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Rovibrational temperature determination of the plasma and the methane flame in a nanosecond DBD microplasma burner using spontaneous Raman spectroscopy

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Department of Mechanical Engineering Power & Flow Research Group

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Abstract

Plasma-assisted combustion has gained interest as technique to make the combustion of fossil fuels leaner and cleaner. To improve the efficiency of plasma-assisted combustion, research needs to be done on how to achieve combustion improvement through the kinetic plasma mechanisms. This can be achieved with a non-equilibrium plasma, which create plasma discharges with non-equilibrium temperatures. A suitable diagnostic technique to determine if a burner creates a non-equilibrium temperatures, is spontaneous Raman spectroscopy.

In this project a moderately accurate Raman scattering model has been developed, which can determine the non-equilibrium temperatures in a plasma and a methane flame. The model has been validated by fitting measurements performed by Lo *et al.* For (non-)equilibrium flames the model can determine the rotational temperature with an accuracy of ± 50 K and the vibrational temperature with an accuracy of ± 80 K. However for strong non-equilibrium plasma, the model is insufficiently accurate to determine the high vibrational temperatures.

A spontaneous Raman spectroscopy measurement has been performed on a methane flame in a nanosecond DBD microplasma burner designed by Elkholy. The Raman scattering model was used to determine the rovibrational temperatures of this flame with and without plasma. It can be concluded that in a stoichiometric flame, the rotational temperature has increased due to the plasma discharges with 294 K, but no non-equilibrium temperatures can be found. However the model does have potential to be useful, when it is used for plasma-assisted combustion configurations, where the plasma and flame are not spatially detached.

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Contents

1 Introduction	4			
	5			
2 Literature study				
2.1 Combustion \ldots	5			
2.1.1 Combustion kinetics	5			
2.1.2 Flat flame burner \ldots	6			
2.2 Non-equilibrium plasma	7			
2.2.1 Dielectric barrier discharge	8			
2.2.2 Plasma-assisted combustion	8			
2.3 Laser diagnostics	9			
3 Raman scattering model	12			
3.1 Energy states and transitions	12			
3.2 Raman scattering	13			
3.3 Spectral intensity	14			
3.4 Thermometry \ldots	14			
3.4.1 Two-temperature Boltzmann distribution	15			
3.4.2 Treanor distribution \ldots	15			
3.4.3 Boltzmann-Treanor distribution	16			
3.5 Fitting of model with measurements	17			
3.5.1 Instrumental function	17			
$3.5.2$ Least squares optimisation $\ldots \ldots \ldots$				
3.5.3 Modelling accuracy				
3.6 Validation	19			
4 Experimental setup	24			
4.1 DBD Microplasma burner	24			
4.2 Optical setup	25			
4.3 Measuring device synchronisation				
4.4 Data processing				
4.5 Experimental accuracy	29			
5 Measurement results	32			
5.1 Measured Raman spectra	32			
5.2 Temperature profile of flame	34			
6 Conclusions and recommendations	38			
6.1 Conclusions				
6.2 Recommendations	39			
References	40			
Appendices	44			
A Biogas combustion improvement using PAC				
B Declaration TU/e Code of Scientific Conduct	19			

Nomenclature

Physical constants

c	Speed of light	$299,792,458{\rm m/s}$
h	Plank constant	$6.62607 \times 10^{-34} \mathrm{Js}$
k_b	Boltzmann constant	$1.38064852\times 10^{-23}{\rm J/K}$
R_u	Universal gas constant	$8.314\mathrm{J/K/mol}$
\mathbf{List}	of symbols	
α	Mean polarisability	m^{6}
α_e	Vibration-rotation interaction constant	cm^{-1}
β	Fitting parameters	
δ	Kronecker delta	
\dot{m}	Mass flow	m kg/s
η	Pseudo-Voigt parameter	

$rac{d\sigma}{d\Omega}$	Differential scattering cross section	m^2
γ	Polarisability anisotropy	m^6
λ	Wavelength	nm

- \mathcal{N} Normal distribution μ Mean residual
- μ Reduces mass of a moleculekg ν Wavenumbercm⁻¹ ω_e Molecular vibration frequencycm⁻¹
- $\omega_e x_e$ Vibrational anharmonicity cm⁻¹ ϕ Equivalence ratio
- σ Accuracy
- σ Standard deviation of residuals

AF Air-fuel ratio

B_e	Molecular rotational constant	cm^{-1}
D_e	Molecular centrifugal distortion constant	cm^{-1}
E	Total internal energy	cm^{-1}
E_a	Activation energy	J

 E_e Internal electron energy cm⁻¹

E_{rot}	Internal rotational energy	cm^{-1}
E_{vib}	Internal vibrational energy	cm^{-1}
F_{imn}	Raman line profile	
G	Gaussian distribution function	
g_J	Degeneracy factor	
HAB	Height above burner	m
Ι	Modelled intensity	W/m^2
Ι	Nuclear spin quantum number	
I_m	Measured intensity	W/m^2
I_{bg}	Background intensity	W/m^2
I_{Ram}	Raman intensity	W/m^2
J	Rotational quantum number	
k	Temperarature dependent reaction rate	s^{-1}
L	Lorentzian distribution function	
M	Molar mass	m mol/kg
N_T	Number density	m ⁻³
$N_{\nu,J}$	Population of certain rovibrational state	
PV	Pseudo-Voigt distribution function	
Q	Partition function	
Q	Volume flow	m^3/s
Q_{rot}	Rotational partition function	
Q_{vib}	Vibrational partition function	
S_L	Laminar burning velocity	m/s
SSR	Sum of squared residuals	
T_e	Electron temperature	Κ
T_g	Gas temperature	Κ
T_i	Ion temperature	Κ
$T_{\nu 01}$	Vibrational temperature for vibrational states $\nu = 0$ and $\nu = 1$	К
$T_{\nu 1 \nu}$	Vibrational temperature for higher vibrational states	K
T_{ad}	Adiabatic flame temperature	Κ
T_{rot}	Rotational temperature	К
T_{vib}	Vibrational temperature	К
V	Voigt distribution function	

- v Vibrational quantum number
- X Molar fraction

List of abbreviations

- AC Alternating current
- CARS Coherent anti-Stokes Raman scattering
- DBD Dielectric Barrier Discharge
- DC Direct current
- FS Full scale
- FWHM Full width half maximum
- GHG Green house gases
- HR High reflective
- HV High voltage
- HW Herman-Wallis factors
- ICCD Intensified charge-coupled device
- LIF Laser induced fluorescence
- MFC Mass flow controller
- Nd:YAG Neodymium-doped yttrium aluminium garnet
- Nd:YLF Neodymium-doped yttrium lithium fluoride
- PAC Plasma-assisted combustion
- PI Princeton Instruments
- PIV Particle image velocimetry
- PRR Pulse repetition rate
- Rd Reading value
- RMS Root mean square

Chemical species

- CH₄ Methane
- CO₂ Carbon dioxide
- H₂O Water
- H^{*} Atomic hydrogen
- N₂ Nitrogen
- NO_x Nitrogen oxides
- O^{*} Atomic oxygen
- OH^* Hydroxyl

1 Introduction

In recent years plasma-assisted combustion (PAC) has gained interest as technique to make the combustion of fossil fuel leaner and cleaner. It has the ability to improve ignition and the lean flammability limit, leading to a decrease in fuel consumption and greenhouse gas emissions. This makes PAC interesting for applications such as domestic boilers and biogas combustion. Prior to this project, research was done on the development of a nanosecond dielectric barrier discharge (DBD) microplasma burner for the premixed combustion of methane. Measurements were performed to assess the influence of the created plasma on the combustion performance. It was concluded that the burner generates a non-equilibrium plasma and improves the lean flammability limit. However, the distribution of plasma generated radicals and the contribution of the kinetic plasma mechanism on the flame is unknown. The reason for this, is that the flame stabilises above the plasma. It has not been measured if excited species and free radicals, which are created in the plasma, still exist in the flame front. To improve the efficiency of plasma-assisted combustion, research still needs to be done on how to achieve combustion improvement through the kinetic plasma mechanisms, instead of the thermal mechanism Joule heating. The contribution of the kinetic mechanisms can be quantified by determining the rotational and vibrational (rovibrational) temperatures of the gas.

For this purpose, a diagnostic technique has to be developed which can distinguish the thermal and kinetic mechanisms in both the plasma and the flame. Laser diagnostics are an extremely suitable technique, as they are non-intrusive, can be accurate and can be performed at small timescales. Spontaneous Raman spectroscopy is such a technique, that can be used for measuring rovibrational temperatures in gases. In previous research, a Raman scattering model has been developed for diatomic molecules. By observing the nitrogen (N_2) Raman spectrum, the temperatures can be determined throughout both the plasma and the flame, as nitrogen is not a reactant in methane combustion. By modifying this model for non-equilibrium plasma, the thermal and the kinetic mechanisms in the DBD microplasma burner can be distinguished. The model and the optical setup are designed to be very flexible and robust, considering further use of this diagnostic technique for other plasma and burner configurations. As Raman scattering is a scarce phenomenon, leading to a relatively weak signal, filtering of the Raman signal is an extensive process. The temperatures with and without plasma are determined as function of the radial location in the flame for lean to stoichiometric equivalence ratios.

The two goals of this project are:

- Develop an accurate Raman scattering model that can determine the rovibrational temperatures in a non-equilibrium plasma and a methane flame.
- Perform spontaneous Raman spectroscopy measurements in the methane flame above a DBD microplasma burner and use the developed model to determine the rovibrational temperatures with and without plasma.

This report starts with a literature study on the various concerned topics in Section 2. Combustion related topics are discussed: combustion emissions and kinetics, and how to determine flame properties in flat flame burners. Followed by information on non-equilibrium plasmas, DBD and PAC. The literature study is concluded with information on various laser diagnostics for combustion and plasma research. Following, in Section 3 the developed Raman scattering model for temperature determination is described. The distribution functions for different (non-)thermal equilibria are given. The fitting procedure and accuracy are explained and validated with measurements from literature. In Section 4 the experimental setup including the DBD microplasma burner, optics and data processing is explained. Measurement results are give in Section 5 and conclusions and recommendations for future work follow in Section 6.

2 Literature study

In this Section information on combustion, plasma and laser diagnostics is given. First it will be explained what the impact of fossil fuel combustion is on the environment, followed by an elaboration on the combustion kinetics. It will be explained how important parameters for combustion science, the adiabatic flame temperature and laminar burning velocity, can be measured with a flat flame burner. Subsequently, information on non-equilibrium plasma, dielectic barrier discharges (DBD) and plasma-assisted combustion research will be given. Various laser diagnostics for combustion applications are explained and the reasons for using spontaneous Raman spectroscopy will be described.

2.1 Combustion

Large fraction of household and industry heating, and transport energy is produced by the combustion of fossil fuels. 80% of the world energy consumption is provided by fossil fuels combustion, making this an indispensable source of energy [1]. However, fossil fuel combustion emits large amounts of greenhouse gases (GHG) especially carbon dioxide (CO_2) and methane (CH_4); a total of 76% of the world GHG emissions. To limit the consequences of the enhanced global warming, CO_2 emissions have to decrease [2]. Furthermore, fossil fuel combustion produces other emissions that have negative effects on the human health and the environment. Incomplete combustion of hydrocarbons emits soot and particulates, which can be carcinogenic in large quantities. At high temperature and lean combustion, nitrogen oxides (NO_x) are produced. This form of emission causes smog and acid rain. Consequently, combustion of fossil fuels faces the challenge of efficiency increase and reduction of emissions. This can be achieved by decreasing the combustion temperature and with lean combustion. At a lower combustion temperature, NO_x emissions decrease and at leaner combustion there are less methane and soot emissions. By decreasing the the activation energy of the ignition, the CO_2 emissions can be decreased. However, flames near the extinguishing temperature and lean flammability limits are less stable due to the slower kinetics and lower free radical concentrations. A promising way to achieve the lower combustion temperature and leaner combustion while maintaining flame stability is the application of PAC, which will be explained further in Section 2.2.2 [1].

2.1.1 Combustion kinetics

Combustion is the process in which, a fuel is oxidised in an exothermic reaction. In this research methane is used as fuel, as this species has a relatively simple chemical structure, is appropriate for Raman spectroscopy and has a well-understood combustion mechanism [3]. Furthermore, this research concentrates on premixed combustion, which is more suitable for plasma-assisted combustion, because the exact location of the plasma discharge becomes less critical. The reaction products of complete methane combustion are water (H₂O) and CO₂, with possibly excess air, depending on the equivalence ratio ϕ [4]. The amount of CH₄ converted can be calculated with the reaction equation using the mass flow \dot{m} and molar mass M [5].

$$\dot{m}_{O_2} + \phi \dot{m}_{CH_4} \longrightarrow \dot{m}_{CO_2} + \dot{m}_{H_2O} + (1 - \phi) \dot{m}_{O_2}$$
(2.1)

$$\phi = \frac{AF_{stoich}}{AF} = \frac{2\left(M_{O_2} + 3.76M_{N_2}\right)/M_{CH_4}}{\left(\dot{m}_{O_2} + \dot{m}_{N_2}\right)/\dot{m}_{CH_4}}$$
(2.2)

In premixed methane combustion, the combustion reaction kinetics is mainly temperature controlled. This means that the amount of species A converted, depends on the temperature T as well as the amount of reactants A and B present. For the first steps of the combustion mechanism of methane these reactants are the fuel $A = CH_4$ and the free radicals atomic hydrogen, oxygen and hydroxyl: $B = H^*$, O^* and OH^* [5].

$$\frac{dA}{dt} = -k(T)[A][B] \qquad k(T) = A \cdot \exp\left(-E_a/R_uT\right)$$
(2.3)

where k(T) is the temperature dependent reaction rate, E_a is the activation energy and R_u is the universal gas constant.

2.1.2 Flat flame burner

When investigating the combustion properties of premixed flames, important parameters are the laminar burning velocity S_L and adiabatic flame temperature T_{ad} [4]. The laminar burning velocity is the velocity of an un-stretched flame front relative to the unburned gas. It gives information about the reaction rates and flame stability. The adiabatic flame temperature is the temperature after complete combustion of a fuel without any work, heat loss or change in kinetic or potential energy. It can be used to compare flame measurements to literature, as it is solely a function of the combustion mixture and inlet temperature. Actual burners will always have a flame temperature that is lower than the adiabatic flame temperature, as energy is lost to the surroundings. An appropriate burner to measure these properties is a flat flame burner, which is a perforated plate through which the gas mixture flow and after which the flame stabilises [3]. The flame stabilises when the laminar burning velocity is equal to the unburned gas velocity. For a flat flame this is the case, when all the heat loss goes to the burner plate, and the burner plate temperature is constant over the entire radius. With this burner, the laminar burning velocity can be measured using the Bunsen burner method or the Heat flux method [3,6]. Using non-intrusive laser diagnostics the flame temperature.

In Figures 2.1 and 2.2 experimental and numerical results from literature are given, which show the relation between the adiabatic burning velocity and flame temperature with the equivalence ratio. At leaner conditions, the adiabatic flame temperature decreases, which is beneficial for lower NO_x emissions. However due to the lower temperature, the reaction rates decrease and subsequently the adiabatic burning velocity decreases. At a certain equivalence ratio, the adiabatic flame temperature and laminar burning velocity are so low that the flame extinguishes. This equivalence ratio is called the lean flammability limit. With PAC this lean flammability limit can be extended and the flame can be made more stable [7].





Figure 2.1: Laminar burning velocity of a premixed methane flame as function of equivalence ratio, determined with: Heat flux method (+), experimental results obtained by Law (Δ) and recalculated results using a nonlinear stretch-correction model (\circ), by Van Maaren *et al.* [4]

Figure 2.2: Adiabatic flame temperature of a premixed methane flame as function of equivalence ratio. determined with: measurements (\circ) , one-step chemical model with (-) and without (--) CO-correction, by Van Maaren et al. [4]

2.2 Non-equilibrium plasma

The well known fundamental states of matter are solid, liquid and gases. However, there is a fourth fundamental state of matter: plasma. Plasma is a quasi-neutral gas, consisting of gaseous molecules, negatively charged electrons, positively charged ions, free radicals, excited species and photons [7]. Due to the presence of charged particles, plasma has conductive properties and due to the free radicals, plasma is highly reactive. It can be found in nature as lightning and the northern light, or man-made among others as fusion plasma or skin-treatment methods. Likely the most common plasma source is the fluorescent lamp.

Plasma discharges can be classified in equilibrium, thermal and non-equilibrium plasma [7]. The first group occurs when all electrons, ions and neutral gas molecules are in equilibrium state, which means that temperatures of all particles are equal: $T_e \cong T_i \cong T_q$. This occurs at high electron temperatures and high electron number density, for example a fusion plasma. Thermal plasma (or quasi-equilibrium plasma) has a lower ionisation level and electron temperature than equilibrium plasma. The kinetic plasma characteristics are mainly determined by high gas temperature, due to significant Joule heating and high power density. This means that a lot of energy has to be put into the plasma, as also the temperature of the relatively heavy gas molecules is increased. In the last group, non-equilibrium plasma, the electron temperature T_e is much higher than the ion and gas temperatures T_i and T_q , which gives the name non-equilibrium [3,7]. This classification of plasma is characterised by its low gas temperature and high excitation selectivity. In non-equilibrium plasma discharge, the energy is firstly transferred to the electrons, as they are the lightest. Following, through inelastic collisions with the gas particles, the energy is transferred and free radicals, excited species and photons are created. The energy transfer to the gas particles, causing vibrational and rotational excitations combined with temperature increases. Conventionally, the relationship between the different plasma temperatures in non-equilibrium plasma is presented as: $T_e >> T_{vib} \ge T_{rot} \approx T_i \approx T_q.$

2.2.1 Dielectric barrier discharge

A plasma is generated when electrons are provided with sufficient energy for the excitation or ionisation of molecules [3]. The energy source can be thermal, beam type or electrical. Electrical energy sources can be subdivided into direct current (DC) discharges, alternating current (AC) discharges and pulsed plasma discharges, each with their own characteristics. The advantage of using pulse discharge sources is their high-power density and ease of control through the duty cycle and pulse repetition rate (PRR).

Non-equilibrium plasmas can be created between a high voltage (HV) anode and cathode with various electric discharge configurations [3]. This configuration determines how efficient the electron energy transfer to the gas particles is. A suitable discharge configuration for transferring the plasma characteristics onto the combustion gas mixture, is a dielectric barrier discharge (DBD). In this configuration, dielectric material is placed between the HV anode, the gas flow and the cathode. The dielectric material accumulates charge on the surface of the dielectric [7]. This energy is released in the form of many microdischarges within a duration of a few nanoseconds. Because of this short discharge time, the microdischarges can be very non-equilibrium with a low gas temperature. The amount of DBD microdischarges depends on the discharge pulse, geometry (e.g. discharge gap and shape of anode) and the pressure [8]. At lower pressures, more microdischarges occur and the plasma can be assumed to be diffuse instead of filamentary. A diffuse plasma is favourable for plasma-assisted combustion, as then maximal plasma-gas interaction is possible.

2.2.2 Plasma-assisted combustion

PAC is a relatively new field in combustion science which can improve ignition and flame stabilisation of (ultra)lean combustion [1]. Especially non-equilibrium plasma is efficient in stimulating combustion, as that specifically generates excited species and free radicals besides increasing the gas temperature. It requires significantly less energy than thermal plasmas and can provide more uniform and well-controlled ignition and stabilisation of flames, which make lean combustion possible [7].

The combustion dynamics and chemistry during non-equilibrium plasma discharges in hydrocarbon flames has been investigated extensively, both for practical applications and in fundamental research [9]. Non-equilibrium plasma improves the combustion through the thermal mechanism of Joule heating. Energy in the electrons of the plasma discharge is transferred to the molecules and increases their temperature. Non-equilibrium also improves the plasma through transport mechanism of ionic winds and the kinetic mechanisms of additional active radical flux and electron impact excitation, dissociation and ionisation of the gas. These mechanisms increase the creation of O^* , OH^* and H^* radicals and the excitation of N₂ and O₂ molecules, which lead to faster reaction chemistry as can be seen from equation 2.3. Many applications of non-equilibrium plasmas have been described, including nanosecond pulsed discharges in subsonic flows for gas turbines [1] and biogas combustion [10], which will be further explained in Appendix A.

A non-equilibrium DBD microplasma burner driven by nanosecond HV pulses, which can be seen in Figure 2.3, has been developed by Elkholy [3]. Electrical and optical measurements were conducted to characterise the plasma discharge [8]. Current and voltage time evolution measurements were used to calculate the pulse energy per channel and electron density. The reduced electric field as function of operating pressure was measured and it was found that the reduced electric field was highest for pressures below ambient. With N_2 emission spectra, the rotational and vibrational temperatures at various pressures were measured [11]. It was found that for this DBD microplasma burner, 85% of the plasma energy went into Joule heating, making it the dominant PAC mechanism. Using CH^{*} chemiluminescence the flame area was calculated, which allowed the calculation of the laminar burning velocity of the microplasma burner at varying equivalence ratios using the Bunsen burner method. For investigation of local plasma effects on burning velocity, particle image

velocimetry (PIV) measurements were performed [3]. It was discovered that the plasma increases the burning velocity. However, this is mainly caused by the thermal mechanism.



Figure 2.3: Image of DBD microplasma burner with methane flame and 445 nm laser, by Elkholy [3]

2.3 Laser diagnostics

Laser diagnostics is a group of measuring techniques which is extremely suitable for short timescale and repetitive measurements in delicate gas flows, where the response time and size of ordinary thermocouples and gas detectors is too limited [12]. This makes laser diagnostics potentially suitable for measuring the temperatures and species densities in the plasma channels and the flame of the nanosecond DBD microplasma burner. Various laser diagnostics techniques have been developed for measuring different aspects of plasma-assisted ignition and combustion. Laser induced fluorescence (LIF) is a technique where a well defined laser beam excites a certain species, which subsequently fluoresces at a certain wavelength. It can be used for the quantitative measurement of active radicals that are formed during the plasma discharge. Thomson scattering is a technique where electromagnetic charge is used to scatter photons when colliding with gas particles. It can be used for measuring electron density and the electron temperature during plasma discharges.

Spontaneous Raman spectroscopy and Coherent anti-Stokes Raman scattering (CARS) are other scattering techniques applicable for thermometry in non-equilibrium plasmas [9]. Raman scattering is a non-resonant process that always occurs when light passes through a medium [13]. When a laser beam with defined wavelength travels through a medium (gas, plasma or a flame) and does not match an allowed transition for the absorption by a molecule, there will always be non-resonant transitions. The incident photon hits a molecule in the medium and is destroyed. Following, a new photon with different properties is created. When the newly created photon has the same wavelength as the incident photon, but different direction of travel, it is called Rayleigh scattering. However, when the wavelength does change, the process is called Raman scattering. As molecules can only take discrete amounts of energy, the photon energy is also discrete. This makes that Raman scattering is a species-specific process. Rayleigh scattering has a significantly higher signal strength than Raman scattering. This can be a complication during measurements as the risk of spectral interference due to Ravleigh scattering needs to be considered. On the other hand, as Raman scattering happens instantaneously, higher order processes, such as quenching and open channel losses do not occur. This makes quantitative analysis of Raman scattering measurements relatively simple.

With CARS, Raman scattering is done with the combination of two lasers, a pumping and probing laser, focused in a small volume. The photons are emitted at a well-defined species-dependent wavelength, which makes CARS a very precise method for temperature measurements [12]. For

example, it can be used to investigate the thermodynamic and kinetic properties of a streamer nanosecond discharge produced between two needles at atmospheric pressure, initialising the combustion of a methane-air mixture. It is shown that the discharge enables combustion for low equivalence ratios by increasing the rotational and vibrational temperatures [14]. CARS can also be used to investigate the temperature, O_2 and H_2 profiles as function of the radial and axial distance from the DBD reactor for a laminar hydrogen flame in a DBD plasma burner [15].

Even though CARS is a very precise and non-intrusive method, it is essentially limited to point measurements. When investigating plasma properties as function of its position, it becomes interesting to use spontaneous Raman spectroscopy [9, 16]. This method enables quantitative temperature and species measurements along a one dimensional direction. Besides, for a CARS setup, multiple precisely aligned lasers are required, making the setup complex. Spontaneous Raman spectroscopy requires only one laser and can give spatial information in one direction. This makes the optical alignment more simple and flexible for various burner and plasma configurations. A spontaneous Raman spectroscopy measurement was performed on a non-equilibrium filamentary nanosecond plasma discharge. With a thermometry model with multiple rovibrational temperatures, the temporal evolution and radial profile of the rovibrational temperatures were investigated [17]. Besides this research, no other research is known to the authors knowledge, where spontaneous Raman spectroscopy is used to investigate non-equilibrium plasma-assisted combustion. No research has been dedicated to non-equilibrium nanosecond discharges in a DBD microplasma burner.

On the topic of laser diagnostic for combustion applications various research has been done. A laminar co-flow burner setup equipped for spontaneous Raman spectroscopy was developed. With this method quantitative temperature and species measurements can be performed for various fuels, e.g. methane, hydrogen and propane. The gas temperature profile and emission species along the centre line of the flame were measured [18]. The gas temperature and mole fraction profile of eight major species along the centre line of the flame were determined with a Raman scattering model and compared to a numerical flame model [19]. The experimental setup and Raman scattering model, which are described above, have been used as foundation for this project. The Raman scattering model has been elaborated for non-equilibrium plasma and the experimental setup has been combined with the DBD microplasma burner.

3 Raman scattering model

Spontaneous Raman spectroscopy is based on the internal energy of molecules and their transitions as a result of the collisions with laser photons. Firstly, it will be elaborated how the internal energy of molecules is quantified, followed by energy state distributions and transitions to other energy states during Raman spectroscopy. Subsequently, the quantification of the Raman scattering spectral intensity will be explained and temperature determination for non-equilibrium plasmas. Lastly, it will be described how the Raman scattering model is fitted to the measurements, including the accuracy assessment and validation.

3.1 Energy states and transitions

Molecules are multi-particle systems that consist of at least two atoms. Therefore, according to the Born-Oppenheimer approximation, molecules have multiple different contributions to the total internal energy E: the electronic energy E_e , vibrational energy E_{vib} and rotational energy E_{rot} [20]. In laser diagnostics the most common unit for this energy is wavenumber [cm⁻¹]. The magnitude of the energy contributions is determined by the energy states/levels, which are discrete values. For spontaneous Raman spectroscopy, all molecules remain in the electronic ground state (e = 0), so this will not be further elaborated. The rotational and vibrational states of the molecules are indicated with J and vrespectively, also referred to as rovibrational quantum numbers. The vibrational energy depends on the internuclear forces, which is described with a harmonic oscillator approximation [13]. For diatomic particles, e.g. N₂ and O₂, there are straightforward equations for calculating the total internal energy as function of the rovibrational quantum numbers to the second order. The energy contributions are products of the rovibrational quantum numbers with the vibrational and rotational constants ω_e , $\omega_e x_e$, D_e , B_e and α_e [13].

$$E(e, v, J) = E_e + E_{vib} + E_{rot} = E_e + \omega_e \left(v + \frac{1}{2}\right) + \omega_e x_e \left(v + \frac{1}{2}\right)^2 + B_v J \left(J + 1\right) - D_e J^2 \left(J + 1\right)^2$$
(3.1)

$$B_v = \left(B_e - \alpha_e \left(v + \frac{1}{2}\right)\right) J \left(J + 1\right) \tag{3.2}$$

As the energy states described above are discrete, each individual molecule will always have a certain quantum number. For a large number of molecules, the distribution of these quantum numbers will depend on the internal energy of the individual molecules, and therefore the temperature of the flame. When molecules are in thermal equilibrium, they will hold to Boltzmann statistics and the energy state population will be a so called single-temperature Boltzmann distribution, which can be seen in Figure 3.1. The population of a certain rovibrational state $N_{v,J}$ depends on the rovibrational energy of that state E(v, J), gas temperature T_g and total number of molecules per unit volume/ number density N_t [21].

$$N_{v,J} = \frac{g_J \exp(-\frac{hcE(v,J)}{kT_g})}{Q(T_g)} N_t$$
(3.3)

where g_J is the degeneracy factor, which describes the amount of individual quantum states that have exactly the same energy. The degeneracy factor depends on the rotational level and the nuclear spin quantum number I. For diatomic molecules the degeneracy factor can be calculated with $g_J = (2J+1)(2I+1)f_I$, where f_I is a molecular constant [22]. It can be seen in Figure 3.1a that the degeneracy may cause an uneven population distribution between odd and even rotation states due to the nuclear spin. h is the Planck constant and c the speed of light. $Q(T_g)$ is the partition function, which is a normalisation factor summing over all rovibrational states. Equation 3.3 and Figure 3.1 show that the population of higher rovibrational states increase as function of species density and temperature. Figure 3.1b shows that for a single-temperature Boltzmann distribution, the vibrational states show an exponential decay.



Figure 3.1: Rovibrational single-temperature Boltzmann population distribution of N₂ at $T_g = 300 \text{ K}$ (blue) and $T_g = 2,000 \text{ K}$ (red).

3.2 Raman scattering

When a photon collides with a molecule, it can be absorbed by the molecule and later emitted (e.g., fluorescence and phosphorescence) or it can be scattered instantaneously. When a photon is Rayleigh-scattered, it changes travelling direction and possibly polarisation. However, in the case of Raman scattering, the photon gains or loses energy to the molecule and causes a transition in quantum state. The photon has a certain amount of energy $E = hc\nu = \frac{hc}{\lambda}$, where ν is the wavenumber and λ is the wavelength, which can increase or decrease due to the collision. The amount of energy the photon gains or loses, known as the Raman shift, is exactly equal to and opposite of the internal energy difference between two quantum states ΔE [13].

$$\Delta E = E(e', v', J') - E(e'', v'', J'') = hc\nu$$
(3.4)

in which E(e', v', J') is the upper energy state and E(e'', v'', J'') is the lower energy state. When the photon loses energy from the collision, it is called Stokes Raman scattering and when the photon gains energy it is called Anti-Stokes Raman scattering. Stokes Raman scattering has certain selection rules, this means that some transitions do occur and others do not. The allowed transitions are $\Delta v = \pm 1$ and $\Delta J = 0, \pm 2$, where the rotational transitions are also known as the Q, O and S branches [13].

The efficiency of a scattering event between quantum states m(v, J) and n(v, J) of species *i* being measured by a detector is given by the differential scattering cross section $\frac{d\sigma_{imn}}{d\Omega}$, where σ is the scattering cross section and $d\Omega$ is the solid angle [21]. The differential scattering cross section for a detector at a 90° angle with the incident light depends on the Raman shift $\nu_{imn} = \nu_0 + E_{im} - E_{in}$, and therefore on the incident wavenumber ν_0 , molecular constants of species *i* and polarisation of the incident light with the scatter plane: perpendicular \perp or parallel \parallel . The relation for a perpendicular polarisation is given in equation 3.5 and for a parallel polarisation it is given in equation 3.6 [19,21].

$$\frac{d\sigma_{imn}}{d\Omega}^{\perp}(\nu_{imn}) = (2\pi)^2 \nu_{imn}^4 (2J_n + 1) \left[\begin{pmatrix} J_n & 0 & J_m \\ 0 & 0 & 0 \end{pmatrix} |\langle m|\alpha|n\rangle|^2 + \frac{4}{45} \begin{pmatrix} J_n & 2 & J_m \\ 0 & 0 & 0 \end{pmatrix} |\langle m|\gamma|n\rangle|^2 \right]$$
(3.5)

$$\frac{d\sigma_{imn}}{d\Omega}^{\parallel}(\nu_{imn}) = (2\pi)^2 \nu_{imn}^4 (2J_n + 1) \left[\frac{3}{45} \begin{pmatrix} J_n & 2 & J_m \\ 0 & 0 & 0 \end{pmatrix} |\langle m|\gamma|n\rangle|^2\right]$$
(3.6)

where the matrices are the Wigner 3-J symbols, which ensure that only the allowed transitions $\Delta J = 0, \pm 2$ have a contribution to the scattering cross section. $\langle m | \alpha | n \rangle$ and $\langle m | \gamma | n \rangle$ are the matrix elements

of the mean polarisability and polarisability anisotropy respectively. These tensor elements can be expanded to the mean polarisability α_0 and its derivative α' , and likewise the polarisability anisotropy γ_0 and its derivative γ' [21].

$$|\langle m|\alpha|n\rangle|^{2} = \alpha_{0}^{2}\delta_{v_{m},v_{n}} + \frac{h}{8\pi^{2}\mu\omega_{e}}\left((v_{m}+1)\alpha'^{2}\delta_{v_{m+1},v_{n}} + v_{m}\alpha'^{2}\delta_{v_{m-1},v_{n}}\right)$$
(3.7)

where μ is the reduced mass of the molecule and $\delta_{i,j}$ is a Kronecker delta that ensures that only allowed transitions $\Delta v = 0, \pm 1$ contribute to the mean polarisability. Therefore, the first term on the right hand side of equation 3.7 corresponds to the Rayleigh and purely rotational Raman scattering and the second term corresponds to the rovibrational Raman scattering [21]. As the mean polarisability is three orders of magnitude higher than its derivative, the Rayleigh scattering efficiency is three order of magnitude higher than rovibrational Raman scattering [19].

3.3 Spectral intensity

Using the Raman scattering cross section, the spectral intensity of Raman scattering I_{Ram} with wavenumber ν_r due to laser irradiation can be calculated. The spectral intensity is a summation of the scattering intensity of all species and state transitions and furthermore depends on the Raman line profile F_{imn} , the population N_{im} from equation 3.3 and the intensity of the laser irradiation I_0 [21].

$$I_{Ram}(\nu_r) = \sum_{imn} \left(\frac{d\sigma_{imn}}{d\Omega} F_{imn}(\nu_r - \nu_{imn}) N_{im} I_0 \right)$$
(3.8)

To make the step to a measurable intensity spectrum I, the instrumental function of the spectral recording devices $\Phi(\nu_r - \nu_{imn})$ and its spectral sensitivity $\varepsilon(\nu_{imn})$ are required. The spectral sensitivity has been obtained from documentation of manufacturers. However, since the properties of measuring devices can change over time, during the measurement data processing spectral sensitivity effects have also been taken into account, see Section 4.4 [23,24]. In Section 3.5.1 an elaboration will be given on the assessment of the instrumental function.

$$I(\nu_r) = \sum_{imn} \left(\frac{d\sigma_{imn}}{d\Omega} (\nu_{imn}) \varepsilon(\nu_{imn}) \Phi(\nu_r - \nu_{imn}) N_{im} I_0 \right)$$
(3.9)

The last step is to translate measurable intensity spectrum as function of wavenumber to a function of pixel p on the intensified charge-coupled device (ICCD) camera. Herefore, non-Raman background signal I_{bg} must be included, as in reality other phenomena than Raman scattering will also influence the pixel count. This will be further elaborated in Section 4.4. Using the ideal gas law, the equation can be rewritten to a function depending on the molar fraction X_i and gas temperature T_g [19].

$$I(p) = \sum_{imn} \left(\frac{d\sigma_{imn}}{d\Omega} (\nu_{imn}) \varepsilon(\nu_{imn}) \Phi(\nu_r(p) - \nu_{imn}) \Delta \nu_r(p) N_{im} \frac{X_i}{T_g} \right) + I_{bg}(p)$$
(3.10)

where $\Delta \nu_r(p)$ is the wavenumber domain corresponding to the *p*th pixel.

3.4 Thermometry

The temperature of a gas can be determined by measuring the spectral intensity, using the equations described in Sections 3.1- 3.3. The temperature is inversely related to the intensity through the ideal gas law, but more importantly related to the population of the rovibrational states through the population distribution of equation 3.3. At higher temperatures, the higher rovibrational states are more populated, which influence the shape of the spectral intensity. As explained in Section 2.2, molecules can be described with multiple temperatures, the gas temperature T_g , as well as the rotational temperature T_{rot} and vibrational temperature T_{vib} . During the post-discharge of a

non-equilibrium nanosecond plasma, high-level rovibrational excitation occurs followed by rovibrational relaxation and temporary gas heating. However, the timescales of these post-discharge events vary, leading to non-equilibrium temperatures [17]. To determine these different temperatures with Raman spectroscopy, equation 3.3 needs to be modified accordingly. In this Section, three different population distributions will be elaborated; two-temperature Boltzmann distribution, Treanor distribution and the Boltzmann-Treanor distribution.

3.4.1 Two-temperature Boltzmann distribution

The two-temperature Boltzmann distribution is caused by differences between rotational and vibrational relaxation rates. Due to fast rotational relaxation, it can be assumed that the rotational temperature is equal to the gas temperature. However, the vibrational relaxation occurs slower and therefore in the two-temperature Boltzmann distribution it is assumed, that $T_g = T_{rot} < T_{vib}$. This distribution can be seen during the vibrational relaxation at hundreds of microseconds after the plasma discharge, until full vibrational relaxation and the end of the non-equilibrium plasma. The two-temperature Boltzmann distribution leads to a separation of rotational and vibrational temperature contributions to the internal energy of the molecules from equation 3.1. The population distribution function is modified to a function with two temperature contributions to the rovibrational state populations and with a separate rotational and vibrational partition function $Q_{rot}(v, T_{rot})$ and $Q_{vib}(T_{vib})$ [17].

$$N_{v,J} = \frac{g_J \exp(-\frac{hcE_{vib}(v)}{kT_{vib}} - \frac{hcE_{rot}(v,J)}{kT_{rot}})}{Q_{vib}(T_{vib})Q_{rot}(v,T_{rot})}N_T$$
(3.11)

$$Q_{rot}(v, T_{rot}) = \sum_{J} g_J \exp\left(-\frac{hcE_{rot}(v, J)}{kT_{rot}}\right)$$
(3.12)

$$Q_{vib}(T_{vib}) = \sum_{v} \exp\left(-\frac{hcE_{vib}(v)}{kT_{vib}}\right)$$
(3.13)

It can be seen that equation 3.11 becomes equal to equation 3.3 if $T_{vib} = T_{rot}$ and $Q(T) = Q_{rot}(v, T_{rot})Q_{vib}(T_{vib})$.

3.4.2 Treanor distribution

In the case of non-equilibrium plasma, there is a higher vibrational energy and the population of the upper vibrational states becomes more significant. When vibration-rotation interactions increase, the higher order terms of the internal energy expression and mean polarisability of equation 3.1 and 3.7 become more relevant. The molecule will deviate from the harmonic oscillator approximation and behave more anharmonic [17]. Due to this behaviour, the population distribution can not be described by a two temperature Boltzmann distribution anymore and a so called Treanor distribution is used [9,25]. This distribution is characterised by an overabundance of population in higher vibrational states compared to the Boltzmann distribution. The vibrational temperature $T_{v_{01}}$ is derived from the relative population of vibrational states v = 0 and v = 1 instead of using the relative populations of all vibrational states. The consequence of this change can be seen in population distribution and the vibrational partition function, whilst the $Q_{rot}(v, T_{rot})$ remains the same as equation 3.12 [25].

$$N_{v,J} = \frac{g_J \exp(-\frac{hcvE_{vib}(v=1)}{kT_{v_{01}}} + \frac{hc(vE_{vib}(v=1) - E_{vib}(v))}{kT_{rot}} - \frac{hcE_{rot}(v,J)}{kT_{rot}})}{Q_{vib}(T_{v_{01}}, T_{rot})Q_{rot}(v, T_{rot})}N_T$$
(3.14)

$$Q_{vib}(T_{v_{01}}, T_{rot}) = 1 + \sum_{v>0} \exp\left(-\frac{hcvE_{vib}(v=1)}{kT_{v_{01}}} + \frac{hc\left(vE_{vib}(v=1) - E_{vib}(v)\right)}{kT_{rot}}\right)$$
(3.15)

3.4.3 Boltzmann-Treanor distribution

For strong non-equilibrium plasmas, at time scales nanoseconds after the plasma discharge, various processes lead to deviations from the Treanor distribution. Electron energy is transferred to the molecule through electron impact, leading to higher vibrational temperatures [9]. The population distribution corresponding to the processed described above, is a Boltzmann-Treanor distribution [26]. The population of higher vibrational states is lower than in a Treanor distribution and therefore modelled as a Boltzmann distribution for $v \ge 1$ with the vibrational temperature $T_{\nu_{1\nu}}$. The lower vibrational states do follow the Treanor distribution with a vibrational temperature $T_{\nu_{01}}$, deduced from vibrational states v = 0 and v = 1, whilst the $Q_{rot}(v, T_{rot})$ remains the same as equation 3.12 [17].

$$N_{v=0,J} = \frac{g_J \exp(\frac{hcE_{vib}(v=1) - E_{vib}(v=0)}{kT_{v_{01}}} - \frac{hcE_{vib}(v=1)}{kT_{v_{1v}}} - \frac{hcE_{rot}(0,J)}{kT_{rot}})}{Q_{vib}(T_{v_{01}}, T_{v_{1v}})Q_{rot}(0, T_{rot})}N_T$$
(3.16)

$$N_{v>0,J} = \frac{g_J \exp(-\frac{hcE_{vib}(v)}{kT_{v_{1v}}} - \frac{hcE_{rot}(v,J)}{kT_{rot}})}{Q_{vib}(T_{v_{01}}, T_{v1v})Q_{rot}(v, T_{rot})}N_T$$
(3.17)

$$Q_{vib}(T_{v_{01}}, T_{v_{1v}}) = \exp\left(\frac{hc(E_{vib}(v=1) - E_{vib}(v=0))}{kT_{v_{01}}} - \frac{hcE_{vib}(v=1)}{kT_{v_{1v}}}\right) + \sum_{v>0} exp\left(-\frac{hcE_{vib}(v)}{kT_{v_{1v}}}\right)$$
(3.18)

The vibrational state populations for all four population distributions can be seen in Figure 3.2. The vibrational population of the single-temperature Boltzmann distribution can be compared to Figure 3.1b. The population of the vibrational ground state at $T_{rot} = 1,000$ K is in between the population of the vibrational ground state at $T_{rot} = 300$ K and $T_{rot} = 2,000$ K. The vibrational state distribution of a single-temperature Boltzmann distribution at $T_{rot} = 2,000$ K and two-temperature Boltzmann distribution at $T_{rot} = 2,000$ K and two-temperature Boltzmann distribution with $T_{rot} = 1,000$ K and $T_{vib} = 2,000$ K give the same vibrational populations. For the Treanor distribution can be seen that the higher vibrational states are overabundant. For the Boltzmann-Treanor distribution. The population of v = 1 of the two-temperature Boltzmann and Boltzmann-Treanor distributions are approximately equal, but the v = 0 of the Boltzmann-Treanor distribution is less populated. This indicates that v = 1 is overabundant and therefore Treanor distribution like. The higher vibrational state populations show an exponential decay, just like the Boltzmann distribution.



Figure 3.2: Vibrational state populations of N₂ for four different population distributions with $T_{rot} = 1,000 \text{ K}, T_{vib} = T_{v01} = 2,000 \text{ K}$ and $T_{v1v} = 4,000 \text{ K}$.

By fitting these different population distributions to the spectral intensity at different stages of the plasma discharge afterglow, conclusions can be drawn about the properties of the plasma. If the two-temperature Boltzmann, Treanor or Boltzmann-Treanor distribution fit the best with the measurements, it can be said that there is a strong non-equilibrium and the production of excited species and free radicals is enhanced. For the plasma discharges to be relevant for plasma-assisted ignition and flame stabilisation, it is also relevant that the gas temperature remains relatively low [1]. In that case, besides the thermal mechanism, also the kinetic (and possibly the transport) mechanism play a role to improve the combustion.

3.5 Fitting of model with measurements

3.5.1 Instrumental function

The instrumental function is a way to incorporate the effects of line broadening, where discrete spectral lines are spread over a wavelength domain with a certain distribution function. Line broadening is caused by a few fundamental optical phenomena and properties of the measuring devices. Due to the natural linewidth of light, photon energy can only be determined up to a certain accuracy [12]. Secondly, due to the Doppler effect of the gas velocity relative to the detector, a wavelength shift occurs. Besides the observation angle of the detector, the Doppler linewidth increases with the temperature, as can be derived from the ideal gas law for constant pressure [19]. Another cause of line broadening is collisional broadening, which is the phenomenon when colliding molecules affect each others internal energy and therefore the wavelength of the scattered photons. Opposite to the Doppler effect, collisional broadening decreases as result of increasing gas temperature at constant pressure, due to a lower species density and therefore less collisions.

The line broadening effects as result of the measuring devices, come from the laser beam that has a certain spectral lineshape, as the crystals in the laser are never perfect and can vary due to the environment. Furthermore, optical misalignment can cause the scattered light to enter the spectrograph under different angles. As the spectrograph slit has finite width, this will also make that the scattered light from different locations of the laser beam enter the spectrograph. The

incidence angle of the scattered light on the diffraction grating influences the reflection angle and therefore a non collimated beam will lead to line broadening. Besides the incident light, imperfections of the grating cause line broadening. Some of the line broadening sources have a significant contribution to the measurement results and others can be neglected.

Line broadening can be represented by different kinds of distribution functions, but the most common distributions are a Gaussian distribution G (caused by Doppler broadening among others) and Lorentzian distribution L (e.g., collisional broadening). The convolution of both distribution functions is a Voigt distribution function V, with V(x) = G(x) * L(x) [27]. Furthermore, a sum of a Gaussian and Lorentzian distribution is called Pseudo-Voigt distribution PV [28]. An extra parameter η determines the weight of both distributions $PV(x) = \eta G(x) + (1 - \eta)L(x)$ [28]. Depending on which line broadening mechanism is dominant, the distribution for the instrumental function will be chosen. The most effective way to determine the influence of the line broadening is measuring the spectral intensity of a well-defined incident light beam and fitting an instrumental function.

3.5.2 Least squares optimisation

The temperatures of the measured spectrum are found by using a least square fitting method. This optimisation approach calculates the sum of squared residuals SSR of the modelled intensity $I(\beta)$ and measured spectral intensity I_m [29].

$$SSR = \sum_{i=1}^{n} \left(I_m(p_i) - I(p_i, \beta) \right)^2$$
(3.19)

where β is a vector containing the fitting parameters and the fitting is performed over a pixel range from p_i till p_n . The model fits the measurement best when the sum of squared residuals is minimum. The residual of every pixel has an equal weight, meaning that the contribution of a intensity peak is equal to the tail of that distribution. For this reason line broadening should be kept minimal, as line broadening increases the relative contribution of the distribution tails. To achieve the minimum sum of squared residuals, the fitting parameters in β are varied to find an optimum. The fitting parameters are the different temperatures T_{rot} , T_{vib} , $T_{\nu_{01}}$ and $T_{\nu_{1\nu}}$, the offset and slope of the background intensity $I_{bg_{A0}}$ and $I_{bg_{A1}}$ (where $I_{bg}(p) = I_{bg_{A0}} \cdot p + I_{bg_{A1}}$) and the wavelength shift λ_{shift} (where $\lambda_r = \lambda_r' + \lambda_{shift}$ with λ_r' is the actual wavelength). The optimisation algorithm used to minimise the sum of squared residuals is the Fmincon solver in Matlab, as this can be a fast and accurate algorithm. This algorithm calculates the gradient of sum of squared residuals as function of the fitting parameters in a Jacobian matrix and makes small increments of the fitting parameters in the direction of the gradient, till it finds the minimum.

3.5.3 Modelling accuracy

The accuracy and robustness of the model is determined by the assumptions made and the chosen solver parameters. Firstly, it is assumed that the intensity is only caused by the Raman scattering of N_2 . However, there could also be emission of other species in the same wavelength region. Especially when measuring during the plasma pulse, there could be unidentified fluorescence or phosphorescence of excited species. For this reason, measurements are performed 100 ns after the plasma pulse. Secondly, the model uses a Placzek-Teller approximation for the Raman cross section, which assumes perfectly perpendicular polarisation directions [30]. Higher-order terms of the polarisability are therefore neglected, which can give a temperature error of 10 K [21]. Furthermore, for the first stages of the post discharge, the anharmonicity corrections using Herman-Wallis (HW) factors can be considered for high vibrational states, to compensate for the effect of vibration-rotation interactions [31]. The HW factors increase the scattering cross section of higher vibrational states. However, as this correction only has a slight effect on the spectral intensity (a

vibrational temperature over-estimation of 1%), it has been neglected [17,32]. Moreover, to limit the computational cost of the spectrum calculation, the number of rotational and vibrational bands are limited to the bands with more than 10^{-10} of the ground state population, limiting the calculation to J = 139 at $\nu = 13$, which is in accordance to Huber *et al.* [22]. Finally, empirical spectroscopic constants for diatomic molecules are used, which obviously have a certain inaccuracy which can influence the shape of the spectrum [22].

Literature on which the model is based, concluded that the rotational temperature according to the N₂ Raman spectrum can be determined with an inaccuracy of $T_{rot} = \pm 50 \text{ K} [16,17,21]$. In the case of nonequilibrium plasma, the inaccuracy increases slightly to $T_{rot} = \pm 90 \text{ K}$ and $T_{vib} = \pm 75 \text{ K} [17]$. This can be checked by performing Monte Carlo simulations on the fitted temperature of the model [33]. This approach is used to create artificial measurement data, which can be used to determine the modelling precision. The first step is to calculate the mean μ and standard deviation σ of the residuals of the measured spectrum and fitted model. With the mean and standard deviation of the residual, pseudorandom noise can be made according to a normal distribution \mathcal{N} . This noise is added to the fitted model to create the artificial measurement I_{am} [33].

$$I_{am}(p_i) = I(p_i) + \mathcal{N}(\mu, \sigma)_i \tag{3.20}$$

For every fitted model, 25 artificial measurements are produced and used as measured intensities to be refitted with the model. This gives 25 new Monte Carlo fitted temperatures, of which the standard deviation can be assumed to be the precision of the fitting model.

In the fmincon solver many parameters can be varied to improve the computational cost, optimisation accuracy and robustness. In this model the interior-point algorithm is chosen, as it is a fast large-scale algorithm. The solver has two stopping criteria, StepTolerance= $|\frac{x_i-x_{i+1}}{1+x_i}| = 10^{-10}$ and OptimalityTolerance = $|\frac{f(x_i)-f(x_{i+1})}{1+f(x_i)}| = 10^{-6}$, which ensure high accuracy of the optimisation. Optimisation robustness is controlled by ensuring that all fitting parameters are sufficiently important with respect to the optimality tolerance. This is indicated by the order of magnitude of the gradients of each fitting parameter. When all gradients are equal, each fitting parameter has an equal influence in finding the optimum. By multiplying the wavelength shift, background offset and slope parameters with a certain factor, their gradients can be tweaked for different measurements. Since optimisation algorithms have risk of finding a local minimum instead of the global minimum, the fitting parameters are initially set to $T_{rot} = T_{vib} = T_{\nu_{01}} = T_{\nu_{1\nu}} = 300$ K and $I_{bg_{A0}} = I_{bg_{A1}} = \lambda_{shift} = 0$. For all temperature fitting parameters, the boundary conditions are T = 250 - 10,000 K and the other fitting parameters have boundary conditions which depend on the multiplication factors.

3.6 Validation

To gain confidence that the model can be applied for a multiple temperature determination with sufficient accuracy, it has to be validated. A comparable measurement on a nanosecond plasma discharge in air has been performed by Lo *et al.* [17]. A 532 nm long-pulse Nd:YAG laser was used to irradiate a point-to-plane non-equilibrium plasma discharge. Using a 1,200 g/mm spectrograph and ICCD camera, the N₂ Raman spectrum has been captured for three stages during the plasma discharge afterglow: 150 ns, 100 µs and 1 ms. Furthermore, a cold air measurement has been made to determine the instrumental function. These four measurements have been used to validate the Raman scattering model.

The validation measurement spectra are obtained from the literature as pixelated images. With Matlab, they are converted to a file that can be used in the model, causing additional inaccuracies of the spectrum. Figure 3.3 shows the N₂ Raman spectrum of cold air. There is one large intensity peak at $\lambda = 607$ nm, which is first vibrational band indicating the transition of v' = 1 to v'' = 0. As

can be seen in Figure 3.1b, this is the only populated vibrational state at T = 300 K. When the temperature increases, higher vibrational states will become populated and higher vibrational bands occur. These will occur at wavelengths lower than $\lambda = 607$ nm, as the Stokes Raman shift becomes smaller for every higher vibrational band, which derived from equations 3.1 and 3.4.

It can be seen that the dots which indicate the experimental results and the fitting residual coincide with the intensity spectrum and increase the line thickness. To obtain a single spectral intensity value, for every horizontal pixel, the median of the line is taken as value. Furthermore, errors can occur when appointing a wavelength value to horizontal pixel location. To find the instrumental function, the N₂ spectrum of cold air is fitted to a single-temperature Boltzamnn distribution model, as can be seen in Figure 3.4. The instrumental function is a Pseudo-Voigt distribution function with $\eta = 0.2$, consisting of a Gaussian with FWHM = 0.2 nm and a Lorentzian with FWHM = 0.3 nm. The residual between the validation measurement spectrum and the fitted model, and the SSR have been added to the Figure to indicate where the deviations occur and to assess the quality of the fit.



Figure 3.3: N_2 spectral intensity of cold air. Validation measurement spectrum by Lo *et al.* [17].



Figure 3.4: N_2 spectral intensity of cold air. Validation measurement spectrum (black) and fitted model using single-temperature Boltzmann distribution (red).

The validation measurements have been fitted with the model twice for each stage after plasma discharge. First to determine the temperatures and secondly to determine the precision of the fitting model with the Monte Carlo method. For the stages after plasma discharge 1 ms, 100 µs and 150 ns, the model fitted to the measured spectral intensities can be seen in Figures 3.5a, 3.6a and 3.7a respectively. The model fitted to the artificial measurements can be seen in Figures 3.5b, 3.6b and 3.7b. In these Figures, the higher vibrational bands become increasingly visible for higher temperatures. For the Boltzmann distribution model at 1 ms and 100 µs after plasma discharge, the intensity of each higher vibrational band is significantly lower than the previous one. For the Boltzmann-Treanor distribution model at 150 ns after plasma discharge, it can be seen that there is an over-abundance of population in higher vibrational states, as the difference in intensity is much lower between higher vibrational bands. This is in agreement with the vibrational population distributions explained in Section 3.4.3.



(a) Spectral intensity model fitted to the measured spectrum

(b) Spectral intensity model fitted to 25 artificial measurements

Figure 3.5: N_2 spectral intensity acquired 1 ms after plasma discharge. Validation measurement spectrum (black), modelled spectrum using two-temperature Boltzmann distribution (red) and artificial measurements (green).



(a) Spectral intensity model fitted to the measured spectrum

(b) Spectral intensity model fitted to 25 artificial measurements

Figure 3.6: N_2 spectral intensity acquired 100 µs after plasma discharge. Validation measurement spectrum (black), modelled spectrum using two-temperature Boltzmann distribution (red) and artificial measurements (green).



(a) Spectral intensity model fitted to the measured spectrum



(b) Spectral intensity model fitted to 25 artificial measurements

Figure 3.7: N_2 spectral intensity acquired 150 ns after plasma discharge. Validation measurement spectrum (black), modelled spectrum using Boltzmann-Treanor distribution (red) and artificial measurements (green).

In Figures 3.5-3.7 can be seen that the SSR of all fitted models is of the same order of magnitude, indicating that the quality of the fit is consistent. Therefore, it can be concluded that model is able to produce a spectral intensity that represents the spontaneous Raman spectroscopy of N_2 at various (non-)equilibrium temperatures. From the determined temperatures can be seen that the model works accurately at relatively low temperatures, when it used the single- and two-temperature Boltzmann distribution. At 1 ms after plasma discharge, the temperature deviation between the measured spectrum and fitted model is $\Delta T_{rot} = 17 \,\mathrm{K}$ and $\Delta T_{vib} = 74 \,\mathrm{K}$, which is roughly within the accuracy stated in literature. At 100 µs after plasma discharge, the temperature deviation is very comparable, with $\Delta T_{rot} = 11$ K and $\Delta T_{vib} = 79$ K. According to the Monte Carlo method, at 1 ms after plasma discharge, the precision of the fitting model T_{rot} is $\pm 27 \text{ K}$ and of T_{vib} is $\pm 22 \text{ K}$. At 100 µs after plasma discharge, the precision of the fitting model is T_{rot} is ± 38 K and of T_{vib} is ± 14 K. For the Boltzmann-Treanor distribution model, the deviations between the measurement and fitting model are significantly larger. The temperature deviations are $\Delta T_{rot} = 51 \,\mathrm{K}, \,\Delta T_{v01} = 158 \,\mathrm{K}, \,\mathrm{and}$ $\Delta T_{v1v} = 342 \,\mathrm{K}$. The fitting model precision of T_{rot} is $\pm 45 \,\mathrm{K}$ and of T_{vib} is $\pm 11 \,\mathrm{K}$. Unlike the rotational temperature, the vibrational temperature is not in agreement with the literature. As described in Section 3.5.3, this can be partially explained by the lack of Herman-Wallis factors. A 1% temperature over-estimation of T_{vib} corresponds to approximately 69 K, giving a remaining $\Delta T_{v1v} = 273 \,\mathrm{K}$. The large vibrational temperature deviation can also have to do with the inaccuracies caused by converting the pixelated images to measurement files. This conversion can have a significant influence on the signal on the signal quality at high vibrational bands.

Altogether, it can be concluded that the model is able to produce a Raman spectrum and fit this to a measured spectrum. An accurate instrumental function can be found using a spectrum with a well defined gas temperature. The model can be used with different population distributions, of which the single- and two-temperature Boltzmann distribution has been validated to give an accurate temperature determination. For the Boltzmann-Treanor distribution, the Raman spectrum is modelled less accurately and the temperature determination is quite imprecise. For the rest of the research the Boltzmann-Treanor distribution will still be used to model the non-equilibrium plasma, but it will not be used for quantitative temperature determination.

4 Experimental setup

In this Section the experimental setup will be described. Firstly, the flat flame burner and DBD microplasma reactor will be explained, followed by the optics used for measuring the Raman scattering. Subsequently, it will be explained how the various devices are synchronised to achieve optimal measurement results. The processing steps undertaken to prepare the measured data for the fitting algorithm are elaborated. Finally, the different sources of measuring inaccuracies will be discussed and assessed.

4.1 DBD Microplasma burner

The burner developed for the experiments is a flat flame DBD microplasma burner. Flat flame burners are very suitable for combustion studies, as the flames can be approximated as one-dimensional, making it convenient for numeric simulations [6]. In the microchannels relatively high-density plasma discharges can be produced, which is beneficial for PAC. Furthermore, the DBD microplasma reactors can be fabricated with photolithography, making it relatively cheap to experiment with different reactor geometries [3].

Compressed air and methane are provided by a lab-wide gas supply. With analogue Bronkhorst mass flow controllers (MFC), the volume flow of both gases is controlled for the required equivalence ratio and gas velocity [34]. These flow controllers are controlled with National Instruments LabVIEW software. The compressed air is supplied at a pressure of 7 Bar and regulated by a 30.0 L/min MFC to 1 Bar and the methane is supplied at 5 Bar and regulated by a 0.9 L/min MFC. After passing the MFC's, the gasses are mixed. For these measurements the total volume flow is 6.0 L/min and the equivalence ratio varies between 0.83 - 1.0. Within the burner, the gas mixture passes through a flow straightener to ensure a uniform flow through the DBD microplasma reactor, above which the flame is stabilised.

The DBD microplasma reactor used in these measurements was designed by Elkholy [8]. In Figure 4.1 a cross section of this reactor can be seen. The dielectric material in the reactor is a composite of woven fiberglass with an epoxy resin and the electrodes are made of copper. Each reactor plate consist of 363 channels of 400 µm diameter and the flow part has a total diameter of 20 mm and thickness of 1.5 mm. Within the reactor there are two sets of HV anodes embedded in the dielectric material, and on the top and bottom are two grounded cathodes. The plasma discharge goes through the microchannels and comes in contact with the gas mixture. At atmospheric pressure, the plasma forms an annulus on the inner wall of the channel, whilst in vacuum, the plasma can fill the entire microchannel.



Figure 4.1: Cross section of DBD microplasma reactor plate designed by Elkholy [11]

The nanosecond HV pulses are triggered by a FeelTech FY2102s frequency generator, of which the pulse repetition rate is set at PRR = 3.00 kHz. The DBD microplasma reactor can also operate at higher PRR, but that reduces the lifetime significantly. It was not possible to measure sufficient

Raman signal within this lifetime. The frequency generator triggers a Mega-Impulse NPG-6/15k semiconductor-based pulse generator, with $4 - 6 \,\mathrm{kV}$ pulses of approximately 7 ns FWHM duration and a 4 ns rise time [8,35]. This creates a non-equilibrium plasma within the channels of the DBD microplasma reactor. During these experiments only the top half of the reactor plates are used to create the plasma. As the HV pulse generator and the plasma create electromagnetic fields, that causes interference with measurement equipment, the HV pulse generator and the reactor are placed in a Faraday cage. To facilitate optical measurements through the Faraday cage, a cylindrical waveguide is made with a metal cylinder in the cage wall that attenuates the electric field by 84 dB, see Figure 4.2 [36].

4.2 Optical setup

The optical setup, which can be seen in Figure 4.2, consists of the laser beam produced by a Photonics Industry DM20-527 Nd:YLF laser with an output wavelength of 527.0 nm, repetition rate of 3.0 kHz, power of 30 W and pulse duration of 170 ns [37]. The laser is shared with another setup, making that the laser beam has to travel a distance of approximately 4.0 m [18]. After the laser beam passes through a Thorlabs half-wave plate, it gets reflected by a flipping mirror and directed to the DBD microplasma reactor. Through a series of high reflective (HR) 532 nm mirrors and lenses the laser beam is focused just above the plasma burner (height above burner HAB = 3.0 mm). As the laser diverges with 8.0 mrad, a f = 1,000 mm and f = 150 mm lens are required to allow the laser beam to pass through the Faraday cage and be focused into a collimated beam above the plasma burner, just before it ends in a beam dump. The laser is controlled by a control unit that is triggered and synchronised with the same frequency generator as the HV pulse generator

Light scattered from above the burner at a 90° angle goes through an Edmund Optics OD4 532 nm notch filter, a 105 mm f/4.5 Nikkon lens, a vertical entrance slit into a Princeton Instruments (PI) Acton SP-2300i 0.3 m Spectrograph which includes a 300, 1, 200 and 2, 400 g/mm grating. The notch filter reduces the Rayleigh-scattered light by a factor 10⁴ and the spectrograph spreads the scattered spectra over the horizontal axis. In these measurements, the 2, 400 g/mm grating is used for maximal spectral resolution [24]. The spectra are captured by a PI-MAX 3, Filmless UniGen II intensified ICCD camera. The shutter of the intensifier is triggered by the same frequency generator as the HV pulse generator and laser, with a time delay to match the laser beam [23]. After 2,000,000 gates with a gate width of 300 ns, the exposure data on ICCD chip is retrieved. Due to the limited lifetime of the DBD microplasma reactor, when turning on the plasma, it was necessary to measure the Raman spectra multiple times for each setting. Four measurements of 200,000 gates are added together for a reasonable signal-to-noise (S/N) ratio. This data is gathered by PI WinSpec 3.2 and analysed by the model in Matlab.



Figure 4.2: Schematic of the optical setup.

4.3 Measuring device synchronisation

For a maximal signal intensity and S/N ratio, the camera should only measure during the laser pulse and at a fixed time after the plasma discharge. To make this possible, all devices should be synchronised in time and frequency. A synchronised frequency can be ensured by triggering all devices with one master; the FeelTech frequency generator. To synchronise all devices at the same time, relative signal delays should be applied. The device output signals are measured and analysed with a Lecroy waverunner 44MXi-A oscilloscope with a sampling rate of 5 GS/s and four BNC input channels (CH1-CH4), as can be seen in Figure 4.3 [38]. The trigger signal of the frequency generator is connected to CH1 of the oscilloscope. The voltage over- and current going through the DBD microplasma reactor are measured with a North Star PVM-4 high-voltage probe (CH2) and a Bergoz CT-F0.5 current transformer (CH3) respectively [39, 40]. The intensity signal of the laser beam is measured by a photodiode (CH4), is located just before the laser beam enters the Faraday cage. As the laser beam travels at the speed of light and the distance from the photodiode to the reactor is approximately 0.5 m, the laser beam is delayed by 1.7 ns, which can be neglected.

From the moment that the trigger signal is sent to all the devices, different delays determine the time at which the measured signals reach the oscilloscope. These delays are caused by signal propagation in the cables, laser light speed and internal device delays. Internal delay of the laser depends on the power, a higher laser power gives a shorter delay. For this reason, all measurements are performed at equal and the maximal laser power. For synchronising the camera with the laser, the camera was set in imaging mode and the intensity has been measured for varying gate width and delay. The optimal settings are those with a maximal intensity and minimal gate width.



Figure 4.3: Schematic of the electrical setup.

4.4 Data processing

As the probability of photons scattering a Raman shifted signal is very small, the measured Raman signal is very low and difficult to distinguish in raw measuring data. For this reason the Raman signal is filtered from other sources of scattered light (e.g. laser-induced fluorescence) and artefacts caused by the measuring devices. Furthermore, multiple pixels of the CCD chip are averaged to give more constant results. In Figure 4.4 the intermediate data processing steps of a N_2 spectrum can be seen.

The first step in the data processing is removing the outliers. These can be caused by saturated or dead pixels on the CCD chip, which can cause problems for the rest of the data processing and when fitting the measurements and model. For this reason a Hampel filter is applied to every measurement. This filter is a less aggressive variant of a median filter, as it takes into account the median of multiple neighbouring pixels to the sample in every direction. If the sample differs more than a certain deviation with the neighbouring medians, it is replaced by the median value. For these measurements, the 10 neighbouring pixels in each direction are used and the threshold is set to one standard deviation [41]. In Figure 4.4a and 4.4b the intensity of each pixel is indicated by the CCD count, which goes from 1 - 65,536 for a 16 bit CCD chip. The horizontal indicates the wavelength range, which is given by the spectrograph. The vertical axis indicates the pixel range of the CCD chip. It can be seen that the flame ends at approximately p = 700, as only first vibrational band is visible due to the low temperature.

As described in Section 3.2, the Raman signal is polarised compared to the incident light. For this reason, two orthogonal polarisations are measured and subtracted from one another to only keep the Raman active signal. The polarisation directions are indicated with perpendicular-perpendicular and parallel-perpendicular. The first term of the polarisation direction stands for the polarisation of the laser beam with respect to the polarisation of the scattering plane. The second term stands for the scattering direction with respect to the propagation direction of the laser beam. As LIF is not polarised, it will be removed from the Raman signal [13]. Furthermore, to decrease sensitivity effects of the spectrograph and ICCD camera, the Raman signal is normalised by a flatfield measurement of which a darkfield measurement is subtracted. A flatfield image can be obtained by measuring the

intensity whilst moving the spectrograph grating in such a way, that the Rayleigh scattering wavelength moves at a constant velocity along the entire CCD chip. It can be assumed that every pixel receives an equal amount of light and the differences in counts is due to pixel-to-pixel sensitivity variations of the spectrograph, intensifier and CCD chip. A darkfield image is obtained by closing the lid of the spectrograph, so no external light can reach the CCD chip. Following, a measurement is made for the same amount of gates and with the same intensifier gain as other measurements. The measured intensity is caused by light leaking into the spectrograph, saturated pixels and measuring noise [20]. In Figure 4.4c the intensity is indicated with arbitrary units, as the CCD count is divided by a CCD count.

As a flat flame shows little variation along the radial direction and to increase the signal quality, 100 pixels in spatial direction are binned to a single spectrum. In Figure 4.4d seven spectra can be obtained, each on corresponding to a certain distance from the flame centre. The spatial binning gives the spectra a spatial resolution of 2.5 mm.

Because of line broadening and the chosen instrumental function, there is limited spectral resolution. However, as can be seen in Figure 4.4d, there is a lot of variation in spectral intensity. To make the vibrational bands more distinct, a Savitzky-Golay filter is used [42]. The spectrum is smoothened, without decreasing the spectral resolution, see Figure 4.4e. This filter is an advanced version of a moving-average filter, as it uses least squares fitting of a higher-order polynomial to each sample point. By using higher-order polynomials, the heights of the peaks remain, while the individual pixels are averaged. The amount of neighbouring pixels considered by the filter should be chosen, so that the considered spectral region can be described accurately by the corresponding higher-order polynomial. For these measurements a third-order polynomial applied to the 40 neighbouring pixels on both sides of a sample pixel is used. The resulting spectra at the centre of the flame can be seen in Figure 4.4f, where the normalised intensity is given as function of the wavelength.



(a) Raw measurement data of CCD chip



(c) After normalising with flatfield and darkfield measurements in [a.u.]



(e) After applying Savitzky-Golay filter in spectral direction in [a.u.]



(b) After applying the Hampel filter



(d) After binning of spatial direction in [a.u.]



(f) Final N_2 spectrum at centre of flame

Figure 4.4: Intermediate data processing steps of a N₂ spectra images of $\phi = 0.83$ methane flame measured at HAB = 3 mm, presented with a false colour scale.

4.5 Experimental accuracy

The experimental accuracies that can be determined are the intensity, wavelength, spatial location and equivalence ratio. In this Section, these accuracies will be quantified. In the measurement results in Section 5, the spatial location and equivalence ratio inaccuracy will be added to the results as error bars.

In the experimental setup various devices influence the intensity of the measured spectrum. The laser creates a beam with 85% circularity, which leads to a 0.30% RMS [37,43]. The sides of the laser beam are blocked by the spectrograph slit, making the captured laser light more homogeneous. The spectrograph has a varying wavelength sensitivity which can be determined with approximately 1% inaccuracy [24]. Likewise, the intensifier has a quantum efficiency which can be determined with approximately 1% inaccuracy [23]. All together, the precision of the measured intensity is 2.3%. However, as temperatures are mainly determined with the relative peak heights of the vibrational bands, the absolute intensity is less relevant. This absolute intensity becomes more relevant, when the spectral intensity of different species are compared to determine the molar fractions. The difference of the relative peak heights due to measurement inaccuracies can be compensated with the slope of the background intensity. Herefore, the inaccuracy due to the measured intensity can be neglected with respect to model fitting inaccuracy, which has been described in Section 3.5.3.

The measured wavelength accuracy is caused by the grating of the spectrograph, as can be seen in Figure 4.5. The offset can be minimised during post processing, by shifting the spectrum till the Rayleigh-scattered light is exactly at $\lambda = 527$ nm. The inaccuracy of this method is $\lambda = 0.1$ nm for the 2,400 g/mm grating. It can be seen that there are minor misalignments and/or imperfections in the spectrograph optics, as the wavelength shift of the Rayleigh line is vertically different. This bias will be removed by the wavelength shift parameter of the fitting model. Furthermore, the instrumental function of the measuring setup was determined with the Rayleigh line and found to be a Gaussian distribution with FWHM = 0.3 nm.



Figure 4.5: Rayleigh-scattered light with a 2,400 g/mm grating and presented with a false colour scale.

The measured height of the laser beam above the burner and distance from the centre of the flame is determined by capturing a 2.5×2.5 mm chequerboard grid with the camera in imaging mode. From the chequerboard the spatial resolution per pixel can be determined with an inaccuracy of approximately 0.5 mm.

The equivalence ratio is determined by the combination of two gas flows, controlled by two mass flow

controllers with an inaccuracy of $\sigma = \pm 0.5\%$ Rd + $\pm 0.1\%$ FS [34]. The propagation of these errors to the accuracy of the equivalence ratio can be calculated with equation 4.1, giving $\sigma_{\phi} = 5.3 - 6.4\%$ for equivalence ratios $\phi = 0.83 - 1.0$ [44].

$$\sigma_{\phi} \approx \sqrt{\phi^2 \left[\left(\frac{\sigma_{Q_{air}}}{Q_{air}} \right)^2 + \left(\frac{\sigma_{Q_{CH_4}}}{Q_{CH_4}} \right)^2 \right]} \tag{4.1}$$

5 Measurement results

In this Section the Raman spectroscopy measurement results on the DBD microplasma burner flame will be presented. The measurements are all performed at $HAB = 3 \pm 0.5$ mm in the centre of the flame. All measurements have been obtained within two weeks of measuring, of which at the beginning of each day, the experimental setup was checked to see if it produced the same measurement results. To check if the day-to-day measurement results were the same, every day the N₂ spectrum of cold air was measured.



Figure 5.1: N₂ spectrum of cold air of four daily measurements.

In Figure 5.1 it can be seen that the wavelength shift has not changed day-to-day, as all ground state peaks are at the same wavelength. However, the peak width of the measured intensity at 12-09-2019 is broader than the other measurements. After this day, it was chosen to use the 2, 400 g/mm grating instead of 1, 200 g/mm grating, as this has more spectral resolution and less line broadening. Furthermore, at 20-09-2019 the spectral intensity around the ground state is less smooth than the other measurements. The reason for this is that the polarisation was accidentally set to parallel-perpendicular instead of perpendicular-perpendicular. For this polarisation, the Raman scattering cross section is smaller and therefore the background noise is relatively high. Altogether, from the daily tests it can be concluded that the different measurements are repeatable and can be compared.

5.1 Measured Raman spectra

To investigate the effects of the non-equilibrium plasma on the combustion, measurements of the N_2 spectral intensity have been performed. One measurement of a flame without plasma and measurements with a plasma discharge at PRR = 3.00 khz. As the reactor would break down between 1 - 2 minutes, it was chosen not to measure continuously. Every time the plasma was turned on, during a 67 s period 200,000 gates were taken. Four of these measurements with the same DBD microplasma reactor were summed to give one N_2 spectrum. In Figures 5.2 and 5.3, the resulting spectral intensities of a methane flame with and without plasma can be seen. The scattering model with a single-temperature Boltzmann distribution has been used, as this proved to be the best fit. Furthermore, artificial measurements for the Monte Carlo method have been fitted to the models to determine the fitting precision.



(a) Spectral intensity model fitted to the measured spectrum



(b) Spectral intensity model fitted to 25 artificial measurements

Figure 5.2: N₂ spectral intensity of $\phi = 1.0$ methane flame without plasma, measured at HAB = 3 mm. Measured spectrum (black), modelled spectrum using a single-temperature Boltzmann distribution (red) and artificial measurements (green).



(a) Spectral intensity model fitted to the measured spectrum



(b) Spectral intensity model fitted to 25 artificial measurements

Figure 5.3: N₂ spectral intensity of $\phi = 1.0$ methane flame with PRR = 3.00 kHz plasma measured at HAB = 3 mm. Measured spectrum (black), modelled spectrum using a single-temperature Boltzmann distribution (red) and artificial measurements (green).

In Figures 5.2 and 5.3 can be seen that the flame without plasma corresponds well with a single-temperature Boltzmann distribution, which would be expected. The flame with $PRR = 3.00 \,\mathrm{kHz}$ plasma measurement shows a moderate fit to single-temperature Boltzmann distribution model. The intensity peaks do correspond with model quite well, indicating that no non-equilibrium temperatures are present in the flame. Due to fewer gates and lower signal-to-noise ratio, the sum of squared residuals is relatively large. It can be seen that there is a larger spread of artificial measurements when measuring with plasma than without, which leads to less precision. Nevertheless, a significant temperature increase is found due to the non-equilibrium plasma. The rotational temperature increases from $T_{rot} = 1,932 \pm 6 \,\mathrm{K}$ to $T_{rot} = 2,226 \pm 49 \,\mathrm{K}$, which is an increase of 294 K.

Since no higher vibrational temperature can be determine, the contribution of the thermal and the kinetic mechanisms cannot be quantified. After the plasma discharge the non-equilibrium plasma

relaxes over time and at the time the gas reaches HAB = 3 mm, due to vibration relaxation the gas could have returned to thermal equilibrium. So even if there was a strong non-equilibrium plasma present within the reactor plate, it cannot be quantified at the measured height or within the measuring inaccuracy. It can concluded that for the DBD microplasma burner the plasma and the flame are spatially detached. Therefore, the combination of this measuring method and burner design are not suitable to quantify the contribution of the thermal and the kinetic mechanisms.

5.2 Temperature profile of flame

The burner choice of a flat flame burner was made to be able to approximate the flame as one-dimensional. To confirm that this approximation is valid, the radial temperature profile can be plotted. If a cross section of the flame area has an equal temperature, the flame can be assumed to be flat. This experimental setup is very suitable for measuring the radial temperature profile, as the laser beam passes through the cross section of the flame area at a certain height above the burner. To compare the the radial temperature profile at different equivalence ratios, measurements have been performed for at a methane flame without plasma with $\phi = 0.77$, 0.83 and 1.0, and for a $\phi = 1.0$ methane with plasma. Since the laminar burning velocity decreases for leaner flames, the flame lift-off height increases. This has influence on the temperature measurement, as the flame temperature develops along the height above burner.

In Figures 5.4 and 5.6 an image of the flame at $\phi = 1.0$ and $\phi = 0.77$ can be seen. Light reflecting from the reactor plate can be seen on the right-hand side of the Figures, from which the flame lift-off can be derived. The location of the laser beam is added to indicate the location of the measured Raman spectrum. It can be seen that the $\phi = 1.0$ flame has a short lift-off height and a flat flame front. The spectrum of this flame is measured completely after the flame front. The $\phi = 0.77$ flame has a large lift-off height and has an irregular shape, indicating that it is close to the flammability limit. The spectrum of this flame is measured within the flame front. This will have significant effects on the measured temperature, as not all methane has been combusted and heat is emitted.

The measured radial temperature profiles of the $\phi = 1.0$ and $\phi = 0.77$ flames can be seen in Figure 5.5 and 5.7. It can be seen that the rotational temperature of the $\phi = 1.0$ flame is approximately a single temperature. This shows that for this equivalence ratio, the flame can be approximated as one-dimensional. The rotational temperature of the five measurements closest to centre of the flame are averaged to a flat flame rotational temperature $T_{rot} = 1,951 \pm 44$ K. The indicated inaccuracy is a summation of the fitting precision and one standard deviation of the five measured temperatures. In Figure 5.7 can be seen that $\phi = 0.77$ flame is not a flat flame and cannot be approximated with a single flat flame temperature.



Figure 5.4: Image of $\phi = 1.0$ methane flame without plasma, measured with spectrograph in imaging mode and presented with a false colour scale. Laser beam added for reference (green).



Figure 5.6: Image of $\phi = 0.77$ methane flame without plasma, measured with spectrograph in imaging mode and presented with a false colour scale. Laser beam added for reference (green).



Figure 5.5: Fitted rotational temperature along the radius of $\phi = 1.0$ methane flame without plasma, measured at HAB = 3 mm.



Figure 5.7: Fitted rotational temperature along the radius of $\phi = 1.0$ methane flame without plasma, measured at HAB = 3 mm.

The radial temperature profiles of all the measured flames can be seen together in Figure 5.8. Here it can be seen that the $\phi = 0.83$ flame without plasma and $\phi = 1.0$ flame with plasma are both flat flames. The rotational temperatures are $T_{rot} = 1,872 \pm 34$ K and $T_{rot} = 2,153 \pm 125$ K, respectively. It can be seen that for the flame with plasma there is no temperature included at 8.1 mm from the flame centre. During this measurement an artefact occurred at the edge of the CCD chip, leading to a S/N ratio that was too low for the model to work reliably. Therefore, it was chosen to exclude that measurement.



Figure 5.8: Fitted rotational temperature of various measured flames along the radius of flame, measured at HAB = 3 mm.

Subsequently, the flat flame temperature can be expressed as function of the equivalence ratio, as can be seen in Figure 5.9. In the Figure the adiabatic flame temperature as function of the equivalence ratio from Section 2.1.2 is added as reference. If there would be no heat loss to the burner plate, the measured flat flame temperature should be equal to the adiabatic temperature. The flame temperature associated with the $\phi = 0.77$ flame is the highest measured temperature $T_{rot} = 1,622 \pm 8 \text{ K}$, which is measured at 5.4 mm from the flame centre. It can be expected that the flame temperature after the flame front is slightly higher. From the flat flame temperatures of flames without plasma can be seen that temperature decreases for lower equivalence ratio and there is a significant difference from the adiabatic flame temperature. At $\phi = 1.0$ can be seen that the temperature of the flame with plasma is very close to the adiabatic flame temperature. This confirms the conclusion from Section 5.1, that there in a gas temperature increase due to the plasma. Which leads to a less heat loss from the flame to the burner plate.



Figure 5.9: Flat flame rotational temperature of various measured flames without plasma (black, red and green) and with plasma (blue), as function of the equivalence ratio, measured at HAB = 3 mm. Adiabatic flame temperature of a premixed methane flame as reference, by Van Maaren *et al.* [4].

6 Conclusions and recommendations

The aim of this research was to develop an accurate method that can determine the rovibrational temperatures of a plasma and a methane flame. Subsequently, use this method to determine if any non-equilibrium temperatures can be measured in a nanosecond DBD microplasma burner. In this Section the conclusions that can be drawn from this research are given, followed by recommendations for future work.

6.1 Conclusions

A literature study has been performed on combustion kinetics and flat flame burners. From the three classes of plasma discharges, non-equilibrium plasma has the most potential to efficiently improve combustion, as that creates free radicals and excited species through the kinetic mechanisms besides Joule heating. To measure this, spontaneous Raman spectroscopy has been used, as this is a laser diagnostic technique that requires a relatively simple setup and can give spatial en temporal information on the plasma and the flame.

A Raman scattering model has been developed that describes the spectral intensity of various diatomic molecules as function of the rovibrational temperatures. The rovibrational state populations are described with four different distribution functions. With a least squares optimisation in Matlab, the model can be fitted to a measured spectral intensity. The precision of the fitting algorithm has been determined with the Monte Carlo method.

The model has been validated with a nanosecond plasma discharge in air measurement performed by Lo *et al.*, where the N₂ Raman spectrum has been measured at 150 ns, 100 µs and 1 ms after the plasma discharge. This resulted in an accurate temperature determination for the model with singleand two-temperature Boltzmann distribution: with a rotational temperature accuracy of ± 50 K and vibrational temperature accuracy of ± 80 K. When using the Boltzmann-Treanor distribution, at higher temperatures, the model can produce the non-equilibrium spectrum, but the vibrational temperature determination is quite inaccurate. One clear contribution to the inaccurate temperature determination for non-equilibrium plasma, is the lack of Herman-Wallis factors, which compensate the anharmonicity effects at high vibrational states.

An experimental setup has been developed to measure the effect of non-equilibrium plasma discharges on a methane flame with spontaneous Raman spectroscopy. A DBD microplasma burner designed by Elkholy has been used to create nanosecond plasma pulses and stabilise the flame. Measurements were performed at $\phi = 0.83$ till 1.0 for flames without plasma and with PRR = 3.00 kHz plasma. From the fitted temperatures it can be concluded that the rotational/gas temperature increases for higher equivalence ratio: $T_{rot} = 1,872 \pm 34$ to $1,951 \pm 44 \text{ K}$ respectively. When applying plasma discharges, the rotational temperature increases to $T_{rot} = 2,153 \pm 125 \text{ K}$. Even in the flame with plasma, the vibrational temperature is equal to the rotational temperature. It is not possible to measure the non-equilibrium temperatures with spontaneous Raman spectroscopy at this height above burner. Either there has been full vibrational relaxation of the gas at the time it reaches the measuring height, or the non-equilibrium temperature difference is within the temperature inaccuracy.

Altogether, it can be concluded that a moderately accurate method to determine the non-equilibrium temperatures in a plasma and methane flame has been developed. However, no non-equilibrium temperatures can be measured in the methane flame in a nanosecond DBD microplasma burner.

6.2 Recommendations

From the conclusions can be derived that there is still a lot of work to be done for making plasma-assisted combustion efficient. The Raman scattering model can be further improved, as can fitting algorithm and the experimental setup.

- As described in Section 3.6, to improve accuracy of the temperature determination of strong non-equilibrium plasmas, Herman-Wallis factors need implemented in the Raman scattering model. This will be relevant for research on plasma-assisted combustion, to be able to quantify the energy from the kinetic mechanisms during the earliest stages of the plasma discharge afterglow.
- The fitting model can still be made more accurate and robust, by using weighted residuals for the least squares fitting method. When the spectral resolution is low due to line broadening, the most important information of the temperature determination is in the relative peak intensities. By increasing the weight of the pixels at the vibrational bands peak wavelengths, the information of the relative peak intensities has relatively large contribution to the SSR. This could improve the accuracy of the vibrational temperature determination for high vibrational temperatures. As can be seen for the validation measurement at 150 ns after the plasma discharge in Figure 3.7, the peak intensities higher vibrational bands are important and distribution tails have a very low S/N ratio. Because every pixel has an equal weight, there is a large inaccuracy of the vibrational temperatures.
- As can be seen in Figure 4.5 there are imperfections in the spectrograph optics, leading to a wavelength offset which is a function of the vertical location of the CCD chip. By determining this curvature and implementing that to the wavelength offset, the wavelength shift fitting parameter can be decreased. This will make the temperature contribution to the gradient larger and subsequently the fitting model more robust.
- As can be seen in the raw measurement data of a Raman spectroscopy measurement in Figure 4.4a, the CCD count can still be increased significantly to increase the S/N ratio. Besides, it is desirable to reduce the measuring time to a period well within the reactor lifetime. To achieve this, the measured intensity can be increased by get more laser irradiation. For this the experimental setup can still be improved by using a more powerful and less divergent laser, and by decreasing the travelling distance of the laser beam and amount of mirrors and lenses. By using a pulse streched Nd:YAG laser at 532 nm, a high energy and long pulse laser beam can be achieved whilst avoiding optical break-down. With this output wavelength, the remaining optics and the Raman scattering model can still be used.
- From these measurements with the DBD microplasma burner can be concluded that it will be very unlikely to measure any non-equilibrium plasma, since the flame and plasma are spatially detached. By using another plasma and burner configuration, where the flame lift-off height is decreased or the free radical and excitated state lifetime is longer, measuring non-equilibrium temperatures should become possible. The most important modification is to change the direction of laser beam with respect to the gas flow. By directing the laser through the plasma and flame, the temperatures can be determined as function height above burner. Secondly, it would be beneficial if the lifetime of the DBD reactor is increased. This can be achieved with a different material and geometry choice or with a more diffuse plasma by operating at lower pressure.

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Appendices

During this project other measurements have been performed on the DBD microplasma burner setup, as this burner design has received international attention. These measurements have been performed for the investigation of plasma-assisted combustion on different fuel mixtures for combustion efficiency and flame stability. This is a research project at the department of Environmental Technology at the Kaunas University of Technology in Lithuania. For a period of two weeks Dr. R. Paulauskas visited the Eindhoven University of Technology. For this the visitation, the gas mixture was expanded to investigate the combustion of methane mixed with additional CO_2 and O_2 . In the following Section some of the measurement results are presented, which lead to a publication in the Experimental Thermal and Fluid Science Journal [10].

Appendix A Biogas combustion improvement using PAC

Biogas is an increasing source of renewable energy, that can be used as alternative to fossil fuels [2]. A disadvantage of using biogas is the large CO_2 fraction (varying from 40 - 70 vol. %), which reduces the flame temperature and stability [45]. One of the possible solutions for this problems is plasma-assisted combustion. By using non-equilibrium plasma, the flame stability increases and the flammability range is extended [10]. However, using plasma-assisted combustion can come to cost of producing NO_x , as non-equilibrium plasma can produces O^* and N^* radicals that can attach to oxygen and nitrogen molecules to produce NO and NO₂.

Measurements on the flammability and emissions have been performed with the nanosecond DBD mictroplasma burner [10], which is described in Section 4. The gas mixture has been expanded with a compressed CO₂ supply, controlled by a 5.0 L/min Bronkhorst mass flow controller. The gas compositions measured vary between $CH_4/CO_2 = 100\%/0\%$ and $CH_4/CO_2 = 20\%/80\%$ (which is the biogas composition known as B₂₀). The equivalence ratio was varied between $\phi = 0.71 - 1.0$. The measurements were performed without plasma and with two different pulse repetition rates: PRR = 3.00 kHz and PRR = 10.00 kHz. The notch filter was removed from the Nikkon lens and replaced by three alternating bandpass filters; for the excited species OH^{*} (282.9 nm), CH^{*} (387.1 nm) and C₂^{*} (514.0 nm). The spectrograph was put into imaging mode and the laser was turned off. Furthermore, an Arex 40-D flue gas analyser was used to measure the CO, CO₂, HC and NO_x emissions [46].



Figure A.1: Flame images of different composition biogas at fuel equivalence ratio $\phi = 0.83$ with plasma switched off. The reactor plate is at the bottom of each image. Images made by Paulauskas *et al* [10].

In Figure A.1 the flame images of the three excited species at different biogas compositions can be seen. As C_2^* emissions only occur in the flame front, with this species the flame shape can be seen. The C_2^* emission has been used to determine the flame lift-off height from the burner, by using the height of the maximum intensity, averaged over the entire width. The decreasing intensity of the OH^{*} and CH^{*} emission at higher CO₂ concentrations indicate the decreasing flame temperature.

In Figure A.2 can be seen how the plasma discharge affect the flame shape at different biogas compositions. The radical emission intensities increase and are spatially more distributed due to the plasma discharges causing the formation of active species. It can be seen that the OH^* emission increases at the plasma zone. This can be associated with excited species such as $O_2(a^1\Delta_g)$, that cause the formation of OH^* in the plasma zone.



Figure A.2: Images of plasma-assisted biogas flames of different compositions at different plasma discharge repetition rates at fuel equivalence ratio $\phi = 0.83$, by Paulauskas *et al.* [10].

Mainly at higher CO₂ concentrations, increasing plasma pulse repetition rates decrease the flame lift-off. This effect becomes even more clear in Figure A.3. For methane combustion at $\phi = 0.76$ the flame lift-off is decreased by 38.8% and 50.4% for plasma repetition rate 3.00 kHz and 10.00 kHz respectively. The flame lift-off decreases even more when applied plasma to flames with high CO₂ concentrations. From these results can be concluded that applying plasma has a positive effect on the flame lift-off for methane and biogas combustion.

However, as described above, plasma-assisted combustion can come at the cost of higher NO_x emissions. In Figure A.4 can be seen how the NO_x emissions increases with increasing plasma discharge repetition rates. Due to the temperature decrease, the NO_x emissions decrease for higher CO_2 concentrations.



Figure A.3: Flame position from the burner nozzle changing fuel-air ratio ϕ at different plasma discharge repetition rates, by Paulauskas *et al.* [10].



Figure A.4: NO_x emissions changing fuel-air ratio ϕ at different plasma discharge repetition rates, by Paulauskas *et al.* [10].

Appendix B Declaration TU/e Code of Scientific Conduct



Declaration concerning the TU/e Code of Scientific Conduct for the Master's thesis

I have read the TU/e Code of Scientific Conductⁱ.

I hereby declare that my Master's thesis has been carried out in accordance with the rules of the TU/e Code of Scientific Conduct

Date 03-12-2019 <u>Name</u> elders ID-number 0898828 Signature

Submit the signed declaration to the student administration of your department.

¹ See: <u>http://www.tue.nl/en/university/about-the-university/integrity/scientific-integrity/</u> The Netherlands Code of Conduct for Academic Practice of the VSNU can be found here also. More information about scientific integrity is published on the websites of TU/e and VSNU

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