Vibrational and gas heating dynamics in molecular plasma assessed by Thomson and Raman scattering

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Abstract: Rotational and vibrational temperatures during ignition of pure CO_2, N_2 and CH_4 microwave plasmas are measured by Raman scattering. A strong vibrational non-equilibrium is observed, followed by rapid gas heating. V-T relaxation mostly explains the observed temperatures in CH_4, but not of N_2 and CO_2. Thomson scattering reveals an electron temperature with limited selectivity to vibrations in N_2 and CH_4, indicating an important role of electronic excitation in N_2 and CO_2 in the gas heating during the ignition of the plasma.

Keywords: Microwave plasma, Thomson scattering, vibrational excitation, electron temperature, Raman scattering.

1. Introduction

Plasma reforming of stable molecules might be attractive as an alternative to conventional gas reforming processes by offering low-inertia, scalability and potentially very high efficiencies [1]. The high efficiencies can be reached by tuning the electron temperature, and thus the electron energy loss fraction, to deposit the majority of the power into vibrations, as illustrated in Figure 1. Molecular vibrations are what unlocks the high efficiencies of plasma processes. Three stable molecules for three plasma reforming processes are studied, N_2, CH_4 and CO_2. Nitrogen can be dissociated through vibrations, breaking the strong triple bond between the atoms, with applications in nitrogen fixation for fertilizer production. Methane reforming to value-added chemical compounds such as ethylene and benzene is possible with a high efficiency and selectivity, which holds great promise for the petrochemical industry [2]. Carbon dioxide dissociation into carbon monoxide for solar fuel production opens a potential route for energy storage in hydrocarbons produced from CO_2. Key in all of these processes is minimizing heat production, for which the electron temperature is a crucial parameter. However, V-T relaxation is an inherent heat source even when all energy goes into vibrations. In this work, pulsed microwave plasmas are studied to unravel these mechanics during ignition, when the gas is at room temperature initially and the effect of product formation is limited.

2. Methodology

A schematic of the experimental setup is shown in Figure 2. Microwave pulses of 200µs are generated by a solid-state power supply and are transported by waveguides to a glass tube, in which the plasma is generated. A three-stub tuner and sliding short are used to tune the field. Tangential gas injection leads to a swirl flow in the tube, which stabilizes the plasma. A 10Hz, frequency doubled Nd:YAG laser of 600mJ per pulse is focused into the centre of the plasma. A 100mm focal distance lens collects and focuses the scattered light into a fiber bundle.

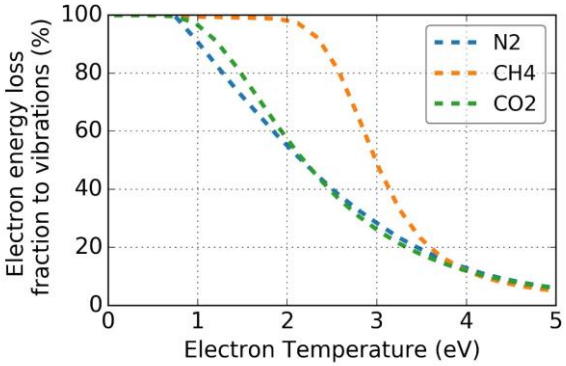

Figure 1 Electron energy loss fractions to vibrations for N_2, CH_4 and CO_2 as a function of T_e. Calculations done with a Boltzmann solver, cross sections from [3] [4].

The fibers relay the scattered light into a 1m focal distance custom built Littrow-configuration spectrometer with an 1800l/mm grating. The spectrally resolved signal is captured by an em-ICCD camera.

In laser scattering experiments rejection of stray light and filtering of the Rayleigh is of extreme importance. Both effects usually are orders of magnitude stronger than Raman or Thomson scattering. For this purpose, a sharp edge longpass filter is used to block the laser frequency. The filter is calibrated by the rotational Raman signal of CO_2 at room temperature, where the spectral response of the filter is fitted with a hyperbolic tangent function, which is illustrated in Figure 3.

Thomson scattering, the elastic scattering of light on free electrons, is a non-intrusive, *in-situ*, time and spatially resolved diagnostic. The scattered light intensity scales linearly with the electron density, provided no collective effects are at play as is expected for our conditions [5].

The electron temperature is calculated assuming a Maxwellian electron velocity distribution, which means that the Thomson spectrum reduces to:

$$s_T(\lambda) = \frac{1}{\sqrt{\pi} s_T} \exp\left(-\frac{(\lambda-\lambda_0)^2}{s_T^2}\right). \qquad \text{eq. 1}$$

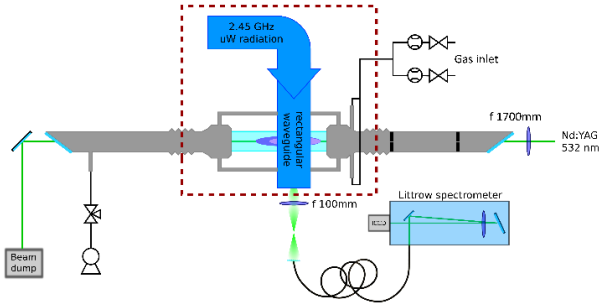

Figure 2 Schematic of the experimental setup used for these experiments, showing a vacuum system with a glass tube where the plasma is created, through the centre of which a laser fires to do laser scattering experiments.

Here, λ is the wavelength, λ_0 the laser fundamental and s_T the $1/e$ width of the Gaussian, which depends upon T_e as:

$$s_T = \sqrt{\frac{4k_b T_e}{m_e c^2}}\lambda_0. \qquad \text{eq. 2}$$

The electron density is calculated based on a calibration of the rotational Raman signal of N_2 at known pressure and temperature[6]:

$$n_e = \frac{I_T}{I_R}\frac{\sigma_{R_{N_2}}}{\sigma_T}. \qquad \text{eq. 3}$$

Here $I_{T,R}$ is the scattered light intensity of respectively the Thomson and Raman scattered light, $\sigma_{R_{N_2}}$ is the differential cross section of rotational Raman scattering for all rotational lines, and σ_T is the differential cross section of Thomson scattering. The ratio of differential cross sections can be evaluated to $8.15 \cdot 10^{-5}$.

Thomson scattering on molecular plasmas is not often considered, since generally molecules emit rotational Raman scattering. Fortunately, methane has a point-group symmetry so that its depolarization reduces to exactly zero [7]. Consequently, there is no depolarization of the Rayleigh scattering, but more importantly no rotational Raman signal obscuring the Thomson scattered light.

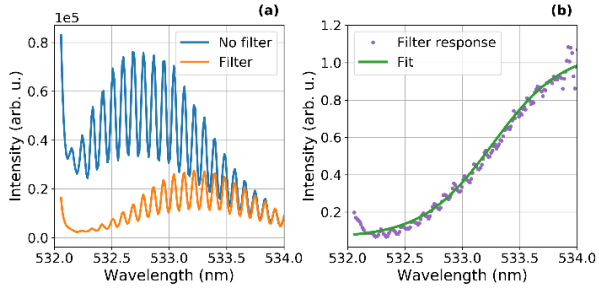

Figure 3 (a) Rotational Raman signal of CO_2 with and without the filter and (b) the fitted response of the filter together with the original signal.

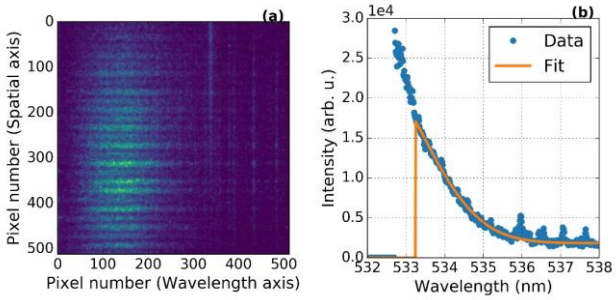

Figure 4 (a) Image of recorded spectrum, together with (b) actual Thomson spectrum and Gaussian fit overlaid. The filter response is taken into account, hence the sharp rise towards 532nm. The electron temperature for this spectrum is 1.8±0.2eV. The electron density is $7.5 \pm 3 \cdot 10^{19} m^{-3}$.

A Thomson scattering spectrum measured in methane is shown in Figure 4. The fit is manually stopped at 533.2nm, up to that point the calibrated filter response is accurate. Spectral signature of products can be seen clearly at $\lambda > 536\text{nm}$. With this method the electron temperature can be measured with relatively high accuracy, the electron density however is prone to errors, since only a fraction of the Thomson signal is recorded. Three checks are passed to confirm that the signal originates from Thomson scattering. Firstly, the polarization is checked to follow the laser polarization. Secondly it is checked that the signal disappears if either the camera gate is out-of-sync with the laser or when the plasma is off. Thirdly, a similar signal should be found in a continuous argon discharge.

3. Results

Figure 5 shows the Thomson scattering results for methane and the absorbed power profile. The absorbed power of the plasma changes over time due to the rapidly developing plasma conditions, which alter the plasma impedance, and thus the matching quality. The error of the electron temperature is estimated based on the quality of the fit at low n_e and high T_e.

Observed is an elevated electron temperature at the start of the pulse. The actual values indicate that this is outside of the parameter range in which energy transfer to vibrational modes is dominating. At electron temperatures of roughly 3±0.4eV the selectivity of electron energy to vibrations is in the order of 50%.

Detection of Thomson scattering signatures in N_2 and CO_2 is more challenging. The Thomson scattered light has a lower intensity than the Raman signal. We take advantage of the fact that the rotational Raman signal is partly depolarized, whereas the Thomson scattering is completely polarized. Subtracting the two polarizations of the scattered light after taking the depolarization ratio into account eliminates the Raman signal. The approach is illustrated in Figure 6 and highlights the possibility to measure Thomson scattering in a molecular plasma.

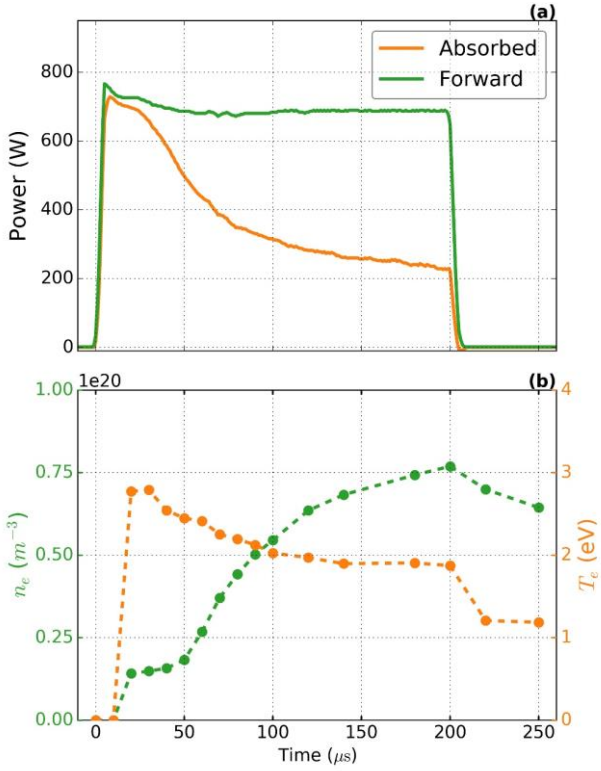

Figure 5 (a) Forward and absorbed power, and (b) the electron density and temperature for pulsed μ-wave CH_4 plasma.

Analysis of the scatter spectra yields an electron temperature of 1.5±0.4eV at 70μs into the pulse, which is lower compared to the methane pulse. Nevertheless, Figure 1 shows more energy going to electronic excitation at a lower electron temperature. For CH_4, with a T_e 2.2eV this is roughly 90%, whereas for N_2 at 1.5eV this is only 70%.

Unfortunately, Thomson scattering contributions could not be retrieved throughout the plasma pulse in N_2. At the onset of the plasma, during the initial 50μs, the electron density was too low to gain sufficient signal-to-noise. As far as it was measurable, electron temperatures were found to be lower in N_2 compared to CH_4.

So far, the approach could not be successfully applied to CO_2 due to its much larger rotational Raman cross section [8] and more complicated and dense rotational spectrum. Where the rotational Raman spectrum of N_2 could be completely resolved, this was not possible for CO_2.

Gas heating dynamics were studied by retrieving the temperature evolutions of CH_4, N_2 and CO_2 over the onset of the discharge from time resolved Raman scattering measurements.

For CH_4 the temperatures are obtained by measuring and fitting the vibrational Raman spectrum in the pentad region. For N_2 the vibrational Raman spectrum of its sole vibrational mode is analysed to give both vibrational and rotational temperatures. For CO_2 vibrational and rotational Raman give insight into the temperature of the asymmetric stretch mode, T_3, the bending and symmetric modes, T_{12}, and the rotational temperature, T_{rot}. The results of these measurements are shown in Figure 7.

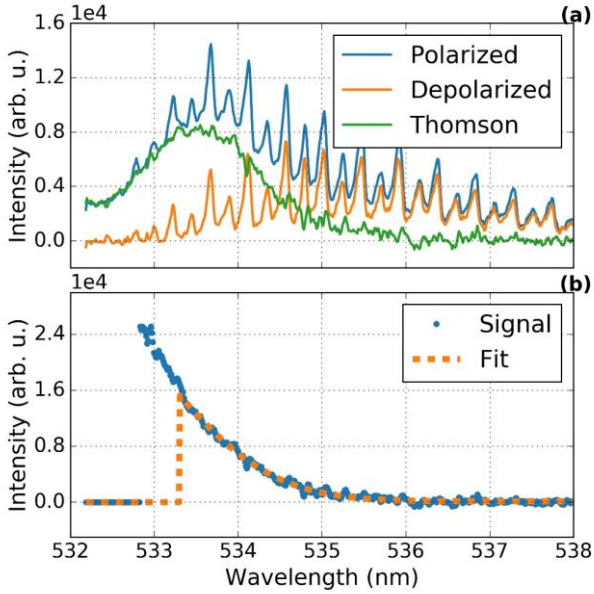

Figure 6 (a) The polarized, depolarized and Thomson signals as measured in a pulsed N2 discharge. (b) The Thomson signal with filter response taken into account together with a Gaussian fit over the data, giving a T_e of 1.5±0.4eV and n_e of $1 \pm 0.5 \cdot 10^{19} m^{-3}$.

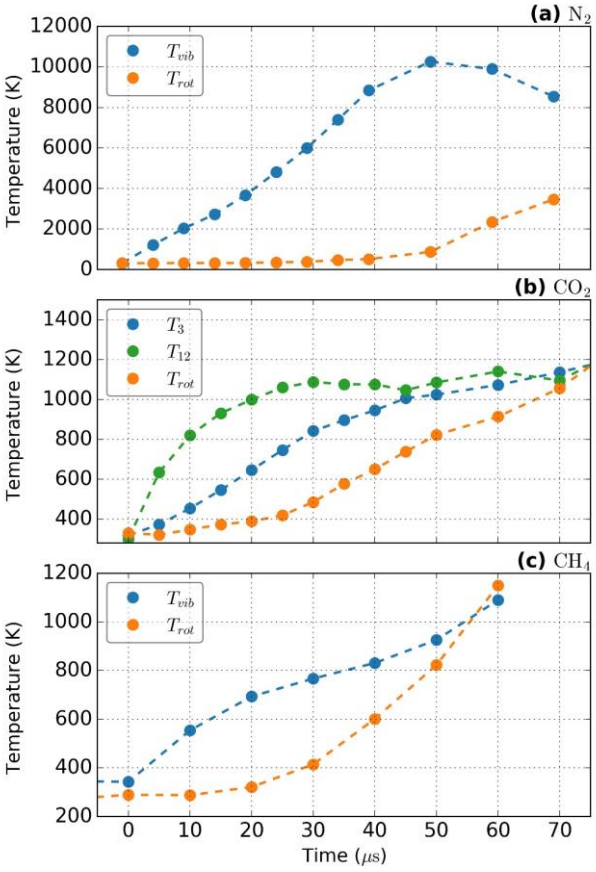

Figure 7 Rotational and vibrational temperature evolutions of (a) N_2 , (b) CO_2 and (c) CH_4 assessed by Raman scattering.

We conclude that the three different gases heat up in significantly different ways. Nitrogen exhibits the largest vibrational excitation, with very limited initial gas heating. Whereas in N_2 the vibrational temperature reaches more than 10^4K, for CO_2 and CH_4 this is only 10^3K, after which the non-equilibrium collapses. In N_2, a rapid temperature increase is observed from 50-70μs, probably leading to thermalisation later in the pulse. While at the onset of the pulse the electron temperature is not suited for selective vibrational excitation, still this is the phase where the non-equilibrium is observed for all three gases. The large non-equilibrium observed in N_2 can partly be explained by the much smaller vibrational heat capacity of N_2, since it only has one vibrational mode. This difference is however not enough to completely explain the recorded temperatures in N_2.

For the few time-steps in the plasma where Thomson signal is obtainable for N_2, we compare the electron temperature with that of methane. For N_2 we see a lower T_e, but a larger fraction of power deposited into electronic excitation. However, quenching of electronic states in N_2 takes much longer than in CH_4 or CO_2, leading to an electronic energy reservoir, whereas the other molecules have short lived electronic states, giving more direct heat production.

For CH_4 the equilibration of T_{vib} and T_{rot} coincides almost perfectly with the characteristic timescale of V-T relaxation at 25mbar and 300K, which is 50μs [9]. This hints at a limited effect of heat produced by other processes. For N_2 the V-T timescales are orders of magnitude longer [10], which strongly suggests that the heat generation near the end of the pulse is caused by other processes than V-T relaxation, such as atomic N recombination.

In CH_4 it is always assumed there is an equilibrium between the vibrational modes, since the V-V equilibration timescales are sub-microsecond. This is not the case for CO_2, where not only a non-equilibrium between vibration and rotation is observed, but also a non-equilibrium between the different vibrational modes. V-T relaxation in CO_2 is mediated by the first excited bending mode, $(0\ 1^1\ 0)$. Relaxation of the first asymmetric stretch level $(0\ 0^0\ 1)$, to the bending mode takes 150μs, while relaxation of this first excited bending mode to translations takes 270μs [11], it is therefore in the case of CO_2 important to know if the energy is deposited into the bending modes or in the asymmetric mode. Taking the small heat capacity of the asymmetric mode into account we see that, while the temperature rise is much smaller initially, most energy goes into the bending and symmetric modes. It cannot be concluded that the bulk of the energy is deposited into the Fermi resonant vibrational modes, these measurements only give temperatures at a specific time. Thus no direct information is obtained on the energy fluxes, a kinetic model would be required for this, which is outside the scope of this work.

The V-T time of the bending mode at different temperatures is known, at $T_{rot} = 900$K, which is reached after only 60μs, the V-T time is 80μs [12]. If the assumption is made all V-T relaxation goes through the bending mode this shows that V-T relaxation alone cannot account for the heat production in the CO_2 plasma.

4. General conclusions

Thomson and Raman scattering were used to obtain a detailed insight in the heating dynamics in the ignition phase of microwave plasmas. For CH_4, N_2 and CO_2 a strong vibrational non-equilibrium is observed during ignition.

This vibrational non-equilibrium in CH_4 is compared with the electron temperature evolution measured by Thomson scattering, where a decreasing electron temperature is observed, going from 3eV to 1.8eV.

Thomson scattering spectra have been measured for the first time in a pure N_2 plasma and yielded lower electron temperatures compared to pure CH_4. For N_2 this still means that significant energy goes into electronic excitation. Nevertheless, the strongest non-equilibrium is observed in N_2.

The ignition of CO_2 appears similar to that of methane, forming a short-lived non-equilibrium. Unlike methane, a difference is observed between the populations of the different vibrational modes. The heat production in CH_4 can almost completely be explained by V-T collisional energy exchange. For N_2 and CO_2 the heating behaviour cannot purely be explained by V-T processes, otherwise the vibrational non-equilibrium would be sustained for longer, hinting at the importance of lowering the electron temperature.

5. References

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