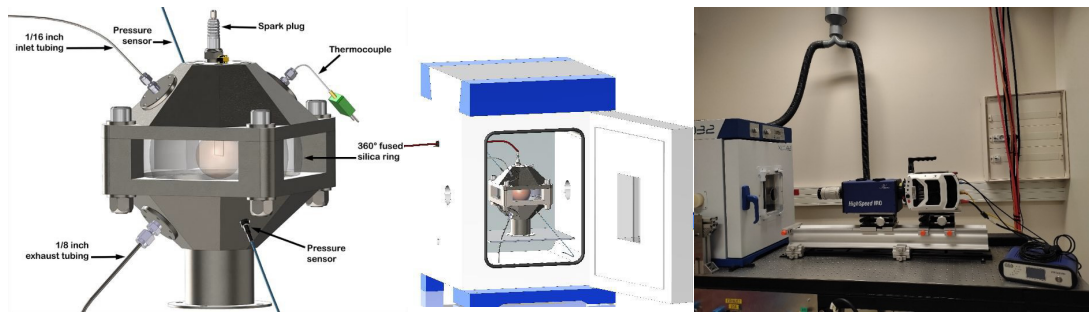


Figure 2.2: Schematic diagram of experimental set-up

2.3.1 Chamber architecture

Two stainless-steel hemispherical shells define the internal volume, clamped around a 360° fused-silica ring that provides optical access. The fused silica ring, with an outer diameter of 144 mm and a wall thickness of 11 mm, is precision-machined to maintain sphericity on both its inner and outer surfaces. This ensures that the internal radius of the chamber remains uniform at 60.85 mm, corresponding to a volume of approximately 0.943 litres. The OPTIPRIME chamber is housed within a 32-litre furnace with a rectangular quartz window that provides optical access and is capable of delivering up to 1050 W of power.

2.3.2 Instrumentation

To minimize flow disturbances and dead volumes, the chamber is equipped with carefully dimensioned inlet and exhaust ports, 1/16 inch and 1/8 inch in diameter, respectively. Pressure was measured using two identical AVL GU21D piezoelectric sensors placed opposite each other in the chamber, one at the top and one at the bottom. These sensors have a high sensitivity of 35 pC/bar, a frequency response of 85 kHz, and linearity within ± 0.3

% of full scale. Temperature monitoring is performed using a type-K thermocouple housed within a stainless steel sheath, providing precise measurement of the initial, unburnt gas temperature. The chamber is designed for operation up to an initial temperature of 473 K.

2.3.3 Mixture preparation and ignition

Fuel-oxidizer mixtures are prepared in a dedicated 3.78-litre high-pressure buffer tank using Dalton's law of partial pressures. The buffer tank's relatively large volume, relative to the chamber volume, ensures homogeneous mixture and repeatability across multiple experimental runs, thereby minimizing compositional variability.

Ignition is initiated by a pair of electrodes connected to a capacitor coil, with the ignition energy precisely controlled by adjusting the coil's charging time. This approach provides consistent and reproducible ignition conditions essential for comparative studies.

2.4 Optical diagnostics

Chemiluminescence was used to track the flame propagation from ignition to the chamber wall. The 360° fused-silica ring enables full optical access of the flame throughout its propagation (isobaric and isochoric), hence further assumptions on the isochoric region would not be necessary. A rapid imaging technique was applied to obtain a series of images. A high-speed CMOS camera, Phantom V1611, was used to obtain a series of images, and a LaVision HS-IRO S20 intensifier was coupled to the camera. The initial spark and the late flame events that occur when the flame contacts the wall were avoided to prevent oversaturation of the intensifier. Therefore, an initial delay was applied to image acquisition, including the decay of the spark, and the number of images to be captured was adjusted accordingly across experiments. A UV lens from Cerco with a focal length of 105 mm was used. The excited state of OH* radical at $A^2\sigma^+ - x^2\pi(0,0)$ is detected using a UV bandpass filter from Edmund centered at 308.5 nm and bandwidth of 10 nm with an optical efficiency of 85 %. This setup enables high temporal and spatial resolution imaging of the flame front, allowing detailed analysis of the evolution of flame radius and structure throughout the combustion event.

An acquisition rate of 10000 fps was used for most of the work, whereas 20000 fps was used for the high-temperature series. Pixel resolution for both cases was 142.85 and 119.04 μm /pixel, respectively. The camera resolution is 1024 * 384 pixels². The camera sensor exposure time was 99 μs . The response linearity with respect to gate time and gain was confirmed by systematically varying these parameters, yielding linear dependencies. To determine optimal image acquisition settings, tests were conducted at $\phi = 1$ and an inlet pressure of 0.5 bar. Constant gain was set, and the gate was modified. Different images were acquired at gate widths of 70, 85, and 100 microseconds. Similarly, a gate of 85 microseconds was further chosen, and the gain was altered between 36, 38 and 40 %. The comparison between different settings was made by calculating the integrated intensity of each frame, which was done by pixel-wise summation across each image. As shown in the

Fig. 2.3, the integrated intensity scales linearly with both gate time (at a fixed gain of 36%) and gain (at a fixed gate of 70 μs), confirming that the chosen acquisition settings operate within the linear response range of the detection system. Changing the gate produces a smaller effect than changes in gain. An optimal gate width of 85 μs and a gain of 40 % were used in all our experiments. The gain and gate are kept constant across experiments to facilitate comparison. Maximum gate and gain settings are chosen as optimal values to avoid saturation.

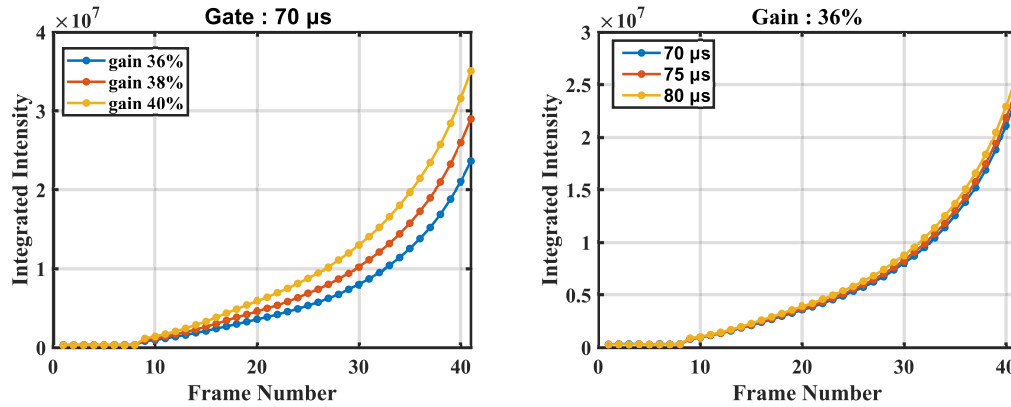


Figure 2.3: Linearity tests for gate and gain conducted at $\phi = 1$.

2.4.1 Schematic diagram

The schematic diagram of the experimental rig and optics is provided below in Fig. 2.4.

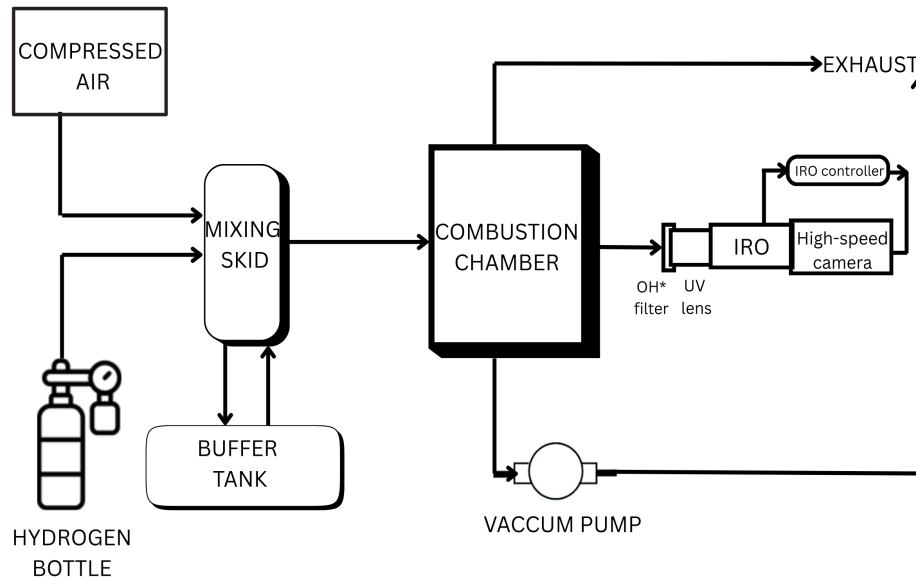


Figure 2.4: Schematic diagram of experimental set-up

2.5 Experimental test conditions

OH* chemiluminescence measurements were performed for various hydrogen-air mixtures, including changes in equivalence ratios, inlet pressures and temperatures. The mixtures were tested at lean, stoichiometric, and rich conditions at $\phi = 0.8, 1.0$, and 1.2 , respectively. Initial pressures were studied at $0.5, 0.75$ and 1.0 bar. Measurements were limited to a maximum inlet pressure of 1 bar due to the onset of thermodiffusive instabilities at higher pressures. The experiments were performed at an inlet temperature of 295 K for all the equivalence ratios, while additional high-temperature tests at 303 K and 353 K were done for $\phi = 1.2$. Repeatability was ensured by performing three tests for each operating condition. The experimental conditions are tabulated in Tab. 2.1

CASE	ϕ	P_i (bar)	T_i (K)
1	0.8	0.50, 0.75, 1.0	295
2	1.0	0.50, 0.75, 1.0	295
3	1.2	0.50, 0.75, 1.0	295
4	1.2	0.8	303, 353
5	1.2	0.8	303
		1.0	323
		1.2	340

Table 2.1: Experimental database

2.6 Experimental treatment

This section outlines the methods for cleaning, processing, and preparing experimental data before analysis. These procedures are used to eliminate the ignition/post-processing artefacts and derive key physical quantities from raw chemiluminescence images.

2.6.1 Data processing techniques

The raw images were first processed to extract the flame edge. A 3×3 Laplacian operator was applied to sharpen edges. The flame edges were detected using the Canny edge detection algorithm. The algorithm computes the image gradient and then applies non-maximum suppression. Double thresholding is applied, and the edge is tracked by hysteresis. A circle-fitting procedure was then applied to the edge-detected raw images to obtain the flame radii. The original raw images were cleaned using background subtraction to remove luminosity contributions from the quartz glass, which increase with flame growth and constitute experimental noise that must be addressed before image analysis. Noise correction was performed by subtracting the maximum intensity value from the glass regions outside the flame radius, accounting for the intensity gradient that rises toward the flame, and any resulting negative values were thresholded to zero to ensure non-negativity. The image cleaning process is shown in Fig. 2.5, where the image on the left is the raw image, the center image is the edge-detected image, and the image on

the right is the background-corrected image. This cleaned image will be further used for deconvolution.

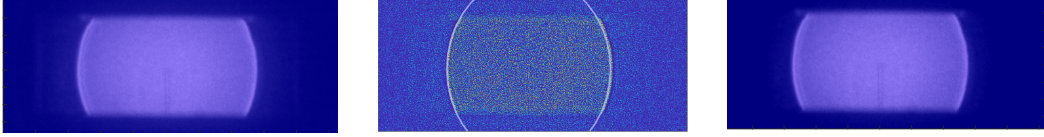


Figure 2.5: Raw (left), Edge detected (center), Background corrected (right) images at $\phi = 1.0$, $P_i = 1.0$ bar and $T_i = 295$ K and time = 3.2 ms

The line-of-sight integrated images obtained from the experiments require further deconvolution to recover the original spatial information. A Fourier-based algorithm originally developed by George Pretzler and Carsten Killer was used for the Abel inversion [34]. The unknown radial distribution $f(r)$ is expanded in a series that is close to a Fourier series. Most methods work from the outer periphery toward the center. The advantage of using this method is that it operates independently and is therefore unaffected by errors. It requires no pretreatment. The measured 2D data are fitted to a cosine expansion based on an integral. The number of cosine expansions impacts the computational time and filtering effects. Higher the expansions longer is the time. The expansion can be performed either algebraically or as a least squares problem. A comparison of algebraic and LSQCURVE fits was conducted, and the resulting intensity distributions during flame evolution are shown below in Fig. 2.6. Both methods exhibit similar temporal evolution, and LSQCURVE was selected for our analysis because it yields lower computational time.

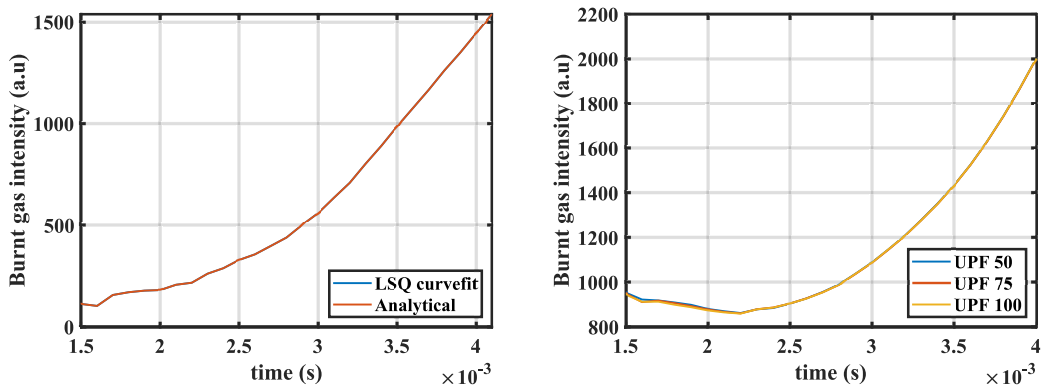


Figure 2.6: Burnt gas intensity distributions as a function of time using different expansions (left) and frequencies (right) fits for $\phi = 1.0$, $P_i = 1.0$ bar and $T_i = 295$ K

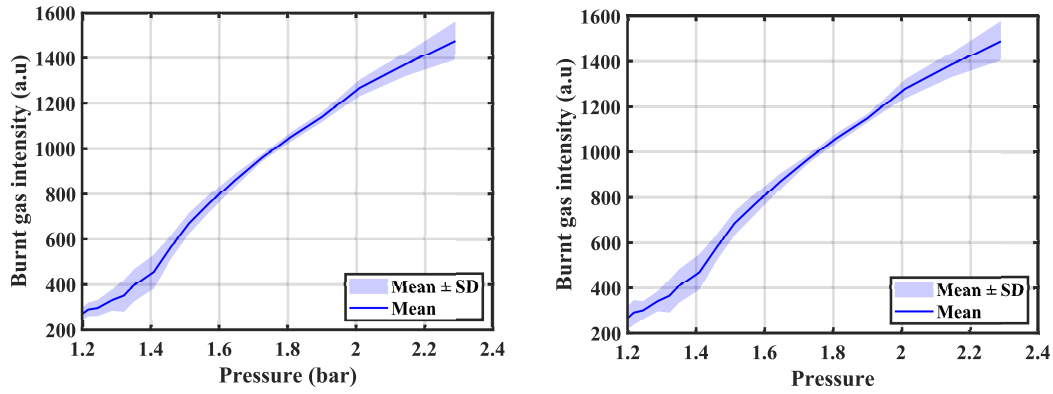


Figure 2.7: Burnt gas intensity distributions as a function of pressure in the left and right core of flame for $\phi = 1.0$, $P_i = 1.0$ bar and $T_i = 295$ K

Upper frequency limit (UPF) determines the number of cosines used in the expansion. Different Upper frequencies of 50, 75, and 100 are applied, yielding comparable intensity distributions as illustrated in right of the Fig. 2.6. A higher UPF helps preserve image features, but it requires more computational time and may introduce noise. An UPF of 75 is further chosen as the optimal threshold for our analysis. The axisymmetric images are input into the algorithm along with the `abelinversion.m`, `computeexpansion.m`, `solvlsq.m`. The transformations are applied row-wise to both the left and right sides of the images. A complete image is reconstructed using both sides. The left- and right-side intensity distributions were comparable, so subsequent processing was restricted to the right side of the flame.

2.6.2 Morphology of the flame

It is essential to understand the chemiluminescence intensity distributions within the flame to compare them with their numerical counterparts. Hence, the morphology of the flame is presented here. To elucidate the evolution of flame structure, spatial intensity maps and temporal traces are extracted and presented below in Fig. 2.8 for a mixture at $\phi = 1.2$, $P_i = 0.5$ bar, and $T_i = 295$ K. The left panel shows the raw image, and the right panel shows the Abel-inverted image. Fig. 2.8 illustrates the intensity distribution at different flame locations. The flame front is outlined in the red circle, and the core of the flame consists of post-combustion gases. Analysis of the flame images indicates that the OH^* intensity is distributed throughout the flame, at the flame front where heat release occurs, and an afterglow is observed in the post-combustion gases. As we move from figure A to B, the intensity in the burnt-gas region increases, and this trend continues as the flame propagates, due to changes in temperature and pressure.

The OH^* signal distribution observed in the experiments is therefore divided into these two zones, and the emission characterization is made separately.

- The intensities within the reaction layer were determined at each radial location via edge detection of the flame front.

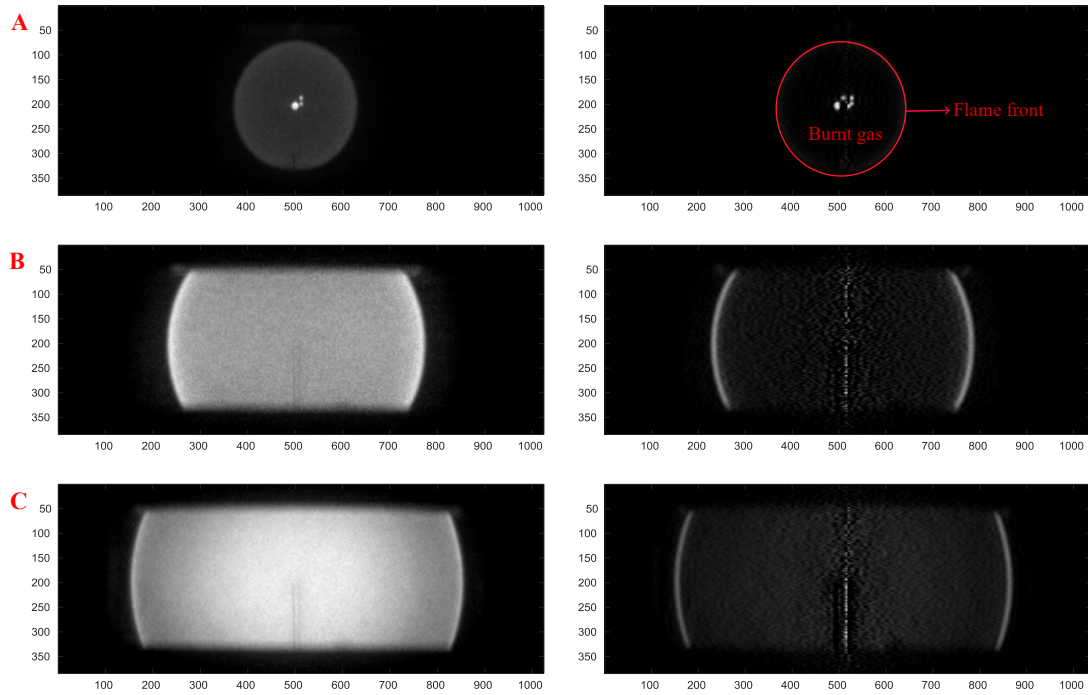


Figure 2.8: Spatial and temporal distributions of OH* chemiluminescence at $\phi = 1.2$, $P_i = 0.5$ bar and $T_i = 295$ K. Raw images (left) and Abel inverted images (right). A: 1.5 ms, B: 3 ms, C: 4 ms

- The burnt-gas intensity was averaged within the burnt-gas region, spanning from 10 pixels beyond the radius to 50 pixels before the center along the horizontal axis.
- Given the substantial volume of burnt gases produced during expansion, their contribution to total chemiluminescence must be evaluated. An intensity ratio is therefore defined as the flame-front intensity divided by the burnt-gas intensity.

As the flame's central region is unaffected by curvature, averaging was performed along 5 vertical lines.

2.7 Numerical treatment: 1D Flame modelling

To complement the experimental observations, detailed one-dimensional simulations were performed using FlameMaster to analyze flame structure, species history, and chemiluminescence formation. FlameMaster [7] is an open-source finite difference solver that can simulate a range of flames from planar premixed flames to spherically expanding premixed flames. FlameMaster employs a Lagrangian coordinate transformation to eliminate the advective terms. The mathematical implementation is based on the work of Maas and Warnatz [35].

The spherically expanding flames using isochoric and isobaric numerical configurations are illustrated in Fig. 2.9.

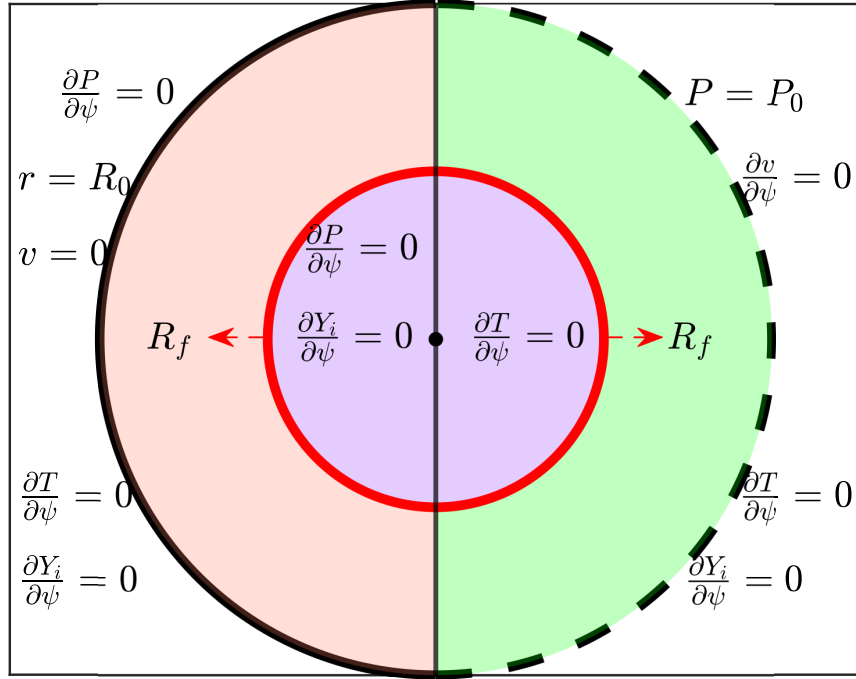


Figure 2.9: Schematic of spherically expanding flames for the isochoric configuration (left half of the circle) and the isobaric one (right half of the circle). The purple shaded regions illustrate the burnt gas region, and the red solid line denotes the flame front of radius R_f while the green shaded region denotes the isobaric region and the red shaded region denotes the isochoric region. 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.

Continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (2.8)$$

Species

$$\frac{\partial \rho w_i}{\partial t} + \nabla \cdot (\rho \mathbf{v} w_i) + \nabla \cdot \mathbf{j}_i = \dot{\omega}_i M_i \quad (2.9)$$

Momentum

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla P - \nabla \cdot \boldsymbol{\tau} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \mathbf{0} \quad (2.10)$$

Energy

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho \mathbf{v} h) - \left(\frac{\partial P}{\partial t} + \mathbf{v} \cdot \nabla P \right) + \nabla \cdot \mathbf{j}_q + \boldsymbol{\tau} : \nabla \otimes \mathbf{v} = \dot{q} - \nabla \cdot \mathbf{q}_{\text{rad}} \quad (2.11)$$

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 use the following relation to translate radial formulation into Lagrangian formulation [36, 35, 37]:

$$\psi = \int_0^r \rho r^2 dr \quad (2.12)$$

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 ($\nabla P = 0$), although unsteady ($\frac{dP}{dt} \neq 0$). The unsteady pressure terms are significant for the isochoric flame configuration. As for isobaric flames, the domain (R_0) expands/contracts to maintain the isobaric nature of the flame [36].

In the Lagrangian formulation, the conservation equations become [36, 35],

Mass

$$\frac{\partial \rho}{\partial t} + \rho^2 \frac{\partial}{\partial \psi} (\mathbf{v} r^2) = 0 \quad (2.13)$$

Species

$$\frac{\partial w_i}{\partial t} + \frac{\partial}{\partial \psi} (\rho r^2 w_i \mathbf{V}_i) - \frac{\dot{w}_i M_i}{\rho} = 0 \quad (2.14)$$

Equation of state

$$P - \frac{\rho R T}{M} = 0 \quad (2.15)$$

Energy in terms of temperature

$$\begin{aligned} \frac{\partial T}{\partial t} - \frac{1}{\rho c_p} \frac{\partial P}{\partial t} - \frac{1}{c_p} \frac{\partial}{\partial \psi} \left(\rho r^4 \lambda \frac{\partial T}{\partial \psi} \right) + \frac{r^2}{c_p} \sum_{i=1}^{n_s} \rho w_i \mathbf{V}_i c_{pi} \frac{\partial T}{\partial \psi} \\ + \frac{r^2}{\rho c_p} \sum_{i=1}^{n_s} \dot{w}_i h_i M_i = -\frac{1}{\rho c_p} (\nabla \cdot \mathbf{q}_{rad}) + \frac{\dot{q}}{\rho c_p} \end{aligned} \quad (2.16)$$

Here,

$$\mathbf{V}_i = \mathbf{V}_{d,i} + \mathbf{V}_{t,i} + \mathbf{V}_c \quad (2.17)$$

with

$$\mathbf{V}_{d,i} = -\frac{1}{w_i} \mathcal{D}_{i,m} \nabla w_i \quad (2.18)$$

$$\mathbf{V}_{t,i} = -\frac{\mathcal{D}_i^T \nabla T}{\rho w_i T} \quad (2.19)$$

$$\mathcal{D}_{i,m} = \frac{1 - w_i}{\sum_{j \neq i} \frac{w_j}{\mathcal{D}_{ji}}} \quad (2.20)$$

Here, $\mathbf{V}_i$ is the diffusion velocity of the species i for the diffusion flux, it accounts for the mass diffusion of species i ($\mathbf{V}_{d,i}$) [38, 39], the thermal diffusion velocity of species i ($\mathbf{V}_{t,i}$) [39] and thermal diffusion coefficient is denoted as ($\mathcal{D}_i^T$), 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 ideal gas law was invoked to compute the thermal conductivity (λ) and diffusion

coefficients ($\mathcal{D}_{i,m}$) [39]. As for the mixture's thermal conductivity and diffusion coefficients, they were evaluated using Mathur and the mixture-averaged formula, respectively [40].

2.7.1 Radiation models

In this subsection, we assess the impact of various radiation models on the OH* and temperature profiles of H₂-air flames. Three classes of radiation models were used:

- Adiabatic (ADI): this model ignores radiative heat transfer
- Optically thin model (OTM): This model assumes the medium to be optically thin and that only radiative emission is important.
- Discrete ordinate method (DOM): This model captures the radiative absorption and emission of the medium. A narrow band model based on the work of Raman et al. [41] was used for the H₂O vapour in the burnt gas.

Fig. 2.10 shows the OH* and temperature profiles at two different flame radii for all the radiation models. We can observe two things:

- The impact of radiation re-absorption is minimal (DOM vs. OTM) due to the high laminar burning velocity of H₂ - air flames. Because of the absence of radiative reabsorption, OTM underpredicts the temperature profile, leading to lower OH* production than DOM as shown in inset of temperature plot in Fig. 2.10.
- Due to the higher temperature predictions by ADI, we have a higher mole fraction of the OH* in the burnt gas.

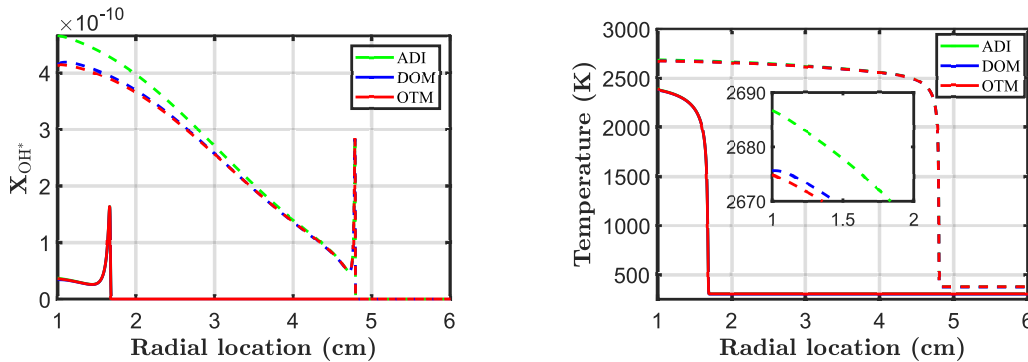


Figure 2.10: Molefraction and temperature profiles with different radiation models for H₂ - air flames at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 303$ K.

Because the difference between OTM and DOM is minimal, OTM is ultimately chosen to model the radiative heat transfer observed in the experiments. Since the computational cost of narrow band DOM is $9.3\times$ more than OTM.

2.7.2 Diffusion models

The performance of different transport models was evaluated by comparing the OH^* profiles. Initially, a constant Lewis approximation is employed, in which the Lewis numbers of all species are assumed constant. Furthermore, a mixture-averaged transport model was used, in which diffusion is considered between a given species and a mixture of other species. Finally, a multicomponent model was used where diffusion between one species and all individual species is considered separately. Fig. 2.11 represents simulation results done at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 303$ K without considering the Soret effect. It is observed that the heat-release rate of the mixture-average model is approximately 20% lower than that of multicomponent diffusion. OH^* mole fractions are severely overpredicted in multicomponent systems due to higher temperatures relative to the other two models. This difference is driven by the multicomponent model's ability to capture the rapid differential diffusion of light radicals, which accelerates chain-branching reactions and elevates local flame temperatures. The mixture-averaged transport model is used hereafter in our simulations due to its lower computational cost.

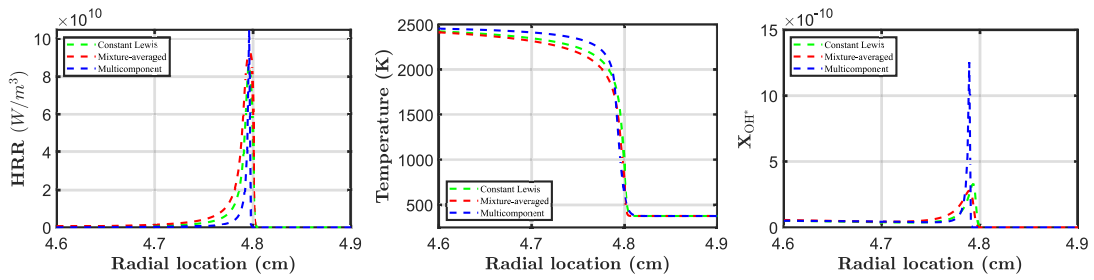


Figure 2.11: Heat release rate (left), OH^* mole fraction (center) and temperature (right) profiles for H_2 (right) for H_2 - air flames at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 303$ K.

2.7.3 Effects of thermodiffusion

Thermodiffusion plays a significant role in hydrogen combustion. Due to high temperature gradients between the flame front and the burnt gas, light species migrate towards the hot region, and heavy species vice versa [42]. To assess the impact of thermodiffusion on OH^* evolution, simulations were performed by including and neglecting Soret diffusion for H_2 - air flames at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 295$ K. Inclusion of Soret diffusion increases H_2 and H diffusion from unburnt gas to burnt gas as previously shown in studies by Yang et al., Faghih et al. and, Zhou et al. and [43, 44, 45]. The Fig. 2.12 shows the contributions from mass and Soret diffusion terms for H and H_2 as functions of temperature. Overall, diffusion is primarily due to mass diffusion. An initial dip in both H and H_2 is observed due to thermodiffusion as we move from the unburnt to the burnt. The mass flux due to thermodiffusion is highest at 1400 K for H and at 700 K for H_2 .

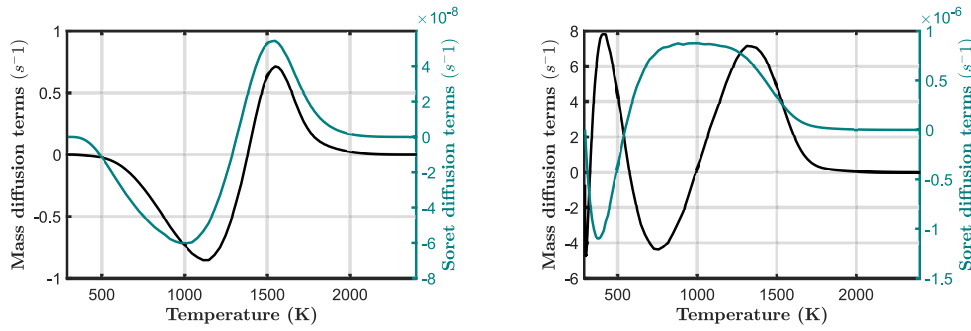


Figure 2.12: Contributions of different terms for H (left) and H₂ (right) for H₂ - air flames at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 295$ K.

In Fig. 2.13, the heat release rate and mass flux of H with and without thermal diffusion are shown. It was observed that the heat-release rate was slightly lower when thermodiffusion was included, due to a reduction in the mass-burning rate. A slightly higher reduction in mass flux in the absence of thermodiffusion is observed, thereby lowering the local H concentration. $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$ is known to be a significant reaction affected by Soret diffusion. The reaction rates are higher with thermodiffusion than without [43, 45, 46], thereby increasing the overall concentrations of OH and OH*. At the flame front, the inclusion of thermodiffusion results in less than 2% change. On further moving towards the burnt gas due to stronger temperature gradients, the impact of Soret diffusion can be a bit more prominent and reaches almost 20 %. Soret diffusion plays an important role in the distribution of OH* across the overall flame morphology and hence has been considered hereafter in our simulations.

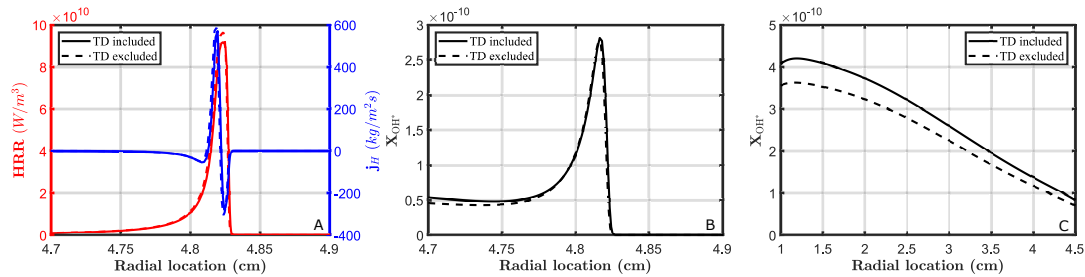


Figure 2.13: A: Heat release rate and mass flux profiles, B: OH* mole fraction profile at flame front, C: OH* mole fraction profile in the burnt gas H₂ - air flames at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 303$ K.

2.8 Chemical kinetic schemes

This section investigates the contributions of the base mechanism and the sub-mechanism to the predicted spatial distribution of OH* chemiluminescence, highlighting their roles in radical formation.

2.8.1 Effects of base mechanism

The profiles of major species involved in hydrogen oxidation are assessed in this study across several base mechanisms to evaluate their effects on OH* formation. The Burke

mechanism, developed by Meng et al. [47], includes 39 species and 268 reactions, and was employed to evaluate reaction kinetics. The effects of species distribution were further assessed by incorporating an OH* sub-mechanism developed by Kathrothia [28], which revealed no impact on the species distribution. An exact overlap of profiles was observed for the Burke mechanism on the addition of the OH* sub-mechanism. Subsequent assessments examined combinations of detailed mechanisms developed by Zhang et al. [48] with the Kathrothia [28] sub-mechanism, involving 44 species and 251 reactions, and the kinetic mechanism of Varga et al. [49] along with the sub-mechanism of Sharipov et al. [32], showing a negligible effect of base mechanisms on overall species distribution profiles. Fig. 2.14 describes heat release rate, temperature and key species distributions in H₂ - air flames. The species profiles are almost identical across all mechanisms. Hence, it can be concluded that the base mechanism may not affect the overall distribution of OH*.

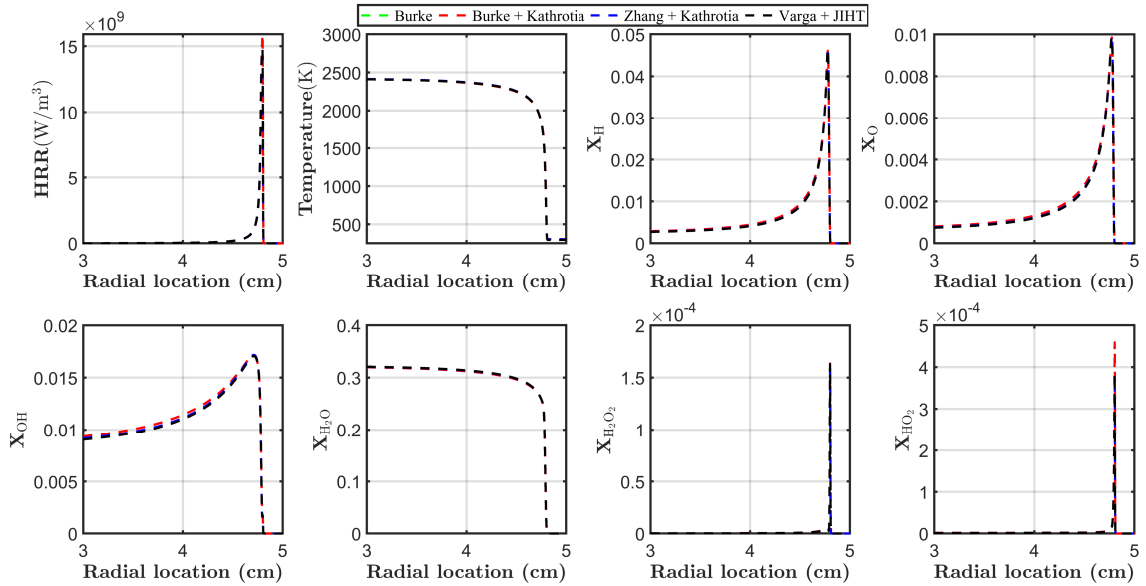


Figure 2.14: Effects of base mechanisms for H₂ - air flames at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 303$ K.

2.8.2 Different sub mechanisms

To evaluate the impact of sub-mechanisms on overall predictions of OH*, three sets of OH* sub-mechanisms, Konnov, Kathrothia and JIHT, were employed for 1D flame simulations. The first set of simulations was performed using a detailed kinetic mechanism of Konnov [29]. A detailed chemical kinetic mechanism by Zhang et al. [48], which includes the OH* sub-mechanism developed by Kathrothia et al. [28], was used as the second set of simulations. The kinetic mechanism of Varga et al. [49] served as the base mechanism, and the OH* sub-mechanism by Sharipov et al. [32] was employed as a final set and will hereafter be referred to as JIHT throughout the paper.

Fig. 2.15 describes the OH* mole fraction profiles with the three sub-mechanisms at two flame radii $R_{f1} = 1.62$ cm and $R_{f2} = 4.78$ cm. It is observed that, at any given radius, Konnov overpredicts at the flame front, whereas Kathrothia and JIHT are almost

comparable. Whilst in the burnt-gas zone, the OH^* profiles are higher with Kathrotia than with the other two, and they evolve similarly in this region. This shows that OH^* predictions are highly dependent on the sub-mechanism. The performance in predicting OH^* chemiluminescence, comparable to experiments, was assessed for Kathrotia, which is well validated, and for JIHT, which is the latest available optimized sub-mechanism.

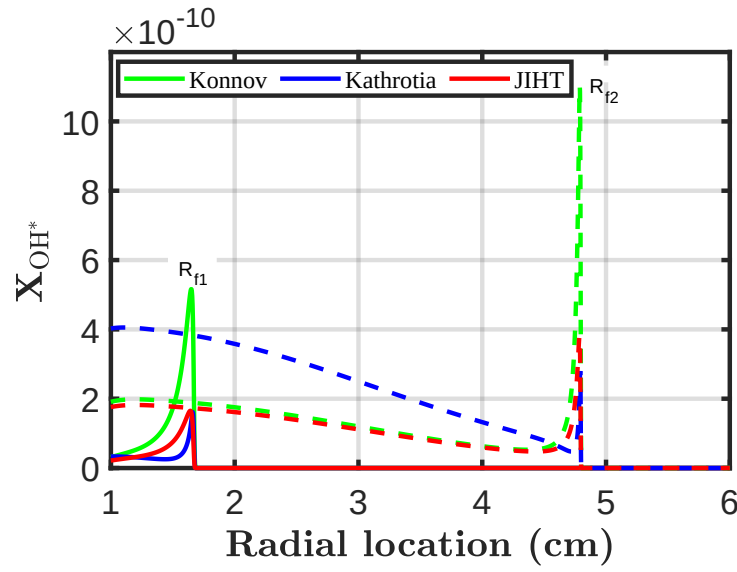


Figure 2.15: Effects of OH* sub mechanisms for H₂ - air flames at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 303$ K.

The Tab. 2.2 and Tab. 2.3 summarize the OH* sub-mechanism for Kathrotia and JIHT, respectively. Units: cm³, mol, s, cal, and K.

No.	Reaction	A	b	E _a
1	$H + O + M \rightleftharpoons OH^* + M$	1.50×10^{13}	0.0	3006.7
2	$OH^* + H_2O \rightleftharpoons OH + H_2O$	5.93×10^{12}	0.5	-432.8
3	$OH^* + H_2 \rightleftharpoons OH + H_2$	2.95×10^{12}	0.5	-223.4
4	$OH^* + N_2 \rightleftharpoons OH + N_2$	1.08×10^{11}	0.5	-625.0
5	$OH^* + OH \rightleftharpoons 2OH$	6.01×10^{12}	0.5	-384.5
6	$OH^* + H \rightleftharpoons OH + H$	1.31×10^{12}	0.5	-84.0
7	$OH^* + Ar \rightleftharpoons OH + Ar$	1.69×10^{12}	0.0	2080.8
8	$OH^* \rightleftharpoons OH$	1.45×10^6	0.0	0.0
9	$OH^* + O_2 \rightleftharpoons OH + O_2$	2.10×10^{12}	0.5	-240.5
10	$N_2O + H \rightleftharpoons OH^* + N_2$	1.60×10^{14}	0.0	50300

Table 2.2: OH* sub-mechanism: Kathrotia

No.	Reaction	A	b	E _a
1	Ar + OH* $\rightleftharpoons$ Ar + OH	6.38×10^{-7}	5.2057	-6559.9
2	Kr + OH* $\rightleftharpoons$ Kr + OH	2.80×10^{12}	0.5	77.50
3	N ₂ + OH* $\rightleftharpoons$ N ₂ + OH	1.08×10^{11}	0.5	-1240.0
4	O ₂ + OH* $\rightleftharpoons$ O ₂ + OH	8.95×10^{11}	0.5	-482.9
5	H ₂ O + OH* $\rightleftharpoons$ H ₂ O + OH	6.09×10^{12}	0.5	-765.1
6	H ₂ + OH* $\rightleftharpoons$ H ₂ + OH	1.00×10^{12}	0.5	-445.1
7	OH + OH* $\rightleftharpoons$ 2OH	1.95×10^{12}	0.5	-1716.9
8	H + OH* $\rightleftharpoons$ H + OH	2.75×10^{13}	0.5	2458.2
9	O + OH* $\rightleftharpoons$ O + OH	1.50×10^{12}	0.5	0.0
10	H ₂ O ₂ + OH* $\rightleftharpoons$ H ₂ O ₂ + OH	4.57×10^{12}	0.5	-270.3
11	O ₂ + OH* $\rightleftharpoons$ HO ₂ + O	6.54×10^{11}	0.5	-482.9
12	H ₂ O + OH* $\rightleftharpoons$ H + H ₂ O ₂	2.40×10^{14}	0.0	42527.2
13	H ₂ O ₂ + OH* $\rightleftharpoons$ H ₂ O + HO ₂	4.73×10^{12}	0.5	-270.3
14	H ₂ + OH* $\rightleftharpoons$ H + H ₂ O	4.70×10^{11}	0.5	-445.1
15	H + OH* $\rightleftharpoons$ H ₂ + O	5.65×10^{12}	0.5	0.0
16	H + OH* + M $\rightleftharpoons$ H ₂ O + M	0.0	0.0	0.0
17	OH + OH* $\rightleftharpoons$ H ₂ O ₂	7.45×10^{13}	-0.37	0.0
18	O + OH* + M $\rightleftharpoons$ HO ₂ + M	0.0	0.0	0.0
19	O + OH* $\rightleftharpoons$ H + O ₂	0.0	0.0	0.0
20	H + O $\rightleftharpoons$ OH*	3.25×10^{23}	-3.5206	27711.95
21	H + O $\rightleftharpoons$ OH*	1.15×10^{-12}	5.5595	-1023.24
22	H + 2OH $\rightleftharpoons$ H ₂ O + OH*	3.88×10^3	3.3199	0.0
23	H ₂ O + O $\rightleftharpoons$ OH + OH*	1.30×10^8	1.3	110460.86
24	H + HO ₂ $\rightleftharpoons$ OH + OH*	0.0	0.0	0.0
25	OH* $\rightleftharpoons$ OH	1.46×10^6	0.0	0.0
26	HO ₂ + OH* $\rightleftharpoons$ H ₂ O + O ₂	4.90×10^8	0.5	0.0
27	NH + NO ₂ $\rightleftharpoons$ N ₂ O + OH*	4.10×10^{12}	0.0	28441.46
28	H + N ₂ O $\rightleftharpoons$ N ₂ + OH*	1.60×10^{14}	0.0	50298.18
29	NNH + O $\rightleftharpoons$ N ₂ + OH*	2.91×10^{12}	0.15	-144.67
30	NH + NO $\rightleftharpoons$ N ₂ + OH*	3.73×10^{12}	-0.17729	25732.34
31	H + NO ₂ $\rightleftharpoons$ NO + OH*	5.47×10^{11}	-0.061112	63789.33
32	NH ₃ + OH* $\rightleftharpoons$ NH ₃ + OH	9.00×10^{12}	0.5	-596.0
33	N ₂ O + OH* $\rightleftharpoons$ N ₂ O + OH	1.99×10^{12}	0.5	-2405.71
34	NO + OH* $\rightleftharpoons$ NO + OH	1.83×10^{10}	0.5	0.0
35	NO ₂ + OH* $\rightleftharpoons$ NO ₂ + OH	4.31×10^{12}	0.5	1272.81
36	H + HNO ₂ $\rightleftharpoons$ HNO + OH*	3.60×10^7	0.0	85449.88

Table 2.3: OH* sub-mechanism: JIHT

Fig. 2.16 describes the rate constants of the main OH* formation reactions as a function of temperature. It can be observed that the reactions that produce OH* differ between the two sub-mechanisms. It is observed that the reaction rates of all reactions increase with increasing temperature. $\text{H} + \text{O} \rightleftharpoons \text{OH}^*$ is highly sensitive to temperature. $\text{H} + 2\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{OH}^*$ and $\text{H} + \text{O} + \text{M} \rightleftharpoons \text{OH}^*$ change comparably. A negligible variation in $\text{NNH} + \text{O} \rightleftharpoons \text{N}_2 + \text{OH}^*$ can be observed as the temperature increases.

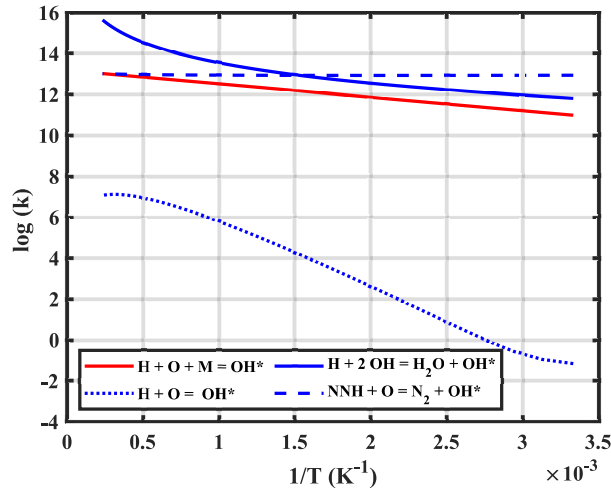


Figure 2.16: Rate constants as a function of temperature from Kathrotia (indicated in red) and JIHT indicated in blue) for H_2 - air flames

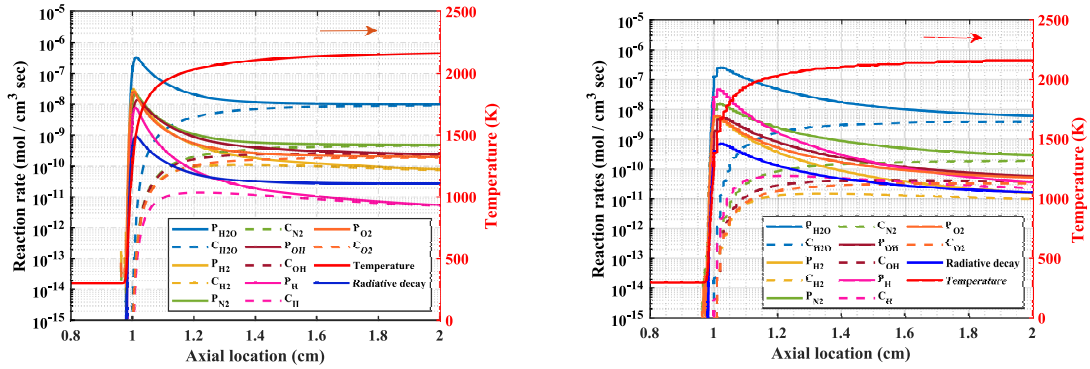


Figure 2.17: Reaction rates as a function of axial distance for a planar for H_2 - air at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 295$ K.

The reaction rates of key reactions involved in production and consumption reaction of OH* is computed for a H_2 - air at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 295$ K in a planar configuration and is shown in Fig. 2.17. Here, P denotes the production of species and C indicates the consumption of species. The main formation reaction is shown only for Kathrotia, since it is a single reaction. It can be noted that in the burnt gas, the contributions from reactions involving H_2O are higher compared to the main reaction; this will be further discussed in Section 2.12. The rate coefficients of H_2O and N_2 are the largest amongst all the other species, and they are the leading collisional partner of OH*. The rate coefficient of OH* due

to radiative decay is smaller compared to other rate coefficients of different species, thereby emphasizing that the de-excitation is comparably higher due to collisions in comparison to photon emission.

2.9 Computational details

Numerical simulations have been conducted under conditions similar to those in the experiments represented in Tab. 3.1. The simulations have been performed using a mixture-averaged transport model, and an optically thin radiation model (OTM) has been considered to account for radiation. Thermodiffusion effects have been evaluated by including the Soret effect. The simulations were performed for a propagation time of 6×10^{-3} s under stoichiometric and rich conditions, and 12×10^{-3} s under lean conditions, because the laminar flame speed is lower under lean conditions. The flames were simulated with radii up to 6 cm, matching the chamber dimensions. An ignition radius of 0.5 cm was used. A grid convergence study was conducted with 4000 and 8000 grid points. Fig. 2.18 represents the heat release rate and mole fraction profiles of OH* at a pressure of 3.98 bar, equilibrium temperature of 2370 K, and a radial location of 5.5 cm, where all our analysis is conducted within this radius. It is observed that even under high-pressure, high-temperature conditions where the flame thickness is low, the two grids yield results that are close to each other, with minimal differences. Hence, 4000 grid points are considered throughout the course of this work.

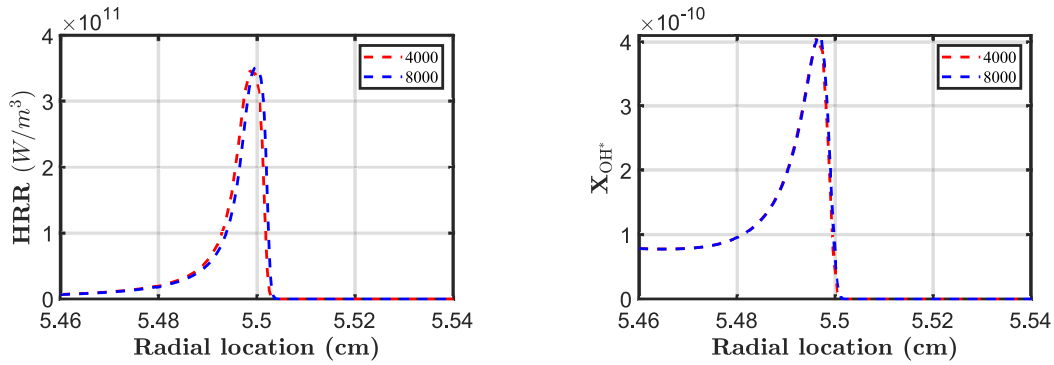


Figure 2.18: Heat release rate and molefraction profiles of OH* using different grid points for H₂ - air at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 295$ K.

2.9.1 Chemiluminescence modelling

Chemiluminescence intensities were calculated using the equation described by Kojima et al. [50]. CLI refers to chemiluminescence intensity and will be used throughout this document [27]. First, concentrations were computed from the simulations. Rate constants for each reaction involved in OH* collisions were calculated using Arrhenius equation.

$$k = A T^b \exp\left(-\frac{E_a}{RT}\right) \quad (2.21)$$

Here k is the rate constant ($\text{kmol}/\text{m}^3/\text{s}$), A is the pre-exponential factor ($\text{m}^3/\text{kmol}/\text{s}$ for 2nd order), b is the temperature exponent (dimensionless), E_a is the activation energy (J/kmol), $R = 8314 \text{ J}/\text{kmol}/\text{K}$ is the gas constant, and T is the temperature (K). Rate parameters were taken individually from each mechanism. An overall quenching rate (Q) was further computed. Subsequently, the quantum and fluorescence yields were calculated, yielding the chemiluminescence intensity.

$$q_i = k_{\text{OH}^*}/k_{\text{all}} \quad (2.22)$$

Here q_i is the quantum yield and k_{OH^*} is the rate constant of radiative decay, and k_{all} is the sum of rate constants of all collisional partners.

$$y_i = A_{21}/(A_{21} + Q) \quad (2.23)$$

Here y_i is the fluorescence yield, A_{21} is the Einstein coefficient s^{-1} and Q is quenching rate in s^{-1}

$$\text{CLI} = y_i \cdot C_{\text{OH}^*} \quad (2.24)$$

Here CLI is the chemiluminescence intensity and the concentration of OH^* ($\text{mol} \cdot \text{cm}^{-3}$).*

2.9.2 Extracted flame properties

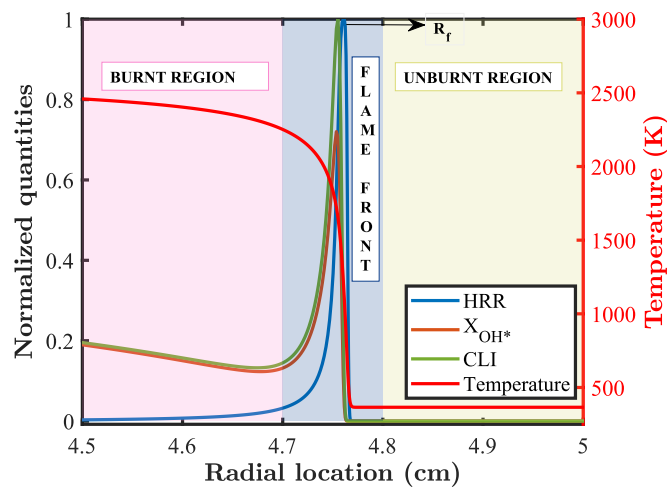


Figure 2.19: Spatial distribution of profiles for H_2 - air at $\phi = 1.0$, $P_i = 1.0$ bar, and $T_i = 295$ K.

The numerical database includes the dynamic evolution of OH^* and other species along with essential flame parameters. Fig. 2.19 describes the normalized profiles of heat release

rate, OH* mole fractions and CLI across different regions of the flame. The fresh gases are denoted in the yellow shaded area, while the flame front is in blue, and the burnt gases further downstream are in pink.

The radius was measured at the flame front, corresponding to the maximum heat-release rate. The OH* mole fraction and CLI at the flame front were also calculated at the flame radius, since describing them at their maximum would not be ideal, as the maximum shifts from the flame front to the burnt region with increasing P and T . While the distributions in the burnt gas region was averaged away from the flame to the core of the flame up to 1 cm to avoid the ignition affected region. The intensity ratio was calculated as the ratio of the CLI at the flame front to that in the burnt gas.

2.10 Results and discussion

This section examines the effects of equivalence ratio, initial pressure, and initial temperature on OH* chemiluminescence and overall behaviour. Each parameter is examined to elucidate its specific role and its combined effects on flame dynamics. Experimental profiles will be compared with the numerical simulations.

Fig. 2.20 displays the line profiles of the flame at the same radial and temporal positions as depicted earlier in Fig. 2.8 for a mixture at $\phi = 1.2$, $P_i = 0.5$ bar, and $T_i = 295$ K. The experimental results are contrasted with numerically simulated intensities using both the OH* sub-mechanisms of Kathrotia and JIHT and are presented in Fig. 2.20. The arrow indicates an increase in the evolving pressure and in the temperature of the unburnt gas due to isentropic compression.

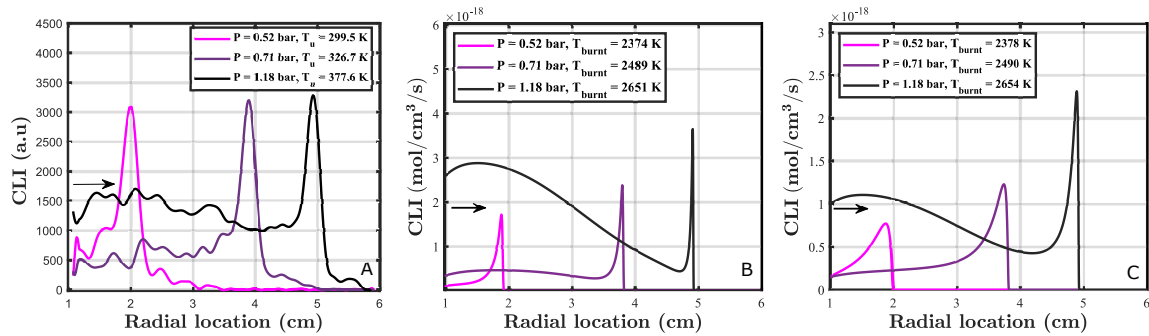


Figure 2.20: Line intensity profiles at $\phi = 1.2$, $P_i = 0.5$ bar, $T_i = 295$ K. A - Experiments, B - Numerical: Kathrotia, C - Numerical: JIHT

At lower pressures and temperatures, the OH* chemiluminescence is predominantly higher at the flame front compared to the post combustion gases in both experiments and simulations. As pressure and temperature increase, a growing contribution to OH* chemiluminescence from the burnt gas region is observed in both experiments and simulations. Line intensity profiles reveal significant OH* emission in the burnt gas region, demonstrating that chemiluminescence persists well beyond the primary reaction zone. Further investigation of how the burnt gas OH* contribution varies with equivalence ratio,

pressure, and temperature is presented in the subsequent sections.

2.10.1 Effects of equivalence ratio

OH* chemiluminescence profiles across varying equivalence ratios were evaluated in the burnt gas zone, and their intensity ratios were subsequently quantified. To elucidate the predictive capability of the Kathrotia and JIHT sub-mechanisms, their performance relative to experimental OH* chemiluminescence profiles is assessed. In the burnt zone, the intensities of each mixture were normalized by its maximum intensity and are represented in the left column, while the intensity ratios are presented in the right column of Fig. 2.21.

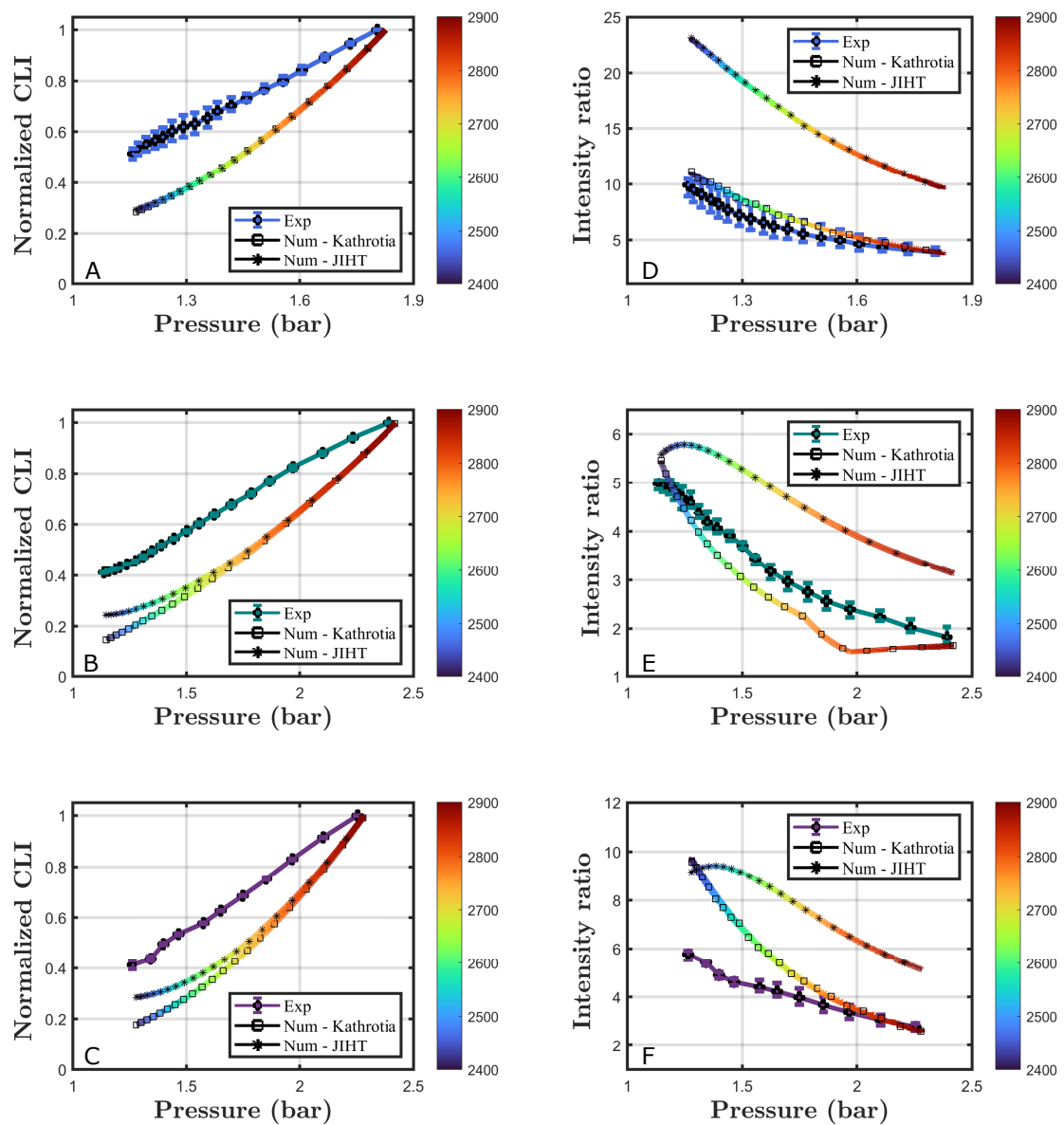


Figure 2.21: Normalized CLI in the burnt gas zone (left column) and intensity ratio (right column) as a function of pressure, the colour bar represents burnt gas temperatures from simulations at $P_i = 0.5$ bar and $T_i = 295$ K. A & D: $\phi = 0.8$, B & E: $\phi = 1.0$ and C & F: $\phi = 1.2$

The quantities are plotted as functions of pressure, with the colour bar indicating the corresponding burnt-gas temperatures, and the numerical results are also presented as functions of this temperature. The first row represents a lean mixture at $\phi = 0.8$, the middle row being a stoichiometric mixture, $\phi = 1.0$ and the last row representing the rich mixture at $\phi = 1.2$. All results are presented at an inlet pressure of 1 bar and an inlet temperature of 295 K.

The results show that the burnt gas intensities and intensity ratios are dependent on pressure and temperature. Among the mixtures, the lean case produces the weakest OH* emission in the burnt gas region, attributable to its comparatively lower post flame temperatures. In contrast, the stoichiometric mixture exhibits the strongest OH* chemiluminescence, driven by higher burnt gas temperatures that increase radical concentrations. Intensity variations are comparable for stoichiometric mixtures and rich mixtures, whereas the lean mixture demonstrates a slightly lower gain. This is mainly attributed to the elevated temperature gradient in the burnt gas of the former.

The intensity ratios between the flame front and the burnt gas region are higher for the lean case and lower for the stoichiometric and rich mixtures. This is primarily because the burnt gas contributes less to the OH* intensity in the lean mixture, resulting in a relatively higher intensity ratio between the flame front and the burnt gas. Interestingly, Kathrotia appears well matched to experiments on lean and stoichiometric mixtures. There are some discrepancies in rich mixtures, although they tend to converge in the final stages of propagation. The JIHT mechanism consistently overpredicts experimental OH* intensity ratios across all conditions. Therefore, Kathrotia was adopted as the primary sub-mechanism for further experimental comparisons.

2.10.2 Influence of pressure and temperature

During isentropic compression of the flame, both pressure and temperature change, resulting in dynamic interactions. To analyze the global evolution of OH* chemiluminescence, inlet pressures and temperatures were systematically varied. The effects of initial temperatures and pressures on OH* chemiluminescence were investigated for a rich mixture of equivalence ratio of 1.2 in the post combustion zone. Experimental results were compared with numerical simulations performed with Kathrotia.

The changes in chemiluminescence intensities across the burnt gas region as a function of unburnt gas temperature are shown in Fig. 2.22. At an initial pressure of 0.8 bar, the inlet temperature was increased from 303 K to 353 K. An increase of 10% in chemiluminescence intensity is observed when the inlet temperature rises by 50 K. Simulations reveal greater modifications in the OH* intensity than experiments for the same increase in unburnt gas temperature. However, as the inlet temperature increases, these differences are slightly reduced.

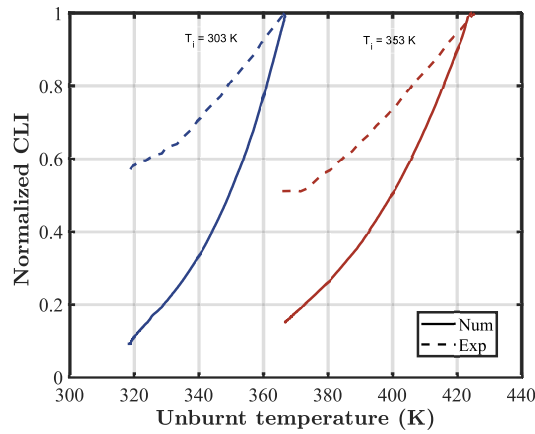


Figure 2.22: normalized intensities in the burnt gas region as a function of temperature at $\phi = 1.2$, $P_i = 0.8$ bar (Kathrotia).

The evolution of chemiluminescence intensities as a function of pressure is shown in Fig. 2.23. As the initial pressure increases while keeping the inlet temperature constant at 295 K, the chemiluminescence intensity in the post-combustion zone rises approximately linearly with pressure. At a subatmospheric pressure of 0.5 bar, this increase in intensity is more rapid compared to higher pressures. Interestingly, the differences between experimental and simulation results are less pronounced for pressure than for temperature variations, suggesting that temperature effects involve more complex interactions that are harder to capture accurately in models.

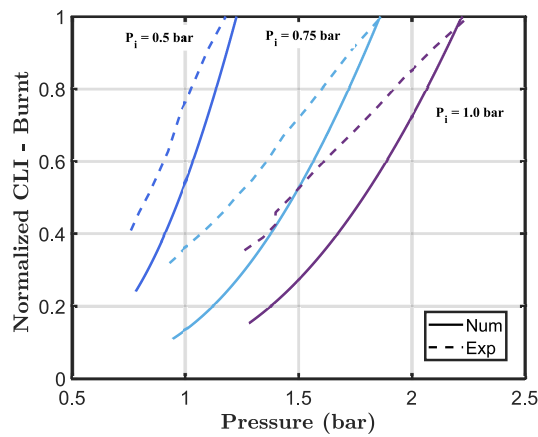


Figure 2.23: normalized intensities in the burnt gas region as a function of pressure at $\phi = 1.2$, $T_i = 295$ K (Kathrotia).

During the isentropic compression of the flame, both pressure and temperature change, creating a dynamic interaction between these factors. To analyze the global evolution of OH^* chemiluminescence, inlet pressures and temperatures were systematically varied, as detailed in the lookup table Tab. 2.1 under Case 5. Fig. 2.24 presents the evolution of CLI in the burnt gas zone, with intensity normalized and depicted on the colourbar,

reflecting variations with radius, pressure, and temperature. The three curves display parallel growth, indicating consistent trends across different pressure and temperature conditions. This suggests a strong correlation between pressure and temperature changes, influencing OH^* production during combustion. The pressure and temperature evolve in parallel, jointly contributing to the OH^* chemiluminescence, with both playing significant roles in the intensity growth.

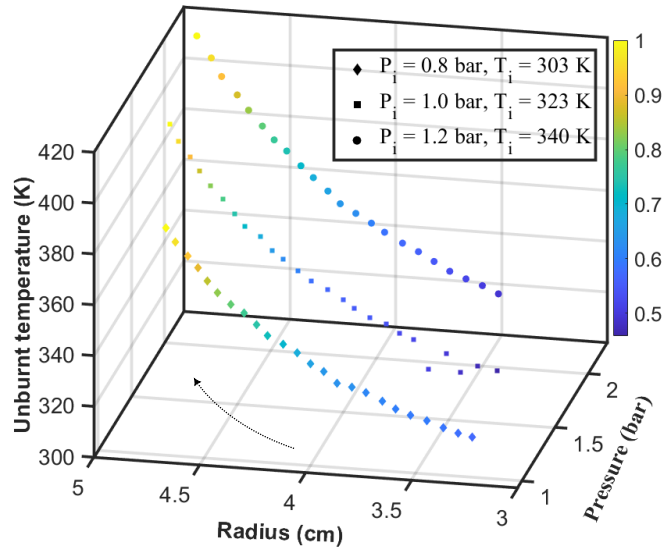


Figure 2.24: Intensity profiles in the burnt gas region (experimental), colour bar represents normalized CLI.

2.11 Isobaric and isochoric flame studies

This section aims to characterize the distribution of OH^* species in flames under isobaric and isochoric conditions. To examine species distributions, we conducted isobaric simulations under identical pressure and temperature conditions at various radial locations, extracted from the isochoric simulations as input parameters. Solid lines will denote the results for the isobaric configuration, while dashed lines will denote those for the isochoric configuration. The different radial locations considered for analysis were at 2.8, 4.8 and 5.5 cm and henceforth will be referred to as R_{f1} , R_{f2} and R_{f3} , respectively.

The left column of Fig. 2.25 presents the simulated mole fraction profiles across the domain. At the radial location of R_{f1} , there is a significantly higher OH^* mole fraction at the flame front in comparison to the burnt gas. As pressure and temperature increased, the flame front and burnt gas became equally distributed at R_{f2} . At a higher radial distance of R_{f3} , the OH^* mole fraction has surpassed the flame front and is higher in the burnt gas. It appears that the burnt gas is much more affected by increasing pressure and temperature than the flame front.

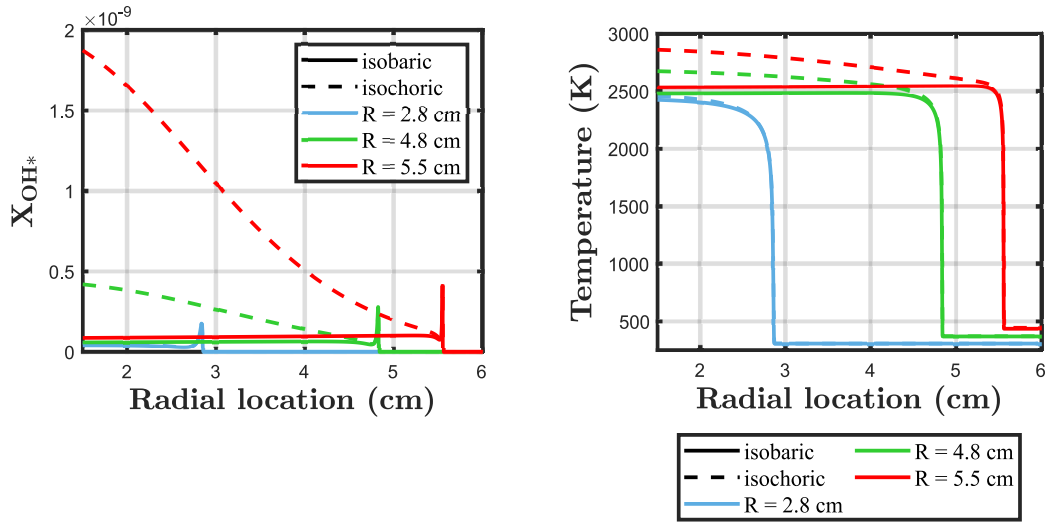


Figure 2.25: Radial profiles of OH* mole fractions and temperature from isobaric and isochoric simulations at $\phi = 1$ (Kathrotia).

The temperature profiles across the flame are represented in the right column of Fig. 2.25. Thermal equilibrium is attained in an isobaric flame, whereas an isochoric flame exhibits a temperature gradient, with temperature increasing as one moves towards the core of the flame. These local temperature profiles in the burnt gas zone support the formation of OH*. At lower radial positions of R_{fl} , temperatures are around 2450 K, which is below the threshold for thermal decomposition [51]. As a result, a flat profile of OH* is observed in the burnt gas zone. As the temperature increases, the thermal excitation pathway for OH* becomes more favourable, enhancing its formation. This temperature-sensitive behaviour explains the radial trends observed in the OH* distribution across the flame.

Given the extensive current research on oxy-combustion systems, we extended our study to these conditions to illustrate the effects of elevated temperatures on the behaviour of OH* chemiluminescence. A set of steady-state simulations was performed by changing the oxidizer ratio. Fig. 2.26 shows the mole fraction and temperature profiles at an oxygen percentage of 21% treated as base case, and further increased to 25% and 30%, and the nitrogen content was adjusted accordingly. It is observed that, initially, the temperatures are below the thermal excitation temperatures of OH*, and hence no substantial amount is observed in the burnt gas. However, as the oxygen level increases slightly to 25%, a high level of OH* is observed in the burnt zone. Further increasing the oxygen content to 30% results in a substantially higher concentration of OH* in the burnt gas than at the flame front. Hence, temperature plays a key role in the distribution profiles of OH*. Similar observations were also reported in the literature by De Leo et al. [20] for the oxycombustion of methane. Therefore, it is vital to consider the implications of using OH* as a flame marker in such scenarios.

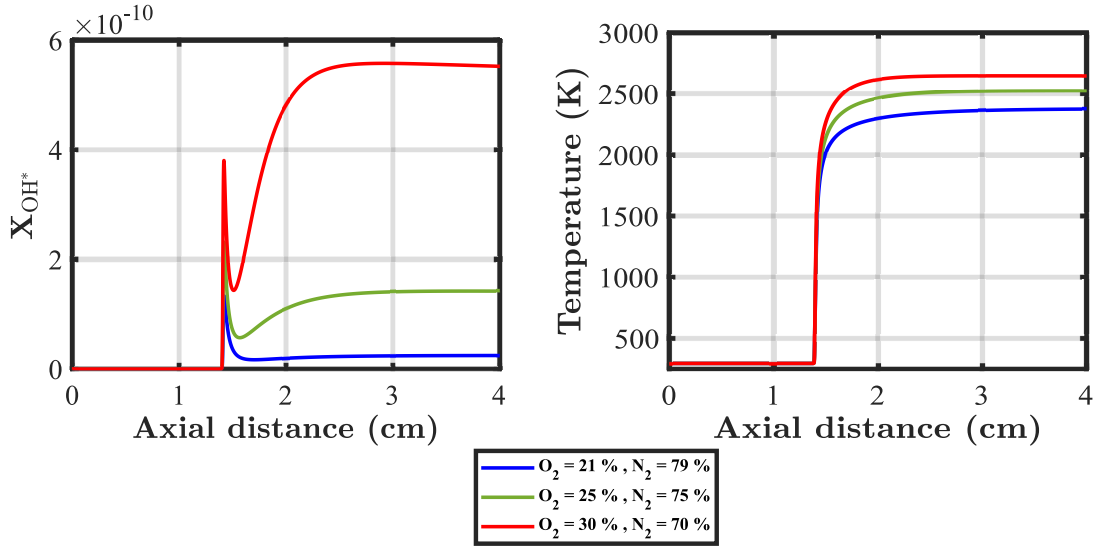


Figure 2.26: Spatial profiles OH^* mole fraction (left) and temperature (right) of OH^* from steady-state simulations at $\phi = 1$ (Kathrotia) for varying oxygen percentages.

2.12 Contributions

To gain deeper insights into the spatial distribution and formation mechanisms of OH^* radicals within the flame, a production-rate analysis was conducted. Contributions from the diffusion and production terms in the species transport equation can be obtained separately from simulations, enabling a quantitative assessment of their influence on OH^* formation across flame zones. The species conservation equation is taken from the study of Mass et al. [38], and is denoted as

$$\frac{\partial w_i}{\partial t} + \frac{\partial}{\partial \psi} (\rho r^\alpha w_i V_i) - \frac{\dot{\omega}_i M_i}{\rho} = 0, \quad (2.25)$$

Here, the first term represents accumulation, the second being transport accounting for both advection and diffusion terms, and the last is the chemical source term due to reactions, where w_i is the mass fraction of species i , ψ is Lagrangian coordinate, r is the radial location, ρ is the density, $\dot{\omega}_i$ is the net rate of production of species i , M_i being the molar mass of species i and V_i is the diffusion velocity of species i . Contributions from different terms are individually evaluated at the flame front and in the burnt gas.

Fig. 2.27 illustrates the rate of production terms and diffusion terms at various radial locations for $\phi = 1.0$. At the flame front, production and diffusion contribute equally to the OH^* mole fraction. Both isobaric and isochoric configurations display similar profiles. In the burnt gas, production terms govern the evolution of species mole fractions, often exceeding diffusion terms by 2 orders of magnitude. It's observed that R_{f2} and R_{f3} isobaric flames show a flat profile, while the isochoric flames show a characteristic curve close to the mole fraction curve seen earlier.

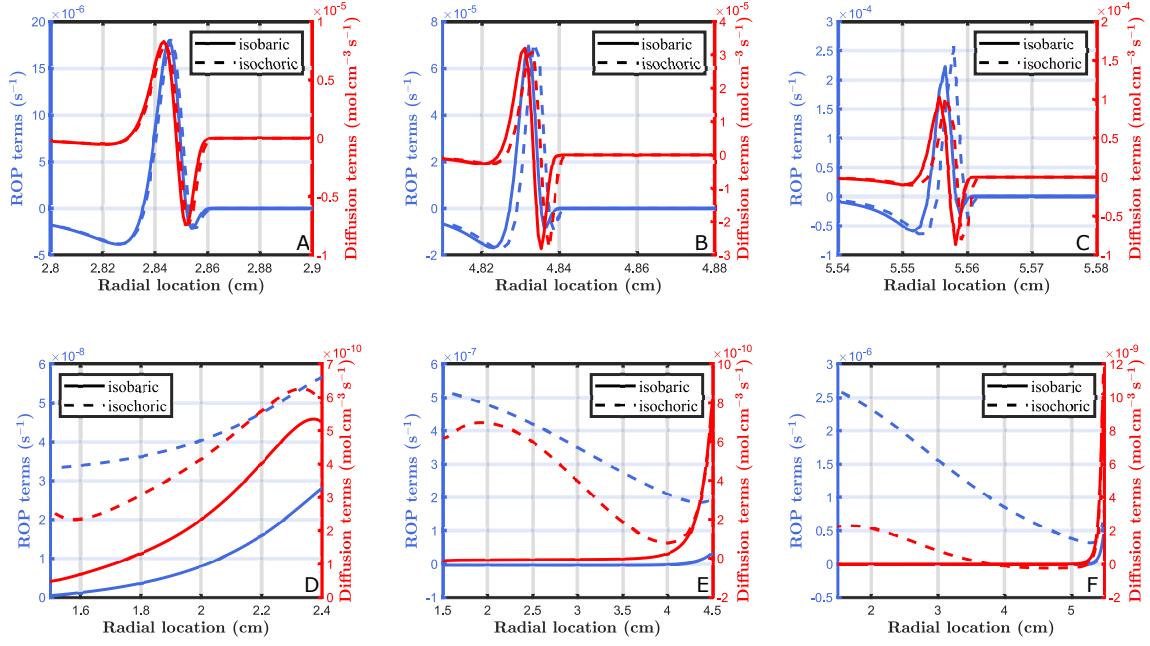


Figure 2.27: Contributions of different terms at flame front (top) and burnt gas (bottom) at $\phi = 1$. A & D: Radial location of 2.8 cm. B & E: Radial location of 4.8 cm. C & F: Radial location of 5.5 cm (Kathrotia).

2.13 Analyses of OH* formations

2.13.1 Thermal excitation

As seen in the previous section, thermal excitation is of significance when interpreting OH* in the burnt zone. A detailed description of thermal and chemical excitation is provided here. Literature reports OH* is mainly formed by chemical excitation of reaction $\text{H} + \text{O} + \text{M} \rightleftharpoons \text{OH}^* + \text{M}$ and above 2800 K this reaction proceeds in the backward direction [52, 53]. At high temperatures, it was also observed that the quenching reaction $\text{OH}^* + \text{M} \rightleftharpoons \text{OH} + \text{M}$ reverses and becomes a significant pathway for OH* formation [28]. Thus, at high temperatures, thermal excitation is one of the main pathways of OH* formation [54, 48, 50]. To illustrate thermal and chemical excitation due to variations in temperature and pressure, the maximum CLI obtained from the Kathrotia simulations is shown for varying equivalence ratios in Fig. 2.28. The CLI location is chosen as the peak CLI within the entire flame domain. Initially, the peak is located at the flame front, and excitation is primarily chemical. With increasing pressure and temperature, thermal excitation dominates, and the peak location shifts to the burnt gas zone, as described earlier. The dashed lines at approximately 2500 K indicate the crossover temperature at which thermal excitation begins.

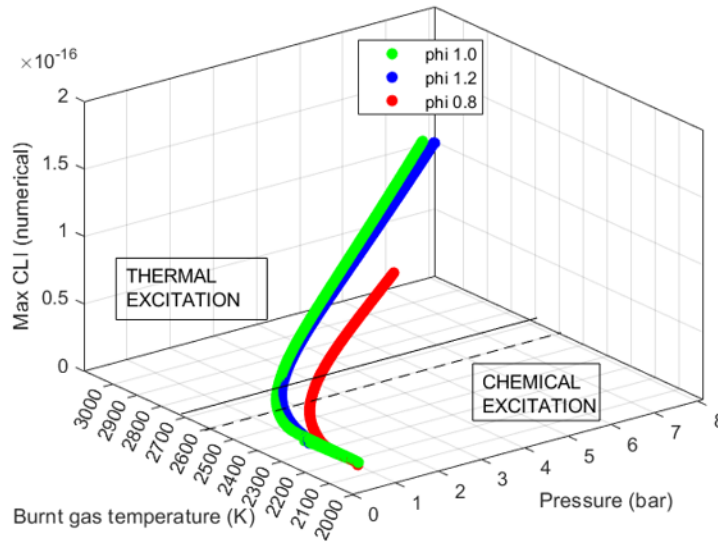


Figure 2.28: Maximum CLI evolution as a function of burnt gas temperature and pressure at varied ϕ from Kathrotia

The crossover temperatures vary depending on the mechanism. A summary of such temperatures, taken from the thesis of Fiala [51], is provided in the Tab. 2.4 below.

Base mechanism	OH* mechanism	Crossover temperature (K)
Ó Conaire et al. [55]	Kathrotia et al. [28]	2725
Ó Conaire et al. [55]	Kaskan [56]	2850
Ó Conaire et al. [55]	Hidaka et al. [52]	2600
Ó Conaire et al. [55]	Koike and Morinaga [53]	2475
Ó Conaire et al. [55]	Dandy and Vosen [57]	Thermal always dominate
Ó Conaire et al. [55]	Smith et al. [58]	2650
Ó Conaire et al. [55]	Hall and Petersen [59]	2900
Jachimowski [60]	Kathrotia et al. [28]	2725
GRI-Mech 3.0 (subset) [61]	Kathrotia et al. [28]	2725
Konnov [62]	Kathrotia et al. [28]	2725

Table 2.4: Crossover temperatures between OH* formation mechanisms from various base mechanisms.

2.13.2 Rate of production analyses

A rate-of-production analysis was conducted to evaluate the key reactions responsible for the production of OH* in both the flame front and the burnt gas region. An assessment of reactions responsible for OH* production was performed using both the Kathrotia and JIHT mechanisms. This revealed mechanism-specific differences in dominant pathways, as well as distinct reaction contributions between the flame front and the burnt gases.

ROP of Kathrotia for isobaric and isochoric simulations at identical P and T at different

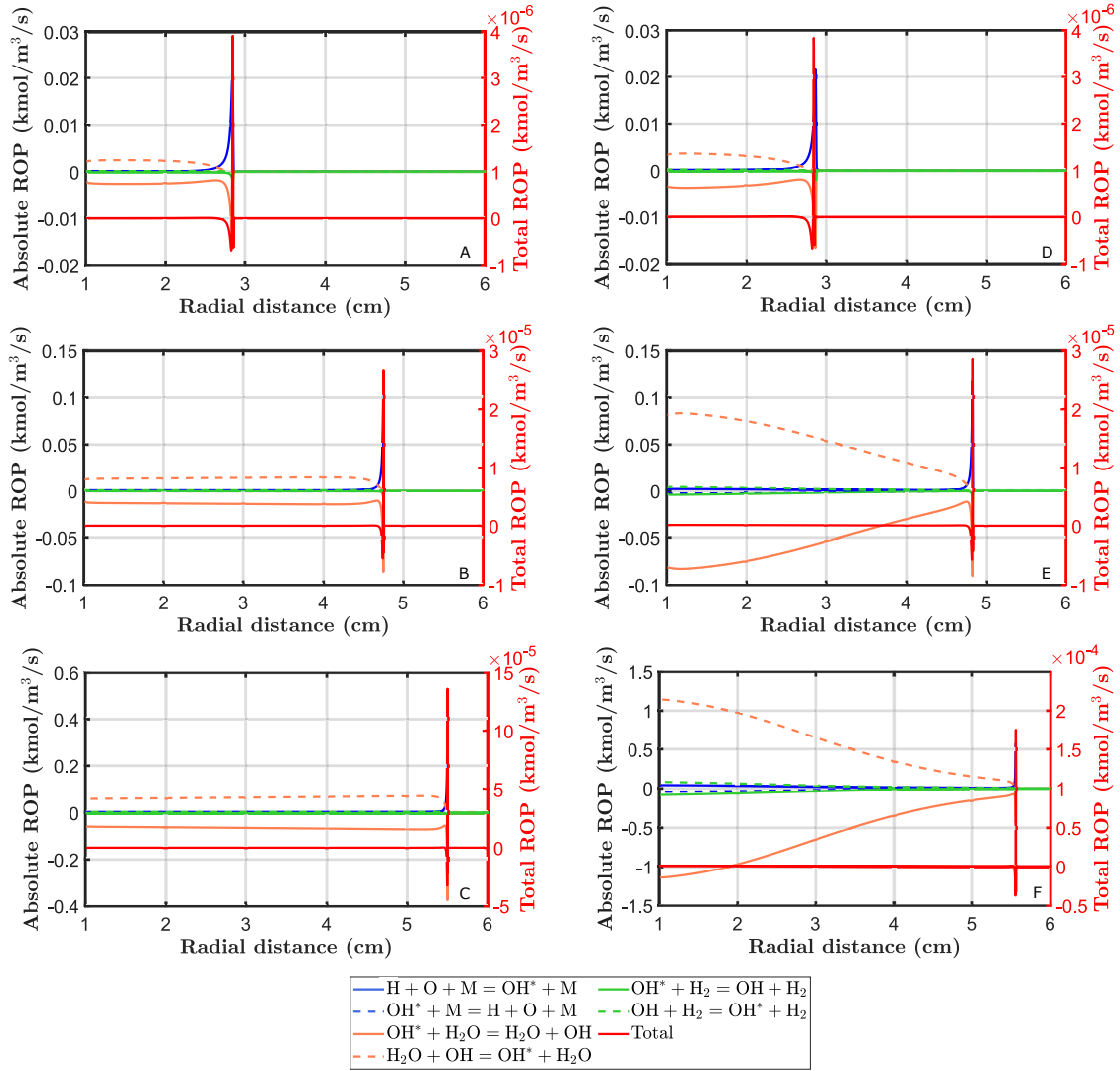


Figure 2.29: ROP analyses from Kathrotia for isobaric (left) and isochoric (right) configurations at $\phi = 1$. A & D: Radial location of 2.8 cm (R_{f1}), B & E: Radial location of 4.8 cm (R_{f2}), C & F: Radial location of 5.5 cm (R_{f3})

flame intervals of 2.8 (R_{f1}), 4.8 (R_{f2}) and 5.5 (R_{f3}) cm are shown below in Fig. 2.29. The left column presents results for isobaric conditions, whereas the right column presents results for isochoric conditions. At any given radial location, the total production rate across both configurations is nearly the same. The production rate at the flame front increases as the flame expands, owing to increases in P and T.

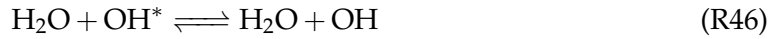
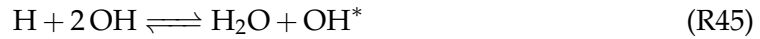
From the simulations of Kathrotia, the key reactions responsible for the formation of OH* are :



At the flame front, OH* is predominantly formed via chemical excitation through three-body collisions in R41 and a small contribution from R43.

The absolute production rate for different reactions is similar at radii R_{f_1} and R_{f_2} under isobaric and isochoric conditions. When moving to radius R_{f_3} , the increase is much greater in the isochoric case than in the isobaric case. At any given radial location, there is no production in the burnt gas zone under isobaric conditions. While in the isochoric configuration, thermal excitation through the reverse of (R42) results in the OH* formation.

The ROP for JIHT is shown in the Fig. 2.30. Left column denotes results of isobaric and right isochoric. In the JIHT mechanism, the production pathways differ from those in Kathrotia. In the flame front, it is mainly formed via R45 in both the isobaric and isochoric configurations. In the burnt gas, no OH* is produced for the isobaric case, whereas at radii R_{f_2} and R_{f_3} , as in Kathrotia, the reverse reaction R46 produces OH* with equal contributions from forward R45. It is to be noted that ROP of R44 is vastly lower in comparison with the other two.



The reactions governing OH* formation at the flame front differ based on sub-mechanism employed. It is to be noted that, as previously discussed in Chapter 1, the OH* is mainly formed by three-body collision reactions through R41, while R45 was used in early studies, it was further discarded and not very widely accepted. Sharipov et al. [32] proposed a bivariate pressure and temperature dependent reaction R44, while this contributes negligibly to the formation of OH* in comparison with others. Thermal excitation was found to be the primary path in the burnt gas, irrespective of the mechanism. Based on these mechanistic differences in OH* formation, these differences in OH* prediction at the flame front could significantly contribute to the intensity ratio interpretation we observed previously in Fig. 2.21. Hence, we have considered the well-validated sub-mechanism of Kathrotia et al. [28].

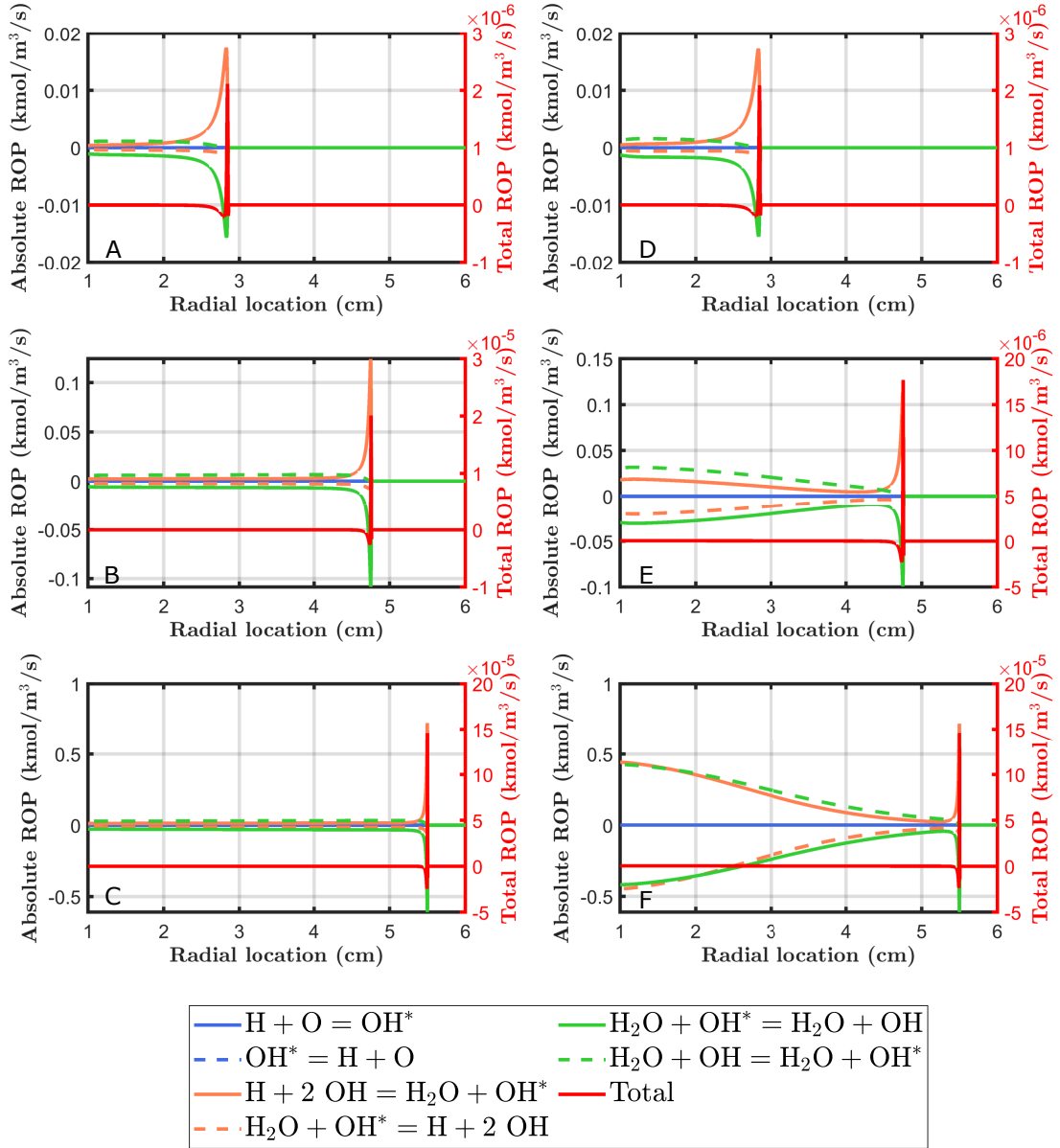


Figure 2.30: ROP analyses from JIHT for isobaric (left) and isochoric (right) configurations at $\phi = 1$. A & D: Radial location of 2.8 cm (R_{f1}), B & E: Radial location of 4.8 cm (R_{f2}), C & F: Radial location of 5.5 cm (R_{f3})

2.13.3 Sensitivity analyses

A sensitivity analysis was conducted in steady-state configuration using Kathrotia sub-mechanism to evaluate the effects of pressure and temperature on OH* in a stoichiometric mixture. The sensitivity coefficients were computed at the flame and burnt-gas zones, at the peak HRR and maximum temperature, respectively. The sensitivity coefficients as a function of temperature are shown in Fig. 2.31. Across the flame front, the most positively sensitive reaction is R47, which increases in inlet temperature. The other sensitive reaction is R48, which has a negative coefficient at 300 K but becomes positive at higher temperatures. The most negative coefficient is of R49. In the burnt gas, R50 is the sensitive (+ve) reaction at 300 K, while R51 is for higher temperatures. Fig. 2.32 displays sensitivity coefficients as a function of pressure; The most sensitive (+ve) reaction across the flame front is R47 and increases with the pressure, and is followed by R51. While the negative coefficient is the same as R49. In the burnt gas, the sensitive reaction is R50 and is important at 1 atm.

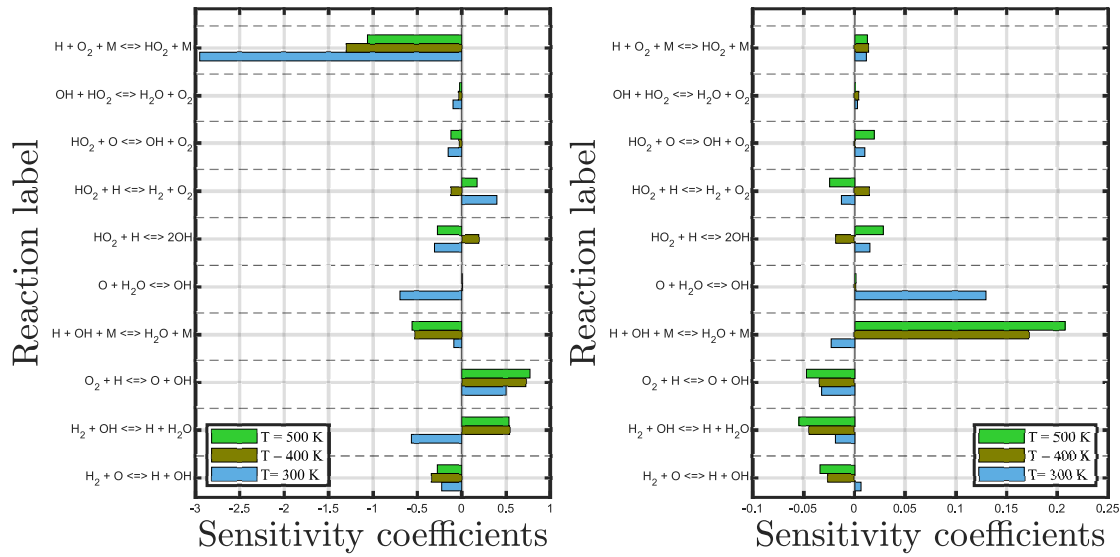


Figure 2.31: Sensitivity analyses from Kathrotia for steady state simulations as a function of temperature at $\phi = 1$.



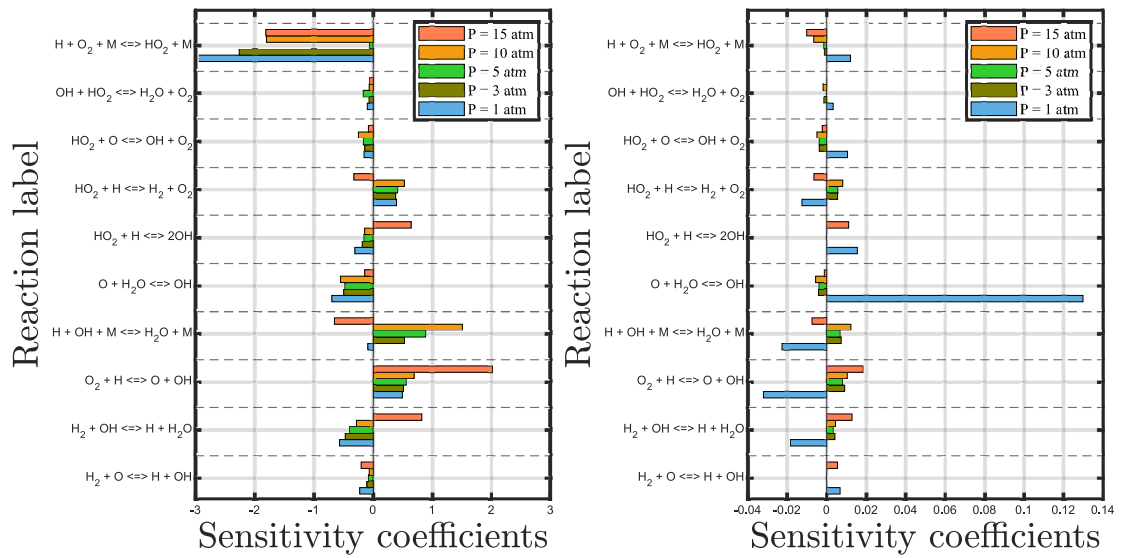


Figure 2.32: Sensitivity analyses from Kathrotia for steady state simulations as a function of pressure at $\phi = 1$.

2.14 Correlation of equivalence ratio, pressure and temperature

To assess the evolution of OH^* and its sensitivity to equivalence ratio, pressure, and temperature, steady-state planar simulations were performed using FlameMaster. The simulations were performed using both the Katorthia and JIHT mechanisms, for equivalence ratios ranging from 0.6 to 3, pressures of 1, 5, 10 and 20 bar, and temperatures of 300, 500 and 700 K. A total of 1,000 grid points were used, and a mixture-averaged transport model and thermodiffusion were considered in the simulations.

From each simulation, the intensities across the flame front and the burnt gas region are computed at the radial location and maximum temperature, respectively. The results in Fig. 2.33 illustrate the variation of CLI across equivalence ratio and pressure, with each column representing a unique temperature. The intensities at the flame front are represented in the top row, while the post combustion zone is described in the bottom row.

The intensity of chemiluminescence follows a non-monotonic bell-shaped curve as the equivalence ratio varies in both regions. As the mixture moves from lean to rich, the intensity increases and peaks at around $\phi = 1.1$. Beyond this point, in richer mixtures, the intensity diminishes, likely due to limited oxygen availability. The variation window of the equivalence ratio is broader at the flame front than in the burnt gas region. At super-rich mixtures beyond $\phi = 2$, the burnt gas intensities are negligible. As described by Wangher et al. [63], the intensity of OH^* increases with temperature and pressure, thereby increasing the reaction rate and the concentration of OH^* . At the flame front, intensity shows an increasing effect of pressure for Katorthia. In the case of JIHT, although CLI increases

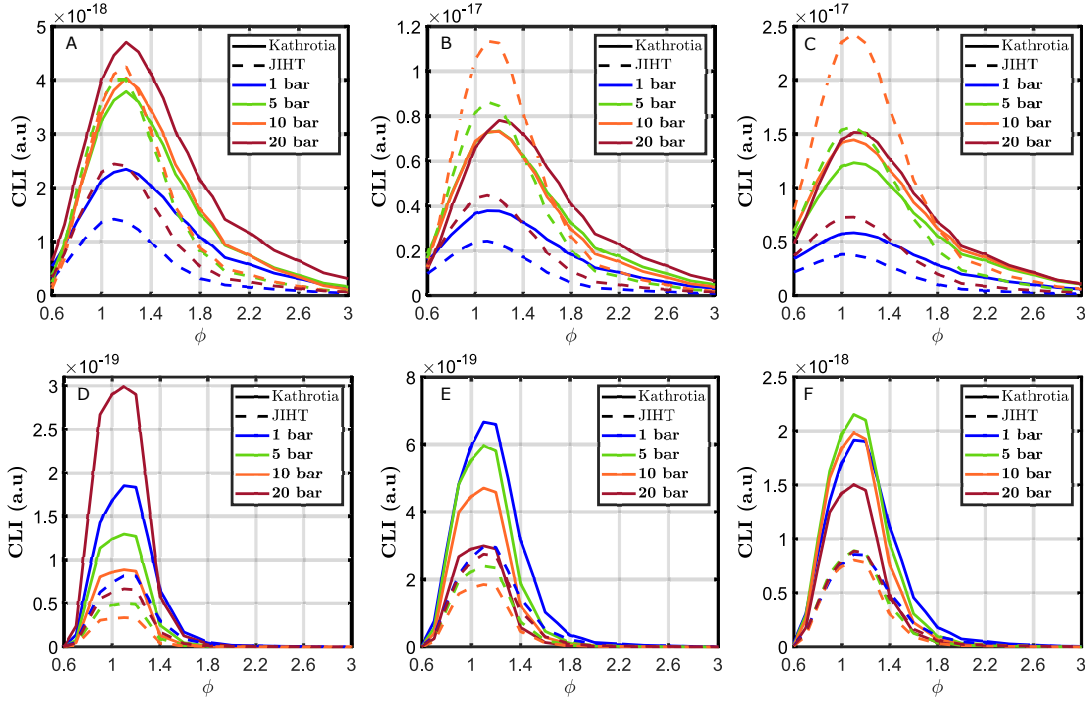


Figure 2.33: CLI as function of ϕ , pressure and temperature, top (flame front) and bottom (burnt gas). A, D : $T_i = 300$ K, B, E : $T_i = 500$ K and C, F : $T_i = 700$ K, steady-state simulations

with pressure at 20 bar, it decreases. The differences in chemiluminescence intensities between mechanisms are likely due to variations in the rate constants of key reactions within those mechanisms. In the burnt gas zone, irrespective of the mechanism, pressure is generally found to have an adverse effect. Quenching increases with pressure, thereby affecting the overall computation of chemiluminescence intensity. Similar observations as a function of pressure are also reported in the study by Li et al. [64], which reported a reduction in intensity due to competition between radiative and non-radiative deexcitation. Temperature shows a strong positive correlation with OH^* intensity. As the unburnt gas temperature increases, both in the flame front and burnt gas regions exhibit a nearly linear increase in OH^* emission, reflecting the enhanced reactivity and radical formation at elevated thermal conditions.

2.15 Predictive models for equivalence ratio, pressure and temperature dependencies

To further establish relationships between equivalence ratios, pressures, and temperatures, a comprehensive set of 650 simulations was performed using the Kathrotia sub-mechanism, spanning a wide range of combustion conditions: pressures from 0.5 to 20 bar, temperatures from 300 to 700 K, and equivalence ratios from 0.6 to 3. The Fig. 2.34 displays chemiluminescence across the flame front and the burnt gas zone.

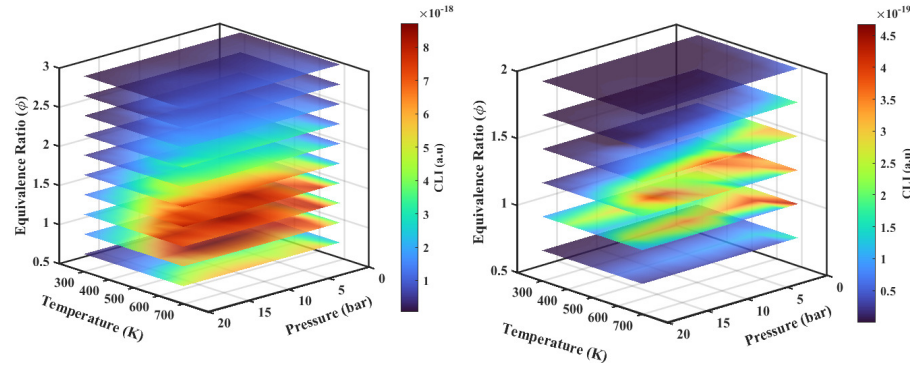


Figure 2.34: CLI as a function of ϕ , pressure and temperature - flame front (left) and burnt gas (right) - (Kathrotia).

To develop a comprehensive framework for analyzing and predicting chemiluminescence characteristics across a wide range of combustion conditions, a nonlinear curve fitting was performed in MATLAB using the least absolute residuals (LAR) criterion with the trust-region-reflective algorithm. The relationship between the equivalence ratio (ϕ), pressure (P), unburnt gas temperature (T), and the resulting chemiluminescence intensity (CLI) is captured by a predictive model, and the fitting equation is given as

$$CLI = a \cdot P^b \exp \left[-c \cdot \frac{(\phi - \phi_{peak})^2}{T} \right] \quad (2.26)$$

where: CLI = chemiluminescence intensity, P = pressure, ϕ = equivalence ratios, $\phi_{peak} = 1.1$, T = temperature, a,b,c = fitting parameters

Prior to training, CLI values were normalized with respect to a reference condition ($\phi = 1.1$, P = 1 bar, and T = 300 K) to enable comparisons across different datasets. The Tab. 2.15 summarizes the fitted parameters.

Temperature	Zone	a	b	c	R ²
300	Flame front	0.893	0.0913	399.3	0.978
300	Burnt gas	0.548	-0.5172	5101.1	0.982
500	Flame front	1.455	0.2609	602.7	0.982
500	Burnt gas	2.176	-0.1811	7790	0.985
700	Flame front	2.374	0.3298	958.1	0.993
700	Burnt gas	7.016	0.0232	9580	0.989

Table 2.5: Fitting parameters for CLI across the flame front and the burnt gas zones.

2.16 Heat release rate versus Chemiluminescence

OH* chemiluminescence plays a vital role in combustion research, serving as a key indicator in premixed hydrocarbon flames for assessing local equivalence ratios and heat release rates [65, 66, 67]. Several studies in literature have indicated that local

chemiluminescence can be a reliable indicator of local heat-release rate [68],[69]. We analyze the local OH* chemiluminescence relative to the local heat-release rate to evaluate its suitability for flame marking. Chemiluminescence, heat release rate, and temperature profiles are extracted at the flame radius. Fig. 2.35 denotes the spatial distribution of HRR and CLI for a H₂ - air mixture at $\phi = 1$, $P_i = 1$ bar and, $T_i = 295$ K. It is observed that the CLI peaks downstream of the maximum of HRR. Similar observations were also made by Schiavone et al. [27].

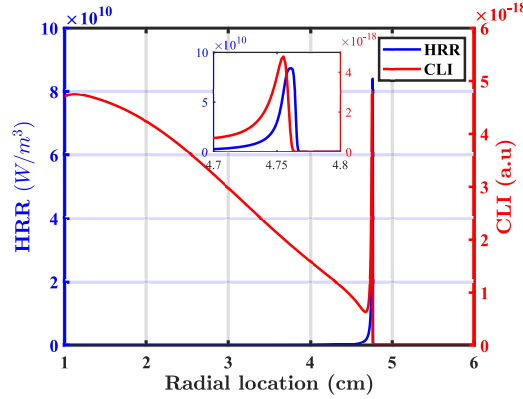


Figure 2.35: Spatial distributions of HRR and CLI for $\phi = 1$, $P_i = 1$ bar and, $T_i = 295$ K.

The evolution of the heat-release rate and the CLI for different ϕ values is presented here. The normalized HRR and CLI as a function of radial location are shown in Fig. 2.36 A and B. The HRR increases exponentially with P and T , whereas the CLI increases rapidly with P and T . To understand the correlation between the heat release rate and the OH* chemiluminescence, the normalized profiles of maximum heat release rate and peak chemiluminescence at the flame front are shown in Fig. 2.36 C.

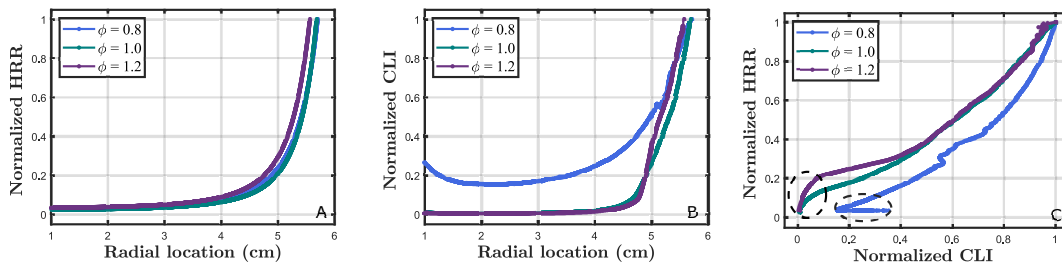


Figure 2.36: A: Normalized HRR versus radial location, B: Normalized CLI versus radial location, C: Normalized HRR versus normalized CLI for H₂ - air mixtures at $P_i = 1$ bar and $T_i = 295$ K.

The ellipses indicate the stretched region. In these stretched zones, the changes in heat-release rate profiles are minimal, and chemiluminescence profiles are negligible relative to the overall evolution. Lean mixtures exhibit an initial temperature drop during flame propagation, which accounts for the observed deviation. Further flame

expansion yields rapid increases in pressure and temperature, boosting both heat release and chemiluminescence. In highly stretched regions, chemiluminescence consistently occurs below the onset of heat release and reverses as pressure and temperature increase, whereas it responds more strongly to these changes. No strong correlation exists between chemiluminescence and heat release rate across the flame.

While the OH^* marker is limited by poor correlation at the flame front itself, burnt gas regions contribute substantially to OH^* intensity, particularly in stoichiometric and rich mixtures, making it less reliable for tracing heat release. Alternative or supplementary markers may be required for accurate diagnosis.

2.17 Conclusions

This study provides a comprehensive analysis of OH^* chemiluminescence for a spherically expanding hydrogen–air flame in a constant-volume chamber, combining experimental data with numerical modelling and analysis of emission features.

- OH^* emission is observed in the burnt gas region, revealing persistent radical activity beyond the flame-front, highlighting unique post-flame chemistry characteristic to hydrogen flames. This prompts us to reconsider its use as a flame indicator across certain thermodynamic conditions, mixture variations, and blend modifications.
- Unlike steady state planar flames, transient flames account for temperature and species history, highlighting the role of temperature in OH^* chemiluminescence within the post-combustion zone.
- The predictive capabilities of the sub-mechanisms show limited accuracy in the burnt gas region compared to experimental data, although Kathrotia's sub-mechanism provides improved agreement for the intensity ratio.
- Different mechanisms govern OH^* formations in specific regions of the flame. Mass diffusion and chemical production both contribute to the OH^* mole fractions near the flame front, whereas chemical production predominates in the burnt-gas zone.
- OH^* intensities are found to be strongly dependent on equivalence ratio, pressure, and temperature. Intensities increase with the pressure and temperature for all mixtures across both the flame front and the burnt-gas zone, with a larger relative increase in the post-flame burnt gases.
- Poor correlation is observed between the heat release rate and the chemiluminescence at the flame front, highlighting the challenges of using OH^* as a flame marker.

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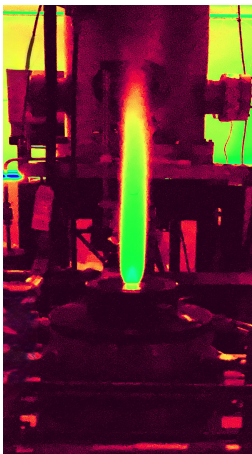
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3 Conical flames: A detailed spatial and spectral characterization of excited species



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This work aims to investigate the flame structure and elucidate the transport effects on radical distribution in a canonical premixed H_2 - air flame across a range of equivalence ratios from $\phi = 0.6$ to 1.4. High-resolution optical emission spectroscopy combined with two-dimensional chemiluminescence imaging was used to investigate the spectral and spatial characteristics of the radicals. Mapping species across the flame front provides information about the chemistry and reaction dynamics within the reaction zone. OH mole fractions and H_2O temperatures were determined quantitatively through spectroscopic modelling. Spatial and spectral variations in the blue emission from hydrogen flames were characterized across the flame domain. Analysis of the exhaust gases revealed the presence of CO. Collectively, this study provides insights into the spatial distribution of reactive species, flame structure, and emissions characteristics, offering a deeper understanding of hydrogen flame chemistry.

3.1 Introduction to Bunsen burners

The Bunsen burner has been the workhorse of various labs across the world to study the combustion characteristics (ignition delay time, speciation data, flame propagation, and heat release rate) of various fuels from H_2 to Al-based fuel mixtures due to their versatility, relatively lower cost, and ease of use. It is one of the oldest examples of stabilized premixed flames [1]. These properties are indispensable for gaining insight into combustion processes. A flame is a region of self-sustaining heat release from chemical reactions that emits thermal and visible radiation. As described previously, the laminar burning velocity (LBV) is defined as the relative velocity, normal to the flame front, with which the unburnt gas moves into the flame front [2]. In the case of a planar flame, there is no ambiguity in determining the laminar burning velocity, whereas we do not have the exact experimental counterpart [2]. Hence, the definition of the flame front location is essential for practical applications and is even more crucial for thicker flames, leading to greater discretion in the selection of experimental diagnostics. The literature recommends the inner region of the luminous zone for calculating the burning velocity. Hence, it requires specialized diagnostics, as opposed to broadband emission, which shows the high-temperature region and is present downstream of the region of interest. Rallis and Garforth [2] recommend diagnostics such as Schlieren and particle-tracking methods because these methods can capture the inner layer. Chemiluminescence has been utilized to capture combustion dynamics since at least the late 1990s [3] and the early 2000s [4, 5]. It helps in mitigating the acquisition of the inner layer (reaction zone) rather than the burnt-gas region. As for the computation of the LBV, special care needs to be taken due to the flame stretch and diffusion branch [6]. The former can be approximated via the

following methods, since the flame front is stabilized at a fixed location, such that the laminar burning velocity can be obtained from the product of the inlet velocity and the sine of the cone angle, or rather from the average burning velocity over the flame front. It is essential to note that these relations overlook the impact of flame stretch on the local burning velocity. This assumption is valid when the flame thickness is significantly lower than the spatial length scale, i.e., $\frac{d}{L} \ll 1$, where d is the flame thickness and L is the spatial length scale can be the flame curvature or flame height. For a detailed evaluation of the LBV, we need to account for the flame curvature-induced stretch. The observations from two significant works are presented below. The experimental study of Echehki and Mungal [7] was pivotal in the identification of the hydrodynamic and curvature-induced stretch in a Bunsen burner for a fuel mixture with minimal preferential diffusion Lewis number ≈ 1 . They highlighted the role of streamline expansion across the flame front and the special care taken in experimental acquisition for relatively thicker flames. Later, Choi and Puri [6] extended the analysis of the premixed Bunsen burner in a slot and cylindrical configuration. They utilized particle image velocimetry for the velocity field, C_2^* for chemiluminescence to identify the reaction zone, and holographic interferometry for the temperature distribution. They highlighted the changes in the local stretched burning velocity from 15-40 cm/s to around 70 cm/s. In addition to the flame tip opening effects observed in Bunsen flames, the local burning velocities were magnified by at least 48%, whereas the local burning velocities near the planar region of the Bunsen flame lie in the region of the laminar burning velocity. They concluded their work after noting ambiguity in the data when local laminar burning velocities were included. Hence, the conventional extrapolation equation cannot be utilized, and a modified equation has to be used, since the former resulted in a negative LBV.

3.2 Literature review

Higgins et al., [5] studied OH^* chemiluminescence of CH_4 -air flames for ϕ 0.66 to 0.86 and pressures ranging between 0.5 and 2.5 MPa. The primary objective was to develop a qualitative or quantitative diagnostic tool as a function of pressure, equivalence ratio, and mass flow rate. They noted that an increase in mass flow rate results in a proportional increase in OH^* . For a fixed ϕ , OH^* intensity decreases with pressure, and for a fixed pressure, the OH^* intensity increases with equivalence ratio. It is crucial to note that the authors have investigated only the lean part of the flames. They observed very good agreement between scaled experimental intensities against the scaled logarithm relation. As for the numerical simulations, they utilized Chemkin-III with GRI 2.11 base mechanism and the OH^* sub-mechanism of Dandy and Vosen [8]. They observed qualitative agreement between experimental and numerical data. Yet, the numerical data were severely over-predicted against the experimental measurements.

Docquier et al., [9] studied OH^* , CH^* , and C_2^* for CH_4 -air flames from 1 atm to 10 atm

(although analysis was limited to 3 atm due to Reynolds number) for $\phi = 0.6$ to 1.1 in a Bunsen burner configuration in addition to the numerical simulations in a PREMIX configuration using detailed chemical kinetics. The aim was to contribute to the description of combustion dynamics for active control of thermo-acoustic instabilities. They observed very good agreement between spatially resolved and spectral measurements. They observed that OH^* was a better flame marker for lean CH_4 flames, and as the equivalence ratio increased, the CH^* and C_2^* were better candidates as flame markers. In the experiments, they observed a non-monotonic response for OH^* with respect to pressure and ϕ . As for the CH^* , the pressure dependency was minimal and increased monotonically with the equivalence ratio. Overall, the agreement between the experiments and simulations was good, but there were still qualitative disagreements, and attributed to the chemical kinetics, specifically in the rich flame region. Due to the non-linear response of the signals, they recommended using the chemiluminescence of two signals to examine the combustion process for a wide range of pressures and equivalence ratios.

Rocha et al., [10] investigated $\text{NH}_3\text{-CH}_4/\text{air}$ flames via Bunsen burners and numerical simulations (2D axisymmetric configuration in OpenFOAM using Okafor mechanism) for $\phi = 0.8$ to 1.2 and pressures between 1 and 3 bar. Additionally, the mole fractions of NH and NO were measured using PLIF. Interestingly, they observed that with an increase in pressure, the flame height increased, while the inlet velocity was slightly lower, indicating a reduction in LBV with pressure. The LBV was computed via the cone angle method. They observed good agreement for the Markstein length between the experiments (NH PLIF surface) and the simulations. As for the NO , to ascertain the NO predictions, they compared the 2D DNS simulations and the experiments against 1D simulations (with detailed mechanisms). The agreement was good, but the 1D simulations did not capture the NO peak downstream of the flame front. This non-monotonic behaviour near the burner rim was attributed to the diffusion branch of the flames.

Jo et al., [11] investigated the characteristics of OH^* , NO^* , flame temperature, and heat-release rate in an inverse diffusion (IDF) hydrogen air flame. They used a CAP burner (circumferentially arranged ports) for experiments, with a central hole diameter of 5.35 mm and 8 circumferential holes of a diameter of 3 mm. A comparative study was also done with a normal diffusion flame (NDF). The experiments were performed in a lean case to nearly stoichiometric conditions, with a total of 6 equivalence ratios from 0.4 - 0.9, while the volumetric rates varied between $0.0003 - 0.0008 \text{ m}^3/\text{s}$ for 6 total volumetric flow rates. Chemiluminescence measurements were performed for OH^* and NO^* , while H_2O radiation was recorded using an infrared camera, and temperatures were subsequently computed from spectral emissivities. Heat release was further calculated using the flame temperatures. They demonstrated that the integrated intensity of OH^* in IDF was initially lower than that in NDF but increased with increasing flow rates, primarily due to the entrainment of H_2 , which enhanced OH^* production. This also affected H_2O , which was found to be higher in IDF than in NDF. The integrated intensities

of NO^* were higher than those of NDF due to higher temperatures and insufficient reaction time. OH^* and NO^* exhibit the highest intensity at the interface between the air and the fuel jet for IDF and NDF. The overall distributions of both OH^* and NO^* are similar. They also showed an increase in temperature with increasing ϕ for IDF, whereas NDF remained nearly constant. Thermal energy generated by IDF is more efficient than that generated by NDF. They indicated that a distinct burner structure in IDF leads to a partially premixed flame, resulting in higher temperatures and heat-release rates than in NDF. This provides an opportunity to use IDF to improve the heat-release rate.

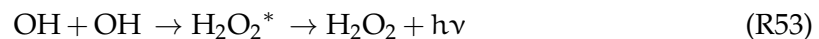
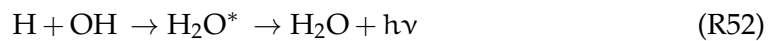
Zhichao et al., [12] investigated NO_x the emission characteristics of a separated stratified swirling flame in a centrally staged lean premixed prevaporator (LPP) module combustor at elevated inlet temperatures of up to 810 K and pressures up to 2.0 MPa. They primarily studied the effects of fuel stage ratio on NO_x emissions and developed an empirical NO_x emission model based on the Lefebvre model. Experiments were performed in TeLESS-II using kerosene-air mixtures with $\phi = 0.55$ to 0.8 and a fuel stage ratio of 8% to 24%. NO_x characterization was through emission gas analysis, while OH^* and NO^* were evaluated using chemiluminescence data. They indicated that NO_x emissions increased with increasing fuel stage ratio. They revealed that the pilot flame and the main flame were independent. OH^* concentration was positively correlated with temperature. It was higher in the pilot flame because the local adiabatic flame temperature was higher. NO^* was also consistent with OH^* and affected by temperature. The thermal mechanism dominated the NO^* formation. They modified the NO_x emission model proposed by Lefebvre and included the processing of coupled weak flames. The PLUS model corrected the pilot-stage temperature by incorporating ϕ corrections. The model is limited to a pressure index of 0.5 and applicable only to weakly coupled flames.

Schefer et al., [13] thoroughly disputed the claim "Hydrogen flames are not visible," through their detailed spectroscopic work, aiming to show that hydrogen flames are not transparent/translucent, although they were first observed in 1867. However, they have a spectral signature in the visible spectrum, which may provide insight into the identification of potential flame markers. They utilized a H_2 -air jet flame in premixed and non-premixed flames. As for the spectroscopic measurements, they used two resolutions, 2 nm and 0.2 nm, which were set by controlling the grating. They observed a broad continuum spectrum between approximately 350 nm and 750 nm. To mitigate the influences of CH^* and CO_2^* , a distinction was made between CP grade (99.0%) and ultra-high purity (99.999%) for the fuel, as for the oxidizer stream, they conducted a few tests with Argon/Oxygen, and the observations were the same. Hence, the blue emission stems from H and O chemistry, for instance, H_2O_2 and H_2O , and it was observed for carbon-based fuels as well (CH_4), and the blue emission increased with the temperature. The work concluded by noting discrepancies among studies on the source of blue emission.

Fiala and Sattelmayer [14] critically examined the sources of the blue radiation in H_2

flames by building upon the previously existing knowledge, specifically, on the chemiluminescent reaction after noting the ambiguity in certain kinetic reactions. They utilized both experimental and numerical studies to examine chemiluminescence. They used a laminar co-flow diffusion flame for experimental measurements, and for simulations, they employed ANSYS Fluent with thermal radiation modelled using a discrete transfer method for the RTE (radiative transfer equation) and WSGG (weighted sum of grey gases) for spectral properties. They ensured the system under study was optically thin to ensure the applicability of the inverse Abel transform. They included additional chemiluminescence reactions based on the concentration of OH and H for H_2O_2^* and H_2O^* . They observed very good agreement between the measured blue emission against the kinetic models (optimized kinetic parameters), although there were slight discrepancies between the experimental and numerical models that might stem from modelling errors, since they observed for H_2O_2^* , H_2O^* , and OH^* . They highlighted that no axiomatic proof was possible due to the nature of the radicals involved. It is not possible to delineate with and without those radicals in experiments. They concluded that the actual source of the blue emission holds a minor role relative to its presence, since blue emission can serve as a flame marker across a range of conditions (including high oxygen content). Although the conclusions by Fiala and Sattelmayer [14] are meritorious, the community would benefit further from investigating the source of the blue emission using detailed spectral models that could inform improvements to kinetic mechanisms.

Matsugi [15] examined the behaviour of blue emission in a time-resolved high-repetition-rate shock tube for $\text{H}_2\text{-O}_2\text{-Ar}$ mixtures, specifically the previously discussed reactions (in R52 and R53) in the literature [13, 14]. He compared the intensity histories against the numerical results from CANTERA with the Konnov [16] mechanism. He observed that the intensity of OH^* chemiluminescence was 2 orders higher than the blue emission. He tested the emission profiles from the shock tubes against the various relevant combinations of the concentrations. He noticed better agreement when radicals from both reactions are used, implying a synergistic role of these reactions in blue emissions. He further emphasized that these are from *a posteriori* and the validity of the mechanism needs to be examined through radiative recombination processes.



Jo [17] investigated the source of blue emissions in $\text{H}_2\text{-air}$ axisymmetric burner. He used a N_2 stream to delineate the effects of the diffusion branch on the premixed flame. A spectrometer coupled with a CCD was used to capture the spectra between 385 nm to 495 nm. He complemented the experimental work with numerical results from Chemkin with the GRI-3.0 mechanism. As for the experimental measurements, he observed several prominent peaks between 390 nm to 460 nm, and the qualitative behaviour was

the same with different levels of gratings (which affect the spectral resolution of the spectrometer). The measurement spectra exhibit a non-monotonic variation, increasing from lean to stoichiometric and decreasing on the fuel-rich side. As the acquisition height was increased, the magnitude of the intensity decreased. He also observed that with an increase in measurement height, the deviations between the rich and stoichiometric flames reduced. The author suggested that the decrease in the intensity of the blue emission can be potentially due to the decrease in OH^* with height and noted that the behavior of blue emission conformed to the behavior of OH^* as a function of ϕ (the non-monotonic behavior discussed above). Additionally, the author discusses the various possible species that could contribute to the blue emission, namely H_2 , H , O_2 , O , H_2O , H_2O_2 , and HO_2 , along with possible reactions that could be the source of the blue emission. The authors evaluated the emission intensity from the experiments against the reaction rates of the possible reactions at different heights. The authors concluded that the blue emission could be from different species contributing to the blue emission at different wavelengths, with notable species being O_2 , H_2 , OH , and O .

3.3 Motivation and objectives

H_2 is an exceptionally clean fuel with a high energy content per unit mass and is known to produce zero-carbon emissions upon combustion. However, the unique transport properties of H_2 , particularly its high diffusivity relative to other reactants [18], introduce significant challenges in predicting and controlling flame structures. In premixed H_2 - air flames, this high diffusivity leads to pronounced preferential diffusion effects, which strongly influence the local equivalence ratio, radical formation, reaction zone thickness, and flame stability [19, 20, 21]. Understanding these effects is essential for improving predictive combustion models and enabling the reliable design of H_2 based energy conversion systems.

Optical emission spectroscopy provides a powerful diagnostic tool for probing the underlying chemical kinetics and thermochemical states within reacting flows. By resolving molecular emission features, spectroscopy enables quantitative measurements of species mole fractions [22, 23], flame temperatures [24, 25, 26, 27]. In this study, we integrate high-resolution pointwise spectroscopy with two-dimensional chemiluminescence imaging to investigate the detailed spectral and spatial signatures of premixed H_2 - air flames. Chemiluminescence imaging provides insight into the spatial organization of reaction zones and their coupling with preferential diffusion, flame stretch, and curvature. Complementary spectroscopic measurements are performed to obtain the spatial and spectral characteristics of species within the flame. By resolving spectroscopically measured OH mole fraction distributions together with temperature (H_2O) fields, we quantify spatial variations in chemiluminescence intensity, enabling characterization of flame structure, and revealing how combustion dynamics affect radical transport. Studies

on NO* chemiluminescence are limited [28, 11], prompting this work to investigate its characteristics and role in flame chemistry. The blue emission typically observed in H₂-air flames has attracted significant interest, and we have conducted investigations to better understand this phenomenon. This approach offers key insights into flame chemistry and species behaviour across different flame regions.

The overarching objective is to establish a mechanistic understanding of how hydrogen's high diffusivity influences flame structure and chemical reactivity. In this context, the influence of equivalence ratio on flame structure and emission characteristics is investigated both spatially and spectrally.

The three main objectives of this work are:

- To evaluate the flame structure through emission characterization across varying equivalence ratios.
- Quantify the spatial distribution of temperature and species mole fractions through spectral measurements.
- To investigate the characteristics of blue flame emission in laminar premixed flames through spatially and spectrally resolved measurements, and to examine its potential as a flame marker.

3.4 Experimental set up



Figure 3.1: Bunsen burner

The experiments were conducted in an aerodynamically stabilized Bunsen burner. The burner consists of a straight circular nozzle with an inner diameter of 7 mm, and it is contoured to minimize boundary-layer separation and ensure a uniform axial flow profile at the exit. A premixed stream of H₂ and air is introduced through the sides of the burner, as shown in the Fig. 3.1, via a 5 mm packed flame strainer filled with glass beads, which promotes homogeneous mixing and flow conditioning. A flame arrester is installed downstream of the mixing section to prevent flashback, a known hazard in hydrogen combustion

due to its high flame speed and low ignition energy.

Dedicated mass flowmeters were used to control the flow of H₂ and air, and the error percentage was less than 3%. H₂ from Air Liquide (ALPHAGAZ 2) was used with purity

99,999 % absolute volume, and compressed air from in-house was used for the tests. Additional tests using Air Liquide synthetic air were conducted with O_2/N_2 mixtures at 20% and 80% volume. The burner was mounted on a high-precision vertical translation stage to allow adjustment of the flame height without disturbing the alignment of the imaging optics or fibre collection system. This rigid optical arrangement kept all diagnostics fixed in space, while the flame position was systematically varied by adjusting the burner position. This configuration enabled consistent diagnostics along the flame axis and minimized experimental uncertainties during flame scanning and data acquisition.

3.5 Optical diagnostics

The schematic diagram of the experimental setup and optical diagnostics is shown below in Fig. 3.2. The optical diagnostics comprised an intensified camera (Princeton Instruments, PI-MAX 4), a digital camera (NIKON Z8), not represented here, and a spectrometer (Princeton Instruments, ISOPlane-160), providing high-resolution chemiluminescence and spectroscopic imaging to analyse flame structure and species emission.

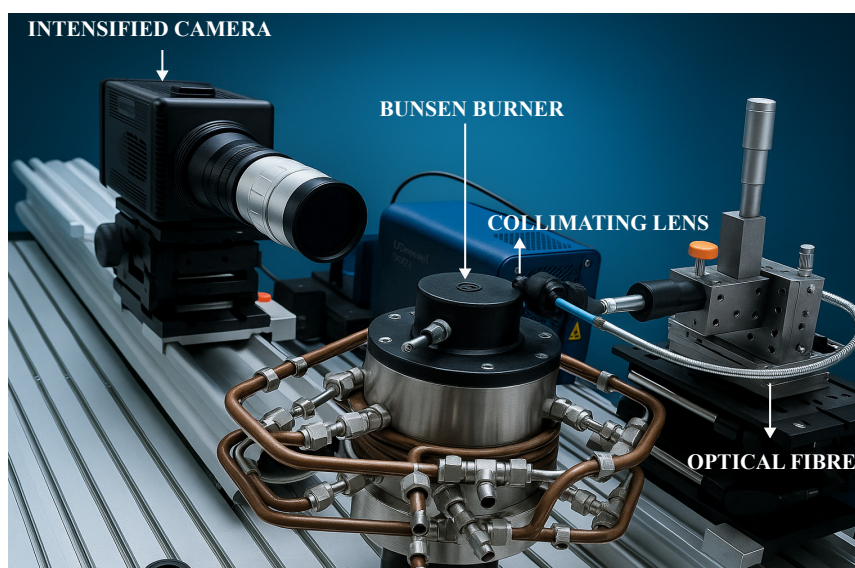


Figure 3.2: Schematic diagram of experimental set-up and optics

The chemiluminescence emissions from various radicals were captured using a 16-bit intensified PI-MAX 4 camera. A Cerco lens with a focal length of 105 mm was utilized, and by adding adapters, the effective focal length was extended to 180 mm, thereby improving spatial resolution to $65.5 \mu\text{m}/\text{pixel}$. A set of six narrowband optical filters was employed to capture chemiluminescence signals from radicals, with a primary focus on OH^* . The blue emission was also studied using broadband imaging across the wavelength range 220 to 900 nm, as well as measurements at selected wavelengths. A short-pass filter between 245 and 270 nm was used to obtain NO^* emissions. The imaging system was further optimized for spatial resolution, achieving a spatial resolution of $14.9 \mu\text{m}/\text{pixel}$, which is sufficient to

resolve the thin hydrogen flame reaction zone. The filter specifications are tabulated in Tab. 3.1.

Manufacturer	CWL (nm)	FWHM (nm)	Diameter (mm)	Transmission efficiency (%)	OD
Semrock	-	-	25	≥ 35	3
Edmund	310	10	50	≥ 70	4
Edmund	337	10	50	≥ 85	4
ThorLabs	390	10	25	≥ 90	5
Edmund	430	10	50	≥ 85	4
ThorLabs	450	10	25	≥ 90	5
Edmund	532	10	50	≥ 85	4
Edmund	632	10	50	≥ 85	4

Table 3.1: Filter specifications

Visible flame images were recorded using a Nikon Z8 camera equipped with a 45.7-megapixel full-frame stacked CMOS sensor. The spatial resolution was 19 $\mu\text{m}/\text{pixel}$.

For spectroscopic analysis, an Ocean Optics spectrometer (Ocean-HDX-UV-VIS) was used for low-resolution (0.369 nm) spectroscopy, whereas a high-resolution spectrometer (Princeton Instruments IsoPlane SCT-320) was used to record high-resolution spectral data. The optical system consists of a 25 mm diameter convex lens positioned 40 mm from the centre of the flame. The light was then collimated using a 5 mm diameter lens and coupled into an optical fibre with a 1 mm core diameter and a length of 2 m. The fibre end was directly connected to the low-resolution spectrometer, and spectral emissions were recorded between 200 and 800 nm with 825 lines/mm, blazed at 325 nm. Whereas, in the case of a high-resolution spectrometer, the end of the fibre passed through a spectrometer slit with a width of 25 μm . Imaging was performed using a high-resolution, back-illuminated ProEM EMCCD camera. Gratings with groove densities of 3600 g/mm, 1200 g/mm, and 300 g/mm, yielding spectral resolutions of 0.01 nm, 0.035 nm, and 0.15 nm, respectively, were used. The integration area was 5 mm², and a total of 10 images were captured, with integration time adjusted for each radical to optimize signal intensity. The depth of field of the optical system was experimentally evaluated using LDLS EQ-99FC for calibration. The optical fibre was translated along the optical axis over a range of distances, and the recorded signal was monitored. No significant variation in intensity was observed. To ensure reproducibility and spatial accuracy, the fibre-optics assembly was mounted on precision translation stages capable of micrometre-scale adjustments in both the x- and y-directions.

CO emission analysis was conducted using the KIGAZ 500 combustion gas analyzer with an electrochemical CO sensor. Measurements were conducted in the plume at a distance of 50 mm from the flame and at a temperature of 500 K.

3.6 Test matrix

The effects of varying the fuel-air mixture composition were systematically studied by maintaining a constant velocity ratio between the bulk flow velocity and the laminar flame speed across all equivalence ratios. The experiments were conducted at atmospheric pressure (1 atm) and ambient temperature (295 K), over a range of equivalence ratios from $\phi = 0.6$ to 1.4. The flame height was kept consistent across all cases to ensure a reliable comparison of the measured parameters. Tab. 3.2 is the summary of all the test conditions.

ϕ	$Q_{H_2}(\text{nlp/m})$	$Q_{air}(\text{nlp/m})$	$U(\text{m/s})$	Re
0.6	1.92	7.61	4.13	1536
0.7	3.02	10.33	5.78	2079
0.8	4.21	12.58	7.27	2550
0.9	5.39	14.35	8.55	2928
1.0	6.55	15.66	9.62	3202
1.1	7.62	16.57	10.48	3406
1.2	8.65	17.16	11.18	3566
1.3	9.49	17.46	11.67	3633
1.4	10.24	17.50	12.02	3646

Table 3.2: Test conditions

3.7 Image processing

High-resolution chemiluminescence of radicals provided a detailed mapping of species within the flame front. A total of 100 instantaneous images were captured and temporally averaged. The line-of-sight integrated intensity was deconvolved into a two-dimensional radial distribution using an in-house MATLAB code based on the BASEX (Basis Set Expansion) method. An edge detection algorithm was applied to identify the flame front. The image treatment sequence is shown in Fig. 3.3, where A, B, C, and D represent the respective image processing explained previously. The peak intensity, later presented in our results, was then evaluated along the direction normal to the flame front and analyzed as a function of height along the burner centerline.

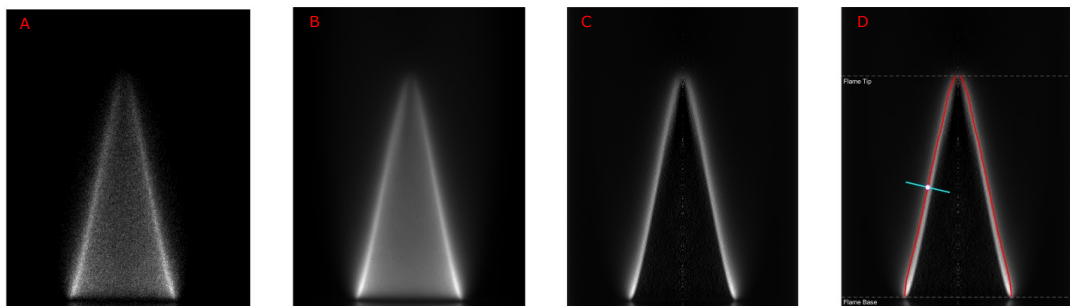


Figure 3.3: Image treatment sequence. A: Raw image, B: Mean image, C: Abel inverted image, D: Edge detected image

3.8 1D flame modelling

One-dimensional numerical simulations were performed using CHEMKINPRO with the premixed laminar flame speed module to model freely propagating laminar flames under steady-state conditions. The governing equations for mass, species, and energy conservation were solved under the assumptions of an ideal gas mixture and adiabatic flame propagation. The computational domain extended over an axial distance of 2 cm and was discretized using a refined grid consisting of 2000 mesh points. The grid adaptation parameters, gradient (GRAD) and curvature (CURV) refinement criteria were both set to 0.01. These values ensured sufficient resolution of the reaction zone while maintaining numerical stability and convergence. Multicomponent transport properties were employed in all simulations to accurately capture species diffusion, which is particularly important for light species such as hydrogen. In addition, thermal diffusion (Soret effect) was enabled.

3.9 Chemiluminescence studies

This section presents a comprehensive analysis of flame structure and emission characterization as a function of equivalence ratio in premixed H₂-air flames. Firstly, the species distribution within the reaction zone is investigated, followed by a detailed study of OH* and NO* throughout the flame, comprising both the flame front and the post-combustion gases.

3.9.1 Flame structure characterization

Spatially resolved chemiluminescence measurements were performed at 14.9 $\mu\text{m}/\text{pixel}$ to investigate the evolution of species. Multiple optical filters were employed in the chemiluminescence measurements to disentangle the contributions of individual emitting species from the underlying broadband emission and to enable comparison with numerical predictions. Narrowband filters centered on specific emission bands were used to preferentially capture OH*, NO*, and other radicals. This multi-filter strategy enhances species selectivity and allows for an experimental basis for validating the chemiluminescence source terms obtained from kinetic simulations. The key reactive intermediates in H₂-air flames, namely OH* centered at 310 nm and NO* between 245 and 270 nm, were investigated in detail by examining their spatial distributions and the underlying reaction layer of the flame. The blue emission was also studied using broadband imaging across the wavelength range of 220 to 900 nm, as well as measurements at selected wavelengths. These complementary observations enabled a correlation between the broadband emission features and their underlying contributions.

A list of potential species in the observed wavelengths is tabulated below in Tab. 3.3

CWL (nm)	Species
245 - 270	NO* [29]
310	OH* [29]
310	OH* [29], N ₂ * [30]
390	OH* [29], O* [31], H* (NIST), O ₂ * [32]
434	H* [31], O* [31]
450	H ₂ * [33], OH* [29]
532	MnO* [32]
632	O* [32], H ₂ O* [34]

Table 3.3: Wavelength and species list

Fig. 3.4 shows a representative edge-detection image at $\phi = 0.8$, with the OH* radical shown on the left and the boundary tracked using all the filters on the right.

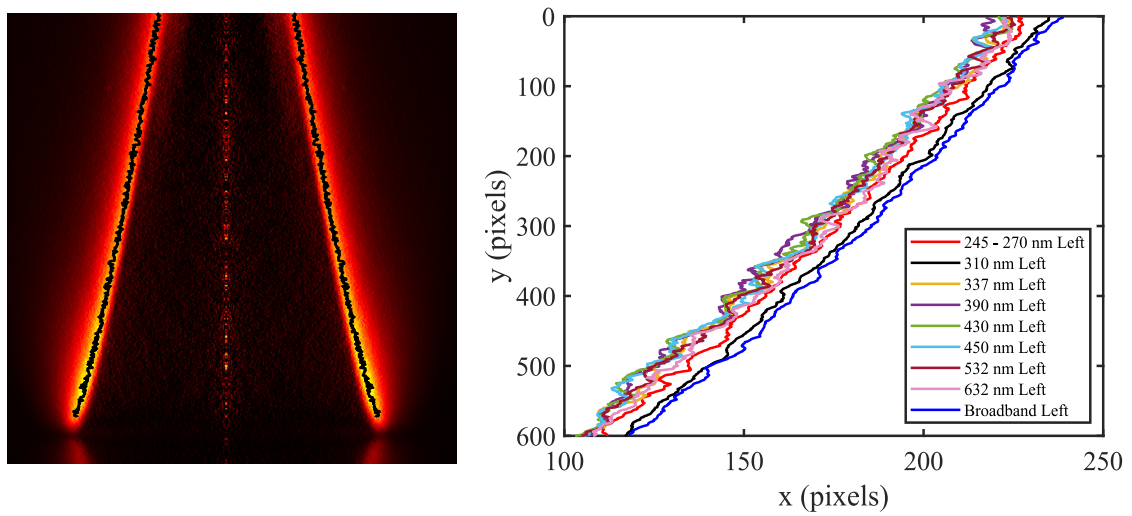
**Figure 3.4:** Edge detection using OH* on the left, edge detection of different species (right) for $\phi = 0.8$.

Fig. 3.5 presents reconstructed flame images obtained after applying Abel deconvolution and the intensity distributions of all the species along the burner centerline for various equivalence ratios. The intensity fields are normalized to their respective maximum values at each equivalence ratio.

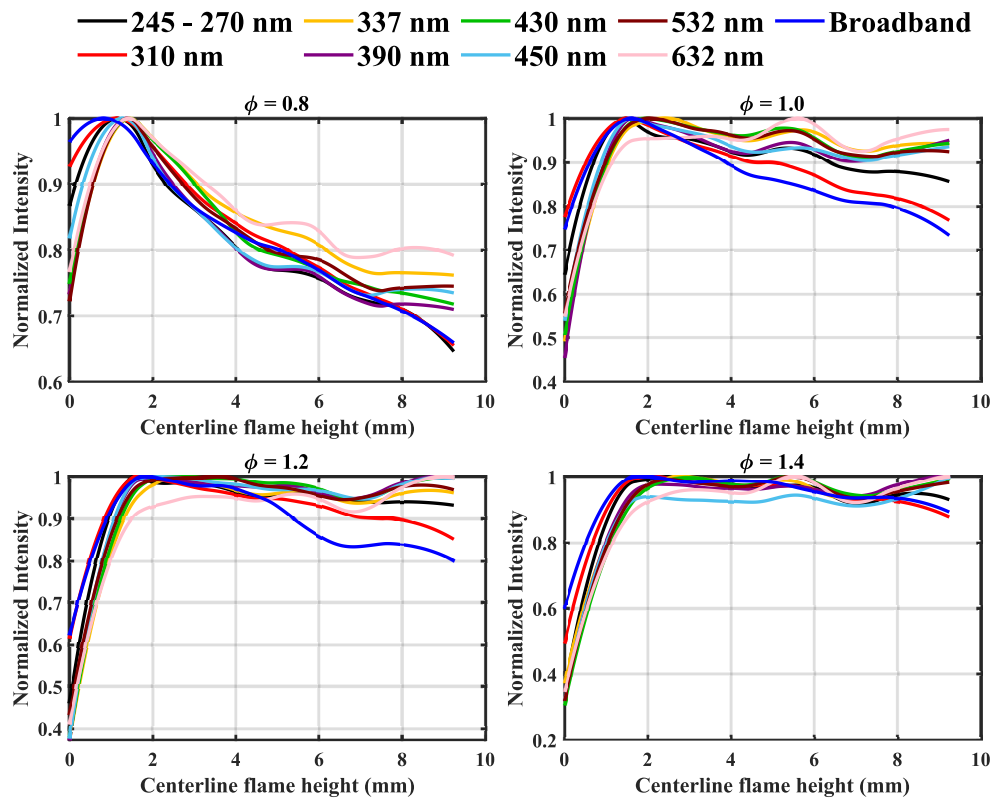


Figure 3.5: Normalized intensity profiles of various species across the centerline flame height.

Upon examining the intensity distributions of reactive intermediates near the flame base, a pronounced increase in emission intensity is observed, with the peak emission appearing about 2 mm above the burner rim, corresponding to the region of maximum local chemiluminescence. This peak varies with the radical and will be described in detail. Beyond this peak point, the intensities tend to decay. The decrease in intensity is more pronounced for a lean mixture and nearly ceases as we approach a rich mixture. For $\phi = 0.8$, OH^* , NO^* and broadband tend to display similar profiles and are comparatively sensitive with respect to other species. H_2O supposedly at 632 nm shows the lowest variation. With further increases in equivalence ratios, the separation among OH^* , NO^* , and broadband increases along the flame waist.

To further understand the evolution of the species along the flame contour, the spatial displacement of species emissions is analyzed to elucidate reaction-zone dynamics. Fig. 3.6 shows the spatial distribution of various emitting species with respect to the OH^* flame front location in a premixed hydrogen-air flame, averaged across the reaction zone. The plots are organized by equivalence ratio $\phi = 0.8, 1.0, 1.2$, and 1.4 , and each graph shows the relative axial displacement, ΔX , of the emission peak across wavelengths. Error bars indicate standard deviations from spatial averaging.

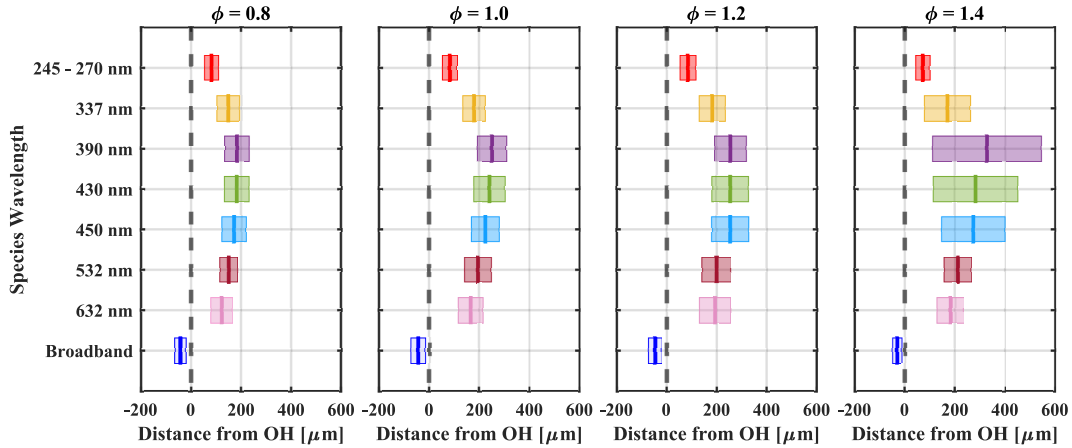


Figure 3.6: . Average spatial displacement ΔX of chemiluminescent species relative to the OH^* flame front, denoted in dashed line, for various $\phi = 0.8, 1.0, 1.2$, and 1.4 . Error bars show the standard deviation across the reaction zone.

Across all equivalence ratios, other species tend to appear downstream positive ΔX from the OH^* front, while the visible broadband appears to be upstream of the OH^* front. In our results, NO^* is observed approximately 1 mm downstream of the OH^* peak, which closely matches the full width at half maximum (FWHM) of the peak mole fraction profiles for both species predicted by the 1D simulations. The separation between OH^* and NO^* becomes more pronounced under rich conditions, consistent with the delayed formation of NO due to slower thermal and prompt NO pathways. It was found that the three wavelengths 390, 437, and 450 nm, which are in the blue region of the visible emission, lie spatially downstream of the OH^* emission. Although suitable radicals may be present in this region, significant interference from H_2O emissions should also be considered. Notably, the wavelengths at 337 nm, 390 nm and 450 nm also overlap with some OH^* bands. The broadband visible emission occurs roughly 0.5 mm upstream of the OH^* peak. These observations suggest that the species responsible for this radiation are formed earlier in the flame before the OH^* radical appears. This aspect will be discussed further in the following sections. As the equivalence ratio increases from lean ($\phi = 0.8$) to rich ($\phi = 1.4$), the peak locations of species shift farther downstream from the OH^* front. This trend indicates that, in richer mixtures, post-flame reactions extend farther downstream due to increased fuel availability and lower flame-temperature gradients, thereby broadening the reaction zone. Additionally, the separation between OH^* and NO^* becomes more pronounced under rich conditions. It is well known that lean flames are affected by preferential diffusion. Hence, higher radical concentrations at the flame base result in overall higher intensities and yield smaller error bars. As the mixture becomes rich, heat loss to the burner rim increases, thereby slightly affecting species formation at the base and producing a significant variation in intensity from the bottom towards the crown.

3.9.2 OH* and NO* Characterization: Effects of equivalence ratio

Chemiluminescence imaging was performed at $65.5\text{ }\mu\text{m/pixel}$ to identify key flame structures and emission zones. OH* and NO* were examined in detail by characterizing emission distribution within the flame front and in the post-combustion region. Effects of mixture equivalence ratios and velocity were investigated.

Fig. 3.7 and Fig. 3.8 present OH* and NO* images after the Abel inversion. A constant flame height is maintained to enable comparison across different equivalence ratios by retaining the same bulk flow velocity. Similar distribution profiles are observed for both radicals. Due to the non-uniform distribution of H_2 in lean mixtures, the radial diffusion leads to the radical pool being mainly concentrated at the base of the flame. As the equivalence ratio increases, a greater distribution of H_2 via radial diffusion and axial convection is expected, leading to higher OH* intensities across the flame. As we move towards the richer mixture beyond stoichiometry, the intensities in the inner cone reduce and an outer diffusion branching is observed. This distribution becomes more pronounced as the equivalence ratio increases, owing to the higher H_2 concentration. The diffusion flame intensity is more prominent for NO* than for OH* due to differences in their primary formation pathways, as discussed in subsequent sections.

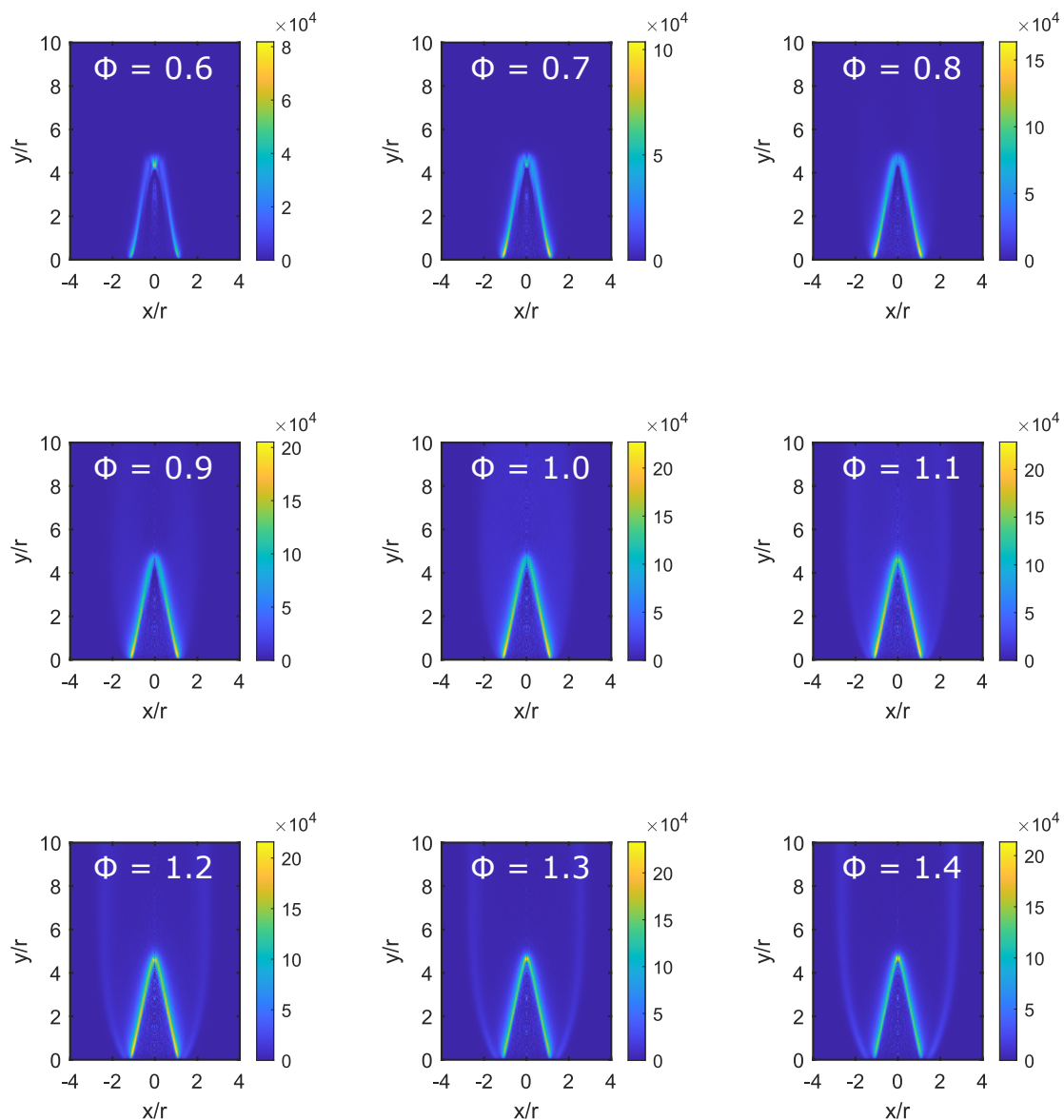


Figure 3.7: OH* images after Abel inversion for varying ϕ

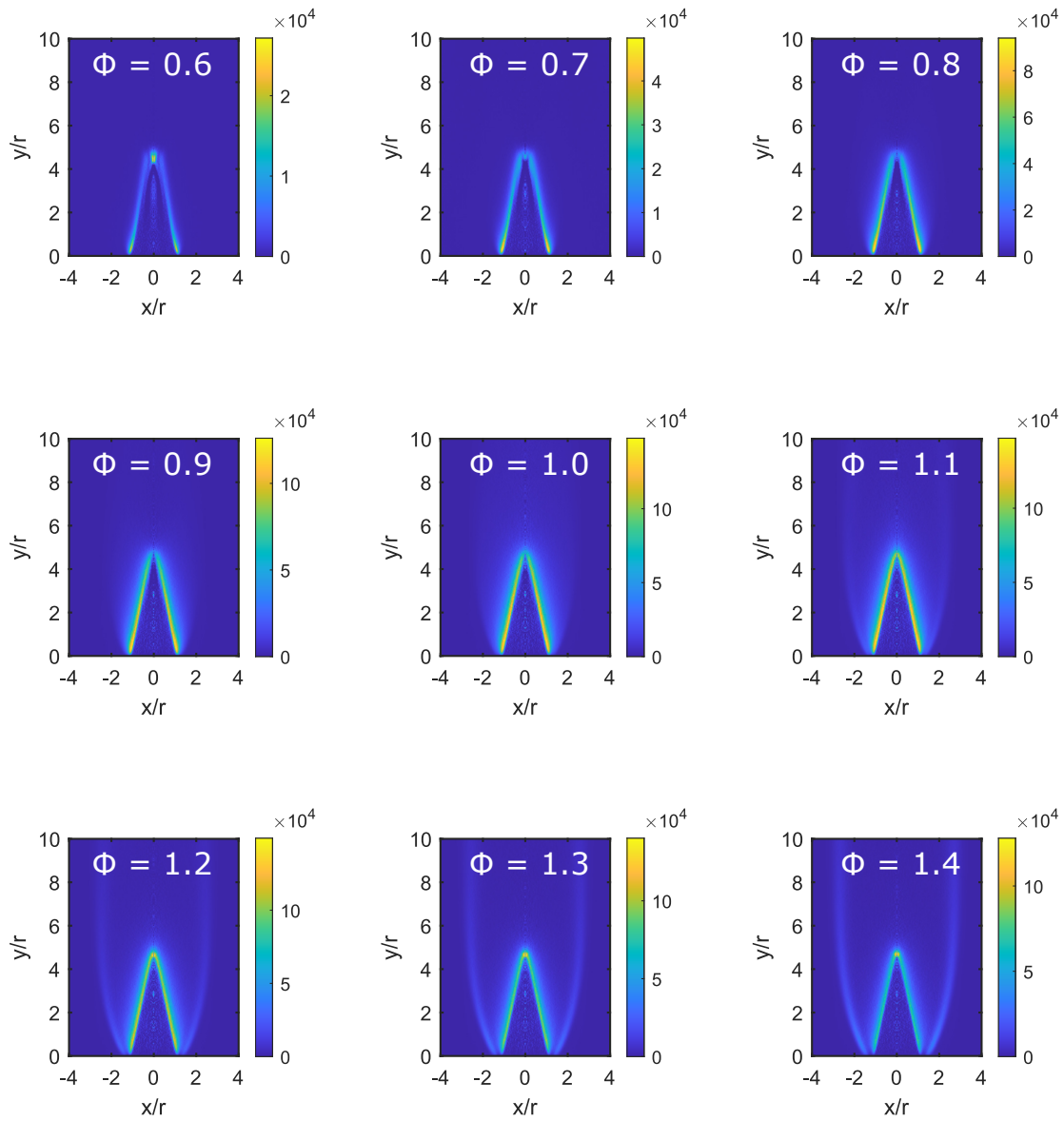


Figure 3.8: NO* images after Abel inversion for varying ϕ

Fig. 3.9 shows intensity maps across the flame contour for OH* represented on the left and NO* represented on the right for varying ϕ . OH* and NO* are localized within the narrow reaction front rather than distributing evenly. Upon evaluating the intensity distributions of various radicals at the base of the flame, a sharp increase in intensity is observed as the mixture becomes richer. In contrast, a smaller increase occurs under lean conditions. This behaviour may be attributed to enhanced quenching losses near the burner's rim in rich flames. Across species, peak intensities consistently occur approximately 2–3 mm from the burner rim, corresponding to the location of the highest local chemiluminescence. Beyond the peak location, as we move higher along the flame waist, the radical intensities gradually decrease. The intensity decay is more pronounced for lean mixtures than for rich ones, indicating greater sensitivity of lean flames to variations in local mixture conditions, resulting in enhanced reactive gradients.

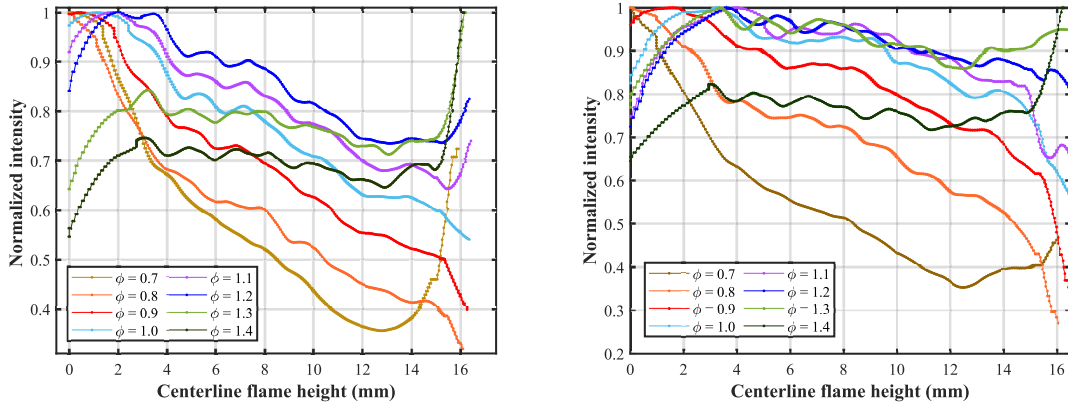


Figure 3.9: Intensity distribution of OH* (left) and NO* (right) across the flame contour for varying ϕ

Preferential diffusion significantly influences species distribution and reaction dynamics in hydrogen flames. The effects of preferential diffusion were evaluated by performing simulations using a detailed kinetic mechanism by Zhang et al. [35] for two cases: one incorporating a multicomponent diffusion model and the other assuming a unity Lewis number for all species. In a 1D simulation, preferential diffusion significantly influenced the mixture's reactivity, affecting local radical concentrations and reaction rates. The progress variable and the mixture fraction were computed, as shown in the literature [20], [21] respectively

$$c = 1 - \frac{Y_F}{Y_{F_u}} \quad (3.1)$$

$$Z = \frac{\nu Y_F - Y_{O_2} + Y_{O_{2,air}}}{\nu + Y_{O_{2,air}}} \quad (3.2)$$

where $Y_{O_{2,air}}$ is the mass fraction of oxidizer in air, and ν is defined as the mass stoichiometric ratio:

$$\nu = \frac{\nu_O W_O}{\nu_F W_F} \quad (3.3)$$

Fig. 3.10 depicts the variation of mixture fraction as a function of the reaction progress variable. A negligible variation can be observed on the unity Lewis number assumption, whereas a difference is seen when applying the multicomponent diffusion model. These changes in the mixture fraction distribution are more pronounced in lean mixtures than in rich mixtures, reflecting the greater sensitivity of lean flames to preferential diffusion and local mixture inhomogeneities. This explains the critical role of preferential diffusion in altering local equivalence ratios, thereby producing the observed distribution patterns.

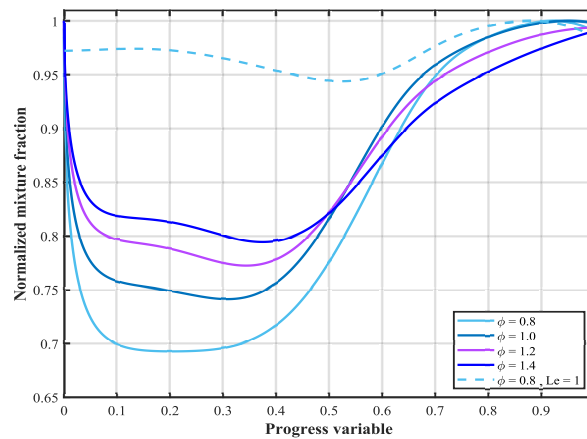


Figure 3.10: Normalized mixture fraction versus combustion progress variable

At the flame tip, both stretch and Markstein length play critical roles in locally increasing the equivalence ratio. The stretch enhances the influx of H and H₂ radicals toward the tip, intensifying reactivity. Lean mixtures typically exhibit negative Markstein lengths, while rich mixtures show positive values. The positive Markstein length in rich mixtures stabilizes species distribution. As demonstrated by Mizomoto et al. [19], preferential diffusion plays a key role in the rich mixtures, it reduces the local equivalence ratios and the mixture burns closer to stoichiometric conditions near the tip, explaining the observed increase in radical intensities. In the lean case, reactant leakage through the tip opening could lead to radical formation, as described by Bouvet et al. [36] and Mizomoto et al. [19].

3.9.3 Rate of production analyses

A rate-of-production (ROP) analysis was performed under stoichiometric conditions and at 1 atm and 295 K, to identify the dominant reaction pathways and the key elementary reactions governing the formation and consumption of electronically excited OH* and NO*. The numerical simulations were conducted using the 2023 detailed kinetic mechanism developed by Konnov [16], which is the only available mechanism that explicitly incorporates a NO* sub-mechanism.

Fig. 3.11 indicates the ROP profiles across the radial distance for the most important reactions where OH* is shown on the left and NO* on the right. From ROP analyses, the

formation of both excited radicals is dominated by three-body recombination reactions. Specifically, OH^* is primarily produced via



while NO^* formation is mainly attributed to



In addition, a minor contribution to NO^* formation arises from the bimolecular reaction



The consumption of OH^* is governed predominantly by collisional quenching processes, with water vapour playing a major role. The most significant pathways are



and



Similarly, NO^* is primarily consumed through collisional quenching reactions involving fuel molecules and radicals. The dominant quenching pathways are



Overall, the ROP analysis highlights the critical role of three-body recombination reactions in forming OH^* and NO^* , as well as the importance of collisional quenching in determining their steady-state concentrations and the resulting emission characteristics under stoichiometric conditions.

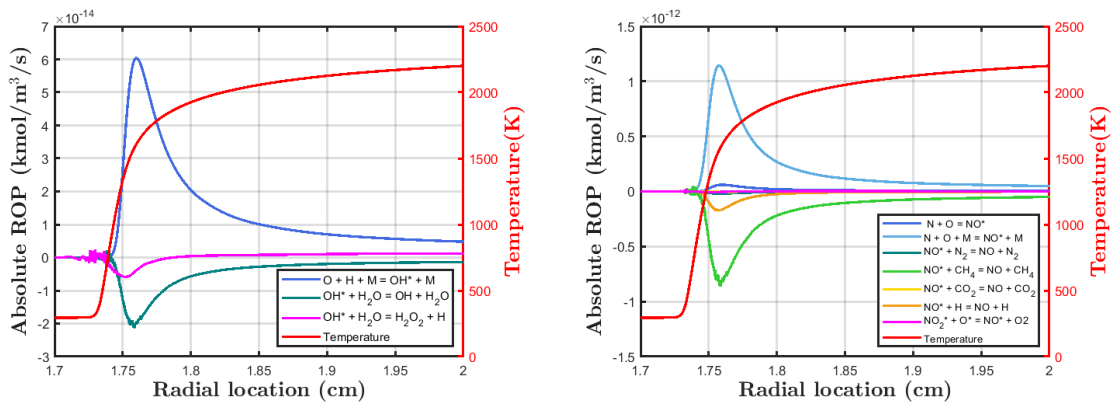


Figure 3.11: Rate of production analysis of OH^* (left) and NO^* (right) at $\phi = 1$, $T_i = 295\text{K}$, $P_i = 1\text{atm}$

3.9.4 Tip opening

To evaluate the effects of tip opening on the intensity distributions in the lean flame, experiments were performed at $\phi = 0.7$ by changing the bulk flow velocities. U/S_L was increased from 4.12 to 4.40 and 4.68, and the intervals of U/S_L were smaller due to the burner geometry. It is observed that as velocity increases, the flame height and tip opening enlarge due to increased residence time.

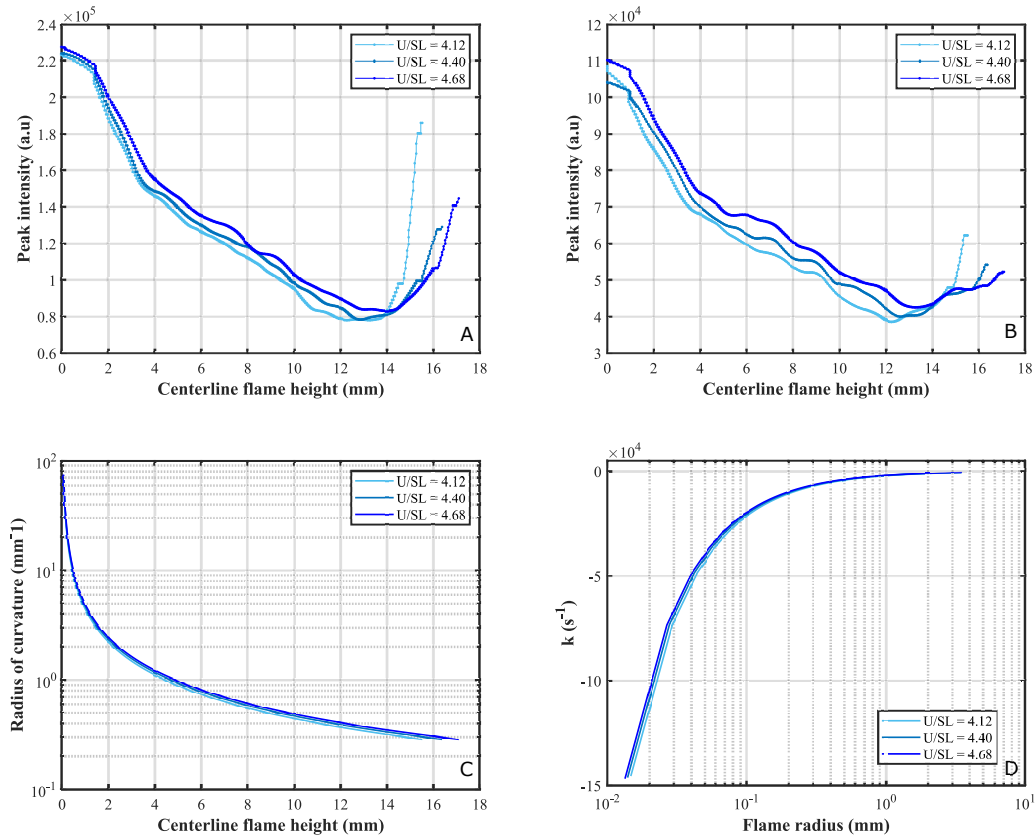


Figure 3.12: A and B: Peak intensity distributions of OH^* and NO^* as a function of centerline flame height, C and D: Profiles of radius of curvature and stretch across the centerline flame height for $\phi = 0.7$

Fig. 3.12, A and B represent the OH^* and NO^* intensity distribution, while C and D represent the radius of curvature and stretch variations across the flame height, respectively. The radius of curvature is computed as the inverse of flame radius R_f , and stretch is calculated using

$$k = \frac{-u \sin 2\alpha}{2R_f} \quad (3.4)$$

Here, k is the flame stretch and α is the cone angle.

The radius of curvature decreases rapidly downstream, indicating an increasing negative curvature toward the tip, consistent with hydrodynamic instabilities that cause tip opening in $Le < 1$ flames. The negative curvature at the flame tip has a defocusing effect on H and H_2 . Closer to the tip, at a given radius, the mixture with lower velocity exhibits greater stretch, leading to local enrichment and increased radical formation.

3.9.5 Emission zone characterization

The emission signal in a premixed flame follows the flame structure. It is strongest at the front, where chemical reactions and heat release are most intense. In the burnt-gas region, ideally, emissions are lower because the reactions are essentially complete. Hence, understanding these emission profiles helps identify flame locations and assess combustion behaviour.

Fig. 3.13 illustrates a representative image of OH^* at $\phi = 1.4$. The Abel inverted image is shown in A, while the premixed cone representing the flame is shown in B, and the post-combustion gases are outlined in C. Mean intensities are computed across the flame front and the post-combustion gases. OH^* and NO^* distributions are individually evaluated across these zones and are shown in Fig. 3.14. A sharp increase in intensity is observed as the mixture transitions from lean to near-stoichiometric conditions, corresponding to enhanced heat release and increased formation of excited radicals. The intensity peaks at $\phi = 1.1$, beyond which a decrease is observed for richer mixtures, which may be attributed to reduced oxygen availability. The intensities are higher for NO^* than for OH^* at both the flame front and the post-combustion zone. In the post-combustion region, OH^* emission decreases rapidly due to the depletion of reactive radicals and efficient collisional quenching. In contrast, NO^* formation is dominated by thermal NO mechanisms, which persist in the high-temperature burnt gases downstream of the flame front. As a result, NO^* emission is more pronounced in the post-combustion zone due to elevated temperatures and longer residence times.

The intensity distribution across several flame heights for OH^* (left) and NO^* (right) is shown in Fig. 3.15 for $\phi = 1.4$, as this is the case with the highest diffusion branching. The intensities are normalized with the maximum intensity at the bottom of the flame. As previously observed, the intensities decrease along the flame contour for both radicals. In the post-combustion zone, the intensity also decreases along the flame height. Higher intensities are observed for NO^* and reach up to 0.375 times the maximum intensities, while for OH^* , 0.175 times. As seen in the previous chapter, significant OH^* was present in the burnt gas at high pressures and temperatures. Even at atmospheric pressure and slightly lower temperatures, OH^* is still present in the burnt gas, casting doubt on its use as a flame marker for rich mixtures in any configuration.

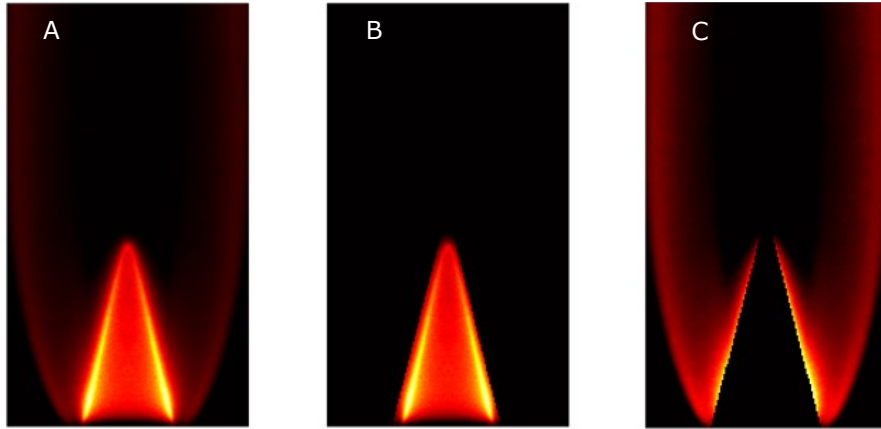


Figure 3.13: Illustration image of flame zones separation of OH^* at $\phi = 1.4$. A: Abel inverted image, B: Flame zone, C: Post flame zone

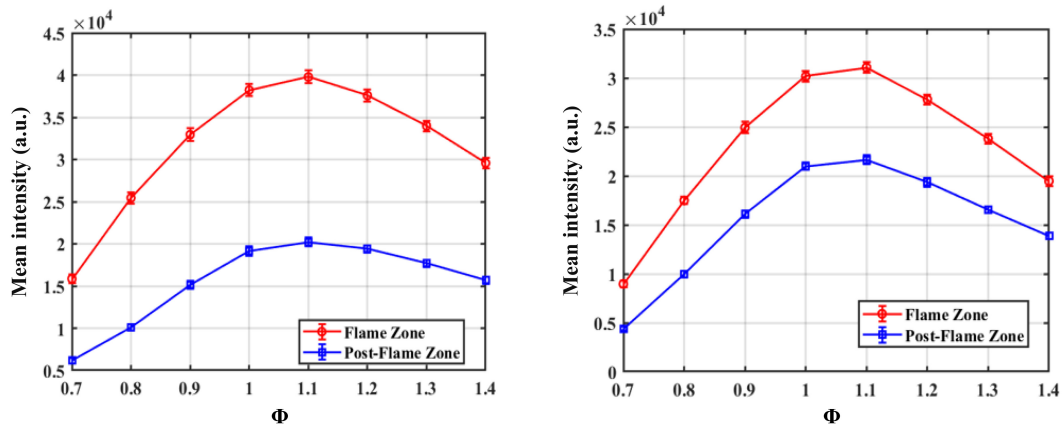


Figure 3.14: Mean intensity distributions OH^* (left) and NO^* (right) across the flame front and post flame zone for varying ϕ .

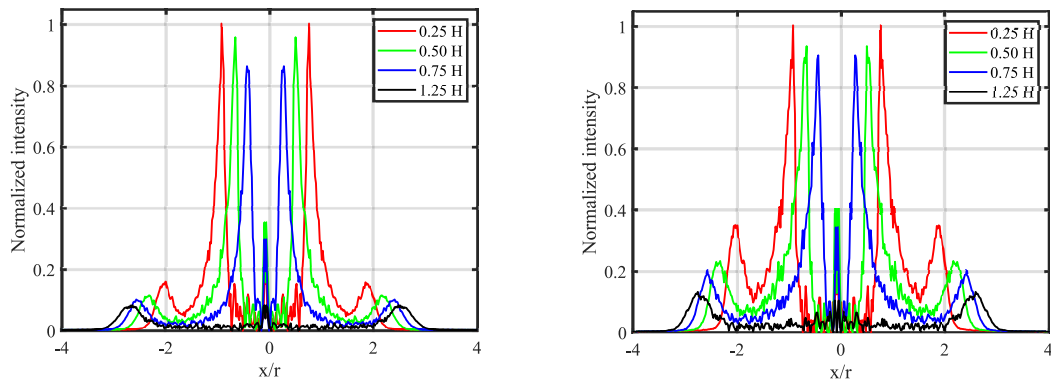


Figure 3.15: Normalized intensity distributions OH^* (left) and NO^* (right) for $\phi = 1.4$, across varying flame heights.

3.10 Spectroscopic studies

Optical emission spectroscopy (OES) is a powerful, non-intrusive diagnostic technique that plays a crucial role in the study of flame chemistry. In hydrogen flames, OH* is the primary emitting species in the reaction zone of the hydrogen–air flame, exhibiting a strong ultraviolet emission at 309 nm, which arises from the $A^2\Sigma^+ \rightarrow X^2\Pi$ from (0,0) and (1,0) transitions of the excited OH radical [25, 37, 27]. Some OH* bands, OH A-X(1,2)/(2,1)/(3,2), near 290 nm, can also be observed [38]. NO* emissions are also expected in the UV region. The literature reports several β bands of NO*, $B^2\Pi^+ \rightarrow X^2\Sigma$ in UV-A (380–315 nm) and UV-B (315–280 nm). Combination of both γ bands $A^2\Sigma^+ \rightarrow X^2\Pi$ and β bands $B^2\Pi^+ \rightarrow X^2\Sigma$ in UV-C (280–200 nm) regions. [39]. A characteristic blue emission in the visible region has been reported in the literature, and this will be discussed in detail in the subsequent sections. Some sodium lines can be found at approximately 588 nm, corresponding to the sodium D-line doublet [40, 11]. H₂O are found in IR regions[25, 27, 22]. By analysing the naturally emitted light from excited chemical species in the flame, OES provides direct insight into the flame. Changes in spectral intensity and relative band emissions can be correlated with variations in flame structure. Ratios of line intensities or of fits to blackbody radiation can be used to estimate the flame temperature. Its ability to deliver spatially and temporally resolved chemical information makes it an indispensable tool for validating numerical simulations. In this study, we used low-resolution spectroscopy to provide an overview of excited species in hydrogen flames. High-resolution spectroscopy revealed finer spectral features, such as the rotational-vibrational structure, enabling precise temperature and species profiling.

3.10.1 Overview spectra

The overview spectra of H₂ - air flames were obtained using Ocean Optics spectrometer at a resolution of 0.369 nm. Optical emission spectra of hydrogen–air flames were acquired across the reaction zone by radially traversing the probe and recording the corresponding peak intensities. Pointwise measurements were performed along the flame, covering fresh gases, the flame front, and burnt gases. A total of 40 measurement points were acquired at an interval of 0.5 mm across both axes. Along the flame contour, three axial points were considered: two in the flame and 1 in the burnt gas, at 0.25, 0.50, and 1.1 times the flame height. Translating into axial distances of 4, 8 and 18 mm from the base of the flame, respectively. Fig. 3.16 is an illustrative image on the left at $\phi = 1.4$ demonstrating the measurement points. On the right, spatially resolved spectra are shown at a height of 4 mm for only one half of the flame. The spectra are acquired radially from the centerline ($r = 0$) outward, with each curve vertically offset to enhance clarity. The x-axis represents the wavelength, covering the ultraviolet (UV) to near-infrared (NIR) range (200–800 nm), while the y-axis shows background-subtracted emission intensity in arbitrary units. A dominant and consistent spectral peak appears near 310 nm, corresponding to OH* emission, along with some minor peaks around 288 and 337 nm. This feature marks regions of active

combustion, as OH^* radicals are formed in the high-temperature reaction zones of the flame. The peak intensity is strongest near the centerline and gradually diminishes with increasing radius, highlighting the concentration of heat release and chemical activity in the flame core. In addition to the OH^* peak, weaker features of NO^* emissions were also observed in the UV regions.

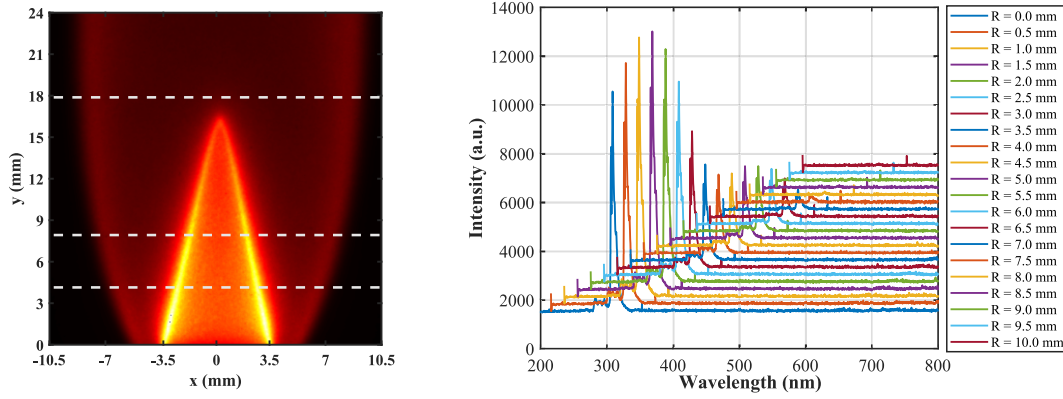


Figure 3.16: (Left) OH^* LOS integrated image at $\phi = 1.4$, and the dashed lines represent measurement locations. (Right) Spatially resolved emission spectra measured at a flame height of 4 mm in a premixed hydrogen-air flame at $\phi = 1.4$. Spectra are taken radially from the flame centerline ($r = 0$) to the outer edge and staggered vertically for clarity.

Radial line-of-sight (LOS) emission profiles are shown in the Fig. 3.17 for different equivalence ratios at a height of 4 mm. These plots illustrate the variation in line-of-sight (LOS) emission intensity across the burner radius. The left subplot shows a narrowband centered at 310 ± 5 nm, dominated by OH^* chemiluminescence from the flame front. The right subplot shows a broader band centered at 260 ± 15 nm, corresponding to NO^* . The integration windows are selected to match the wavelength ranges of the filters used in previous chemiluminescence studies.

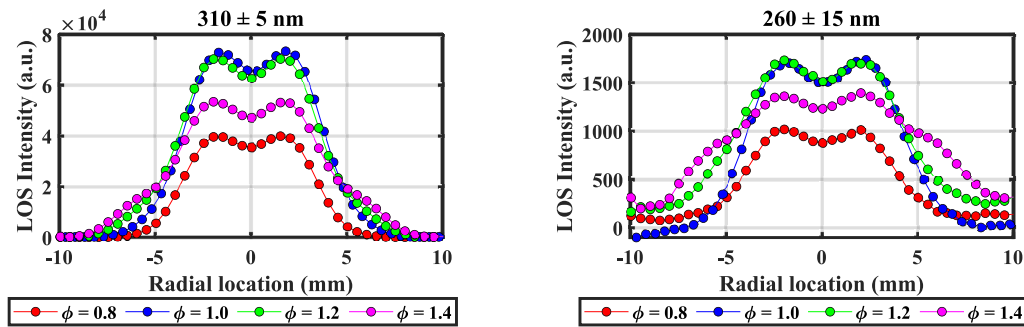


Figure 3.17: LOS intensities of OH^* (left) and NO^* (right) at an axial location of 4 mm across the burner axes for varying ϕ .

Both plots display a roughly bell-shaped radial profile, reflecting the maximum reaction intensity and radical concentrations in the conical core, and taper down towards the burnt gas. At the flame front, ϕ increases from 0.8 to 1.2, the peak intensities of both bands

increase, indicating enhanced chemiluminescence near stoichiometry, where heat release is maximized. However, the intensity then plateaus and declines at $\phi = 1.4$ due to rich-side quenching. Whereas in the post-combustion region, the intensities of both the bands tend to increase with increasing ϕ due to a pronounced diffusion branch as we move to rich mixtures.

Complementary to chemiluminescence measurements, spectroscopic measurements of OH^* and NO^* for $\phi = 1.4$ are shown in Fig. 3.18. The line-of-sight radial emission profiles change significantly from the base ($H = 4$ mm) to the post-combustion zone ($H = 18$ mm). A strong signal is observed near the base, reflecting maximum line-of-sight (LOS) integration through the luminous flame cone, and a decay signal is observed as we move to a higher height. Potentially, a negligible diffusion of the radicals from the premixed cone to the diffusion branch may occur. The main contribution of the intensities in the diffusion flame may be through convective transport.

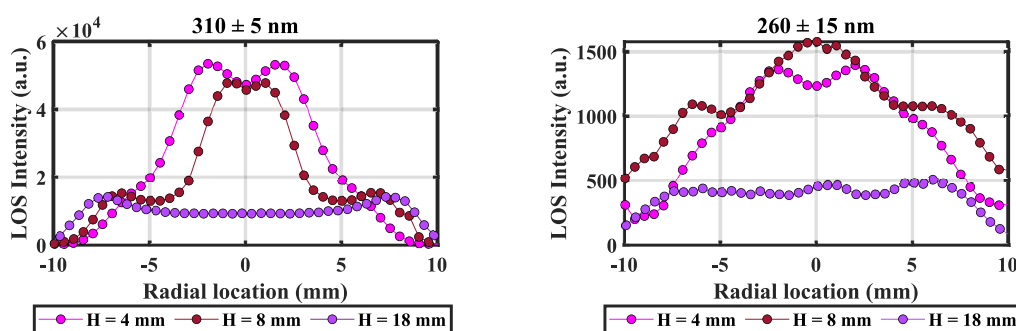


Figure 3.18: LOS intensities of OH^* (left) and NO^* (right) across different flame heights at $\phi = 1.4$.

3.10.2 High-resolution imaging

High-resolution spectroscopic measurements were acquired using a Princeton Instruments IsoPlane SCT-320 to resolve the different radicals in the reaction layer. Measurements were performed at 6 axial points along the flame contour. These points were at heights of 1, 2, 8, 11, 14, and 16.5 mm above the burner. Fig. 3.19 illustrates representative background corrected emission spectra obtained for a stoichiometric mixture at $\phi = 1.0$ at selected axial locations, highlighting the spectral intensity variations. The spectra were recorded using a diffraction grating with 300 grooves/mm, which provided a broad spectral range suitable for capturing emission features across the ultraviolet and visible regions. The spectra indicate that OH^* is the dominant species emitting in the reaction zone of the hydrogen–air flame, with strong ultraviolet emission at 310 nm and a smaller emission at 288 nm. Several bands of NO^* were also observed between 240 and 260 nm. A broadband continuum across the visible region, spanning wavelengths from 380 to 500 nm, was also observed. As previously observed in the literature, some sodium lines were present at 588 nm. These sodium emissions increased with richer mixtures and likely originated from the burner, as high temperatures vaporized trace sodium impurities, contributing to the

flame's yellowish hue. Considerable H_2O emission is also observed as one moves from the far-visible region toward the infrared.

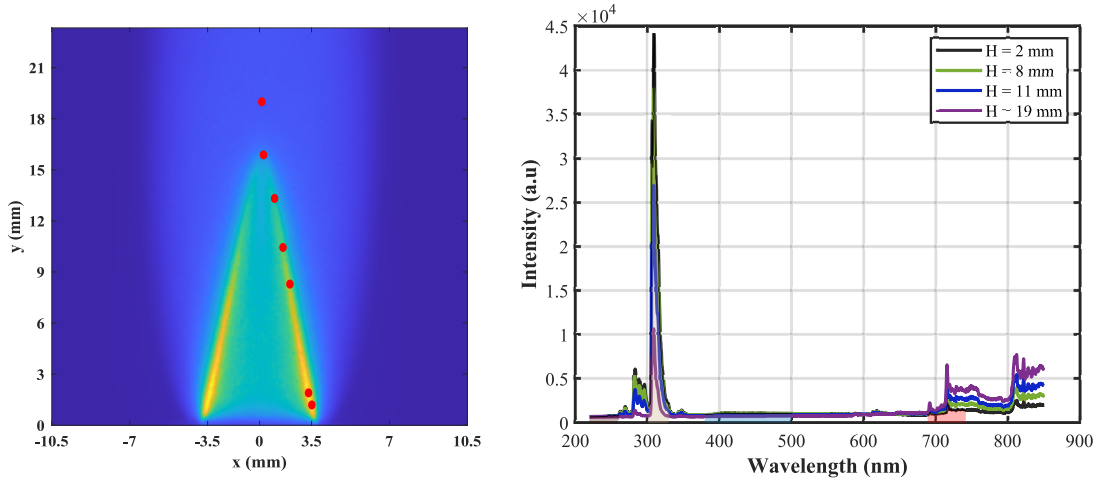


Figure 3.19: Emission spectra for $\phi = 1.0$ across varied axial distances

To interpret the contributions of these radicals, the intensities were integrated along the spectral bandwidths, as shown in the shaded regions in Fig. 3.19. The integration ranges were set based on the spectral regions corresponding to the main emission bands. They were 220 - 260 nm for NO^* , 302 - 320 nm for OH^* , 380 - 500 nm for the Blue emission, and for the water vapour radiation in the region between 689 - 741 nm. Peak intensities were observed at an axial location 2 mm from the burner rim, consistent with the chemiluminescence measurements described earlier. Further along the contour, the intensity tends to decrease. This holds for OH^* , NO^* , and blue emission, whereas H_2O behaves conversely. The concentration of H_2O is known to increase with flame height; hence the observed increase in intensity.

To estimate the role of the various radicals and their effect on the equivalence ratio, the intensity distribution as a function of the equivalence ratio is demonstrated in Fig. 3.20. The intensities were measured at a height of 2 mm above the burner rim and normalized to the stoichiometric reference case, which represents the maximum emission level. The integrated intensities tend to increase as the mixture moves from lean to stoichiometric conditions, owing to the rise in the adiabatic flame temperature. A maximum is reached in stoichiometric conditions, while beyond this point, intensities decrease. A pronounced variation in OH^* intensity with equivalence ratio was observed, followed by the blue continuum emission, while NO^* showed only minor changes. This indicates that OH^* chemiluminescence is still considerably more sensitive to variations in equivalence ratio.

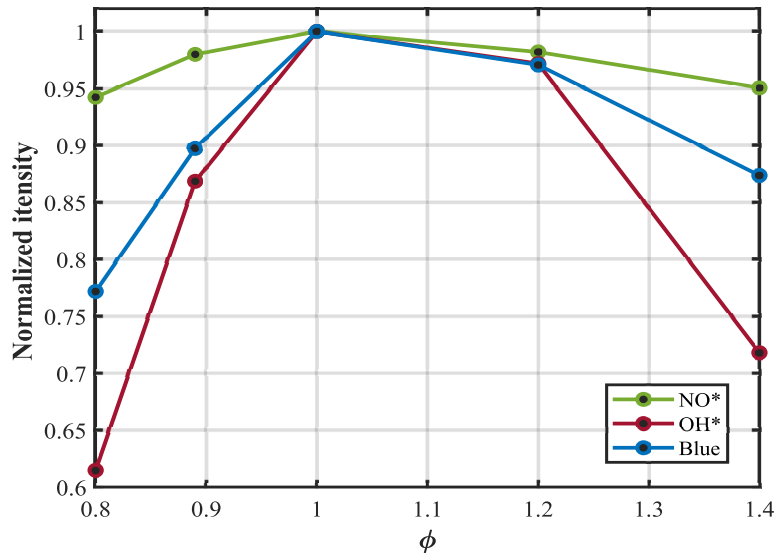


Figure 3.20: Normalized intensity profiles as a function of equivalence ratios for various bands

To resolve the detailed emission characteristics, measurements of the NO* and OH* radicals were performed using a 3600 g/mm diffraction grating, covering wavelengths from 242 to 258 nm and from 300 to 316 nm, respectively. The broadband blue emission was captured between 380 to 500 nm using a 300 g/mm diffraction grating, as a larger spectral range was required. As shown by Moskalenko et al.[41], H₂O contains weak emission bands at 693 and 718 nm in the red region of the visible spectrum. Hence, H₂O* measurements were performed between 690 and 740 nm for H₂O* at 1200 g/mm. Fig. 3.21 represents the distributions of normalized intensities across different ϕ acquired for OH* (A), NO* (B), Blue (C) and H₂O* (D), respectively.

NO* emissions were acquired at an integration time of 20 s and are shown in A. Several NO* γ and β bands, as indicated in the literature, can be observed. However, the fits are a bit noisy and not as good as OH*. OH* intensities were acquired for an integration time of 1s and are shown in B. A low and nearly flat signal observed below 305 nm indicates minimal contribution from OH* emission. Several rotational lines are observed, with peak bands at R and P around 306 and 309 nm, respectively. The overall spectral shape is similar across all equivalence ratios. The broadband blue emissions were acquired with an integration time of 20 s and are shown in C. The intensities are sensitive to variations in wavelength. They are more resolved for leaner mixtures and flatten at several wavelengths as the mixture becomes richer. H₂O* emissions were acquired with an integration time of 1s and are plotted in D. The spectra are well resolved, similar to those of OH*.

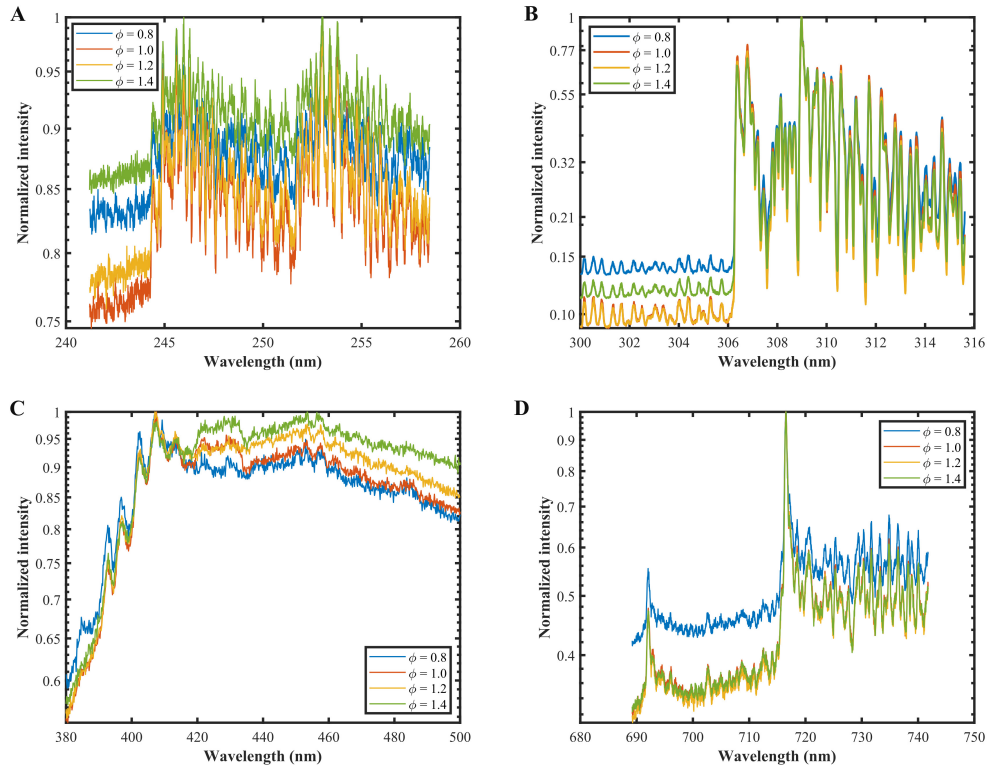


Figure 3.21: Emission spectra for varying $\phi = 1.0$ at an axial height of 2 mm. A: NO* (3600 g/mm), B: OH* (3600 g/mm), C: Blue (300 g/mm), D: (H₂O)* (3600g/mm)

3.10.3 Spectral modelling

Quantification of species provides direct insight into the chemical reactivity of the flame. Resolved measurements are vital for validating kinetic models and identifying the key zones of combustion. Using highly resolved spectroscopic measurements, both rotational temperatures and concentrations were determined for OH, and rotational temperatures for H₂O. Rotational states are generally distributed according to Boltzmann distributions, where the ground and excited states are assumed to be in equilibrium. Hence, rotational temperatures can be computed either from Boltzmann plots or by comparing experimental and synthetic spectra.

Rotational temperature can be obtained by [42]

$$I_{JJ'} \propto h\nu_{JJ'}(2J+1)A_{JJ'} \exp\left(-\frac{B_v h c J(J+1)}{k_B T_{\text{rot}}}\right) \quad (3.5)$$

where, $I_{JJ'}$ = intensity distribution of rotational population distribution, $\nu_{JJ'}$ = frequency of the transition from rotational, level J to level J' , $A_{JJ'}$ = transition probability, B_v , k_B , h = Rotational, Boltzmann and Planck constant respectively, E (cm⁻¹) = Rotational energy, E (cm⁻¹) = $B_v J(J+1)$

Spectral fitting was performed using an in-house optimization routine. Spectral properties were imported from the HITEMP [34] database. The L-BFGS-B algorithm was used for optimization, and the best fit of synthetic spectra to the measured spectra was obtained by iteratively varying gas temperatures and mole fractions. Voigt line broadening was used, accounting for both collisional and line broadening. The pressure is set to 1 atm, and the path length is 4 cm, and a line intensity cut off is set to $S_{\text{cut}} = 10^{-40}$ cm/molecule. Fig. 3.22 represents the normalized intensity profiles between experimental and simulated spectra. The black lines represent experiments, and the red lines represent simulations. Several rotational lines in this spectral interval can be found where below 309 nm, low quantum rotational states (J) exist, and above this, higher quantum rotational states are present [43]. There is good agreement between the experiments and simulations for the OH* branches at R (306.8 nm) and P (309 nm). Similarly, the H₂O spectra also show excellent agreement.

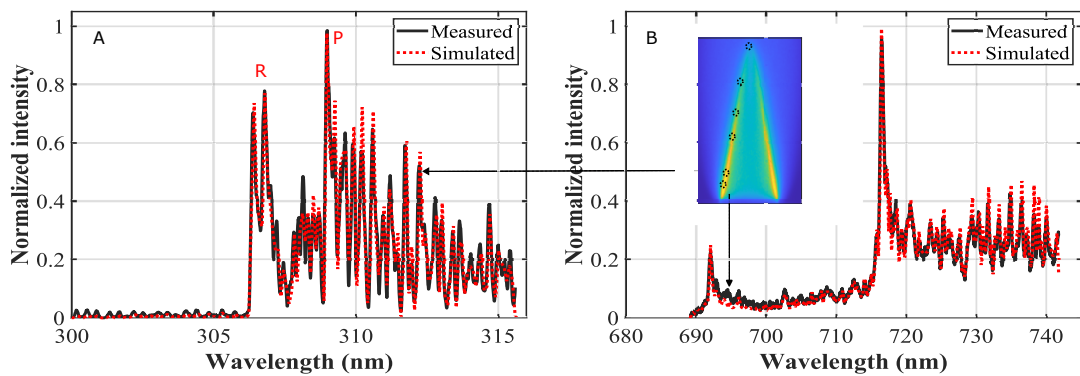


Figure 3.22: Representative spectra for $\phi = 1.0$ at HAB 2 mm: A - OH* (3600 g/mm), B - H₂O* (1200 g/mm)

The number density alongside the rotational temperatures is evaluated in this work. Hydrogen flames are generally optically thin, and lab-scale hydrogen flames may have a very low self-absorption [44]. The effects of reabsorption are also accounted for in our simulations. To illustrate the impact of species concentration on the overall spectral distribution, mole fractions of OH and H₂O ranging from 0.001 to 1 were considered. Spectra were simulated at a gas temperature of 2200 K. Fig. 3.23 presents the normalized intensities of OH* on the left and H₂O* on the right. It is observed that, for OH*, the intensity peaks between R and P at lower mole fractions. In contrast, as the mole fraction increases, lines in higher rotational quantum numbers become more pronounced. Similar observations have been reported in the literature [45]. For H₂O, the spectral distributions are unaffected by concentration.

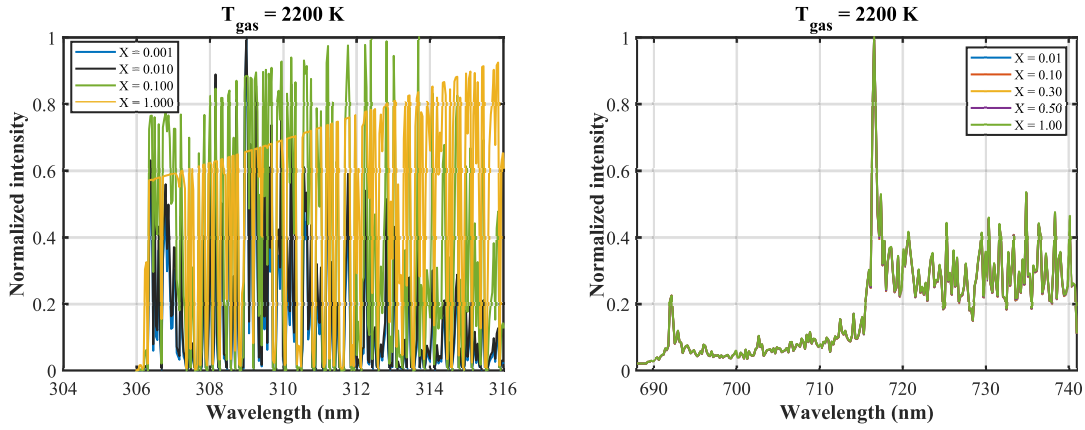


Figure 3.23: Normalized intensity profiles OH* (left) and H₂O* (right) for varying mole fractions and at a gas temperature of 2200 K.

The emission intensity from a rotational level is proportional to the product of the density in that level and the Einstein A coefficient of the observed line. Thus, the number density ($n_{J'}$) can be obtained by [46]

$$I_{J'J''} \propto n_{J'} A_{J'J''} \nu_{J'J''} \quad (3.6)$$

$I_{J'J''}$ = intensity distribution of rotational population distribution,
 $\nu_{J'J''}$ = frequency of the transition from rotational level J' to level J'' ,
 $A_{J'J''}$ = transition probability

Fig. 3.24 shows the temperature obtained from the spectral fitting of OH. It was observed that a very high temperature was required to achieve a good match between experiments and simulations. To validate our results, we performed simulations with LIFBASE [29] and obtained the same results. The temperature increases from the base of the flame, attains a peak of around 8 mm, and then decreases along the contour.

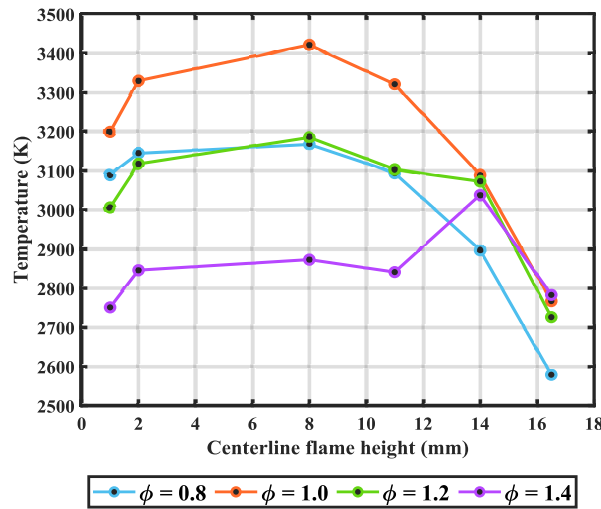


Figure 3.24: Temperature profiles derived from OH* spectra.

A non-equilibrium between the ground and excited states would necessitate such high temperatures. A larger population of higher- J states can lead to non-distribution. The low J states are expected to be in a Boltzmann distribution. The nascent rotational population distributions primarily depend on rotational energy transfer (RET) and effective lifetimes. RET governs the thermalization rate of the rotational population distribution. The RET time scale is around 0.2 to 0.6 ns in H_2O . If H_2O is considered one of the important quenching partners of OH, it has a quenching time of 0.5 ns. It is observed that the quenching rate is nearly equal to the RET rate, thereby preventing thermalization of OH. The effective lifetime τ is the time required for radiative decay, and it depends on the Einstein coefficient $A_{J''J'}$, collisional quenching $k_{q,i}$ and predissociation rates A_{pd} . The quenching rate of air is 1.3 ns, while H_2O is 0.5 ns, leading to τ of 0.8 ns and 0.2 ns, respectively. The radiative lifetime is comparable to the quenching timescale of H_2O and is shorter in the air. Therefore, multiple collisions can occur before decay, leading to non-equilibrium. [46]

$$\tau = \sum_{J''} \frac{h\nu_{J''J'}}{A_{J''J'} + \sum_i k_{q,i}\nu_{J'}n_i + A_{pd}} \quad (3.7)$$

Here, $\nu_{J''J'}$ is the frequency of the transition from rotational, level J' to level J''

Therefore, it is important to note that the temperatures obtained by OH spectra are apparent and do not represent the kinetic gas temperatures.

Fig. 3.25 shows the mole fraction profiles of OH obtained from the spectra. It was observed that the OH mole fraction increases from the burner rim, peaking at approximately 2 mm, before decaying further. These measurements complement the previous chemiluminescence measurements and show a good correlation between the excited and ground states.

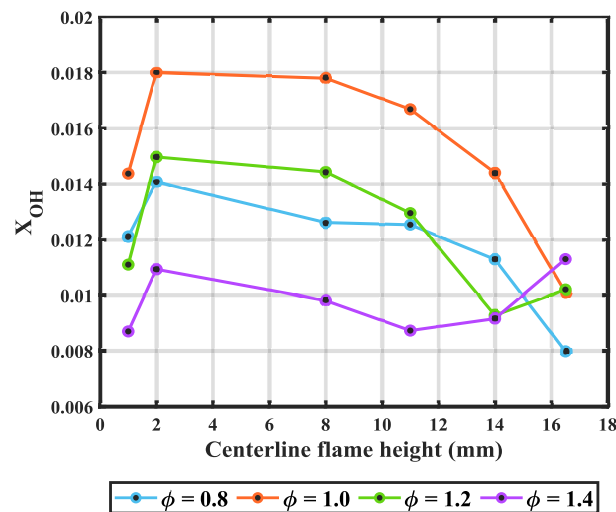


Figure 3.25: Mole fraction profiles derived from OH* spectra.

A spectral fitting with H_2O was performed to determine gas temperatures. Fig. 3.26 represents the temperature profiles of H_2O varying across the flame. The maximum flame temperature increases along the flame contour as the heat-release rate increases. The temperature plots show an increasing trend with increasing flame height. For lean mixtures, the temperature increase along the flame appears less consistent, likely due to weaker reaction zones and enhanced sensitivity to local flow variations. Near the base of the flame, the temperature decreases by approximately 2 mm, primarily due to heat loss to the burner's rim. At the base of the flame, preferential diffusion can lead to a local enrichment of fuel, resulting in higher local equivalence ratios and thus elevated temperatures in lean mixtures.

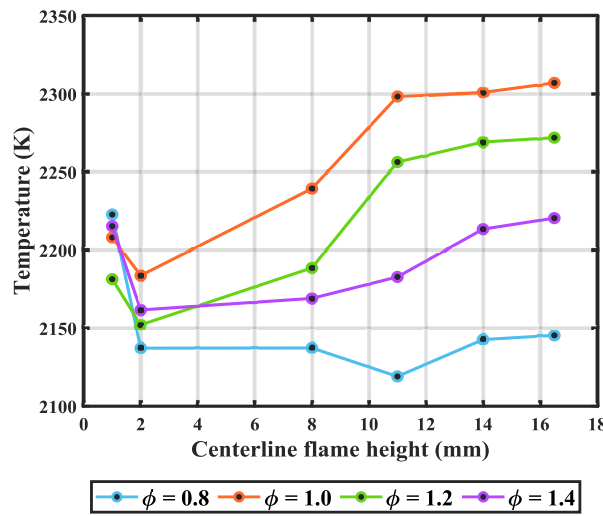


Figure 3.26: Temperature profiles derived from H_2O^* spectra

The experimentally determined mole fractions of OH at the peak location at 2 mm were compared against values predicted by 1D numerical simulations. While for H_2O , the temperature profiles in the burnt gas region of experiments at height = 19 mm are compared with the temperature profiles in the burnt gas region of simulations. A good agreement

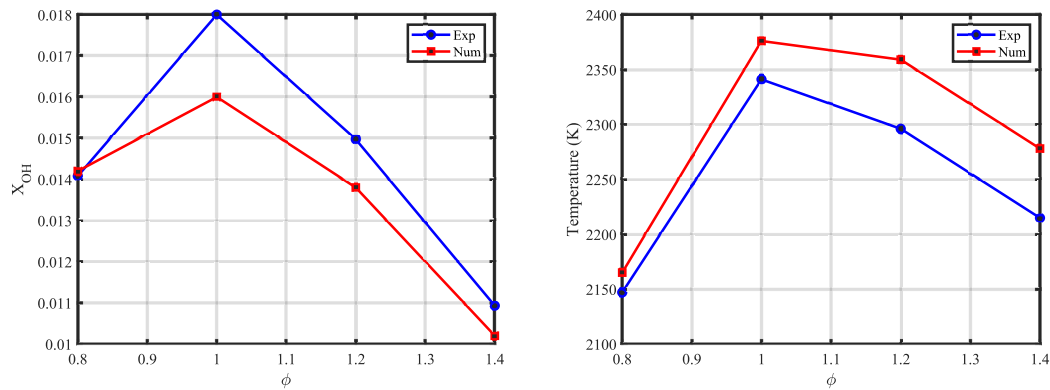


Figure 3.27: Comparison of profiles of OH mole fraction (left) and H_2O temperature (right) between experiments and numerical simulations as a function of ϕ

between the experiments and simulations is evident. Although the experiments slightly overpredict X_{OH} and underpredict the temperature profiles, the average errors between experiments and simulations for both profiles are less than 9% and 2%, respectively. Therefore, in general, OH provides a measure of local radical concentration, whereas H_2O serves as an equilibrium tracer for temperature.

3.11 A study on blue emission

Hydrogen flames are generally expected to be colourless, but they emit a characteristic blue emission. While ultraviolet radiation and water vapour in the infrared are important emissions in the flames, the distinctive blue colour makes these emissions particularly interesting to study. Several studies [13, 14, 15] in the past have indicated



to be the main reactions contributing to this blue emission. Recent studies by Jo et al. [17] also indicated that blue emission can be affected by OH, H_2 , O_2 and O. Building on existing knowledge, we have attempted to investigate the blue emission in hydrogen flames, focusing on its origin and identifying the possible contributing species responsible for this characteristic radiation. Visible imaging and spectroscopic measurements were conducted to analyse this emission in detail.

3.11.1 Visible imaging

Fig. 3.28 represents the visible images obtained from the colour camera. The flame zone appears to be blue, while the post-combustion zone appears to be reddish. A prominent reaction zone, along with a darker hue, is observed in both the blue and red regions for lean mixtures and becomes slightly paler as the equivalence ratio increases. The flame zone appears to broaden and blunt, while the post-combustion zone becomes much longer and broader. A secondary diffusion flame, surrounding the premixed cone, is also observed and becomes prominent in rich conditions.

The RGB components were further extracted from the digital images for analysis. Fig. 3.29 left shows the extraction of RGB components at $\phi = 1.4$, while the right quantifies the mean emission intensity per pixel shown as a function of equivalence ratio for both the flame-front and post-flame regions in hydrogen flames. The flame-front region, corresponding to the visually blue core, exhibits a steady increase in intensity from $\phi = 0.6$ to 1.0, peaking near stoichiometric conditions. This trend reflects enhanced chemical activity and higher populations of excited radicals in the reaction zone under optimal fuel–oxidizer balance, beyond $\phi = 1.0$, the flame-front intensity decreases. In contrast, the post-flame region,

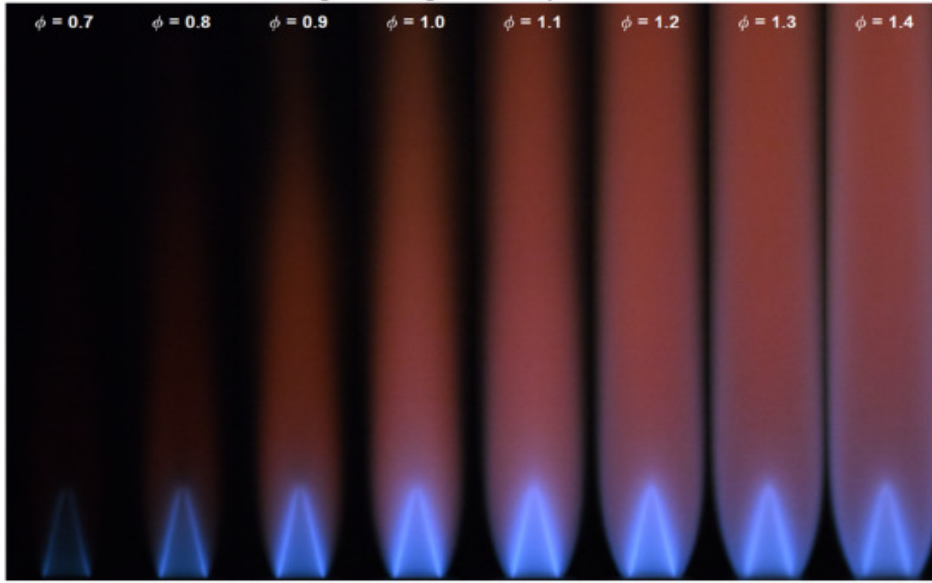


Figure 3.28: Digital images of H₂ - air flames.

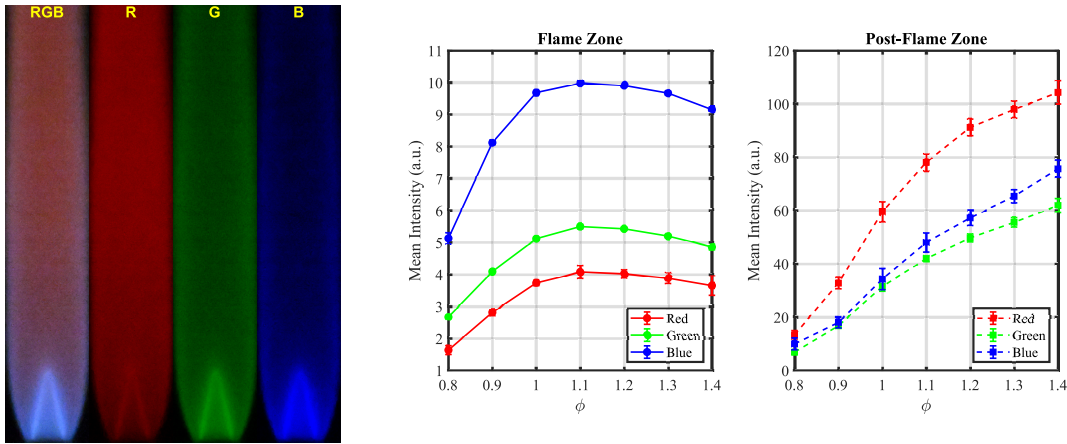


Figure 3.29: RGB component separation at $\phi = 1.4$ (left), mean intensity in flame and post-flame zones across varied ϕ (right).

corresponding to the reddish zone above the flame front, shows a continuous increase in mean intensity with equivalence ratio. This increase becomes more pronounced under rich conditions, where broadband emission and post-flame recombination processes dominate. The post-flame region captures emission that persists longer than the brief flame-front signal, resulting in higher integrated intensities in the longer-wavelength channels. These observations indicate that the RGB channels primarily reflect broadband, camera-weighted emission rather than species-specific chemiluminescence.

3.11.2 Spectral measurements

The spectroscopic measurements were performed using a diffraction grating with 300 grooves/mm, and the spectra were recorded in the blue region of the visible spectrum, spanning wavelengths between 380 and 500 nm. Fig. 3.30 shows the intensity distribution

across the wavelength as a function of equivalence ratios, and in B, the distributions across various heights at $\phi = 1$. In terms of absolute intensity, the signal is lowest at $\phi = 0.8$, increases with the equivalence ratio, and reaches a maximum under stoichiometric conditions. As the mixture becomes fuel-rich, the intensity decreases progressively. With respect to the axial distance, the intensity peaks near the base of the flame and then decreases with increasing height above the burner. Overall, the intensities peak near stoichiometric conditions and decay rapidly away from the flame base.

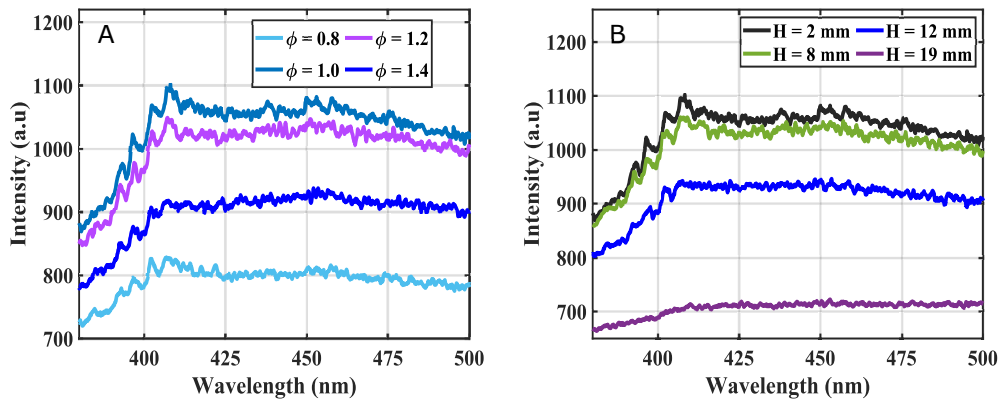


Figure 3.30: Blue emission profiles: A - as a function of equivalence ratios, B - as a function of axial heights at $\phi = 1$.

The spectroscopic measurements revealed a broadband continuum with distinct peaks at wavelengths of 384.65, 392.71, 396.65, 402.18, 407.55, and 409.27 nm. Additional peaks were detected within the broadband at 413.21, 418.41, 421.24, 429.11, 438.30, 440.26, 442.46, 450.50, 452.96, 457.66, and 461.80 nm. The broad spectral component arises from the combined emissions of several radicals and thermal radiation. A detailed analysis of different radicals is presented here to investigate their contributions to the signal. Studies have suggested that atomic hydrogen Balmer series transitions, specifically $H\delta$ near 410 nm and $H\gamma$ near 434 nm, contribute to the blue emission spectrum [13]. Corresponding atomic oxygen emission lines are also present at 384.78, 392.65, 407.58, 409.29, 413.28, 418.54, and 429.12 nm, as catalogued by NIST [31]. From LIFBASE [29], some OH emission lines were noted at 384.70, 392.83, 392.73, 393.35, 397.65, 403.79, 451.00, and 457.70 nm. Important species and their relevant transition bands, including fundamental bands for NH and CO, are taken from the atlas by Barrow and Rosen [47] and are summarized in Tab. 3.4. H_2O exhibits spectral bands between 380 and 500 nm and is sourced from the HITEMP database [34]. Its emission intensity increases with flame height, unlike the pattern observed for blue emission, indicating minimal H_2O influence on this spectral region. Some studies have reported the presence of H_2O_2 in the visible region [48], which may also contribute.

Wavelength (nm)	Species	Transition	v', v''
392.54	N ₂	$C^1 \rightarrow B^3\Pi_g$	0, 8
396.98	NO	$B^2\Pi \leftrightarrow X^2\Pi$	2, 13
402.10	O ₂	$B^3\Sigma_u^- \leftrightarrow X^3\Sigma_g^-$	0, 18
438.30	CO	$C^1\Sigma^+ \rightarrow A^1\Pi$	0, 3
450.02	NH	$C^1\Pi \rightarrow b^1\Sigma^+$	0, 0
451.09	CO	$B^1\Sigma^+ \rightarrow A^1\Pi$	0, 0
450.32	NH	$C^1\Pi \rightarrow b^1\Sigma^+$	0, 0
457.43	N ₂	$C^3\Pi_u \rightarrow B^3\Pi_g$	1, 6

Table 3.4: Summary of emission lines with assigned transitions.

Studies by Cole et al. [49] have indicated that trace amounts of CO and CO₂ may arise in hydrogen flames due to ambient CO₂ entrainment. Atmospheric CO₂ concentration is 420 ppm, and taking that into account, we performed some equilibrium calculations, and the residual CO₂ and CO content are shown in Fig. 3.31. It is seen that the CO₂ is highest for lean mixture and gradually decreases with increasing ϕ , whereas CO content tends to increase with increasing ϕ . We conducted exhaust gas analysis to detect the CO content in our exhaust gas. In our work, CO levels in the flame exhaust increased with the equivalence ratio, reaching about 40 ppm, values were below equilibrium predictions due to experimental limitations. Notably, the intensity of both CO emissions and the blue colour of the flame increased with rising CO₂ content, suggesting that reactions involving CO and CO₂ may also contribute to this blue emission. Studies by Raposo et al. [50] indicated CO flame band emissions in the visible spectrum. Several emission peaks attributable to CO are also present within the 400 to 450 nm wavelength range derived from the atlas by Barrow and Rosen [47].

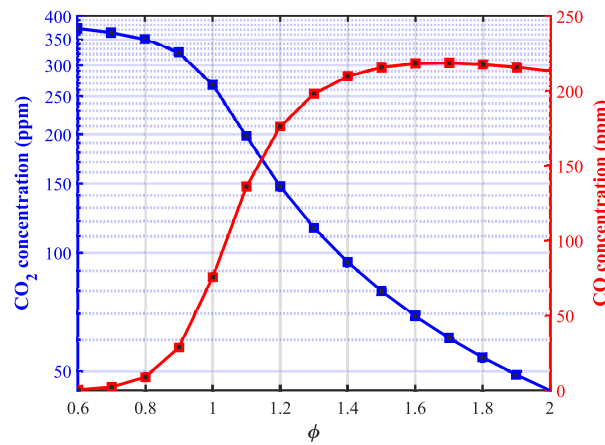


Figure 3.31: CO₂ and CO concentrations as a function of ϕ from equilibrium calculations

A comparative study was conducted by correlating experimentally observed intensities with species profiles and by evaluating numerous combinations of such profiles derived

from 1D numerical simulations. Fig. 3.32 shows the normalized mole fraction profiles across the domain computed for $\phi = 1$, and needs to be compared with the OH^* . As shown in the previous section, broadband emission appears spatially upstream of OH^* . Although the simulated $[\text{H}][\text{OH}]$ profile appears to be spatially upstream of OH^* , the absolute mole fraction profiles of these species are significantly high and hence are discarded. $[\text{OH}][\text{OH}]$ seems to be spatially downstream and of a higher magnitude; thus could be neglected. $5[\text{OH}][\text{OH}][\text{H}][\text{OH}]$ appears to be spatially offset, while the magnitude seems to agree well with OH^* . The combination of the radicals H_2 , H , O_2 , O , OH and H_2O_2 seems to have a best fit with respect to both spatially upstream of OH^* , approximately around $100\text{ }\mu\text{m}$, and slightly lower in magnitude with respect to OH^* . A combination of these species, coupled with thermal radiation, most likely tends to emit the blue emission of hydrogen-air flames.

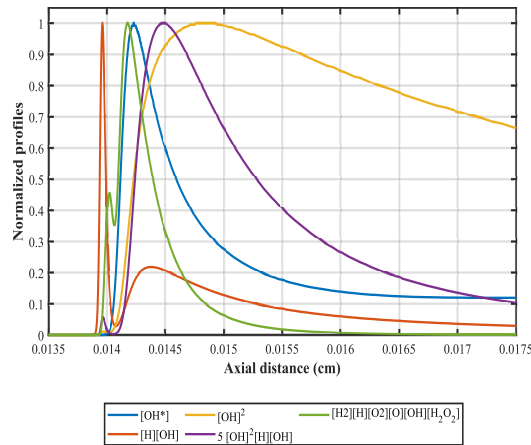


Figure 3.32: Normalized mole fraction profiles of various species at $\phi = 1$.

We examined and contrasted this blue emission with that of OH^* to assess its potential use as a flame marker. It was observed that the absolute intensities of the blue emission were substantially lower than those of OH^* . The comparison is shown for representative lean and rich mixtures at $\phi = 0.8$ and 1.4 , respectively. The intensities are measured at two locations; one at the flame front at the maximum intensity (2 mm HAB) and the other in the post-combustion gases at (19 mm HAB). The intensities of the post-combustion gases are normalized by intensities at the flame front and are shown in Fig. 3.33, where the left is OH^* and the right is blue emission. For both mixtures, the intensity peaks at the flame front. In the case of OH^* , the post-combustion intensities are below 0.2, whereas for the blue emission, they reach up to 0.75. Thus, blue emission has a much greater contribution from post-combustion gases and can, therefore, be excluded as a candidate for flame marking.

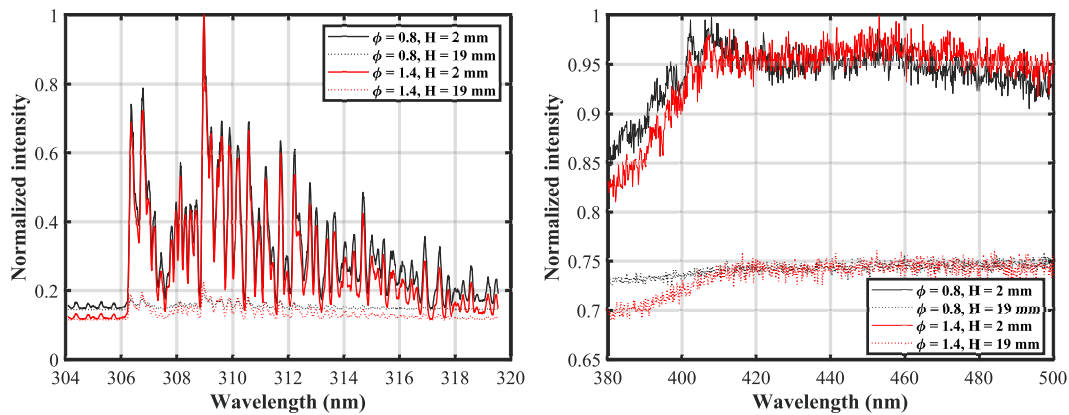


Figure 3.33: Normalized intensity profiles at HAB 2 and 19 mm, and $\phi = 0.8$ and 1.4. Left : OH*, Right: Blue

3.12 Conclusions

High-resolution chemiluminescence imaging combined with spectroscopy was used to investigate spectral and spatial signatures in premixed H₂-air flames, as the equivalence ratio was systematically varied. The present work aimed to characterize the emissions of key species in a laminar premixed flame, along with a combination of spatially and spectrally resolved measurements of temperature, species mole fractions, and blue flame emission, and to analyze the distributions of these quantities. These measurements allowed for a comprehensive assessment of flame structure, radical distribution, and the spatial characteristics of chemiluminescence.

The key conclusions from this study are:

- From the spectral and spatial measurements, it is observed that the flame structure and emission behaviour of premixed hydrogen-air flames are strongly dependent on the equivalence ratio. The experimental observations reveal that, under lean and near-stoichiometric conditions, emissions are distributed in a premixed cone, whereas as the equivalence ratio increases beyond stoichiometric, a diffusion-branching regime is observed accompanying the premixed cone. This transition reflects the interplay between fuel availability and local reaction dynamics.
- The chemiluminescence measurements indicate that preferential diffusion significantly influences radical distributions across the reaction zone. Coupled with stretch and curvature effects, these phenomena induce local deviations in radical distributions. The emission characterization across the flame front and postcombustion gases denoted the presence of OH* in the postcombustion region, but not as prominently observed in the spherical flames as seen in the previous chapter, due to considerably lower temperatures in this configuration. NO* intensities are considerably higher in post-combustion gases with respect to OH*.
- Spectroscopic analysis quantified OH mole fractions and gas temperatures from

H₂O emissions, respectively, enabling characterization of species concentrations and temperature fields. Due to the nonequilibrium nature of OH*, the emission spectra cannot be used to determine gas temperature.

- The blue emission in the flame was investigated and interpreted as resulting from a combination of multiple chemiluminescent species. This broadband chemiluminescence accounts for the characteristic blue colour of hydrogen flames. The significant presence of emissions in post-combustion gases precludes the use of blue emissions for flame marking.

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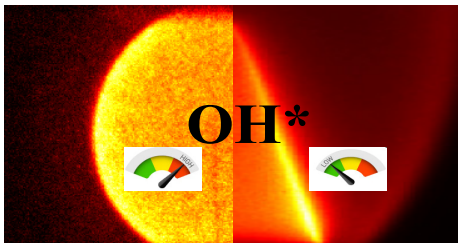
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4 Summary



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This chapter provides an overview of the thesis, summarizing its main findings. It outlines the implications of these results for our understanding of OH* chemiluminescence. Finally, perspectives and directions for future research are presented.

4.1 Overview

Hydrogen combustion has become a major focus as an important technology for future low-carbon energy systems. It offers high energy density and wide flammability limits. However, using hydrogen as a fuel poses various challenges related to flame stability, safety, combustion efficiency, and accurately describing reactive flame structures across different operating conditions. To develop reliable and efficient hydrogen-based combustion systems, it is crucial to understand how hydrogen flames behave under different pressures, temperatures, and mixture compositions.

In this thesis, firstly, we investigated the OH* emission characteristics in a laminar premixed H₂ - air flames. Experiments were conducted in spherically expanding flame configurations, which enabled the study of flame evolution over a wide range of equivalence ratios, pressures, and temperatures. High-speed chemiluminescence imaging was employed to capture temporally and spatially resolved OH* signals. The emissions were characterized across the flame front and the burnt gas zones, and the intensity ratios across these two zones were computed. These measurements were complemented by detailed 1D simulations in FlameMaster using different chemical kinetic mechanisms, allowing for direct comparison between experiments and simulations.

In addition to the enclosed flame configurations, this work was further extended to a Bunsen burner, where OH* chemiluminescence was studied at atmospheric pressure and ambient temperature. High-speed imaging and spectroscopic measurements were performed to capture OH*. The study also investigated additional chemiluminescent emissions, including NO* and blue emissions associated with H₂-air flames. Spectral modelling was conducted to obtain the mole fractions and rotational temperatures of OH*.

Overall, through this work, we aimed to deepen the understanding of hydrogen flame dynamics through chemiluminescence diagnostics.

4.2 General Conclusions

The results of this study show that OH* chemiluminescence exhibits pronounced spatial variation across different flame zones, with chemical excitation dominating at the flame front and thermal excitation contributing primarily in the burnt gas region. This distinction plays a critical role in interpreting OH* as a flame diagnostic. In open flame configurations, such as Bunsen burners, OH* remains a reliable flame marker. However, in closed configurations, its applicability must be carefully evaluated under different operating conditions. The analysis further demonstrates that OH* emission is strongly influenced by mixture composition, pressure, and temperature. Under very lean or highly rich conditions, OH* continues to serve as an effective flame marker, while at elevated pressures, the contribution from the burnt gas region is substantially reduced. At lower burnt gas temperatures, OH* retains its diagnostic usefulness provided that excitation mechanisms are properly considered. The assessment of the predictive accuracy of OH* sub-mechanisms appears to be more effective when using Kathrotia.

4.3 Outlook

The following are some of the future works that can be pursued in relation to the current study:

- The interactions of diffusion branching with the premixed cone and the OH* distribution for rich mixtures, for example, by diluting with nitrogen, are of interest.
- The usage of OH* as a flame marker at higher pressures and temperatures in turbulent configurations needs to be evaluated.
- Quantitative analysis of OH* in the burnt gas and NO* overall is needed and this could be useful to further develop kinetic mechanisms.
- Blue emissions need to be further assessed through spatial and spectral studies targeting species-specific wavelengths, like for HO₂ or H₂O₂. Firstly, the emission wavelengths of these species need to be obtained. Currently, data on H₂O₂ is limited to 410 nm. Quantum calculations are needed to compute the wavelengths and rate constants to further interpret the possible reactions.

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Évaluation de l'OH* comme marqueur de flamme dans les flammes
prémélangées H₂ - air

Cette thèse propose une étude approfondie de la chimiluminescence du radical OH* dans les flammes d'hydrogène prémélangées laminares, en couvrant une large gamme de rapports d'équivalence, de pressions et de températures. L'objectif est d'évaluer son utilisation comme marqueur de flamme. Des études expérimentales sont d'abord menées à l'aide de flammes à expansion sphérique. Les intensités de OH* sont caractérisées à travers le front de flamme et la zone des gaz brûlés, révélant une émission significative dans les gaz brûlés attribuable à l'excitation thermique. Les observations expérimentales sont comparées à des simulations numériques 1D, apportant de nouvelles perspectives sur la chimie des flammes d'hydrogène et soutenant l'affinement ainsi que le développement de mécanismes cinétiques détaillés. L'investigation s'étend ensuite aux flammes de brûleur Bunsen, permettant une analyse approfondie de la dynamique globale de la flamme et une caractérisation détaillée de la zone de réaction sous différentes configurations. De plus, on utilise une modélisation spectrale pour extraire les températures de rotation et les fractions molaires d'OH, ce qui fournit des informations quantitatives sur la structure de la flamme et sur son état chimique.

Mots-clés : Chimiluminescence du radical OH*, Hydrogène, Flammes à expansion sphérique, brûleur type Bunsen, Excitation thermique, Spectroscopie à haute résolution.

Assessment of OH* as a flame marker in premixed H₂ - air flames

This thesis presents a comprehensive investigation of OH* chemiluminescence in laminar premixed hydrogen flames over a wide range of equivalence ratios, pressures, and temperatures to evaluate its usage as a flame marker. Experimental studies were initially conducted using spherically expanding flames, with OH* intensities characterized across the flame front and burnt gas zone, revealing significant emissions in the burnt gas attributable to thermal excitation. The experimental observations are compared with 1D numerical simulations, providing novel insights into hydrogen flame chemistry and supporting the refinement and development of detailed kinetic mechanisms. The investigation is further extended to the Bunsen burner, enabling a thorough analysis of global flame dynamics and detailed characterization of the flame zone under different configurations. Additionally, spectral modelling is employed to extract rotational temperatures and OH mole fractions, providing quantitative information on the flame structure and chemical state.

Keywords: OH* chemiluminescence, hydrogen, spherically expanding flames, Bunsen burner, thermal excitation, high-resolution spectroscopy.



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