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

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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 model of non-equilibrium vibrational kinetics in N_2-CO_2. The value of γ_{N2} was determined for SiO_2, TiO_2, Al_2O_3, Pyrex and anodized aluminium.

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 laboratory plasmas, relaxation on the reactor walls is the most efficient $N_2(v)$ loss mechanism for pressures up to few tens of mbars. Therefore, the knowledge of the heterogeneous deactivation probability of $N_2(v)$ (γ_{N2}) is crucial for plasma modelling. The number of experimental studies devoted to the determination of $N_2(v)$ loss probabilities on different surfaces is rather limited [1-4]. Typically, the measurements of γ_{N2} were performed in a flowing afterglow zone and the state of the studied surfaces was prone to an uncontrolled evolution in the course of the experiments as pointed out by the authors [2-3]. The development of a simple and reliable technique for *in-situ* γ_{N2} determination was therefore the main motivation of the present study. A special emphasis was made on the elucidation of the effect of low pressure plasma exposure on the value of γ_{N2}.

In this work we use the idea [4] of titrating vibrationally excited N_2 by a small admixture of infrared (IR) active molecules - CO_2, N_2O or CO. Gas mixtures containing 0.05-1 % of 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 [5] dedicated to time resolved *in-situ* gas sensing. 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. Experiments were performed in a single pulse mode (no signal accumulation) in static (no gas flow) conditions; after every discharge pulse the gas mixture in the reactor was renewed. Before a series of measurements the reactor was pre-treated by a flowing discharge in argon, oxygen or nitrogen at a pressure of 26-50 Pa for 30 min.

Extensive data on the rates of vibrational relaxation in N_2-CO_2 system are available in the literature [6]. Therefore, modelling of the vibrational kinetics in pulsed DC discharge in N_2-CO_2 was performed. The model is zero dimensional and it incorporates excitation of vibrations by electronic impact (e-V), V-V and V-T exchange in the N_2 subsystem as well as the V-V´ exchange between N_2 and CO_2 and intra-molecular vibrational relaxation in CO_2 [7]. The relaxation probability γ_{N2} was the *only* adjustment parameter of the model. In the model, the dependence of γ_{N2} on the vibrational quantum number v of nitrogen was assumed to be linear $\gamma_{N2}(v) = \gamma_1 \cdot v$ where γ_1 is the quenching probability of $N_2(v=1)$. The value of γ_{N2} was found from the best agreement between the model and the experiment.

With laser absorption spectroscopy we actually measure 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 [7]. Figure 1 shows the time evolution of $(N_0 - \beta N_1)$ for different initial concentrations of CO_2 in a silica discharge tube. 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 the γ_{N2} determination by the fitting procedure was estimated to be 15%. It was found that the value of γ_{N2} increases with increasing concentration of the added CO_2, what indicates the possibility of the energy transfer between vibrationally excited gas phase nitrogen molecules and adsorbed CO_2 molecules. The value of the $N_2(v=1)$ relaxation probability on silica and Pyrex surfaces found by extrapolation to zero CO_2 admixture $\gamma_1=(1.1\pm0.15)\cdot10^{-3}$ is in good agreement with the literature data. In addition to the γ_{N2} measurements, time evolution of the vibrational temperature of N_2 (T_v) was determined from the measured depletion of $(N_0 - \beta N_1)$. At the end of a 5 ms discharge pulse the measured value of $T_v=3500K$ was found to be in good agreement with the modelling.
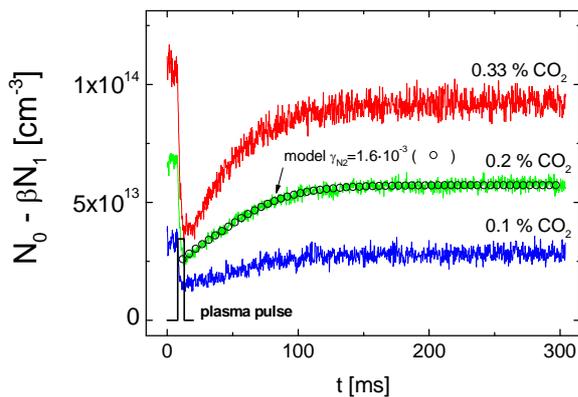

Fig. 1: Time evolution of $(N_0 - \beta N_1)$ after a I=50 mA, τ=5 ms pulse at p=133 Pa in the silica discharge tube. Different curves correspond to different initial concentrations of CO_2.
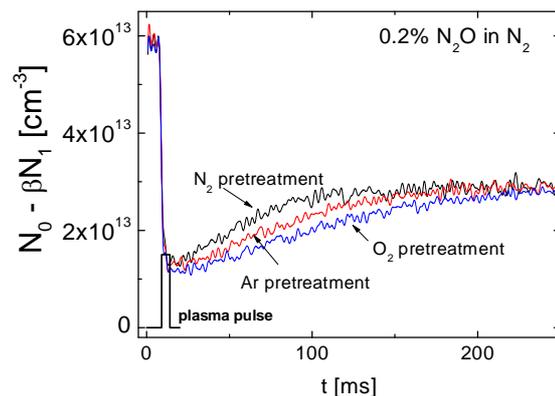

Fig. 2: Time evolution of $(N_0 - \beta N_1)$ after a I=50 mA, τ=5 ms pulse at p=133 Pa, 0.2% N_2O in N_2. Different curves correspond to different plasma pretreatments of the silica tube surface.

Figure 2 illustrates the influence of low pressure plasma pretreatment on the value of γ_{N2} on silica. In these experiments N_2O was used as a titrating molecule. The relaxation after N_2 plasma exposure is about two times more efficient than in the case of O_2 plasma pretreatment. Identical effects were observed when the mixtures of N_2 with CO or CO_2 were used. It should be noted that the observation of such effects was possible because short single plasma pulses were used for the excitation of the gas mixture and the whole relaxation kinetics in the post discharge was measured in a single pulse without data accumulation; therefore, the state of the surface after the pretreatment was not strongly modified.

Using the described technique surface quenching probabilities were determined for several materials: (i) sol-gel films of TiO_2 ($\gamma_1=(1.8\pm0.3)\cdot10^{-3}$) and (iii) Al_2O_3 ($\gamma_1=(1.5\pm0.2)\cdot10^{-3}$) deposited on the inner surface of a silica discharge tube and (iii) at anodized aluminum ($\gamma_1=(2.9\pm0.4)\cdot10^{-3}$). It was found that for catalytic materials the value γ_1 depends on the pretreatment of the surface and on the titrating molecule that is used. The work is in progress in order to better understand these new effects.

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