Surface vibrational relaxation of N\textsubscript{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 $\gamma_{N2}$ of vibrationally excited N\textsubscript{2} on different surfaces has been developed. A short DC discharge pulse was applied to a mixture containing 0.05-1\% of CO\textsubscript{2}, N\textsubscript{2}O or CO in N\textsubscript{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\textsubscript{2}-CO\textsubscript{2}. The value of $\gamma_{N2}$ was determined for SiO\textsubscript{2}, TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Pyrex and anodized aluminium.

In nitrogen containing plasmas, vibrationally excited N\textsubscript{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\textsubscript{2}(v) loss mechanism for pressures up to few tens of mbars. Therefore, the knowledge of the heterogeneous deactivation probability of N\textsubscript{2}(v) ($\gamma_{N2}$) is crucial for plasma modelling. The number of experimental studies devoted to the determination of N\textsubscript{2}(v) loss probabilities on different surfaces is rather limited [1-4]. Typically, the measurements of $\gamma_{N2}$ 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 $\gamma_{N2}$ 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 $\gamma_{N2}$.

In this work we use the idea [4] of titrating vibrationally excited N\textsubscript{2} by a small admixture of infrared (IR) active molecules - CO, N\textsubscript{2}O or CO. Gas mixtures containing 0.05-1\% of CO\textsubscript{2}, N\textsubscript{2}O, CO in N\textsubscript{2} were excited by a single DC discharge pulse (I=50 mA, $\tau$=1-10 ms) at a pressure of 133 Pa. The relaxation kinetics of CO\textsubscript{2} (N\textsubscript{2}O, 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\textsubscript{2} and CO\textsubscript{2} (N\textsubscript{2}O, CO), the excitation of titrating molecules reflects the degree of vibrational excitation of N\textsubscript{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\textsubscript{2}-CO\textsubscript{2} system are available in the literature [6]. Therefore, modelling of the vibrational kinetics in pulsed DC discharge in N\textsubscript{2}-CO\textsubscript{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\textsubscript{2} subsystem as well as the V-V' exchange between N\textsubscript{2} and CO\textsubscript{2} and intra-molecular vibrational relaxation in CO\textsubscript{2} [7]. The relaxation probability $\gamma_{N2}$ was the only adjustment parameter of the model. In the model, the dependence of $\gamma_{N2}$ on the vibrational quantum number $v$ of nitrogen was assumed to be linear $\gamma_{N2}(v)=\gamma_1 \cdot v$ where $\gamma_1$ is the quenching probability of N\textsubscript{2}(v=1). The value of $\gamma_{N2}$ 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\textsubscript{2}(00'0')]=N\textsubscript{0}) and the upper ([CO\textsubscript{2}(00'1')]=N\textsubscript{1}) vibrational levels [7]. Figure 1 shows the time evolution of $(N_0 - \beta N_1)$ for different initial concentrations of CO\textsubscript{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\textsubscript{2} upon the application of the discharge pulse. Vibrational relaxation takes place in the
afterglow, the difference between the CO₂ concentrations before the pulse and when the relaxation is finished is ascribed to the dissociation of CO₂ in the discharge. The result of the modeling for 0.2% CO₂ is shown on the same graph, the relative uncertainty of the γ₂N₂ determination by the fitting procedure was estimated to be 15%. It was found that the value of γ₂N₂ increases with increasing concentration of the added CO₂, what indicates the possibility of the energy transfer between vibrationally excited gas phase nitrogen molecules and adsorbed CO₂ molecules. The value of the N₂(ν=1) relaxation probability on silica and Pyrex surfaces found by extrapolation to zero CO₂ admixture γ₁=(1.1±0.15)·10⁻³ is in good agreement with the literature data. In addition to the γ₂N₂ measurements, time evolution of the vibrational temperature of N₂ (Tᵥ) was determined from the measured depletion of (N₀ − βN₁). At the end of a 5 ms discharge pulse the measured value of Tᵥ=3500K was found to be in good agreement with the modelling.

![Graph](image)

Fig. 1: Time evolution of (N₀ − βN₁) after a 1=50 mA, τ=5 ms pulse at p=133 Pa in the silica discharge tube. Different curves correspond to different initial concentrations of CO₂.

![Graph](image)

Fig. 2: Time evolution of (N₀ − βN₁) after a 1=50 mA, τ=5 ms pulse at p=133 Pa, 0.2% N₂O in N₂. 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 γ₂N₂ on silica. In these experiments N₂O was used as a titrating molecule. The relaxation after N₂ plasma exposure is about two times more efficient than in the case of O₂ plasma pretreatment. Identical effects were observed when the mixtures of N₂ with CO or CO₂ 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 TiO₂ (γ₁=(1.8±0.3)·10⁻³) and (iii) Al₂O₃ (γ₁=(1.5±0.2)·10⁻³) deposited on the inner surface of a silica discharge tube and (iii) at anodized aluminum (γ₁=(2.9±0.4)·10⁻³). It was found that for catalytic materials the value γ₁ 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.

References