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Letter

Ultrafast laser-collision-induced fluorescence in atmospheric pressure plasma

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Abstract
The implementation and demonstration of laser-collision-induced fluorescence (LCIF) generated in atmospheric pressure helium environments is presented in this communication. As collision times are observed to be fast (~10 ns), ultrashort pulse laser excitation (≤100 fs) of the 2S to 3P (388.9 nm) is utilized to initiate the LCIF process. Both neutral-induced and electron-induced components of the LCIF are observed in the helium afterglow plasma as the reduced electric field (E/N) is tuned from <0.1 Td to over 5 Td. Under the discharge conditions presented in this study (640 Torr He), the lower limit of electron density detection is ~10\(^{12}\) e cm\(^{-3}\). The spatial profiles of the 2S helium metastable and electrons are presented as functions of E/N to demonstrate the spatial resolving capabilities of the LCIF method.

Keywords: atmospheric pressure plasma, diagnostics, laser-collision-induced fluorescence, ultrafast laser, laser-induced fluorescence, helium

(Some figures may appear in colour only in the online journal)

1. Introduction

The field of low-temperature plasma physics is experiencing an expanding interest in higher pressure, higher collisionality plasmas for their strong promise in a broad range of applications [1, 2]. During the last decade, the focus of research on high-pressure non-equilibrium plasmas has expanded to address a variety of novel application areas, including ignition and low-temperature combustion [3, 4], material synthesis such as nanostructured materials [5], the deposition of coatings [6, 7], chemical synthesis [8], plasma catalysis [9], sterilization [10, 11], plasma-induced wound healing [12, 13], tissue ablation, blood coagulation and cancer treatment [14–16].

The vast majority of what has been done to characterize these plasma systems is derived from analysis of the optical emission emanating from the plasma. Most of these measurements consist of imaging the propagation of the ionization front with the use of high-speed devices such as intensified CCD cameras [17, 18]. A few studies have reported assessments of the electric fields by the analysis of ion-neutral line ratios in nitrogen [19, 20] or forbidden-allowed line ratios in helium [21]. Measurements of electron densities have been obtained from methods based on line-broadening [22] or the broadband continuum [23, 24]. As is the case with most passively based optical emission methods, these measurements are inherently line-of-sight in nature, which requires some form of inversion to obtain more localized information. These inversions are typically based on an assumed configuration or...
the inherent symmetry of the discharge. Laser-based methods, such as CARS [25–27], have been utilized to assess electric fields, while other methods, like Thomson scattering [28, 29] and microwave scattering [30], have been utilized to assess electron densities. While these methods are capable of providing 2D information, they are essentially point measurements necessitating the movement of the source or the interrogation region. While considerable progress in the development of the diagnostics capable of assessing these systems has been made, methods capable of measuring the key plasma parameters of interest, such as electron densities and electric fields on time scales and spatial scales relevant to the highly collisional plasma environment, are sorely needed [16].

In this fast-track communication, we report on the development and demonstration of laser-collision-induced fluorescence (LCIF) generated in atmospheric pressure helium plasma discharges initiated by the utilization of short pulse (<100 fs) broadband (>10 nm) laser excitation. The material presented in this communication is significant, as the results demonstrate that laser-induced fluorescence can be readily induced by these broadband laser pulses, where much of the bandwidth (~10 nm) provided by the laser in essence is not utilized in exciting the targeted transition (~0.1 nm at 1 atm). Furthermore, the short-pulse nature of laser excitation occurs over time scales much faster (~100 fs) than the anticipated decay rates of the laser excited states (~10 ns) in this highly collisional environment. Finally, the most important finding is the observation and demonstration of collision-induced fluorescence and the correlation of this induced fluorescence to energetic electrons in the discharge environment. In section 2, an overview of the principles that govern the LCIF method, a brief description of the laser system utilized to induce the LCIF process, and general procedures for generating and manipulating an atmospheric pressure plasma generated in helium are provided. In section 3, demonstrations of the electron density dependence of the observed LCIF are provided, as the reduced electric field (E/N) in the plasma discharge is manipulated. In section 4, concluding remarks are offered on the prospects and limitations of LCIF as a diagnostic platform for atmospheric pressure discharges.

2. LCIF generation and detection

2.1. General overview of the LCIF process

The concept of laser-collision-induced fluorescence is illustrated in figure 1, and has been demonstrated in various gas systems utilizing both continuous wave and nanosecond laser [31–34] excitation schemes. In general, for both methods, there is a redistribution of the laser-excited state due to a combination of radiative and collisional processes, as can be described by a simplified 0D rate equation taking the form of

\[
\frac{dN_i}{dt} = \left[ \sum_{j < i} K_{ji} N_j - \sum_{i > j} K_{ij} N_i \right] n_e + \sum_k \left[ \sum_{i > j} K_{ki} N_j - \sum_{i < j} K_{ik} N_i \right] N_k + \left[ \sum_{i > j} A_{ij} N_j - \sum_{i < j} A_{ji} N_i \right].
\]

As articulated in equation (1), the change in population of a given state \(N_i\) due to the population of other states \(N_j\) is a function of the electron-driven processes (first bracketed term), gas-phase-driven processes (second bracketed term) and radiative-driven processes (third bracketed term). In this expression, the kinetic-dependent collision rates \(K^{e,a}\) describe the strength or likelihood of interactions in the given state by either electrons \(n_e\) or energetic neutrals \(N_i\), while photon emission \(A_{ij}\) describes the radiative decay into or out of the state. With increasing gas density and an increased number of different collision partners (excited atoms, ions and molecules) associated with the atmospheric pressure plasma environment, separating out electron-induced processes from non-electron-induced processes becomes non-trivial. In general, a detailed collisional-radiative model, like that described in equation (1), is needed to describe and ultimately predict the evolution of the interrogated atomic system after laser
excitation. The solution of the model becomes even more challenging when the species participating in the collision process are unquantified, and the rates between the active species participating in the collision process are uncertain, meaning it is unknown whether or not the transport of the radiation should be accounted for.

The results presented in this communication for the laser excitation pathway and key rates [35] associated with the various productions and losses into states that are associated with the LCIF process are presented in figure 1. In the utilized excitation scheme, metastable helium (2⁢S) serves as the laser-excited species. As has been reported in lower-pressure plasma environments [32], the excitation of the 2⁢S to the 3⁢P state (at 389 nm) was performed with a nanosecond laser, while LCIF caused by the redistribution of some of the laser-excited 3⁢P states into nearby but energetically up-hill states, including the 3⁢D (0.07 eV above 3⁢P) or the 4⁢D (~0.7 eV above 3⁢P), was observed. In the reported lower-pressure systems containing predominantly atomic helium, a much more simplified treatment was possible, and only electron and neutral collisions with atomic helium needed to be accounted for to describe the collisions from the 3⁢P into the 3⁢D state. Furthermore, little neutral dependence was observed for collisions from the 3⁢P into the 4⁢D state due to the larger (0.7 eV) energy spacing between the two states. In our discussion, we do not consider contributions from the 3⁢S state, which is populated by both radiation and collisions from the laser-excited 3⁢P state. At atmospheric pressures, as is the case at lower pressures, it is anticipated that the neutral-collision interactions will set a lower bound for the electron densities than can be detected. An estimate of the bound placed on the electron density at atmospheric pressure can be made for atomic species near room temperature by assuming a neutral collision rate of Kₐ ~ 10⁻¹¹ cm³ s⁻¹ and an electron collision rate of Kₑ ~ 10⁻⁵ cm³ s⁻¹, and comparing the products of KₑNₑ to KₐNₐ. For neutral densities of ~10¹⁹ neutrals cm⁻³, the bound for electron density detection is ~10¹³ e cm⁻³. As this bound was established by setting the two contributions to be equal, it is anticipated that densities comparable to or lower than ~10¹³ e cm⁻³ will be resolved.

2.2. Generation of LCIF

At higher pressures and the associated higher collision rates, the lifetime of the excited states becomes greatly reduced. For collision rates and densities associated with atmospheric pressure conditions, excited state lifetimes (KₑNₑ)⁻¹ approach 10 ns or less. To simplify the interpretation of the LCIF, it is advantageous to use a laser excitation process that is much faster than the response of the system to decouple the two processes. This decoupling cannot be realized using nanosecond-based YAG lasers, like the one utilized in earlier studies that was nominally 5–7 ns in duration. Therefore, in this communication we utilize a broadband (10 nm), short pulse laser (<100 fs) to excite the 2⁢S helium metastable state to 3⁢P and initiate the LCIF process. A 1 kHz regenerative amplifier (Spectra-Physics SpitFire) generates an a ~ 1 mJ, ultrafast (<80 fs) broadband (~10 nm) pulse, centered around 780 nm by tuning the input of the seed oscillator (Spectra-Physics Tsunami). The amplified output is attenuated (~100 µJ) and doubled by a thin BBO crystal to generate 10–20 µJ of UV light (389 nm ± 5 nm) which is utilized for laser excitation. While it is expected that there will be some temporal broadening of the initial 80 fs pulse due to dispersion, this broadening is relatively small (30 or 40 fs) compared to the anticipated timescales associated with redistribution kinetics (~ns).

Finally, it is of interest to note that because of the short pulse nature of the laser light, it has an intrinsically much broader band (100 cm⁻¹ or 500 GHz) compared to the more commonly employed seeded, grating-based nanosecond laser systems (0.1 cm⁻¹ or 0.5 GHz). Using the published pressure broadening values of helium (~0.1 GHz Torr⁻¹) [36], the linewidths of atomic helium are ~70 GHz at atmospheric pressure conditions. Clearly, while only 10% of the short pulse laser bandwidth is utilized in the laser excitation process, all of the absorption profile of the helium transition is accessible. In contrast, not all of the absorption profile of the helium transition is accessed by the narrowband nanosecond laser. The combination of a high repetition rate, large metastable densities and strong absorption of the interrogated transition yield a reasonable LIF, despite the relatively inefficient utilization of the laser’s bandwidth.

2.3. Plasma generation and manipulation

The general arrangement utilized in this communication is depicted in figure 2(a). The measurements are performed in an evacuated chamber (~10 mTorr) that is backfilled to ~640 Torr of helium gas (99.999% purity). The plasma-generating electrodes are arranged in a point-to-point geometry consisting of two tungsten rods that are 3 mm in diameter and separated by ~10 mm.

The plasma is generated and manipulated by the ‘double pulse’ method utilized in earlier studies [34]. A high voltage pulse with a magnitude of ~3 kV and a duration of 150 ns is utilized to generate the breakdown of the helium gas. The magnitude and duration of the voltage pulse establishes an upper bound on the electron densities. After the termination of the voltage pulse, the electrons rapidly thermalize to temperatures that are anticipated to be comparable to the background gas temperatures (<0.1 eV). Based on the published reports [37] and observed optical emission, this cooling occurs faster than 100 ns.

At 5000 ns after the initial voltage pulse is terminated, a second voltage pulse of varying magnitude (tens to thousands of volts) and a fixed duration of 500 ns is applied across the electrodes to drive the current through the afterglow. Initially thermalized, cold electrons obtain an induced drift velocity (vdrift) as they are energized or heated through the applied electric field that is generated by the second voltage pulse. The temporal evolution of the current driven through the afterglow is depicted for varying applied voltages in figure 2, while the voltage dependence of that current (measured ~250 ns after application of the voltage pulse) is plotted in figure 3(a).
As a direct measurement of the electron density was not performed, estimates of both the electron density and $E/N$ were assessed from the observed current–voltage trends and measured cross-sectional area ($A$) of the plasma by relating the measured current ($I$) to the density ($n_e$) and the induced drift velocity ($I = en_eV_{\text{Drift}}A$). For the initial estimates, the knees in the published drift parameters relating $V_{\text{Drift}}$ to the reduced electric field ($E/N$) [38] correlate to the knees in the observed current–voltage trend at 350 V and 1300 V. The $E/N$ values at these voltages correspond to $\sim$0.1 Td at 350 V and 5 Td $\sim$ 1300 V. For measured currents of 2 mA at an $E/N$ of 0.1 Td, inducing a drift velocity of $10^5$ cm s$^{-1}$ through a 2 mm diameter plasma (FWHM), the average electron densities are estimated to be $\sim$10$^{13}$ e cm$^{-3}$ in the center of the discharge. It is noted that the shape of the discharge did not change with the applied voltage (figures 2(b) and 4) until the $E/N$ was high enough ($>5$ Td) to ionize the residual energetic species in the afterglow plasmas.

2.4. LCIF detection

Laser-induced fluorescence and laser-collision-induced fluorescence are monitored with a gated, intensified CCD (Andor I-Star) that is synchronized to the firing of the 1 kHz laser. As the radiative lifetimes of the excited states are short, the typical gate widths were $\sim$10 ns to suppress the contribution of the plasma-induced emission to the total measured signal. As the plasma-induced emission can contribute significantly to the measured signal, even with relatively short gates, it must be subtracted from the total measurement. Therefore, for every observation, two measurements must be made: one consisting of the total emission (laser-induced and plasma-induced) and one consisting of plasma-induced emission. To acquire the latter, an electronic shutter is utilized to block the laser. The laser-induced contribution is obtained by subtracting the two measurements.

Figure 3. Key scaling trends in extracted current (a), normalized LIF from the laser excited $3^3P$ state (b) and the ratio of the LCIF from the $3^3D$ state to the LIF from the $3^3P$ state (c) as functions of voltage applied across the gap and reduced electric field. Dashed lines are utilized to indicate changes in discharge behavior used to assess or assign $E/N$ values.

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To identify the states that emit LCIF and to eliminate possible contributions from other potential sources of plasma-induced emission (PIE), spectrally resolved measurements were made by attaching the ICCD to the output of a high-resolution spectrometer. Light from the central core of the plasma was imaged into a fiber coupled to the input of the spectrometer. The representative LIF and LCIF spectra are illustrated in figure 2 to demonstrate that the latter was observed from several helium states, and that the observed lines were well isolated from other potential sources of emission.

Having identified the LCIF transitions of interest, the ICCD is utilized as a camera to image the discharge region. Narrowband interference filters (~5 nm FWHM) centered on the transitions of interest are placed in front of the camera lens to isolate the target LCIF lines. The representative images of the plasma-induced emission are also presented in figure 2 to demonstrate that there is little change in the structure of the discharge as a function of $E/N$.

**3. Electron- and neutral-density-dependent LCIF**

The key scaling of the normalized LIF emanating from the laser-excited $3^3P$ state (at 389 nm) and the collision-induced fluorescence from the energetically nearby $3^3D$ state (at 588 nm) normalized to the LIF from the laser-excited $3^3P$ state is plotted in figures 3(b) and (c) as a function of the amplitude of the second voltage pulse (and $E/N$). Both the LIF and LCIF are spatially averaged over a 1 mm$^2$ region extracted from the center of the discharge. Prior to discussing the specifics of the LIF and LCIF trends, it is beneficial to review the characteristics of the plasma as the second voltage pulse is applied and $E/N$ is tuned. As mentioned in the previous section, the second voltage is applied ~5000 ns after the first pulse generates the plasma, while the LIF and LCIF measurements are made 250 ns after the application of the second voltage pulse. Because of the 5000 ns delay, little to no optical emission is observed emanating from the plasma without the application of the second voltage pulse. This observation indicates that the electron energies are too small to excite optical transitions, which is consistent with the reported rapid cooling of the electrons after the voltage is terminated [37]. Over most of the applied voltage range of the second pulse, $E/N$ remains sufficiently low (<5 Td, figure 3(a)), such that metastable production and ionization rates are low enough that appreciable excitation and ionization does not occur (figure 1(b)). As a result, the structure of the plasma remains unchanged (figure 2(b)), and more importantly the electron density is expected to be unchanged over these lower $E/N$ conditions. Finally, it is important to note that as prescribed in equation (1), the observed LCIF is the sum of the constant neutral contribution ($K^Nn_e$) and the variable electron contribution ($K^e n_e$). For most of the observed $E/N$ range, $K^e$ is electron-temperature-dependent below $E/N \sim 1$ Td and remains flat for higher $E/N$ values (figure 1(b)). Again, $n_e$ is postulated to remain constant at a value of $1 \times 10^{13}$ e cm$^{-3}$ in the center of the discharge, because ionization rates are low. Of course, at higher $E/N$ values, $n_e$ increases due to ionization in the plasma column, while $K^e$ is essentially constant.

For lower applied voltages (0–750 V) and lower $E/N$ (<0.1–1 Td), it is observed that the LCIF from the $3^3P$ state, which serves as a measure of the laser-excited $2^3S$ metastable state, remains unchanged, while at moderate voltages (750–1200 V) and moderate $E/N$ (1–3 Td) it begins to decrease. At higher voltages (~1250 V) and higher $E/N$ (>5 Td) there is an increase in the LIF. The initial decrease corresponds to the redistribution of the metastable state to other states by the modest increase in electron energies ($kT_e \sim 0.5$ eV), while the subsequent increase corresponds to the generation of metastable states from the neutral background ($kT_e \sim 3$ eV).

With regards to the normalized LCIF emanating from the nearby, but energetically uphill $3^3D$ state, it is observed that the LCIF is not initially zero but has a finite value of roughly half the LIF from the laser-excited $3^3P$ state. Upon increasing the voltage above 350 V ($E/N > 0.1$ Td) there is an increase in the LCIF which then levels out until the voltage exceeds 1200 V ($E/N > 3.5$ Td). For the lower voltage and $E/N$ range, where the electrons are thermalized and the average temperature is close to the gas temperature, the dominant contribution to the LCIF is due to the collision of the laser-excited $3^3P$ state with the neutral background. With an increased voltage, there is a stronger contribution to the LCIF by heating of the electrons. After the transition, the normalized LCIF remains constant.
as the electron excitation rate from the $3^3P$ to $3^3D$ state is a relatively weak function of the $E/N$ and electron temperature at values greater than the threshold. At higher voltages and higher $E/N$ the electrons have sufficient energy to not only deplete (and ultimately repopulate) the metastable state, but also to ionize (initially from the metastable state and then the ground state).

To illustrate the spatial resolution capabilities of the LCIF technique, the radial profiles of the LIF from the $3^3P$ state (at 389 nm) as well as the ratio of the LCIF from the $3^3D$ (at 588 nm) to the LIF from the $3^3P$ state are plotted in figure 4 for select voltage ($E/N$) values, where the electron densities are not significantly modified. The radial profiles are extracted from the central 2 mm region of the discharge and the dotted profiles correspond to the profiles measured with no applied voltage across the afterglow. As discussed in the previous paragraph, at lower applied voltages, there is no change in the structure of the discharge, as illustrated by the radial distribution and magnitude of the metastable states as measured by the LIF from the $3^3P$ state. At higher values of applied voltage, some depletion is observed due to the (suspected) redistribution of the metastable state to other states. In contrast to the behavior of the metastable states, the normalized LCIF nominally has a ‘flat-top-like’ distribution at lower $E/N$ values, resulting predominantly from the uniform distribution of the background neutrals populating the $3^3D$ state from the laser-excited $3^3P$ state. With an increasing voltage, the distribution of the normalized LCIF becomes significantly modified and more like the observed metastable distribution. As the anticipated $E/N$ values presented in figure 4 are not expected to generate significant changes in the distribution or magnitude of the electron densities (via the ionization of diffusion), it is concluded that the afterglow electrons are initially too cold to add significantly to the LCIF signal. With the applied $E/N$, these electrons gain sufficient energy to significantly contribute to—and even dominate—the observed LCIF. From the analysis presented in section 2, the average electron densities are $\sim 10^{13}$ e cm$^{-3}$. These electrons generate LCIF signals that are $\sim 3$–4 times greater than the background neutral helium ($640$ Torr or $\sim 2 \times 10^{18}$ atoms cm$^{-3}$), indicating that the lower limit of electron detection at or near atmospheric pressure conditions is $\sim 10^{12}$ e cm$^{-3}$.

4. Concluding remarks

In this letter, a demonstration of ultrafast laser-collision-induced fluorescence for spatially resolving electron densities in atmospheric pressure helium discharges was presented. The highly collisional environments that exist under these conditions make the straightforward application of earlier, low pressure, utilization of the LCIF method considerably more challenging. The short lifetimes of laser-excited states ($< 10$ ns) encourage the use of very fast ($< 1$ ns) or ultrafast ($< 1$ ps) laser excitation, such that relaxation processes can be separated from excitation events. Likewise, the high rate of collision between laser-excited species and various, often unknown, plasma species (atoms, molecules, ions, electrons, etc) imposes further challenges and uncertainties in interpreting the observed LCIF. The results presented here represent an important first step in extending earlier efforts on rather simplified low-pressure systems to more challenging atmospheric pressure environments. Subsequent work to be performed includes looking at other spectroscopic pathways in helium and other species of interest that may better be used to limit many of the uncertainties that limit LCIF implementation.

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