DETERMINATION OF QUENCHING COEFFICIENTS BY TIME RESOLVED EMISSION SPECTROSCOPY

T. Gans, V. Schulz-von der Gathen, and H. F. Döbele

Universität Essen, Institut für Laser- und Plasmaphysik, Universitätsstr. 5, 45117 Essen, Germany
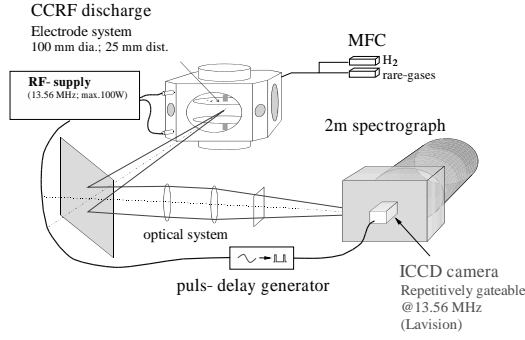
1   Introduction

In gas discharges at elevated pressure radiation-less collisional de-excitation (quenching) has a strong influence on the population of excited states. The knowledge of quenching coefficients is therefore important for discharge simulations taking into account excited states. The knowledge of quenching coefficients is also essential for the correct analysis of the experimental data for plasma diagnostics based on optical emission spectroscopy (OES) [1, 2] and laser induced fluorescence spectroscopy (LIF) with one or two photon (TALIF) excitation [3], since the spontaneous emission intensities indicating the population of the excited states are affected by quenching. Quenching coefficients of noble gases, e.g., are of particular interest, because these are finding widespread application as tracer gases in molecular discharges.

Quenching coefficients are usually determined from measurements of the effective lifetime of excited states. The effective lifetime of excited states can be obtained from the fluorescence decay after a pulsed excitation. The pulsed excitation can be performed by laser radiation. The disadvantages of laser excitation are limitations by optical selection rules and the problem to overcome the energy gap from the ground state to the excited states. For noble gases such as xenon [4], krypton [4] and argon [5] it is possible to cover the energy gap with two photon excitation in the UV or VUV, but for neon and helium the energy gaps are too large for a direct laser excitation. Excitation from metastable levels to higher levels by laser radiation represents a possibility to yield information on self-quenching coefficients in discharges, however. Since the population density of noble gas metastables is very low in the presence of molecules in discharges, the determination of quenching coefficients by laser excitation for neon and helium does not work with molecules (e.g. hydrogen).
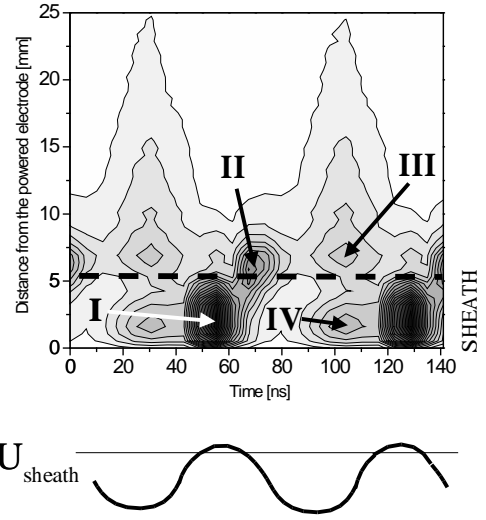
Capacitively coupled RF discharges (CCRF discharges) at 13.56 MHz in hydrogen exhibit a field reversal phase of about 10 ns during which an intense electron current provides collisional excitation within the sheath region [6, 7]. After this strongly dominant short pulsed electron impact excitation, it is possible to determine quenching coefficients from the lifetime of the fluorescence at various pressures by time resolved OES even for high energy levels and without any restrictions of optical selection rules. This novel technique allows the measurement of quenching coefficients for atomic and molecular emission lines of hydrogen itself, as well as for emission lines of small admixtures (e.g. noble gases) to the hydrogen discharge, since with a fast gate-able ICCD camera operating at 13.56 MHz it is possible to measure even faint emission lines temporally resolved [8].

2   Experiment

The measurements are performed in an asymmetric (one electrode grounded) CCRF discharge at 13.56 MHz in hydrogen with small admixtures of noble gases. The setup is described in detail elsewhere [8]. The flat cooled stainless steel electrodes, 100 mm in diameter, are 25 mm apart. The gas pressure ranges between 20 Pa and 400 Pa at an RF power of 100 W. The discharge axis is imaged onto the entrance slit of a 2m-spectrograph, see figure 1 (a). A fast gateable ICCD-camera samples spectral intervals of about 4.5 nm with a spectral resolution of 0.34 nm/mm and a spatial resolution of about 0.5 mm. Time resolved measurements are possible by locking the gate to a fixed phase position within the RF cycle. The intensities measured over the gate time of 3 ns can be integrated over many RF cycles for this fixed phase setting. A variable delay between the fixed phase and the gate allows one to cover the complete RF cycle.

(a) Experimental set-up of the discharge chamber and the eletronic and optical system for the time resolved emission spectrocopy

(b) Space and time resolved emission profile of H_α within a hydrogen discharge at 141 Pa and 100 W. Sketched is the time development of the sheath voltage as measured by Czarnetzki et al.

Figure 1: Experimental set-up (a) and space and time resolved emission profile of H_α (b)

3   Measurements and results

Understanding the excitation dynamics [6, 7] in a hydrogen CCRF discharge is essential for the measurement of quenching coefficients by time resolved OES. Figure 1 (b) displays the space-time evolution of the H_α line emission. The abscissae comprises two 74 ns RF periods. The transverse axis gives the distance from the powered electrode located at the bottom of the figure. Several emission structures (I-IV) can be distinguished. Structures I and II can be explained on the basis of E-field measurements [7]. Structure I is caused by a field reversal across the space charge sheath - typical for hydrogen RF discharges. Electrons are accelerated towards the powered electrode and induce a strong impact excitation. This excitation in front of the electrode is exploited for the measurement of quenching coefficients, since, when the sheath potential becomes negative again, electrons are pushed out of the sheath towards the plasma bulk. Note that there is no electron impact excitation for the rest of the RF cycle in front of the powered electrode, and the fluorescence decay with the effective lifetime influenced by quenching is observable. Structure II is related to the sheath expansion heating of the electrons moving to the plasma bulk. Structure III results from fast secondary electrons created by ion impact [6]. The secondary electrons are accelerated to energies beyond the maximum of typical excitation cross sections already within a distance shorter than the mean free path for collisions. They can contribute to the excitation only after loosing part of their energy in collisions with the background gas in the plasma bulk where no further acceleration occurs [6]. Structure IV is related to fast hydrogen atoms created at the electrode surface by the impact of hydrogen ions [6]. These fast hydrogen atoms can excite the background gas by heavy particle collisions. Due to the light mass of hydrogen ions they are able to follow the applied electric field with a small delay because of their inertia. Thus, this time dependent ion bombardment of the electrode determines the time dependence of secondary electrons and fast hydrogen atoms related to Structure III and Structure IV, respectively.

In order to determine quenching coefficients for species other than hydrogen, these species have to be admixed in small amounts to the hydrogen discharge. Figure 2 (a) shows the time resolved emission of the Kr $2p_2$ line in front of the powered electrode. After the strong electron impact excitation due to the field reversal, the fluorescence decay with the effective lifetime influenced by quenching with molecular hydrogen can be observed. With the known [4] quenching coefficient and natural lifetime of the Kr $2p_2$ line, the excitation function $E_j(t)$ of the observed level j can be calculated from the emission (proportional to the population density n_j) in the following manner

$$E_j(t) = \frac{dn_j(t)}{dt} + A_j n_j(t) \qquad ,$$

because a population by cascading processes is comparable low for this level [9]. The excitation function in figure 2 (b) shows a weak excitation related to heavy particle collisions of fast hydrogen atoms (max. at $\approx$70 ns), after a strong excitation due to the field reversal (max. at $\approx$20 ns) and a weak excitation due to the sheath expansion

(a) Emission of Kr 2p$_2$

(b) Excitation function of Kr 2p$_2$

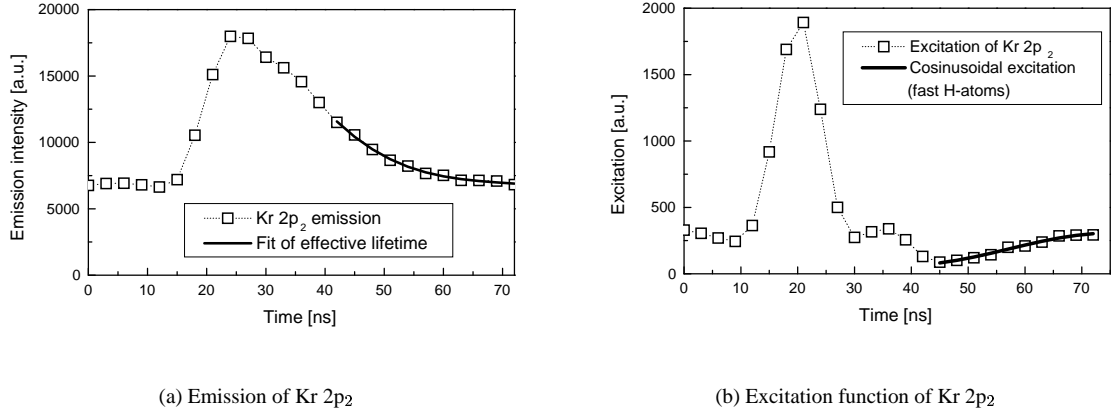Figure 2: Time resolved emission (a) and excitation function (b) of the krypton 2p$_2$ line in front of the powered electrode.

(max. at $\approx$35 ns). The time dependence of this excitation

$$H_{fast} + X \rightarrow H_{fast} + X^* \qquad ,$$

where X represents the observed species, can be described by a sinusoidal function including a delay with respect to the applied voltage.

The time dependence of the population of an excited level including the additional population by heavy particle collisions and cascading processes can, therefore, be described in the interval after electron impact excitation by the following rate equation

$$\frac{dn_j(t)}{dt} = -A_j n_j(t) + A_{ij} n_i(0) \exp(-A_i t) + \frac{U_0}{2}\left[1 + \cos\left(\frac{(t - t_{heavy})2\pi}{T_{RF}}\right)\right] \qquad ,$$

where j and i denote the observed level and a higher level responsible for population by cascades, respectively. The effective lifetime can be obtained in this interval by fitting the analytical solution of the rate equation to the measured data.
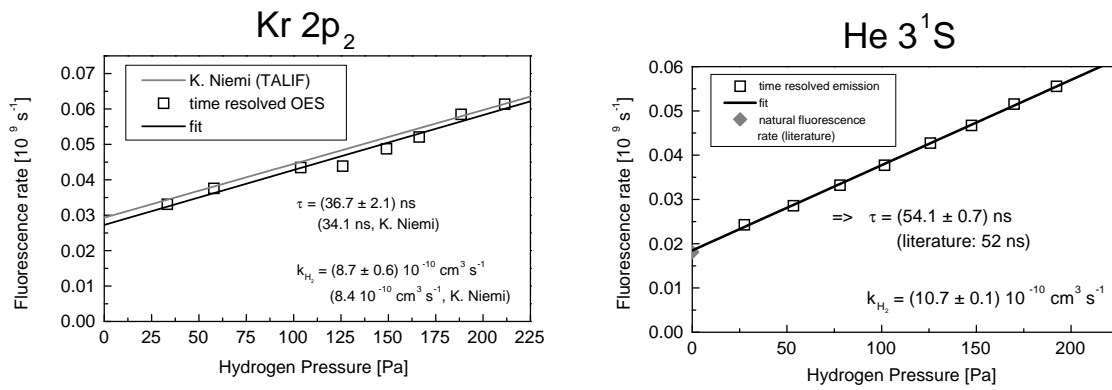
$$n_j(t) = n_j(0)\exp(-A_j t) + F_{cascade}(t, n_i(0), A_{ij}, A_i, A_j) + F_{heavy}(t, t_{heavy}, U_0, A_j)$$

The parameters $n_i(0)$, A_{ij} and A_i describing the cascade contribution can be determined by taking into account the information of optical measurements of electron impact excitation cross-sections by continuously operating electron guns. Since these measurements are also affected by cascades, these cascade contributions were investigated in detail (see [9] and references in it).

The measurement of effective decay rates at various hydrogen partial pressures allows to determine the quenching coefficient of the observed level with molecular hydrogen from the slope in a so called Stern-Volmer-plot. The natural lifetime can be determined from the axis intercept at zero pressure. Since the natural lifetime of the observed level is usually known from literature, this result is a good check for measurements of levels with unknown quenching coefficients. Figure 3 (a) is a Stern-Volmer-plot for the Kr 2p$_2$ line with known values for the quenching coefficient and natural lifetime. The agreement of the time resolved OES with this TALIF measurement [4] is very good. Figure 3 (b) is an example for a measurement of a helium line with unknown quenching coefficient. The agreement with the natural lifetime from literature is very good again. The measurements were performed at a gas temperature slightly above room temperature ($\approx$400 K). The temperature was determined by a time resolved OES measurement of the Fulcher bands of molecular hydrogen [8].

4 Conclusions

The excitation dynamics in a capacitively coupled hydrogen RF discharge was investigated with a fast gateable ICCD camera. This allows a novel time resolved OES technique for the measurement of quenching coefficients based on field reversal excitation for various species (e.g. noble gases) with molecular hydrogen. The technique is independent - in contrast to laser techniques - of the energy gap between the ground state and the observed excited level. It is, therefore, also possible to measure quenching coefficients for helium and neon. Furthermore, the electron impact excitation is independent of optical selection rules. The agreement with known quenching coefficients from TALIF experiments [4, 5] is very good.

(a) Comparison with the known quenching coefficient of krypton $2p_2$

(b) Determination of the quenching coefficient of the helium 3^1S line

Figure 3: Stern-Volmer-plots of the time resolved emission spectroscopy for Kr $2p_2$ (a) and He 3^1S (b).

5 Acknowledgment

References

[1] V. Schulz-von der Gathen, H.F. Döbele, Plasma Chem. Plasma Process. **16** (1996) 461

[2] H.M. Katsch, A. Tewes, E. Quandt, A. Goehlich, T. Kawetzki, H.F. Döbele, J. Appl. Phys. **88** (2000) 6232

[3] A. Goehlich, T. Kawetzki, H.F. Döbele, J. Chem. Phys. **22** (1998) 9362

[4] K. Niemi, V. Schulz-von der Gathen, H.F. Döbele, Proceedings Hakone VII **1** Greifswald (2000) 199

[5] A. Francis, U. Czarnetzki, H.F. Döbele, N. Sadeghi, Eur. Phys. J. **AP 4** (1998) 239

[6] T. Gans, V. Schulz-von der Gathen, H.F. Döbele, Contr. Plasma Phys., Whype (2000/1)

[7] U. Czarnetzki, D. Luggenhölscher, H.F. Döbele, Plasma Sources Sci. Technol. **8** (1999) 230

[8] T. Gans, V. Schulz-von der Gathen, H.F. Döbele, Plasma Sources Sci. Technol. **10** (2001) 17

[9] J.E. Chilton, M.D. Stewart, Jr., C.C. Lin, Phys. Rev. A **62** (2000) 32714