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

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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 of flammability limits of premixed gas flames are still not 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]. Since these losses are eliminated by employing large combustion vessels at microgravity, heat loss via gas-to-gas radiation is probably the dominant extinction mechanism [8–11].

Nevertheless, it is unclear whether radiative loss causes 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 Planck mean absorption length (Lp), defined as the mean monochromatic absorption coefficient (κ) weighted by the Planck function:

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

\[ G(u) = \frac{15}{\pi^3} \frac{u^3}{e^u - 1}; \quad u = h c \omega k T \]  

where \( h, c, k, and T \) denote Planck's constant, light speed, wavenumber, Boltzmann's constant, and temperature, respectively. In the experiments in Refs. [6,7], the optical thickness \( \tau = X/L_p \), 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 \( \Phi_0 \) decreases compared with values without reabsorption.

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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 $S_i$ 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, $\tau \sim 1$ 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 S$_6$ 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 $x = +L_1 = +400$ cm, respectively. Upstream boundary conditions were ambient temperature (300 K), and composition with inflow velocity $S_i$ 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 ($Q_R = 4\sigma(T^4 - T)^3/L_p$, where $\sigma$ is the Stefan-Boltzmann constant and $T_0$ the ambient temperature, is always positive (upper plot). With reabsorption, $Q_R$ 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 ($T_0$). 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 $\delta = \alpha/S_i \sim 0.1$ cm, where $\alpha$ 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 $L_p$ ($\sim 19$ cm).

Fig. 2a shows that reabsorption effects in CH$_4$-air mixtures ($\gamma = 0$) are minor because $\Phi_0$ is reduced.
thin radiative absorption narrowband line strength equations 50 and 9:300 S discrete for CO, \( \text{CH}_4 \) necessary spectral radiation is [11]. Fur- thermore, the upstream temperature was 325 K for the upper boundary with secondary temperature boundaries. 

- \( \gamma \text{N}_2 \) and even with reabsorption \( S_\text{r} \) is always lower than the adiabatic burning velocity \( (S_\text{a}) \). However, \( S_{\text{lim}} \) is reduced by 25%, and \( S_{\text{lim}} \) for the limit mixture decreases similarly (26%). For both optically thin and reabsorption models, \( S_{\text{lim}}/S_{\text{lim}} \) is close to the theoretical prediction \( e^{-\frac{1}{2}} \) [6,7]. A simple picture emerges from these results. Radiation from hot \( \text{CH}_4 \) and \( \text{CO}_2 \) can escape only if it is emitted upstream, because downstream radiation will be reabsorbed by other \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) molecules. Thus, reabsorption approximately halves the net heat loss. Surprisingly, for optically thin flames \([6,7]\) predicts \( S_{\text{lim}}/S_{\text{lim}} \) to be 0.5, but if \( \Phi_0 \) were halved, \( S_{\text{lim}} \) should decrease 29%. Consequently, the classical quenching mechanism approximately applies in this case.

Flame characteristics are quite different with \( \gamma = 0 \). At \( \gamma = 0 \), for optically thin reabsorption, \( S_\text{r} \) and \( T_\ast \) are lower than adiabatic values, but with \( \text{CO}_2 \) substitution, because of reabsorption, these quantities are significantly higher than adiabatic values. The effect on \( \Phi_0 \) is substantial (0.682 for optically thin conditions vs. 0.442 with reabsorption). Nevertheless, flammability limits still exist.

Figure 3 elucidates two mechanisms that cause net
heat loss and thus flammability limits even with reabsorption, designated I and II. Mechanism I is that \( \kappa(\omega) \) is very different for \( \mathrm{H}_2\mathrm{O} \) and \( \mathrm{CO}_2 \) (Fig. 3a); because \( \mathrm{H}_2\mathrm{O} \) is absent from the unburned gas, most \( \mathrm{H}_2\mathrm{O} \) radiation emitted upstream cannot be reabsorbed. Mechanism II is that \( \kappa(\omega) \) for \( \mathrm{CO}_2 \) is broader at \( T_0 \) than \( T_e \) (Fig. 3a); thus, some \( \mathrm{CO}_2 \) radiation emitted upstream from temperatures near \( T_e \) cannot be reabsorbed farther upstream where \( T = T_0 \). Mechanism II can also occur for \( \mathrm{H}_2\mathrm{O} \) but not for the dry reactants studied here. Both mechanisms apply for arbitrarily large domains. The manifestation of these mechanisms is seen in the spectrally resolved radiative flux at the upstream boundary \( (x = -L_i) \) (Fig. 3b). The spectrum for \( \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} + \mathrm{CO} \) is similar to the \( \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \) spectra at 1300 K (Fig. 3a) less the \( \mathrm{CO}_2 \) spectrum at 300 K, indicating that losses arise mainly from the differences between the burned-gas emission and unburned-gas absorption. \( \mathrm{H}_2\mathrm{O} \) emission comprises most of the loss (mechanism I), but some occurs from \( \mathrm{CO}_2 \) emission (mechanism II).

These observations show that fundamental flammability limits due to radiative losses will exist in gaseous flames no matter how large the domain or what absorbing gases are present, because some radiation emitted from the high-temperature region cannot be reabsorbed by the unburned gases (mechanism II). These limits depend on the temperature 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 \( (x = L_f) \) is much less important for several reasons. A disappearing reactant (e.g., \( \mathrm{CH}_4 \)) can produce some loss at \( x = L_f \) via mechanism I, but \( \mathrm{CH}_4 \) radiation was not considered, and the loss would be much less than the upstream \( \mathrm{H}_2\mathrm{O} \) and \( \mathrm{CO}_2 \) loss because \( \mathrm{CH}_4 \) 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 \( L_f \). Thus, \( T_e \) and \( T_0 \) are unaffected, as was verified by changing \( L_f \) 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 \( \alpha/D_i \) are close to unity, \( \delta \) is an appropriate scale for both species and temperature changes. Hence, these criteria become

\[
I: \quad \left| \frac{d\chi}{dx} \right| > \left| \frac{d\chi}{d(1/\kappa(\omega))} \right| = \frac{d \ln(\kappa(\omega))}{d \ln(\chi)} \Rightarrow \frac{d \ln(\kappa(\omega))}{d \ln(\chi)} > \kappa(\omega)\delta \Rightarrow \kappa(\omega)\delta < 1
\]

\[
II: \quad \left| \frac{dT}{dx} \right| > \left| \frac{dT}{d(1/\kappa(\omega))} \right| = \kappa(\omega)\delta \Rightarrow \frac{d \ln(\kappa(\omega))}{d \ln(T)} < \frac{d \ln(\kappa(\omega))}{d \ln(T)}
\]

where \( \chi \) is the mole fraction of species \( i \) and the fact \( \kappa = \chi \), has been used. Fig. 3b shows evidence of these criteria. The loss due to \( \mathrm{H}_2\mathrm{O} \) mimics \( \kappa(\omega) \) except where \( \kappa(\omega) \) is very large and reabsorption can occur within the convective-diffusive zone where \( \chi_{\mathrm{H}_2\mathrm{O}} \) changes rapidly. For \( \mathrm{CO}_2 \), 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 \( dx/dT \) is large.

The convective-radiative zone at \( x < 0 \) has a characteristic thickness \( L_f \). Thus, \( L_f \) can influence reabsorbing flames drastically. Fig. 4 shows that \( \Phi_0 \) decreases as \( L_i \) increases because \( \Phi_0 \) decreases as \( L_i \) increases because more reabsorption (thus lower net \( Q_b \)) occurs with larger \( L_i \). Because \( S_{1,\text{lim}} \sim Q_b^2 \), \( S_{1,\text{lim}} \) also decreases. Significant reabsorption effects occur even for \( L_i = 1 \) cm (\( \tau = 0.0654 \)) because \( \mathrm{CO}_2 \) 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 \( L_i = 1 \) cm, \( \chi_{\text{H}_2\mathrm{O}} = 0.19 \), thus, significant absorption occurs on the scale \( (0.190 \times 40 \text{ cm}^{-1})^{-1} = 0.13 \text{ cm} \). This estimated
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Fig. 5. Effect of substitution of CO₂ for N₂ on burning velocities under adiabatic conditions, with optically thin radiative 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 \( T_\text{ad} \) to total heat release rate and thus measures the potential for radiative preheating to increase \( S_1 \). For nonscattering media [12]

\[
B = \frac{\beta \epsilon(T_\text{ad}^4 - T^4)}{2\rho_0 S_\text{ad} C_p T_\text{ad}^3}, \quad \beta = \frac{E}{RT_\text{ad}}
\]

where \( \beta, E, R, \rho_0, \) and \( C_p \) 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, CO₂ substitution increases \( \Phi_0 \) and \( S_\text{Lad} \) because the additional radiating CO₂ increases \( Q_{\text{R}} \). With reabsorption, small amounts of CO₂ substitution actually decrease \( \Phi_0 \) and \( S_\text{Lad} \) due to greatly reduced \( Q_{\text{R}} \), whereas larger amounts increase \( \Phi_0 \) slightly due to reduced \( T_\text{ad} \). Fig. 6b shows that for optically thin conditions, \( S_\text{Lad}/S_\text{Lad} \) is always close to the theoretical prediction [6,7] \( e^{-1/2} \), whereas with reabsorption \( S_\text{Lad}/S_\text{Lad} \) can be greater than 20.

Comparison with Experiment

For CH₄-air flames (Fig. 2a), comparison between computation and microgravity experiments in spherically 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 extend flammability limits considerably, fundamentally. It was found that effects may be important.

For the configuration of Refs. [9, 26], the optically thin model clearly overpredicts the limit fuel concentration (by 13%) and $S_{L,\text{lim}}$ (by 350%); thus, reabsorption extends this limit. With reabsorption, $S_{L,\text{lim}}$ 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 $L_1 = L_2 = 0.35$ cm; this might explain why in Ref. [27] numerical predictions of $S_{L}$ could not be obtained. In Ref. [27], results were extrapolated to zero strain to estimate the planar $S_{L}$. Although the accuracy of this method for reabsorbing conditions has not been established, with reabsorption the computed and experimental values of $S_{L}$ 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 $H_2O$, $CO_2$, and $CO$. It was found that while reabsorption can increase burning velocities and extend flammability limits considerably, fundamental limits independent of the system dimensions 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 spatially 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
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