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Picosecond two-photon absorption laser induced fluorescence (ps-TALIF) in krypton: the role of photoionization on the density depletion of the fluorescing state Kr $5p^{\prime}[3/2]_2$

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Abstract

The present study focuses on the application of a picosecond (ps) TALIF technique in krypton (Kr) at variable pressure (0.1–10 mbar). The laser intensity (I , units $\text{W}\cdot\text{cm}^{-2}$) is tuned between 1 and 480 $\text{MW}\cdot\text{cm}^{-2}$, and the depletion of the density of the Kr $5p^{\prime}[3/2]_2$ fluorescing state through photoionization (PIN) and amplified stimulated emission (ASE) is investigated. This is done by combining TALIF experiments with a simple 0D numerical model. We demonstrate that for a gas pressure of 3 mbar and $15 < I \leq 480 \text{ MW}\cdot\text{cm}^{-2}$, a saturated fluorescence signal is obtained, which is largely attributed to PIN, ASE being negligible. Also, a broadening of the two-photon absorption line (i.e. $4p^6 \ ^1S_0 \rightarrow 5p^{\prime}[3/2]_2$) is recorded due to the production of charged species through PIN, inducing a Stark effect. For $I \leq 15 \text{ MW}\cdot\text{cm}^{-2}$, though, PIN is significantly limited, the absorption line is noticeably narrowed, and the quadratic dependence of the TALIF signal intensity versus the laser energy is obtained. Thus, in this case, the investigated Kr TALIF scheme, using the $5p^{\prime}[3/2]_2 \rightarrow 5s[3/2]_1$ fluorescence channel, can be used for calibration purposes in ps-TALIF experiments. These results are of interest for fundamental research since most ps-TALIF studies performed in Kr do not investigate in detail the role of PIN and ASE on the depletion of the Kr $5p^{\prime}[3/2]_2$ state density. Moreover, this work contributes to the development of ps-TALIF for determining absolute densities and quenching coefficients of H and N atoms in plasmas. The use of ps-TALIF can allow sub-ns measurements of quenching rates that are necessary for absolute atomic densities determination in atmospheric pressure plasmas. Thus, the present study is linked to many experimental works focused on plasma physics and applications. In fact, the investigation of the application of ps-TALIF in Kr and the definition of regimes where the TALIF signal intensity scales quadratically with the laser energy is essential to calibrate H and N atom densities in reactive plasmas.

Keywords: picosecond, TALIF, ultrafast laser, laser diagnostics, krypton.

1. Introduction

The implementation of fast (nanosecond–ns) and ultrafast (picosecond–ps and femtosecond–fs) optical diagnostics for the study of ionized gases is nowadays among the principal research axes of different research groups [1-16]. Such diagnostics aim for the precise identification and fine tuning of essential physical quantities, leading to a better understanding of transient phenomena in reactive plasmas. Typical examples refer to the use of (i) two-photon absorption laser induced fluorescence (TALIF) to obtain atomic densities [1,5,7–14], (ii) electric-field-induced second harmonic generation to infer electric field

42 dynamics [1,6,10], and (iii) Thomson scattering to access electron density and temperature [15,16]. These
43 measurements can help in the development of diverse plasma-based applications, e.g. synthesis of
44 advanced nanomaterials [17,18], biomedical [19,20], public security [21], and environmental applications
45 [22,23], where the above plasma quantities can play a key role.

46 Particularly, TALIF is a reliable technique that has been extensively applied over the last decades
47 to probe reactive atoms (mostly H, N, and O) in collisional media [1]. TALIF offers high sensitivity with
48 a very good spatial and temporal resolution. The latter is defined by the duration of the laser pulse, which
49 can be either in the ns [7–10,24,25], ps [14,26–28] or fs [11–13,29] time-scale. In general, ns-TALIF is
50 consistent for measurements at gas pressures lower than 10 mbar [30]. However, with increasing gas
51 pressure, the collisional quenching can become the major loss mechanism of excited states of interest
52 depending on the species and the quencher nature [7]. For instance, the quenching time of laser-excited H
53 atoms in flames falls well below ns at atmospheric pressure [27], which is shorter than the pulse duration
54 of ns lasers (typically few ns [7–10,24,25]). In this case, to infer the quenching rate of species from the
55 fluorescence signal, the laser pulse duration must be much shorter than the TALIF decay time. Otherwise,
56 more complex model-based signal corrections need to be performed [8,31]. For accurate measurements at
57 pressures close to the atmospheric (or even higher [13]), a better approach would be to use ultrafast lasers.
58 These can deliver (i) sufficient peak intensities (I , units $\text{W}\cdot\text{cm}^{-2}$) to achieve the necessary two-photon
59 transitions, and (ii) pulse widths down to the ps and fs timescales.

60 The use of ultrafast lasers for probing reactive species in flames has been already reported in the
61 past decades in interesting works of different groups [1,26–28,32]. However, the implementation of
62 mostly ps- [14], and fs-TALIF [11–13,29] for quench-free measurements in collisional plasmas is very
63 recent. In ps/fs TALIF, the relatively high peak intensities of the laser pulses used can lead to saturated
64 fluorescence regimes [5]. This is due to a substantial depletion of the densities of the laser-excited states
65 through photoionization (PIN) and/or amplified stimulated emission (ASE) [1,5,26–28,33]. These
66 processes must be studied in detail so as to be carefully avoided when absolute density measurements are
67 sought from TALIF signals.

68 Such an understanding is particularly needed in the case of ps-TALIF in krypton. This rare gas
69 has been well-utilized as a calibrating species for the measurement of H- and N-atom densities in plasmas
70 with ns-TALIF [7–10,25,30]. Non-saturating regimes with a quadratic dependence between the TALIF
71 signal intensity and the laser energy (E_{Laser}) were reported [8,10,25,30]. Within these regimes, the kinetic
72 of the fluorescing state is dominated by the processes involved in the TALIF scheme, and the
73 fluorescence signal intensity is proportional to the ground-state Kr atom density. However, the use of Kr
74 gas in ps-TALIF for studies of reactive plasmas is very recent [14,34], and requires further assessment of
75 the conditions where Kr atom may be still considered for calibration purposes.

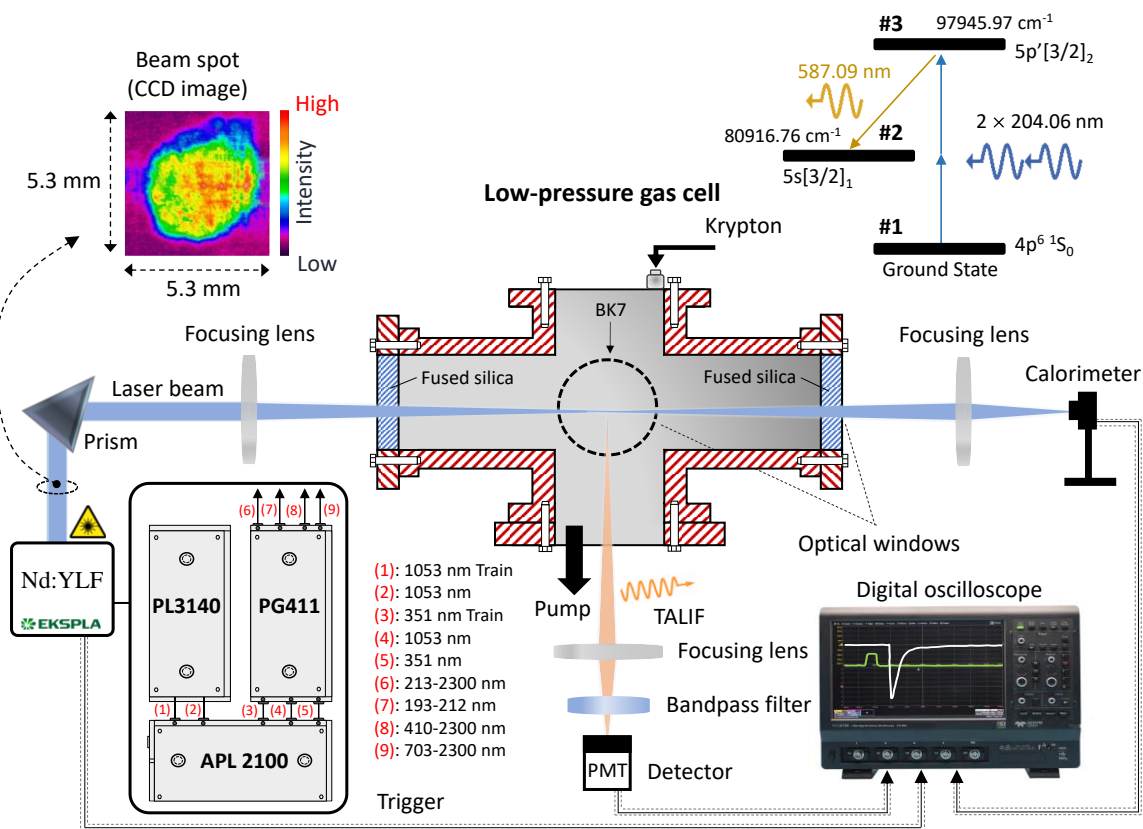
76 Based on the above, the present study focuses on the fundamental investigation of the relative
 77 predominance of the processes involved in the ps-TALIF scheme of Kr atom. In particular, the critical
 78 role of PIN on the depletion of the Kr $5p^1[3/2]_2$ fluorescing state at high E_{Laser} , as well as conditions
 79 leading to a minor PIN effect are demonstrated. The later also allow for the quadratic dependence on
 80 E_{Laser} of the TALIF-signal intensity to be ensured. Thus, besides being a fundamental investigation, our
 81 work contributes to the development of ps-TALIF in Kr gas to calibrate measurements of H- and N-atom
 82 densities in reactive plasmas.

83

84 2. Experimental setup

85 **Fig. 1** illustrates the experimental setup used to perform ps-TALIF studies in krypton gas (Air liquide,
 86 99.998% purity). The gas was introduced in a low-pressure gas cell, which offered optical accesses
 87 through two fused silica (for the laser) and one BK7 (for the TALIF) windows, suitable for TALIF
 88 diagnostics in the UV–NIR range. Besides, it allowed for the precise control ($\pm 5\%$) of the Kr gas pressure
 89 (P_{Kr}) between 0.1 and 10 mbar using a MKS Baratron[®] capacitance manometer (pressure range: 0.01–10
 90 mbar).

91



92 **Figure 1.** Experimental setup of ps-TALIF in Kr gas. The two-photon excitation scheme and the
 93 investigated fluorescence transition are given at the top right. The laser beam at the output (7) of PG411
 94 (EKSPLA®) is fairly homogeneous as shown at the top left (measured with a CCD camera beam-profiler).

95 In the following parts of the paper, one will note the ground-state of Kr ($4p^6\ ^1S_0$) as level #1, the
 96 laser-excited state Kr $5p\ [3/2]_2$ as level #3, and the de-excitation state Kr $5s\ [3/2]_1$ as level #2. To induce a
 97 two-photon excitation from level #1 to level #3, and analyze the subsequent fluorescence decay to level
 98 #2 (i.e. #3→#2 transition at $\lambda=587.09$ nm, as that used in [9], see **Fig. 1**), an ultrafast laser from
 99 EKSPLA® was used. It was composed of three units: i) a Nd:YLF pump laser (PL3140, 50 mJ max
 100 output, ~10 ps pulse width) selectively producing a fundamental output of 1053 nm in two modes: pulse
 101 train or 5 Hz repetition rate, ii) a harmonic generator (APL2100, 50 mJ max output, <15 ps pulse width)
 102 for fundamental frequency doubling (527 nm) and tripling (351 nm), and iii) a solid state optical
 103 parametric generator (PG411, 2 mJ max output, 10 ps pulse width, ~4 cm^{-1} linewidth as it is assessed by
 104 the manufacturer) generating laser pulses between 193 and 2300 nm at different tuning ranges ((6)–(9)).
 105 For the present study, the laser pulse repetition rate was kept at 5 Hz (output (2) of PL3140). The suitable
 106 experimental wavelength for the two-photon excitation of ground-state Kr in our case was $\lambda_{c_{Kr}}=204.06$
 107 nm ($\tilde{\nu}_{c_{Kr}}=1/\lambda_{c_{Kr}}=49005.19\ \text{cm}^{-1}$) and was tuned within the range 193–212 nm of the output (7) of PG411.
 108 The laser spot after the output (7) of PG411 was fairly homogeneous with a diameter of less than 5 mm
 109 (an indicative laser beam profile, using a linear color scale to represent the intensity, is shown in the upper
 110 left side of **Fig. 1**). Using a series of prisms, the laser light was guided to a lens (35 cm focal length)
 111 focusing it at the center of the gas cell. Then it was collected with a second identical lens, as shown in
 112 **Fig. 1**. A calorimeter (Coherent J-10MB-LE, 11630 V/J) was placed after the second lens to measure the
 113 laser energy per pulse (the energy measurement was not affected by the presence of Kr gas in the gas
 114 cell). Its output was recorded with a high-definition oscilloscope (Lecroy HDO6104, 1 GHz, 2.5 Gs/s).
 115 TALIF was collected at 90° angle with respect to the laser beam by using a third focusing lens, and a
 116 bandpass filter (Semrock FF02-586/15-25, center wavelength: 586 nm, bandwidth: 20.5 nm) to eliminate
 117 any stray light. Then, it was focused to the entrance slit (500 μm width) of a fast photomultiplier tube
 118 (PMT, Hamamatsu R9110) and stored in the same oscilloscope. It should be noted that the sensitivity of
 119 the PMT is maximal between 500 and 600 nm. That is why we chose to perform TALIF studies on the Kr
 120 I transition at $\lambda=587.09$ nm instead of using more classic lines (e.g., that at 826.3 nm [7]). Also, the
 121 corresponding recorded fluorescence with the PMT was less prone to perturbations from other Kr I lines
 122 as it is shown further in the text. The features of the TALIF signal were studied for E_{Laser} values ranging
 123 between 0.1 and 13 $\mu\text{J}/\text{pulse}$, corresponding to $I=4$ and 52 $\text{MW}\cdot\text{cm}^{-2}$ ($I=E_{\text{Laser}}/(D \times \tau_L)$), respectively,
 124 for a beam diameter (D) of $500\pm 100\ \mu\text{m}$ at the collection point, and $\tau_L=10$ ps (laser pulse duration of

125 PG411 indicated by the manufacturer; the precise measurement of the width of the laser pulse is planned
 126 for a later study by our group using a streak camera). The variation of E_{Laser} was achieved by combining
 127 different neutral density filters placed after the output (7) of PG411. The shot-to-shot energy fluctuation
 128 was $<10\%$ (measured over 1000 laser pulses during different days, the room's temperature being
 129 controlled *via* air conditioning). The room temperature was equal to $20\text{ }^\circ\text{C}$ which was also assumed to be
 130 the temperature of Kr in the gas cell.

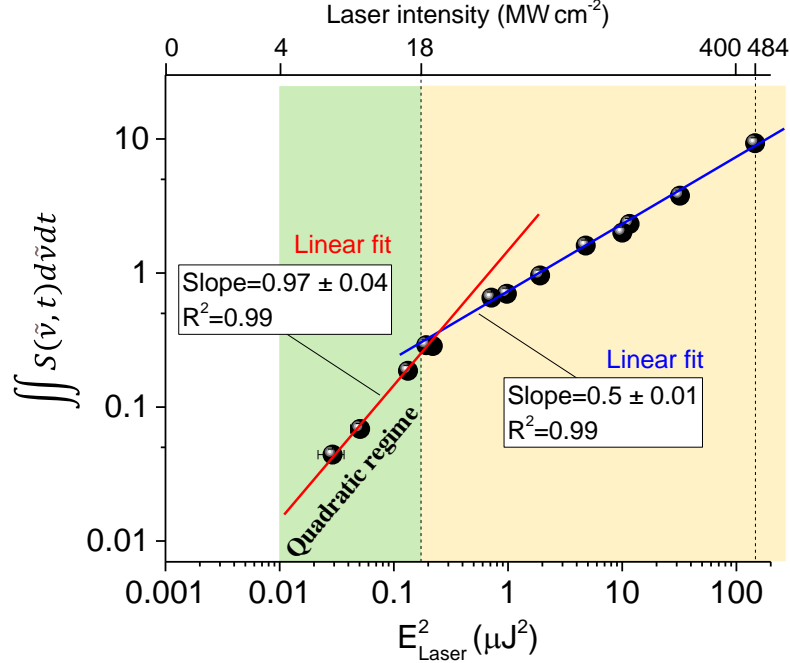
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132 3. Results and discussion

133 The spectrally- and temporally-integrated TALIF signal ($\iint S(\tilde{\nu}, t) d\tilde{\nu} dt = S_{\tilde{\nu}t}$) depends on the PMT
 134 quantum efficiency (η), the transmission of the optics used (T), the solid angle of detection ($\Delta\Omega$), the
 135 fluorescence yield ($a_{32} = A_{32}/(A_3 + Q_3)$), where A_{32} is the Einstein coefficient for the fluorescence
 136 channel $\#3 \rightarrow \#2$, A_3 is the sum of Einstein coefficients for all radiative channels from level $\#3$, and Q_3 is
 137 the quenching rate of level $\#3$, the Kr-atom density (n_{Kr}), the photon statistic factor ($G^{(2)}$), the two-
 138 photon absorption cross-section ($\sigma^{(2)}$), the time-integrated squared laser intensity ($\int I^2 dt \propto E_{\text{Laser}}^2$), the
 139 squared laser photon energy ($(h\nu)^2$), and the observed excitation volume (V), as follows [7]:

$$140 \quad S_{\tilde{\nu}t} = \eta T \frac{\Delta\Omega}{4\pi} a_{32} n_{\text{Kr}} G^{(2)} \frac{\sigma^{(2)}}{(h\nu)^2} V \int I^2 dt \rightarrow S_{\tilde{\nu}t} \propto E_{\text{Laser}}^2 \quad (1)$$

141 This is experimentally evaluated by capturing TALIF signals at different laser frequencies around the
 142 peak two-photon excitation frequency, followed by temporal and spectral integration. In the present work,
 143 the spectral profile of the two-photon absorption line was acquired over a laser-wavelength range of 250
 144 pm with a step of 2 pm (see later in the text). Based on eq. (1), for reliable density measurements, $S_{\tilde{\nu}t}$
 145 should exhibit a quadratic dependence on E_{Laser} (quadratic regime) [7]. Thus, a linear regression of the
 146 experimental data on $S_{\tilde{\nu}t}$ versus E_{Laser}^2 should give a slope of 1. This is plotted in **Fig. 2**. For $E_{\text{Laser}} < 0.45$
 147 $\mu\text{J/pulse}$ (i.e. $I < 18\text{ MW.cm}^{-2}$, green zone), a slope of 0.97 ± 0.04 is obtained (red line), validating the
 148 quadratic regime. However, for $I \geq 18\text{ MW.cm}^{-2}$, a slope of 0.5 ± 0.01 is found (blue line within the yellow
 149 zone). This implies that other physical processes are involved in the depletion of the fluorescing state,
 150 namely PIN and possibly ASE [5,27]. Thus, eq. (1) is not valid for $I \geq 18\text{ MW.cm}^{-2}$.



151

152 **Figure 2.** $S_{\tilde{\nu}t} = \iint S(\tilde{\nu}, t) d\tilde{\nu} dt$ versus E_{Laser}^2 for $I < 500 \text{ MW}\cdot\text{cm}^{-2}$ (top) and $E_{\text{Laser}} = 0.1\text{--}13 \text{ }\mu\text{J/pulse}$
 153 (bottom) at $P_{\text{Kr}} = 3 \text{ mbar}$. The green and yellow zones indicate quadratic and saturation regimes,
 154 respectively.

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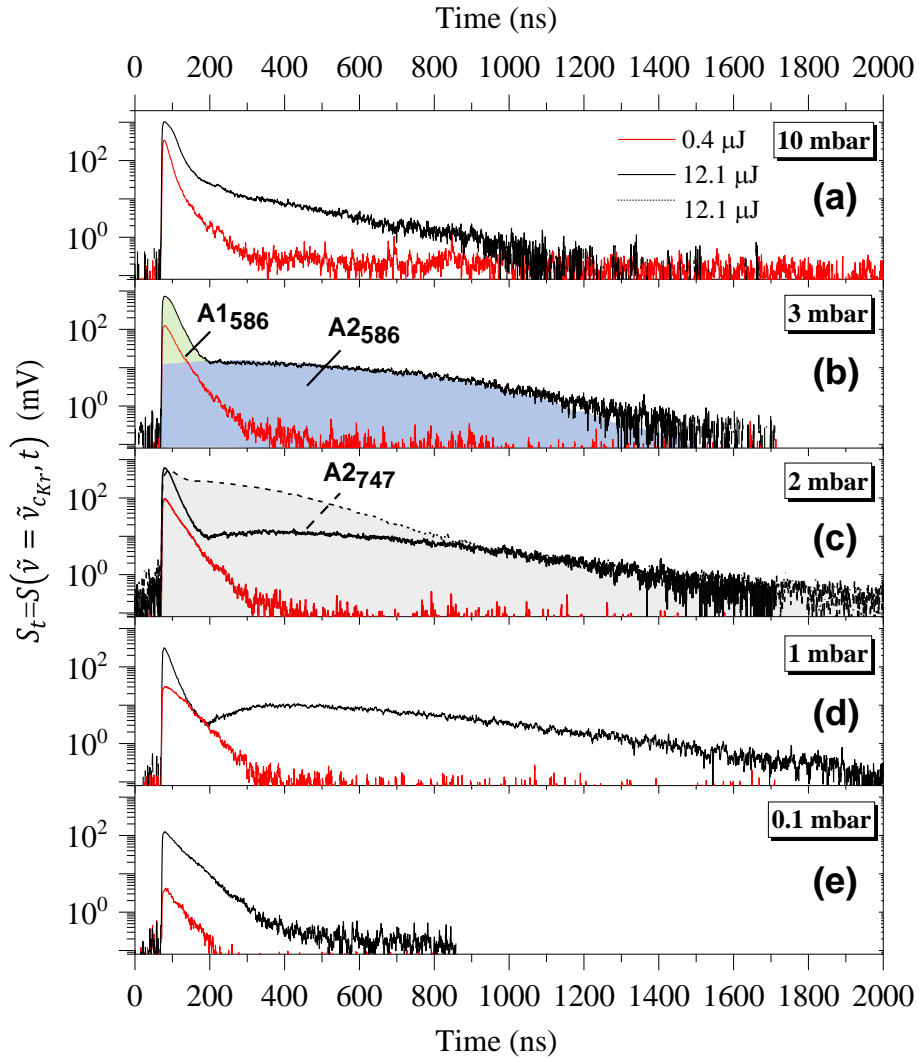
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When using ultrafast TALIF to probe atomic densities, the validity of eq. (1) (quadratic regime) is ensured if two conditions are satisfied [5]: (c1) the depletion of an atomic ground state (i) by the laser is negligible; to achieve that, τ_L must be much lower than the characteristic time of the two-photon absorption process, $1/W_{ij}$, where W_{ij} is the frequency of the two-photon excitation from the ground to an excited state (j). This translates to $W_{ij} \times \tau_L \ll 1$. (c2) the depletion rate of the laser-excited state (level #3) through PIN and ASE must be much lower than A_3 and Q_3 .

In Fig. 2, the above two conditions should be valid for $I < 18 \text{ MW}\cdot\text{cm}^{-2}$, where the quadratic regime is obtained (green zone). Similarly, in [14,34], the quadratic regime was clearly achieved when using ps-TALIF (30 ps laser pulses) in Kr gas. However, in those studies, Kr gas was mostly used to calibrate absolute density measurements of H atoms in plasma jets. Concerning Kr atoms, they were laser-excited at $E_{\text{Laser}} = 0.28 \text{ }\mu\text{J/pulse}$, which was well-below the TALIF saturation limit. Thus, for a laser-beam diameter of $\sim 250 \text{ }\mu\text{m}$ (given in [34]) at the TALIF collection point, $I_{[14,34]} \cong 8.2 \text{ MW}\cdot\text{cm}^{-2}$, which is consistent with our finding above. Our study here aims further to analyze the processes leading to the depletion of the fluorescing state. Quadratic regimes have been also achieved when using fs-TALIF in Kr gas by constructing laser sheets so as to significantly decrease I [12,35]. Therefore, our work and studies [12,14,34,35], contribute to the development of ultrafast TALIF diagnostics for determining absolute densities and quenching coefficients of H and N atoms in reactive plasmas.

172 For $I \geq 18 \text{ MW.cm}^{-2}$ in **Fig. 2** (yellow zone), a lower slope (~ 0.5) of the linear regression is
 173 revealed, indicating a non-quadratic dependence on E_{Laser} of the TALIF signal intensity. To understand
 174 this behavior, the validity of the above conditions (c1) and (c2) must be checked. For condition (c1) we
 175 have $W_{ij} = \frac{\sigma_{Kr}^{(2)} g(v_0) G^{(2)} I^2}{(hc)^2 \tilde{\nu}_{Kr}^2}$ [5] and $\tau_L = 10 \text{ ps}$. The value of $\sigma_{Kr}^{(2)}$, inferred from $\sigma_{Kr}^{(2)}/\sigma_H^{(2)} = 0.62$ [7] (with
 176 50% uncertainty) and $\sigma_H^{(2)} = 1.77 \times 10^{-35} \text{ cm}^4$ [5,36], is of $1.09 \times 10^{-35} \text{ cm}^4$. For $I_{\text{max}} = 484 \text{ MW.cm}^{-2}$
 177 ($E_{\text{Laser}} = 12.1 \text{ }\mu\text{J/pulse}$), i.e. the highest laser intensity in **Fig. 2**, and $g(v_0)G^{(2)} \approx \frac{0.94}{\sim 4 \text{ cm}^{-1}} \times 2 \approx 1.56 \times 10^{-11} \text{ s}$
 178 (considering a Gaussian absorption-line profile dominated by the laser linewidth [5]), $W_{ij} \cong 4.19 \times 10^7 \text{ s}^{-1}$
 179 and, thus, $W_{ij} \times \tau_L \cong 4.19 \times 10^{-4} \ll 1$, satisfying the condition (c1) within the yellow zone. Thus, the
 180 condition (c2) regarding PIN and ASE should not be valid in the yellow zone, which is checked below by
 181 analyzing the time-decay of fluorescence signals.

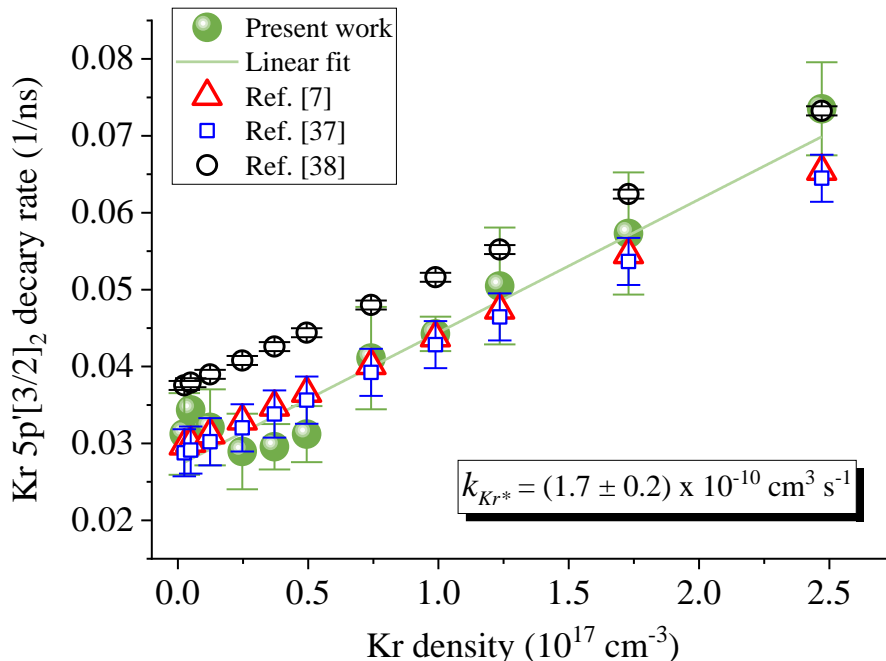


183 **Figure 3.** PMT signals $S_t = S(\tilde{\nu} = \tilde{\nu}_{c_{Kr}}, t)$ for $P_{Kr} = 0.1\text{--}10$ mbar at low ($0.4 \mu\text{J/pulse}$ – solid red) and high
 184 ($12.1 \mu\text{J/pulse}$ – solid black) E_{Laser} , recorded with a 586 nm-centred interference filter. Black solid signals
 185 are saturated consisting of two areas: A_{1586} and A_{2586} (indicated in (b) for $P_{Kr} = 3$ mbar). It should be noted
 186 that A_{2586} is clearly observed in (a)-(d), but it is also present in (e) for the lower P_{Kr} studied, i.e. 0.1 mbar.
 187 In (c), the black dashed signal, which is essentially defined by the grey area A_{2747} (A_{1747} being very
 188 weak), is recorded when using a 747 nm-centred interference filter.

189 The impact of P_{Kr} and E_{Laser} on the experimentally-obtained PMT signal $S_t = S(\tilde{\nu} = \tilde{\nu}_{c_{Kr}}, t)$ is
 190 shown in **Fig. 3**. The solid red and black lines refer to an S_t recorded using a 586 nm-centred interference
 191 filter for the corresponding E_{Laser} values: i) $0.4 \mu\text{J/pulse}$, i.e. within the quadratic regime (at $P_{Kr} = 3$ mbar),
 192 and ii) $12.1 \mu\text{J/pulse}$, which is the upper E_{Laser} limit studied outside the quadratic regime (see **Fig. 2**). For
 193 $E_{Laser} \leq 0.4 \mu\text{J/pulse}$ and P_{Kr} up to 10 mbar in **Fig. 3**, the decaying part of the TALIF (solid red) follows an
 194 exponential variation with a time-constant τ . Then, the total decay rates of the excited state ($1/\tau$) are in
 195 fact the sum of the natural (radiative) decay rate ($1/\tau_{Kr^*}$) and the collisional quenching rate of Kr
 196 $5p^{[3/2]}_2$ such that

$$197 \quad \frac{1}{\tau} = \frac{1}{\tau_{Kr^*}} + k_{Kr^*} n_{Kr} \quad (2)$$

198 Where k_{Kr^*} and n_{Kr} are the collisional quenching rate and the Kr atom density, respectively [7]. τ_{Kr^*} was
 199 evaluated for $E_{Laser} \leq 0.4 \mu\text{J/pulse}$, and $P_{Kr} = 0.1\text{--}0.2$ mbar, for which the collisional quenching was
 200 negligible. It was found to be of 34.6 ± 2.3 ns, which is consistent with the values of 34.1 ns, 35.4 ± 2.7 ns,
 201 and 33.6 ± 1.1 ns reported in [7,12,37]. Further, from the Stern-Volmer plot [7], i.e. plotting of $\frac{1}{\tau}$ versus
 202 n_{Kr} in the pressure range 0.1–10 mbar, k_{Kr^*} was found to be of $1.7 \pm 0.2 \times 10^{10} \text{ cm}^3 \text{ s}^{-1}$, which is in the
 203 range of values reported in the literature [7,12,37,38]. This is illustrated in **Fig. 4**, where our results
 204 (green) are compared to those from references [7] (red), [37] (blue), and [38] (black).

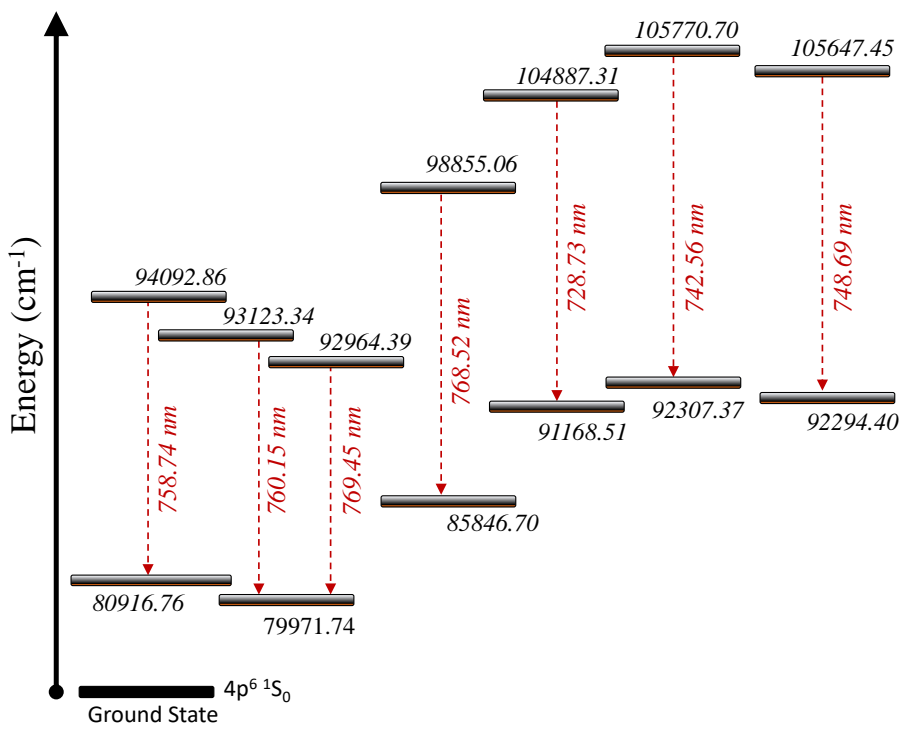


205
 206 **Figure 4.** Stern–Volmer plots showing the decay rate of Kr 5p'[3/2]₂ fluorescing state against the krypton
 207 density in the gas cell. The results of the present work are given in green and compared to other published
 208 studies in the literature [7,37,38].

209 Interestingly, for temporal signals in the saturated regime ($E_{\text{Laser}}=12.1 \mu\text{J/pulse}$ and $P_{\text{Kr}} \geq 0.1 \text{ mbar}$
 210 in **Fig. 3**), two distinct signal-decay areas are revealed: A_{1586} and A_{2586} , as indicated in **Fig. 3b**. The
 211 transition from A_{1586} to A_{2586} is observed at around 200-300 ns almost independently of P_{Kr} . Indeed,
 212 A_{2586} is still present even at $P_{\text{Kr}}=0.1 \text{ mbar}$ (**Fig. 3(e)**). However, it is less significant than in the case of
 213 higher pressures because reactions (3) and (4) (see below) are less important at 0.1 mbar as compared to
 214 higher pressures. A_{1586} has a short duration and corresponds to the decay of Kr 5p'[3/2]₂ laser-excited
 215 state, which is characterized by an exponential function with a time constant τ . On the other hand, A_{2586} ,
 216 which forms almost immediately after the laser pulse (see below for justification), and is responsible for
 217 the inflection point at around 200-300 ns, has a larger duration depending on the gas pressure. This
 218 suggests that there could be additional mechanisms leading to the formation of different excited states of
 219 Kr atom. In fact, the 586 nm-centred interference filter used in this work could capture only three Kr I
 220 emission lines, which emanate from different excited states of Kr atom, i.e. 586.68, 587.09, and 587.99
 221 nm, as also reported in [39]. That said, it would be impossible to discriminate with this filter the different
 222 excited states that could lead to the observed emissions corresponding to the area A_{2586} .

223 In order to verify if other excited states of Kr are produced, emission was recorded using a
 224 broader filter (Semrock FF01-747/33-25, centered at 747 nm, 41.1 nm bandwidth). With this filter, the
 225 emissions recorded do not emanate from Kr 5p'[3/2]₂ and would consist of seven Kr I lines, i.e. 728.73,

226 742.56, 748.69, 758.74, 760.15, 768.52, and 769.45 nm, exhibiting much larger relative intensities than
 227 the three previous lines [39]. Those seven transitions are illustrated in Fig. 5. In fact, temporal signals
 228 captured using this filter were similar to those recorded with the previous one, where a single exponential
 229 decay region (i.e. only A1₇₄₇) was always observed for laser energies within the quadratic regime (i.e.
 230 $E_{\text{Laser}} \leq 0.4 \mu\text{J/pulse}$ for $P_{\text{Kr}} = 3 \text{ mbar}$), while for the saturated regime two distinct areas were produced:
 231 A1₇₄₇ over very short timescales, and A2₇₄₇ over long timescales (indicated in Fig. 3c, black dashed line at
 232 $P_{\text{Kr}} = 2 \text{ mbar}$). However, A2₇₄₇ is seen to be much more predominant when compared to A1₇₄₇. These
 233 signals became stronger with krypton pressure and laser energy, especially in the saturated regime.



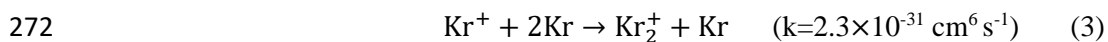
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 235 **Figure 5.** Krypton energy level diagram illustrating seven Kr I emissions (red dashed arrows) and their
 236 corresponding wavelengths recorded when using a 747 nm-centred interference filter. The energies of the
 237 upper and lower Kr I levels are taken from NIST [40] and they are given in units of cm⁻¹. The population
 238 of the upper Kr I levels is due to radiative recombination of Kr₂⁺ ions.

239 Kr-atom emission that is not exclusively attributed to the relaxation of the fluorescing state Kr
 240 $5p^{\prime}[3/2]_2$ starts almost immediately after the laser pulse, and lasts for a relatively long time as compared
 241 to the lifetime of Kr $5p^{\prime}[3/2]_2$ state. Its presence suggests the existence of additional emission
 242 mechanisms. These mechanisms are rapidly induced by the laser pulse and remain active over almost 1
 243 μs . It means that these mechanisms are able to produce several emitting excited species over almost 1 μs
 244 time-scale.

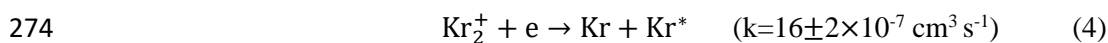
245 Furthermore, the presence of the secondary decay region (A₂₅₈₆ or A₂₇₄₇) for signals recorded in
 246 the saturated regime using both interference filters, clearly points towards the existence of a secondary
 247 much slower chain of reactions leading to the formation of different excited states of krypton. One of the
 248 likely mechanisms which could explain this observation is PIN from Kr 5p[°][3/2]₂ state through the
 249 absorption of a third laser photon [4,5]. This leads to the formation on Kr⁺ ions, which through
 250 transformation to Kr₂⁺ ions, and subsequent radiative recombination, could produce several Kr excited
 251 states [39,41], which de-excite radiatively in the spectral range 420-900 nm [39]. Additional Kr I lines in
 252 the TALIF spectrum at high E_{Laser} were also observed in [42] while studying two-photon absorption from
 253 Kr atom at 215 nm, and were also attributed to PIN, which further validates our findings. In fact, the
 254 energy of Kr 5p[°][3/2]₂ is of 97945.97 cm⁻¹ (12.1436 eV), and the ionization threshold of Kr is of
 255 112914.47 cm⁻¹, resulting in an energy gap of 14968.5 cm⁻¹ [40]. The laser photon energy in our case is of
 256 49005.19 cm⁻¹, which is more than enough to produce Kr⁺ ions from the 5p[°][3/2]₂ level. This would in
 257 fact explain the departure from the quadratic regime at the higher E_{Laser} studied.

258 In order to understand the relative significance of the different physical mechanisms involved in
 259 the TALIF scheme, a simple 0D model was developed (similar to that used in [24]). For the very short
 260 time scales corresponding to the laser pulse, the model takes into account the two-photon excitation rate
 261 of the ground-state Kr atom, PIN from Kr 5p[°][3/2]₂ and Kr 5s[3/2]₁ states, and ASE, in addition to the
 262 decay of the Kr 5p[°][3/2]₂ fluorescing state by spontaneous emission (fluorescence) and collisional
 263 quenching (τ values obtained from this work). Ionization from Kr(5p) (cross-section: $\sigma_i \cong 3.6 \times 10^{-18}$ cm²)
 264 and Kr(5s) states ($\sigma_i \cong 2.8 \times 10^{-21}$ cm²) [43] leads to the formation of Kr⁺ ions. Also, ASE results from a
 265 population inversion between Kr 5p[°][3/2]₂ and Kr 5s[3/2]₁ states [33,44], leading to an amplification of
 266 the fluorescence along the laser beam [45]. ASE has been implemented in the model through the
 267 analytical solution given in [46]. PIN and ASE would deplete the Kr 5p[°][3/2]₂ state leading to saturated
 268 fluorescence regimes.

269 For the large time scales (after the laser pulse), in addition to the A₃ + Q₃ loss channels,
 270 mechanisms related to the ions Kr⁺ and Kr₂⁺ have been considered in the model. The main modes of loss
 271 of Kr⁺ ions are known to be through diffusion or by the formation of Kr₂⁺ ions, as follows [47,48]:



273 Then Kr₂⁺ undergoes dissociative recombination, as follows [39]:

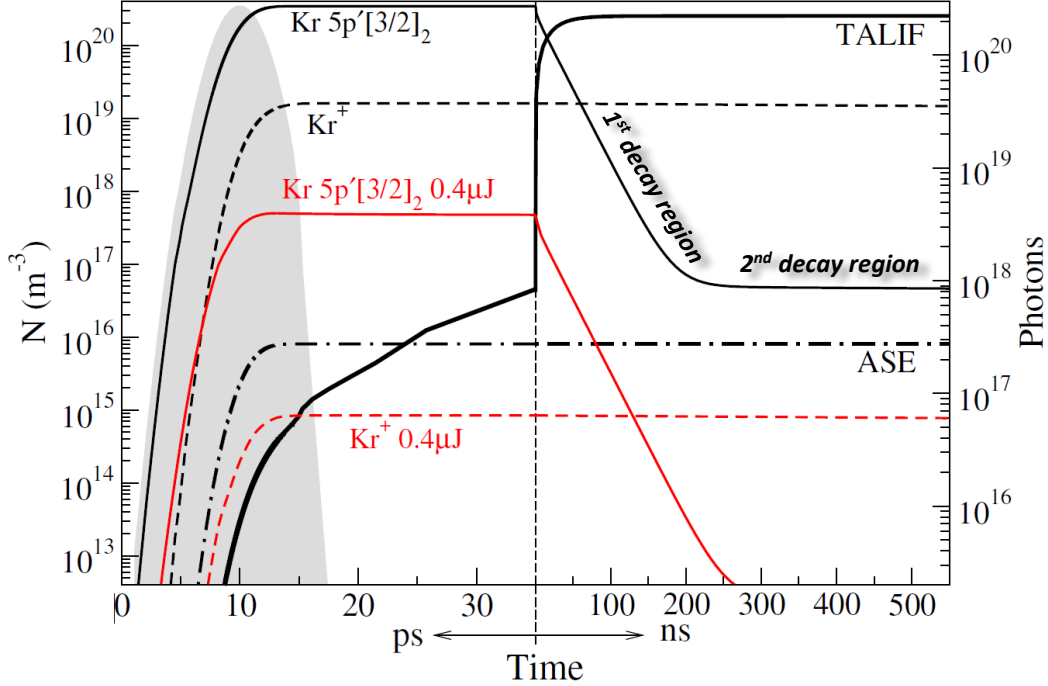


275 However, the model is not able to discriminate the various Kr* excited states formed in (4) since we do
 276 not have the corresponding statistical weights. Therefore, we have assumed that the Kr* excited-state

277 density is equally distributed (i.e., with 50% probability) between Kr $5p^{\prime}[3/2]_2$ and Kr $5s[3/2]_1$ states,
278 which are the only excited states that have been considered in the model.

279 **Fig. 6** shows the results of the numerical model performed at $P_{\text{Kr}}=3$ mbar (as in **Fig. 2**) for the
280 same two E_{Laser} values as in **Fig. 3**. Firstly, the effect of ASE was found to be negligible when compared
281 to PIN even at the higher laser energy. In fact, the intensity of ASE was only significant within the laser
282 pulse (~ 10 ps), and the depletion of the laser-excited state through ASE was negligible as it accounts for
283 less than 0.1% of the total number of TALIF photons. This is consistent with reference [27], where it was
284 shown experimentally that ASE from H atoms in a H_2/O_2 flame was only formed during the laser pulse
285 (35 ps) and for less than 30 ps after it. Unfortunately, the ASE signal was not possible to be measured
286 experimentally in the present study. The ASE effect on the fluorescence signal was reported in different
287 works when performing ps-TALIF studies of O and H atoms in flames. Agrup *et al.* [26] compared the
288 laser power dependence of ps-TALIF and ASE from O atoms in a H_2/O_2 flame. For $I > 400$ $\text{MW}\cdot\text{cm}^{-2}$,
289 ASE started perturbing more and more the TALIF signal. In another example, Kulatilaka *et al.* [28]
290 performed ps-TALIF and ASE studies of H atoms in different flames. The lowest ASE threshold fluence
291 was found for a H_2/O_2 flame and was of 0.03 $\text{J}\cdot\text{cm}^{-2}$, i.e., 300 $\text{MW}\cdot\text{cm}^{-2}$ (100 ps laser pulse). For
292 $\text{CH}_4/\text{O}_2/\text{N}_2$ and $\text{H}_2/\text{O}_2/\text{N}_2$ flames, though, the corresponding ASE thresholds were of 700 and 1500
293 $\text{MW}\cdot\text{cm}^{-2}$. Based on the above, ASE could possibly affect the TALIF signal at $I_{\text{max}}=480$ $\text{MW}\cdot\text{cm}^{-2}$ in our
294 experiments. In this case, the effect of ASE would be significant only during the laser pulse (or slightly
295 after it) [27] leading to a faster TALIF decay. However, the TALIF system investigated in our work (Kr)
296 and its pressure are not the same as in [26-28]. Furthermore, we did not observe a fast decay on the
297 TALIF signal up to $I_{\text{max}}=480$ $\text{MW}\cdot\text{cm}^{-2}$, which is also supported by the model. Thus, the major mode of
298 depletion of the laser-excited state is through PIN.

299 Similarly, PIN can lead to a significant depletion of different fluorescing atomic states when
300 using much shorter laser pulses (fs range). As it was shown by Dumitrache *et al.* [13], the use of 100 fs
301 laser pulses and a strongly focused beam (beam waist: 52 μm) resulted to laser peak intensities of ~ 4
302 $\text{TW}\cdot\text{cm}^{-2}$. In those conditions, PIN led to a departure from the quadratic regime for both N (produced in a
303 ns repetitive discharge) and Kr (used for calibration) atoms. Schmidt *et al.* [11] also investigated 100 fs
304 TALIF in O (produced in a plasma jet) and Xe (used for calibration) atoms. But instead of strongly
305 focusing the laser beam, they constructed a laser sheet (2 $\text{mm} \times 0.09$ mm). In this way, they were able to
306 define adequate conditions in order to obtain the quadratic regime for both atoms by avoiding PIN effect.
307 Finally, Wang *et al.* [35] studied fs-TALIF in Kr (80 fs laser pulses) by also constructing a laser sheet (25
308 mm high). They also demonstrated that the effects from PIN and ASE can be limited at specific laser
309 energies (lower than 4 $\mu\text{J}/\text{pulse}$ in their case). Thus, even for fs-TALIF it is possible to determine
310 conditions leading to the quadratic regime.



311
 312 **Figure 6.** Indicative modelling results referring to $P_{Kr}=3$ mbar. Black and red solid lines are the Kr
 313 $5p'[3/2]_2$ densities (N) obtained for $E_{Laser}=12.1$ and $0.4 \mu\text{J/pulse}$, respectively. Also shown for $E_{Laser}=12.1$
 314 $\mu\text{J/pulse}$ are: i) the cumulative number of photons corresponding to ASE (dash-dot) and TALIF (thick
 315 black), and ii) the density (N) of Kr^+ ions at both E_{Laser} values (dash). The shaded grey curve represents
 316 the laser pulse.

317 The results obtained by the model may be better understood by a simple rate analysis. As a matter
 318 of fact, using the available experimental information, the PIN rate (Γ) of $\text{Kr}(5p)$ states can be qualitatively
 319 estimated as follows [27]:

320

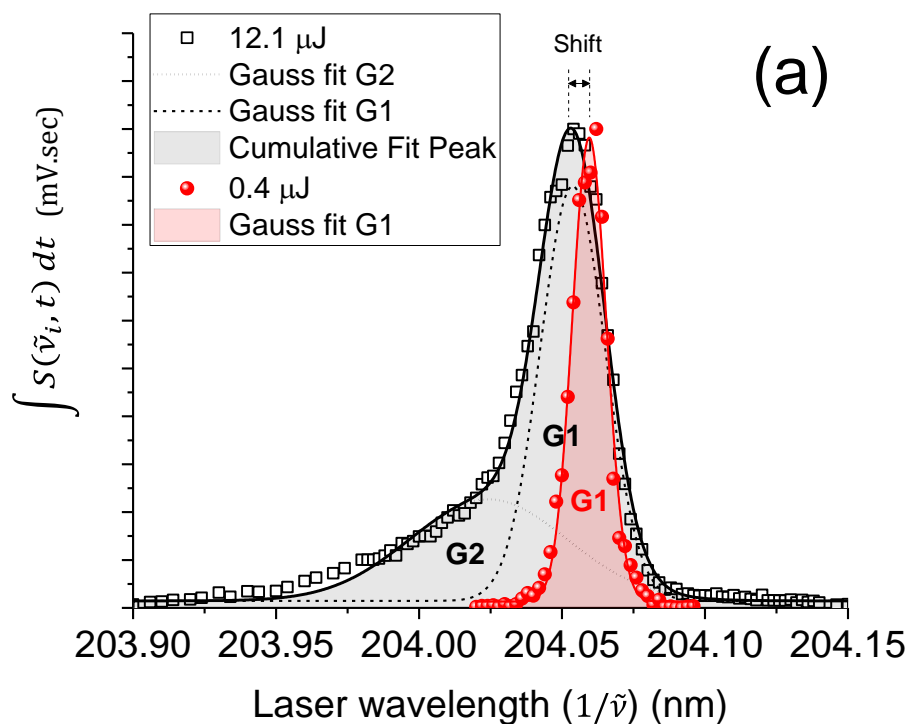
$$\Gamma = \frac{\sigma_i I}{hc\nu_{c_{Kr}}} \quad (5)$$

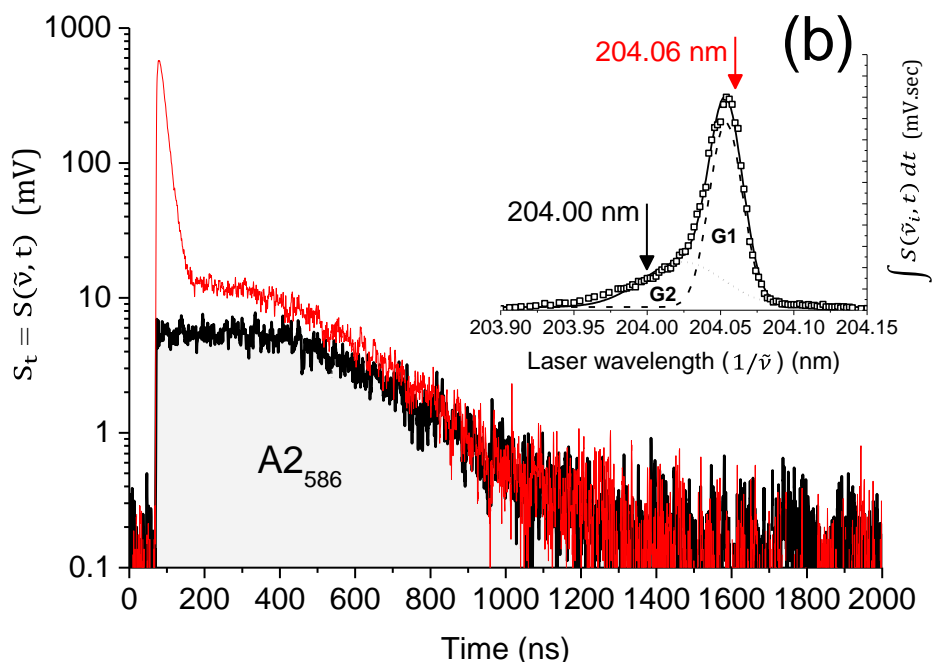
321 For $I=I_{max}=484 \text{ MW}\cdot\text{cm}^{-2}$, eq. (5) gives $\Gamma=1.79\times 10^9 \text{ s}^{-1}$. This is almost two orders of magnitude
 322 larger than $A_3 + Q_3$, which herein is estimated to be of $\sim 4.25\times 10^7 \text{ s}^{-1}$ at $P_{Kr}=3$ mbar, and $\sim 6.5\times 10^7 \text{ s}^{-1}$ at
 323 $P_{Kr}=10$ mbar, in good agreement with references [7,37,38] (see Fig. 4). Furthermore, for $I=18 \text{ MW}\cdot\text{cm}^{-2}$,
 324 i.e. the upper intensity limit of the quadratic regime in Fig. 2, $\Gamma=6.67\times 10^7 \text{ s}^{-1}$, which is still slightly higher
 325 than $A_3 + Q_3$ at 3 and 10 mbar. Therefore, similarly to what is suggested by the model, PIN determines
 326 the population of the fluorescing state and, thus, the TALIF signal intensity beyond the quadratic regime.
 327 On the other hand, for $I=4 \text{ MW}\cdot\text{cm}^{-2}$ ($E_{Laser}=0.1 \mu\text{J/pulse}$, i.e. the lowest E_{Laser} giving an acceptable TALIF
 328 signal-to-noise ratio in our work), Γ decreases to $1.48\times 10^7 \text{ s}^{-1}$. This is $\sim 65\%$ and $\sim 77\%$ lower than $A_3 +$
 329 Q_3 at 3 and 10 mbar, respectively. This result is also supported by Fig. 6, where the density of Kr^+ ions at

330 $E_{\text{Laser}}=0.4 \mu\text{J/pulse}$ (dashed red) is 4 orders of magnitude lower than that at $E_{\text{Laser}}=12.1 \mu\text{J/pulse}$ (dashed
 331 black). Thus, PIN and ASE effects are limited in the quadratic regime, fulfilling the condition (c2) above.

332 Further, for the higher E_{Laser} in **Fig. 6**, the model captures the transition from a 1st to a 2nd signal-
 333 decay region (both indicated in the figure), which starts at the inflection point around 200 ns. This
 334 transition is similar to that captured experimentally in **Fig. 3b** ($P_{\text{Kr}}=3 \text{ mbar}$), the corresponding signal-
 335 decay regions denoted by $A1_{586}$ and $A2_{586}$, respectively. This establishes that PIN is the major saturation
 336 mechanism of the TALIF signal due the creation of Kr^+ ions, followed by reactions (3) and (4), and
 337 radiative relaxations of Kr^* (formed through reaction (4)). In fact, the slope of $S_{\tilde{\nu}t}$ versus E_{Laser}^2 in the
 338 saturation regime is of ~ 0.5 (**Fig. 2**), which also strongly suggests that depletion of $\text{Kr } 5p^{\prime}[3/2]_2$ takes
 339 place through PIN. Also to be noted is that the contribution of the 2nd decay region to the fluorescence
 340 yield is negligible.

341 The key-contribution of PIN to the TALIF signal properties may be also inferred from the
 342 spectral analysis of the two-photon absorption line (**Fig. 7**).





344
 345 **Figure 7.** (a) Experimental high-resolution two-photon absorption line profiles (symbols), $\int S(\tilde{\nu}_i, t) dt$,
 346 fitted with Gaussians (solid/dashed lines) for low (0.4 $\mu\text{J/pulse}$ – red) and high (12.1 $\mu\text{J/pulse}$ – black)
 347 E_{Laser} , respectively, at $P_{\text{Kr}}=3$ mbar. At the higher E_{Laser} , the center of the absorption line is shifted by -6
 348 pm. (b) PMT signals $S_t=S(\tilde{\nu}, t)$ at $P_{\text{Kr}}=3$ mbar and $E_{\text{Laser}}=12.1$ $\mu\text{J/pulse}$, recorded with a 586 nm-centred
 349 interference filter at two laser wavelengths (indicated by the arrows on the corresponding cumulative
 350 spectral profile in the inset): 204.00 nm (black) and 204.06 nm (red).

351 **Fig. 7a** illustrates two normalized spectral profiles obtained at $P_{\text{Kr}}=3$ mbar for the lower- and
 352 upper-limit values of E_{Laser} in **Figs. 3** and **6**. To the best of our knowledge, such a detailed analysis of the
 353 two-photon absorption line profile, especially for E_{Laser} values outside the quadratic regime, has not been
 354 performed in the literature regarding ultrafast TALIF studies in Kr. The experimental data points (black
 355 squares and red spheres) were obtained through the temporal integration of $S(\tilde{\nu}_i, t)$, which was recorded
 356 at different laser wavelengths around the central laser frequency. For $E_{\text{Laser}}=0.4$ $\mu\text{J/pulse}$, the spectral
 357 profile (red spheres) is narrow and can be well-fitted with one Gaussian (red line, denoted as G1). In this
 358 case, the main broadening mechanism of the two-photon absorption line is the laser instrumental function,
 359 which has a Gaussian shape. As a matter of fact, the only other broadening effect that can enter into play
 360 is the Doppler broadening for Kr atoms that turns out to be much smaller than the laser linewidth (0.14
 361 versus ~ 17 pm, respectively). For $E_{\text{Laser}}=12.1$ $\mu\text{J/pulse}$, however, the recorded spectral profile (black open
 362 squares) can be well-fitted only by combining two Gaussians (denoted as G1 and G2 in **Fig. 7a**). While
 363 the peak G1 corresponds to a two-photon excitation to the Kr fluorescing state of interest (i.e. $4p^6$
 364 $^1S_0 \rightarrow \text{Kr } 5p^1[3/2]_2$ transition), as expected, the appearance of the peak G2 strongly indicates a

365 contribution from other processes. In fact, as it can be seen in **Fig. 7b**, the formation of the peak G2 is
 366 directly associated to the appearance of the emissive region A_{2586} in the time-range ~ 80 – 1000 ns of the
 367 PMT signal. Indeed, when the laser is tuned to 204.00 nm (black signal, see corresponding black arrow in
 368 the inset spectral profile), only emission from region A_{2586} is recorded. Furthermore, when tuning the
 369 laser at the peak two-photon absorption frequency (red signal/arrow), A_{2586} is still present along with the
 370 fluorescence peak, which is seen between ~ 80 and 200 ns. Thus, at the higher E_{Laser} , the existence of
 371 A_{2586} and G2 indicates the presence of additional emission channels that are initiated by the laser, they
 372 last over almost 1 μs , and they are captured when using this filter. PIN is a process that may explain this
 373 behavior, as follows. First, it initiates the slow chain of reactions (3) and (4), as discussed through the
 374 analysis of **Figs. 3** and **6**, which would result to the creation of different Kr^* states after the laser pulse.
 375 Therefore, these would contribute to the formation of the long-lasting part of the region A_{2586} through
 376 spontaneous emissions [39,41,42,51]. Second, the formation of A_{2586} in **Fig. 7b** happens very fast, almost
 377 immediately after the laser pulse. This may be also attributed to PIN through the generation of photo-
 378 electrons. Depending on their energy and density, these would rapidly enter into collisions with Kr atoms,
 379 leading to their fast excitation, especially if the photo-electrons are substantially heated by the laser
 380 electric field and the ionization degree is high. This seems to be the case at the higher E_{Laser} studied
 381 herein, as revealed by the model (**Fig. 6**). It should be noted that at the higher E_{Laser} , a slight deformation
 382 of the spectral profile can be possible due to non-linear processes happening during the passage of the
 383 ultrafast laser through the UV fused silica window of the gas cell. But this is almost negligible as
 384 compared to that due the other processes discussed above.

385 Putting it all together, a likely sequence of processes that would explain the obtained results at the
 386 higher E_{Laser} is the following: (i) the application of the laser pulse leads to two-photon excitation of Kr at
 387 the fluorescing state $\text{Kr } 5p^{\prime}[3/2]_2$, (ii) laser-induced photoionization of this state happens very fast (within
 388 the laser pulse), leading to the production of photo-electrons; their energy is estimated to be of ~ 4.2 eV in
 389 our case (based on the difference between the laser photon energy, and the energy gap between the Kr
 390 ionization threshold and the $\text{Kr } 5p^{\prime}[3/2]_2$ state energy, as discussed above), (iii) generated photo-electrons
 391 may be further heated by the laser electric field, inducing a fast excitation of Kr (depending on their
 392 energy and density), and a subsequent early emission, which is seen in the very beginning of the PMT
 393 signal in **Fig. 7b**, (iv) the moderately-fast reaction (3) leads to the formation of Kr_2^+ ions, which through
 394 radiative recombination (reaction (4) – slow process) lead to the creation of Kr^* states, (v) radiative
 395 relaxation of Kr^* states induces the long-lasting emission part of the region A_{2586} in **Figs. 3** and **7b**.

396 However, in spite of having the peak G2 close to the main excitation peak G1, this does not
 397 prevent using G1 for calibration purposes when aiming on the measurement of H- and N-atom densities in
 398 plasmas. This is due to the negligible contribution from G2 when using the 586 -centred filter for E_{Laser}

399 values in the quadratic regime, as seen in **Fig. 7a** for $E_{\text{Laser}}=0.4 \mu\text{J/pulse}$ (red signal). Besides, the area
 400 A_{2586} in the time variation of the PMT signal also disappears for $E_{\text{Laser}} \leq 0.4 \mu\text{J/pulse}$ (see **Figs. 3b** and **6**,
 401 red signals).

402 Furthermore, in **Fig. 7a**, we also observe that at the higher E_{Laser} the line G1 is noticeably broader,
 403 and its central wavelength is shifted by -6 pm from the central laser wavelength. This should be attributed
 404 to an AC Stark shift induced by the linearly-polarized electromagnetic field of the laser [26,27,44,49].
 405 Besides, the possible mechanism for the observed broadening may be the Stark effect due to the presence
 406 of charged species [44,52]. Indeed, the results obtained from the investigation of the fluorescence time-
 407 decay, the laser-induced emission, the spectral analysis of the two-photon absorption line, and the laser-
 408 absorption-induced collisional-radiative kinetics, give a strong indication for the presence of charged
 409 species, which create a strong local micro-field resulting in a Stark effect. This induces the two-photon
 410 absorption-line broadening and shift. Our results would indicate that this effect would quickly dominate
 411 the laser absorption mechanism and result in the deviation from the quadratic regime when E_{Laser} is
 412 increased. In fact, this mechanism has been also proposed in [44], where the excitation line profiles
 413 corresponding to the two-photon excitation of ground-state Kr atom to the $5p[5/2]_2$ state, and its
 414 subsequent transitions to the Kr $5s[3/2]_1$ or Kr $5s[3/2]_2$ states, were broader than the laser line, similar to
 415 our case. It should be noted that broadening due to power-saturation [50] of the optical transition is ruled
 416 out for our conditions since $W_{ij} \times \tau_L \ll 1$. Besides, the power saturation broadening always comes with a
 417 much less increase of the peak fluorescence with E_{Laser} (not seen in **Figs. 3** and **6**).

418

419 **Conclusions**

420 In summary, ps-TALIF in Kr between 0.1–10 mbar was fundamentally investigated in this work. The
 421 laser intensity (I) was varied between 1 and 480 MW.cm^{-2} . The influence of photoionization (PIN) and
 422 amplified stimulated emission (ASE) on the TALIF signal properties was detailly studied for a Kr gas
 423 pressure of 3 mbar. PIN was the dominant process leading to the depletion of the laser-excited state
 424 ($5p[3/2]_2$), which became increasingly significant for $15 < I \leq 480 \text{ MW.cm}^{-2}$. Thus, a saturated
 425 fluorescence regime was obtained, and broader two-photon absorption-line profiles probably due to the
 426 Stark effect. However, for $I \leq 15 \text{ MW.cm}^{-2}$, the PIN effect was significantly limited, the two-photon
 427 absorption line was narrow, and the quadratic dependence of the TALIF-signal intensity versus the laser
 428 energy was revealed. Thus, in this case the investigated Kr TALIF scheme, including two-photon
 429 excitation to the $5p[3/2]_2$ state and fluorescence at 587.09 nm can be used for calibration purposes in ps-
 430 TALIF studies. Besides its fundamental interest, this work contributes to the development of ps-TALIF
 431 diagnostics for measuring absolute densities and quenching coefficients of H and N atoms in reactive
 432 plasmas and/or flames.

433 The determination of atomic species densities and quenching coefficients in reactive plasmas is
434 generally difficult. This is because the quenching kinetic scheme of species de-excitation is complex and
435 depends on the type, the density and the temperature of colliding species. In this case, the species
436 quenching rate can only be measured from the decay of fluorescence signals if the laser decay is faster
437 than that of the fluorescence. Thus, TALIF techniques with excitation time-scales lower than the
438 quenching de-excitation of species can be extremely useful. The use of ps-TALIF proposed in this work
439 can allow sub-ns measurements of quenching rates that are necessary for absolute atomic densities
440 determination. Thus, the present study is linked to many experimental works focused on plasma physics.
441 In fact, the investigation of the application of ps-TALIF in Kr and the definition of regimes where the
442 TALIF signal intensity scales quadratically with the laser energy is extremely useful for the plasma
443 community. This is because Kr is an essential gas to calibrate H and N atom densities in plasmas when
444 using ns- and, more recently, ps- and fs-TALIF diagnostics. Particularly, the measurement of H-atom
445 density, quenching rates, and lifetime in atmospheric pressure plasmas is quite challenging. Indeed, the
446 quenching time of laser-excited H atoms can fall well-below ns at atmospheric pressure [27]. In this case,
447 the use of ps-TALIF would be beneficial. Therefore, this work provides adequate conditions for which the
448 use of ps-TALIF in Kr can be valid and adopted subsequently for calibrating H-atom densities in
449 atmospheric pressure plasmas. Furthermore, the quenching coefficients of H and N atoms by different
450 quenchers in collisional plasmas can be obtained using ps-TALIF and performing well-known Stern-
451 Volmer plots. The obtained information would be especially useful in numerous plasma-based
452 applications (e.g. thin film synthesis, biomedical treatments, plasma-assisted combustion, ...), for which
453 the knowledge of the densities and kinetics of those reactive species is crucial for the optimization of the
454 related processes.

455

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465 **Data Availability Statement**

Availability of data	Template for data availability statement
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Data available on request from the authors	The data that support the findings of this study are available from the corresponding author upon reasonable request.
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