EFFECTS OF RADIATIVE EMISSION AND ABSORPTION ON THE PROPAGATION AND EXTINCTION OF PREMIXED GAS FLAMES

YIQUANG JU, GORO MASUYA AND PAUL D. RONNEY

1Department of Aeronautics and Space Engineering
Tohoku University
Aoba-ku, Sendai 980, Japan
2Department of Aerospace and Mechanical Engineering
University of Southern California
Los Angeles, CA 90089-1453, USA

Premixed gas flames in mixtures of CH₄, O₂, N₂, and CO₂ were studied numerically using detailed chemical and radiative emission-absorption models to establish the conditions for which radiatively induced extinction limits may exist independent of the system dimensions. It was found that reabsorption of emitted radiation led to substantially higher burning velocities and wider extinction limits than calculations using optically thin radiation models, particularly when CO₂, a strong absorber, is present in the unburned gas.

Two heat loss mechanisms that lead to flammability limits even with reabsorption were identified. One is that for dry hydrocarbon-air mixtures, because of the differences in the absorption spectra of H₂O and CO₂, most of the radiation from product H₂O that is emitted in the upstream direction cannot be absorbed by the reactants. The second is that the emission spectrum of CO₂ is broader at flame temperatures than ambient temperature; thus, some radiation emitted near the flame front cannot be absorbed by the reactants even when they are seeded with CO₂. Via both mechanisms, some net upstream heat loss due to radiation will always occur, leading to extinction of sufficiently weak mixtures. Downstream loss has practically no influence. Comparison with experiments demonstrates the importance of reabsorption in CO₂-diluted mixtures. It is concluded that fundamental flammability limits can exist due to radiative heat loss, but these limits are strongly dependent on the emission-absorption spectra of the reactant and product gases and their temperature dependence and cannot be predicted using gray-gas or optically thin model parameters. Applications to practical flames at high pressure, in large combustion chambers, and with exhaust-gas or flue-gas recirculation are discussed.

Introduction

Flammability limit studies are important for assessing fire safety in many environments and for determining the operation limits of combustion devices. Despite many years of study, the mechanisms that cause apparatus-dependent extinction limits including flame stretch [1, 2], buoyant convection [3, 4], and heat losses to cold walls [5–7], have not been well understood. In particular, it has not been established whether “fundamental” limits exist independent of apparatus size and geometry. Many mechanisms cause apparatus-dependent extinction limits including flame stretch [1, 2], buoyant convection [3, 4], and heat losses to cold walls [5–7]. When these losses are eliminated by employing large combustion vessels at microgravity, heat losses via gas radiation is probably the dominant extinction mechanism [8–11].

Nevertheless, it is unclear whether radiative loss affects fundamental limits because emitted radiation can be reabsorbed, a factor not considered by the theories [6, 7] and computations [10, 11]. Whether reabsorption is important is usually assessed by comparing the system dimension to the burned-gas mean Planck absorption length (Lp), defined as the mean monochromatic absorption coefficient (κ) weighted by the Planck function:

\[ L_p = \int_0^\infty \kappa(u)G(u)du; \]

\[ G(u) = \frac{15}{\pi^2} \left( \frac{u}{e^u - 1} \right); \quad u = hcω/kT \]  

where h, c, ω, k, and T denote Planck’s constant, light speed, wavenumber, Boltzmann’s constant, and temperature, respectively. In the experiments in Refs. [8, 9], the optical thickness τ = X/Lp, where X is an apparatus dimension, was generally small (with exceptions noted later), consequently optically thin conditions (no reabsorption) applied. Theoretical studies of premixed-gas flames seeded with inert particles [12] predict that with reabsorption, net heat losses decrease, burning velocities (S_b) increase, and the flammability limit equivalence ratio (Φ_d) decreases compared with values without reabsorption.
Corresponding microgravity experiments in particle-laden methane-air mixtures [13] support these predictions. Gaseous flame behavior should be different from that of particle-laden flames because gases emit and absorb in spectral bands, whereas particles exhibit approximately gray-gas behavior. No computational studies of gaseous flames with detailed radiative emission/absorption models have been performed to test their effects on $S_0$ and $\phi_0$. Consequently, our goal is to model premixed-gas flame propagation with detailed radiative emission/absorption effects and compare results with experiments and theoretical predictions.

In addition to microgravity studies, modeling of premixed-gas flames with reabsorption is relevant to combustion at high pressures and in large furnaces because frequently $\tau > 1$. For example, at 40 atm, a typical pressure for premixed-charge internal combustion engines, $\tau \approx 1$ for cylinders of radius 4 cm. Similarly, $\tau > 1$ in atmospheric-pressure furnaces larger than 1.6 m. Moreover, significant amounts of absorbing CO$_2$ and H$_2$O are present in the unburned mixtures of combustion devices employing exhaust-gas or flue-gas recirculation.

**Numerical Model**

The energy and chemical species conservation equations for steady planar premixed-gas flames were solved using a CHEMKIN-based code [14] with arc-length continuation [15,16]. This code was employed previously to model optically thin radiating counterflow flames [16]. For this study, radiative transport including both emission and absorption was computed using the statistical narrowband model with exponential-tailed inverse line strength distribution [17]. The radiative transfer equations were solved for wavenumbers between 150 and 9300 cm$^{-1}$ with 25 cm$^{-1}$ resolution using the S6 discrete ordinate method. Radiation parameters for CO$_2$, H$_2$O, and CO were taken from Ref. [18]. CH$_4$ radiation was not included because the necessary spectral data were not available, but CH$_4$ radiation is minimal even for optically thin conditions [11]. Further details of the model, including accuracy considerations, are presented elsewhere [19]. Methane oxidation was modeled using an 18-species, 58-step chemical mechanism [14]. The spatial position ($x$) = 0 was defined as the location where $T = 325$ K for radiation-free flames. Except where noted, the upstream and downstream boundary locations were $x = -L_1 = -30$ cm and $x = +L_2 = +400$ cm, respectively. Upstream boundary conditions were ambient temperature (300 K), and composition with inflow velocity $S_1$ and downstream boundary conditions were zero-gradient. Ambient-temperature blackbody walls were assumed at both boundaries.

Mixtures of CH$_4$ + (0.21O$_2$ + (0.79 - $\gamma$)N$_2$ + $\gamma$CO$_2$) were examined, with $\gamma$ varied to assess reabsorption effects by substituting emitting/absorbing CO$_2$ for radiatively inactive N$_2$. Ambient H$_2$O was not considered because experiments at standard conditions allow at most 3% H$_2$O without condensation.

**Results**

Figure 1 shows typical computed results. For optically thin conditions, the volumetric radiative loss ($Q_p$) = $4\pi (T^4 - T_0^4)/L_p$, where $\pi$ is the Stefan-Boltzmann constant and $T_0$ the ambient temperature, is always positive (upper plot). With reabsorption, $Q_p$ is negative at $x < 0$ because some radiation emitted at high $T$ ($x > 0$) is reabsorbed at lower $T$ ($x < 0$). This decreases the net loss and preheats the unburned mixture so that, consistent with the theory in Ref. [12], the peak temperature ($T_p$) exceeds adiabatic ($T_{ad}$). With optically thin radiative loss, $T$ decays downstream to $T_0$ (lower plot). With reabsorption, $T$ still decays downstream (but on a much longer scale); thus, some net loss still occurs. All flames exhibit conventional convective-diffusive zones of thickness $\delta = a/S_1 = 0.1$ cm, where $a$ is the temperature-averaged thermal diffusivity. The reabsorbing flame additionally exhibits a much longer upstream convective-radiative zone (lower plot) whose length is comparable to $L_p$ ($\approx 19$ cm).

Fig. 2a shows that reabsorption effects in CH$_4$/air mixtures ($\gamma = 0$) are minor because $\phi_0$ is reduced.
Radiative reabsorption effects on premixed flames

For optically thin radia-

tion, reabsorption nar-
rowband
ine strength
er equa-
tions 50 and 9300
86 discrete
rs for CO,
6. CH4 ra-
cessarv spec-
ration is
9. Fur-

racy eonsld.
lethane
ies. 58-step
osition ,xJ =
325 K for
ed. the up-
ons were
ations were
osition with
mary con-
temperature
urs.
- gN2 +
ss reab-
absorbing
H2O was
standard
it condens-

\[ \text{Fig. 3. Radiative properties of combustion gases as a function of wavenumber (}\lambda\text{)}. (a) Absorption coefficients}\ x(\lambda)\text{for pure CO2 and H2O at 1300 K and 300 K. (b) Radiative heat flux at cold (upstream) boundary for}\ \Phi =
0.50, \gamma = 0.30 (t = 2.39)\text{with reabsorption effects included. Note that the units on the vertical axes are W/m}^2\text{per m}^{-1} = \text{Wm}^-1\text{per unit wavenumber. Also shown is}\ \pi_T\text{where}\ \pi_T\text{is the Planck function for a blackbody at} \ T^*\text{for this flame (i.e., the maximum possible flux).}\]

3.8% and, even with reabsorption $S_I$, is always
than the adiabatic burning velocity ($S_{I,ad}$). How-
S_{I,lim}$ is reduced by 25%, and $S_{I,ad}$ for the limit
x increases similarly (26%). For both optically
and reabsorption models. $S_{I,lim}/S_{I,ad}$ is close to
theoretical prediction $e^{-1/2}$ [6,7]. A simple pic-
emerges from these results. Radiation from hot
O and CO2 can escape only if it is emitted up-
stream, because downstream radiation will be reab-
rased by other H2O and CO2 molecules. Thus,
absorption approximately halves the net heat loss.
ary for optically thin flames [6,7] predicts $S_{I,lim}$
29%. Consequently, the classical quenching
mechanism approximately applies in this case.

\[ \text{Fig. 2. Predicted burning velocities and peak flame tem-
peratures under adiabatic conditions, with optically thin
ative losses and with a radiative model including reab-
ption effects. In this and subsequent figures, the turn-
point limit is shown, but for clarity, the unstable lower
ation branch is omitted. (a) Lean CH4-air mixtures. (b)
CH4(0.21O2 + 0.49N2 + 0.30CO2) mixtures (t =
3.8b). As with $\gamma = 0$, for optically thin radia-
tion, $S_I$ and $T$ are lower than adiabatic values,
but with CO2 substitution, because of reabsorption,
these quantities are significantly higher than adia-
atic values. The effect on $\Phi_0$ is substantial (0.682
for optically thin conditions vs. 0.442 with reab-
sorption). Nevertheless, flammability limits still exist.

Figure 3 elucidates two mechanisms that cause net
heat loss and thus flammability limit properties: equivalence ratio ($\Phi_0$) and burning velocity ($S_{1,\ln}$) for $\gamma = 0.20$. The corresponding flammability limit for optically thin conditions is $\Phi_0 = 0.62$.

FIG. 4. Effect of upstream domain length ($L_1$) on flammability limit properties: equivalence ratio ($\Phi_0$) and burning velocity ($S_{1,\ln}$) for $\gamma = 0.20$. The corresponding flammability limit for optically thin conditions is $\Phi_0 = 0.62$.

Mechanism II is because $x(t_0)$ heat absorption and unburned-gas absorption effects on the absorption spectrum and cannot be predicted via simple mean absorption coefficients, as optically thin limits can. Of course, if sufficient quantities of inert particles, soot, or other quasi-graybody absorbers are present, complete reabsorption could occur.

Loss at the downstream boundary ($x = L_2$) is much less important for several reasons. A disappearing reactant (e.g., CH$_4$) can produce some loss at $x = L_2$ via mechanism I, but CH$_4$ radiation was not considered, and the loss would be much less than the upstream H$_2$O and CO$_2$ loss because CH$_4$ disappears near $x = 0$ just as $T$ rises to values where significant radiation could be emitted. Some downstream loss via mechanism II can occur because of the downstream temperature gradient, but the gradient and total decrease in $T$ are much less than the corresponding upstream values, leading to much lower downstream loss. A third mechanism of radiative loss occurs at the downstream boundary because of the blackbody wall with $T = T_0$, but due to reabsorption, its influence is confined to the adjacent region of thickness $L_p$ ($=18$ cm). Thus, $T_*$ and $S_*$ are unaffected, as was verified by changing $L_2$ from 400 to 100 cm.

Losses via mechanisms I or II can occur only for wavenumbers where $\kappa(\omega)$ is nonzero on one side of the flame but changes to zero over a length smaller than the scale $(\kappa(\omega))^{-1}$ over which reabsorption occurs. Changes occur on the scale $\delta$ for temperature and $D/S_1$ for species $i$, where $D_i$ is the diffusion coefficient. Because the Lewis numbers $\alpha_i/D_i$ are close to unity, $\delta$ is an appropriate scale for both species and temperature changes. Hence, these criteria become

$$I: \quad \frac{d\chi}{dx} > \frac{d\chi}{d(1/\kappa(\omega))} \Rightarrow \frac{d\ln(\kappa(\omega))}{d\ln(\chi)} > \kappa(\omega)\delta = \kappa(\omega) < 1$$

$$II: \quad \frac{dT}{dx} > \frac{dT}{d(1/\kappa(\omega))} \Rightarrow \kappa(\omega)\delta < \frac{d\ln(\kappa(\omega))}{d\ln(T)}$$

where $\chi$ is the mole fraction of species $i$ and the fact $\kappa = \chi_i$ has been used. Fig. 3b shows evidence of these criteria. The loss due to H$_2$O mimics $\kappa(\omega)$ except where $\kappa(\omega)$ is very large and reabsorption can occur within the convective-diffusive zone where $X_{H_2O}$ changes rapidly. For CO$_2$, practically no loss occurs where $\kappa(\omega)$ is large at both 300 K and 1300 K (Fig. 3a), but substantial loss occurs for $\omega$ on the "wings" of these peaks where $dv/dT$ is large.

The convective-radiative zone at $x < 0$ has a characteristic thickness $L_p \gg \delta$; thus, $L_1$ can influence reabsorbing flames drastically. Fig. 4 shows that $\Phi_0$ decreases as $L_1$ increases because more reabsorption (thus lower net $Q_k$) occurs with larger $L_1$. Because $S_{1,\ln} \sim Q_k^2$, $S_{1,\ln}$ also decreases. Significant reabsorption effects occur even for $L_1 = 1$ cm ($\gamma = 0.054$) because CO$_2$ has absorption bands with $\kappa(\omega)$ up to 4000 m$^{-1}$ atm$^{-1}$ (40 cm$^{-1}$ atm$^{-1}$) (Fig. 3a). For the limit conditions at $L_1 = 1$ cm, $X_{H_2O} = 0.19$, thus, significant absorption occurs on the scale $(0.190 \times 40$ cm$^{-1})^{-1} = 0.13$ cm. This estimated
Radiative reabsorption effects on premixed flames

Fig. 5. Effect of substitution of CO$_2$ for N$_2$ on burning velocities under adiabatic conditions, with optically thin reabsorption losses, and with a radiative model including reabsorption effects.

Second, $\Phi = 0.5$ mixtures have much higher Boltzmann numbers ($B$), which is a scaled ratio of blackbody emissive power at $T_a$ to total heat release rate and thus measures the potential for radiative preheating to increase $S_1$. For nonscattering media $[12]$

$$B = \frac{\beta (T_a^4 - T_o^4)}{2\rho_0 S L_{ad} \varepsilon T_a} = \frac{E}{RT_a}$$

where $\beta$, $E$, $R$, $\rho_0$, and $\varepsilon$ represent nondimensional activation energy, overall activation energy, gas constant, ambient density and specific heat, respectively. Values of $B$ for $\gamma = 0$ mixtures are about 11.3 and 127 for $\Phi = 1.0$ and 0.50, respectively; thus, reabsorption can increase $S_1$ much more in $\Phi = 0.5$ mixtures.

Figure 6a shows that, for optically thin conditions, CO$_2$ substitution increases $\Phi_o$ and $S_{L,ad}$ because the additional radiating CO$_2$ increases $Q_R$. With reabsorption, small amounts of CO$_2$ substitution actually decrease $\Phi_o$ and $S_{L,ad}$ due to greatly reduced $Q_R$, whereas larger amounts increase $\Phi_o$ slightly due to reduced $T_{ad}$. Fig. 6b shows that for optically thin conditions, $S_{L,ad}/S_{L,ad}^i$ is always close to the theoretical prediction $[6,7]$ of $20$, whereas with reabsorption $S_{L,ad}/S_{L,ad}^i$ can be greater than 20.

Figure 7 shows comparisons of our computed effects of reabsorption on $S_1$ to the theoretical prediction of Ref. [12] $S_1/S_{L,ad}^i \ln(S_{L,ad}/S_{L,ad})^i = B$ for gray gases. The theory requires that $(T_a - T_o)/T_{ad}$ be a small, $O(1/\beta)$ quantity, which is justified for our conditions (Fig. 2b). Agreement is poor because the computation allows substantial net spectral heat loss (Fig. 3b), which is not considered by the theory. Agreement is improved with H$_2$O and CO radiation suppressed (mechanism I eliminated) and still better with temperature broadening of $\kappa(\omega)$ also suppressed (mechanism II eliminated) so that the flame is practically adiabatic. Still, $S_1/S_{L,ad}$ is much lower than theoretical predictions because the theory assumes graybody radiation, whereas gases radiate only in certain spectral bands and thus accelerate $S_1$ more than graybody radiators would. When gray-gas conditions are applied ($\kappa(\omega)$ constant = 26 m$^{-1}$ $L_{ad}^4$), the agreement is more satisfactory, though calculated results are now above theoretical predictions, probably because the theory assumes constant thermodynamic and transport properties and single-step chemistry. Thus, our model is believed to capture the essential elements of flame propagation with graybody reabsorption plus the nuances of spectrally radiating gases.

Comparison with Experiment

For CH$_4$-air flames (Fig. 2a), comparison between computation and microgravity experiments in spherical expanding flames $[20,21]$ and tubes $[22]$ and earth-gravity experiments specially designed for low
while reabsorption can increase burning velocities were studied using a detailed emission-absorption mental limits independent of the system dimensions and extend flammability limits considerably, fundamentally limited by the partitioning model for H+O, COoo, and CO. It was found that effects may be important. For reabsorbing conditions has not been established, the planar results were extrapolated to zero predictions of this might explain why in Ref. [27] numerical predictions, with reabsorption the computed and experimental values of SL agree moderately well (Fig. 8). Therefore, even for these small-scale flames, reabsorption effects may be important.

Conclusions

The effects of radiation on premixed-gas flames were studied using a detailed emission-absorption model for H2O, CO2, and CO. It was found that while reabsorption can increase burning velocities and extend flammability limits considerably, fundamentally limited independent of the system dimensions.

The only relevant SL data that may exhibit optically thick conditions are microgravity spherically expanding flame experiments [9,26] in (CH4 + 4O2)+CO2 mixtures and counterflow twin-flame experiments [27] in CH4-(0.21O2 + 0.79CO2) mixtures (γ = 0.79). Neither configuration corresponds to our planar flames, but comparisons are nonetheless considered useful. To compare with Refs. [9,26], we chose L1 = L2 = 6 cm, which corresponds to a flame radius half the vessel radius. By this radius, SL was steady, yet the pressure rise in the constant-volume vessel was small (<10%). To compare with Ref. [27], we chose L1 = L2 = 0.35 cm, which corresponds to twin flames located midway between the nozzle exits and stagnation plane for 1.4-cm nozzle separation. For both experiments, ambient values of Lp are about 5.4 cm, but even for L1 = L2 = 0.35 cm, some reabsorption is anticipated (Fig. 3a).

For the configuration of Refs. [9,26], the optically thin model clearly overpredicts the limit fuel concentration (by 13%) and SLamb (by 350%); thus, reabsorption extends this limit. With reabsorption, SLamb is predicted well, indicating that the net loss is correctly predicted, but the limit fuel concentration is underpredicted (by 16%), perhaps because in spherical geometry the radiative flux divergence causes less radiative preheating than would occur in planar geometry. For the configuration of Ref. [27], no numerical solutions could be obtained for adiabatic or optically thin conditions with L1 = L2 = 0.35 cm; this might explain why in Ref. [27] numerical predictions of SL could not be obtained. In Ref. [27], results were extrapolated to zero strain to estimate the planar SL. Although the accuracy of this method for reabsorbing conditions has not been established, with reabsorption the computed and experimental values of SL agree moderately well (Fig. 8).

Exist due to the nature of gas radiation, specifically, (1) differences between the spectral characteristics of reactants and products and (2) temperature broadening of the emission/absorption spectra. The results agree well qualitatively and in some cases quantitatively with theory and experiments. In future work, we will examine stationary "flame balls," since modeling of recent space experiments [25] suggests dominant reabsorption effects in some cases. The spherically expanding flame configuration will be studied to compare with the microgravity experiments already cited [9,26]. The effects of elevated pressures will be examined because of their
RADIATIVE REABSORPTION EFFECTS ON PREMIXED FLAMES

FIG. 7. Comparison of theoretical predictions [12] of reabsorption effects on $S_t$ to numerical results with all radiation included, with CO$_2$ radiation only, with CO radiation only with the temperature broadening of the absorption spectrum artificially suppressed, and with $\kappa(\omega) = \text{constant} = 26 \text{ m}^{-1}$ to simulate a gray gas.

FIG. 8. Comparison of numerical predictions of $S_t$ with experiments on microgravity spherically expanding flames (CH$_4$ + 4O$_2$)-CO$_2$ mixtures [9] and counterflow twin-tube experiments in CH$_4$-air mixtures with $\gamma = 0.79$ (all replaced by CO$_2$) [27].

specifically characteristics temperature spectra. The some cases primary flame experiments effects in some configuration gravito-effects of ele-

Relevance to the internal combustion engine and gas turbine flames. Collisional broadening of the absorption spectrum will likely be important in these cases. Finally, the effects of exhaust-gas or flue-gas recirculation will be examined via computations at elevated temperatures with CO$_2$ and H$_2$O addition.

Acknowledgments

PDR acknowledges support by NASA-Lewis grant NAG3-1523 and NAG3-2124. Dr. Fengshan Liu (National Research Council, Canada) contributed to building the computational code.

REFERENCES


