Surface vibrational relaxation of N_2 studied by infrared titration with time resolved Quantum Cascade Laser diagnostics

D Marinov[1,2], D Lopatik[3], O Guaitella[1], M Hübner[3], Y Ionikh[2], J Röpcke[3] and A Rousseau[1]

[1]*LPP, Ecole Polytechnique-91128 Palaiseau, France E-mail: daniil.marinov@lpp.polytechnique.fr*
[2]*St Petersburg State University, Institute of Physics, Ulianovskaya 1, 198904 St Petersburg, Russia*
[3]*INP Greifswald, Felix-Hausdorff-Str, 17489 Greifswald , Germany*

A new method for determination of the de-excitation probability γ_{N2} of vibrationally excited N_2 on different surfaces has been developed. A short DC discharge pulse was applied to a mixture containing 0.05-1% of CO_2, N_2O or CO in N_2. In the afterglow, the vibrational relaxation of titrating molecules was monitored *in-situ* using quantum cascade laser absorption spectroscopy (QCLAS). The experimental results were interpreted in terms of a numerical model of non-equilibrium vibrational kinetics.

1. Introduction

In nitrogen containing plasmas, vibrationally excited $N_2(v)$ acts as an energy reservoir that affects electron kinetics, chemistry and thermodynamic properties of the plasma. In bounded low pressure laboratory plasmas, relaxation on the reactor walls is the most efficient $N_2(v)$ loss mechanism. Therefore, the knowledge of the heterogeneous deactivation probability of $N_2(v)$ (γ_{N2}) is crucial for plasma modeling. The development of a simple and reliable technique for *in-situ* γ_{N2} determination based on the titration with IR active molecules [1,2] was therefore the main motivation of the present study.

2. Experimental

Gas mixtures containing 0.05-1 % of titrating molecules (CO_2, N_2O, CO) in N_2 were excited by a single DC discharge pulse (I=50 mA, τ=1-10 ms) at a pressure of 133 Pa. The relaxation kinetics of CO_2 (N_2O, CO) was followed using a 3-channel quantum cascade laser (QCL) spectrometer TRIPLE Q [3] with time resolution up to 10 μs. Experiments were done in a single pulse mode without accumulation.

Due to a very efficient vibrational coupling between N_2 and CO_2 (N_2O, CO), the excitation of titrating molecules reflects the degree of vibrational excitation of N_2.A model of vibrational kinetics in N_2 with CO_2 (N_2O, CO) admixtures was developed and the value of γ_{N2} was determined from the best agreement between the model and the experiment.

3. Results

With laser absorption spectroscopy a combination $(N_0 - \beta N_1)$ of the populations of the lower ($[CO_2(00^00)] \equiv N_0$) and the upper ($[CO_2(00^01)] \equiv N_1$) vibrational levels is actually measured. Figure 1 shows the time evolution of $(N_0 - \beta N_1)$ in a silica discharge tube for different initial concentration of CO_2. One can see a depletion of the measured value of $(N_0 - \beta N_1)$ due to the vibrational excitation of CO_2 upon the application of the discharge pulse. Vibrational relaxation takes place in the afterglow, the difference between the CO_2 concentrations before the pulse and when the relaxation is finished is ascribed to the dissociation of CO_2 in the discharge. The result of the modeling for 0.2% CO_2 is shown on the same graph, the relative uncertainty of γ_{N2} determination by fitting procedure was estimated to be 15%.

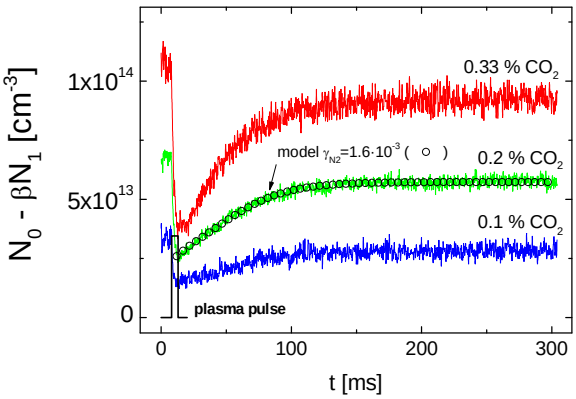

Fig. 1: Time evolution of $(N_0 - \beta N_1)$ after a I=50 mA, τ=5 ms pulse in silica discharge tube.

It was found that the value of γ_{N2} depends on the partial pressure of titrating molecules, what suggests a vibrational energy transfer mechanism between $N_2(v)$ and physisorbed CO_2 (N_2O, CO). Using the described technique the value of γ_{N2} was determined for SiO_2, TiO_2, Al_2O_3, Pyrex and anodized aluminium. The effect of plasma exposure on the efficiency of vibrational $N_2(v)$ quenching on different materials was observed and studied for reactive (N_2, O_2) and non-reactive (Ar) plasma pre-treatments.

References

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