

# Time-resolved quantum cascade laser diagnostics of pulsed plasmas with strong vibrational excitation.

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## 1. Introduction

Quantum cascade laser absorption spectroscopy (QCLAS) is a powerful tool for diagnostics of reactive plasmas because of its high sensitivity and time resolution. In addition to the measurements of species concentrations, laser absorption spectroscopy can provide valuable information about the gas temperature and the degree of vibrational excitation in the plasma. The latter would require simultaneous detection of multiple absorption lines belonging to the same molecule. However, the tuning range of the QCLs is often limited to just a few roto-vibrational transitions. In this case, the sensitivity to the gas heating and to the vibrational excitation complicates the interpretation of the absorption measurements. In pulsed plasmas, different processes (e.g. gas heating, vibrational relaxation, chemical reactions) occur on different time scales. Therefore, using the excellent time resolution of the QCLs one can separate different contributions and get insight in the chemical and vibrational kinetics in the discharge [1].

In the present study we investigate the kinetics of a pulsed dc discharge in N<sub>2</sub> with admixtures of CO<sub>2</sub> (N<sub>2</sub>O or CO) using a three channel quantum cascade laser spectrometer TRIPLE Q [2]. This system allows simultaneous detection of up to 3 different species with sub-microsecond time resolution. In the gas mixtures under study a strong vibrational excitation of CO<sub>2</sub> (N<sub>2</sub>O, CO) is reached because of the efficient energy transfer from vibrationally excited N<sub>2</sub>(v) molecules. Therefore, by following the kinetics of the infrared (IR) active admixtures, relaxation processes of N<sub>2</sub>(v) can be investigated.

## 2. Results and Discussion

Figure 1 shows the time evolution of the normalized absorbance of CO<sub>2</sub>, CO and N<sub>2</sub>O (absorption transitions around 2200 cm<sup>-1</sup>) in N<sub>2</sub> with 0.3% admixture concentration. As one can see, the absorbance drops abruptly during the 5 ms discharge pulse and then it relaxes to a steady state (10 – 50 % lower than the initial value) on a time scale of 100 ms. During the pulse, the gas heating, vibrational excitation and dissociation contribute to the reduction of the measured absorbance. In the afterglow, the relaxation of the gas temperature occurs within 1-2 ms and the depletion of the absorbance with respect to the new steady state is

caused solely by the vibrational excitation. During the afterglow, V-V' transfer from N<sub>2</sub>(v) determines the degree of vibrational excitation of the admixtures. Therefore, the magnitude of the depletion of the absorbance reflects the degree of vibrational excitation of N<sub>2</sub>(v). And the characteristic relaxation time deduced from the QCLAS measurements represents the vibrational relaxation time of N<sub>2</sub>(v) in the afterglow.

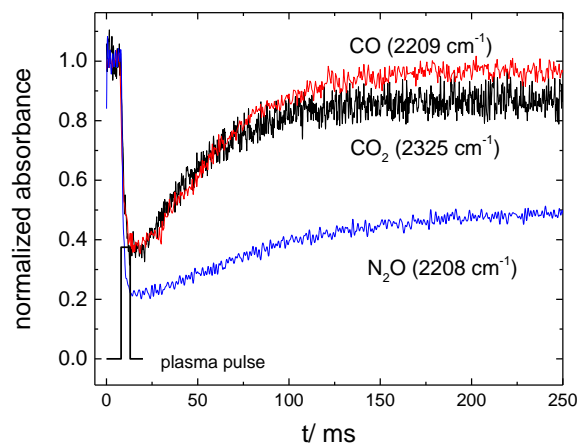


Figure 1. Normalized absorbances of selected IR transitions in N<sub>2</sub>-0.3% CO<sub>2</sub> (N<sub>2</sub>O, CO) mixtures at p=1.33 mbar, I = 50 mA, 5 ms pulse.

QCLAS relaxation measurements have been interpreted using a model of non-equilibrium vibrational kinetics in N<sub>2</sub> taking into account molecular admixtures. We have shown that quenching of N<sub>2</sub>(v) on the reactor walls is the main relaxation process and the surface vibrational deactivation probability  $\gamma_{N_2}$  has been determined from the best agreement between the experiment and the model. The value of  $\gamma_{N_2}$  for different surface materials and different plasma pretreatment has been measured. The advantage of the proposed technique is that the value of  $\gamma_{N_2}$  can be determined *in-situ* in a single discharge pulse so the initial state of the surface is not affected by the plasma.

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## References

- [1] Marinov *et al.* 2014 *J. Phys. D* **47** 015203
- [2] Hubner *et al.* 2011 *Rev. Sci. Instrum.* **82**, 093102