On Calibration of Laser-Induced Fluorescence Measurements in Plasma Flows Using Rare Gases

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Abstract In plasma flows intended for the qualification of atmospheric re-entry maneuvers of spacecrafts, the plasma wall interaction strongly affects the heat load to the thermal protection system. Therefore, ground state densities have to be known for plasma flow characterization, where laser-induced fluorescence measurements are applied. Calibration can be performed using rare gases, while one interest is to calibrate atomic nitrogen using xenon. Three excitation schemes for two-photon laser-induced fluorescence (TALIF) on neutral xenon are presented. These excitation schemes include 5f and 6f states, lying energetically close to the 2x211 nm resonance in atomic nitrogen. Characterization of these transitions will qualify them as reference transitions for same-order calibration procedures. Results of lifetime and collisional deactivation rate measurements for 5f levels are given in pressure regimes between 4 and 60 Pa. Lifetimes are found to be consistent with literature values. Collisional deactivation plays an extensive role in the studied pressure regime. Two-photon excitation of 6f states has been verified at pressures between 69 and 224 Pa, weak signal intensities require further investigations.

1. Introduction

Plasma flows are widely used in technological applications such as plasma spraying or plasma coating. In a particular application, namely the re-entry research, high-enthalpy plasma flows are generated for the simulation of conditions as expected during an entry maneuver in a planet’s atmosphere. These high temperature plasma flows are commonly used to qualify heat shield materials (Laure 1996). With respect to an Earth (re-)entry maneuver, an air plasma flow has to be investigated. Here, the problematic in gas-surface chemistry occurring from the presence of the atomic particles nitrogen and oxygen is a wide field of research. The heat load strongly depends on gas-surface interaction processes which are mainly dependent on the atomic particle density, i.e. atomic nitrogen and atomic oxygen, and the surface catalytic efficiency. Rough calculations show that materials with high catalytic efficiency can lead to a heat flux increase with a factor of 3 to 4 (Fertig 2007). However, for a thorough measurement of material properties the decisive plasma parameters have to be known, which in the sense of gas-surface interaction are the particle densities of atomic oxygen and atomic nitrogen.

First and foremost for such high temperature gas dynamics, optical measurement techniques are favored for their non-intrusive approach and the possibility to access particle densities. In case of plasma flows, where dissociation and ground state excitation have to be accounted for, a main interest focuses on the determination of ground-state densities of atoms. Besides some fancy probe techniques and more complex four wave mixing laser diagnostic approaches, laser-induced fluorescence measurements are an appropriate technique to assess ground state densities (Eckbreth 1988). The technique is used since the late 1970s (Areppalli 1989). To access ground states of atoms, research focuses on the application of two-photon absorption laser-induced fluorescence (TALIF). Here, the atoms of interest are excited by the absorption of two photons simultaneously via a virtual intermediate state. Usually, both photons are provided by the same laser system.

However, calibration of two-photon laser-induced fluorescence measurements with respect to line intensities is a non-trivial problem. Detected intensities depend on instrumental sensitivities and
geometrical quantities of the experimental apparatus, but also on the geometrical properties of the excitation volume. For multi-photon processes, the transition probability for simultaneous absorption of n photons is given by a power law of the laser intensity $\propto I^n$. Calibration by same-order processes is therefore generally preferred, which also might explain discrepancies found by Löhle and Auweter-Kurtz (2007) comparing two-photon rare gas calibration to techniques based on Rayleigh scattering in oxygen plasma flows. Goehlich et al (1998) and Niemi et al (2001) calibrate TALIF measurements of atomic nitrogen (2x207 nm) and atomic oxygen (2x225 nm) in plasma flows by two-photon reference measurements in neutral krypton and neutral xenon, respectively. With respect to the 2x225nm transition of atomic oxygen, an applicable reference transition in neutral xenon is well characterized and has already been applied to high enthalpy plasma flows of pure oxygen and air by the authors (Löhle et al 2008, Löhle and Auweter-Kurtz 2006). For the 2x211nm excitation scheme in atomic nitrogen, which is easier to achieve with the laser system than the 2x207 nm transition, lack of data concerning appropriate transitions in neutral xenon calls for some fundamental research in order to characterize atom specific quantities related to signal intensities.

Within this paper, high energetic levels in neutral xenon are investigated by TALIF spectroscopy as candidates for two-photon transitions in a reference medium to calibrate TALIF signals of atomic nitrogen in plasma flows. Lifetimes and collisional deactivation rates are studied as key quantities to relate corresponding fluorescence signals for absolute calibration procedures.

2. Theory

One way to model TALIF processes consists in the construction and solution of a system of rate equations, which has been often discussed in literature (e.g. Bamford et al 1986). In a simple model including two-photon excitation from the ground state and fluorescence decay of the two-photon excited state, the fluorescence signal $S$ can be written as

$$S = D \frac{E^2 A_{21}}{a^2} \frac{\hat{\sigma}^{(2)} n_0}{A + Q} \int_{-\infty}^{\infty} F^2(t) dt,$$

as long as saturation of the absorption process can be neglected. Herein, $E$ represents the energy of the laser pulse, $a$ the beam waist at the detection area, $n_0$ the particle density, $\omega$ and $F(t)$ the frequency and the temporal profile of the laser beam respectively, $A_{21}$ the Einstein coefficient for the fluorescence transition, $A$ the transition rate including all possible radiative decays of the two-photon excited state, $Q$ the collisional deactivation rate and $\hat{\sigma}^{(2)}$ the two-photon absorption cross section (which includes information of the line shape of the absorption transition). The calibration constant $D$ involves all factors with influence on the sensitivity of the detection system,

$$D = L \Omega \eta I \eta_\phi e KG \frac{G_a}{C}$$

with $\eta_I$ denoting the transmission function of all windows and filters, $\eta_\phi$ the quantum efficiency of the photomultiplier, $G_p$ the photomultiplier tube gain, $K$ including sensitivities of further analyzing instruments, $G_a/C$ the ratio of preamplifier gain to preamplifier capacitance (in V/C), $e$ the elementary charge (in C), $L$ the effective length of the collection system (in cm) and $\Omega$ the solid angle (in sr) of the fluorescence collection lens. The units of $S$ and $D$ are V and V·cm·sr, respectively.
The calibration constant can, in principle, be cancelled out by taking measurements in a reference medium at known particle concentrations. In order to obtain absolute calibrated TALIF signals, Goehlich et al (1998) combined two TALIF measurements, one in an atomic oxygen plasma flow and one in neutral xenon at defined pressure. From equation (1) follows for an unknown plasma flow particle density ($n_p \equiv \text{const.}$)

$$n_p = \gamma \left( \frac{A_{21}}{A + Q} \right)_{Xe} \left( \frac{A + Q}{A_{21}} \right)_p \frac{\sigma^{(2)}_p}{\sigma^{(2)}_{Xe}} \frac{S_p}{S_{Xe}} n_{Xe}$$

(3)

wherein $\gamma$ accounts for those different sensitivities of the fluorescence detection system with respect to optical components (interference filters), which can not be kept unchanged applying rare gas reference measurements. However, this method requires the knowledge of atom specific quantities as the respective transition rates $A_{21}$, $A$ and $Q$ (or at least their ratio $A_{21}/(A+Q)$ at defined pressure), as well as the two-photon absorption cross sections $\sigma^{(2)}$, with only two published values concerning one $6p'$ and one $7p$ transition (Goehlich et al 1998, Niemi et al 2001, Niemi et al 2005). An accurate determination of these quantities is a prerequisite for application of rare gas calibration techniques. Additionally, equation (3) only holds if temporal and spatial laser profiles remain constant for both measurements. This may be best fulfilled by comparing two signals with two-photon absorption transitions in direct spectral vicinity.

With respect to the $2x211.0 \text{ nm}$ transition in atomic nitrogen, calibration in xenon seems possible.
due to a variety of possible levels to be excited, but is not applicable up to now as those energy levels are rarely studied in literature, yielding a remarkable lack of data concerning even transition rates. Extensive two-photon investigations of 6p, 6p', and 7p levels (e.g., Böwering et al. 1986, Bruce et al. 1990, Whitehead et al. 1995) are not appropriate as their spectral gap is too wide and can not be excited within the range of one single laser dye. Results from two-photon excitation of 8p and 4f-levels have been published by Miller (1989), but in collisional dominated pressure regimes without determination of radiative or collisional transition rates. Verdugo et al. (1986) report spontaneous lifetimes measurements in low pressure regimes ($\sim 10^{-3}$ Pa) for some nf (n=4-8) states, but used delayed coincidence methods as excitation mechanism and did not measure pressure dependencies.

Fig.1 shows an excerpt from the level scheme in neutral xenon, including excitation/fluorescence transitions discussed in this paper. Following two-photon electric dipole selection rules, in the case of equal polarized photons, allowed two-photon transitions from the ground state are restricted to even parity states with total angular momentum numbers J=0,2. Multiplets of np (n$\geq$8) and nf (n$\geq$5) can be found within the range of the used laser dye Stilbene-3, qualifying them as potential candidates for atomic nitrogen calibration reference transitions. The studies concentrate on the excitation of 5f, 6f levels with J=2. To the knowledge of the authors, investigations of these levels via two-photon excitation are not formerly published.

3. Experimental

Re-entry maneuver testing can be divided in roughly two parts. For aerodynamic behavior testing of a foreseen vehicle shock tubes are the appropriate test facilities. However, the aerothermodynamic behavior can not be investigated in these experiments due to the short measurement times. Therefore, the thermochemical behavior is tested in so-called plasma wind tunnels. The aim of these facilities is to rebuild the thermal and chemical loads on the surface of material probes. Meanwhile, high enthalpy facilities with steady-state flow conditions have been generated for plasma flows up to 150 MJ/kg. In the present case the Plasmawindkanal 3 (PWK3) is used because of the possibility to generate pure nitrogen flows at discharge power levels from zero up to 120 kW. The plasma wind tunnel consists of a vacuum vessel 2 m in diameter and 2.5 m in length. Optical accesses on both sides of the vacuum chamber are provided in order to measure and observe the plasma flow. On the rear end, the vacuum chamber is connected to the IRS’s vacuum system.

![Figure 2: Experimental set-up](image-url)
As calibration has to be performed in situ, no geometrical changes of the laser spectroscopic set-up should be introduced between measurements in the plasma flow and in the reference medium. The experimental setup for laser spectroscopy is shown in Fig. 2. Measurements in neutral xenon as reference gas are performed in a fluorescence cell, which is placed inside the PWK. Thus, the experimental geometry is saved, while fluorescence intensities have only to be corrected for optical filters and transmission windows of the cell.

The laser system is installed in parallel to the vacuum chamber. It consists of a pulsed dye-laser (LAMBDA PHYSIK SCANMATE 2E) pumped by a Nd:YAG laser (QUANTEL Brilliant B). The 5ns output of the dye laser is frequency doubled by a beta barium borate (BBO) crystal to generate laser radiation around 211 nm, using Stilbene-3 as laser dye. A maximum output energy of about 1 mJ per pulse is reached. The laser beam is adjusted to the measurement location on the plasma jet axis, and the fluorescence cell respectively, in the center of the vacuum chamber by three prisms and a focusing lens system. In order to have a better focussing a Galilean telescope is used.

Laser-induced fluorescence is detected at right angles to the laser and the flow direction, i.e. on top of the vessel. A gated photomultiplier tube (PMT) of type HAMAMATSU R636-10 is used. Two achromatic lenses image the fluorescence plane onto the detector. In front of the entrance slit, interference filters are used to separate the fluorescence from the laser and the plasma radiation. Moreover, interference filters with very small bandwidths are used to avoid line blending effects.

The data acquisition equipment consists of two BOXCAR integrator channels (STANFORD RESEARCH SYSTEMS SR250) and a computer interface (STANFORD RESEARCH SYSTEMS SR245). Data acquisition is controlled by a LABVIEW program together with a trigger generator (STANFORD RESEARCH SYSTEMS DG535) in order to switch the photomultiplier gate with respect to the laser pulse. Laser energy measurement is performed using an energy monitor (POLYTEC RJP735). A beam splitter is used that splits a small amount of laser energy to the energy monitor. The time-resolved fluorescence measurements of the present investigation are acquired using a fast 1-GHz oscilloscope (GAGESCOPE 82G).

4. Results

The investigations first concentrated on the excitation of the levels 5f \([5/2]\) J=2 at 214.1 nm and 5f \([3/2]\) J=2 at 214.2 nm. Both levels show comparably large signal intensities. Fluorescence signals are fitted to a single or a sum of exponentials. With respect to spontaneous lifetime \(\tau_0\) and collisional deactivation rate \(Q(p)\) determination, the effective lifetime \(\tau\) in dependence of pressure is measured and the values are plotted in Stern-Volmer representation,

\[
\frac{1}{\tau} = \frac{1}{\tau_0} + Q(p)
\]

Measurements have been taken within a pressure range of 4 and 60 Pa. Each decay curve represents the summation of the fluorescence of 800 to 1700 laser pulses at constant laser energy, which have been taken at the central wavelength of the absorption line determined in a previous spectral scan. Fig. 3 shows, as an example, the decay curve of 5f \([3/2]\) J=2, detected at fluorescence wavelength 747.2 nm, at 15.3 Pa xenon pressure. In this case, a strong fast component is visible, while the noisy signal >60 ns after the excitation pulse suggests a weaker slow component. On the left side of Fig. 4, the corresponding Stern-Volmer plot for this level is presented, based on measurements at seven defined pressures. A spontaneous lifetime of 98±16 ns and a collisional deactivation rate coefficient of 4.5±0.5 cm\(^3\) s\(^{-1}\) is found. The value of lifetime is in good agreement with Verdugo et al (1986),

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who give two values $105\pm6$ ns and $99\pm6$ ns, the first one being measured at the same fluorescence channel as in the case presented here, the latter at 394.8nm. Derived collisional deactivation rates are significantly larger than reported for 6p, 6p’ and 7p states (Bruce et al 1990, Whitehead et al 1995), what is not surprising as the density of states is higher in the region of 5f levels. However, since presence of collisions reduces effective lifetimes considerably in our pressure regime,
Figure 5: Sample data of the time-dependent fluorescence signal of the 6f [5/2] J=2 level

extrapolation to small pressures introduces our comparatively larger errorbar for the lifetime. This may, in principle, be circumvented by analyzing decay curves at pressures < 4 Pa, what is difficult here as reduced signal intensities introduce larger errors for the respective effective lifetime value. The discussion of the weaker slow component is rather complex. As the FWHM of the used interference filter is 3.4 nm, we can not fully prevent a possible line blending effect of the fluorescence line belonging to the 5f [3/2] J=1 level. Although excitation is state selective (note additionally that two-photon excitation of 5f [3/2] J=1 is excluded as forbidden by selection rules), this level might be populated by collisions. However, as population by collisional deactivation should affect a variety of levels, it is assumed that there results no significant fraction yielding dominant contribution to the fluorescent decay from this level. Measurements by Miller (1989) and Whitehead et al (1995) suggest that collisional processes do not necessarily populate levels in direct vicinity (although they studied higher pressure regimes). Additionally, Verdugo et al (1986), who also had difficulties to separate radiation from 5f levels, argued that lifetimes within the 5f multiplet do not differ significantly based on their theoretical predictions. It is therefore believed that the weak component is the result of more complicated collision kinetics, leading to re-population of the originally excited 5f [3/2] J=2-state.

Regarding the 5f [5/2] J=2 state detected at 745.1nm, smaller collisional deactivation rates (by a factor 0.7) and a spontaneous lifetime of 99±36 ns (103±7 ns given in Verdugo et al (1986)) are found, a value to be increased in accuracy by further measurements at lower pressures. Comparatively, measurements of this level at the 871.0 nm fluorescence line give a spontaneous lifetime value of 127±17 ns, but with an interference filter of 10 nm bandwidth allowing possible line blending also from 7p-states.

The study of the 6f [5/2] level detected at the 568.8 nm fluorescence, which is of particular interest due to its excitation wavelength of 2x211.1 nm almost identical with the atomic nitrogen transition to be calibrated, exhibits extensive quenching and manifestly weaker signal intensities. In Fig. 5, the decay curve is shown for 69 Pa xenon pressure. So far, signals could only be analyzed at pressures ≥ 69 Pa, so that the Stern-Volmer representation yielded no consistent result due to the
low effective lifetimes. However, optimization of detection optics and the laser pulse energy are expected to gain improvements to achieve measurements in lower pressure regimes.

5. Conclusions

The two-photon excitation of 5f, 6f J=2 levels in neutral xenon have been verified, intended as rare gas calibration transitions for TALIF measurements of atomic nitrogen species in plasma flows. 5f J=2 levels have been discussed with respect to lifetime and collisional deactivation rates, whose knowledge is a prerequisite to determinate two-photon absorption coefficients. Values of lifetimes have to be increased in accuracy during future investigations. Levels have been found to be appropriate for upcoming determination of two-photon absorption cross sections, completing the qualification as reference transitions. Modifications in the experimental set-up to increase detection limits for 6f levels as well as the extension to the 8p and 9p manifolds are subjects of present experiments.

Acknowledgments

C. Eichhorn thanks the Evangelisches Studienwerk Villigst for financial and idealistic support through a PhD scholarship. Authors gratefully acknowledge funding by the Deutsche Forschungsgemeinschaft (DFG) within project Au 85/24-1.

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