Gas temperature and vibrational temperature in a pulsed N_2 microwave plasma: a combined experimental and computational study to explore non-equilibrium conditions

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Abstract: Plasma is gaining increasing interest for N_2 fixation, i.e. the conversion of N_2 into small molecules (like NH_3 or NO_x), which can be used as building blocks for life on earth. The most energy-efficient conversion occurs by vibrational-induced dissociation of N_2. An important challenge in using non-equilibrium plasmas, to maximize this vibrational-induced dissociation, lies in preventing VT relaxation processes, in which vibrational energy is lost to gas heating. We present here both experimental and modeling results for a pulsed MW N_2 plasma, to gain a deeper insight in how power pulsing can suppress these unfavourable VT relaxation processes.

Keywords: Plasma technology, Nitrogen fixation, Microwave plasma, Pulsed plasma

1. Introduction

Nitrogen is a crucial element, being a major building block for proteins, nucleic acids and other cellular constituents, responsible for life on earth. On earth we are surrounded by this vital element, as almost 79% of the earth's atmosphere consists of molecular nitrogen gas (N_2). However, this abundant nitrogen source is not available to the majority of living organisms, as the molecule's strong triple bond and very stable electronic configuration prevents organisms to easily incorporate it in any biosynthetic pathway. Our agricultural system, and life on earth in general, thus depends on nitrogen fixation processes that convert molecular nitrogen into simple nitrogen compounds, such as ammonia or nitric oxides, which in turn can be further used as precursors for the synthesis of more complex molecules [1]. This issue led in 1908 to the development of the Haber-Bosch process, which to this day remains the conventional standard for producing ammonia through N_2 fixation. Today the Haber-Bosch process produces more than 130 million tons of ammonia per year, indirectly feeding 40% of the world population through fertilizer production [2]. Unfortunately, the process consumes almost 2% of the world's total energy production through fossil fuel consumption and emits 300 million metric tons of CO_2 each year [3]. As major environmental concerns associated with fossil fuels require a short-term transition from a carbon-based energy economy to a sustainable one, energy intensive chemical processes like the Haber-Bosch process are detrimental in our present-day society. The Haber-Bosch process was significantly optimized the past 100 years, essentially reaching its theoretical optimization limits [3]. As a result, the environmental impact of N_2 fixation processes can only be improved by considering new, innovative approaches, which are very different from the Haber-Bosch process [3]. Among several solutions, the use of non-equilibrium plasmas seems very promising. Non-equilibrium plasmas enable high energy electrons to forcefully interact with the stable nitrogen bond, while the bulk gas remains close to room temperature. This solely electricity driven, fossil fuel-free solution harmonizes greatly with a future of renewal energy from wind and solar cells [4]. Furthermore the theoretical energy consumption limit of the plasma-based process is 2.5 times lower than that of the Haber-Bosch process, giving it an edge over the classical process when it is optimized towards this limit [5].

The plasma-based NO_x formation has already been tested in different kind of plasma reactors [4]. A microwave (MW) reactor delivers the best results at reduced pressure, yielding an energy cost of 0.3 MJ/mol for an NO_x yield of 14 % [6]. Second in place is a gliding arc reactor, with a 2% NO_x yield and 2.8 MJ/mol energy consumption [7]. The reason why MW discharges (and also GA discharges) yield the most promising result is because they create significant vibrational excitation of N_2. As revealed by recent computer modeling, the most efficient way of breaking the N≡N bond is not achieved by direct electronic excitation with high energy electrons, but by gradually exciting the vibrational states of N_2 [8]. These vibrationally excited N_2 molecules collide with each other, inducing vibrational-vibrational relaxation (VV relaxation) and exchanging their vibrational energy. Going through a series of these vibrational relaxation collisions, molecules can gradually populate higher vibrational energy levels, a process which is often referred to as vibrational ladder climbing [9]. Through this vibrational ladder climbing, a N_2 molecule eventually reaches energy levels close to the bond dissociation energy of the N≡N bond (9.765 eV), facilitating the breakage of the bond. However, as a response to the non-equilibrium between vibrational and thermal energy caused by vibrational ladder climbing,

vibrational-translational (VT) relaxation occurs [9]. This relaxation process causes the energy of N_2 to be transferred from vibrational to translational energy upon collision with another species. This is deemed highly unfavourable, as the vibrational energy, which is required to overcome the reaction energy barrier, is lost to gas heating. As revealed by computer modeling, this energy loss mechanism becomes more important at high gas temperature [8]. Avoiding the temperature rise and the thermalization of the vibrational energy is thus of very high priority in N_2 fixation through non-equilibrium plasmas [9]. One option to prevent the gas temperature rise exists in supplying the power source of the plasma, like the MWs of a MW plasma, in a pulsed manner, so that time is provided for the plasma to cool down between pulses [4]. This last option is relatively easy to apply on a plasma setup and indeed looks very promising for N_2 fixation, but lacks a fundamental understanding to fully exploit its advantages. To address these fundamentals of the vibrational excitation mechanism of N_2 in a pulsed plasma, we perform a combined experimental and computational study of a pulsed pure N_2 MW plasma.

2. Methodology

To observe vibrationally excited N_2 species in the MW plasma, vibrational Raman spectroscopy is conducted. Raman spectroscopy is the ideal spectroscopic technique to observe low frequency modes of molecules, like the vibrational modes of N_2 [10]. This is achieved by analyzing light from a 532 nm pulsed Nd:YAG laser, described in [11], that has scattered inelastically on the excited N_2 molecules. This inelastically scattered light is focused onto an iCCD camera, which captures the light signals into a Raman spectrum. In this spectrum the intensity of the signals that represent the vibrational modes are in proportion to the density of the vibrationally excited species, while the signals that represent the rotational modes deliver information about the gas temperature.

The vibrational mechanisms inside the pulsed MW plasma are studied by modeling the MW setup using the zero-dimensional (0D) model ZDPlasKin (Zero-Dimensional Plasma Kinetics solver) [12]. In this model the time evolution of the plasma species densities is calculated by balance equations, taking into account the various production and loss terms by chemical reactions. Such a balance equation of a species density is given by:

$$\frac{dn_i}{dt} = \sum_j \left[\left(a_{ij}^R - a_{ij}^L \right) k_j \prod_l n_l^L \right] \quad (1)$$

In which n_i is the density of species i and a_{ij}^R and a_{ij}^L are the stoichiometric coefficients of species i on the right-hand and left-hand side of the reaction j. n_l is the density of species l, the reaction product on the left side of the reaction. k_j is the reaction rate constant of reaction j, which has the general form:

$$a_A A + a_B B\ (+\delta\varepsilon) \xrightarrow{k_j} a_c C + a_D D\ (+\delta\varepsilon) \quad (2)$$

In which A,B,C and D are the species and a_A, a_B, a_C and a_D their stoichiometric coefficients. $\delta\varepsilon$ represents the possible energy change during the reaction, used to calculate the gas temperature self-consistently as the reactions progress. The rate coefficients of these reactions are adopted from literature for the heavy particle reactions, whereas the rate coefficients for the electron impact reaction are calculated with a Boltzmann solver, BOLSIG+, built in ZDPlasKin. As we are particularly interested in the vibrational ladder climbing mechanism of plasma-based nitrogen fixation, the chemistry of the model focusses excessively on the vibrational excitation and relaxation mechanisms in the plasma. For this reason, 45 vibrational energy levels up to the dissociation limit of N_2 (9.765 eV) are included in the model, resulting in 50 plasma species and 4000+ reactions. These reactions include: electron impact reactions, various ion and neutral reactions, VT relaxation, VV relaxation and dissociation.

3. Results and discussion

To obtain an initial understanding of the vibrational excitation in pulsed MW plasmas, the excitation process is first studied when only one single pulse is applied to the gas. This will provide very fundamental information about the non-equilibrium between the vibrational and gas temperature that exists in pulsed plasmas. This one pulse plasma is experimentally achieved by pulsing at such a low frequency (30 Hz) that no gas molecule will ever see more than one pulse when passing through the plasma tube. This is combined with a high flow rate of 4 slm, constantly providing new gas to the plasma. The duration of the pulse is chosen to be 233 µs, while the pressure is kept at 25 mbar. By using Raman spectroscopy at different time frames in the 233 µs pulse, the profile of the vibrational and rotational temperature through the pulse is captured in figure 1. This temperature evolution shows a clear non-equilibrium formed between the vibrational temperature and the gas temperature: While the vibrational temperatures reaches values up to 4000 K, the gas temperature never peaks above 1500 K. The gas temperature is clearly not able to establish thermal equilibrium in the plasma before the 233 µs pulse ends. This clear non-equilibrium is further elucidated by the 0D modeling results shown in figure 2, displaying the reaction rates of the three most important excitation and relaxation processes in the plasma: electron impact vibrational excitation, VV relaxation and VT relaxation. The relative ratio of these three major plasma processes provides an explanation for the current situation: The electron impact vibrational excitation and VV relaxation rates are very high, inducing high vibrational temperatures instantly as the pulse begins. VT relaxation, however, occurs on a much slower time-scale, explaining the slow gas heating of this system. The pulsed situation represented here takes advantage of these different time scales: terminating the

power supply frequently, as done in this pulsed plasma, inhibits the rates of the slow VT relaxation process to grow to high values, while fast reactions, like electron impact vibrational excitation and VV relaxation, have no problem to occur on this short time scale.

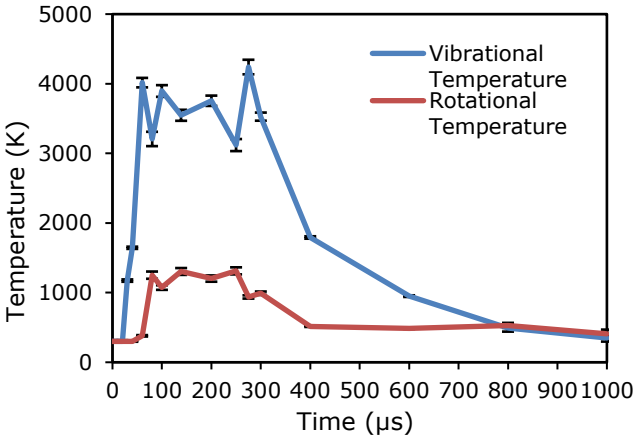

Fig. 1: Evolution of the measured vibrational and gas temperature in the centre of the plasma during one single 233 µs pulse and its afterglow

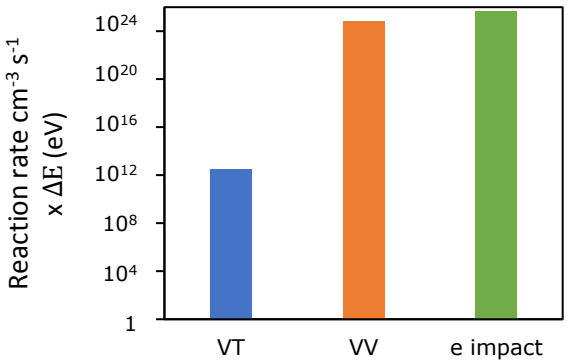

Fig. 2: Calculated reaction rates of electron impact vibrational excitation, VV relaxation and VT relaxation, multiplied with the energy difference caused by these processes and averaged over all transitions in the model, in one single 233 µs pulse

While a lot of fundamental information can be extracted from these one pulse experiments, their application potential for industrial N_2 fixation is unlikely. Indeed, pulsing the power at 30 Hz with a gas flow rate of 4 slm allows a large portion of the gas to pass through the reactor in the pulse off-time, missing out on any vibrational excitation. Therefore, using the knowledge acquired in this one pulse experiment, regimes of higher frequencies are also investigated. The following cases will thus elucidate to which degree the fundamentals of the one pulse plasma extend to more realistic, higher frequency situations. To fully explore the influence of pulsed power deposition, both the pulse frequency and the pulse length are varied.

Figure 3 shows the vibrational and gas temperature, obtained from the Raman experiments as well as the 0D simulations, for pulse frequencies of 1, 2, 5 and 7 kHz with a 50 µs pulse width, a flow rate of 4 slm and a pressure of 25 mbar. For all four cases, a good agreement between experiments and simulations is achieved, clearly indicating the same trend: as more pulses are applied in the same period of time, i.e. due to a higher frequency, more power is put into the plasma, which leads to more vibrational excitation and thus a higher vibrational temperature. However the gas temperature also raises notably upon rising frequency, indicating that VT relaxation also gains significance. This is again confirmed by the 0D modeling results. Unlike the one pulse regime, higher pulse frequencies, like 7 kHz, do display high VT relaxation rates. These higher rates indicate that more vibrational energy is wasted to gas heating in these higher frequency regimes, explaining the higher gas temperatures that were observed. Indeed, since computer calculations already pointed out that VT rates increase drastically upon rising temperature [8], the self-accelerating effect that is induced by significant VT relaxation will eventually nullify the advantages of a pulsed regime at high frequencies. This observation suggests that at some point a high pulse frequency will be unfavourable for the non-equilibrium in the plasma. The extent to which this occurs for the regimes studied here, is shown in table 1. We define thermal non-equilibrium based on the difference between vibrational and gas temperature, so the ratio between the vibrational and gas temperature is used in this table as a measure for the non-equilibrium. Overall, the 5 kHz regime achieves the highest degree of non-equilibrium, as it allows the gas to be exposed long enough to the MW radiation to achieve high vibrational temperatures through vibrational excitation, and at the same time, it is not too high for VT relaxation to significantly accelerate itself, as observed at 7 kHz. Hence, at this frequency an ideal balance is achieved.

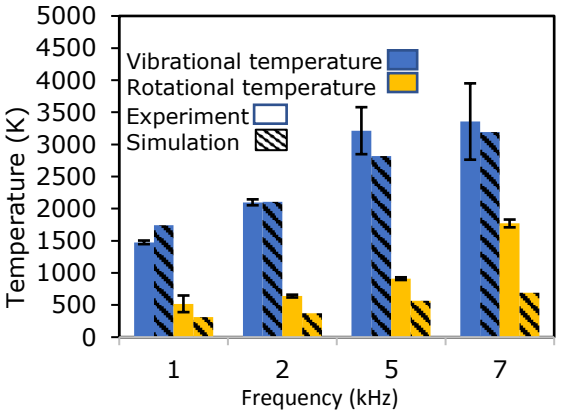

Fig. 3: Measured and calculated spatially-averaged vibrational and gas temperatures in a pulsed MW plasma at four different frequencies

Table 1: Ratio between measured vibrational and gas temperature for four different pulse frequencies, averaged over the whole plasma

1 kHz	2 kHz	5 kHz	7 kHz
2.2±0.2	3.0±0.2	3.7±0.3	2.2±0.2

All results presented up to now were obtained using a constant pulse width of 50 µs. However, just like the pulse frequency, the pulse width also defines the amount of power that is applied to the plasma and will thus also have an impact on the vibrational excitation process. Figure 4 show the vibrational and gas temperatures in the plasma, obtained from the experiments and the 0D simulations, for a pulse length of 10, 50, 200 and 400 µs at a pulse frequency of 1 kHz, a flow rate of 4 slm and a pressure of 25 mbar. Again, the four cases deliver a good agreement between simulations and experiment, clearly demonstrating the same trend. Similar to the effect of a higher pulse frequency, a longer pulse length both delivers a higher vibrational temperature and higher gas temperature. 0D modeling results show that these long pulses give electron impact vibrational excitation reactions the opportunity to occur for a long period of time, explaining the high vibrational temperature in this regime. However, as VT relaxation was shown to work on a longer time scale, the modeling results also indicate that these long pulses encourages the VT relaxation rates to build up to high values throughout each pulse, inducing significant gas heating. The extent to which this significant gas heating is deterring for the non-equilibrium is again deduced from the ratio between the vibrational and gas temperature shown in table 2. This table clearly shows that the pulsed MW plasmas with a longer pulse width of 200 µs and 400 µs do not provide a significantly more pronounced non-equilibrium than the 50 µs pulse regime. Although they implement a long excitation time for vibrational ladder climbing, the significant gas heating compensates for the additional vibrational excitation that occurs.

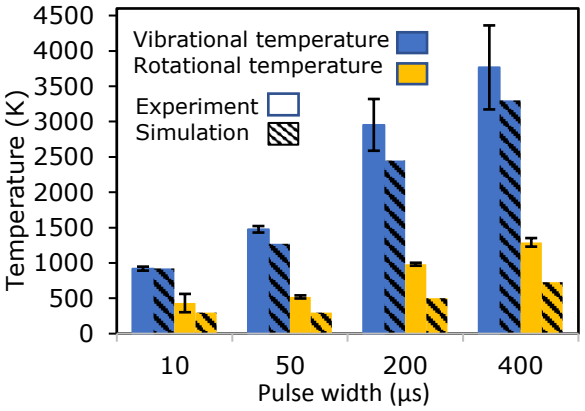

Fig. 4: Measured and calculated spatially-averaged vibrational and gas temperatures in a pulsed MW plasma at four different pulse widths

Table 2: Ratio between vibrational and gas temperature for four different pulse widths averaged over the whole plasma

10 µs	50 µs	200 µs	400 µs
1.79±0.2	2.38±0.4	2.56±0.5	2.53±0.5

4. Conclusion

The common understanding has been developed that a transition from our carbon-based energy economy towards a sustainable one is necessary rather sooner than later. This includes an electrification of energy-intensive chemical processes like the Haber-Bosch process. A promising potential green alternative to the Haber-Bosch process is plasma-based N_2 fixation, for instance through pulsed MW plasmas. It has been demonstrated that a pulsed plasma takes advantage of the different time scales of the three major vibrational mechanisms in the plasma, i.e., electron impact vibrational excitation, VV and VT relaxation. By pulsing the plasma, the unfavoured VT relaxation, which operates on a long time scale, is inhibited. By varying the pulse parameters, it has been demonstrated that the advantage of pulsing is diminished if the frequency or the pulse length become too high (i.e., pulse frequency around 7 kHz and pulse length above 400 µs). As soon as gas heating becomes too dominant, the VT rates grow rapidly, accelerating themselves even more upon gas heating. We observe that an ideal balance can be found in pulse frequency and pulse length, at which vibrational excitation occurs excessively, populating the higher vibrational levels, while the gas heating is limited. In our study, the highest non-equilibrium was achieved for a frequency of 5 kHz and a pulse width of 50 µs, reaching a vibrational temperature of 3200 K, while the gas temperature was kept at only 900 K, yielding a very promising non-equilibrium.

5. References

[1] B. S. Patil, Q.Wang,V.Hessel, Jüergen. Lang, Catal. Today, **256**,49-66 (2015)

[2] Aste, T. J. Phys. Condens. Matter, **17** , 2361–2390 (2005)

[3] Canfield, D. E.; Glazer, A. N.; Falkowski, P. G. Science, **330**, 192–196 (2010)

[4] Bogaerts, A.; Neyts, E. C. *ACS* Energy Lett, **3**, 1013–1027 (2018)

[5] V. D. Rusanov, A. A. Fridman, G. V. Sholin, Sov. Phys. Usp, **24**, 447 – 474 (1981)

[6] Asisov, R. I.; Givotov, V. K.; Rusanov, V. D.; Fridman, A. Sov. Phys, **14**, 366 (1980)

[7] Patil, B. S.; Rovira Palau, J.; Hessel, V.; Lang, J.; Wang, Q. Plasma Chem. Plasma Process, **36**, 241–257 (2016)

[8] Wang, W.; Patil, B.; Heijkers, S.; Hessel, V.; Bogaerts, A. ChemSusChem, **10**, 2110 (2017)

[9] Berthelot, A.; Bogaerts, A. J. Phys. Chem. C, **121**, 8236–8251 (2017)

[10] Plasma Sources Sci. and Technol., Gatti, N., Ponduri, S., Peeters, F. J. J., van den Bekerom, D. C. M., Minea, T., Tosi, P., van de Sanden, M. C. M. & van Rooij, G. J., **27**,5 (2018)

[11] van den Bekerom, DCM. Vibrational excitation for efficient chemistry in CO2 microwave plasmas, Technische Universiteit Eindhoven (2018)

[12] Hagelaar, G. J. M.; Pitchford, L. C. Plasma Sources Sci. Technol., **14**, 722–733. (2005)