Quantification of the Raman Scattering and LIF Data
3.1 General introduction

In the present work the non-intrusive laser diagnostic methods described in Ch. 2 have been used to derive species concentrations and temperatures in laminar diffusion flames. Extracting quantitative information using these techniques, however, requires special considerations [1]. For example, knowledge of the temperature-dependent scattering cross-sections of the species of interest is needed for obtaining mole fractions and temperature using spontaneous Raman scattering technique. Similarly, quantitative use of laser induced fluorescence (LIF) for flame diagnostics requires knowledge of temperature and composition dependent parameters such as quenching rates, line widths, etc. In most cases, for extracting quantitative information, separate calibration procedures must be conducted in media where composition and temperatures are known. This chapter describes the procedures followed to quantify the spontaneous Raman scattering and LIF data used in this work.

3.2 Quantitative information from Raman measurements

As shown in Eq. 2.1, the measured Raman intensity is dependent upon the incident laser power, effective Raman scattering cross-section and the concentration of the species of interest [2,3]. The effective scattering cross-section in turn depends on the local temperature, excitation wavelength and experimental parameters such as the quantum efficiency of the detector, spectrometer bandwidth, etc. In one approach, the effective cross-sections of all species at the laser wavelength are determined through calibration in flames with known composition and temperature [4-7]. But, this procedure is tedious, because the calibration needs a large number of flames and the temperatures of these flames should be measured independently, preferably maintaining the same composition at different temperatures.

Major species concentrations and temperatures can also be obtained by fitting the experimental Raman spectrum, provided the functional dependence of the Raman cross-sections of all flame components on wavelength and temperature is known [8]. In this approach, the calibration procedure is simplified to the determination of the apparatus function and the overall response of the detector system, which can be achieved by a single daily measurement of the Raman signal in a medium having known composition and temperature, such as room-temperature air. More importantly, this procedure uses all spectral information, which can potentially increase precision, and interfering signals in the measured spectrum can be detected and removed.
The Raman cross-sections of diatomic molecules are known with good accuracy, and their use in the fitting code is straightforward [8-11]. The knowledge of the cross-sections of polyatomic molecules, however, is limited and may require calibration. The Raman spectrum of CO$_2$ has been adequately described over the range from room to flame temperatures [8,12] and the spectral data can be used reliably in the fit. The Raman spectrum of CH$_4$ is currently available only at lower temperatures (<1000 K), and requires more information at higher temperatures. Fortunately, in most of the cases, CH$_4$ is hardly present in substantial quantities in hydrocarbon combustion at temperatures above 1500 K, and therefore one can approximate its concentration to zero at these temperatures. Thus, for quantitative work, uncertainty remains about the CH$_4$ Raman spectrum in the temperature region 1000 - 1500 K. However, in this work the CH$_4$ Raman spectrum was not measured in this temperature range, and this problem was avoided. Water is formed in substantial quantities during combustion of hydrogen-containing species. The calculation of the Raman spectrum for this asymmetric-top molecule is far more complicated than for the diatomic and linear triatomic molecules [13]. Lapp [14] obtained the vibrational-rotational Raman signature of water molecules, which is dependent upon temperature, but he called attention to the need for more information on the broad spectrum of water at high temperatures. A better characterization of the spectra at high temperatures is especially important for flame studies.

In this chapter, an approach is presented to conduct quantitative Raman measurements in the hot gases of laminar premixed CH$_4$/air and H$_2$/air flames and to assess the capability of the Raman system for obtaining concentrations and temperatures accurately by spectral fitting. For this purpose, a computer program was written to fit the calculated spectra to the experimental spectra. To include fitting of the water spectrum, the Raman spectra of water in a wide range of temperature were measured. To assess the accuracy of the measurements, the Raman temperatures were compared to those obtained by CARS. The species mole fractions in post-flame gases were compared with those expected at equilibrium. As will be seen below, use of this fitting procedure simplified the quantification to a single daily calibration measurement.

3.3 Calculation of Raman spectra

As given in Ch. 2, the intensity of the measured Raman signal of species $j$ can be written in general as
\[ I_j(v) = P_j N_j \left( \frac{d\sigma(v)}{d\Omega} \right)_j \Delta\Omega \lambda \epsilon, \quad (2.1) \]

where \( \left( \frac{d\sigma(v)}{d\Omega} \right)_j \) is the differential cross-section of species \( j \) at frequency \( v \). For the Raman signal of species \( j \) measured by one pixel of the photodetector, Eq. 2.1 can be rewritten as

\[ I_{pj}(v_i) = \frac{C' \epsilon(v_i) \left( \frac{d\sigma(v_i)}{d\Omega} \right)_j}{v_i} \frac{x_j}{T}, \quad (3.1) \]

where \( I_{pj} \) is the intensity in photons/s, \( x_j \) is the mole fraction of species \( j \) and \( v_i \) is the frequency corresponding to the \( i^{th} \) pixel of the photodetector, respectively. In this equation, \( \epsilon(v_i) \) is the spectral sensitivity of the detection system, which can be determined by measuring radiation of a light source with known emission characteristics, such as tungsten lamp. In Eq. 3.1, \( C' \) is a constant which includes the laser power, collecting solid angle and length of measurement volume, and can be written as

\[ C' = \frac{P}{hc} \Delta\Omega l \frac{P}{k} \quad (3.2) \]

The measured Raman intensity for a multicomponent system can be written as

\[ I_{\text{meas}}^i = C' \sum_j \frac{\epsilon(v_i) \left( \frac{d\sigma(v_i)}{d\Omega} \right)_j}{v_i} x_j \frac{1}{T} + I_{bg}^i, \quad (3.3) \]

where \( I_{\text{meas}}^i \) is the measured intensity of the raw spectrum, \( I_{bg}^i \) is the measured background signal. The measured background signal \( I_{bg} \) is added to Eq. 3.3 to account for intensities arising from other (non-Raman) radiating processes. In Eq. 3.3, the values of mole fractions \( (x_j) \) and temperature \( (T) \) are unknown parameters, while the values of the rest of the parameters are known either theoretically or determined through calibration. As the cross-sections of diatomic molecules are known, the values of the calibration constants \( C' \) can be retrieved when the Raman spectra are measured in media (such as ambient air) with known concentrations of these species. When the number of measured spectral points (number of pixels of the photodetector) is larger than the number of unknowns; the unknown parameters can be found using a least-square fitting method.
3.4 Experimental procedure for calibrating the Raman system

Flat flame burners, such as McKenna Products burner, have been proven as an excellent system for calibrating Raman signals [5,6,15,16]. Using these burners, good spatial uniformity of the post-flame region can be obtained and a wide range of temperatures and gas compositions can be achieved by varying stoichiometry or flow rates. In the present calibration procedure, a McKenna burner, along with specially built heat exchangers, were used to obtain a wide range of temperatures and compositions of the hot gas for the Raman measurements. The burner and heat exchanger are shown schematically in Fig. 3.1. The heat exchanger consisted of a bundle of stainless tubes. The stainless tubes were welded together to obtain a uniform radial temperature distribution (maximum difference ~ 30 K) across the exit plane. A cooling coil was wrapped around the tubes just above the burner. Similar heat...
exchangers of different lengths were constructed to obtain different gas temperatures at the measuring location. Each heat exchanger was placed as close to the burner as possible to prevent mixing of the flue gases with the surrounding air. This ensured that the composition of the flue gases downstream at the measuring point remained unchanged. Temperatures ranging from \( \sim 2200 \) K (above the CH\(_4\)/air premixed flame without any heat exchanger) to \( \sim 450 \) K were obtained with a step of about 150 K.

The optical scheme used for the Raman scattering measurements is described in detail in Ch. 2. The Raman and CARS measurements were performed on premixed CH\(_4\)/air and H\(_2\)/air flames. The flow rates of methane, hydrogen and air were measured by mass flow meters (Bronkhorst) and the equivalence ratios were determined by measuring the methane and oxygen concentrations in the fuel-air mixtures by an infrared and paramagnetic analyzer, respectively, in the Maihak Unor 710 module.

### 3.5 Results and discussion for the Raman data

The coefficient \( C' \), as we can see in Eq. 3.2, is dependent only upon parameters of the experimental setup. Before proceeding further, the constancy of \( C' \) was examined. For this purpose, the Raman spectra of pure gases and air were measured at room temperature, and the coefficient \( C' \) was determined by fitting each Raman spectrum. The coefficients \( C' \), obtained in this manner were normalized to that of pure N\(_2\), and plotted as a function of wavelength of the Raman transition, shown in Fig. 3.2.

![Figure 3.2 Calibration coefficients calculated for different species.](image-url)
As can be seen in the figure, the normalized coefficients determined in CO₂, CH₄ and H₂ remain within 10% of that for N₂. However for oxygen, the normalized coefficient is significantly higher than those derived for the other species. One possible reason for this discrepancy is the resonant enhancement of the O₂ Raman signal because of the proximity of the B₃Σ_u electronic state, as indicated in [17]. We remark here that the Raman cross-section has been measured using low-power CW laser, in contrast with the pulsed high-power laser used here. This could have an impact on the resonance-enhanced Raman cross-section. To correct for this discrepancy, in the Raman fitting program the scattering cross-section of O₂ is decreased by 30% the literature value.

The Raman signatures of water in the temperature range 450 – 2200 K were obtained using the burner arrangement shown in Fig. 3.1 and stored as a library of spectra in the fitting program. As an example, Fig. 3.3 shows the water Raman spectra at four different temperatures in CH₄/air flames at ϕ = 1. In this figure, we see the

![Raman spectra of water at different temperatures](https://via.placeholder.com/150)

Figure 3.3 Raman spectra of water at different temperatures, as obtained through the calibration study on premixed CH₄/air flames at ϕ = 1
progressive change in the Raman signal intensity and shape over the range of temperatures from 790 (Fig. 3.3a) to 2200 K (Fig. 3.3d). Particularly interesting is the considerable spread in the Raman spectrum at high temperatures.

Whereas the Raman spectra are fitted in the present work for deriving the temperature and species concentrations, it is interesting to assess the double harmonic approximation for calculation of the vibrational Raman spectrum. In this approximation, the differential Raman scattering cross-section for species \( j \) is given by [11] as

\[
\frac{d\sigma}{d\Omega}_j = \frac{h(v_0 - v_j)^2 \left\{ (a')^2 + \frac{4}{45} (\gamma')^2 \right\}}{8\mu e^4 v_{shf,j}^2 [1 - e^{-hv/\Delta T}]},
\]

where \( a' \) and \( \gamma' \) are the mean and anisotropy invariants of the polarizability tensor, \( h \) is the Planck’s constant and \( \mu \) is the reduced mass of the species. Using this equation, we can estimate the behavior of the scattering cross-section of any species as a function of temperature. For \( N_2 \) in the temperature range from 400 to 2000 K, the value of the differential cross-section remains relatively constant due to only 20% variation in the factor \( [1 - e^{-hv/\Delta T}] \) in Eq. 3.4, and the Raman signal intensity is estimated to vary roughly linearly with \( 1/T \), as can be seen in Fig. 3.4. Similarly, Eq.

![Figure 3.4 Integrated Raman signal intensity for \( N_2 \) and \( H_2O \) molecules as a function of temperature.](image-url)
3.4 predicts the H$_2$O Raman scattering cross-section to vary only by $\sim 7\%$ over the temperature range 400 to 2000 K and the Raman signal intensity for this molecule is also expected to vary linearly with $1/T$ in this temperature range. The integrated Raman intensities are plotted against $1/T$ for N$_2$ and H$_2$O in Fig. 3.4, which supports the use of double harmonic approximation for the H$_2$O molecule.

Figure 3.5 shows the results of fitting flame spectra of a stoichiometric premixed CH$_4$/air flame with and without the heat exchanger; the corresponding CARS measurements indicate that the temperatures in the flames in Fig. 3.5a and 3.5b are 785 K and 2170 K, respectively. The Raman measurements at the lower temperatures were conducted at the laser energies $\sim 135$ mJ/pulse to avoid the optical breakdown, and at higher temperature, the laser energy was increased up to 185 mJ/pulse. The signal intensities (counts) in these plots are absolute.
Figure 3.5 Plots showing experimental and fitted Raman spectra in the stoichiometric CH<sub>4</sub>/air flames at different temperatures. The table shows the results obtained from fitting the Raman spectra and their comparison against the equilibrium species compositions of the burnt gas mixture for the conditions used.
In Fig. 3.5, as expected for the post-flame gases of a stoichiometric CH₄/air flame, the measured Raman spectra show mainly N₂, CO₂ and H₂O. The temperature dependence of the Raman spectrum can be observed through the shapes and peak intensities of the Raman bands. Particularly, the spread in the Raman bands and the reduction of the peak intensities at higher temperature is seen for all the species. The results obtained from the fit show excellent agreement between the CARS and the Raman temperatures. The difference in the measured and equilibrium mole fractions of N₂, CO₂ and H₂O is no more than 10% (relative). The results of the fit even reflect small quantities of CO (Fig. 3.6), which is barely seen in the magnified scale of Fig. 3.5b.

![Figure 3.6](image_url)

Figure 3.6 The magnified image of the spectrum shown in Fig. 3.5b. Here, the spectral fit detects the presence of trace CO at the measuring location.

The results obtained in a stoichiometric premixed H₂/air flame, shown in Fig. 3.7a and 3.7b, are also in excellent agreement with the equilibrium approximation. As expected, the composition at the measuring location mainly consists of N₂ and H₂O. Here too, the spectral intensities and lineshapes at different temperatures are well reproduced by the fit.
Figure 3.7 Plots showing experimental and fitted Raman spectra in stoichiometric H$_2$/air flames at different temperatures. The table shows the results obtained from fitting the Raman spectra and their comparison against the equilibrium species compositions present in the burnt gas mixture for the conditions used.
In the current work on coflow diffusion flames, where sharp radial gradients in species distributions were present, only 4 CCD pixels in the spatial direction were binned to increase the spatial resolution, which decreased the signal-to-noise ratio (SNR) of the Raman spectrum compared to that obtained above by binning 256 pixels. This was especially of concern when collecting data in the hot regions of the hydrogen diffusion flames, where the Raman signal intensities were low and the data possessed significant noise. Thus it was essential to test the ability of the spectral fitting program to obtain mole fractions and temperatures accurately using the noisier data at high temperatures. This test was performed by measuring the Raman spectra with different exposure times. Figure 3.8a shows a flame spectrum with 10s exposure time and 10 accumulations, while Fig. 3.8b shows the flame spectrum with 1s exposure time and 10 accumulations. The values obtained by fitting are reported in the corresponding table.
Figure 3.8 Plots showing experimental and fitted Raman spectra in stoichiometric CH\(_4\)/air flames. The experimental Raman data were collected in the same flame with different signal collection time to obtain different signal to noise ratios (SNR) in the plots.
The mole fractions and temperatures obtained after fitting the experimental spectra in Fig. 3.8a and 3.8b are in excellent agreement, in spite of the substantially poorer SNR in Fig. 3.8b.

3.6 Conclusions for the quantitative Raman diagnostics

Spectral fitting of the measured Raman spectra greatly simplifies the experimental procedure; only a single daily calibration measurement of the Raman signal is required. Comparing the measured composition in post-flame gases with equilibrium concentrations, we can conclude that the accuracy of the present Raman setup is better than 10% (relative) for major species with mole fraction $\geq 0.1$ and 0.01 mole fraction for lower concentrations. The temperatures obtained by the Raman measurements in methane and hydrogen flames are in excellent agreement with those obtained by CARS, with a maximum of 50 K difference between them. The excellent agreement achieved in the species mole fractions and temperatures by fitting the experimental spectra with different SNR indicates that the fitting code can even be used to fit moderate quality spectra.

3.7 Quantification of the LIF data: introduction

In last few decades, much effort has been devoted towards measuring the hydroxyl (OH) radical, which is an important participant in many key chemical reactions involved in the ignition of the fuel mixture, flame propagation and processes in the burnt flue gases. Laser induced fluorescence (LIF) has proved to be the best method for OH diagnostics in flame due to its sensitivity, selectivity and spatial resolution [18].

For a simple two level system in the linear regime, the following expression for the LIF signal is obtained by modifying Eq. 2.4 in Ch. 2:

$$ F = \frac{h\nu}{c} A_{21} \frac{\Omega}{4\pi} I_A \frac{N^0_i B_i^2 I^*}{(Q(T) + A_{21})} G(T), \quad (3.5) $$

where $G(T) = \int_{-\infty}^{\infty} L(\nu) g(\nu, T) d\nu$, is the overlap of the laser line $L(\nu)$, and the absorption profile $g(\nu, T)$. The rest of the symbols were defined in Ch.2. Based on this expression, the measured LIF signal can be simply written as
\[ F = C f_b(T) X_{abs} \frac{1}{T} \frac{A_{21}}{A_{21} + Q(T)} G(T), \]  

(3.6)

where \( C \) is a calibration coefficient that contains the geometrical factors and detection efficiencies, \( f_b(T) \) is the Boltzmann fraction and \( X_{abs} \) is the mole fraction of the species \([19, 20]\). It is clear from Eq. 3.6 that to quantify the LIF signals, the geometrical and the temperature dependent parameters should be determined. The geometrical factor can be determined experimentally, for example, by measuring the intensity of Rayleigh scattering. In the present work, the total partition sum for OH molecule was calculated using the method described in [21], while the values of the initial state energies were taken from [22]. Collisional quenching rates and the convolution integral can also be calculated, provided collider concentrations and their collisional cross-sections are known. The temperature dependent OH quenching cross-sections for \( O_2, H_2, H_2O, CH_4, CO \) and \( CO_2 \) molecules were taken from [23]. Absorption lines of OH in flame spectra can be described by a Voigt profile, which is the convolution of the Lorentzian line shape due to intermolecular collisions with the Gaussian line shape arising from molecular motions (Doppler broadening). The collisional line broadening parameters have been taken from [24, 25]. The spontaneous emission coefficients were taken from reference [26].

![Figure 3.9 Plot showing temperature dependent function \( Y(T) \) as a function of temperature for different species](image-url)
To illustrate temperature dependence of fluorescence signal, the temperature-dependent term \( Y(T) = (F/C)X_{OH} \) is shown in Fig. 3.9 for different collisional partners. In this figure, we see that the value of \( Y(T) \) calculated for \( \text{N}_2 \) is significantly higher than other major species over the range of temperature because of the low quenching cross-section of \( \text{N}_2 \). Thus, in the flames regions having significant nitrogen concentrations, we can expect the higher values of \( Y(T) \).

### 3.8 Quantifying the OH LIF data in diffusion flames

To determine the absolute value of the OH mole fraction, we make use of a calibration flame; here, a lean-premixed flat flame was used [27]. In this case, the local OH mole fraction in diffusion flames was calculated using Eq. 3.6 as

\[
X_{OH, \text{diff.}} = \frac{F_{\text{diff.}}}{F_{\text{cal.}}} \frac{Y(T)_{\text{cal.}}}{Y(T)_{\text{diff.}}} \left( X_{OH, \text{cal.}} \right),
\]

where \( X_{OH, \text{cal.}} \) denotes the OH mole fraction obtained in the calibration flame, and subscripts (diff) and (cal) denote diffusion and calibration flame, respectively. For measurements in the diffusion flames, the following procedure was followed. First the LIF signal in the center of the calibration flame was collected. Then the diffusion flame burner was placed at the measuring location, and the profiles of the LIF signals in the diffusion flames were measured. The consistency in the LIF data was then verified by repeating the measurement of the LIF signal in the premixed flame. In all experiments, the settings of the detection system were unchanged.

For calibration purposes, the direct OH measurements are preferred over calculations, because OH mole fraction is very sensitive to the operational conditions [28]. In this work, the results of direct laser absorption measurements in a lean-premixed flame [27] were used to calibrate the OH LIF data. The calibration measurements were performed using a flat near-adiabatic premixed \( \text{CH}_4/\text{air} \) flame at \( \phi = 0.8 \) (mass flux \( \rho \phi = 0.028 \text{ g/cm}^2\text{s} \)), stabilized on the McKenna burner. In this flame, at height of 15 mm above the burner surface, the OH mole fraction derived from the absorption measurements was 1550 ppm and temperature 1970 K (CARS measurements); these data were used for calibration purposes.
Figure 3.10 Plots showing the distribution of the major species, temperature (a) and temperature dependent factor $Y(T)$ (b) as a function of radial distance at $z = 3$ mm in H$_2$/air diffusion flame ($\delta = 18$ cm/s).

To calculate $Y(T)$, the local temperatures and concentrations of the major species are required. In the calibration flame, the mole fractions of the major species were obtained from the calculations using the PREMIX code in CHEMKIN II [29] with the GRI-MECH 3.0 [30] chemical mechanism. For diffusion flames, the major species and temperature data obtained from the Raman scattering and CARS measurements were used to calculate $Y(T)_{diff}$. Figure 3.10 shows an example of the distribution of $Y(T)$ along the radial distance in a diffusion flame at $z = 3$ mm (Ch. 4, 18 cm/s exit).
velocity). As expected from the results of the calculations shown in Fig. 3.9, the factor $Y(T)$ in Fig. 3.10 is seen decreasing from the regions of high N$_2$ concentrations to a minimum in the high temperature zones (caused by the high quenching rate of water). The strong dependence of the fluorescence signal upon composition is also illustrated by Fig. 3.11. In this figure, $Y(T)$ shown in Fig. 3.10 is plotted as a function of the measured local temperature. The figure shows two “branches”, one following the temperature increase from the center line $(r = 0, \text{center of the fuel jet})$, and one branch following the temperature increase beginning in pure air at $r \sim 12$ mm. As can be seen, a difference of a factor of three can be observed between the fluorescence signals at the same temperature on the fuel lean side of the flame as compared to the rich side of the diffusion flame.

This strong dependence of LIF signals upon flame composition results in a propagation of noise from the Raman measurements into the derived OH concentrations. This effect is especially distinguishable at high temperatures, where the Raman data possess significant noise. As an illustration, Fig. 3.12 shows data
Figure 3.12 Plots showing (a) the measured LIF signal distribution (b) the major species and temperature profiles and (c) the measured (points) and smoothed (line) OH concentration data in H₂/air diffusion flame (18 cm/s average exit velocity) at $z = T_{\text{max}}$. 
obtained from radial profiles measured at the position of the maximum centerline temperature in a pure H$_2$/air diffusion flame (Ch. 4, 18 cm/s average exit velocity). We see that the measured LIF signal (Fig. 3.12a) and temperature (Fig. 3.12b) profiles at this axial distance show a smooth distribution, while the derived OH mole fractions (Fig. 3.12c, points) possess significant scatter. The noise in the OH concentration profiles originates from the major species profiles (see Ch. 4). To derive a smooth distribution of the OH mole fraction, the major species data have been smoothed first and then used for quenching corrections (Fig. 3.12c, solid line).

### 3.9 Conclusions for quantifying LIF measurements

The LIF data in the diffusion flames are quantified by correcting for the temperature and collisional dependent factors based on the CARS and Raman measurements, using measurements in a “calibration” flame to derive the absolute values. We see that the noise in the Raman data can make a substantial contribution to the noise in the LIF results.

### References