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Measurement of collisional quenching rate of nitrogen states $N_2(C^3\Pi_u, \nu = 0)$ and $N_2^+(B^2\Sigma_g^+, \nu = 0)$

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Abstract

This paper presents an experimental investigation of the effect of the electric field strength on the collisional quenching rate of nitrogen states $N_2(C^3\Pi_u, \nu = 0)$ and $N_2^+(B^2\Sigma_g^+, \nu = 0)$ by nitrogen and oxygen molecules. In experiments, the pulses of non-self-sustained electrical discharge excite gas molecules. The range of reduced electric field strength is from 240 to 4000 Td at pressure range from 70 to 4300 Pa. The experiments show that the field strength has no effect on the quenching rate. The paper discusses the probable reasons for discrepancy of results obtained by different authors and proposes the preferable values for rate coefficients. These coefficients can be used for electric field determination in low temperature gas discharge plasmas via nitrogen emission spectrum, and are of interest to atmospheric air fluorescence investigations.

1. Introduction

The intensity ratio of molecular nitrogen spectral bands corresponding to $N_2^+(B^2\Sigma_g^+, \nu = 0) \rightarrow N_2^+(X^2\Sigma_g^+, \nu = 0)$ and $N_2(C^3\Pi_u, \nu = 0) \rightarrow N_2(B^3\Pi_g, \nu = 0)$ transitions, denoted below as $R_{391/337}$, is frequently used for electric field strength estimation in nitrogen containing gas discharge plasmas. Our recent papers (Paris *et al* 2004, 2005, 2006) present experimentally determined ratio $R_{391/337}$ as a function of reduced field strength E/n in air. Here E denotes the electric field strength and n the gas number density. At pressures above 10 kPa this ratio is independent of pressure and is solely a function of E/n . At lower pressures, this ratio depends on the gas density, in addition to the E/n dependence. This is caused by the differences both in values of the radiative lifetime and the collisional deactivation coefficients of the states $N_2(C)$ and $N_2^+(B)$. Based on this assumption, Paris *et al* (2005) proposed a reduction procedure for reduction of the measured intensity ratio to the standard conditions (pressure $p = 100$ kPa and absolute temperature $T = 273$ K). As a result, the ratio $R_{391/337}$ was obtained as a function of only one variable, E/n . The values of radiative lifetimes τ_0 and rate constants k for quenching of these states with N_2 and O_2 molecules must be known for performing the reduction procedure. However, there is a number of different from each other values of these constants available in the literature. Using different constants, different values for reduced ratio $R_{391/337}$ will be obtained.

An overview of lifetimes and de-excitation rate coefficients of the states $N_2(C)$ and $N_2^+(B)$ is given in papers (Dotchin *et al* 1973, Chen *et al* 1976, Erman 1993, Belikov *et al* 1995, Pancheshnyi *et al* 1998 and 2000, Kozlov *et al* 2001). We have found there up to twenty different from each other values for quantities under interest. Bar diagrams in Figures 1 and 2 compare the values obtained by different authors. Several of cited authors presented in their papers instead of the rate constant k some of related quantities like the quenching pressure, p_q , (the pressure where collisional de-excitation frequency is equal to $1/\tau_0$) or the quenching cross-

section, σ_q . We derived k from these quantities using next formulae: $k = \frac{k_B T}{p_q \tau_0} = \sigma_q \langle v \rangle = 4\sigma_q \sqrt{\frac{k_B T}{\pi m}}$,

where k_B is the Boltzmann constant, $\langle v \rangle$ is the mean relative velocity of the colliding particles and m is the mass of quenching molecule, in the case of quenching by molecules of parent gas. The measurement uncertainties $u(\tau)$ or $u(k)$ are also denoted in the Figures 1 and 2 if the uncertainty (or measurement error) information is available in cited papers.

In most of measurements of quenching rate described in cited papers, gas is excited by stationary or pulsed beam of high energy electrons, protons or x-rays. The gas resides under zero or low electric field ($E/n < 100$ Td). The field strength can be estimated also low in experiments where laser-induced fluorescence was used for excited state lifetime measurements (Jolly and Plain 1983, Plain and Jolly 1984, Dilecce *et al* 2007). A different excitation method is described by Pancheshnyi *et al* (1998 and 2000) where the high voltage pulses with E/n up to some thousand Td were used. However, also in these papers the value of E/n during fluorescence decay was estimated being low, below 600 Td. At the same time in a lot of applications

e.g. in gas discharge investigation, the radiation is emitted under high electric field conditions, where ion-neutral collisions could be affected by the electric field. The effect of electric field on ion-neutral collisions is present in the nitrogen ion conversion reaction $N_2^+ + N_2 + M \rightarrow N_4^+ + M$, rate constant of which is a function of E/n (McKnight *et al* 1967, Moseley *et al* 1969). If the conversion reaction participates in some way in the quenching process as proposed by Pancheshnyi (2006) then the dependence of quenching rate of $N_2^+(B)$ state on E/n should appear.

An expectation for the possible effect of the electric field on the quenching rate of excited ions comes also from the dependence of quenching rate on the temperature, reported by Belikov *et al* (1995). At higher temperature the kinetic energy of colliding particles (gas molecules and ions) is higher. Kinetic energy of ions becomes higher also under high electric field. Thus, we can expect the dependence of quenching rate of nitrogen ion on the E/n .

We were unable to find in literature any remark about the dependence of depopulation rate of excited state of nitrogen ion on the electric field strength, neither any paper regarding the study of this problem. Therefore we undertook the experiment to measure this dependence. In this paper we present the results of our measurements and discuss possible reasons for discrepancy between results obtained by different authors.

2. Experimental set-up and measuring conditions

Figure 3 presents the sketch of the experimental set-up.

The gas was excited by pulses of non-self-sustained electrical discharge between parallel plate electrodes in homogeneous electric field. The anode was made of brass. A thin semitransparent aluminium coating evaporated on a quartz plate side facing to the anode served as a cathode. The distance, d , between the electrodes was adjustable with an accuracy of 0.01 mm. The electrodes were installed in a vacuum chamber (volume about 80 cm³) equipped with quartz windows. The gas, N₂ or mixture of N₂ and O₂, (both gases supplied by AGA, with purity 99.95%) was directed to the chamber via flow controllers. The gas flow rate through the chamber was maintained constant in the region 17 - 170 ml/s during all the measurements. A vacuum gauge, equipped with piezoelectric and micro Pirani transducer, measured the pressure in the chamber. The accuracy of the transducer was 1% at pressures above 1.3 kPa and 10% at pressures below 1.3 kPa. The valves helped to obtain the desired value of the pressure. The gas temperature we estimated to be approximately equal to the room temperature (difference less than 1 K) which was in the range 294 - 303 K.

The anode was grounded via resistor $R_2 = 50 \Omega$. The signal from R_2 was used to monitor the discharge current. A high voltage (below the breakdown) was applied to the cathode. The UV ($\lambda = 248$ nm) excimer laser PSX-100 flash with 4 ns half-width liberated the electrons from the cathode. The repetition rate of laser flashes was up to 20 pulses per second and the energy was 3 mJ per pulse. The scatter dispersed the laser beam ensuring homogeneous illumination of the cathode. The diameter of the illuminated area of the cathode was 18 mm.

An achromatic quartz lens of 75 mm in focal length focused the radiation from the discharge on the input slit of a monochromator. The linear dispersion of the monochromator was 1.3 nm mm⁻¹. The slits width was 0.6 mm and the monochromator was adjusted to signal maximum (337.1 nm for $N_2(C^3\Pi_u, \nu = 0)$ state investigation, and to 391.4 nm for $N_2^+(B^2\Sigma_g^+, \nu = 0)$ state investigation). The tail of spectral band corresponding to $N_2(C^3\Pi_u, \nu = 2) \rightarrow N_2(B^3\Pi_g, \nu = 5)$ transition overlaps the wavelength region chosen for $N_2^+(B^2\Sigma_g^+, \nu = 0)$ state investigation. According to our calculations, in the selected wavelength region the contribution of C(2→5) band to the B(0→0) emission is 15% at $E/n=240$ Td and $p = 4300$ Pa, and much less at higher values of E/n and lower pressures because the intensity ratio of spectral bands corresponding to $N_2^+(B^2\Sigma_g^+, \nu = 0) \rightarrow N_2^+(X^2\Sigma_g^+, \nu = 0)$ and $N_2(C^3\Pi_u, \nu = 2) \rightarrow N_2(B^3\Pi_g, \nu = 5)$ transitions increases rapidly with E/n (Paris *et al* 2005). This overlapping is not taken into account and causes systematic error of lifetime measurements at low values of E/n . This error has about the same percentage as the overlapping.

A photomultiplier PM with rise time of about 0.5 ns (PMH-100-4, Hamamatsu) in the photon-counting mode detected the radiation of the discharge. Digital oscilloscope Tektronix TDS 540B (time resolution 0.5 ns) recorded the PM pulses. A high speed photodiode was used to trigger the oscilloscope. The jitter between the laser pulse and plasma emission was less than 0.5 ns. The oscilloscope performed averaging of about 200 - 400 pulses. PC stored this averaged signal synchronously with the current pulse (voltage pulse from resistor

R₂). The high speed photodiode recorded the temporal profile of the laser flash before and after the spectral measurements.

The applied to the cathode voltage and the number of initial electrons liberated from the cathode by the laser flash control the intensity of the non-self-sustained discharge (the amplitude of the discharge current pulse). Changing the distance between the laser beam scatter and the cathode enabled us to change the number of initial electrons. We have chosen the number of initial electrons and the inter-electrode voltage such that the space charge field, E_ρ , of ions generated by the discharge between electrodes always stayed much lower than the Laplacian field, $E = \frac{U}{d}$, to avoid the electric field distortion by the discharge. Our earlier paper (Paris *et al* 2004) describes the estimation of the space charge field. In experiments, the discharge current value was adjusted to satisfy the condition $\frac{E_\rho}{E} \leq 1\%$. Typical current pulse amplitudes were in the range of 1 - 4 mA.

Changing both the distance, d , between electrodes and the applied voltage, U , enabled us to achieve different reduced electric field strength values, E/n . In our discharge chamber they remained in the range of 240 - 4000 Td. To distinguish between the two effects: the dependence of the quenching rate on the reduced electric field strength and on the pressure, respectively, we recorded the experimental points at a given pressure for different electrode distances, d , and therefore for different electric field strengths, E . Though the distance, d , could be changed 16 times (5.6 mm/0.35 mm), the corresponding change in the reduced electric field strength, E/n , was about 2 to 5 times at certain pressure, depending on the gas pressure. The uncertainty in E/n was estimated to be between 3% - 10% depending on pressure, p , and inter-electrode distance, d .

One effect, that needed to be taken into account, was that at lower pressures and shorter inter-electrode distances (high E/n , high ion drift speed) the N_2^+ ($B^2\Sigma_g^+$, $\nu = 0$) state was quenched by ion-cathode collision in addition to ion-molecule collisions, typically when $p \times d < 0.4$ Pa·m ($E/n > 3000$ Td). This was because the ion drift speed was high enough for nitrogen ions to reach the cathode before quenching by the gas molecules. The number of ions quenched by the cathode was calculated using ordinary discharge model (Wen 1989), though it was only necessary for a small minority of experimental points. The neutral N_2 ($C^3\Pi_u$, $\nu = 0$) diffusion loss was very low compared to loss via collisional quenching or irradiation.

4. Data processing

According to the model of quenching via two body collisions, the following differential equation describes the number density of excited particles as a function of time:

$$\frac{dN_+^*(t)}{dt} = -\frac{1}{\tau} N_+^*(t) + \alpha I_e(t), \quad (1)$$

where

$$\frac{1}{\tau} = k_{N_2} n_{N_2} n + k_{O_2} n_{O_2} n + \frac{1}{\tau_0}. \quad (2)$$

Here N_+^* is the number of excited particles, $I_e(t)$ is the electron component of the discharge current and α is the coefficient of proportionality. k_{N_2} is the quenching constant of certain state with N_2 molecules, k_{O_2} is that for quenching with O_2 molecules, n_{N_2} and n_{O_2} are relative number densities of nitrogen and oxygen molecules, respectively. The solution of equation (1) has a form

$$N_+^*(t) = \alpha e^{-\frac{t}{\tau}} \int_0^t I_e(t') e^{\frac{t'}{\tau}} dt'. \quad (3)$$

We chose values for α and τ such that the curve according to the equation (3) gives the best match with the recorded PM signal. We calculated the electron component of a current pulse, proceeding from the laser pulse temporal profile, as a convolution of two signals:

$$I_e(t) \propto i_e(t) * q(t), \quad (4)$$

where $q(t)$ is the laser intensity as a function of time, and

$$i_e(t) = \frac{e \times v_e}{d} \int_0^d \rho_e(x,t) dx \quad (5)$$

is the current pulse caused by single electron starting from the cathode.

Here $\rho_e(x,t)$ is the number density of electrons between cathode and anode, e is the elementary charge and v_e is the drift velocity of electrons. To find $\rho_e(x,t)$ in nitrogen – oxygen mixtures, we took into account, in addition to ionization, the attachment of electrons to oxygen molecules resulting in formation of unstable negative ions, detachment of electrons from unstable negative ions, and conversion of unstable negative ions to stable ones. Number density of electrons, positive and negative ions as a function of time, t , and distance, x , from the cathode was found solving the set of partial differential equations with appropriate boundary conditions:

$$\begin{aligned} \frac{\partial \rho_e(x,t)}{\partial t} + v_e \frac{\partial \rho_e(x,t)}{\partial x} &= (\alpha - \eta) v_e \rho_e(x,t) + \delta v_e \rho_{nu}(x,t) \\ \frac{\partial \rho_p(x,t)}{\partial t} - v_p \frac{\partial \rho_p(x,t)}{\partial x} &= \alpha v_e \rho_e(x,t) \\ \frac{\partial \rho_{nu}(x,t)}{\partial t} + v_{nu} \frac{\partial \rho_{nu}(x,t)}{\partial x} &= \eta v_e \rho_e(x,t) - (\delta + \beta) v_e \rho_{nu}(x,t) \\ \frac{\partial \rho_{ns}(x,t)}{\partial t} + v_{ns} \frac{\partial \rho_{ns}(x,t)}{\partial x} &= \beta v_e \rho_{nu}(x,t) \end{aligned} \quad (6)$$

Here $\rho_p(x,t)$ is the number density of positive ions, $\rho_{nu}(x,t)$ and $\rho_{ns}(x,t)$ are that of unstable and stable negative ions, respectively. v_p , v_{nu} and v_{ns} are drift velocities of positive, unstable-, and stable negative ions. α , η , β and δ are accordingly ionization, attachment, conversion and detachment coefficients.

We solved the set (6) for each condition using formulae proposed by Wen (1989). We evaluated the values of ionization- and attachment coefficients and electron mobility using software BOLSIG+ (2005). We took the coefficients for detachment and conversion reactions and ions mobilities from paper (Badaloni and Gallimberti 1972). We calculated also the total current. The coincidence of the calculated current pulses with measured pulses proved the accuracy of the current pulse calculations. It turned out that the difference between the electron component and the measured current was typically less than 5%.

One more problem that needed to be addressed was the secondary emission from the cathode due to ion bombardment. This phenomenon interfered typically at field strengths higher than 2000 Td at lower values of $n \times d$ where time of flight of positive ions to the cathode became comparable to the time of radiation of excited particles. As the secondary emission was difficult to take into account, we used for data processing only the recorded signals starting period where the contribution of the secondary emission was negligible. This resulted in higher measurement uncertainty for those points.

The procedure for estimation of quenching time constant τ was therefore the following:

1. measure the shape of the laser pulse $q(t)$;
2. calculate the electron component of the discharge current $I_e(t)$ by calculating $i_e(t)$ first;
3. evaluate α and τ and compare the measured PM pulse to the curve $N_+^*(t)$ calculated from equation (3).

Figure 4 presents the examples of the above-mentioned curves. In Figure 4a, the PM signal is long compared to the current pulse. In this case it is possible to find τ also directly as time constant of the exponential decay of the PM signal. In Figure 4b, the PM signal duration is close to that of the current pulse, and we need the deconvolution to get the correct value of τ .

5. Results and discussion

Figures 5-7 present typical Stern-Volmer dependencies. As one can see in the figures, points corresponding to certain gas composition lay on a straight line in accordance with the model of collisional quenching which accounts only two body collisions. The intercept of the straight line gives natural lifetime τ_0 of the state under investigation, and the slope of the line – the collisional quenching rate constant k . For the gas mixture

$$k = k_{\text{N}_2}n_{\text{N}_2} + k_{\text{O}_2}n_{\text{O}_2}. \quad (7)$$

We calculated the quenching rate constants for oxygen molecules using Equation (7). Points at the same pressure but different distance between electrodes (0.7 and 2.8 mm in Figures 5 - 6) correspond to values of E/n differing about 2 - 3 times. Points obtained at different E/n lay on the same line – there is no evident dependence of quenching rate on the electric field strength neither in the case of $\text{N}_2(\text{C})$ state nor in the case of $\text{N}_2^+(\text{B})$ state. The deviation of $k_{\text{N}_2}(\text{B}^2\Sigma_g^+, \nu=0)$ from average due to the change of E/n stay in the limits $0.12 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ that is much less than our measurement uncertainty. The same holds for $k_{\text{O}_2}(\text{B}^2\Sigma_g^+, \nu=0)$: the changes with E/n were less than our measurement uncertainty and had occasional direction. Values evaluated from our measurements are presented in the Table 1 and in Figures 1 – 2.

As it is seen in the Figure 1, lifetimes for the state $\text{N}_2^+(\text{B})$, obtained by different authors, are very consistent if we exclude the results obtained before the year 1968, and result of Nagano *et al* (2003) as an exception. Average of these selected results is $\tau_0(\text{B}^2\Sigma_g^+, \nu=0) = 62.2 \text{ ns}$. Our result for $\tau_0(\text{B}^2\Sigma_g^+, \nu=0) = 62 \pm 3 \text{ ns}$ coincides with average of selection with high accuracy. Lifetimes of the state $\text{N}_2(\text{C})$ are less consistent. The results scatter much more than the individually quoted errors. The weighted average of many observers' values, derived from measurements prior to year 1977 is presented by Lofthuis and Krupenie (1977) as $\tau_0(\text{C}^3\Pi_u, \nu=0) = 36.6 \pm 0.5 \text{ ns}$. Later Erman (1993) recommends $\tau_0(\text{C}^3\Pi_u, \nu=0) = 37.4 \pm 1 \text{ ns}$. Our result for $\tau_0(\text{C}^3\Pi_u, \nu=0)$ is higher than average of previous results, however, it coincides with many of earlier results (Simon *et al* 1994, Wuerker *et al* 1988, Carr and Dondes 1977, Chen *et al* 1976) within the limits of measurement uncertainty.

The dispersion of the quenching rate constants, obtained by different authors, for the state $\text{N}_2(\text{C})$ is about the same as dispersion of lifetimes. The rapid increase of quenching rate up to some times at low pressures ($p < 50 \text{ mTorr}$) is mentioned by Erman (2001), and Dilecce *et al* (2007). The average value $0.11 \times 10^{-10} \text{ cm}^3/\text{s}$ is quoted in a number of high pressure measurements (see for example (Pancheshnyi *et al* 2000 and references given therein). Our result $k_{\text{N}_2}(\text{C}^3\Pi_u, \nu=0) = 0.132 \pm 0.005$ coincides with those obtained at pressure range close to ours (Pancheshnyi *et al* 2000, Dilecce *et al* 2007, Morozov *et al* 2008). For the average quenching rate of the same state with O_2 we will get $k_{\text{O}_2}(\text{C}^3\Pi_u, \nu=0) = 2.8 \times 10^{-10} \text{ cm}^3/\text{s}$ if the lowest (Anton 1966) and the highest (Asinovskii 1979) are excluded. This average of selection is close to overall average $2.7 \times 10^{-10} \text{ cm}^3/\text{s}$ and to our result $2.9 \times 10^{-10} \text{ cm}^3/\text{s}$ as well. Almost all results coincide in the limits of measurement uncertainties given by the authors. The coincidence of our results with those presented in literature confirms that our method of measurements is appropriate for evaluation of quenching rate and lifetimes of nitrogen states.

In the case of the state $\text{N}_2^+(\text{B})$ the dispersion of the quenching rate values is the most prominent. The maximum and minimum values of $k_{\text{N}_2}(\text{B}^2\Sigma_g^+, \nu=0)$ differ more than 4 times, whereas the measurement uncertainties stay near 10% in most of cases. The discrepancy between values given by different authors exceeds highly the measurement uncertainty.

Table 1. Lifetimes and quenching rate constants of nitrogen states.

State	$\text{N}_2^+(\text{B}^2\Sigma_g^+, \nu=0)$			$\text{N}_2(\text{C}^3\Pi_u, \nu=0)$			
	quantity	$\tau_0, \text{ ns}$	$k_{\text{N}_2}, \text{ cm}^3 \text{ s}^{-1} \cdot 10^{-10}$	$\tau_0, \text{ ns}$	$k_{\text{N}_2}, \text{ cm}^3 \text{ s}^{-1} \cdot 10^{-10}$	$k_{\text{O}_2}, \text{ cm}^3 \text{ s}^{-1} \cdot 10^{-10}$	
Average of all results in Figures 1 – 2		59.9	4.6	6.8	39.3	0.115	2.7
Present study		62 ± 3	3.0 ± 0.4	8 ± 3	41.9 ± 1.7	0.132 ± 0.005	2.9 ± 0.1

Our results for $k_{\text{N}_2}(\text{B}^2\Sigma_g^+, \nu=0)$ coincide in the limits of measurement uncertainties with results of Lillicrap (1973) and Chen *et al* (1976). Discrepancy with results of other authors is higher than measurement uncertainty. For $k_{\text{O}_2}(\text{B}^2\Sigma_g^+, \nu=0)$ the coincidence of our result with results of other authors is better but only due to higher measurement uncertainty.

The great difference in results obtained by the different authors is probably caused by difference in experimental conditions and measurement methods. Measurements in wide region of pressure give complicated pressure dependence instead of the linear one in Stern-Volmer plots for the $N_2^+(B)$ state (Lillicrap 1973, Nagano *et al* 2003, Mitchell 1970) as well as for $N_2(C)$ state (Erman 1993, 2001, Pancheshnyi *et al* 2000). Pancheshnyi's opinion is that the most likely reason for the acceleration of depopulation at lower pressures in experiments with high voltage pulse discharge is an increase of electron concentration and the contribution of super-elastic collisions in the process of collisional deactivation. It was shown by Pancheshnyi *et al* (1999) that relaxation of the electron energy distribution function in the energy range associated with inelastic processes ($e > 10$ eV) proceeds for a time comparable with the time of radiative depopulation of investigated levels.

By our opinion the above explanation is applicable also for the results of experiments with excitation by particles of high energy. High energy particles used for gas excitation produce a lot of secondary electrons what are the main agents of excitation of states under interest. In the absence of electric field these secondary electrons stay in the region where gas fluorescence is registered. We estimated the electron energy relaxation time τ_E in nitrogen gas using data obtained by Kanzari *et al* (1998). For $n = 10^{16}$ cm⁻³ (40 Pa at 293 K) we got τ_E about 10 ns in electron energy range 10 – 100 eV with tendency to grow at higher energies. Several nanoseconds for τ_E at pressure of several Torr is also proposed by Pancheshnyi *et al* (1999) referring to Slinker *et al* (1990). Presence of high energy electrons due to long electron energy relaxation time may, in principle, affect the fluorescence decay time.

In addition to the electrons, excited N_2 molecules could produce intensive quenching effects on $N_2^+(B^2\Sigma_g^+)$ levels in an electrical discharge, as proposed by Jolly and Plain (1983) and Plain and Jolly (1984) to explain the high value of $k_{N_2}(B^2\Sigma_g^+, \nu = 0)$ they obtained using LIF (Laser Induced Fluorescence) method.

In the case of the pulsed non-self-sustained discharge, what we used for gas excitation, there are no electrons in the discharge gap during the decay period of excited states. Electrons are removed by the electric field. During the pause between laser flashes the gas flow removes also probable long lived excited molecules whose quenching ability may be different from that of molecules in the ground state. Gas flow removes also products of reactions in N_2 - O_2 gas mixture that can accumulate in the case of stagnant medium. Density of molecules in excited state is low in dark discharge so that interaction between excited particles can be excluded. Therefore we are of the opinion that our method of measurement gives the accurate value of quenching rate by molecules in the ground state. However, the excitation mechanism of our method is not selective, meaning that the discharge pulse populates also the higher vibrational levels. The cascading from those higher levels, in principle, can influence the lifetime measurements. To clarify the role of cascading, another experiment has to be made. Despite the last circumstances, our values for rate coefficients can be used for electric field determination in low temperature gas discharge plasmas via nitrogen emission spectrum in pressure range 70 - 4300 Pa.

6. Conclusions

A new method for quenching rate measurements is implemented. The characteristic and novel detail of the method is that the gas is excited by pulses of non self-sustained discharge and electrons are removed by the DC field from the excited gas. Thus the participation of electrons in collisional processes during the de-excitation period is excluded. For the first time the dependence of collisional quenching rate coefficients of nitrogen molecular ion on the electric field strength was investigated in the region of E/n up to 4000 Td. The collisional quenching rate was independent of the reduced electric field strength. The linear dependence of $1/\tau$ on pressure indicates the two body nature of the quenching reaction in investigated pressure range (0.07 – 4.3) kPa.

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Figure captions

Figure 1. Radiative lifetimes, proposed by different authors: a) $N_2^+(B^2\Sigma_g^+, \nu = 0)$ state, b) $N_2(C^3\Pi_u, \nu = 0)$ state. The red line denotes the overall average μ and σ denotes the sample standard deviation.

Figure 2. Quenching rate coefficients, proposed by different authors: a) $N_2^+(B^2\Sigma_g^+, \nu = 0)$ state, quenching by N_2 molecules; b) $N_2(C^3\Pi_u, \nu = 0)$ state, quenching by N_2 molecules; c) $N_2^+(B^2\Sigma_g^+, \nu = 0)$ state, quenching by O_2 molecules; d) $N_2(C^3\Pi_u, \nu = 0)$ state, quenching by O_2 molecules. The red line denotes the overall average μ and σ denotes the sample standard deviation.

Figure 3. Sketch of the experimental setup.

Figure 4. Examples of recorded and calculated pulses: a) $N_2(C^3\Pi_u, \nu=0)$ state, PM pulse calculated with $\tau = 39\text{ns}$, PM pulse recorded at $d = 0.70\text{ mm}$, $p = 0.8\text{ kPa}$, $E/n = 1779\text{ Td}$, $n_{N_2} = 100\%$, $n_{O_2} = 0\%$; b) $N_2^+(B^2\Sigma_g^+, \nu = 0)$ state, PM pulse calculated with $\tau = 3.8\text{ns}$, PM pulse recorded at $d = 0.70\text{ mm}$, $p = 3.2\text{ kPa}$, $E/n = 614\text{ Td}$, $n_{N_2} = 100\%$, $n_{O_2} = 0\%$.

Figure 5. Typical Stern-Volmer dependencies for $N_2(C^3\Pi_u, \nu = 0)$ state.

Figure 6. Typical Stern-Volmer dependencies for $N_2^+(B^2\Sigma_g^+, \nu = 0)$ state.

Figure 7. Experimental points registered at different E/n values. $N_2^+(B^2\Sigma_g^+, \nu = 0)$ state, $n_{O_2} = 0\%$.

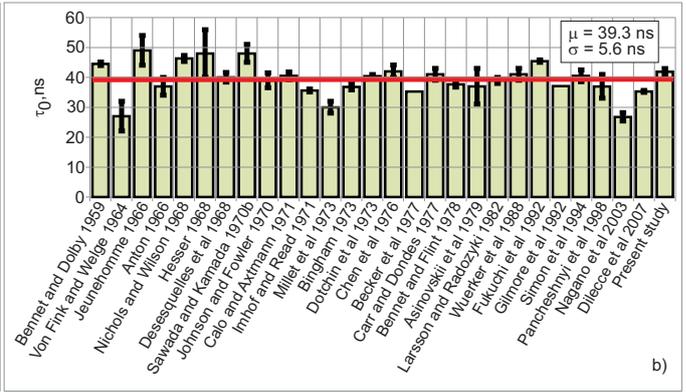
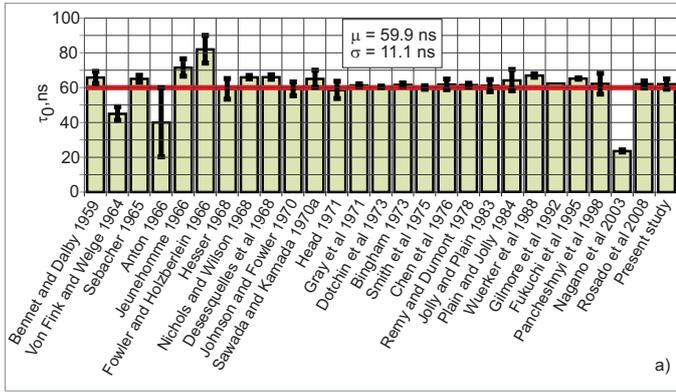


Figure 1 (Figure1.eps)

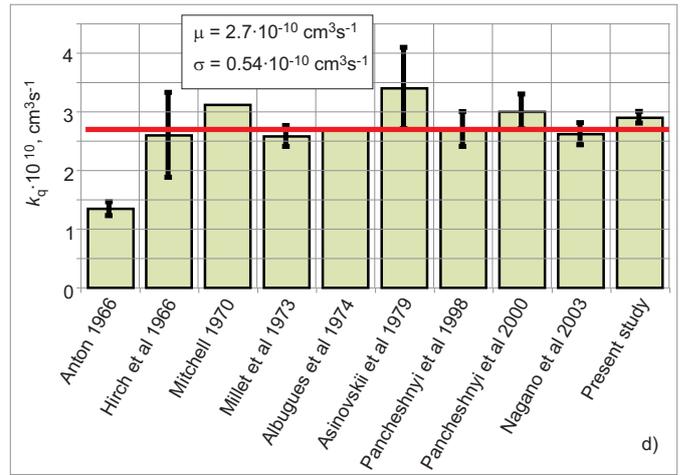
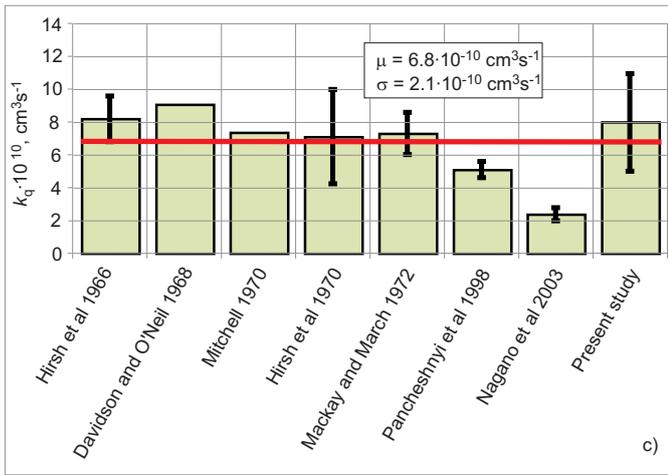
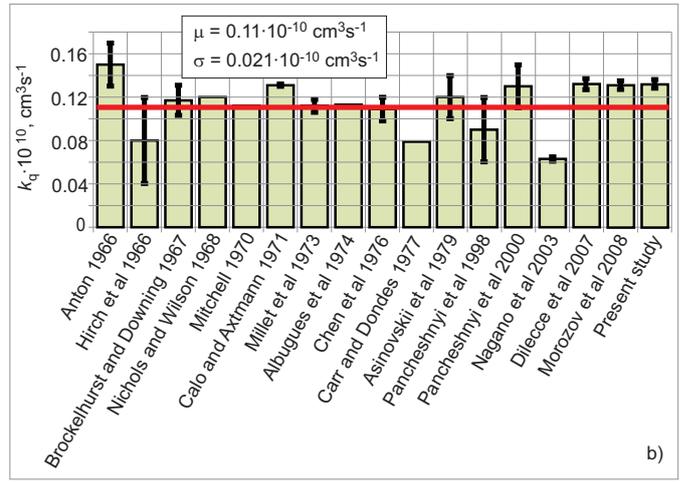
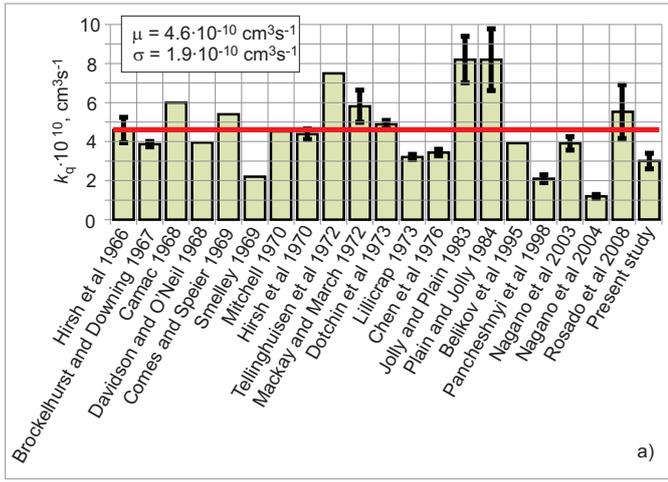


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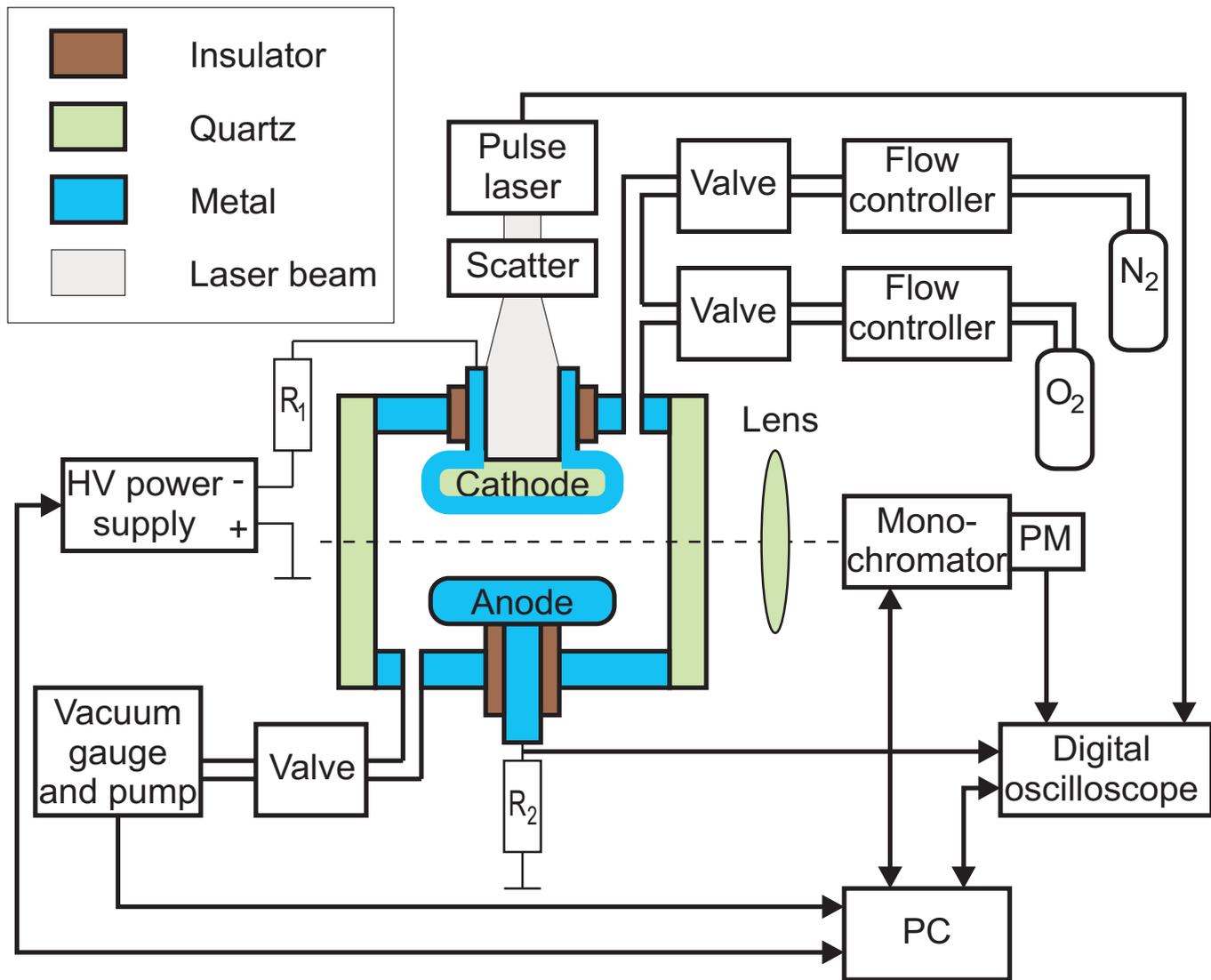


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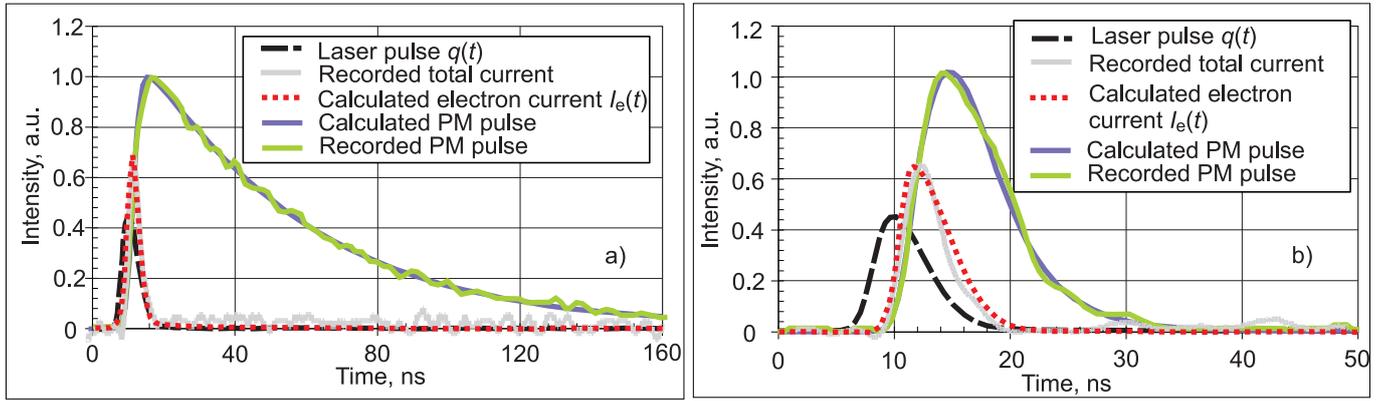


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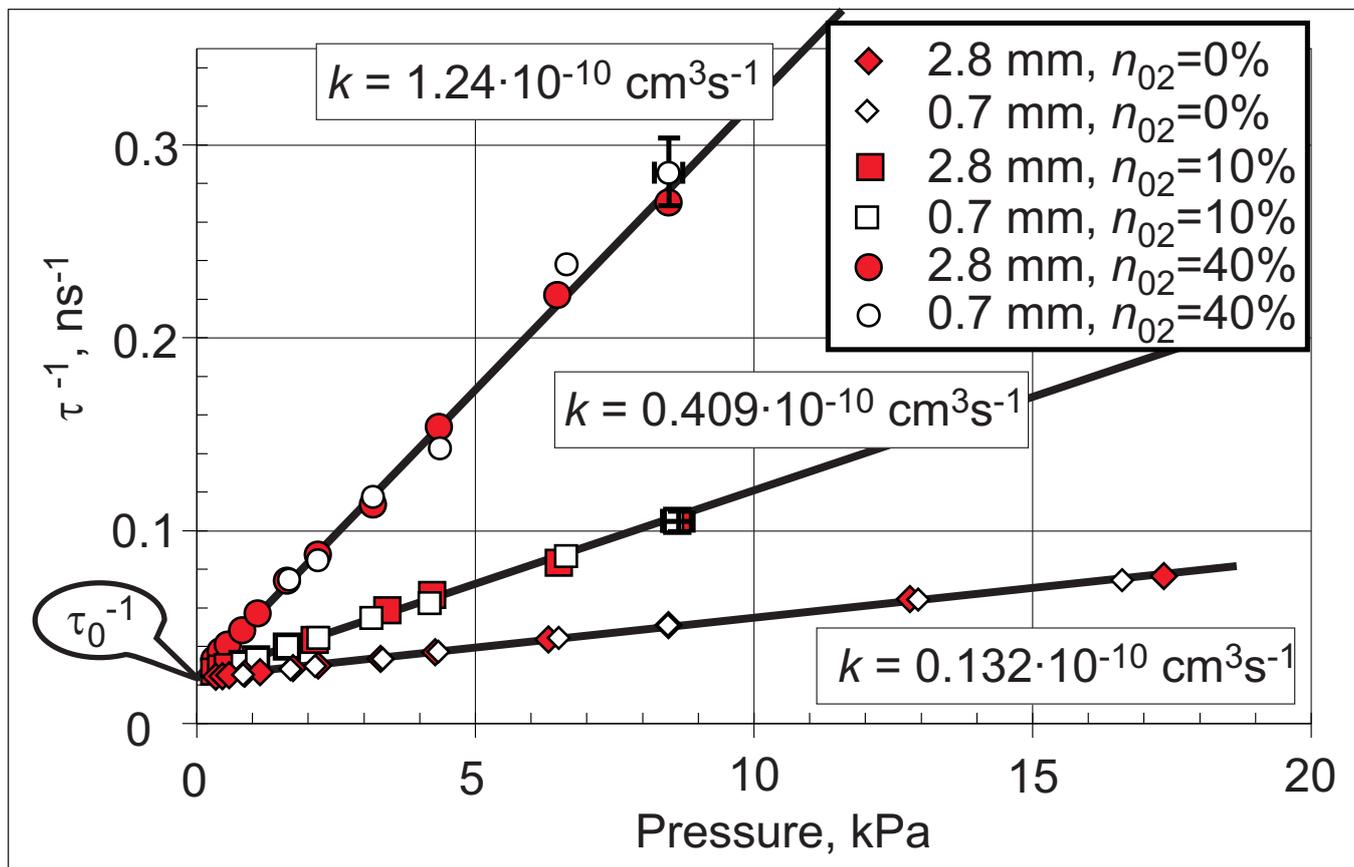


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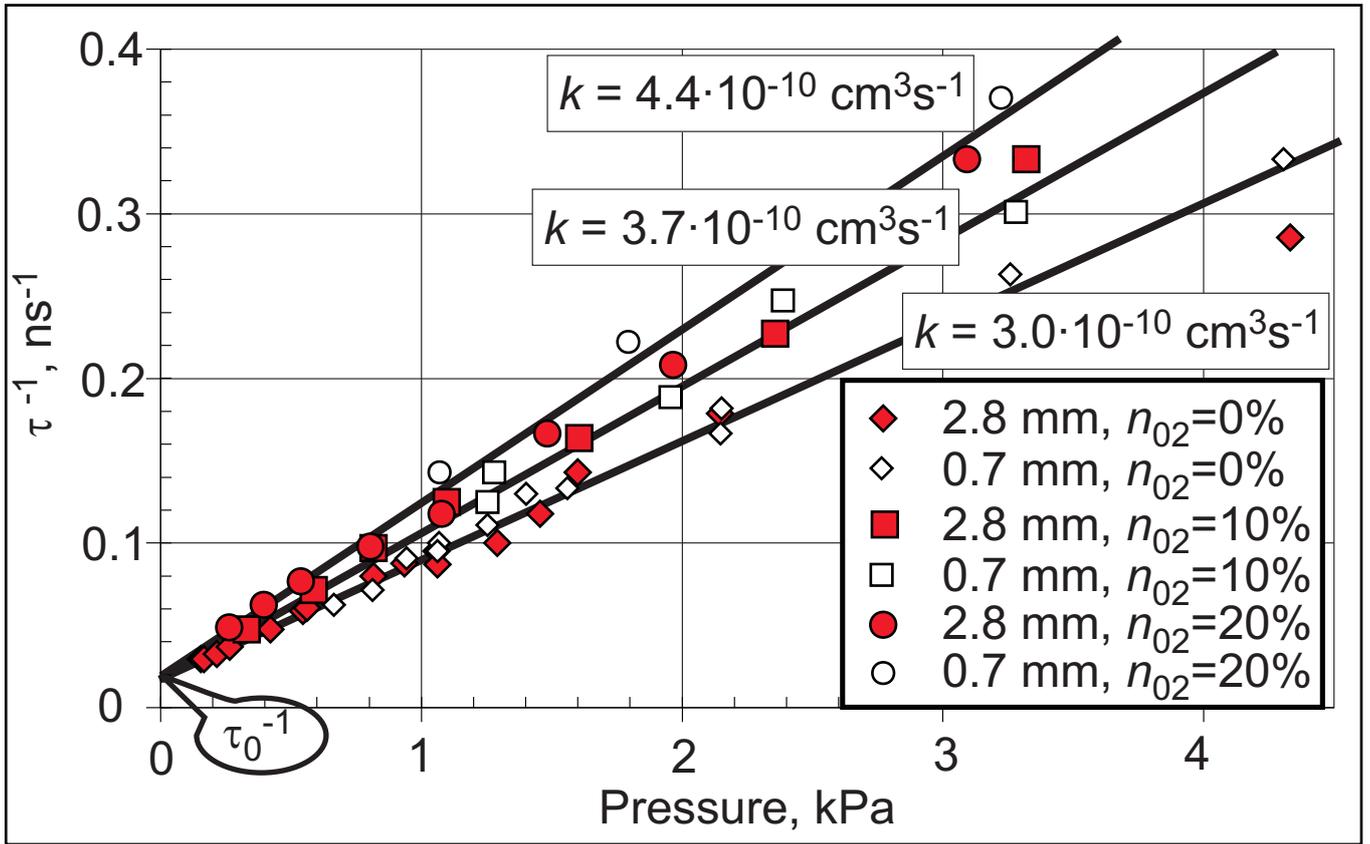


Figure 6 (Figure6.eps)

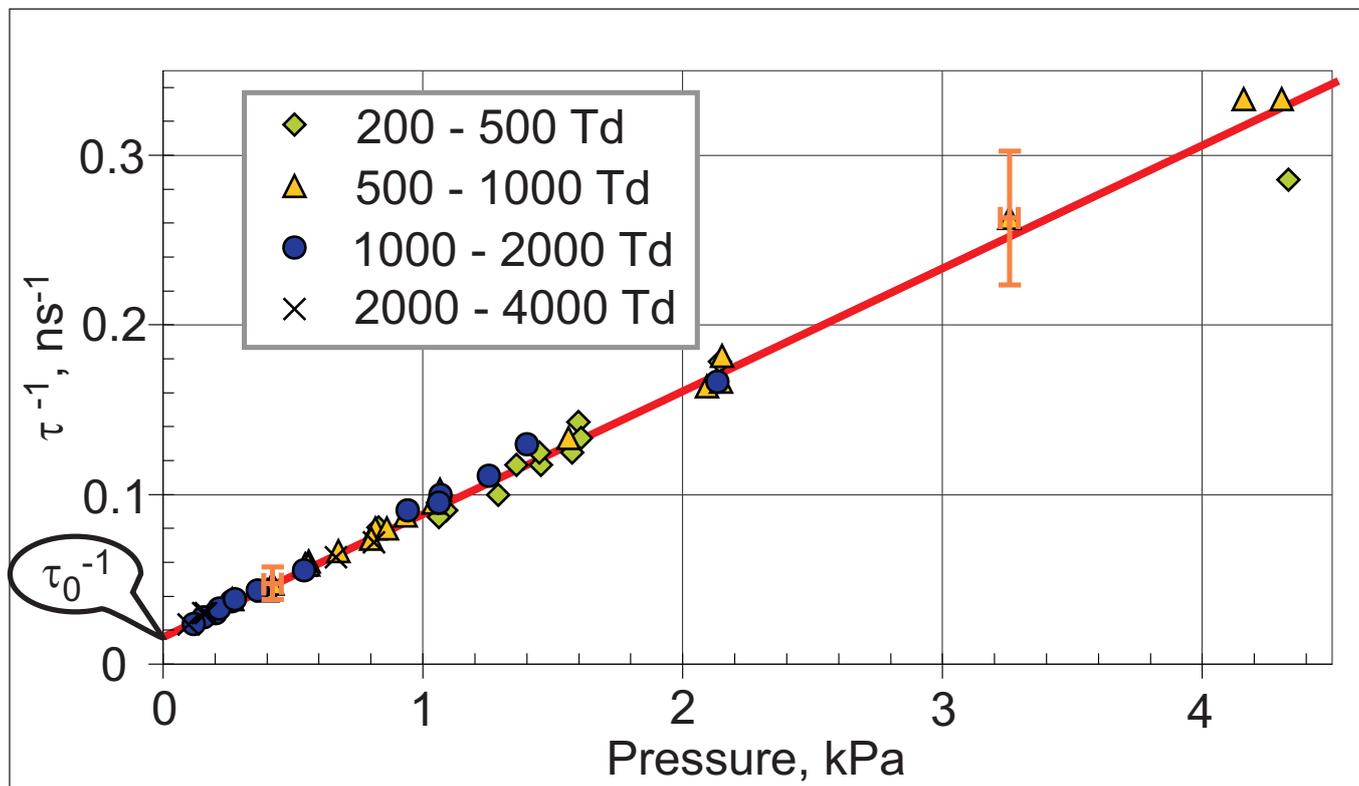


Figure 7 (Figure7.eps)