

TALIF CALIBRATION WITH NOBLE GASES FOR QUANTITATIVE ATOMIC DENSITY MEASUREMENTS

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1 Introduction

Fluorescence spectroscopy is a well established diagnostic to measure atomic ground-state densities in plasmas with high spatial and temporal resolution [1]. The atomic species - usually in its ground state - is excited by resonant absorption of tunable narrow bandwidth laser radiation to a higher electronic state. The subsequent fluorescence radiation yields information on the ground-state density. In order to obtain absolute values, not only a suitable calibration technique is necessary, but effects of collisional quenching of the generated population have to be included.

Only in the low pressure case will the excited state be depleted by spontaneous emission only, independently of plasma parameters. Collisional processes become competitive with increasing pressure and lead to an additional radiationless decay which depends on the density of all effective collision partners. A detailed knowledge of the quenching coefficients is required in this situation in order to obtain quantitative results.

Laser induced fluorescence spectroscopy based on single-photon absorption can be calibrated by a comparative Rayleigh scattering measurement performed under identical excitation and detection conditions with a reference gas of known Rayleigh scattering cross-section. For light atoms, however, the excitation wavelengths are located in the VUV spectral range and are difficult to generate. Furthermore, VUV radiation is strongly absorbed in air, many other gases and at elevated pressure even in the investigated medium itself (optical thickness).

Two-photon Absorption Laser Induced Fluorescence spectroscopy (TALIF) circumvents these problems. The excitation is, however, much less efficient, and focused laser radiation is used in most cases to generate a measurable TALIF signal. Good spatial resolution - determined by the focal dimensions - is an additional welcome consequence. The applicability of Rayleigh calibration is lost due to the nonlinear character of the excitation process. So-called "flow tube reactors" which generate well-defined atomic densities with the aid of titration methods [3] can be applied as reference sources in this situation. This procedure requires that the reference source can be attached to the experimental chamber in accordance with the vacuum requirements.

2 Experiment

The objective of this work is to provide an alternative calibration method for TALIF diagnostics to determine atomic hydrogen, nitrogen and oxygen ground-state densities even in plasmas where collisional effects are present. The method is based on a comparative measurement with a noble gas with a two-photon resonance spectrally close to the investigated atomic transition [2]. It requires no additional measurements nor major modifications of the TALIF set-up. Suitable transitions in krypton and xenon exist for the two-photon excitations of atomic hydrogen at $\lambda = 2 \times 205.1$ nm, nitrogen at $\lambda = 2 \times 206.6$ nm and oxygen at $\lambda = 2 \times 225.5$ nm. We investigated these resonances using the TALIF schemes listed in table 1 in order to measure the atomic data required for this calibration: the radiative lifetimes of the excited states, their quenching coefficients for collisions with several important species and the relevant ratios of two-photon excitation cross-sections.

The experiment was performed at a vacuum system equipped with a flow tube reactor. Figure 1a) shows the scheme of the experimental set-up. The pump radiation around $\lambda = 205$ nm is generated with a Nd:YAG-laser (second harmonic at $\lambda = 532$ nm) pumped dye-laser system by mixing the frequency doubled dye radiation with the frequency double Nd:YAG output (max. energy 0.5 mJ, pulse duration 8 ns, repetition rate 10 Hz). The pump radiation at $\lambda = 225$ nm is generated with an excimer-laser pumped dye-laser with frequency doubling (max. energy 2 mJ, pulse duration 10 ns, repetition rate of 2 Hz). The focused laser beam ($f = 30$ cm) is adjusted

Atom	Two-photon excitation	$\lambda_{Laser}(nm)$	Final state	$\lambda_{Fluorescence}(nm)$
Kr	$4p^6 1S_0 \rightarrow 4p^5 5p'[3/2]_2$	204.2	$4p^5 5s'[1/2]_1$	826.3
H	$1s^2 S_{1/2} \rightarrow 3d^2 D_J$	205.1	$2p^2 P_J$	656.3
N	$2p^3 4S_{3/2}^0 \rightarrow 2p^2 3p^4 S_{3/2}^0$	206.6	$2p^2 3s^4 P_J$	742-746
Xe	$5p^6 1S_0 \rightarrow 5p^5 7p[3/2]_2$	225.5	$5p^5 6s[3/2]_2$	462.4
O	$2p^4 3P_2 \rightarrow 2p^3 3p^3 P_2$	225.6	$2p^3 3s^3 S$	844.6

Table 1: TALIF schemes of the investigated atoms

through orifices in the flow tube. The energy dependencies of the excitation processes are investigated with a variable attenuator consisting of two coated substrates, rotatable in opposite sense, to avoid a beam displacement.

Figure 1b) shows the experimental arrangement of the flow tube reactor. The atomic species are produced in a microwave discharge (2.45 GHz, 100 W, 900 Pa, $\phi_{He} = 700$ sccm, $\phi_{H_2, N_2, O_2} = 5$ sccm) and are passed along the flow tube. The TALIF measurements are performed downstream through holes in the tube. The absolute atomic density in the observation region is determined by titration [3] on the basis of the fast reactions: $H+NO_2 \rightarrow OH+NO$, $N+NO \rightarrow N_2+O$, $O+NO_2 \rightarrow NO+O_2$. Atomic hydrogen and nitrogen densities in the order of 10^{13} cm^{-3} and atomic oxygen densities in the order of 10^{14} cm^{-3} are generated under typical conditions. The composition of the applied NO/He and NO₂/He mixtures are verified by FTIR-spectrometry.

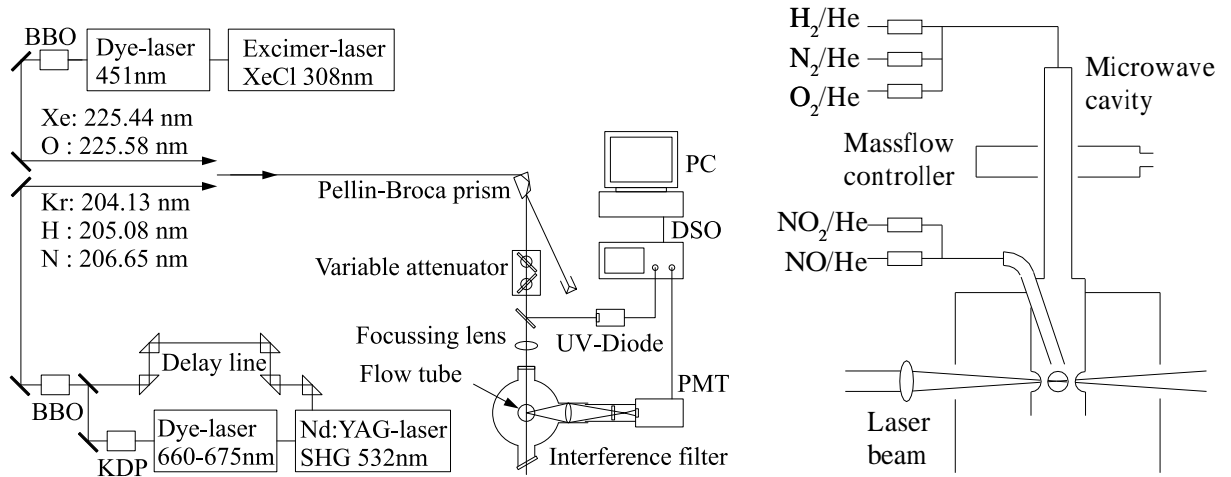


Figure 1: a) Experimental set-up, b) Experimental arrangement of the flow tube reactor.

3 Measurements and results

3.1 Radiative lifetimes and quenching coefficients

The radiative lifetimes of the excited states and the quenching coefficients for collisions with H₂, N₂, O₂, He, Ar, Xe, Kr and CH₄ were determined from time resolved measurements. As an example, figure 2a) shows the influence of an additional H₂ pressure on the TALIF signal obtained with a fixed H-atom density. Stern-Volmer plots for the decay rate of the signal versus the partial pressure of different collision partners are shown in figure 2b).

The pressure was increased until the quenching lead to signals whose duration was limited by the laser pulse duration and the time resolution of the detection system. The dependence was linear throughout. The quenching coefficients are deduced from the slopes of these plots and a conversion to the unit [cm³/s] according to the ideal gas law for $T = 300$ K. The gas temperature was verified by measuring the thermal population distribution in the fine-structure-split ground state of atomic oxygen. The radiative lifetimes are deduced from the zero pressure intercepts of the plots accounting for quenching by the molecular fraction and the carrier gas helium as well as self-quenching of the noble gases. The results (with an estimated uncertainty of 15%) are summarized in table 2. Satisfactory agreement with published data is found [4, 5, 6, 7, 8].

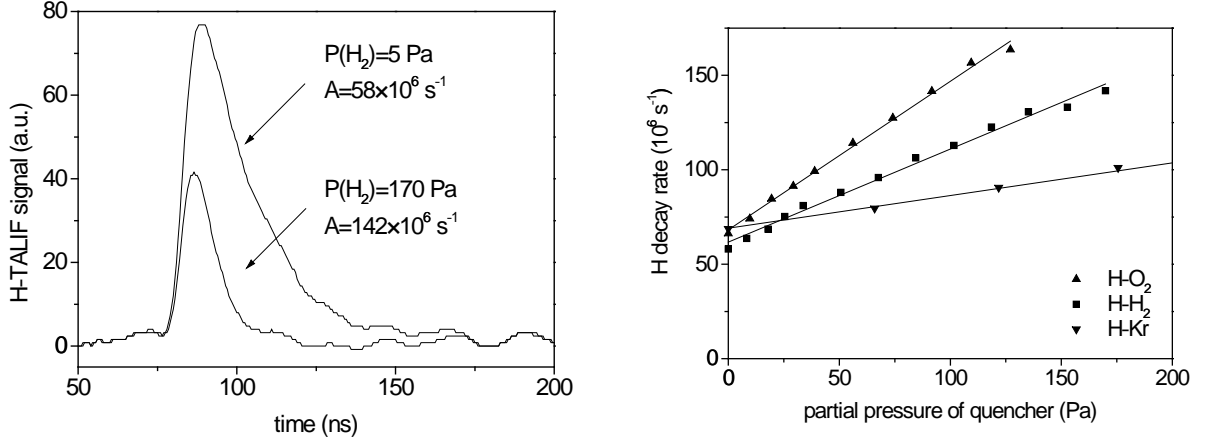


Figure 2: a) Time resolved $H(3d^2D_J)$ TALIF signals at different H_2 pressures. b) Decay rate of the $H(3d^2D_J)$ TALIF signals versus partial pressure of O_2 , H_2 and Kr .

Reagent		H_2	N_2	O_2	He	Ar	Kr	Xe	CH_4
Excited state	τ (ns)	$k_q(10^{-10}cm^3s^{-1})$							
$Kr(5p[3/2]_2)$	34.1	8.44	3.35	6.34	0.78	1.29	1.46	3.78	6.27
$H(3d^2D_J)$	17.6	20.4	20.1	32.6	0.18	3.93	7.15	19.8	25.0
$N(3s^4P_{3/2})$	29.6	1.11	0.41	6.63	0.11	0.37	3.16	7.75	5.81
$Xe(7p[3/2]_2)$	105.6	28.5	14.0	20.6	2.33	3.71	5.91	5.05	-
$O(3p^3P_J)$	35.1	10.9	5.9	9.3	0.07	0.25	-	-	-

Table 2: Radiative lifetimes τ and room temperature quenching coefficients k_q of the investigated states.

3.2 Ratios of two-photon excitation cross-sections

The procedure used to determine ratios of excitation cross-sections of neighbouring two-photon resonances is the same as for the calibration except that it is performed with a known atomic density generated in the flow tube reactor. The time and spectrally integrated TALIF signal is measured with a fixed density of an atomic species as a function of the laser energy. This series of measurements is repeated with a known density of the appropriate noble gas under otherwise identical experimental conditions. The fluorescence signals exhibit at small energy the quadratic intensity dependence of an unsaturated two-photon excitation process. This low energy range was used to fit the straight lines shown in figure 3. Their comparison yields:

$$\frac{I_F(X)}{I_F(R)} = \chi \frac{n_X}{n_R} = \gamma \frac{a(X)}{a(R)} \frac{\sigma(X)}{\sigma(R)} \frac{n_X}{n_R}. \quad (1)$$

X denotes the investigated atomic species, R the noble gas, I_F the integrated TALIF signal normalized to the square of the laser energy and χ the calibration factor which depends only on experimental and atomic constants. γ is the ratio of the detection sensitivities for the fluorescence wavelengths (transmission of the observation optics and the quantum efficiency of the PMT), a the branching ratio of an observed transition corrected by the effective quenching rate and σ the two-photon excitation cross-section. The branching ratios, effective at the measurements, were calculated using results from section 3.1. Because the excited states of the noble gases decay each via several fluorescence transitions in contrast to the excited atomic states, two further reference values were used for the calculation: $A_{ik}/A_i = 0.958$ the branching ratio of the krypton 826.3 nm line in absence of quenching from [8] and $A_{ik} = 2.18 \times 10^6 s^{-1}$ the transition probability for of the xenon 462.4 nm line from [9]. The following ratios of two-photon cross-sections were deduced from experimentally determined calibration factors:

$$\frac{\sigma(Kr)}{\sigma(H)} = 0.62 \quad \frac{\sigma(Kr)}{\sigma(N)} = 0.67 \quad \frac{\sigma(Xe)}{\sigma(O)} = 0.36 \quad (2)$$

The estimated uncertainty of these values is 50% due to the numerous input parameters and the reproducibility of the laser beam profile. Note that the laser radiation is linearly polarized and the fluorescence radiation is observed parallel to the direction of polarization. If the fluorescence characteristics of two compared species are different, the stated cross-section ratio includes a correction factor which is only valid in the present geometry.

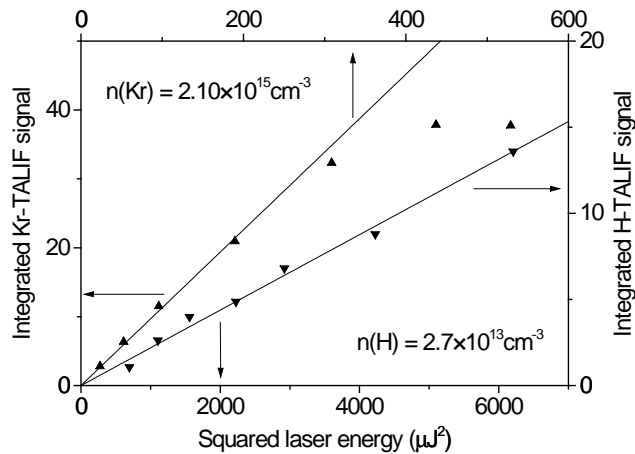


Figure 3: Dependence of the $\text{Kr}(5p'[3/2]_2)$ and $\text{H}(3d^2 D_J)$ TALIF signal on the laser energy.

4 Conclusion

The required atomic data - radiative lifetimes, quenching coefficients and ratios of two-photon cross-sections - are now available to calibrate atomic hydrogen, nitrogen and oxygen densities in low temperature plasmas by reference measurements with krypton and xenon. The determination of quenching coefficients extends the range of applicability to higher pressures.

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