

**Chapter 10**

**Applications for**

**Chemiluminescence in Combustion**

**Diagnostics**

## 10.1 Interpretation of experimental results

In Section 1.1, the lack of understanding of chemiluminescence formation was blamed for the lack of quantitative measurement applications. The experimental results found in Chapter 5 will be interpreted in the present section in light of the chemiluminescence formation path understanding gained through the analysis presented in Chapter 9.

### 10.1.1 Normalization of experimental results

In Section 5.1.1, the Bunsen flame chemiluminescence data is normalized to find the residual function of chemiluminescence with equivalence ratio.  $\text{OH}^*$  chemiluminescence data is divided by the fuel flow-rate and multiplied by the square root of the Reynolds number.  $\text{CH}^*$  chemiluminescence data however is only divided by the fuel flow-rate. Analysis of the formation path and the experimental setup allows the difference in the normalization between the two chemiluminescence species to be explained.

The stainless steel tube on top of which the flame sits is only five inches long (see Section 2.2). The boundary layer developing from the upstream end of the stainless steel tube does not have enough length to develop fully. The heat conducted from the burner rim causes the stainless steel tube to heat up significantly and the heat-transfer to the gas cannot be neglected. Due to the developing boundary layer the heat-transfer to the fluid is not only a function of the flame temperature but more importantly the heat-transfer becomes a function of the gas flow-rate. The convective heat-transfer coefficient from the stainless steel tube to the gas is a function of the square-root of the free-stream Reynolds number. The variable heat-up experienced by the gas as the flow-rate changes also affects the  $\text{OH}^*$  chemiluminescence yield.

An increase in the flow-rate causes an increase in the temperature of incoming mixture. The temperature increase in the incoming mixture in turn produces an increase in the flame temperature. The flame temperature increase is not equal to the increase in the incoming mixture temperature due to higher heat-losses by radiation,

conduction as well as product dissociation. The increase in temperature within the flame affects OH\* formation detrimentally by favoring higher activation energy formyl radical (HCO) consumption reactions (see Figure 9.2).

CH\* chemiluminescence is only normalized by fuel flow-rate and the Reynolds number effect seen for OH\* chemiluminescence is not observed. The reason for this characteristic can also be found by investigating the formation path diagram shown in Figure 9.2. In contrast to the formyl radical where some consumption reactions have a high activation energy and others have a low activation energy, all C<sub>2</sub>H consumption reactions have a low activation energy, causing the CH\* production to remain relatively unaffected.

Finding the reason behind the different chemiluminescence behaviour is important due to the proposed use of chemiluminescence as indicator of heat-release rate. Both types of chemiluminescence are sensitive to the overall heat liberated as indicated by the dependence on the fuel flow-rate. The total heat liberated is however not always a good measure of the heat released to the product gases in their temperature increase. The important heat-release rate measure useful in gas turbine combustion is the temperature increase in the gases. The heat-up effect induced by the heat-transfer from the stainless steel flame tube to the incoming gas mixture, causes a net decrease in the temperature change of the gases. An adequate indicator of heat-release rate for gas turbine combustors should be sensitive to this change. OH\* is sensitive to the change whereas CH\* is not sensitive to the change.

### 10.1.2 Chemiluminescence as measure of heat-release rate

The normalization used to collapse the Bunsen flame chemiluminescence showed how OH\* chemiluminescence is more sensitive to small changes in heat-release rate than CH\* chemiluminescence. The honeycomb chemiluminescence data was not able to be collapsed but the analysis of the fuel flow-rate specific chemiluminescence measurements is still worthwhile, especially with respect to heat-release rate.

Early research (Price et al., 1968), (Hurle et al., 1968) claimed that chemiluminescence is proportional to heat-release rate because of the linear behaviour of

chemiluminescence with fuel flow-rate. In the case of both  $\text{OH}^*$  and  $\text{CH}^*$ , the linearity is not given because the fuel flow-rate specific chemiluminescence still shows a significant residual trend with fuel flow-rate. To be able to continue to consider chemiluminescence a viable heat-release rate indicator, the observed non-linearity with fuel flow-rate in the chemiluminescence must be mirrored by nonlinear behaviour of heat-release rate with fuel flow-rate in the honeycomb burner.

Indeed, the non-linearity seen in the behaviour of chemiluminescence with fuel flow-rate coincides or is caused by a non-linearity in the heat-release rate, forced by the particular combustion process in the honeycomb burner. The flow-rate per unit area of the honeycomb burner is very low when compared to the maximum laminar burning rate. The highest flow-rate studied corresponds to a flow-rate one third of the maximum laminar burning rate. In the honeycomb burner, the flame area is always constant and the reaction rate increases to accommodate increases in flow-rate. Closely tied to increases in reaction rate are increases in the flame temperature.

Reaction rate is an exponential function of temperature. Radiation heat-loss from the flame is a function of the flame temperature raised to the fourth power. For an overall activation temperature ( $E_a/R_u$ ) of 16000 °K, a base temperature of 1800 °K and a required increase in the reaction rate of 30%, the increase in flame temperature only has to be about 3%. A 3% increase in the flame temperature results only in a 13% increase in radiation heat-loss. The radiation heat-loss is thus relatively lower at a higher burner flow-rate. Note also that since the flame temperature is higher, the temperature rise through the flame is higher. The increase in fuel flow-rate specific chemiluminescence with fuel flow-rate thus corresponds to an increase in the fuel flow-rate specific heat-release. In the honeycomb burner especially, the idea of a universal heat of reaction for a given fuel has to be abandoned with respect to the temperature rise through the gases. The heat chemically liberated is a very different quantity from the heat added to the gases.

## 10.2 Interpretation of modeling results

The arguments put forth on a rational basis above in Section 10.1 can be quantified using the models developed in the study. Both the honeycomb burner modeling results and Bunsen type burner results give quantitative insight into the relationship between heat-release rate (as given by the enthalpy increase in the gases) and the candidate indicators considered in the present study:  $\text{OH}^*$  and  $\text{CH}^*$ . In the calculation of heat-release rate an average specific heat is used, not varying with the conditions of the particular flame considered. The correct average specific heat varies from case to case, but the variation is negligible when compared to the overall variation of heat-release rate with the other parameters considered such as flow-rate and equivalence ratio.

### 10.2.1 Bunsen flame heat-release rate modeling results

#### $\text{OH}^*$ chemiluminescence

Figure 10.1 shows heat-release rate as a function of  $\text{OH}^*$  yield for four air flow-rates. Each of the four curves is made up by using a variation in equivalence ratio from 0.75 to 1.10. The results show that heat-release rate is a non-unique function of  $\text{OH}^*$  yield. Beyond equivalence ratios of 1.00,  $\text{OH}^*$  yield is found to decrease while the heat-release rate continues to increase. Furthermore, a certain single value of heat-release rate reached by two different combinations of air flow-rate and equivalence ratio will have two different  $\text{OH}^*$  chemiluminescence yields. However, if the equivalence ratio is held constant, heat-release rate is a near linear function of  $\text{OH}^*$ .

The normalized sensitivity of  $\text{OH}^*$  chemiluminescence yield to changes in heat-release rate is shown in Figure 10.2. The figure shows that the sensitivity is very equivalence ratio dependent. Considering only equivalence ratios below 1.00, the sensitivity varies only slightly. Overall, inspection of the figure shows that moderate increases in flow-rate such as those studied, do not change the sensitivity of the  $\text{OH}^*$  chemiluminescence yield measurement significantly.

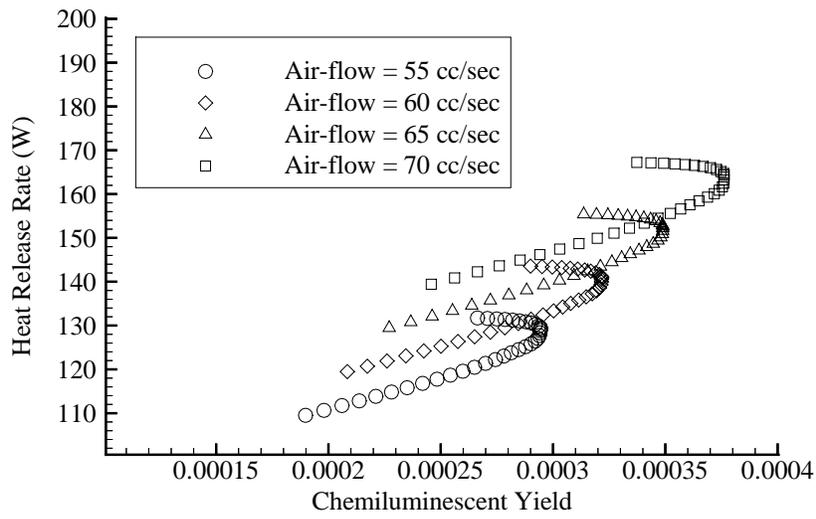


Figure 10.1: Heat-release rate as a function of OH\* chemiluminescence

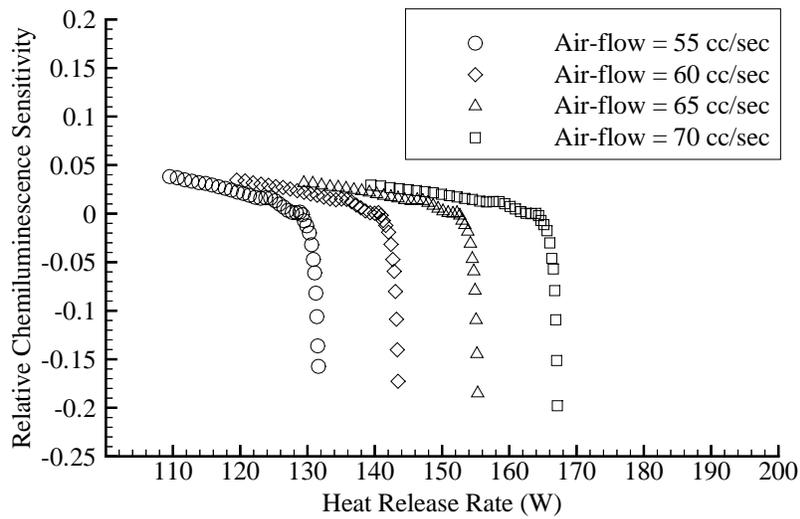
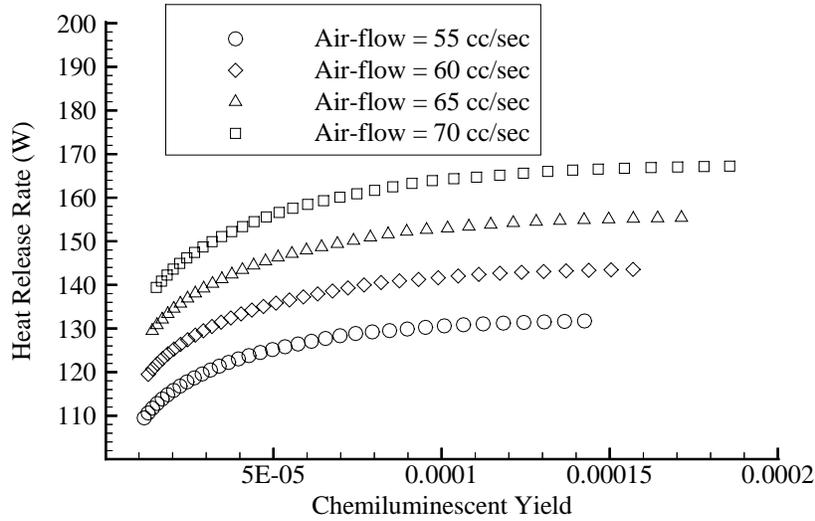


Figure 10.2: OH\* chemiluminescence sensitivity to changes in heat-release rate

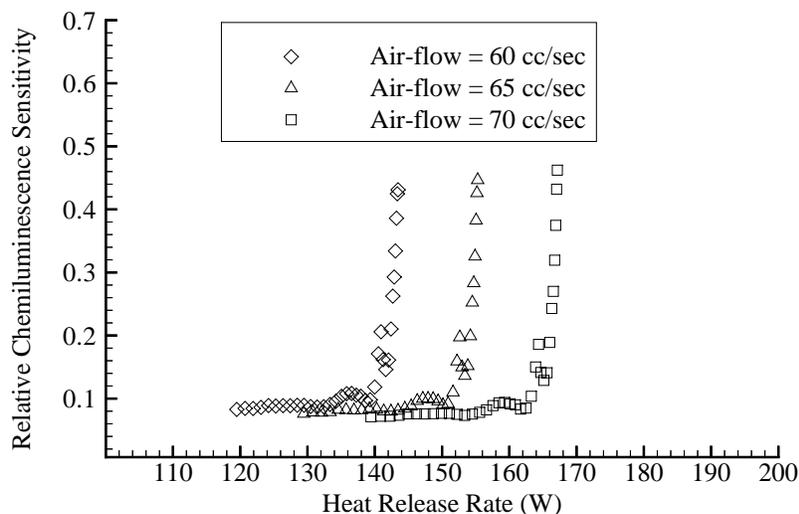


**Figure 10.3:** Heat-release rate as a function of CH\* chemiluminescence

### CH\* chemiluminescence

Figure 10.3 shows heat-release rate as a function of CH\* yield for four air flow-rates. Each of the four curves is made up using a variation in equivalence ratio from 0.75 to 1.10. The results show that heat-release rate is a non-unique function of CH\* yield. CH\* chemiluminescence yield does not decrease with increasing heat-release rate above equivalence ratios of 1.00 in the same way OH\* chemiluminescence did. As observed for OH\* chemiluminescence, a certain single value of heat-release rate reached by two different combinations of air flow-rate and equivalence ratio, will have two different CH\* chemiluminescence yields. Also parallel to observations made for OH\* chemiluminescence, CH\* is a near linear function of flow-rate when the equivalence ratio of the mixture is held constant. (See Section 7.4.3)

The normalized sensitivity of CH\* chemiluminescence yield to changes in heat-release rate is shown in Figure 10.4. The figure shows that the sensitivity is very equivalence ratio dependent. Considering only equivalence ratios below 1.00, the sensitivity varies only slightly. Overall, inspection of the figure shows that moderate



**Figure 10.4:** CH\* chemiluminescence sensitivity to changes in heat-release rate

increases in flow-rate such as those studied, do not change the sensitivity of the CH\* chemiluminescence yield measurement significantly. The results in terms of sensitivity are very similar to those obtained for OH\* chemiluminescence. The CH\* sensitivity to changes in heat-release rate appears to vary slightly less than OH\* heat-release rate sensitivity over the equivalence ratio range from 0.75 to 1.00. The large sensitivity observed around an equivalence ratio of 1.00 and higher is due to the fact that CH\* chemiluminescence yield continues to increase strongly while the heat-release rate flattens out to near zero slope. At zero slope any increase of chemiluminescence would yield an infinite sensitivity.

### Illustrating dynamic response

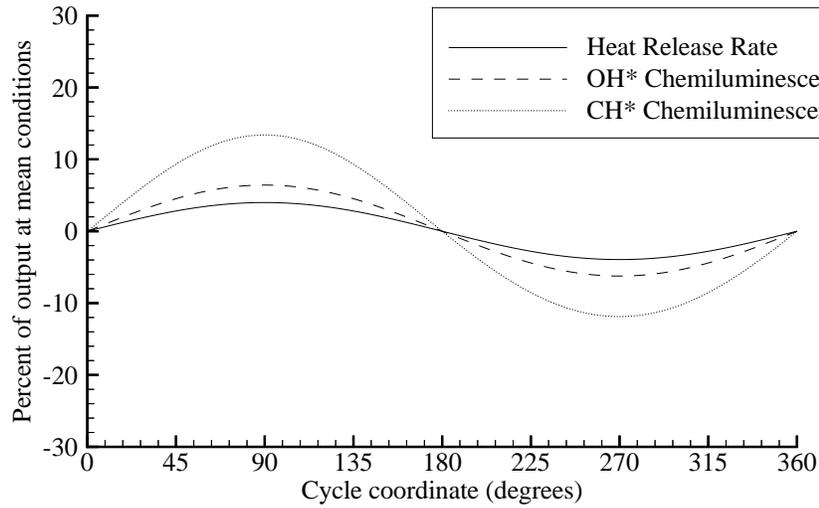
The Bunsen burner model involves only steady calculations. However, to illustrate some of the non-linear relationships alluded to in the previous subsections, an ideal response of the flame to fluctuations in mass-flow and equivalence ratio is calculated. The ideal response assumes that the flame instantaneously adjusts to the varying equivalence ratio and mass-flow. In other words, the flame is assumed

to react to changes in equivalence ratio or mass-flow much faster than the changes themselves take place. A series of Bunsen type burner model calculations were performed for a continuous variation in flow-rate and equivalence ratio. The calculations were performed using the modeling procedure described in Section 7.4.1. The calculations form a detailed interpolation table with one dimension describing equivalence ratio variation and the other dimension representing mass-flow variation. Using the interpolation table and MATLAB's spline 2-D interpolation scheme, it is possible to calculate the variation of all relevant output variables based on a prescribed variation of equivalence ratio and mass-flow. The following paragraphs show how simultaneous variations of equivalence ratio and mass-flow affect the theoretically observed heat-release rate, OH\* chemiluminescence and CH\* chemiluminescence. The mean condition for the start and end of the cycle is chosen to be a mass-flow of 62.5 scc/sec and an equivalence ratio of 0.80.

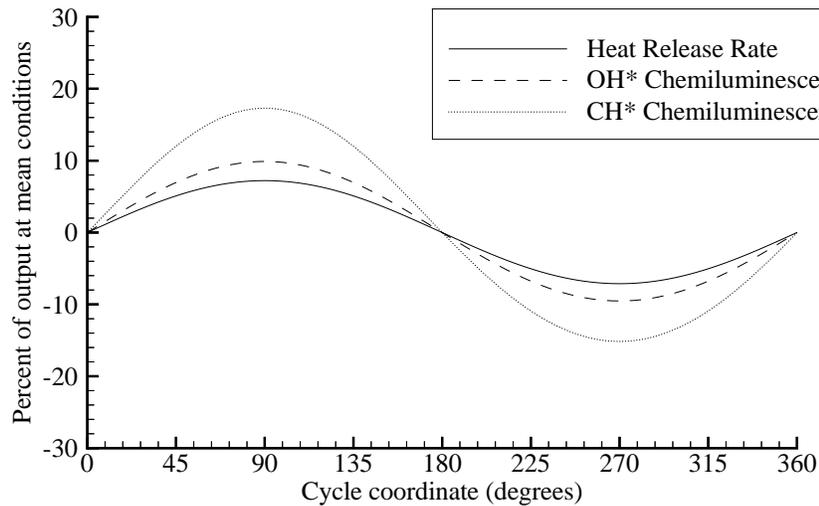
The first condition studied is a 0.01 amplitude oscillation in equivalence ratio and an in-phase 2 scc/sec amplitude mass-flow oscillation. The results of the calculations are shown in Figure 10.5. The results are given as a percentage of the mean value at the prescribed mean conditions given previously. The results show the high sensitivity of CH\* chemiluminescence relative to OH\* chemiluminescence. All the oscillations, as expected based on the ideal response assumption, are in phase and both chemiluminescence species may be said to represent heat-release rate oscillations well. Some of the large amplitude difference observed in Figure 10.5 is caused by the high equivalence ratio sensitivity of CH\* chemiluminescence.

For Figure 10.6 the amplitude of the mass-flow oscillation is increased while the equivalence ratio fluctuation is kept the same. The figure shows that the amplitude difference between OH\* and CH\* chemiluminescence has decreased, illustrating the increased importance of oscillating mass-flow in the oscillation.

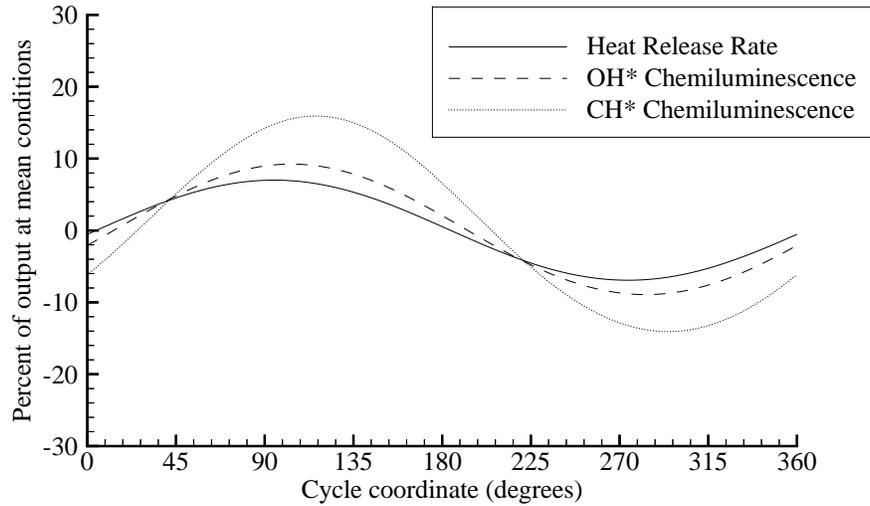
Figure 10.7 shows the variation of heat-release rate, OH\* chemiluminescence and CH\*chemiluminescence for a 45 degree phase shifted oscillation in equivalence ratio, relative to the oscillation in mass-flow. The amplitude for the equivalence ratio oscillation is 0.01 and the amplitude for the mass-flow oscillation is 2 scc/sec.



**Figure 10.5:** Ideal dynamic response with in-phase variation of equivalence ratio and mass-flow at amplitudes of 0.01 and 2 scc/sec respectively



**Figure 10.6:** Ideal dynamic response with in-phase variation of equivalence ratio and mass-flow at amplitudes of 0.01 and 4 scc/sec respectively

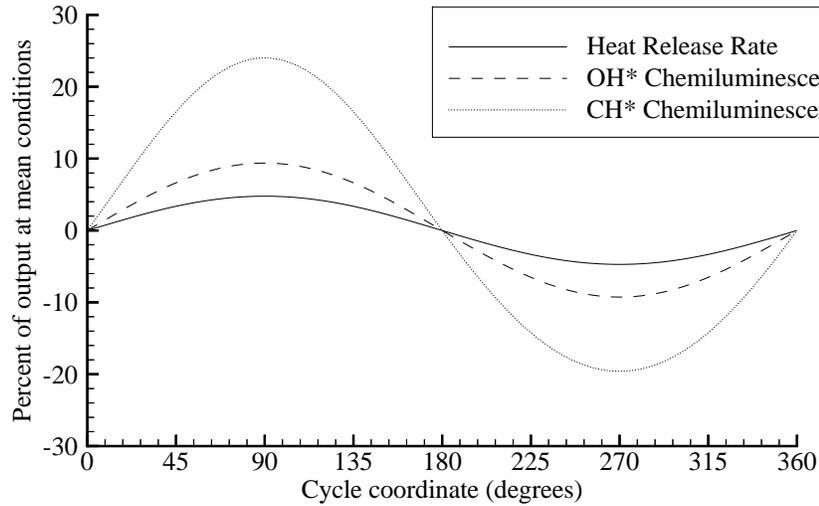


**Figure 10.7:** Ideal dynamic response with a 45 degree phase shift between the oscillations of equivalence ratio and mass-flow of amplitudes of 0.01 and 4 scc/sec respectively

The chart shows that the CH\* sensitivity to equivalence ratio fluctuations alluded to previously causes the CH\* curve to lag significantly behind the heat-release rate and OH\* chemiluminescence curves. There also is a delay in the OH\* chemiluminescence response to the heat-release rate changes, but the phase error is less than half that of CH\* chemiluminescence response.

An in-phase modulation of mass-flow and equivalence ratio with amplitudes of 2 scc/sec and 0.02 respectively is shown in Figure 10.8. The figure again emphasizes the sensitivity of CH\* chemiluminescence to changes in mixture equivalence ratio. The amplitude of the equivalence ratio fluctuation has now reached the level where the oscillation of CH\* chemiluminescence becomes non-linear as seen by the asymmetric response. OH\* chemiluminescence meanwhile maintains approximate symmetry with respect to the mean operating point along with the heat-release rate.

Figure 10.9 shows the ideal dynamic response for a flame subjected to the same oscillation amplitudes, 0.02 in equivalence ratio and 2 scc/sec in mass-flow but with a 180 degree phase difference between the oscillations. Figure 10.9 shows that the

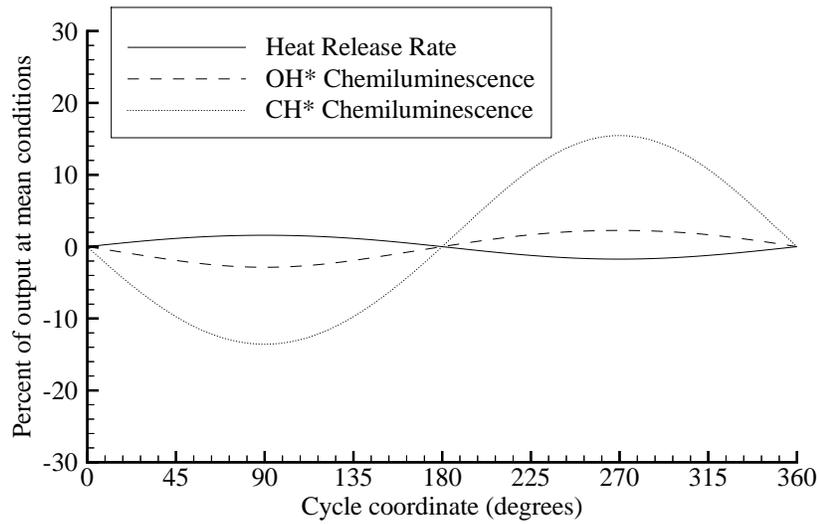


**Figure 10.8:** Ideal dynamic response with in-phase variation of equivalence ratio and mass-flow at amplitudes of 0.02 and 2 scc/sec respectively

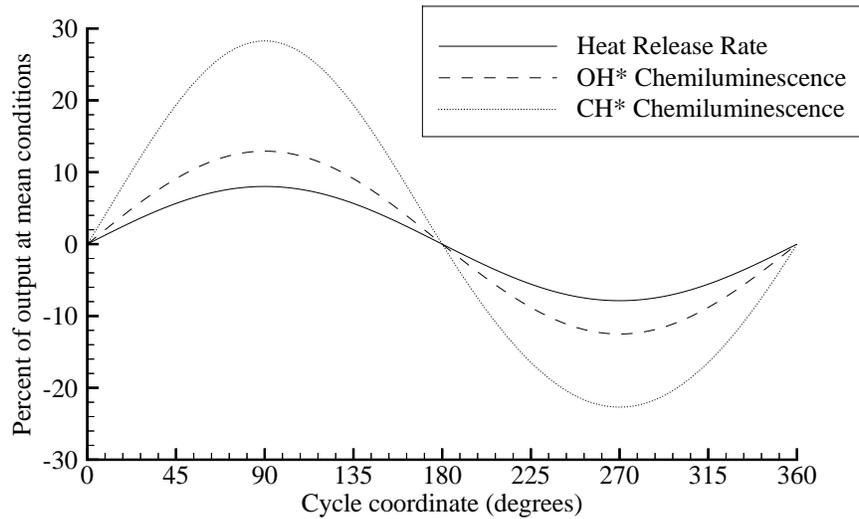
heat-release rate response is almost flat, slightly increasing with increasing mass-flow in the cycle. CH\* chemiluminescence on the other hand, again due to the high sensitivity to equivalence ratio fluctuations, decreases significantly during the cycle with increasing mass-flow, parallel to the decrease in equivalence ratio. The OH\* chemiluminescence response is also decreasing when heat-release rate is increasing, although the amplitude of the out-of-phase oscillation is greatly diminished compared to that of CH\* chemiluminescence.

Figure 10.10 shows that the situation observed in Figure 10.5 is recovered when the amplitude of mass-flow oscillation is doubled once more to 4 scc/sec and the equivalence ratio fluctuation is kept the same at 0.02. The amplitudes of oscillation of OH\* chemiluminescence and heat-release rate are comparable whereas the CH\* chemiluminescence oscillation amplitude is significantly higher.

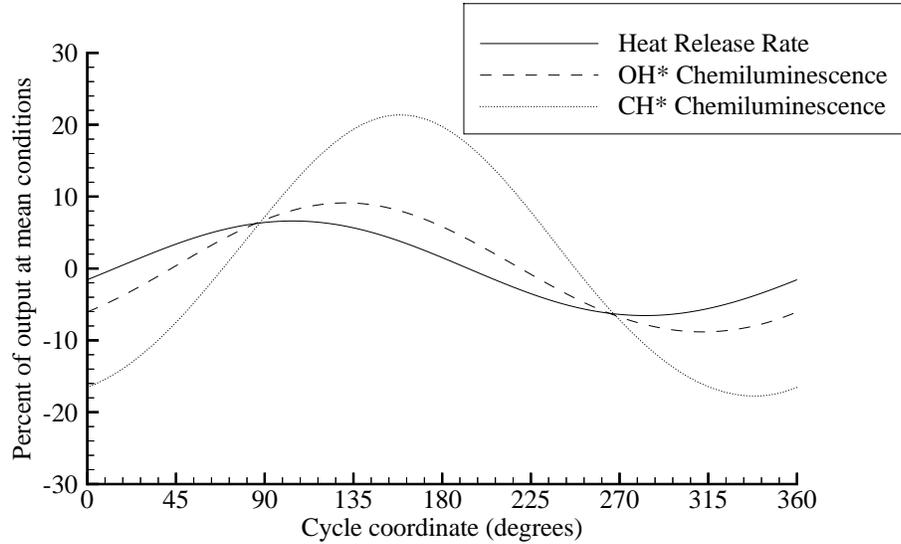
Figure 10.11 shows the response of the flame to oscillations in mass-flow of 4 scc/sec and equivalence ratio of 0.02, phase-shifted with respect to each other by 90 degrees. The figure confirms the trend already observed in Figure 10.9, in that OH\* chemiluminescence follows heat-release rate more closely than does CH\*



**Figure 10.9:** Ideal dynamic response with a 180 degree phase shift between the oscillations of equivalence ratio and mass-flow of amplitudes of 0.02 and 2 scc/sec respectively



**Figure 10.10:** Ideal dynamic response with in-phase variation of equivalence ratio and mass-flow at amplitudes of 0.02 and 4 scc/sec respectively

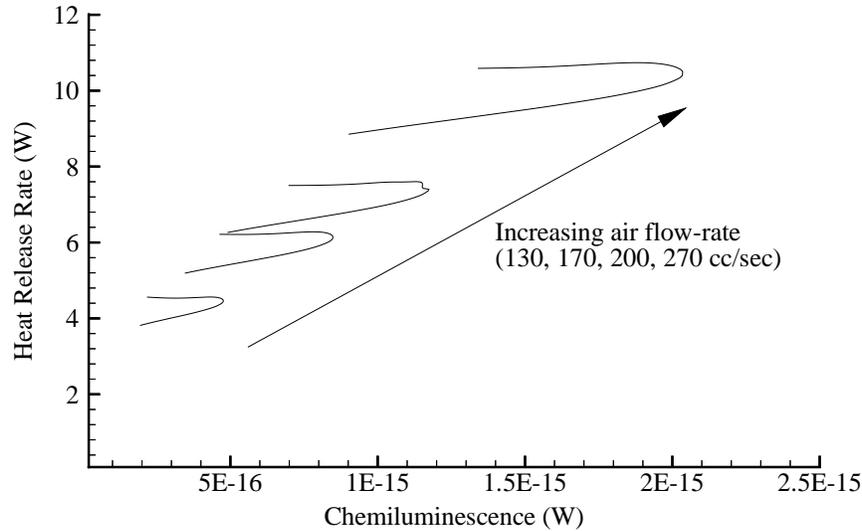


**Figure 10.11:** Ideal dynamic response with a 90 degree phase shift between the oscillations of equivalence ratio and mass-flow of amplitudes of 0.02 and 4 scc/sec respectively

chemiluminescence. The heat-release rate is least affected by the equivalence ratio oscillation. OH\* chemiluminescence is somewhat more sensitive to the fluctuation in equivalence ratio. CH\* chemiluminescence again is shown to exhibit the highest sensitivity to the equivalence ratio fluctuations.

### 10.2.2 Honeycomb burner heat-release rate modeling results

The interpretation of heat-release rate in the honeycomb burner is an interesting problem, considering the axial variation of temperature as shown in Figure 8.12. There is a significant temperature increase of the gas prior to the flame-front. In the gas heat-up region, there is no chemical reaction and consequently no chemiluminescence. However, the temperature increase experienced by the gases is due to energy originating from the flame-front in the form of radiative heat-transfer to the honeycomb surface. Using the definition that heat-release rate is the maximum total enthalpy change of the gases, all of the temperature increase due to heat-transfer from the honeycomb walls must be included. The proportionality of heat-release rate and

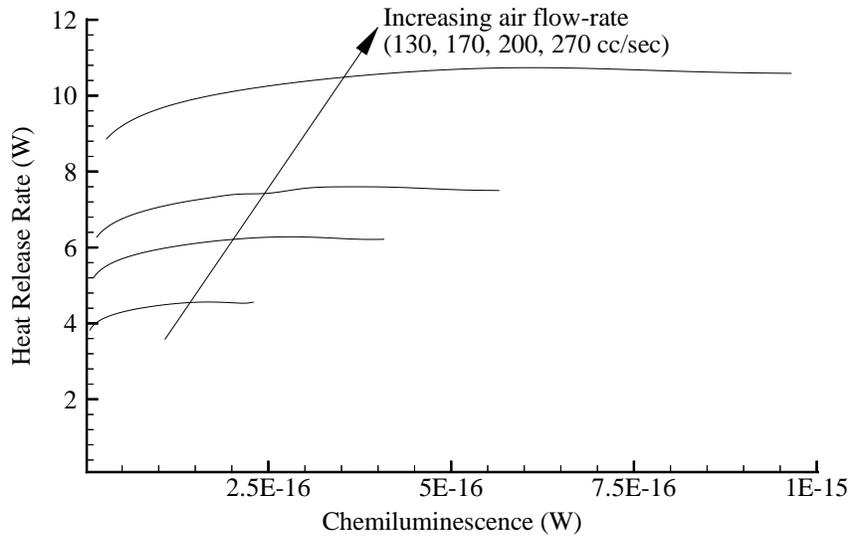


**Figure 10.12:** Heat–release rate as a function of OH\* chemiluminescence for four air flow–rates and varying equivalence ratio

chemiluminescence may however be affected since part of the temperature increase does not occur at the same spatial location as the chemical reaction. Some relationship between chemiluminescence and the defined heat–release rate should remain because the energy obtained by the gas through heat–transfer from the honeycomb does have its ultimate origin in heat lost from the flame.

Figure 10.12 shows the variation of heat–release rate as a function of OH\* chemiluminescence for four air flow–rates and varying equivalence ratio. Figure 8.9 showed that OH\* chemiluminescence peaks around an equivalence ratio of 0.90. The non–unique relationship between heat–release rate and OH\* chemiluminescence shown in Figure 10.12 is caused by the fact that OH\* chemiluminescence peaks at an equivalence ratio of 0.90 while the heat–release rate continues to increase.

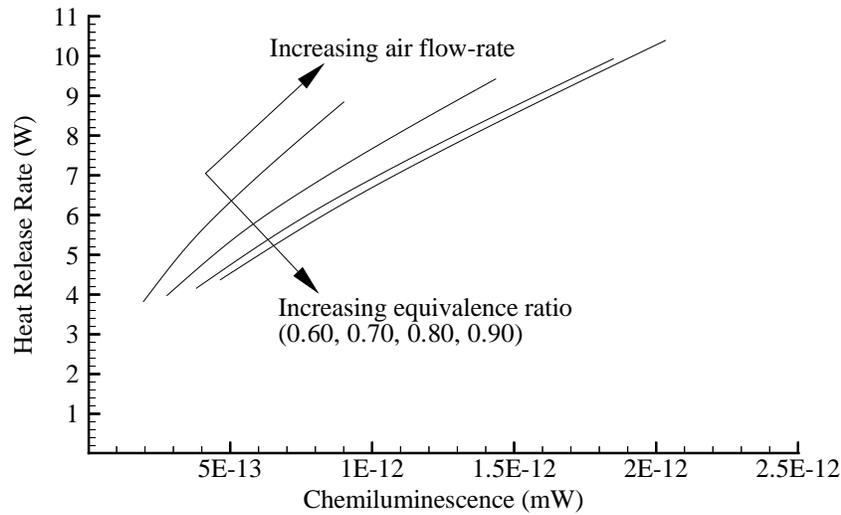
Figure 10.13 shows the variation of heat–release rate as a function of CH\* chemiluminescence for four air flow–rates and varying equivalence ratio. Since CH\* chemiluminescence is a monotonic function of equivalence ratio, the functional dependence between CH\* and heat–release rate appears simpler. The heat–release rate peaks near an equivalence ratio of 1.025, preventing CH\* chemiluminescence from providing a



**Figure 10.13:** Heat–release rate as a function of  $\text{CH}^*$  chemiluminescence for four air flow–rates and varying equivalence ratio

one–to–one sensor relationship for heat–release rate given the flow–rate.

Another interesting way of looking at the data presented above in Figures 10.12 and 10.13 is to look at the variation of heat–release rate with flow–rate for a constant equivalence ratio. In some combustion systems, combustion instabilities occur without variation of equivalence ratio in the flame. For these systems, the oscillations are in flow–rate only and not in equivalence ratio. Flame dynamics studies using the  $\text{OH}^*$  chemiluminescence signal as heat–release rate indicator have been conducted recently for the honeycomb burner (Khanna et al., 2000). The validity of the study partially depends on an assumption of direct proportionality between heat–release rate and  $\text{OH}^*$  chemiluminescence. Figure 10.14 shows the variation of heat–release rate as a function of  $\text{OH}^*$  chemiluminescence for a continuous variation of flow–rate and four distinct equivalence ratios. The figure shows that the assumption of direct proportionality for a given equivalence ratio is good, particularly when the perturbations in flow–rate considered are small. The figure also shows that there is a somewhat significant change in the proportionality constant between  $\text{OH}^*$  and heat–release rate as the equivalence ratio is changed. The observed change in the proportionality constant



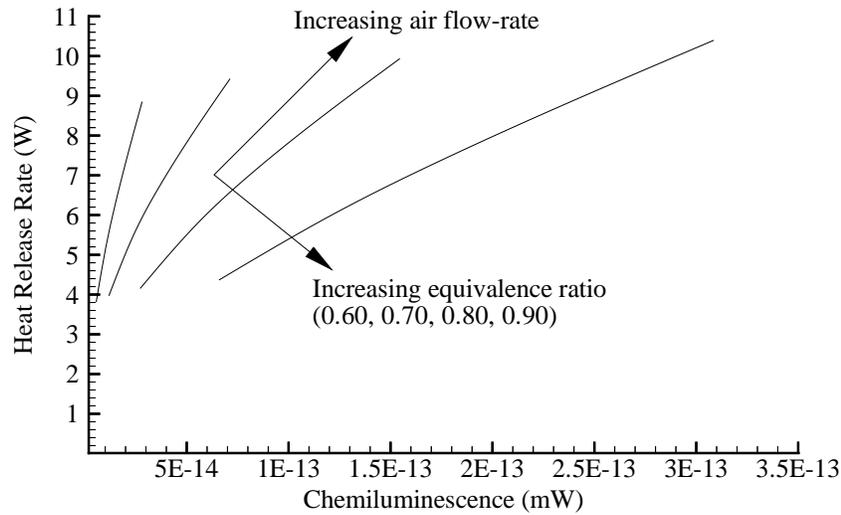
**Figure 10.14:** Heat–release rate as a function of OH\* chemiluminescence for four equivalence ratios and varying flow–rate

affects the interpretation of relative results from flame dynamics studies.

Figure 10.15 shows the relationship between CH\* chemiluminescence and heat–release rate analogous to Figure 10.14. The figure shows that an assumption of direct proportionality between heat–release rate and CH\* chemiluminescence is also valid for variations in flow–rate. The proportionality constant between heat–release rate and chemiluminescence which varied mildly for OH\* under changes of equivalence ratio varies greatly for CH\* chemiluminescence. The variation of the proportionality constant with equivalence ratio reflects the exponential dependence of CH\* chemiluminescence on equivalence ratio.

### 10.3 Application of OH\* Measurements

The original motivation for beginning the present study was to measure heat–release rate in premixed flames using chemiluminescence as the measured quantity. Ideally, such a measurement of chemiluminescence is not only able to measure the time–averaged heat–release rate but also the dynamic component of heat–release rate.

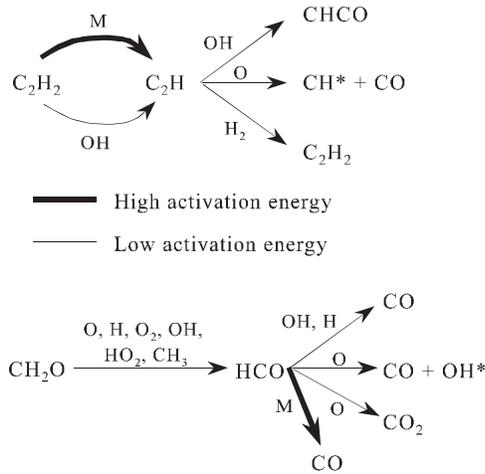


**Figure 10.15:** Heat–release rate as a function of CH\* chemiluminescence for four equivalence ratios and varying flow–rate

Measuring the dynamic component of heat–release rate is very important in monitoring modern ultra–lean premixed gas turbine combustors which are susceptible to combustion instabilities. A quantitative measure of dynamic heat–release rate is also important in combustion instability research for the purpose of system identification.

Based on the work presented in this report, OH\* appears to be the best candidate for heat–release rate measurement in premixed methane flames. OH\* chemiluminescence is tied directly to a major intermediate in the formyl radical, the break–up of which is responsible for a significant proportion of the total heat–release obtained in the conversion from methane to carbon dioxide. OH\* chemiluminescence measurement offers several advantages over the measurement of CH\* chemiluminescence for heat–release rate.

First, the calculations discussed in Chapter 8 show that OH\* formation is understood not only on a qualitative basis but also on a quantitative basis. The ability to accurately predict OH\* chemiluminescence makes the conclusions drawn from the honeycomb burner model more meaningful. The accuracy achieved in modeling OH\* chemiluminescence provides a solid foundation for the assumption that OH\* chemi-



**Figure 10.16:** Chemiluminescence formation path diagram

luminescence is proportional to heat-release rate in other burner systems.

Second, for methane combustion,  $OH^*$  chemiluminescence is more closely associated with the major heat-releasing chemical kinetic species. As shown in Figure 10.16, all consumption reactions of the formyl radical yield carbon monoxide or carbon dioxide. The production of these molecules is always associated with significant heat-release. Only the  $CH^*$  producing reaction is associated with significant heat-release in the consumption of the  $C_2H$  radical.

A third reason for choosing  $OH^*$  chemiluminescence as heat-release rate indicator over  $CH^*$  chemiluminescence lies in the relative sensitivity of each species to equivalence ratio variations. Heat-release rate, on a per unit mass of fuel basis, does not vary significantly with equivalence ratio. The inherent lack of sensitivity of heat-release rate to equivalence ratio fluctuations makes the choice of  $CH^*$  chemiluminescence as indicator of heat-release rate difficult to justify given its exponential sensitivity to equivalence ratio changes.  $CH^*$  chemiluminescence based on the Bunsen type burner and honeycomb burner experiments discussed in Chapter 5, increases by an order of

magnitude over the equivalence ratio range 0.6 - 1.0, whereas OH\* chemiluminescence increases by about 50% over the same range. Heat-release rate can be expected to only change by on the order of 5 - 10% over the same range. The equivalence ratio sensitivity of CH\* chemiluminescence becomes important in dynamic measurement applications where the mixture equivalence ratio varies in time. Measurement of CH\* would over-estimate the variation of heat-release rate significantly. The measurement of OH\* chemiluminescence does not eliminate this problem, but the calculations of ideal flame response discussed in Section 10.2.1 and illustrated in Figure 10.11, for example, showed that the OH\* chemiluminescence response follows heat-release rate more accurately than CH\* chemiluminescence.

Finally, OH\* chemiluminescence measurement is preferable to CH\* chemiluminescence measurement for experimental reasons. CH\* chemiluminescence light emissions occur at 431 nm whereas OH\* chemiluminescence light emissions occur at 308 nm. The relative proximity of CH\* chemiluminescence light emissions to the red spectrum causes the measurement of CH\* chemiluminescence to be much more susceptible to background radiation, as observed in Figure 5.18. More importantly, time-varying background radiation may contaminate the desired measurement of unsteady heat-release rate.

## 10.4 Application of CH\* Measurements

CH\* chemiluminescence is an attractive measurement quantity due to the fact that the light is measured in the visible range of the spectrum and does not require a special UV sensitive light-measuring device. As seen in the honeycomb spectrum in Figure 5.18 however, the location of the CH\* emission peak in the visible spectrum makes the measurement susceptible to contamination by other radiation sources such as hot surfaces in the combustor.

Based on the formation chemical kinetics of CH\*, its chemiluminescence is anticipated to be a poorer quality indicator of heat-release rate than OH\* for premixed methane flames. The consumption of the C<sub>2</sub>H radical does not always cause signif-

icant heat-release as Figure 9.2 shows. The energy contained in the carbon-carbon bond is only released in the reaction yielding  $\text{CH}^*$ . More significantly however, the  $\text{C}_2\text{H}$  radical branch is significantly less populated than the formyl radical branch, especially at low equivalence ratios, and thus contributes less to the total amount of heat released.

It is important to stress that  $\text{CH}^*$  chemiluminescence may be an appropriate indicator of heat-release rate in higher hydrocarbon fuels such as acetylene or propane.  $\text{C}_2\text{H}$ , the precursor of  $\text{CH}^*$  is a much more important intermediate in higher hydrocarbon combustion and may prove to be a good indicator of heat-release rate in these environments, provided the measurement can be made without interference from background radiation.

## 10.5 Application of Combined Measurements

The local Bunsen type burner measurements have shown that the ratio of  $\text{OH}^*$  to  $\text{CH}^*$  chemiluminescence may be used to obtain meaningful information about local burning conditions. In the case of the ratio of  $\text{OH}^*$  to  $\text{CH}^*$  chemiluminescence, the quantity measured locally is the equivalence ratio. Global measurements on both burners studied showed that even for different flow-rates on different burners, an exponential fit through all the data points collected can predict equivalence ratio to within 10%. Calibration for each burner improves the accuracy of the curve-fit considerably to below 5% in each case. The difficulty in making the chemiluminescence ratio measurement lies in the equipment required. Using a monochromator and manually changing the measurement wavelength is not practical in any application other than pure research. To perform chemiluminescence ratio measurements efficiently and dynamically, the collected light has to be split evenly and achromatically and then measured using relatively calibrated intensity measurement devices of which at present only PMTs are sensitive enough to be suitable for the application. Implementation of this type of setup is at present cost-prohibitive but possible.

Finally, it is important to note that the accuracy of the measurement is severely

hampered by a loss in accuracy in the measurement of  $\text{CH}^*$  chemiluminescence. At lean equivalence ratios, the weakness of the  $\text{CH}^*$  light signal causes both a good sensitivity of the chemiluminescence ratio to variations in equivalence ratio but also could introduce significant error if measurement precision cannot be maintained at lower light levels. It is also important not to forget to check for possible stray radiation contamination of the  $\text{CH}^*$  signal as discussed above in Section 10.4.

A further application of  $\text{OH}^*$  chemiluminescence measurement, or  $\text{CH}^*$  chemiluminescence measurement for that matter is the identification of flame structure. Both  $\text{OH}^*$  and  $\text{CH}^*$  correctly identified the Bunsen type burner flame–tip burning structure. The very tip of the Bunsen flame studied consumes very little of the fuel originally contained in the center stream–tube. It would thus make sense that a local minimum in chemiluminescence would be observed in the flame–tip as shown in the figures of Section 5.1.2. The chemiluminescence ratio as well helps to identify the flame structure as the ratio is seen to increase in the center of the flame, again confirming the studies of Poinso et al. (1992), that there is a fuel deficit in the flame center causing the flame to actually burn leaner in the center. Leaner burning increases the chemiluminescence ratio.

## 10.6 Dynamic heat–release rate measurement

The application of chemiluminescence in the measurement of time varying heat–release rate requires some further attention. Although the present calculations all involve steady state assumptions, important conclusions can be drawn from the results that affect how dynamic chemiluminescence measurements should be interpreted.

In Section 10.2.1, the ideal response of chemiluminescence and heat–release rate to oscillations in equivalence ratio and heat–release rate was illustrated. The calculations showed the excessive sensitivity of chemiluminescence to equivalence ratio compared to the low sensitivity of heat–release rate to the same variable. For dynamic measurements conducted under conditions of time–varying equivalence ratio and flow–rate, the limitation presented by the excessive sensitivity to equivalence

ratio is severe if the equivalence ratio oscillations are on the same order as the flow-rate oscillations. Equivalence ratio variations in time have been postulated to occur in modern ultra lean premixed gas turbine combustors (Richards and Janus, 1998) when combustion oscillations are observed, but these oscillations are generally not considered to have very high amplitude. Even in the absence of equivalence ratio fluctuations, consideration must be given to the relationship between chemiluminescence and equivalence ratio.

Consider Figure 10.14 which shows the relationship between OH\* chemiluminescence and heat-release rate for varying flow-rate at for different equivalence ratios. In the comparison of dynamic measurements performed at one equivalence ratio to those at another equivalence ratio, the excessive sensitivity of OH\* to equivalence ratio must be considered. In order to illustrate this point, consider Equation 10.1 which captures the essential functional relationship between OH\*, heat-release rate, flow-rate and equivalence ratio. Equation 10.1 casts the relationship between OH\* chemiluminescence and heat-release rate into linear form with the slope and intercept varying with equivalence ratio. In the identification of flame dynamics, the mean component of heat-release rate is rarely of interest, the focus is on the dynamic component of heat-release rate, i.e. the derivative of Equation 10.1. The time derivative operation removes the function  $G(\phi)$ . What remains is the variation of the slope in the linear relationship between OH\* chemiluminescence and heat-release rate, giving a single proportionality constant to relate the time-derivative of OH\* chemiluminescence to the time-derivative of heat-release rate. The function  $F$  which determines the proportionality constant is relatively invariant at high equivalence ratios but becomes important as lean blow-out conditions are approached.

$$\dot{Q} = F(\phi)OH^* + G(\phi) \quad (10.1)$$

The result of the analysis shows that assuming a direct proportionality between the time derivative of heat-release rate and OH\* chemiluminescence is appropriate only in a limited range of equivalence ratio. At lower equivalence ratios, the change in the proportionality factor with equivalence ratio becomes significant and must be

accounted for.  $\text{CH}^*$  chemiluminescence is more sensitive to changes in equivalence ratio than  $\text{OH}^*$  chemiluminescence, as seen in Figure 10.15, and the assumption of direct proportionality cannot be defended for any lean equivalence ratio. It is also important to note that as the equivalence ratio is lowered, the proportionality constant increases. Neglecting the variation of the proportionality constant with equivalence ratio will thus under-predict the magnitude of the heat-release rate variation actually occurring in flame-dynamics measurements.

All of the above points rely on the assumption that the curves shown in Figure 10.14 and Figure 10.15 remain valid in a dynamic combustion environment. In order for the assumption to be valid, the heat and mass transport characteristics of the dynamic combustion environment must be similar to the corresponding steady environment. Future work will examine, in detail, how similar the environments have to be to allow extrapolation of steady results into dynamic environments. Recent qualitative measurements taken in an unstable ceramic honeycomb tube combustor have indicated a 10% change in mean chemiluminescence emission over the entire radiation spectrum, clearly illustrating the limitations of the results contained in this thesis with respect to their applicability in unsteady burning environments. However, the ceramic honeycomb tube combustor represents an extreme case where velocity fluctuations are of the same order as the mean velocity. Dynamic models for the relationship between chemiluminescence and unsteady heat-release rate remain an intriguing issue for research in virtually all types of combustors.