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Laser-induced fluorescence measurements of absolute atomic densities: concepts and limitations

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Abstract

The potential of laser-induced fluorescence spectroscopy of atoms is reviewed with emphasis on the determination of absolute densities. Examples of experiments with single-photon and two-photon excitation are presented. Calibration methods applicable with the different schemes are discussed. A new method is presented that has the potential to allow absolute measurement in plasmas of elevated pressure where collisional depletion of the excited state is present.

1. Introduction

The fast progress in plasma technology and the development of suitable plasma sources require detailed information on the spatial distribution of particles involved in the plasma processes of interest and of velocity distributions and time dependences. In this context absolute measurements become increasingly important.

Optical emission spectroscopy is the technically most simple non-intrusive method to yield important information on the species present in the plasma and on their velocity distributions. This information is line-of-sight integrated, however, and seldom quantitative as far as densities are concerned. Furthermore, only excited particles are accessible to this diagnostic. This is an important shortcoming, since the populations of the excited states are, as a rule, orders of magnitude lower than the ground state populations, and theoretical models of approximative character have to be applied to provide the necessary link to the ground state.

Absorption spectroscopy and laser-induced fluorescence (LIF) spectroscopy are techniques that have direct access to ground state (and metastable) populations. Whereas the former is again restricted to line-of-sight integration, the latter can provide spatially resolved information in view of the angle between the exciting laser beam and the optical detection path—see, e.g. figure 1—defining a scattering volume determined by the overlap of both. A second advantage is that the fluorescence signal is free from the

intense background of the irradiated laser light—unlike the case of absorption measurements. The plasma background light (of which the absorption signal is virtually free) may play a limiting role in specific cases.

We want to focus in this contribution on fluorescence spectroscopy of atomic radicals because of their dominant importance in processing plasmas with particular emphasis on the discussion of the possibilities of quantitative measurements.

2. LIF spectroscopy with single-photon excitation

LIF spectroscopy is an active optical method allowing us to measure population densities and velocity distributions (temperatures) of atoms, molecules and ions including electric fields in some cases [1, 2]. Narrow-bandwidth tunable radiation is used to excite particles by absorption of a photon into a higher state. The fluorescence radiation emitted when the particle makes a transition to an energetically lower state—often again the ground state—is analysed in order to obtain information on the population, the lifetime of the upper state and the velocity distribution of the particles. The cross section for this fluorescence process is comparatively high so that together with the sensitivity and high amplification capabilities of modern photodetectors a powerful diagnostic technique results. Modern laser systems provide, in addition, focusing and pulsing possibilities that usually meet all requirements with respect to space and time resolutions in plasma discharges.

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Several basic prerequisites have to be warranted in the context of LIF measurements. The species of interest has to have bound states accessible according to optical selection rules. The excitation should not result directly in ionization or dissociation. Sufficient optical transparency of the medium for the laser radiation and the fluorescence radiation is also an important condition. The particle density—assumed homogeneous over the scattering volume of length L —must not change within characteristic times such as the laser pulse and the fluorescence lifetime. In other words: the fraction of particles leaving the scattering volume after excitation has to be negligible.

The intensity of the fluorescence radiation is directly proportional to the mean density in the scattering volume, if the spatial and temporal resolutions are determined by the focusing and the pulse duration of the laser beam. Saturation effects and collisional de-excitation (quenching) from the level into which the optical excitation has occurred may require consideration.

Saturation effects become important when the laser radiation power is so high that the populations of the states involved are substantially affected by the laser radiation field. Photon absorption and stimulated photon emission can then become the dominant effects. In the ultimate situation in which the stimulated photon emission rate equals the absorption rate the spontaneous photon emission rate (and also quenching rate) is negligible, and further increase of the laser power will not change this balance between the populations of the states considered. Full saturation of the fluorescence signal is then reached. When saturation occurs, the laser power spectrally corresponding to the line wings becomes important, resulting in high photon absorption rates outside the central frequency of the transition. This fact induces a broadening in the measured fluorescence line. The saturation of a homogeneous line profile differs from the saturation of an inhomogeneous line profile. In the latter case spectrally selective saturation occurs—called hole burning (Bennet-hole, Lamb-dip).

So-called saturation spectroscopy takes advantage of this effect. In most LIF applications for the determination of particle densities one will try to avoid saturation by suitable choice of the laser intensity.

Finally it should be mentioned that the spatial beam profile of the laser may also affect the overall broadening and saturation intensity of the measured fluorescence line. A complete discussion of saturation-related laser broadening effects is a lengthy task and no attempt is made to approach it in this paper. With respect to this topic we refer to the literature [1, 3]. We assume, therefore, in the following discussion that the laser intensity is below the limits for which saturation effects become important. This can be controlled in the experiment by varying the irradiated laser power and verifying the linearity of the fluorescence.

If the detection system has the transmission $T(\omega_{21})$ at the central transition frequency ω_{21} and if ϕ_L is the number of laser photons, one obtains for the number of fluorescence photons ϕ_F emitted per laser pulse into the solid angle $\Delta\Omega$

$$S_F = \int \frac{\phi_F}{\phi_L} d\omega = T(\omega_{21}) \Delta\Omega L \frac{A_{21}}{A_{21} + Q_2} \sigma_S^\omega K_F(\theta) n_1. \quad (1)$$

$K_F(\theta)$ describes the radiation pattern depending on the angle of observation θ (measured with respect to the polarization

vector of the linearly polarized laser beam) and on the angular momentum quantum numbers of the transition under consideration [4] with $\int K_F(\theta) d\Omega = 1$. $\sigma_S^\omega \equiv \pi r_0 c f_{12}$ is the spectrally integrated scattering cross section (f_{12} is the absorption oscillator strength and r_0 the classical electron radius), A_{21} is the transition probability, Q_2 the collisional de-excitation rate and n_1 the particle density to be found.

3. Calibration with Rayleigh scattering

We see from equation (1) that the determination of absolute densities requires knowledge of spectroscopic data of the transitions involved and a calibration of the optical detection system. For the case of single-photon excitation this is relatively simple with the aid of Rayleigh scattering. This calibration is based on a comparison—under identical conditions of laser irradiation and signal detection—of the LIF signal with the signal generated by Rayleigh scattering from a reference gas—usually a noble gas—of known density [5–7]. The method is applicable if the wavelengths of excitation and fluorescence coincide, if the fluorescence is linearly dependent on the excitation intensity (i.e. no saturation) and if the Rayleigh cross section of the reference gas is known.

The dipole radiation pattern applies for non-resonant Rayleigh scattering from the bound electrons of ground state noble gases

$$K_R(\theta) = \frac{1}{4\pi} \frac{3}{2} \sin^2(\theta). \quad (2)$$

The total Rayleigh scattering cross section is [8]

$$\sigma_R = \frac{24\pi^3}{n_{R,0}^2 \lambda^4} \left(\frac{\kappa_R^2(\lambda) - 1}{\kappa_R^2(\lambda) + 2} \right)^2. \quad (3)$$

$n_{R,0}$ is the number density of the gas atoms (Ar, Kr, Xe, ...) for which the refractive index $\kappa_R(\lambda)$ applies, where λ is the vacuum wavelength. In the case of molecular gases an additional frequency dependent correction factor accounts for the anisotropy of the non-spherical symmetry of the molecules (N_2 , O_2 , ...) [8–10].

The Rayleigh scattering cross section is expressed here with the aid of the Clausius–Mosotti relation through the macroscopic quantities gas density and pertinent refractive index. The resulting scattering cross section is independent of the particle density as expected for a microscopic single-particle cross section.

If the detection system is characterized by the transmission $T(\omega_L)$ at the central laser frequency ω_L , one finds the number of photons ϕ_R scattered by the angle θ into the solid angle $\Delta\Omega$ to be

$$S_R = \frac{\phi_R}{\phi_L} = T(\omega_L) \Delta\Omega L \sigma_R K_R(\theta) n_R. \quad (4)$$

Since the Rayleigh scattered signal is proportional to n_R , $S_R = S_R(n_R)$ will exhibit a linear dependence unless there is additional stray light. This influence can be identified and eliminated by extrapolating the scattered signal to $n_R = 0$.

The absolute population density to be calibrated is found from the ratio of S_F and S_R as

$$n_1 = \frac{S_F}{S_R} \frac{\sigma_R K_R}{\sigma_S^\omega K_S} \left(1 + \frac{Q_2}{A_{21}} \right) n_R. \quad (5)$$

The method of absolute calibration by Rayleigh scattering from noble gases is limited to the case of negligible saturation. Cunge *et al* [11] have communicated a scheme based on fluorescence scattering from NO that allows us, under certain circumstances, to perform absolute calibration even if saturation is not negligibly low.

Fluorescence diagnostics of light atoms (e.g. H, N, O, Cl and F) with single-photon excitation has to cope with the problem that the resonance lines are located in the vacuum ultraviolet (VUV) so that tunable radiation in this spectral region is necessary for excitation [12, 13]. The measurement of velocity distributions of particles represents a characteristic application for LIF with VUV radiation [14]. Figure 1 shows the experimental set-up and the velocity distribution of carbon particles sputtered from a graphite target by bombardment with argon ions (1 kV, 50 mA). The VUV radiation tunable around $\lambda = 166$ nm is generated by stimulated anti-Stokes Raman scattering (SARS) in cold hydrogen gas and is irradiated through a small bore to the scattering volume close to the target surface. Tuning the VUV light over a spectral interval linked by the Doppler effect to the width of the velocity distribution allows recording of the latter by collecting the fluorescence light under 90° . The zero mark of the distribution has to be established separately, since all sputtered particles move away from the surface. This zero mark is realized by a second LIF set-up whereby the symmetric carbon atom

Figure 1. Determination of velocity distributions of sputtered carbon atoms by VUV-LIF at $\lambda \sim 166$ nm: (a) experimental set-up and (b) results. The smooth curve corresponds to the theoretical expectation [15].

velocity distribution in a small filamentary gas discharge with a carbon cathode is recorded (35 mA, 200 mbar argon)—left symmetric distribution in figure 1(b).

4. Fluorescence spectroscopy with two-photon excitation (TALIF)

In many applications the problem will arise that with increasing particle density the excitation radiation will no longer be transmitted sufficiently and the medium becomes optically thick in the centre of the resonance line. This problem is aggravated in the case where the fluorescence transition occurs back to the ground state. It is also not uncommon that the irradiated VUV radiation is absorbed by other species in the plasma which are not being probed. One possible solution is two-photon excitation in the UV spectral range (TALIF; two-photon absorption LIF) which can be realized with efficient commercial laser systems on the basis of second harmonic generation (SHG) and frequency mixing in nonlinear crystals.

The optical transitions involved with LIF and TALIF are different according to the optical selection rules. Figure 2 shows several excitation schemes for single-photon and two-photon absorption together with the fluorescence transition for the TALIF case.

Two-photon excitation is considerably less efficient, and the excitation rate scales with the square of the laser intensity. The fluorescence occurs to an intermediate state because of the selection rules and is usually in the visible spectral range. The problem of reabsorption is usually absent. It is worthwhile to note that single-photon and two-photon absorption schemes are not competing techniques. Single-photon LIF is much more sensitive but restricted by the requirement of transmission to smaller densities (typically $<10^{11} \text{ cm}^{-3}$). The domain of TALIF are plasmas with higher densities where limitations may arise by collisional quenching.

The determination of the spatial distribution of hydrogen atoms in a capacitively coupled RF discharge (GEC reference cell) can serve as an example for TALIF [16]. Radiation at $\lambda = 205$ nm is sent through the discharge without focusing as two counterpropagating collimated beams (~ 5 mm diameter) so that the excitation is Doppler-free. Figure 3 shows the experiment and the results.

The fluorescence light at $\lambda = 656$ nm is collected under 90° as indicated in the figure. A linear segment extending from the centre to the edge is imaged onto the intensified charge coupled device (ICCD) camera. The full range between the electrodes can be covered by irradiating the probing laser beams at different heights in succession. The results of figure 3

Figure 2. Excitation schemes for single-photon and two-photon excitations for some relevant atomic species.

Figure 3. Doppler-free two-photon LIF imaging in a CCRF hydrogen discharge: experimental set-up (a) and measured atomic hydrogen distributions (b) at $p = 50$ Pa and $P = 50$ W and (c) at $p = 50$ Pa and $P = 20$ W. z denotes the distance from the lower electrode; x denotes the lateral direction. (The geometrical centre of the discharge does not coincide with $x = 0$.)

are obtained by combining the results of 15 linear segments to obtain a complete mapping of the atomic density.

The method of calibration by Rayleigh scattering is not applicable for TALIF measurements because of the inherent nonlinearity of the latter. One possibility is the absolute calibration of the sensitivity of the detection system

(see, e.g. [17]). With an additional measurement of the laser intensity distribution in the scattering volume the absolute density can be inferred, if the two-photon excitation cross section is known [18]. Such a concept is, of course, critically dependent on the careful determination of all quantities of influence.

In specific situations where the degree of dissociation is high ($\sim 20\%$) calibration can be performed on the basis of relative measurements as demonstrated by Dilecce *et al* [19, 20] for atomic oxygen in a supersonic $N_2/O_2/NO$ RF plasma jet.

We describe in the following TALIF calibration methods based on reference measurements.

5. Calibration with a reference source: the flow-tube reactor

The use of a reference source in which a known absolute density of the species under investigation is established is considerably simpler and reduces the calibration process to the comparison of two signal amplitudes recorded under otherwise identical conditions. The so-called flow-tube reactor is a suitable source for many applications. This particle source generates a stationary gas flux of atomic (or molecular) radicals. The absolute radical concentration in the reactor is warranted by gas phase titration techniques [21]. Although the titration method is considered as well established, particularly in chemistry, it is experimentally quite elaborate and complex. We will describe the set-up of our flow-tube reactor, the radical generation, suitable titration schemes and the titration procedure itself.

The scheme of our flow-tube reactor is shown in figure 4. An appropriate molecular gas dissolved in helium or argon (typical dilution 1 : 100) is admitted through the quartz tube (inner diameter 9 mm) placed in the centre of the cylindrical microwave resonator which is cooled by compressed air. Radicals are generated in the microwave discharge (2.45 GHz, 50–100 W) by electron impact dissociation. The resulting gas flux expands into the main flow-tube (inner diameter 19 mm), made of Teflon in order to minimize wall recombination losses (typical rate 50 s^{-1}). The active species in the carrier gas are transported to the detection volume located some decimetre downstream the discharge either a few millimetres below the end of the flow-tube or accessible through holes in the flow-tube on its perimeter. The distance between the discharge and the location of the scattering volume provides sufficient relaxation of the radicals and thermalization of the gas mixture under typical operational conditions (total gas flux ~ 700 sccm at ~ 1000 Pa total pressure). The mean flux velocity is estimated to be $\sim 4\text{ m s}^{-1}$ and the Reynolds number is estimated to be ~ 6 for the helium carrier gas at room temperature (300 K). Since turbulent flux conditions usually occur at Reynolds numbers exceeding 1700, this flow can safely be considered as laminar. Radial gradients of the radical density are negligible over the flow-tube cross section under the conditions stated, as demonstrated in [16].

The titration technique is based on fast chemical reactions between the generated radicals and an appropriate titration gas added to the main gas flux in a well-controlled manner—in

Figure 4. Scheme of the flow-tube reactor.

our case through a narrow Teflon tube orifice in the flow-tube ~ 5 cm upstream the detection volume. Concerning H, O, N and F atoms, the following reactions with rate constants corresponding to room temperature are commonly accepted:

Assuming ideal mixing and complete reaction within the corresponding reaction time each titration gas molecule leads to the consumption of one atomic radical. A linear decrease of the fluorescence signal with increasing flux of the titration gas is expected until the signal amplitude tends to zero. At this so-called titration endpoint the flux ϕ_T of titration gas molecules equals the initial flux of atoms, so that the corresponding atomic density n_A is obtained as

$$n_A = \frac{\phi_T}{\phi_{\text{tot}}} n_{\text{tot}} \approx \frac{\phi_T}{\phi_{\text{tot}}} \frac{p}{k_B T_g} \tag{7}$$

with the total gas flux ϕ_{tot} , the total pressure p , Boltzmann's constant k_B and the gas temperature T_g according to Dalton's law and the ideal gas law.

The kinetics of the titration reaction can be described in more detail according to the rate equation

$$\frac{d}{dt} n_A = \frac{d}{dt} n_T = -k_T n_A n_T = v \frac{d}{dx} n_A = v \frac{d}{dx} n_T \tag{8}$$

with rate constants k_T and the flux velocity $v = x/t$ connecting the space and time coordinates of particles transported from the point of admixture to the point of detection. For equal densities $n_A(0) = n_T(0)$ at the point of admixture we get the particular solution corresponding to the situation at the titration endpoint:

$$n_A(t) = \frac{n_A(0)}{1 + k_T n_A(0) t}. \tag{9}$$

Completion of the reaction and a well-defined titration endpoint obviously require the condition $k_T n_A(0) t \gg 1$ to be fulfilled. In a specific situation with given values for k_T , $n_A(0)$ and v , a compromise has to be found for the reaction length x : the reaction time t must be sufficiently long in view of full completion of the titration reaction but also sufficiently short to avoid detrimental slower secondary or wall reactions.

Direct generation of defined atomic densities is also possible by titration techniques, for example O atoms can be produced via the $\text{N} + \text{NO}$ reaction. In this scheme the generated O density increases linearly with the flux of titration gas and can be quantified according to equation (7) as long as N atoms are in excess.

6. TALIF calibration with noble gases

A technically simple alternative to the flow-tube reference source is the use of a noble gas as a reference with a two-photon resonance close to the transition of the investigated species as shown in figure 5. Xenon is well suited to calibrate atomic oxygen, krypton matches sufficiently well with atomic hydrogen and nitrogen as does argon with atomic fluorine.

Several rules have to be observed, however. The two-photon resonances of the reference gases have to be sufficiently close to those of the species to be absolutely determined so that identical excitation conditions can be assumed. In addition the experimental conditions have to be such that saturation effects like ground state depletion, photoionization out of the excited state, or amplified spontaneous emission (ASE) via the fluorescence channel for both the species under investigation and the noble gas can safely be disregarded. The signal amplitudes will then vary quadratically with the irradiated laser intensity in both cases.

The unknown atomic ground state density $n(X)$ is then related to the reference gas density $n(R)$ by

$$n(X) = \frac{T(R)\eta(R)\sigma^{(2)}(R)a(R)S(X)}{T(X)\eta(X)\sigma^{(2)}(X)a(X)S(R)} n(R) \tag{10}$$

with the fluorescence signal S (integrated over fluorescence and excitation wavelengths and normalized to the squared laser pulse energy), the branching ratio a of the observed fluorescence transition, the transmission T of the detection optics, the detector's quantum efficiency η at the fluorescence wavelength and the two-photon excitation cross section $\sigma^{(2)}$.

Figure 5. Matching two-photon excitation schemes. Transitions are denoted by vacuum wavelength. For the fine structure of atomic oxygen, see figure 12.

Collisional quenching at elevated pressures reduces the branching ratio a_{ik} of a radiative transition $i \rightarrow k$

$$a_{ik} = \frac{A_{ik}}{A_i + Q_i} \quad (11)$$

with the fluorescence rate $A_i = \sum_{k < i} A_{ik} = \tau_i^{-1}$ equivalent to the inverse of the radiative lifetime τ_i and the effective quenching rate $Q_i = \sum_q k_q^i n_q$ expressed by collision partner densities n_q and the corresponding quenching coefficients k_q^i .

Table 1. Radiative lifetimes (ns) and room temperature quenching coefficients ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$) of $\text{O}(3p^3 P_J)$ and $\text{Xe}(6p'[3/2]_2)$ atoms.

	This work	Others
Excited state	Radiative lifetime (ns)	
$\text{O}(3p^3 P_J)$	34.7 ± 1.7	35.1 ± 3.0^a 36.2 ± 0.7^b
$\text{Xe}(6p'[3/2]_2)$	40.8 ± 2.0	40 ± 6^c 37 ± 2^d
Reagent	$\text{O}(3p^3 P_J)$ atoms	
O_2	9.4 ± 0.5	9.3 ± 0.4^a 6.3 ± 0.1^b 8.6 ± 0.2^c
Ar	0.14 ± 0.007	0.25 ± 0.08^a 0.21 ± 0.07^b
He	0.017 ± 0.002	0.07 ± 0.02^a 0.15 ± 0.05^b
	$\text{Xe}(6p'[3/2]_2)$ atoms	
Xe	3.6 ± 0.4	4.2 ± 0.5^c 4.3 ± 0.1^f

^a Ref. [23]. ^b Ref. [29]. ^c Ref. [30]. ^d Ref. [31]. ^e Ref. [32].

^f Ref. [33].

Note that not only the collision partner densities depend on the gas temperature T_g according to the ideal gas law but also the quenching coefficients according to kinetic theory. For a thermal velocity distribution the following relation holds:

$$k_q^i = \sigma_q^i \langle v \rangle = \sigma_q^i \sqrt{\frac{8k_B T_g}{\pi \mu}} \quad (12)$$

with the collision cross section σ_q^i (assumed to be temperature independent), the mean collision velocity $\langle v \rangle$ and the reduced mass μ of the colliders.

The atomic data required to warrant the applicability of the calibration method for atomic oxygen (using the ‘old’ reference scheme—upper left in figure 5) [22] as well as for atomic hydrogen and nitrogen have been provided [23] by measurements at the flow-tube reactor: the radiative lifetimes of the excited states, the corresponding room temperature quenching coefficients for the important gases H_2 , N_2 , O_2 , He, Ar, Kr, Xe and CH_4 as well as the relevant two-photon excitation cross section ratios $\sigma^{(2)}(R)/\sigma^{(2)}(X)$. The resulting values for the cross section ratios are believed to be reliable within 50%. To exclude a systematic error of the titration technique, as an example, we tested the $\text{H} + \text{NO}_2$ titration scheme by an independent diagnostic (section 7). This calibration method has meanwhile found application with other plasma sources [24–27].

Furthermore, we investigated a second TALIF scheme for xenon (upper right in figure 5) which allows a more reliable atomic oxygen density calibration. This reference scheme provides not only spectral matching of the two-photon resonances but also of the fluorescence transitions. Both fluorescence wavelengths can be detected by using one interference filter and a red-sensitive photomultiplier tube (PMT) so that errors in the determination of the detection sensitivity connected with widely spectrally distant detection wavelengths are significantly reduced.

Our measurements yield the values for lifetimes and quenching coefficients listed in table 1, the corresponding

Figure 6. Measured decay rate of the $O(3p\ ^3P_J)$ TALIF signal versus the partial pressure of helium, argon and molecular oxygen.

Stern–Volmer plots are shown in figure 6, as well as a value of 1.9 for the first-time measured two-photon excitation cross section ratio of $\sigma^{(2)}(\text{Xe})/\sum_{J'}\sigma_{J\rightarrow J'}^{(2)}(O)$, where J' is the quantum number of the upper fine structure levels. The accuracy is estimated to be 20% in this case. A detailed presentation of this work is given in [28].

7. Testing the $H + NO_2$ titration by VUV-LIF

In order to critically analyse the widely used $H + NO_2$ titration scheme we generate in our flow-tube reactor hydrogen/deuterium atom densities which are diagnosed by single-photon LIF spectroscopy on the Lyman- α transition. Absolute ground state densities are determined both by titration and by Rayleigh calibration with argon. The latter method is considered to be reliable so that it can serve as a test for the titration technique. The required tunable narrow-bandwidth VUV radiation at $\lambda \sim 121.5$ nm is generated by SARS from LN_2 -cooled molecular hydrogen. The H-Lyman- α transition is completely optically thick for typical operation parameters of the flow-tube reactor. Therefore, we operate the flow-tube reactor with a 0.5% $D_2/99.5\%$ H_2 mixture. This value was specified by the manufacturer (Messer-Griesheim) on the basis of a mass spectroscopic analysis. We now can use the spectrally shifted D-Lyman- α transition ($\Delta\nu = 22.5\text{ cm}^{-1}$) for quantitative measurements under optically thin conditions. We do not know of arguments that the atomic isotope ratio should not be identical to the molecular isotope ratio in view of the similarity of the generation and loss processes in the flow-tube reactor.

The experimental set-up is shown in figure 7; details are described in [34]. Frequency doubled dye laser radiation at $\lambda \sim 223$ nm is focused into a Raman cell where the required VUV radiation is generated by SARS [35]. The ninth anti-Stokes component is singled out by a concave grating from all radiation components leaving the Raman cell. The narrow-bandwidth VUV radiation can be tuned over the Lyman- α transition by scanning the output wavelength of the dye laser.

Figure 8 shows a measured titration curve: the on-resonance D-Lyman- α fluorescence signal as a function

Figure 7. Experimental set-up for testing the $H + NO_2$ titration.

Figure 8. Titration curve (710 sccm He flux, 10 sccm 0.5% D_2/H_2 flux, 930 Pa total pressure and 80 W microwave power) in comparison with the results of the Rayleigh calibration.

of the NO_2 density calculated from the admixed titration gas flux according to equation (7). The extrapolation of the titration endpoint yields a total atomic density of $n_{D+H} = (5.4 \pm 0.6) \times 10^{12}\text{ cm}^{-3}$. The criterion for complete reaction ($k_{TD+H}t$ assumes a value of ~ 9 for a reaction time of ~ 13 ms) can explain the deviations close to the titration endpoint; the measured signal exhibits a flat plateau far beyond the titration endpoint, however. This phenomenon is not understood so far. It has, fortunately, no influence on the result of the titration measurement.

In addition, a second straight line is shown in figure 8: the ordinate intercept is the on-resonance D-Lyman- α fluorescence signal obtained from an independent measurement without NO_2 admixture and the abscissa intercept is the atomic density derived for this measurement on the basis of Rayleigh calibration. This line is almost ideally parallel to the upper section of the titration curve—the difference in the slopes amounts to less than 10%. This indicates that the result of the titration measurement derived on the basis of ideal stoichiometric behaviour is reliable within an error comparable to the uncertainty in the titration endpoint.

From the discrepancy between the ordinate intercepts—the signals obtained without NO_2 admixture—we can conclude that in both cases the flow-tube reactor was producing different

Figure 9. Experimental set-up for TALIF and PICLS. The 338 nm laser beam is present only in the case of PICLS.

absolute atomic densities. Repeating the measurements, we in fact found long-term drifts of the atomic density of the order of 30% occurring on a characteristic time scale of 30–60 min even after hours during which the flow-tube reactor was operated at constant external parameters.

8. Quantitative atomic oxygen density measurements in an RF-excited atmospheric pressure plasma jet by TALIF

The atmospheric pressure plasma jet (APPJ) operates with a high helium flux of $1\text{--}2\text{ m}^3\text{ h}^{-1}$ and small molecular admixtures such as oxygen, fluorine or hydrogen [36]. The plasma is generated by capacitive RF excitation (13.56 MHz, up to 300 W) in the gap between concentric electrodes (10 and 14 mm diameter) over an effective length of ~ 10 cm. The effluent contains high concentrations of radicals $\sim 10^{15}\text{ cm}^{-3}$ at a comparatively low temperature below 100°C at the exit. This is the key property for a variety of applications such as etching of organic films, coating, disinfection and decontamination of temperature sensitive surfaces and possibly *in situ* medical treatment.

The reaction processes in the discharge volume and in the effluent are only partly understood. The concentration of the ‘key-role’ species has been inferred in the past in an indirect manner.

We performed absolute atomic oxygen density measurements in the jet effluent on the basis of a new TALIF calibration scheme in xenon. This scheme (see figure 5) has the advantage over the one previously reported [22, 23] that both the two-photon resonance and the fluorescence wavelength are spectrally close to that of atomic oxygen.

The experimental set-up is shown in figure 9. The jet is operated inside an evacuable chamber in order to have well-defined conditions concerning gas flux and ambient

Figure 10. TALIF signal dependences on laser pulse energy for xenon and atomic oxygen measured in the APPJ effluent.

environment. The plasma source is mounted on a stepper-motor-controlled manipulator that allows three-dimensional movement with respect to the fixed optical diagnostic beams. The detection sensitivities for both fluorescence wavelengths are nearly equal according to manufacturer’s data for the quantum efficiency of the photomultiplier (Burle C31034A) and for the transmission of the interference filter: $(T(\text{Xe})\eta(\text{Xe}))/ (T(\text{O})\eta(\text{O})) = 0.94$, see equation (10). It turned out that the use of a conventional quartz lens ($f = 40$ cm) leads to laser-induced generation of oxygen atoms. In this case a dependence of fluorescence signal versus pump power increasing steeper than quadratic was obtained (not shown). This problem could be removed—as demonstrated in figure 10—by using an $f = 35$ cm cylindrical quartz lens oriented to produce a horizontal focal line in which the power density is sufficiently reduced, so that the signal response

Figure 11. Temperature field and map of absolute atomic oxygen density in the APPJ effluent.

is now nearly quadratic. With this irradiation geometry we have sufficient fluorescence signal amplitude at the expense of reduced spatial resolution in radial direction (~ 2 mm).

At atmospheric pressure collisional quenching is of great importance. The advantage in the present case is that we know the dominant collision partners—helium and molecular oxygen. We have performed lifetime measurements at the flow-tube reactor, e.g. with large helium admixtures up to 8000 Pa, in order to determine the corresponding quenching coefficients as accurately as possible (see figure 6).

The determination of absolute oxygen atomic densities is performed in the following way. After recording a two-dimensional fluorescence map of the jet effluent the calibration measurement with xenon is performed at one spatial position. Individual corrections including collisional quenching and the Boltzmann-fraction of the probed ground state sub-level are then applied to all measurement points according to the temperature field measured by a thermocouple. Vignetting, i.e. shadowing of the detection solid angle by the APPJ nozzle leading to spatially inhomogeneous detection sensitivity, is corrected on basis of a spatially resolved TALIF measurement with the homogeneously distributed noble gas. The temperature field measured and the distribution of atomic oxygen for an RF-power of 150 W, a He flux of $2 \text{ m}^3 \text{ h}^{-1}$, and an O_2 flux of $0.01 \text{ m}^3 \text{ h}^{-1}$ is shown in figure 11.

Detailed information on the APPJ properties and operation as well as details on the fluorescence measurements will be communicated in a separate article [28].

9. Extension to the case of arbitrary quenchers: photoionization-controlled TALIF

Photoionization-controlled loss spectroscopy (PICLS) was proposed by Lucht *et al* [37] as a quenching-independent fluorescence diagnostic method for the measurement of relative density distributions. The basic idea is to introduce an additional controllable space independent loss mechanism—photoionization—that can be made dominant compared to collisional quenching (and spontaneous emission).

This concept was applied by Salmon and Laurendeau [38] for investigating the atomic hydrogen distribution in a flame at 20 Torr. By overlapping two focused laser beams—one for two-photon excitation with $\lambda = 205$ nm and the other for photoionization at $\lambda = 550$ nm with a peak power of 2.3 MW and a three times larger waist of $850 \mu\text{m}$ —the authors achieved a photoionization rate about 10 times higher than the decay rate. They were, therefore, able to obtain relative density distributions without knowledge of the spatially varying de-excitation efficiency.

Following our earlier proposal [39] we present here an extension of the PICLS concept that allows us to determine effective quenching rates by measuring the fluorescence signal decrease induced by a controlled photoionization loss, and to infer, consequently, absolute particle densities. It is sufficient to generate an ionization loss of the same order as the quenching loss. The fluorescence output is then reduced by less than an order of magnitude. We use, in order to demonstrate this novel scheme, a particle source for which we know the quenching rate from measured quenching coefficients, so that we have a basis for comparison. The flow-tube reactor for the generation of O atoms is well suited to this purpose. It can be operated in the ‘collisionless’ standard mode (O_2 flux 5 sccm, He flux 700 sccm, total pressure 1000 Pa, and O atom density $\sim 2 \times 10^{14} \text{ cm}^{-3}$ determined by titration with NO_2) or in a ‘collision-dominated’ mode with an additional O_2 flux of 700 sccm admixed through the titration gas tube. In this case the quenching rate of the excited O atoms by collisions with the O_2 molecules amounts to 277 MHz.

The experimental set-up is shown in figure 9. The flow-tube reactor is mounted in the centre of the evacuable chamber. The laser system provides frequency tripled dye laser radiation at $\lambda = 226$ nm for TALIF and frequency doubled radiation at $\lambda = 338$ nm for photoionization, according to the level scheme shown in figure 12.

The 338 nm beam is directed through a delay line providing synchronization of both laser pulses of nearly equal duration $T_p \sim 5$ ns. The collimated laser beams are overlapped by a dichroic mirror and are then focused by a spherical Suprasil lens ($f_{\text{vis}} = 45$ cm). The 226 nm focus is located

Figure 12. Simplified energy level scheme of atomic oxygen (energies given in cm^{-1} and J -values ordered from lowest to highest energy).

Figure 13. Photoionization-controlled TALIF measurements. For the definition of the quantities involved see text.

on the axis of the flow-tube exit whereas the 338 nm focus is located $\sim 3 \text{ cm}$ behind due to chromatic aberration. This ensures that the photoionization rate is nearly constant over the fluorescence volume. Its imaged longitudinal dimension is limited by the photocathode size to 1 cm . The laser radiation with $\lambda = 226 \text{ nm}$ is sufficiently attenuated to avoid saturation of the two-photon excitation process.

In each mode of operation of the flow-tube reactor the on-resonance fluorescence signal is measured as a function of the photoionizing laser pulse energy. Figure 13 shows the corresponding ratios Y of the fluorescence signals obtained with and without photoionization.

The measurement is analysed on the basis of a simple model. In case of unsaturated two-photon excitation the change of the excited state population n_3 is given by

$$\frac{d}{dt}n_3 = R_{13}n_1 - (A_3 + Q_3 + \Gamma_3)n_3 \quad (13)$$

with the excitation rate R_{13} , the ground state population n_1 , the fluorescence rate A_3 (including all spontaneous transitions from level 3), the quenching rate Q_3 and the photoionization rate Γ_3 . Two assumptions concerning the ionizing pulse are made: the photoionization rate is constant during the duration T_p of the excitation pulse and zero before and after. It is also assumed constant over the effective two-photon excitation volume. The exciting pulse may have, in contrast, an arbitrary temporal and spatial shape. The number of fluorescence photons per pulse $N_F(\Gamma_3) = A_{32} \int n_3 dt dV$ can then be expressed explicitly (by analytical integration of the above rate equation, not shown) in addition to the corresponding ratio $Y = N_F(\Gamma_3)/N_F(0)$ of the fluorescence signals in the cases with and without photoionization under otherwise identical conditions:

$$Y = \left\{ \frac{A_3^*}{A_3^* + \Gamma_3} \right\} \left[1 + \frac{\Gamma_3 \exp(-(A_3^* + \Gamma_3)T_p)}{A_3^* (A_3^* + \Gamma_3)T_p} \right] \quad (14)$$

with the overall de-excitation rate $A_3^* = A_3 + Q_3$. The term in curly brackets represents the solution for stationary conditions ($T_p \rightarrow \infty$) and the term in square brackets the corresponding correction factor accounting for the imperfect temporal overlap of photoionization and fluorescence in case of finite pulse duration.

Note that the two-photon excitation rate scales with the square of the local laser irradiance, so that in our situation the two-photon exciting pulse is embedded within the photoionizing pulse both temporally and spatially. The real time shape of the photoionizing laser pulse is, of course, not ideally rectangular, so that the photoionization rate (as defined in the model) is an effective quantity that is obtained by the measurement in the collisionless mode.

One can evaluate the earlier expression for $T_p = 5 \text{ ns}$ and $A_3 = 28.8 \text{ MHz}$ for different values of the photoionization rate Γ_3 . The data set obtained for the collisionless mode ($Q_3 \approx 0$) can be scaled to yield a best fit to the experimental points corresponding to this case. Once this scaling established, one can vary the quenching rate Q_3 until the best fit to the experimental points for the collision-dominated mode is obtained. The best agreement is obtained for $Q_3 = 250 \pm 32 \text{ MHz}$. This value obtained by PICLS compares favourably with the value of 277 MHz calculated on the basis of quenching coefficients (table 1).

This novel scheme has the great advantage to allow local absolute measurements with conventional nanosecond laser systems in collision-dominated situations without information on the quenching processes required. We note that the radiation intensities required for photoionization are quite substantial, and possible effects (e.g. photodissociation) on measured radical densities in plasma conditions are yet to be determined. If in a specific situation additional atoms are generated, one can take recourse to alternative excitation schemes—see figure 14 for atomic oxygen [40]. The photon energies necessary for photoionization can be substantially reduced if two-photon

Figure 14. Alternative two-photon excitation schemes of atomic oxygen with corresponding upper-limit-wavelengths λ_{ion} for photoionization out of the excited state.

excitation is performed with shorter wavelengths (as, e.g., easily available by SARS).

We feel that this issue bears interesting diagnostic possibilities for plasmas at elevated pressures. Many alternative schemes seem possible—among those also with excitation into bound states close to the ionization limit.

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