Laser-induced photodetachment of negative oxygen ions in the spatial afterglow of an atmospheric pressure plasma jet

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Laser-induced photodetachment of negative oxygen ions in the spatial afterglow of an atmospheric pressure plasma jet

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Abstract

Negative ions are an important constituent of the spatial afterglow of atmospheric pressure plasmas, where the fundamental plasma-substrate interactions take place that are vital for applications such as biomedicine, material synthesis, and ambient air treatment. In this work, we use laser-induced photodetachment to liberate electrons from negative ions in the afterglow region of an atmospheric pressure plasma jet interacting with an argon-oxygen mixture, and microwave cavity resonance spectroscopy to detect the photodetached electrons. This diagnostic technique allows for the determination of the electron density and the effective collision frequency before, during and after the laser pulse was shot through the measurement volume with nanosecond time resolution. From a laser saturation study, it is concluded that $\text{O}^-$ is the dominant negative ion in the afterglow. Moreover, the decay of the photodetached electron density is found to be dominantly driven by the (re)formation of $\text{O}^-$ by dissociative attachment of electrons with $\text{O}_2$. As a consequence, we identified the species and process responsible for the formation of negative ions in the spatial afterglow in our experiment.

Keywords: photodetachment, negative ions, spatial afterglow, laser-induced photodetachment, microwave cavity resonance spectroscopy, atmospheric pressure plasma jet, oxygen

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

1. Introduction

Atmospheric pressure (low-temperature) plasmas [1, 2] are promising for biomedical applications [3–5], deposition and synthesis of (nano)materials [6–10], and the treatment of air pollution [11–14]. The key advantage of such plasmas resides in their capability to generate charged species, radicals, and ultraviolet (UV) radiation in large quantities under low-temperature and atmospheric pressure conditions, which allows for easy integration in existing processes aiming to treat delicate materials. Such low-temperature plasmas operate far from thermal equilibrium [15], because the electrons are energized by the (driving) electric field, while the heavy species—such as (negative) ions, metastables and neutrals—remain near room temperature.

Oxygen-based reactive species are among the most important contributors to bacterial inactivation [16, 17], surface modification [18], and the formation of complex negative...
ions and molecules [19]. Although the properties and dynamics of various neutral and positively charged plasma species has been extensively investigated [20–22], there is a lack of understanding with respect to the role of negative ions.

Negative ions—such as O\(^{-}\), O\(_2\)\(^{-}\), O\(_3\)\(^{-}\), NO\(^{-}\), NO\(_2\)\(^{-}\), and OH\(^{-}\)—are created in the spatial afterglow downstream from the active plasma region, where the plasma species mix and react with nitrogen, oxygen and water vapor. The relative yields of various negative ion species were measured by Bruggeman et al [23] in a radio-frequency (RF) excited atmospheric pressure glow discharge in a mixture of helium and water vapor using mass spectrometry, where OH\(^{-}\) was found as the dominant anion. It was concluded that negative ions had an equally important effect in case of oxygen-containing discharges. Also, negative oxygen ions, and specifically O\(^{-}\), play a vital role in corona discharges [19] during the production of negatively charged molecules and other reactive species. Despite the importance of negative ions for the chemistry and targeted performance of atmospheric pressure plasmas, the role of negative ions is less understood compared to the role of other species. The lack of this understanding is mainly caused by the limited diagnostic capabilities for detecting negative ions and, correspondingly, the limited availability of experimental data.

In this work, we present measurements of the negative oxygen ion density in the spatial afterglow of an atmospheric pressure plasma jet driven by a 13.56 MHz RF voltage signal. This discharge was created in a capacitively-coupled cylindrically symmetric geometry, where the plasma was confined between the RF-powered needle electrode and a dielectric (quartz) tube covering the inside of the grounded electrode. The spatial afterglow, formed downstream of the discharge, culminated in a chamber with a controlled atmosphere where the negative ions were formed by the interaction of afterglow electrons with the argon-oxygen gas mixture. A pulsed UV laser (\(\lambda_{\text{laser}} = 355\) nm) was used to liberate electrons from the negative oxygen ions by photodetachment. The contribution of the photodetached electrons to the free electron density was measured by microwave cavity resonance spectroscopy (MCRS) with a sampling time of 4 ns. By determination of the photodetached electron density as a function of laser pulse energy towards saturation, the photodetachment cross section and local number density of negative ions were found.

The current paper is structured as follows. Section 2 describes the experimental setup and measurement methodology, and explains the MCRS diagnostic in more detail. Section 3 presents the experimental results obtained in this work, of which three main features are highlighted in detail: the argon discharge afterglow before the laser pulse, the saturation study, and the temporal decay of the photodetached electron density. Section 4 provides an interpretation of the results leading to the identification of the major negative ion species, a discussion on the probed volume, the reactions governing the decay of the photodetached electron density, and a discussion of the energy relaxation mechanisms. This work is concluded in section 5 with a brief summary of the main findings.

2. Experiment

An atmospheric pressure plasma in pure argon was created using a cylindrically symmetric dielectric barrier discharge as is shown in figure 1, of which the plasma species reacted with an argon-oxygen mixture in the spatial afterglow downstream of the glow discharge region. The glow discharge was produced in the gap between the RF-powered electrode (a needle with a diameter of 1 mm and having a sharp tip) and the grounded electrode (hollow copper cylinder with an inner diameter of 4 mm) which was covered on the inside by a dielectric (quartz tube with inner diameter of 2 mm and outer diameter of 4 mm). The distance between the RF needle tip and the end face of the quartz tube was 3.2 mm, and the distance between the end face of the grounded electrode and the quartz tube end face was 2 mm. The powered electrode was connected to an RF power supply delivering a continuous power of \(P_{\text{RF}} = 13.5(+/-0.9)\) W to the discharge, of which the electrical characteristics were monitored during the experiments using a power probe [24] to ensure steady state plasma conditions and to measure the plasma power. Pure argon gas (99.999% purity) was introduced into the discharge gap via the top at a flow rate of 3000 sccm, while a mixture of argon(93%)-oxygen(7%) gas was introduced into the vessel as background gas (99.999% purity) using mass flow controllers at a flow rate of 2000 sccm argon and 150 sccm oxygen. The plasma jet was integrated in a vacuum-tight vessel so that the ambient air could be removed down to a pressure of \(\leq 9.8 \times 10^{-1}\) mbar prior to each experiment. During the experiments, a controlled atmosphere inside the vessel was maintained at 1 bar using the mass flow controllers for the background and discharge gases, by closing the valve to the vacuum pump, and by opening a valve connecting the vessel to the central exhaust of the laboratory. Thereby, the experimental setup allowed to generate a stable argon plasma, which created negative oxygen ions in the afterglow located downstream of the discharge gap.

A microwave cavity (with an interior diameter of 66 mm and an inner height of 16 mm) was mounted directly below the plasma jet such that the plasma-produced species could enter the probing volume and, subsequently, the number density of free electrons could be measured using MCRS. The MCRS technique relies on the dependence of the resonant behavior of a resonant microwave mode on the complex permittivity of the medium inside the cavity’s probing volume. The complex permittivity was perturbed by changes in the number density and collision frequency of free electrons inside the cavity volume. Moreover, electrons were released from negative oxygen ions in the spatial afterglow of the plasma jet by photodetachment in addition to the electrons generated by the continuously driven discharge.

The change in resonance frequency \(f_{\text{res}}\) and quality factor \(Q_{\text{res}}\) of the resonant mode are formalized through the Slater perturbation theorem, which relates the resonant mode characteristics to the (spatially-dependent) change in complex permittivity [25–27].
Figure 1. Schematic overview of the experimental setup. The overview depicts the plasma jet discharge geometry, the gas flows, the UV laser beam, and the microwave cavity. The plasma jet comprised several elements, where the argon flow entered the discharge gap from the top into the annular space between the RF-powered needle electrode, the dielectric (quartz) tube and the grounded electrode. The actual measurement volume was a combination of the spatial plasma afterglow and the UV laser beam, which perturbed the microwave cavity simultaneously. Next to the argon flow, a background gas flow comprised the argon-oxygen mixture was introduced into the vessel via an additional inlet, which could freely enter the vessel and the microwave cavity volume. The RF power sensor (printed circuit board; PCB) was located at the top, outside the vessel, which monitored the RF current, voltage, and power.

\[
\frac{\Delta f}{f_1} + \frac{1}{2} \Delta \left( \frac{1}{Q} \right) = -\frac{\iiint_{V_{\text{cav}}} \Delta \bar{\varepsilon}(r)|E(r)|^2 \, dr}{2\varepsilon_0 \iiint_{V_{\text{cav}}} |E(r)|^2 \, dr}. \tag{1}
\]

Here, the shift in resonance frequency is \(\Delta f = f_2 - f_1\) and the change in inverse quality factor is \(\Delta (1/Q) = 1/Q_2 - 1/Q_1\), where the subscript 2 denotes the perturbed state (caused by the argon discharge and laser-detached electrons) and the subscript 1 denotes the cavity state with only neutral gas. Furthermore, the imaginary unit is denoted by \(\ii\), the cavity volume by \(V_{\text{cav}}\), the spatial dependent (microwave) electric field corresponding to the excited TM_{010} mode by \(E(r)\), the vacuum permittivity by \(\varepsilon_0\), and the shift in complex permittivity by \(\Delta \bar{\varepsilon}\), with

\[
\Delta \bar{\varepsilon} = \frac{\omega_{pe}^2}{\nu_{\text{eff}}^2 + \omega^2} + \frac{\nu_{\text{eff}}}{\omega} \frac{\omega_{pe}^2}{\nu_{\text{eff}}^2 + \omega^2}. \tag{2}
\]

Here, \(\omega_{pe} = 2\pi f_{pe}\) and \(\omega = 2\pi f\) with \(f_{pe}\) the electron plasma frequency and \(f\) the applied microwave frequency. As can be seen, the change in complex permittivity depends on the number density and the (effective) collision frequency of the electrons. When assuming a homogeneous plasma region, the free electron density and effective collision frequency are given, respectively, by:

\[
n_e = \frac{2e_0 n_e}{\varepsilon_0} \frac{\nu_{\text{eff}}^2 + 4\pi^2 f_1^2 \Delta f}{\nu_{\text{eff}} f_1}. \tag{3}
\]

and

\[
\nu_{\text{eff}} = \frac{\pi f_1^2 \Delta (1/Q) \Delta f}{\Delta f}. \tag{4}
\]

Here, \(\Delta f\) and \(\Delta (1/Q)\) are determined from the measured signals, \(\nu_{\text{eff}}\) denotes the (microwave-electric-field-weighted) volume ratio (see appendix A.1), \(n_e\) represents the (microwave-electric-field-weighted volume-averaged) free electron density, and \(\nu_{\text{eff}}\) represents the (microwave-electric-field-weighted volume-averaged) effective collision frequency. Please consult appendix A.2 for the specific equations used for the calculation of the (additional) electron density and the (change in) effective collision frequency caused by the discharge and the laser photodetachment events.

The time-resolved measurement scheme to determine the resonance frequency and quality factor was deployed previously at atmospheric pressure to study pulsed high-voltage discharges in nitrogen [28] and RF discharges in helium.
interacting with ambient air [29, 30]. From an experimental point of view, first, microwave power was introduced via an antenna into the cavity to excite the TM$_{010}$ resonant mode. This was done by injecting sequentially microwaves with frequencies in the spectral neighborhood of the resonant mode. This mode had a resonance frequency $f_1 = 3.5029$ GHz and a quality factor $Q_1 = 725$ in case the cavity volume was only occupied by the argon-oxygen gas mixture, i.e. without the discharge or laser perturbation, and at a (measured) cavity temperature $T_1 = 26.642$ °C. After the creation of the discharge, a continuous flow of plasma species entered the cavity, which increased the resonance frequency to $f_2$ and decreased the quality factor to $Q_2$. Depending on the frequency of the injected microwaves—ranging $f = 3.498–3.510$ GHz with frequency step size of 250 kHz—and the complex permittivity in the cavity volume, part of the microwave power was reflected. This reflected power was then converted by a logarithmic power detector to an analog voltage signal, which was measured using a transient recorder sampling at a rate of 250 MHz. For each applied microwave frequency and laser pulse energy, the temporal response was sampled for 4096 (photodetachment) events and averaged afterwards. By measuring the reflected power as a function of time, for each microwave frequency, each average cavity response at a fixed time instant could be reconstructed due to the excellent repeatability of the experiment.

The photodetachment events were induced by short UV laser pulses from an EdgeWave InnoSlab IS6III-E (Nd:YAG) laser at a wavelength $\lambda_{\text{laser}} = 355$ nm, corresponding to a photon energy $E_{ph} = 3.49$ eV. The laser pulses were generated at a repetition frequency of $f_{\text{laser}} = 1$ kHz with a duration between $\tau_{\text{laser}} = 9.0$ ns for $E_{\text{laser}} = 1.26$ mJ and $\tau_{\text{laser}} = 9.2$ ns for $E_{\text{laser}} = 0.14$ mJ. The laser pulse energy was measured using a laser power sensor (Ophir PE50-DIF-C pyroelectric sensor with an Ophir Starbright meter). The laser beam propagated through two thin slit (each on opposite sides of cavity, 2 mm wide and the height matching that of the cavity interior height) located in the side walls of the cavity, just below the glass tube exit, and through the radial center of the cavity. It was verified that no electrons were released from the walls inside the cavity by measuring the response of the gas-filled cavity to the UV laser pulses. The laser beam cross section was determined equal to $S = 8.9 \times 10^{-3}$ cm$^2$, and details of the beam cross section measurement can be found in appendix A.3. The volume initially perturbed by the laser beam resulted from the intersection of the laser beam and the spatial afterglow of the plasma column, which is further substantiated by the discussion in section 4.2.

In summary, MCRS and laser-induced photodetachment were applied to detect negative ions in the spectral afterglow of an RF-driven atmospheric pressure plasma jet. Synchronized with the laser pulses, MCRS provided the time-resolved shift in the resonance frequency and the reciprocal quality factor due to photodetached electrons for the different laser pulse energies. The cavity response was used to determine the photodetached electron density as a function of laser pulse energy, which in turn provided the negative ion density and the photodetachment cross section.

![Figure 2. Time-resolved shift of the relative resonance frequency $\Delta f/f_1$ resulting from laser-induced photodetachment for different laser pulse energies. The change in resonance frequency, for $t < 0 \mu s$, originates from electrons in the spatial plasma afterglow of the continuous argon discharge. At $t = 0 \mu s$, the laser was shot and electrons were liberated from negative ions by photodetachment up to a peak value. The signal decays again after reaching the peak value due to loss processes.](image)

3. Results

This section discusses the results obtained from the time-resolved MCRS measurements before, during and after the moment that the laser was shot. In section 3.1, the change in resonance frequency and inverse quality factor are shown as a function of time for several values of the laser pulse energy. In section 3.2, the values of the free electron density and the effective collision frequency before the laser shot are discussed, which allows to characterize the spatial afterglow of the continuous argon discharge. In section 3.3, the change in free electron density and effective collision frequency due to laser-induced photodetachment are discussed, from which valuable information is derived about the photodetachment process. In section 3.4, the decay time of the photodetached electron density and the relaxation of the effective collision frequency are treated providing insight in the decay process and the thermalization of the photodetached electrons with the afterglow electrons.

3.1. Time-resolved cavity response

The time-resolved scheme discussed in section 2 directly results in the determination of the relative shift in resonance frequency $\Delta f(t)/f_1 = (f(t) - f_1)/f_1$ and the shift in reciprocal quality factor $\Delta(1/Q(t)) = 1/Q_2(t) - 1/Q_1$, which are depicted for several laser pulse energies in figures 2 and 3, respectively.

The shifts measured for $t < 0 \mu s$, with respect to the neutral gas-filled cavity $f_1$ and $Q_1$, are caused by the plasma electrons in the spatial afterglow. As the diagnostic method is very sensitive, the temperature of the structure forming the cavity
was measured with mK resolution in order to correct the monitored resonant behavior for thermal expansion of the metal structure. Appendix A.4 presents a description of this correction method. The resulting variations in $\Delta f/f_1$ (roughly $\sim 5.5 \times 10^{-6}$) and in $\Delta (1/Q)$ (roughly $\sim 3.4 \times 10^{-5}$), measured before the laser shot, for the different laser experiments, are attributed to fluctuations in the plasma absorbed power. The standard deviation between the different background (electric-field-weighted) electron density values, as found in figure 4, compared to the mean of the background values is about $0.1/2.8 \approx 3.6\%$. The standard deviation of the plasma absorbed power, compared to the mean value, is $0.9/13.5 \approx 6.7\%$. If we assume that the measured (electric-field-weighted) electron density depends linearly on the plasma absorbed power, it is reasonable that the background electron density is expected to fluctuate over the course of consecutive laser experiments.

Additional shifts for $t > 0 \mu s$ were caused by the laser photodetached electrons, which added to that induced by the plasma. Photodetached electrons increased the shifts temporally, which vanished again after several $\sim \mu s$. Consequently, the change in resonance frequency and the inverse quality factor can be used to calculate the free electron density and effective collision frequency in the perturbed volume occupied by the intersection of the spatial afterglow and laser volume.

A peculiar feature in the signal is apparent after about $1–2 \mu s$ after the laser shot, where it can be seen from figure 2 that the shift in resonance frequency dives temporarily below the pre-laser shot value. However, it is not trivial that the free electron density decays below the density that was present before the laser shot. Given the relationship between the shift and the electron density, as defined by equation (2), there are two possible reasons stated here that could explain this phenomenon. First, it could be that the electrons are transported to regions where the microwave electric field is less sensitive. This would result in a lower electric-field-weighted volume-averaged electron density temporarily. The observation that the electric-field-weighted value returns to its original value indicates that the spatial distribution of the electron density is again restored within $\sim 4 \mu s$. Second, the plasma properties could be altered due to the energy deposited into the system by the laser such that the balance of physical processes (e.g. attachment and detachment reactions) shifts temporarily. The addition of energy (via the photodetached electrons) could improve the rate of attachment reactions, which results in a temporarily lower electron density. Although this effect directly relates to the electron density and the effective collision frequency, the absolute value of the negative shift in resonance frequency is much smaller than that of the positive shift caused by the laser photodetached electrons. Consequently, this effect is not relevant for the interpretation of the measurements and the purpose of this work, and therefore it is not discussed further in this work.

### 3.2. Argon discharge afterglow

The shifts of the resonance frequency and the inverse quality factor, as shown in figures 2 and 3, can be used directly in combination with equations (3) and (4) to obtain the free electron density and the effective collision frequency of the medium perturbing the microwave cavity. It should be noted that the definition of both quantities involves the assumption of a homogeneous medium such that the change in (complex) permittivity can be taken out of the electric-field-weighted...
averaged) electron density inside the laser volume, caused by the continuous argon discharge, is about 1.1 \times 10^{19} \text{ m}^{-3}, which is reasonably close to the experimental value \( n_e^* \). Therefore, it is concluded that the background electron density inside the laser volume is about 89 times higher than the electric-field-weighted electron density.

Based on theoretical calculations (see appendix A.6), it is found that \( \nu_{\text{eff}} \approx 28 \text{ GHz} \) for a mean electron energy \( \bar{\varepsilon} = 0.032 \text{ eV} \) (= 370 K) considering electron momentum transfer collisions with argon neutrals. Because the neutral argon number density is much higher than the neutral oxygen number density in the afterglow, only the electron collisions with argon are considered. This shows that the mean electron energy is significantly lower than the mean electron energy in the glow discharge region where \( \bar{\varepsilon} \sim 1–3 \text{ eV} \) [32, 33, 35–37].

3.3. Laser-induced photodetachment

Due to laser-induced photodetachment events, a sudden rise in the electron density and effective collision frequency is observed in figures 4 and 5, respectively, for \( t > 0 \mu s \). This sudden rise is caused by the laser shot with a pulse duration of \( \tau_{\text{laser}} = 9.0–9.2 \text{ ns} \) (dependent on laser pulse energy, and the fixed repetition frequency \( f_{\text{laser}} \)) leading to changes in resonant behavior on a timescale that follows from the cavity response time \( \tau_{\text{cav}} = Q_1/(\pi f_1) = 66 \text{ ns} \). This cavity response time determines the typical time it takes to charge energy into or from a resonant mode. In fact, the cavity was made from stainless steel in order to decrease the cavity response time compared to the copper cavity (with the same geometry) used by Platier et al. [29]. However, the effective collision frequency decreases during the first 40–70 ns—being limited by the response time of the cavity—before rising gradually to a peak value which exceeds the values determined for \( t < 0 \mu s \). This peak value is also limited by the cavity response, while the loss process already sets in during the rise time. The initial rapid decline of \( \nu_{\text{eff}} \) is caused by the relatively stronger increase of \( \Delta f \) with respect to the relative increase of \( \Delta(1/Q) \), where it should be noted that \( \nu_{\text{eff}} \approx \Delta(1/Q)/\Delta f \). A possible explanation of this behavior is that the resonance frequency shift due to the photodetached electrons temporarily increases more strongly than the quality factor does due to elastic collision losses. Therefore, the effective collision frequency of the medium as a whole is likely to decrease.

As shown in figure 4, it can be observed that the maximum number of photodetached electrons increases with the laser pulse energy, given the fixed beam cross section. The photodetached electron density in the laser perturbed volume provides valuable information on the negative ion species, which is analyzed in two steps.

First, the additional electron density caused by laser photodetachment \( N_e \) is calculated by correcting the free electron density \( n_e(t) \) with the base line electron density created by the argon discharge afterglow \( n_e^* \) (i.e. the values for \( t < 0 \mu s \) in the figures), and scaling the photodetached electron density with the (microwave-electric-field-weighted) ratio of the plasma and laser volume (see appendix A.1). The maximum value of the photodetached electron density, \( N_{e_{\text{max}}} \), for all applied
laser pulse energies, $E_{\text{laser}}$, is depicted in figure 6 (by the colored data points). It should be noted here that the experiments for different laser pulse energy were performed in a random order on purpose to ensure that (possible) one-way drifts, e.g. in RF power or gas composition, did not obscure the saturation study. In this figure, it can be seen that the maximum number of photodetached electrons increases as a function of laser pulse energy. As the number of negative ions is finite, a sufficient fluence of laser photons results in the saturation of the number of photodetached electrons as can be observed clearly from figure 6.

Second, the trend in $N_e^{\text{max}}$ can be fitted with the photodetachment saturation model, as shown in figure 6 by the dotted line, to derive the photodetachment cross section $\sigma_{\text{pd}}$ and saturated photodetached electron density $N_{e}^{\text{sat}}$:

$$N_e^{\text{max}} = N_e^{\text{sat}} \left( 1 - \exp \left( \frac{\sigma_{\text{pd}} E_{\text{laser}}}{E_{\text{ph}} S} \right) \right).$$

Here, the photon energy is denoted by $E_{\text{ph}} = 3.49 \text{ eV}$, and the laser beam cross section $S = 8.9 \times 10^{-3} \text{ cm}^2$ is based on the 1/e-diameter of the laser beam cross section (see appendix A.3). The quotient $\sigma_{\text{pd}} / (E_{\text{ph}} S)$ is used as one of the two parameters in the model fitted to the data, which in this experiment results in the photodetachment cross section $\sigma_{\text{pd}} = 8(\pm 2) \times 10^{-15} \text{ cm}^2$, and the saturated photodetached electron density $N_e^{\text{sat}} = 2 \times 10^{18} \text{ m}^{-3}$. The uncertainty in $\sigma_{\text{pd}}$ originates directly from the uncertainty in $S$, which is due to the Gaussian fit to the (spatially-resolved) laser intensity profile, resulting in an uncertainty of $\tilde{S} = 2.0 \times 10^{-3} \text{ cm}^2$. At saturation, the (saturated) photodetached electron density $N_e^{\text{sat}}$ equals the negative ion density in the laser volume assuming singly charged negative ions.

Finally, it should be noted that a homogeneous plasma volume was assumed during the derivation of equations (3) and (4). However, the uniformity of the electron density is not guaranteed due to the complex interplay of the (undetermined) spatial mixing of oxygen and electrons in the afterglow forming negative ions, and the Gaussian distribution of the laser beam intensity. For verification of the uniformity of $\nu_{\text{rel}}$, the thermalization time of the electrons was studied [38]. This time is about 9.5 ns for electrons with a mean electron energy $\bar{\varepsilon} = 2.02 \text{ eV}$ in argon at atmospheric pressure (see section 4.4 for a detailed analysis). Here, the mean electron energy $\bar{\varepsilon} = E_{\text{ph}} - E_A$ follows from the difference between the photon energy $E_{\text{ph}} = 3.49 \text{ eV}$ and the electron affinity of the negative ions $E_A = 1.47 \text{ eV}$ (for O$^-$ [39], which is expected as the dominant negative ion species (see section 4.1). Consequently, the electrons quickly lose their energy in the afterglow, and the effective collision frequency can serve as a measure for both the plasma and laser volume.

### 3.4. Decay of photodetached electrons

After reaching the temporal peak value, the photodetached electron density follows an exponential decay back to the steady state value, which equals the pre-laser shot value of the spatial afterglow of the plasma. An exponential curve fit was applied to the determined signals for the free electron density, which are shown for the considered time frame by the solid lines in figure 7. The exponential curve fits are depicted in figure 7 by the dashed lines. The data was fitted for measurement times between $t = 0.320 - 0.376 \mu s$ (i.e. the moment of the peak value) and $t = 2.0 \mu s$ (where the signal...
approximated the pre-laser shot value). Likewise, an exponential curve fit was also applied to data measured for the effective collision frequency. For all settings, the mean and standard deviation of the decay time of the free electron density is 0.366(+/−0.029) µs, and a mean and standard deviation of 0.368(+/−0.007) µs was found for the decay time of the effective collision frequency. The fact that the decay of the signals agrees well with an exponential curve indicates that the loss of electrons and the relaxation of their energy is caused by a first-order process, which is discussed in detail in sections 4.3 and 4.4.

4. Discussion

This section contains the interpretation of the major findings from the experimental results presented in this work. Section 4.1 covers the interpretation of the found photodetachment cross section and negative ion density, and concludes with the identification of the major negative ion species present in the afterglow. Section 4.2 provides the validity of using the interaction of the spatial afterglow and the laser beam cross section as the perturbed volume, which is substantiated by investigation of the lifetime of the major negative ion species. Section 4.3 discusses the different mechanisms for the loss of electrons by negative ion formation and recombination, of which the timescales are compared to the experimentally determined decay time of the electron density and effective collision frequency. Section 4.4 treats the relaxation of the electron energy in detail with a specific focus on the thermalization of the electron energy after the photodetachment events, and the relaxation of the mean electron energy as observed from the determined effective collision frequency signals.

4.1 Identification of anion species

The found photodetachment cross section of $\sigma_{pd} = 8(+/−2) \times 10^{-19}$ cm$^2$ agrees well with experimental and theoretical values, obtained from literature, for the negative atomic oxygen ion at $\lambda_{laser} = 354$ nm: $8 \times 10^{-18}$ cm$^2$ by Branscomb et al [40], $10 \times 10^{-18}$ cm$^2$ by Génévérez et al [41], and—to a lesser extent—to the value $12 \times 10^{-18}$ cm$^2$ by Jackson and Garrett [42]. By contrast, the cross section obtained from the measurement is significantly higher than those reported in literature for $O_2^−$ and $O_3^−$, which equal $\sigma_{O_2^−} = 3.7 \times 10^{-18}$ cm$^2$ and $\sigma_{O_3^−} = 2 \times 10^{-18}$ cm$^2$, respectively, at 350 nm [43, 44]. Besides oxygen species, the formation of anions containing hydrogen is likely due to water vapor left prior to the experiment (the pre-experiment vacuum pressure was $\leq 9.8 \times 10^{-1}$ mbar). Common negative ions involving hydrogen are H$^-$ and OH$^-$, for which the respective photodetachment cross sections equal $\sigma_{H^-} = 20 \times 10^{-18}$ cm$^2$ at 354 nm [45] and $\sigma_{OH^-} = 7.6 \times 10^{-18}$ cm$^2$ at 350 nm [46], respectively. As a consequence, based on the photodetachment cross sections, the fitted cross section suggests that the dominantly present negative ions can be O$^-$ and/or OH$^-$.

The absolute value of the negative ion density is the main outcome of the saturation study, which hints towards the negative ion species that is predominantly formed by the interaction of the argon discharge with the argon-oxygen background gas mixture. Numerical modeling by van Gaens and Bogaerts [34] shows that the number density of the negative oxygen ion O$^-$ is dominant over other negative ion species such as $O_2^−$, $O_3^−$, H$^-$, OH$^-$, and NO$^-$ in the early afterglow, i.e. within a distance of 2 mm from the nozzle exit. In that model [34], in which an argon jet propagates in ambient air (containing nitrogen, oxygen and water molecules), the density of negative atomic oxygen ions equaled $n_{O^-} \approx 1 \times 10^{16}$ m$^{-3}$, and this value was found to be approximately three orders of magnitude smaller than the electron density. In a model by Park et al [37], however, values of $n_e \approx 3 \times 10^{17}$ m$^{-3}$ and $n_{O^-} \approx 1 \times 10^{15}$ m$^{-3}$ were found in an argon-oxygen mixture using a power density of $1 \times 10^8$ W m$^{-3}$ at a RF of 13.56 MHz. The power density ($0.9 \times 10^8$ W m$^{-3}$) during our experiment was similar to that, but the oxygen density in the afterglow could have been higher due to mixing of the argon discharge with the argon-oxygen background mixture. In a (geometrically) similar plasma jet studied by van Gessel et al [47], the partial air density quickly reached values close to 20% of the discharge gas density (argon in our experiment) due to mixing of ambient air with the discharge gas flow. By comparison of our experiment to the model by Park et al [37], it is found that the negative ion density measured in our experiment is an order of magnitude higher than calculated from models under similar discharge conditions. This is most probably due to a higher mixing ratio in our experiment compared to the mixing ratio used in their model. Comparing to the model by van Gaens and Bogaerts [34], it can be concluded that the chemistry in our argon-oxygen mixture is potentially much simpler by the lack of nitrogen- and (dominant) hydrogen-containing species.

In conclusion, the photodetachment cross section suggests that the negative ion species detected are most likely O$^-$ and/or OH$^-$, and/or O$_2$$^-$, while the saturated photodetached electron density provides a measure for the negative ion density. Comparing this value to those found from numerical models suggests that negative atomic oxygen ions are probably dominant in the early afterglow (directly following the exit of the discharge region, or glass tube in our experiments). It was also confirmed experimentally, in atmospheric pressure helium-oxygen (dielectric barrier) discharges, that the negative atomic oxygen ion is the dominant anion species [48, 49]. Considering the low content of water vapor in our measurement, it is concluded that atomic oxygen most probably is the major negative ion species present at a density of $2 \times 10^{18}$ m$^{-3}$ in the early spatial afterglow.

4.2 Detachment processes from O$^-$

With the identification of the major negative ion, the validity of the assumed perturbed volume can be further investigated by studying the lifetime of O$^-$. The volume governed by the intersection of the spatial afterglow and the laser beam cross section was used as the perturbed volume by laser-induced photodetachment, which is included in the calculation of the electric-field-weighted volume ratio $\gamma$. However, it is not excluded...
that negative ions are present outside this volume, for instance, through radial diffusion if their lifetime is long enough.

The lifetime of the negative ions created in the spatial afterglow can be estimated by studying processes of detachment. Detachment processes occur through collisional detachment with neutrals, electron-induced three-body collisional detachment, and associative detachment. Electron-induced collisional detachment is expected to be negligible compared to the neutral variant [50], because the electron density is much smaller than the neutral gas density (of Ar and O2). Collisional detachment with neutrals can proceed by collisions with, e.g. oxygen [51],

$$O^- + O_2 \rightarrow O + O_2 + e, \quad \text{(R1)}$$

but the timescale for this process goes to infinity for ion temperatures near room temperature. On the other hand, associative detachment follows from collisions between negative atomic oxygen ions with atomic [52] and molecular oxygen [53],

$$O^- + O \rightarrow O_2 + e, \quad \text{(R2)}$$

$$O^- + O_2 \rightarrow O_3 + e. \quad \text{(R3)}$$

The timescale $\tau_i$ for the $i$th first-order reaction scheme, i.e. for reactions (R1) to (R3), is derived in appendix A.7 using the reaction rate coefficient $k_i$ and the density of reacting species $n_i$:

$$\tau_i = \frac{1}{k_i n_i} \quad \text{(6)}$$

The values of the species densities $n_i$ are listed in table 1, which are based on the numerical model of van Gaens and Bogaerts [34]. Equation (6) is used to calculate the timescale for each reaction resulting in $\tau_{K2} = 71 \text{ ns}$ and $\tau_{K3} = 13 \text{ ns}$.

The detachment timescale implies that negative ions are quickly destructed by collisions with neutral gas particles, leading to a short lifetime. This means that the negative ions cannot travel far from the spatial afterglow region. Consequently, the intersection of the spatial afterglow and the laser beam cross section provides an excellent estimate for the perturbed volume.

4.3. Decay of the photodetached electron density

The decay of the photodetached electron density back to its pre-laser pulse value can be caused by various processes, including diffusion, advection, wall losses, recombination with positive ions, and negative ion formation.

First, diffusion and advection can move electrons to regions where the resonant microwave mode is less sensitive to perturbations, for example, at locations away from the radial center, whereas wall losses can lead to the physical loss of free electrons. The movement of electrons through the cavity is considered based on the length scales associated with (ambipolar) diffusion and advection. Ambipolar diffusion governs the diffusive movement during the experiment for which $n_e \approx 10^{17} \text{ m}^{-3}$. This can be verified by studying the ratio of the characteristic diffusion length $\Lambda = 4.8 \text{ mm}$ [54], which is more than 100 times larger than the Debye length $\lambda_\text{De} \approx 20 \mu\text{s}$ in our experiment. Therefore, this characteristic length ratio largely exceeds the threshold for the transition to the free diffusion regime [54–56]. The length scale for (ambipolar) diffusion is $\Lambda_\text{diff} = \sqrt{D_\text{amb}/\tau_\text{decay}} \approx 0.3 \text{ mm}$ using the ambipolar diffusion coefficient [57] equal to $D_\text{amb} = 0.3 \text{ m}^2 \text{s}^{-1}$ (at $E/N = 0.1 \text{Td}$) and $\tau_\text{decay} = 0.37 \mu\text{s}$ as obtained from the experiment in section 3.4. The length scale for advection, i.e. electrons carried by the gas flow, is estimated (in worst-case) by using the gas velocity in the glass tube ($v_e \approx 15 \text{ m s}^{-1}$) such that $\Lambda_\text{adv} = v_e \tau_\text{decay} = 5.8 \mu\text{s}$. From the above, it can be directly concluded that the electrons are not able to reach the walls within the timescales of the observed decay. Furthermore, the expansion of the electron cloud due to diffusion and advection leads to at most a factor 1.3 increase in plasma volume, because the radial expansion is leading the volumetric expansion of the spatial afterglow such that $((R_\text{plasma} + \Lambda_\text{diff})/R_\text{plasma})^3$. This implies that diffusion, advection and wall losses are not dominant processes under the current conditions.

Second, a major electron loss channel could be due to recombination, which is stimulated in the spatial afterglow by an electron mean energy that is decreasing over time after the laser pulse. Recombination of electrons with positive ions can proceed by a two or three body process, where Ar$^+$ [58], Ar$^+_2$ [59], and O$^+$ [60] are considered as positive ion species:

$$e + Ar^+ \rightarrow Ar(4P), \quad \text{(R4)}$$

$$e + Ar_2^+ \rightarrow Ar(4P) + Ar, \quad \text{(R5)}$$

$$e + O^+ + Ar \rightarrow O + Ar, \quad \text{(R6)}$$

$$e + O^+ + O_2 \rightarrow O + O_2. \quad \text{(R7)}$$

Third, the formation of atomic negative oxygen ions (found as the main species in section 4.1) proceeds by radiative attachment, electron-impact dissociative attachment, and three-body stabilized attachment [50]. Radiative attachment [50] produces a negative oxygen ion and a photon $h\nu$:

$$e + O \rightarrow O^- + h\nu. \quad \text{(R8)}$$

Dissociative attachment occurs by interaction of an energetic electron with O$_2$ [50] or O$_3$ [37].
Concerning recombination, the smallest timescale follows coefficients found from the literature stated for each reaction. species densities listed in table 1 and the reaction rate coefficients based on the energy gained by the electrons directly after photodetachment well in agreement with the measured decay time. Considerably high:

$$R_5: 2.96 \mu s$$

$$R_4: 40.31 \text{ s}$$

By electron impact (reaction (R10)) provides a timescale for an electron mean energy close to room temperature. Considerably high:

$$R_{11}: 400 \text{ ms}$$

$$R_6: 2680 \text{ s}$$

$$R_7: 268031 \text{ s}$$

$$R_8: 7.69 \text{ s}$$

$$R_9: 100 \text{ s}$$

$$R_{10}: 0.40 \mu s$$

$$R_{11}: 400 \text{ ms}$$

$$R_{12}: 4 \text{ ms}$$

Electron attachment stabilized by a third body \[60\] occurs, with $O_2$ or $Ar$ as the stabilizing agent, in case its density is sufficiently high:

$$e + O_3 \rightarrow O^- + O_2,$$  \hspace{1cm} (R9)

$$e + O_2 \rightarrow O^- + O.$$  \hspace{1cm} (R10)

The electron-neutral mean free path $\lambda_{ne}$, the Debye length $\lambda_{De}$ and the distance of closest approach between electrons $r_0 = \lambda_{De}/(2N_{De})$ (where $N_{De}$ denotes the Debye number, i.e. the number of electrons in the Debye sphere) \[38\]. The electron-neutral mean free path for photodetached electrons with energy $\epsilon = 2.03 \text{ eV}$ equals $\lambda_{ne} = v_e\lambda^{-1}$ with the electron velocity $v_e = \sqrt{2\epsilon/m_e}$ in this work. The electron-neutral collision frequency of the photodetached electrons directly after photodetachment equals, for argon, $\nu_{en} \approx 571 \text{ GHz}$, and for oxygen, $\nu_{en} \approx 1413 \text{ GHz}$ (see appendix A.6). This results in an electron-neutral mean free path of $\lambda_{e-Ne} \approx 1.5 \mu s$ for argon collisions and $\lambda_{e-O_2} \approx 0.6 \mu s$ for collisions with oxygen. The Debye length is defined as $\lambda_{De} = \sqrt{\varepsilon_0\varepsilon_\mu}/(n_e e^2) \approx 20 \mu s$, and consequently, the distance of closest approach $r_0 = 0.035 \mu s$. Clearly, the following ordering applies to our experiments where $r_0 < \lambda_{en} < \lambda_{De}$, which implies that the electrons collide frequently with neutrals in the Debye sphere. As a result, the energy equilibration between electrons occurs on a timescale $\tau_{en} = N_{De}/(2\pi r_0^2) = 9.5 \text{ ns}$, and the electron energy gained by photodetachment is rapidly distributed among the electrons in the afterglow.

4.4. Electron energy relaxation

The change in the effective collision frequency depends strongly on the mean electron energy. During the laser photodetachment phase, a gradual rise of the effective collision frequency is observed. This value for $\nu_{eff}$ is used for the determination of the electron density created by the argon discharge and that created by the photodetachment events. The first part of this subsection discusses the validity of $\nu_{eff}$ for the entire perturbed volume by investigating the thermalization of energetic electrons—resulting from photodetachment—and afterglow electrons with a mean energy close to room temperature.

Collisions of photodetached electrons with afterglow electrons govern the electron energy distribution, and thereby the relaxation of the photodetached electrons’ energy to the cold afterglow electron temperature. The timescale of the electron–electron collisions depends strongly on the ratio of the electron-neutral mean free path $\lambda_{en}$, the Debye length $\lambda_{De}$ and the distance of closest approach between electrons $r_0 = \lambda_{De}/(2N_{De})$ (where $N_{De}$ denotes the Debye number, i.e. the number of electrons in the Debye sphere) \[38\]. The electron-neutral mean free path for photodetached electrons with energy $\epsilon = 2.03 \text{ eV}$ equals $\lambda_{en} = v_e\lambda^{-1}$ with the electron velocity $v_e = \sqrt{2\epsilon/m_e}$ in this work. The electron-neutral collision frequency of the photodetached electrons directly after photodetachment equals, for argon, $\nu_{en} \approx 571 \text{ GHz}$, and for oxygen, $\nu_{en} \approx 1413 \text{ GHz}$ (see appendix A.6). This results in an electron-neutral mean free path of $\lambda_{e-Ne} \approx 1.5 \mu s$ for argon collisions and $\lambda_{e-O_2} \approx 0.6 \mu s$ for collisions with oxygen. The Debye length is defined as $\lambda_{De} = \sqrt{\varepsilon_0\varepsilon_\mu}/(n_e e^2) \approx 20 \mu s$, and consequently, the distance of closest approach $r_0 = 0.035 \mu s$. Clearly, the following ordering applies to our experiments where $r_0 < \lambda_{en} < \lambda_{De}$, which implies that the electrons collide frequently with neutrals in the Debye sphere. As a result, the energy equilibration between electrons occurs on a timescale $\tau_{en} = N_{De}/(2\pi r_0^2) = 9.5 \text{ ns}$, and the electron energy gained by photodetachment is rapidly distributed among the electrons in the afterglow.

After the photodetachment peak, the effective collision frequency decays analogous to the electron density and on a similar time scale $\tau_{decay} \sim 0.26–0.46 \mu s$. The energy relaxation of the electron cloud proceeds by electron-neutral collisions, during which an electron transfers part of its energy to the heavier particle. The timescale of energy exchange $\tau_{en} = \nu_{en}^{-1}m_N/m_e$ equals $\tau_{e-Ne} = 0.129 \mu s$ for argon, and $\tau_{e-O_2} = 0.021 \mu s$ for oxygen. It should be noted that during each electron-neutral encounter, part of the electron’s energy is lost, which decreases the momentum transfer collision frequency $\nu_{en}$ and increases the energy exchange timescale along the process. In conclusion, this means that the energy exchange timescale provides a lower limit, whereas the timescale for energy relaxation will be larger in practice.

In conclusion, the distribution of excess energy between background and photodetached electrons in the afterglow proceeds on $\sim0.01 \mu s$ timescales through electron–electron collisions. These collisions are responsible for the energy equilibration between energetic photodetached electrons and cold
afterglow electrons, and serve as a motivation for the use of \( \nu_{\text{eff}} \) determined by MCRS for the calculation of the electron density by the argon discharge afterglow and photodetached electron density. On longer timescales of the order \( \sim 0.1 \mu s \), the energy relaxation (i.e., the loss of electron mean energy to the neutral gas) proceeds by electron-neutral collisions during which energy is efficiently exchanged to the cold neutral gas. This timescale is observed from the measurements.

5. Conclusion

This work demonstrates that negative ions can be detected in the spatial afterglow of an atmospheric pressure discharge using laser-induced photodetachment in combination with MCRS as a diagnostic technique for detecting the density and effective collision frequency of the electrons photodetached from negative ions. The temporal behavior of the photodetached electrons was successfully determined using MCRS, which provided the free electron density and effective collision frequency as a function of time before, during and after the laser shot. As a consequence, the number density and collision frequency caused by the discharge afterglow and the photodetachment events could be determined providing insight in the dynamics of the major negative ion species. Based on the photodetachment cross section and negative ion density estimated from our experiments, it was found that the atomic oxygen ion formed the major negative ion species. After the photodetached electron density and the effective collision frequency reached their respective maxima, dissociative attachment was most probably responsible for the decay of the photodetached electron density after the laser shot. The combination of laser-induced photodetachment and MCRS opens a path for studying negative ions created by atmospheric pressure discharges, which are vital plasma agents in the formation of reactive oxygen species and the plasma afterglow chemistry as a whole. Future experiments in the same setup could be targeting the spatial dependence of the negative ion species, and selectively probing different negative ions due to the distinct electron affinity by using different laser wavelengths. In addition, the technique demonstrated in this work could be extended towards gas discharges excited by, e.g., pulsed high-voltage or microwaves, and in different gas mixtures.

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Data availability

The data that support the findings of this study are available upon reasonable request from the authors.

Conflicts of interests

The authors declare no competing interests.

Code availability

The computer code used for the data analysis and interpretation is available from the corresponding author upon reasonable request.

Appendix A

A.1. Electric-field-weighted volume ratio

The electric-field-weighted volume ratio is an important factor in the determination of the free electron density based on the cavity response. The solution of the microwave electric field is shown in figure 8, which was obtained using COMSOL Multiphysics® by solving the Maxwell equations for the cavity and plasma jet geometry for the (fundamental) resonant mode TM010. This solution was used in a custom MATLAB program to evaluate the electric-field-weighting integrals over the plasma and laser volumes with respect to the total cavity volume. As a result, the fact that the cavity was only partially perturbed in a region should be corrected for using \( V \) in the evaluation of the electron density based on the determined \( \Delta f \) and \( \Delta (1/Q) \) from MCRS measurements.

The expression for \( V \) follows by definition, when converting the Slater perturbation equation to equations defining the
free electron density and effective collision frequency, as:

\[
\mathcal{V}_p = \frac{\iiint \mathcal{V}_V |\mathbf{E}(\mathbf{r})|^2 \, d\mathbf{r}}{\iiint \mathcal{V}_V |\mathbf{E}(\mathbf{r})|^2 \, d\mathbf{r}} = 7.3 \times 10^{-4},
\]

(7)

\[
\mathcal{V}_l = \frac{\iiint \mathcal{V}_l \mathbf{E}(\mathbf{r})^2 \, d\mathbf{r}}{\iiint \mathcal{V}_l \mathbf{E}(\mathbf{r})^2 \, d\mathbf{r}} = 4.2 \times 10^{-6}.
\]

(8)

Here, \( \mathcal{V}_p \) denotes the electric-field-weighted plasma volume ratio, and \( \mathcal{V}_l \) the electric-field-weighted laser volume ratio. The integral in the numerator of each of the equations is calculated over the estimated plasma or laser volume. The plasma volume was observed by camera images and it resembles a cone with a base that coincides with the inner cross section of the quartz tube, i.e. a circle with a diameter of 2.0(+/−0.1) mm and a height along the z-direction in figure 8 of 20(+/−1) mm. The laser volume is formed by the region where the plasma and laser volume intersect, whereas the laser cross section is obtained by charge-coupled device (CCD) camera images (see appendix A.3). The integral over the whole cavity volume \( \mathcal{V}_{\text{cav}} \) was obtained by integrating over the complete extent of the radial and axial axes.

A.2. Calculation of the photodetached electron density

The relation between the change in complex permittivity \( \Delta \bar{\varepsilon} \), the shift in the resonance frequency \( \Delta f \), and the change in inverse quality factor \( \Delta (1/Q) \) are formalized by the Slater equation [25, 27, 61]:

\[
\frac{\Delta f}{f_1} + i \frac{1}{2} \left[ \frac{\Delta \left( \frac{1}{Q} \right)}{\frac{1}{Q}} \right] = -\frac{\iiint \mathcal{V}_V \Delta \bar{\varepsilon} |\mathbf{E}|^2 \, d\mathbf{r}}{2\varepsilon_0 \iiint \mathcal{V}_V |\mathbf{E}|^2 \, d\mathbf{r}}.
\]

(9)

For a homogeneous medium, \( \Delta \bar{\varepsilon} \) in the numerator integral in equation (9) is non-zero only inside the perturbed volume (due to electrons from the plasma or created by photodetachment). Hence, the change in complex permittivity can be taken outside the integral due to homogeneity and the numerator integral can be taken over the perturbed volume, \( V \), only:

\[
\frac{\Delta f}{f_1} + i \frac{1}{2} \Delta \left[ \frac{1}{Q} \right] = -\Delta \bar{\varepsilon} \mathcal{V},
\]

(10)

with the electric-field-weighted volume ratio \( \mathcal{V} \) defined as:

\[
\mathcal{V} = \frac{\iiint \mathcal{V}_V |\mathbf{E}|^2 \, d\mathbf{r}}{\iiint \mathcal{V}_V |\mathbf{E}|^2 \, d\mathbf{r}}.
\]

(11)

The volume ratio equals \( \mathcal{V}_p = 7.3 \times 10^{-4} \) for the plasma volume, i.e. \( V = V_p \), and \( \mathcal{V}_l = 4.2 \times 10^{-6} \) for the volume perturbed by the laser photodetachment events, i.e. \( V = V_l \). The electron density and effective collision frequency are found by relating the real and imaginary part of the left- and right-hand sides in equation (10). In this experiment, two homogeneous regions—with the same collision frequency—will be assumed as explained below.

For the continuous gas discharge, the shift in resonance frequency and inverse quality factor for \( t < 0 \) \( \mu s \), the electron density and effective collision frequency can be derived as follows:

\[
\frac{\Delta f}{f_1} = \frac{e^2}{2\varepsilon_0 m_e \nu_{\text{eff}, p} + \omega_2^2} \mathcal{V}_p
\]

(12)

where the subscript \( p \) indicates plasma-related quantities. Similarly, the inverse quality factor can be defined in terms of measured quantities:

\[
\frac{\Delta (1/Q)}{Q} = \frac{e^2}{2\varepsilon_0 m_e \nu_{\text{eff}, p} + \omega_2^2} \mathcal{V}_p \mathcal{V}_l.
\]

(13)

By rewriting the equation for \( n_{e,p} \) and \( \nu_{\text{eff}, p} \), the expressions can be evaluated based on the measured shifts \( \Delta f \) and \( \Delta (1/Q) \):

\[
n_{e,p} = \frac{2\varepsilon_0 m_e \nu_{\text{eff}, p}^2 + \omega_2^2}{e^2} \frac{\Delta f}{f_1} \mathcal{V}_p.
\]

(14)

\[
\nu_{\text{eff}, p} = \pi^2 \frac{\Delta (1/Q)}{\Delta f} \mathcal{V}_l.
\]

(15)

For \( t > 0 \) \( \mu s \), when the signals start to change due to photodetachment, the situation is a bit more complicated due to the presence of two volumes with a different permittivity. The first volume is the plasma volume described above without the laser perturbed volume. This volume is occupied by the electron density determined from the signals for \( t < 0 \) \( \mu s \). The second volume is the laser perturbed volume, which contains a different electron density. Hence, the following equation can be derived for the electron density in the laser volume based on the measured frequency shift for \( t > 0 \) \( \mu s \):

\[
\frac{\Delta f}{f_1} = \frac{e^2}{2\varepsilon_0 m_e \nu_{\text{eff}, p} + \omega_2^2} \mathcal{V}_p \mathcal{V}_l \left( \mathcal{V}_p - \mathcal{V}_l \right) + \frac{n_{e,p} + n_{e,1}}{\nu_{\text{eff}, l}^2 + \omega_2^2} \mathcal{V}_l.
\]

(16)

The effective collision frequency is assumed to be equal in both volumes as discussed in section 4.3. Using \( \nu_{\text{eff}, p} = \nu_{\text{eff}, l} \), the following expression for the laser-induced electron density can be derived:

\[
n_{e,1} = \frac{2\varepsilon_0 m_e \nu_{\text{eff}, l}^2 + \omega_2^2}{e^2} \frac{\Delta f}{f_1} \mathcal{V}_l - \mathcal{V}_p \mathcal{V}_l.
\]

(17)

This equation is used for the calculation of the photodetached electron density, which provides the peak values for figure 6 and the data for curve fitting for figure 7.

A.3. Beam cross section

The cross section of the laser beam \( S \) is required for the evaluation of the saturation curve and to determine the laser perturbed volume. To obtain the value of this parameter, the experimental setup was slightly adapted with the following changes. First, the second vacuum window (quartz) was removed to obtain better images of the laser beam shape monitored in the way it interacted with the plasma afterglow. Second, a CCD camera was placed after the cavity to capture the laser light. Third, a neutral density filter with reduction order 2.0 was placed in front the CCD camera so that the laser intensity was reduced by a factor of \( 1 \times 10^2 \).
Figure 9. Beam cross section of the pulsed UV laser. The image was obtained by directing the laser light, at low laser pulse energy, onto a CCD camera via a 2.0 neutral density filter reducing the intensity by a factor of $1 \times 10^2$.

Figure 10. Gaussian beam fit based on measured laser intensity distribution. The Gaussian beam fit provides an experimental value for the beam cross section $S = 8.9 \times 10^{-3}$ cm$^2$.

As can be seen at the top of figure 9, the beam is approximately circular with a peak intensity in the center that falls off radially. The top figure depicts an average of 50 images obtained under the same conditions to average out fluctuations in the laser intensity. A Gaussian beam fit was applied to the measured data, which resulted in figure 10.

The beam cross section is obtained by numerically integrating the region with significant light intensity, i.e. $I > 1/e \times I_0$. First, each pixel, sized 3.75 μs in width and height direction, gains a value equal to 0 if the intensity is below this threshold, or 1 if the intensity exceeds the threshold. This resulted in a beam cross section equal to $S = 8.9 \times 10^{-3}$ cm$^2$, which corresponds to a beam radius of 0.53 mm. By calculating the difference between the Gaussian fit and the original data, the error in the beam cross section is determined to be $\tilde{S} = 2.0 \times 10^{-3}$ cm$^2$.

Figure 11. Resonance frequency with only neutral (argon-oxygen) gas mixture $f_1$ as a function of the average cavity temperature $T_{cav}$ measured during the MCRS experiments. The average cavity temperature during each MCRS experiment, providing a certain resonance frequency at that temperature, are shown by the solid red dots. The linear curve fit is depicted by the dashed line, which provides the thermal expansion coefficient of the cavity to corrected for temperature effects in the reference resonance frequency $f_1(T_{cav})$.

Figure 12. The numerical profile of the electron density $n_{e\text{NUM}}$ obtained from van Gaens and Bogaerts [34], was used to assess the ratio between the electric-field-weighted volume-averaged electron density $n_{e\text{NUM,MCRS}}$ and the (background) volume-averaged electron density inside the laser volume $n_{e\text{NUM,LV}}$. A (non-weighted) volume-averaged electron density $n_{e\text{NUM,VA}}$ was also calculated to indicate the effect of the electric-field weighting, where the electric field strength increases (towards the cavity center) with increasing $z$.

A.4. Temperature-correction of resonance frequency

The resonance frequency of the cavity depends strongly on its temperature. An NTC thermistor was mounted on the cavity to monitor the temperature with 1 mK resolution for each microwave frequency probed during the MCRS measurements. Figure 11 depicts the average cavity temperature...
Theoretical analysis of effective collision frequency for momentum transfer collisions between electrons and argon. (a) The momentum transfer cross section $\sigma_{e^- Ar}^{m}$ for collisions between electrons and argon is shown as a function of the electron energy $\varepsilon$. (b) The momentum transfer collision frequency $\nu_{e^- Ar}^{m}$, calculated using equation (19), is depicted as a function of electron energy $\varepsilon$. (c) The theoretical calculation of the effective collision frequency $\nu_{e^- Ar}^{eff}$ for electron-argon collisions as a function of the mean electron energy $\bar{\varepsilon}$.

A.5. Estimation of background density in laser volume

In order to compare the negative ion density with the (background) electron density produced by the gas discharge, this section provides an interpretation of the electric-field-weighted volume-averaged electron density, $n_{1e}$, that directly results from the MCRS measurements. For clarity, it is noted again that the MCRS signal before the laser shot provides this electron density value, which is a measure for the average electron density across the whole spatial afterglow volume probed by the diagnostic. Because the electron density falls off by several orders of magnitude over a few centimeter length, the electric-field-weighted electron density $n_{1e}$ is much lower than the (local) background electron density in regions closer to the gas discharge such as the laser volume.

The following analysis is based on the numerical profile of the electron density as obtained from simulations performed by van Gaens and Bogaerts [34], using the following approach:

- The one-dimensional numerical electron density profile (superscript: NUM) as shown in figure 2 in the paper by van Gaens and Bogaerts [34] was digitized, loaded into a custom Matlab program, interpolated on a uniform grid, and depicted in figure 12.
- The microwave electric field solution, used for the calculation of the electric-field-weighted volume ratios $V'$, was loaded into the same program.
A.6. Theoretical analysis of collision frequency

The electron-neutral momentum transfer cross section $\sigma_m$ has been obtained from the LXCat database for both argon and oxygen [57]. The dependence of $\sigma_m$ on the (directed) electron energy $\varepsilon$ can be seen from the panels (a) in figures 13 and 14. Based on the momentum transfer cross section $\sigma_m(\varepsilon)$, the momentum transfer collision frequency for electron-neutral collisions can be calculated as follows:

$$\nu_m = n_e \sigma_m(\varepsilon) v_e, \quad (19)$$

where $n_e$ denotes the neutral gas density (equals $2.5 \times 10^{25} \text{ m}^{-3}$ at atmospheric pressure), and $v_e = \sqrt{2\varepsilon/m_e}$ the electron velocity. The momentum transfer collision frequency $\nu_m$ is shown in the panels (b) of figure 13 for argon, and figure 14 for oxygen.

The (microwave-)electric-field-weighted volume average electron density along the axial dimension (superscript: NUM, MCRS) was calculated using the formula:

$$n_e^{\text{NUM,MCRS}} = \int_0^L n_e^{\text{NUM}}(z) E^2 \, dz / \int_0^L E^2 \, dz \quad \text{with} \quad E = \sqrt{E(r = 0, z)}.$$

$L = 15 \text{ mm}$ and $z$ is the coordinate along the axial dimension (parallel to the primary gas flow direction).

The volume-averaged electron density, inside the laser volume (superscript: NUM, LV), was calculated by averaging the numerical profile values for the first 2 mm (along the $z$-axis) such that:

$$n_e^{\text{NUM,LV}} = \int_{\text{laser}} n_e^{\text{NUM}}(z) \, dz / D_{\text{laser}} = 2 \text{ mm}.$$

The ratio of $n_e^{\text{NUM,LV}} / n_e^{\text{NUM,MCRS}} \approx 89$.

This shows that the local (volume-averaged) electron density in the laser volume can be about two orders of magnitude higher than the electric-field-weighted volume-averaged value, if a similar electron density profile as used for this assessment is also established in our experiment.

$\bullet$ The (microwave-)electric-field-weighted volume averaged electron density along the axial dimension (superscript: NUM, MCRS) was calculated using the formula:

$$n_e^{\text{NUM,MCRS}} = \int_0^L n_e^{\text{NUM}}(z) E^2 \, dz / \int_0^L E^2 \, dz \quad \text{with} \quad E = \sqrt{E(r = 0, z)}.$$

$L = 15 \text{ mm}$ and $z$ is the coordinate along the axial dimension (parallel to the primary gas flow direction).

$\bullet$ The volume-averaged electron density, inside the laser volume (superscript: NUM, LV), was calculated by averaging the numerical profile values for the first 2 mm (along the $z$-axis) such that:

$$n_e^{\text{NUM,LV}} = \int_{\text{laser}} n_e^{\text{NUM}}(z) \, dz / D_{\text{laser}} = 2 \text{ mm}.$$

$\bullet$ The ratio of $n_e^{\text{NUM,LV}} / n_e^{\text{NUM,MCRS}} \approx 89$.

$\bullet$ The momentum transfer collision frequency $\nu_m$ is shown in the panels (b) of figure 13 for argon, and figure 14 for oxygen.

It should be noted that such momentum transfer collisions have been measured using a directed electron beam onto a neutral gas target, where the neutral gas particles are essentially at rest. Hence, this means that we need to integrate over the electron energy distribution $F(\varepsilon)$ when a plasma or gas discharge is considered. This idea is captured in the definition of the effective collision frequency, which—assuming a Maxwellian distribution function—can be defined as follows [28]:

$$\nu_{\text{eff}} = \frac{\int_0^\infty \varepsilon^{3/2} \frac{\rho_{\text{e}}(\varepsilon) F(\varepsilon)}{\rho_{\text{e}}(\varepsilon)} \, d\varepsilon}{\int_0^\infty \varepsilon^{3/2} \frac{\rho_{\text{e}}(\varepsilon) F(\varepsilon)}{\rho_{\text{e}}(\varepsilon)} \, d\varepsilon}. \quad (20)$$

Here, the energy distribution function is denoted by $F(\varepsilon)$, and $\omega (= 2\pi f)$ describes the angular microwave frequency. The effective collision frequency is depicted in the panels (c) of figures 13 and 14, for electron-argon and electron-oxygen collisions, respectively.

With regard to the discussion, the following values have been evaluated numerically in the program to facilitate the analysis. Please note that room temperature $T = 300 \text{ K}$ equals $T = 0.026 \text{ eV}$, and that the number density of argon in the spatial afterglow is significantly higher than oxygen density.

The electron-argon effective collision frequency $\nu_{\text{eff}} \approx 36 \text{ GHz}$ at $\varepsilon = 0.025 \text{ eV}$ and $\nu_{\text{eff}} \approx 28 \text{ GHz}$ at
where \( \epsilon \) occurs around for elastic electron-argon collisions, where the minimum Ramsauer minimum in the momentum transfer cross section of electron-argon collisions, where the minimum occurs around \( \epsilon \approx 0.25 \) eV. The electron-O\(_2\) effective collision frequency \( \nu_{\text{eff}} \approx 55 \) GHz at \( \epsilon \approx 0.025 \) eV and \( \nu_{\text{eff}} \approx 41 \) GHz at \( \epsilon \approx 0.032 \) eV.

### A.7 Timescale of first-order reaction

The timescale for a first-order reaction follows from the solution of the first-order differential equation, which describes the rate of change of the (photodetached) electron density:

\[
\frac{d n_e}{dt} = -k_i n_i n_e, \tag{21}
\]

where \( i \) indicates the type of reaction (reaction \( R_i \) in section 4.2), \( k_i \) represents the corresponding reaction rate coefficient, \( n_i \) denotes the electron density, and \( n_e \) describes the density of the reacting species, i.e., atomic or molecular species that react with the electrons. This differential equation has the following solution,

\[
n_e(t) = n_e^0 \exp \left(-\frac{t}{k_i \tau_i}\right), \tag{22}
\]

with \( n_e^0 \) the initial electron density, from which the timescale of electron loss can be defined as:

\[
\tau_i = \frac{1}{k_i \tau_i}. \tag{23}
\]

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