

Chapter 1

Introduction

1.1 Motivation

Monitoring and measurement systems for combustion systems are difficult to develop because of the harsh environment inside the combustor. Optical methods are attractive because the measurements are non-intrusive and optical materials can survive the high temperatures of combustors. Another advantage of optical methods is the generally fast time response of optical sensors. High-speed monitoring devices are important in the monitoring of dynamic systems, such as modern premixed gas turbine combustors.

Chemiluminescence (described below in Section 1.2.1) has been used frequently in combustion research. Unfortunately the formation of the light emissions has not been clearly understood and quantitative diagnostic measurement applications have therefore been very difficult to develop.

Chemiluminescence is intricately tied to the chemical kinetics that support the combustion process. Chemiluminescence has therefore received renewed attention recently as a possible means of measuring unsteady heat-release rate in unstable combustion systems.(see (Paschereit and Polifke, 1998) and (Cho et al., 1998)) A reliable well understood measurement of chemiluminescence can provide quantitative insight into the details of the combustion process. Chemiluminescence measurement may provide the ability to monitor the combustion system at a level of detail traditionally thought impossible.

1.2 Background

1.2.1 Chemiluminescence

Definition

Chemiluminescence is radiation emitted from electronically excited molecules when these return to a lower energy state. The wavelength of radiation which is emitted is characteristic of the particular molecule and the particular transition the molecule undergoes. The more complex the molecule, the more complex the char-

acteristic radiation spectrum observed. For some simple (diatomic) molecules, the spectrum exhibits one major peak and relatively few, weak secondary peaks. For complicated molecules, the radiation spectrum observed appears continuous. OH^* , CH^* and C_2^* are examples of molecules exhibiting a simple spectrum with major peaks at 308 nm, 431 nm and 513 nm respectively, whereas CO_2^* is an example of a molecule with a radiation spectrum that appears continuous. (Gaydon, 1974) (See Section 4.1 for examples of flame-spectra)

Flame chemiluminescence

Flame chemiluminescence is the chemiluminescence emitted in flames. Chemiluminescence from flames is especially interesting because the concentrations of excited molecules seen in flames exceed the equilibrium concentrations expected at the same temperature without chemical reaction by several orders of magnitude. It is possible to deduce from this fact that excited molecules are not only produced by thermal excitation but also are produced as the products of reactions. Since the amount of radiation observed in the flame at a particular wavelength is proportional to the concentration of the associated excited molecule, a measurement of the radiation can be directly related to the concentration of the excited molecule.

It is important to mention that the excess energy contained in an excited molecule is not always removed by radiation. The excited molecule could react with another molecule or lose its excess energy in a non-reactive collision. Such a collision occurs without the emission of light and therefore is called a quenching collision. Not all molecular collisions are effective in removing excess energy from the excited molecule. The process of quenching is strongly dependent on the colliding molecules. The quenching efficiency of a given unexcited molecule is a measure of how likely the molecule is to remove the excess energy from a given excited molecule in a collision. Quenching efficiency varies greatly from molecule to molecule and is very often a strong function of temperature. (Garland and Crosley, 1986)

1.2.2 Chemical kinetics and reaction mechanisms

Chemical kinetics deals with all the detail molecular reactions that describe the process of converting the incoming reactants to the final products observed in steady state. The chemical kinetics of a reacting system is described by a reaction mechanism. A reaction mechanism is a system of molecular reactions with associated rate expressions to model all important molecular collisions. Reaction mechanisms vary in complexity from one or two reactions to several hundred.(Turns, 1998)

The accuracy of a reaction mechanism is measured by how well the model predicts reactor output variables such as stable molecule concentrations and exit temperature as well as the overall location of the reaction zone. Increasing the number of reactions in a reaction mechanism does not necessarily increase its accuracy. Larger reaction mechanisms are used primarily to obtain insight into the details of the reaction process. Large reaction mechanisms allow the study of reaction intermediates which hold the key to explaining such important phenomena as pollutant formation, flame extinction and ignition and non-equilibrium molecule formation. In the research discussed in the present thesis document, a large reaction mechanism is used to be able to observe the modeled concentrations of chemiluminescent species.(See Section 6.2.3)

1.2.3 Combustion modeling

Combustion modeling is concerned with simulating all relevant processes inside a reactor. The relevant processes inside a reactor depend on the reactor model. In some idealized systems such as the well-stirred reactor, the number of relevant processes has been reduced to the reactions governing the conversion of reactants to products and the heat-up experienced by the mixture while inside the reactor. More physically relevant models require the resolution of mixing processes and flow-fields inside the reactor. In the case of liquid fuel combustion the model must also include phase interchange processes such as evaporation and the influence of these processes on momentum, species and energy balances.

Most combustion modeling efforts are plagued by the same difficulty. The equa-

tions to be modeled are very non-linear and stiff. A set of equations is said to be stiff if the time-scales of the various processes to be modeled vary greatly. In a combustion system, the reactions occur on a very fast time-scale whereas other processes such as diffusion occur on a much slower time-scale. The problem is that the smallest time scale needs to be resolved everywhere in the computational domain, even though the process requiring this resolution only occurs in a very small part of the computational domain. The problem of stiffness is most important in unsteady calculations. Steady calculation is more straightforward because the spatial resolution can be varied over the computational domain. Still, any level of combustion modeling is numerically difficult and special solvers are required to obtain stable accurate solutions.

1.3 Literature Review

1.3.1 Experimental use of chemiluminescence

Chemiluminescence measurement is not a novel idea. Researchers as early as 1958 (Clark, 1958) measured chemiluminescence from flames and attempted to find correlations between the measured chemiluminescence and experimental variables. The dependence of the signal strength of several types of chemiluminescence on fuel type, flow-rate and equivalence ratio were measured by Clark (1958). The study laid the ground work for a lot of the chemiluminescence research to follow. Four types of chemiluminescence were measured: OH^* , CH^* , CO_2^* and C_2^* . Today, these four species are still the most commonly measured chemiluminescent species.

Clark (1958) used Bunsen type burners of various diameters and a wide range of flow-rates in his study. The study was the first to show the linear dependence of chemiluminescence on fuel flow rate, in the same flow regime. The linear dependence varied from laminar flow to turbulent flow, with a very narrow transition regime around a Reynolds number of 6000. The slopes of the observed linear dependence varied with mixture composition (equivalence ratio) and type of chemiluminescence. The behavior of the chemiluminescent species with equivalence ratio is species specific.

OH^* and CO_2^* both have peaks near the maximum laminar flame speed, with CO_2^* decreasing at a slower rate beyond the maximum on the rich side than OH^* . Both CH^* and C_2^* have maxima well on the rich side of the equivalence ratio spectrum.

The idea of using chemiluminescence in dynamic measurements was explored early on by Price et al. (1968) and Hurle et al. (1968) who related the noise from turbulent flames to oscillations in the strength of the chemiluminescence signal. Price et al. (1968) used premixed ethylene-air and ethylene diffusion flames in the experiments and found excellent correlation between the time derivative of the chemiluminescent light signal strength and the root mean square pressure as measured by a microphone some distance away from the flame. The research was conducted using C_2^* and CH^* chemiluminescence. The unsteadiness in the flames was caused by the introduction of turbulence into the flow by means of perforated plates. The relation derived in their work relied on the chemiluminescence strength being proportional to heat-release rate. The proportionality was considered verified by the linear relationship between fuel flow and chemiluminescence emission strength at a given mixture composition.

Due to the development of lean premixed gas turbine systems, and the associated occurrence of combustion instability in such systems, interest in measuring heat-release rate dynamically has once again surfaced. In combustion dynamics research, oscillating heat release is often assumed to be at least illustrated by the oscillating strength of a chemiluminescence signal from the reaction zone. Paschereit (1998) used spatially resolved OH^* chemiluminescence measurements to show the dynamic behavior of the flame in their experimental test facility. Cho (1998) and Langhorne (1988), assumed C_2^* chemiluminescence to be proportional to heat-release rate in their studies. For all these researchers the basis of the direct proportionality between heat-release rate and chemiluminescence is the work of Price et al. (1968) and Hurle et al. (1968) described above. Langhorne's (1988) research is particularly interesting as the paper presents a calibration of C_2^* for heat-release rate. The calibration is then used in the modeling of unsteady pressure oscillations (Bloxsidge et al., 1988b) as well as the design of a control system using an automotive fuel injector (Bloxsidge et al., 1988a).

More sophisticated research in correlating heat-release rate and chemiluminescence was performed by Samaniego et al. (1995) who used CO_2^* as heat release indicator. Unfortunately the work of Samaniego et al. (1995) is limited to numerical modeling of chemiluminescence and no experimental verification of his findings has taken place. The results were however promising as CO_2^* chemiluminescence was found to be a good indicator not only of heat-release rate but also of H-atom concentration in steady and unsteady combustion under moderate strain-rate.

Najm et al. (1998) performed an extensive study of experimental observables that are considered indicators of heat-release rate. The study focused on the various observables' ability to predict heat release for the case of the unsteady interaction between a flame sheet and a counter-rotating vortex pair. Among the observables studied were CH^* chemiluminescence, CH fluorescence (laser-induced) and HCO fluorescence (laser-induced). The study concluded that HCO is an excellent indicator of heat-release rate everywhere. CH^* and CH are poor indicators of heat-release rate in areas of high flame strain and curvature immediately prior to extinction. The study also encompassed a very important modeling effort to be discussed in more detail below in Section 1.3.3.

The study of Najm et al. (1998) points out an important limitation of the assumption that chemiluminescence is proportional to heat-release rate. The proportionality breaks down in regimes of very high strain and curvature, near extinction. Earlier studies, showing the proportionality of heat release and chemiluminescence used relatively low levels of unsteadiness. The unsteadiness in the work of Price et al. (1968) and Hurle et al. (1968) was generated using a perforated plate yielding a very low level compared to the effect of a counter-rotating vortex pair. Samaniego et al. (1998) modeled unsteady strain effects in his calculations but did not perform any calculations under time-varying flame-curvature, which has an important effect on flame structure and can lead to extinction. The combustion instability phenomena as occurring in ultra-lean premixed combustion exhibit very high levels of unsteady flow and therefore all measurements involving chemiluminescence in such environments must be interpreted very carefully.

Chemiluminescence measurement has not only been applied in the combustion dynamics field. Chemiluminescence has been used to monitor the reaction zone location in the burning of droplets in micro-gravity experiments (Marchese et al., 1996). Schefer (1997) investigated the interaction of the flame sheet with vortical structures using CH^* chemiluminescence as the main reaction zone marker. Santavicca (1999) has calibrated CO_2^* chemiluminescence as an indicator of mixture strength at a given flow rate. Chemiluminescence measurements have also been used to identify flame structure and flame stabilization mechanisms in gas turbine type combustors (Chomiak, 1972) (Beyler and Gouldin, 1981). Three of the major types of chemiluminescence, OH^* , CH^* and C_2^* have also been used to measure Damköhler numbers in turbulent flames (Ikeda et al., 2000). Ikeda et al. (2000a and 2000b) used a Cassegrain optical system to obtain sub-millimeter spatial resolution in their measurements of the spatial distribution of chemiluminescence intensity inside the flame.

1.3.2 Chemiluminescence chemical kinetics

OH^* chemiluminescence

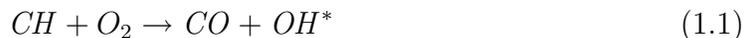
The chemical kinetics leading to the measured chemiluminescence signal hold the key to fully understanding the signal collected. Experimental determination of all the reaction rate constants involved to a precision necessary to achieve such an understanding is very difficult. Most methods deduce rate constants of one or a set of reactions by measuring the concentrations of molecules involved in the reactions in time.

Early research in chemical kinetics was hindered by the difficulty of experimental access in most all combustion environments. The result was that many chemical kinetics experiments were conducted in low pressure reactors, where the reaction zone is thick enough to allow spatially resolved measurements of species profiles by laser-induced fluorescence. Based on the species profiles measured and an assumed network of reactions, the reaction rate constants were then deduced.

Recent experiments have been aided by the advent of laser photolysis which allows

the controlled production of unstable molecules found inside the flame.(Davidson et al., 1991) Individual reaction rates can thus be identified, greatly increasing the accuracy of the obtained reaction constants. Even using the most modern equipment however, it is rare that reaction rate constants can be specified to within $\pm 50\%$.

Accurate data on chemiluminescence chemical kinetics is very difficult to obtain. The currently accepted production path of OH^* was proposed in 1961 by Krishnamahari and Broida (1961) :



The reaction rate for Equation (1.1) was derived by Porter et al. (1967) by correlating measured CH, O_2 and OH^* profiles through the flame. Based on some assumptions concerning the quenching cross-section, a reaction rate coefficient of 1×10^{-13} cc/(molecule-sec) was calculated. The study used both acetylene and methane flames in a low-pressure reactor to arrive at the given rate constant.

Since then, several researchers have found supporting evidence for the reaction given in Equation 1.1. Becker et al. (1977) reported on OH^* chemiluminescence in hydrocarbon atom flames. They found that the proposed reaction adequately explained the observations made in their two-hydrocarbon atom flames. Reactions of CH with O and HCO with O_2 were rejected as formation paths for OH^* because of lack of energy release in these reaction paths to produce the excited OH radical. Dandy and Vosen (1992) used the reaction given in Equation 1.1 in chemiluminescence modeling calculations and had some success at equivalence ratios below 0.9, as described in more detail below in Section 1.3.3.

Another aspect of chemiluminescence chemistry is the destruction of chemiluminescent species. As mentioned above in Section 1.2.1, there are three paths for the removal of excess energy from the excited molecule. The most common path is by quenching through a collision with another molecule. The typical quenching reaction is given by:



The observable path is energy loss by spontaneous emission. The radiation reaction

involves only the excited molecule and is described by:



The rate of the reaction given in Equation 1.2 varies for different collision partner molecules M. Depending on the level of modeling desired, an average rate of quenching is specified or separate quenching reactions for all important quenching molecules are specified. Dandy and Vosen (1992) used data given by Garland and Crosely (1986) to calculate the quenching rates of the most important quenching molecules of OH*. The reaction rates have strong temperature dependencies that vary widely from one molecule to another. The quenching reactions are shown in detail in appendix A which lists the reaction mechanism used in the Chemkin modeling calculations. (See also Section 6.2.3)

The third path of destruction for OH*, by reaction, is not significant based on the work performed by Dandy and Vosen (1992).

CH* chemiluminescence

CH* formation has received more attention than OH* formation. The production path for CH* has been more difficult to identify because the radicals involved were not possible to be measured reliably. Reactions proposed include combinations of C₂ with OH (Gaydon and Wolfhard, 1979) and then later of C₂H with molecular oxygen (Renlund et al., 1981). Research by Glass et al. (1965) first introduced the reaction of C₂H with atomic oxygen as a source for CH*. Experiments and modeling performed by Joklik et al. (1986) first showed that although the reaction of C₂H with molecular oxygen may contribute to CH* formation, the dominant source of CH* appears to be the reaction of C₂H with atomic oxygen (Equation 1.4). Devriendt and Peeters (1997), using sophisticated sampling techniques confirmed the results found by Joklik et al. (1986). The research also was able to provide the reaction rate coefficient for the reaction of C₂H with atomic oxygen: $k = 2.4 \times 10^{-11} e^{-230/T(K)}$ cc/(molecule-sec). The error for the coefficient is a factor of two due to the uncertainty in the C₂H

concentration calibration factor.



The consumption reactions for CH^* are similar to those of OH^* in that CH^* goes to its ground state through the same three paths described for OH^* . However, quenching of CH^* , the major consumption path, is not nearly as well understood as it is for OH^* . Garland and Crosley (1986) were able to give detailed quenching data for OH^* because a molecular model they had developed for OH^* quenching agreed well with experimental data. The same model was not able to predict quenching of CH^* observed in experiments. The experiments showed quenching that was extremely temperature dependent (more so than OH^*). The model was not able to capture this dependence. Nevertheless, if sufficient consistent experimental data were available the quenching of CH^* could be adequately modeled in the context of a reaction mechanism. Some experimental data does exist but it is not nearly complete. Quenching of CH^* by O and H atoms for example is well understood. Quenching data for these molecules was extremely important for Devriendt and Peeters (1997) to be able to calculate the reaction rate reported. Data for important quenching molecules in flames such as water, molecular oxygen and carbon dioxide (a.o.) is however not nearly as complete. The difficulty of modeling CH^* quenching is dealt with in greater detail in Section 6.2.3.

As was the case for OH^* consumption of CH^* by reaction with another molecule can be ignored.(Joklik et al., 1986)

1.3.3 Chemiluminescence modeling

The modeling of chemiluminescence has been difficult until recently due to the large uncertainties involved in the reaction rates forming the chemiluminescent species and their precursors. Modeling the quenching reactions has also been a particular challenge. Large, detailed, reliable reaction mechanisms can now be developed thanks to the availability of more detailed experimental data for validation of such models. Furthermore, to decrease the influence of individual reaction rate uncertainties on the

final modeling result, optimization techniques have been applied to reaction mechanisms.(Frenklach et al., 1992)

The first attempt to model experimentally measured chemiluminescence was made by Joklik et al. (1986) for CH^* . In the study, a water-cooled porous plug burner was used with a reactant mixture of acetylene and oxygen. The burner was operated in a low pressure environment to increase the reaction zone thickness and provide the ability of making spatially resolved measurements of species concentrations. The study predates the research of Devriendt and Peeters (1997) and so, the reaction rates used for the production of CH^* were inaccurate. Nevertheless, Joklik et al. (1986) succeeded in showing that the production reaction given in Equation 1.4 was the dominant production path for CH^* . A qualitative agreement between model and experiment was also achieved.

OH^* was first modeled by Dandy and Vosen (1992). The reaction mechanism used for OH^* production is as described above in Section 1.3.2. The experiment modeled by Dandy and Vosen (1992) is the burning of a methane air mixture in a shock tube. The researchers obtained excellent agreement between modeled chemiluminescence and integrated chemiluminescence intensity. The model also accurately predicted the time dependence of chemiluminescence in the shock tube. Experiments were reported for equivalence ratios between 0.65 and 0.9. Modeling experiments were carried out in a wider range for equivalence ratios from 0.65 to 1.4. OH^* chemiluminescence rises exponentially for lean equivalence ratios and reaches a maximum on the rich side at an equivalence ratio of 1.2, as may be expected considering the OH^* chemiluminescence formation path in Equation 1.1. It is important to note that the research of Clark (1958) observed the maximum of OH^* chemiluminescence at an equivalence ratio close to 1. The experimental work described in this thesis confirms the results found by Clark (1958) and the discrepancy between modeled OH^* and measured OH^* will be addressed in greater detail in Section 9.1.

OH^* was also modeled by Marchese et al. (1996) for the burning of fuel droplets in micro-gravity. The reaction mechanism describing the production of OH^* was taken from Dandy and Vosen (1992). OH^* was predicted accurately for n-heptane droplets

but failed to predict OH^* chemiluminescence in methanol droplets. The authors concluded that the observed OH^* chemiluminescence was due to thermal excitation.

The most complete chemiluminescence modeling effort to date has been published by Samaniego et al. (1995). The study is however a purely computational one with no comparison to experimental data. In the study, CO_2^* is modeled as a possible heat-release rate indicator in unsteady premixed flames. The work was briefly mentioned above in Section 1.3.1. Model calculations were performed for freely-propagating and steady and unsteady counter-flow flames using both propane-air and methane-air mixtures. The calculations showed that CO_2^* chemiluminescence is an adequate indicator not only of heat-release rate but also of hydrogen atom concentration. To determine the adequacy of CO_2^* as indicator of heat release, local values of CO_2^* intensity were compared to local values of heat-release rate. The relationship between CO_2^* and heat release changed with external parameters such as equivalence ratio and flow rate but remained very close to linear in each case.

Najm et al. (1998) used the combination of experimental data and modeling calculations to show that HCO is a universally good indicator of heat-release rate. The study also investigated CO_2^* and CH^* along with CH . CH was assumed to be an indicator of how OH^* would perform given the accepted formation path given in Equation 1.1. The conclusion of the study was that in highly strained and curved flames, chemiluminescence of any sort is not a good indicator of heat-release rate. The model showed why this is the case for methane combustion in the case of the chemiluminescent species OH^* and CH^* . In the conversion from fuel to products, several paths are available for fuel consumption. The most stable and likely path is that through HCO which explains why the molecule is such a good indicator of heat-release rate. A small amount of fuel (20%) is converted in a path through CH and an even smaller amount (5%) of fuel is converted through a branch of C_2X type molecules. As the flame approaches extinction the less populated paths become empty first leaving the path through HCO as the last path available for conversion immediately prior to extinction. CO_2^* is thought to be produced by a reaction between carbon monoxide and atomic oxygen so that the argument above cannot be

applied to CO_2^* . However, CO_2^* was also found to be a less than adequate indicator of heat-release rate in regions of high flame strain and curvature. At present, no chemiluminescence species can be directly associated with the path through HCO and so chemiluminescence cannot be a good indicator of heat-release rate in flame environments where intermittent extinction may occur.

1.4 Research Goals

The research effort described in this report was directed at establishing a clearer understanding of the formation mechanism of chemiluminescent light. The understanding gained will support the development of quantitative measurement applications, and immediately contribute to the correct qualitative interpretation of chemiluminescence measurements. In greater detail, the research goals were as follows:

- Understanding chemiluminescence formation:
 - Examine validity of existing chemiluminescence reaction kinetics:
 - * Critical evaluation of currently accepted formation paths
 - * Evaluation of alternate formation paths
 - Investigate dependence of chemiluminescence on flame parameters:
 - * Heat-loss
 - * Flow-rate
 - * Fuel to air ratio (equivalence ratio)
- Quantitative modeling of chemiluminescence:
 - Full simulation of 1-D laminar flame geometry
 - Semi-empirical modeling of more complex 2-D axis-symmetric flame
- Evaluation of possible measurement applications:
 - Heat-release rate
 - Equivalence ratio