Modelling the time-dependent gas heating in low-pressure CO_2 and N_2 pulsed DC discharges

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Abstract: This work presents a modelling study of the time-dependent variation of the gas temperature in CO_2 and N_2 plasmas, with the analysis of the relevant gas heating processes. The calculations are validated through a comparison with experimental data obtained in pulsed DC glow discharges at 1-5 Torr. The role of vibrational kinetics is shown to be paramount for gas heating in both CO_2 and N_2 plasmas under these conditions.

Keywords: kinetic modelling, gas temperature, gas heating mechanisms, Raman spectroscopy, CO_2, N_2

1. Introduction

Gas temperature and heat transfer mechanisms in plasmas are important for fundamental research and many applications. There are several methods available to determine the gas temperature experimentally. However, modelling of heat transfer in plasmas is crucial for understanding the gas heating mechanisms. Of particular interest is the dynamics describing the temporal evolution of the gas temperature, allowing a more detailed investigation than addressing steady-state conditions. One ideal system for this study is the case of a pulsed DC discharge, where it is possible to analyse the raise of the gas temperature during the pulse and its decrease in the afterglow phase.

Gas temperature calculations are usually based on the solutions of the gas thermal balance equation under steady-state or time-dependent situations, according to the working conditions of the plasma. To determine the temperature evolution in plasmas it is important to consider the interplay between electron, vibrational and chemical kinetics. Moreover, at low pressures and discharge tubes of a small radius, surface processes also play an important role and should be included in the overall kinetics.

This work presents a modelling study of the time-dependent evolution of the gas temperature in CO_2 and N_2 millisecond pulsed DC glow discharges produced in a cylindrical tube of inner radius R=1 cm at low pressures (p=1-5 Torr) and current I=50 mA. The modelling results are compared to experimental data obtained in FTIR, optical emission spectroscopy and rotational Raman experiments.

2. Heat transfer equation

In the discharges under study, the plasma is axially homogenous. Therefore, the model considers a radially averaged gas temperature, given by

$$T_g(t) = \frac{1}{\pi R^2}\int_0^{2\pi}\int_0^R T(r,t)rdrd\theta, \qquad (1)$$

where the gas temperature $T(r,t)$ is described by a parabolic radial profile. Under isobaric conditions and assuming that heat conduction is the dominant cooling mechanism, the time-dependent gas thermal balance equation may be written as

$$n_m c_p \frac{\partial T_g}{\partial t} = Q_{in} - \frac{8\lambda_g(T_w - T_g)}{R^2}. \qquad (2)$$

In this equation, n_m and c_p are, respectively, the molar density and the molar heat capacity at constant pressure. The term Q_{in} represents the mean input power transferred into gas heating from the energy released in volume and wall processes. The last term on the right-hand side represents the heat conduction to the discharge tube and it depends on the thermal conductivity, λ_g, and the wall temperature, T_w.

3. Temporally resolved gas temperature in CO_2

To obtain accurate solutions of equation (2), it is necessary to have a detailed knowledge of the thermal conductivity λ_g and the molar heat capacity c_p. The values of these quantities as a function of T_g are used as input to the calculations. The thermal conductivity of CO_2 used in the present work is given by the expression reported in [1]

$$\lambda_g = (0.071\,T_g - 2.33) \times 10^{-5}\ \mathrm{W\,cm^{-1}\,K^{-1}}, \qquad (3)$$

based on the experimental data from Vesović et al [2]. The molar heat capacity used in the model is reported in [3]. Although the values of these parameters do not include the contribution from the vibrational and electronic degrees of freedom, for the case under study they provide reasonably good predictions, as these contributions are expected to be small.

The time-evolution of T_g in a plasma is governed by different elementary processes. For millisecond pulsed discharges, the populations of CO_2 vibrational levels become important, leading to energy exchanges that contribute significantly to the temperature increase during the discharge and to its decrease in the afterglow. In the present work, the term Q_{in} in equation (2) includes i) the power consumed or released in heavy particle reactions, and ii) the power transferred from the electrons to the heavy particles in elastic collisions. The only heavy particle interactions considered in the model are vibration–translation (V-V) and vibration–vibration (V-T) energy exchanges. Our simulations are based on a 0D kinetic model that determines the solutions of a coupled system of time-dependent rate balance equations for ~70 vibrational levels of CO_2. The collisional data used in this work are detailed in [4, 5] and references therein. Once the solutions are known for some pulse duration, they are used as initial conditions for the same system of equations to obtain the solutions corresponding to the afterglow, with the assumption that the electron density is negligible.

The results are validated by comparing the calculated gas temperature with the experimental data obtained from time-resolved *in situ* Fourier transform infrared spectroscopy in a pulsed DC glow discharge, 5 ms plasma-on time and 150 ms off time, at p=5 Torr and I=50 mA. Due to a high flow rate and long off time, all dissociation products leave the reactor between two subsequent pulses. For this reason, the experiment is suitable for the comparison with the present model that does not include chemical kinetics.

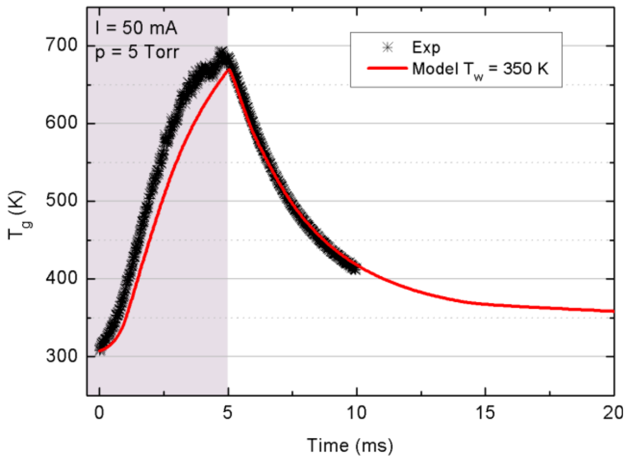

Fig. 1. Temporal evolution of the radially averaged gas temperature T_g for a pulsed discharge in CO_2 at a pressure of 5 Torr with a pulse duration of 5ms and a current of 50mA and the corresponding afterglow. The red curve represents the modelling results, whereas the symbols are experimental data from [4].

Fig. 1 presents the results of our simulations, compared with the experimental data recently reported in [4]. We have used the reduced electric field measured in the experiment, *i.e.* E/N=55 Td. The wall temperature, T_w, which is an input parameter in our model, is assumed to have a constant value of 350 K. Clearly, the calculated temperature compares very well with the experiment. although the model predictions for the active part exhibit some observable discrepancies, especially during the last 2 ms of the pulse. The good agreement of the model predictions with the measured data implies that the role of vibrational kinetics is paramount in gas heating mechanisms in CO_2 plasma under studied conditions.

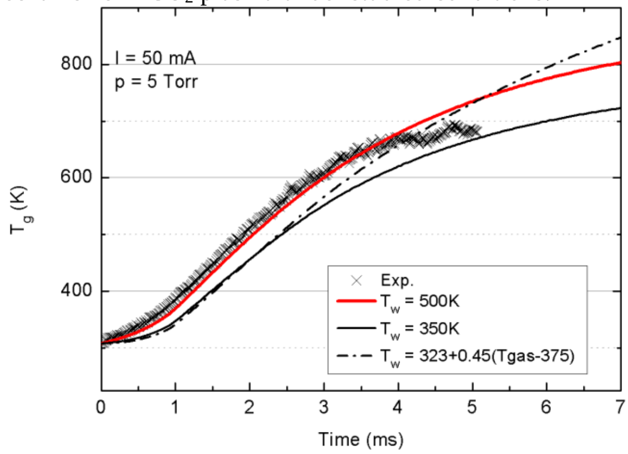

Fig. 2. Temporal evolution of the radially averaged gas temperature T_g in CO_2 during the active discharge. The different curves correspond to calculations made imposing different wall temperature values as input. The symbols represent the experimental data from [4].

To test the sensitivity of the model to different values of T_w, we performed calculations for the active part of the discharge using different values for the wall temperature, as shown in Fig. 2. It can easily be seen that using T_w = 500 K, we obtain a very good agreement with the experiment, with some overestimation at the end of the pulse. Calculations made with a T_w profile that is dependent on the gas temperature, as suggested in some works [6] compare better with the data at later times.

4. Temporally resolved gas temperature in N_2 discharge

Similarly to CO_2, the complex vibrational kinetics of N_2 plasmas at low pressures is shown to play an important role in heat transfers. A thorough modelling study of the time-dependent variation of the gas temperature in N_2 and N_2-O_2 was previously presented in several publications [7-9], with a systematic analysis of the corresponding heating mechanisms, such as

i) Elastic collisions of electrons with N_2 molecules;
ii) Nitrogen dissociation by electron impact collisions through pre-dissociative states N_2*;
iii) Electron-ion recombination;
iv) Non-resonant vibrational-vibrational (V-V) energy exchanges in N_2-N_2 collisions;

v) Vibrational-translational (V-T) energy exchanges in N_2-N_2 and in N_2-N collisions;
vi) Vibrational deactivation of $N_2(X, v)$ at the wall;
vii) Exothermic chemical reactions;
viii) Diffusion and subsequent deactivation of molecular and atomic metastable states to the wall;
ix) Recombination of N atoms at the wall.

The results show that the main mechanisms for the heat transfer in N_2 plasma are the following:
1) Exothermic pooling reactions involving collisions between electronically excited molecules $N_2(A^3\Sigma_u^+)$. The products of this process are a vibrationally excited molecule $N_2(X, v{=}2)$ and electronically excited $N_2(B)$ or $N_2(C)$ followed by 4 eV and 0.4 eV released to the gas heating, respectively. Some works also consider creation of $N_2(B)$+$N_2(X, v{=}8)$ with a lower available energy of 2 eV.
2) Non-resonant V-V energy exchanges in N_2-N_2 collisions.
3) V-T energy exchanges in N_2-N collisions involving multi-quantum transitions.

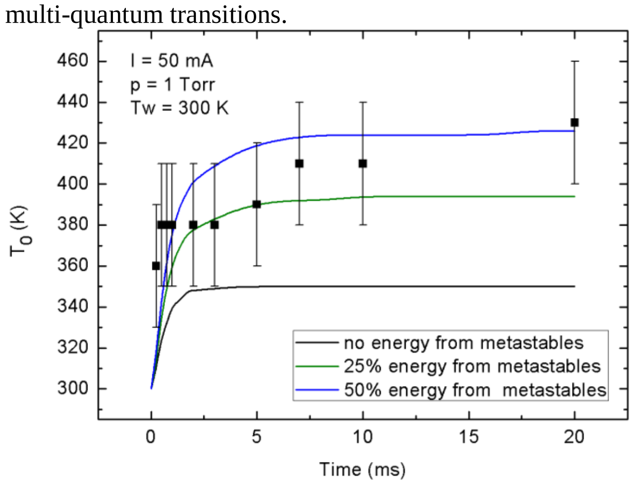

Fig. 3. Comparison between the temporal evolution of the gas temperature at the axis of the reactor T_0 calculated for different amount of energy transferred from metastables for a 20 ms pulsed discharge in 1 Torr with a current of 50 mA in a tube radius of 1 cm, and the experimental measurements (symbols).

However, there is still an open question regarding the amount of energy that is transferred to gas heating from the following processes involving the quenching of N_2 or N electronically excited species:

$$N_2(B) + N_2 \rightarrow N_2(A) + N_2$$
$$N(^2D) + N_2 \rightarrow N(4S) + N_2$$
$$N(^2P) + N_2 \rightarrow N(4S) + N_2. \qquad \text{(R1)}$$

These three reactions can be an energy source to gas heating that can go respectively up to 1.2, 2.38 and 3.58 eV. Fig. 3 shows the simulation results assuming different amounts of energy transferred to the gas heating by reactions (R1). The calculated temperatures represent the gas temperature at the axis of the reactor, which is suitable for the comparison with the measurements that were obtained by optical emission spectroscopy, where the diameter of the laser beam is much smaller than the tube.

It is evident from Fig. 3 that the inclusion of the energy released from (R1) improves the modelling predictions. Fast gas heating observed in the first millisecond of the pulse is attributed to energy released in the pooling reactions $N_2(A) + N_2(A) \rightarrow N_2(B) + N_2(X)$ and $N_2(A) + N_2(A) \rightarrow N_2(C) + N_2(X)$. At later instance of time, contribution from V-V and V-T processes become dominant heating mechanisms [10].

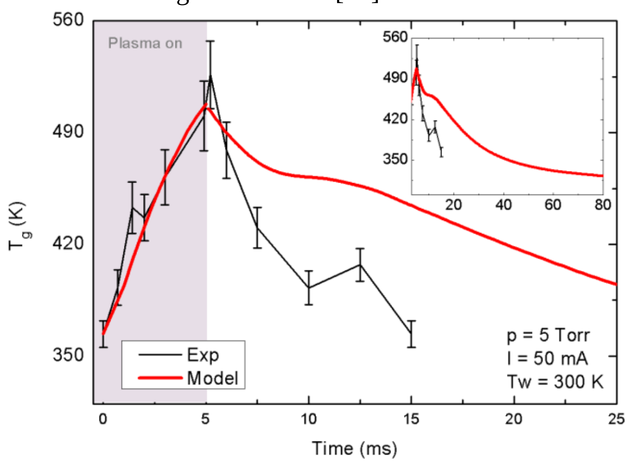

Fig. 4. Calculated temporal evolution of the gas temperature in N_2 plasma at 5Torr (red solid line), *I*= 50 mA and 5ms pulse duration. Calculations include 50% of the energy released in (R1). Experimental results are obtained by rotational Raman spectroscopy.

This is confirmed by the comparison with more recent experimental campaign, shown in Fig. 4. Simulation results shown in the figure correspond to the radially averaged temperature taking into account 50% of available energy transferred to gas heating from reactions (R1). Experimental data used for the validation of the model were obtained from the *in situ* rotational Raman measurements in a pulsed glow DC discharge, with 5 ms plasma-on time and 10 ms off time, at *p*=5 Torr and *I*=50 mA. The calculated temperature corresponding to the active part compares very well with the data, whereas the afterglow predictions exhibit a slower relaxation. An important aspect worth considering when dealing with the average temperature calculations and its comparison with experiment is the agreement between the cross section over which the temperature is averaged. In the present experiment, the measured temperature corresponds to the temperature at the axis of the reactor, while the calculations show the temperature averaged along the reactor radius. Therefore, as stated in [9], this issue should be regarded with caution and it will be addressed in a future study. However, the work presented in [11] shows that the temperature obtained with rotational Raman is nearly equal to the values measured with FTIR, where the IR beam waist is much wider than the laser beam in Raman experiment.

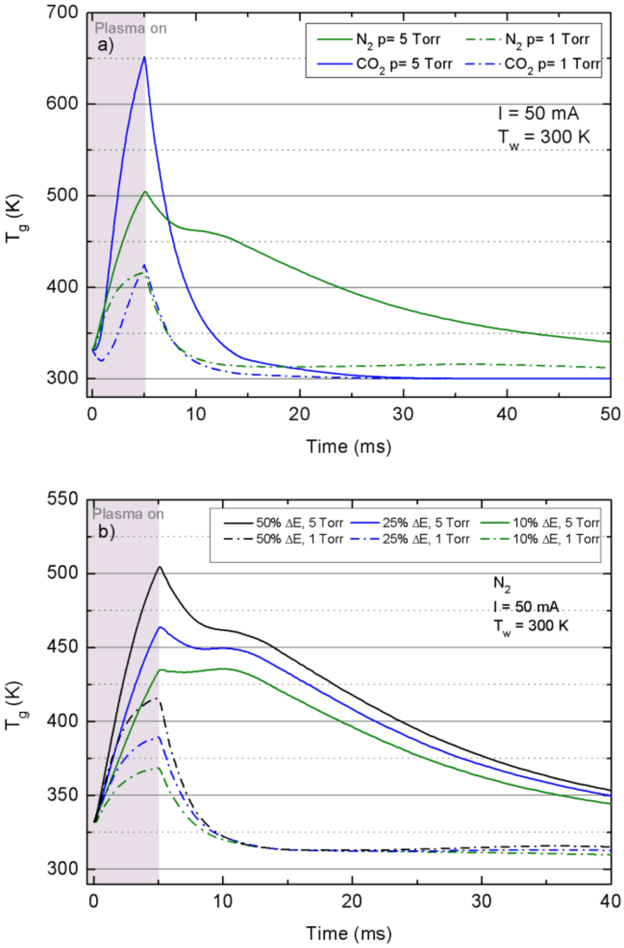

Fig. 5. Calculated temporal evolution of the gas temperature a) in CO_2 and N_2 plasmas at 1 Torr (dot-dashed line) and at 5 Torr (solid lines). Calculations made for N_2 include 50% of the energy released in (R1). b) Gas temperature in N_2 plasmas including 10, 25 and 50% of the energy released in (R1). In all simulations we consider I= 50 mA and 5ms pulse duration.

Fig. 5a) represents the temporal evolution of the gas temperature calculated for CO_2 and for N_2 at 1 and 5 Torr and 5 ms pulse duration. Calculations made for N_2 include 50% of the energy released in (R1). It can be observed that the temperatures in CO_2 are significantly higher at later times in the pulse, *i.e.* after ~2 ms. Before this time, the temperatures in CO_2 exhibit a slower increase than in N_2. Reason for this might be the energy released to gas heating from the quenching of the electronically states that is included in the model for N_2 and that is responsible for the fast heating. Electronically excited states are not considered at present in our model for CO_2. The afterglow part shows slower relaxation in N_2 than in CO_2, easily observed at 5 Torr. This is due to the vibrational levels that remain populated during the afterglow in N_2 discharges [12]. Fig. 5b) shows modelling results for N_2 plasma at the same conditions, considering 10, 25 and 50% of energy transferred to heating from the reactions (R1). Clearly, more energy transferred into heating results in higher magnitude of the gas temperature, as expected.

5. Conclusions

This work presents a modelling study of gas heating mechanisms in CO_2 and N_2 plasmas. Vibrational kinetics is found to be of a great importance for gas heating in both gases. Fast gas heating due to pooling reactions involving $N_2(A)$ mestastables is observed in the first millisecond of N_2 discharges. The contribution of processes involving the quenching of N_2 or N electronically excited species is found to affect strongly the magnitude of the calculated gas temperature. Model predicts a slow relaxation in N_2 plasmas, especially at higher pressures, that is not observed in CO_2. Future studies will consider different contributions to gas heating in CO_2 plasma and address the discrepancies between the simulation results and experimental data.

6. Acknowledgments

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