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A passive measurement of dissociated atom densities in atmospheric pressure air discharge plasmas using vacuum ultraviolet self-absorption spectroscopy

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We demonstrate a method for determining the dissociation degree of atmospheric pressure air discharges by measuring the self-absorption characteristics of vacuum ultraviolet radiation from O and N atoms in the plasma. The atom densities are determined by modeling the amount of radiation trapping present in the discharge, without the use of typical optical absorption diagnostic techniques which require external sources of probing radiation into the experiment. For an 8.0 mm spark discharge between needle electrodes at atmospheric pressure, typical peak O atom densities of $8.5 \times 10^{17} \text{ cm}^{-3}$ and peak N atom densities of $9.9 \times 10^{17} \text{ cm}^{-3}$ are observed within the first $\sim 1.0 \text{ mm}$ of plasma near the anode tip by analyzing the OI and NI transitions in the 130.0–132.0 nm band of the vacuum ultraviolet spectrum. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4869895>]

I. INTRODUCTION

Plasma formation^{1,2} is a limiting factor in the design of a variety of pulsed power modulators which require the dielectric support structure to sustain a high DC electric field across the device, especially considering the trend towards higher power applications. This plasma (in the form of spark breakdown) is especially prevalent when the device is deployed to environments with a large background of UV or x-ray radiation which can lead to free electron buildup. Such applications include power modulators in high current sources for high power microwave (HPM) vacuum diodes,³ mega-ampere current pulse generators in dense nuclear fusion experiments,⁴ induction accelerator cavities used to generate intense electron beams for radiographic studies,⁵ and as well as general problems with propagating high power electromagnetic waves for applications in communications.⁶ Studies⁷ have discussed the effectiveness of UV radiation in seeding the background electron density required for spark breakdown at atmospheric pressures, but most investigations are limited to studying optical wavelengths longer than 200 nm due to the experimental difficulty in measuring vacuum ultraviolet (VUV) radiation. Despite this, VUV irradiation has demonstrated⁸ an increased ability to generate free electrons in N_2 environments, and recent studies⁹ have investigated the earliest VUV production from N atoms in the streamer and spark phases of breakdown. As a result, it is desired to passively measure the dynamics of atom production from molecular dissociation in air discharge plasmas, without using a potentially invasive optical absorption diagnostic technique, such as two-photon laser induced fluorescence (TALIF) spectroscopy¹⁰ or broadband absorption spectroscopy,¹¹ which can artificially increase the dissociation degree.

We recently reported¹² favorable results in passively measuring the dissociated density of H and N atoms in H_2/N_2 plasmas by monitoring the HI/NI spectrum in the 120–125 nm range using the vacuum ultraviolet self-absorption spectroscopy (VUV-SAS) method, with measured atom densities on the order $\sim 10^{17} \text{ cm}^{-3}$. This was possible due to the strong self-absorption characteristics of $2p \rightarrow 1s$ Lyman- α transition of HI at 121.57 nm. However, the usefulness of this technique was limited due to the small number of plasma studies outside of the research environment which use H_2 as a medium. Therefore, it was desired to extend the VUV-SAS method to plasmas generated in atmospheric pressure air, thereby demonstrating applicability to a large number of pulsed power and plasma experiments under investigation today as well as practical importance to breakdown studies in traditional high voltage environments.

II. RADIATION TRANSPORT PHYSICS

We demonstrate a passive method for determining the dissociated density of O atoms in air plasmas by measuring the absorption characteristics of the $2s^2 2p^3 3s \rightarrow 2s^2 2p^4$ transition(s) in OI at 130.22/130.49/130.60 nm. Note that these transitions have been used to measure atom densities previously,¹³ but only at the expense of using probing radiation from a high pressure micro-discharge hollow cathode lamp to measure broadband absorption in the plasma structure. This method has the drawback of injecting energetic photons at high radiative intensities into the plasma, which during absorption potentially alters the fundamental plasma kinetics under investigation. The method presented in the present study instead uses the intrinsic self-radiation produced from the plasma structure itself, which undergoes partial radiation

trapping as it attempts to escape the plasma medium (see Fig. 1). Under the assumption that most of the atomic population is energetically in the ground state, VUV photons which result from electronic de-excitation into the ground state are likely to be re-absorbed due to the high probability of encountering another ground atom within the path length leading out of the plasma. However, UV/VUV photons which result from higher de-excitations are less likely to be re-absorbed as they escape the plasma due to the lower probability of finding an excited atom in the correct energy state for re-absorption. Therefore, application of the VUV-SAS technique reduces to modeling the radiation trapping physics in the desired plasma structure. Note that by similarly monitoring the emission of the nearby $2s^22p^23d \rightarrow 2s^22p^3$ transition(s) of NI at 131.05/131.10 nm, the N atom density is simultaneously derived from the experiment by comparing the relative intensity of the NI and OI spectral profiles.

Modeling the radiation trapping physics inherently involves calculating the effective line profiles for emission and absorption, and the general treatment¹⁴ of the various line broadening mechanisms is well discussed in literature. The recorded line profiles contain a Lorentzian and Gaussian component, which are additionally convolved with the apparatus profile used in measurement. The Lorentz full-width at half maximum ($\delta\nu_L$) is primarily the sum of the effects from pressure broadening, Stark broadening from charged particle interaction, and instrumentation. In first order, the effects of Stark broadening for NI and OI atomic systems are assumed to be much smaller than the Lorentz component for instrumentation and are therefore neglected. The pressure broadening estimated¹⁵ from resonance or Van der Waals collisions with neutral particles is calculated to be on the order <1% of the total line width due to instrumentation. Therefore, the effect of instrumentation (due to pixel cross-talk between CCD pixels on the detector) is the primary source of Lorentz broadening in the current study. The normalized Lorentzian distribution takes the form

$$I_L(\nu) = \frac{\left(\frac{\delta\nu_L}{2}\right)^2}{(\nu - \nu_0)^2 + \left(\frac{\delta\nu_L}{2}\right)^2}, \quad (1)$$

where ν_0 is the center frequency of the electronic transition. The normalized Gaussian profile (with full-width at half maximum $\delta\nu_G$) is primarily determined by the Doppler broadening of radiation released from the plasma, which is a function of gas temperature (T_g)

FIG. 1. Overview of the VUV-SAS methodology: radiation from one section of plasma passes into the adjacent section, undergoing partial radiation trapping on the way to the optical detector. Radiation from lower atomic states is likely to be re-absorbed, while radiation from higher atomic states mostly passes into the detector.

$$I_G(\nu) = \exp\left[-4 \ln(2) \frac{(\nu - \nu_0)^2}{\delta\nu_G^2}\right], \quad (2)$$

$$\delta\nu_G = 2\sqrt{\ln(2)} \frac{\nu_0}{c} \sqrt{\frac{2k_B T_g}{m_A}}, \quad (3)$$

where c is the speed of light in vacuum (2.99×10^{10} cm/s), k_B is Boltzmann's constant (1.38×10^{-23} J/K), and m_A is the mass of the radiating atom. The normalized Voigt profile (I_V) is generated by numerical convolution of the Lorentzian and Gaussian profiles, along with a rectangular profile (I_R) from instrumentation accounting for the spectrograph entrance slit.

The amount of radiation self-absorption in a section of plasma is determined by the absorption coefficient (κ) at that location, which is assumed to have the same line width (population of atomic energy states) as the emission line profile, i.e., the Voigt distribution. As a result, the absorption coefficient takes the form

$$\kappa(r) = \frac{q^2 n_i(r) f_{ij}}{4\pi\epsilon_0 m_e c} I_V, \quad (4)$$

where q and m_e are the charge (1.6×10^{-19} C) and mass (9.11×10^{-31} kg) of the electron, respectively, n_i is the population density of absorbing atoms in the lower energy state, and ϵ_0 is the permittivity of free space (8.85×10^{-14} F/cm). The oscillator strength (f_{ij}) of the transition takes the form

$$f_{ij} = 1.499 \times 10^{-14} A_{ji} \lambda_0^2 \frac{g_j}{g_i}, \quad (5)$$

where A_{ji} is the Einstein coefficient for spontaneous emission of the transition given in s^{-1} , λ_0 is the transition wavelength of the radiation in nm, and g_j and g_i are the statistical degeneracies of the upper and lower states, respectively.

The population density of atoms is assumed to be in partial local thermodynamic equilibrium (LTE) condition determined as a function of a common Boltzmann electronic temperature (T_e). The peak atom density of each species in the core of the plasma can then be calculated by estimating the dissociation percentage (η_d)

$$\bar{n}_i = 2\eta_d n_c n_0 \frac{g_i}{\Gamma} \exp\left(-\frac{E_i}{k_B T_e}\right), \quad (6)$$

where η_c is the concentration of each species in the plasma (i.e., for laboratory air: $\eta_c = 0.79$ for N_2 molecules and $\eta_c = 0.21$ for O_2 molecules), n_0 is the background number density of molecules in the plasma (2.5×10^{19} cm⁻³ for STP laboratory conditions), E_i is the energy level of the state, and Γ is the statistical partition function of the total number of available states. The factor of two is due to the fact that each dissociated molecule creates two free atoms in the plasma. Note that if all other parameters are known or inferred, η_d (i.e., the dissociation kinetics) is determined by comparing the calculated line profiles to the ones measured from the experiment.

The spark channel is in first order assumed to be cylindrically symmetric, and so the absorption calculations are

formed by integration in 1D over the radial profile in the center of the cross section within the line of sight of the spectral instruments. The density of atoms in the plasma is not uniform in the radial direction, and other spark discharge studies¹⁶ with similar currents have shown that the luminosity (and therefore atomic population) is highest in the middle of the plasma channel. In first approximation, the spatial profile is assumed to be of Gaussian cylindrical shape, which takes the form

$$n_i(r) = \bar{n}_i \exp\left(-\frac{r^2}{r_0^2}\right), \quad (7)$$

where r_0 is the radial normalization given by

$$r_0 = \left(-\frac{\left(\frac{d}{2}\right)^2}{\ln\left(\frac{n_{edge}}{n_{core}}\right)} \right)^{1/2}, \quad (8)$$

where d is the diameter of the plasma column and n_{edge}/n_{core} is the estimated plasma density taper at the edge of the spark channel. The amount of radiation produced from each location in the plasma is determined by the spontaneous emission of the local atom density. The resulting differential intensity packet produced by the local atom density, which escapes the plasma volume, is then given by the total absorption by inhomogeneous plasma within the path length from that position to the plasma edge

$$dI_\ell(r) = dt A_{ji} n_j(r) \times (I_V * I_R) \exp\left(-\int_{r_{edge}}^r \kappa(r) dr\right), \quad (9)$$

where dr is the discrete numerical thickness of each plasma slab, n_j is the population density of atoms in the upper energy state, and dt is the discrete numerical time step over which radiation is released. It follows that calculating the total emission profile observed at the detector reduces to integration of dI_ℓ from radiation produced from all locations (in 1D) in the plasma over time. Radiation which originates from locations near the plasma edge is absorbed less due to the decreased path length to the detector, but the intensity is lower due to the overall lower atom density in this region. However, radiation which is released from the dense plasma core is much more intense but must travel through a longer path length to reach the plasma edge, leading to increased absorption of this core radiation. Thus, the final shape of the resulting profile observed at the detector is ultimately dominated by the dynamics of the intense core radiation escaping the dense plasma center. Direct evaluation of the radiation transport and spectral line profiling calculations are performed in the MATLAB[®] environment and accelerated via graphics processing unit (GPU) processing resources using the NVIDIA[®] CUDA[™] architecture. The transition probabilities, statistical degeneracies, and atomic energy levels for OI and NI species relevant to this study are available online from NIST.¹⁷

III. EXPERIMENT AND DISCUSSION

The experiment¹⁸ consists of an 8.0 mm discharge between two needle electrodes in air at atmospheric pressure. The discharge is triggered via ~ 100 ns rise-time 15 kV high voltage pulse (1.0 Hz rep-rate), with typical peak discharge currents during the spark phase of ~ 20 A lasting up to 5.0 μ s. Previous measurements⁹ of the relative emission line strengths for the NI spectrum in the range of 140–150 nm established an estimated Boltzmann electron temperature of 3.0 eV in partial-LTE condition during the spark phase of plasma development (i.e., the first ~ 200 ns after voltage collapse). The plasma forms very near to a MgF₂ surface which acts as the interface between the experiment and a vacuum spectrograph (vacuum vessel pressure = 10^{-7} Torr) installed with VUV sensitive intensified CCD electronics as the detector. The plasma is positioned so only radiation from the first ~ 1.0 mm of plasma near the anode is viewable during the experiment, for a 100 ns exposure recorded 100–200 ns into the spark phase.

The measured and calculated intensity profiles in the wavelength range of 130–132 nm are shown in Fig. 2. The calculated spectrum is generated to best fit the profile of the entire spectrum, normalized to the NI intensity peak at 131.10 nm which is weakly self-absorbed. The calculated spectrum is corrected for the attenuation due to the spectrograph optics, quantum efficiency of the detector, and diffraction grating efficiency. The experiment consists of determining η_d from five sets of ten averaged measurements and calculating the standard deviation. The gas and atom densities are assumed to be at laboratory temperature (300 K) during the short timescales of the experiment. Previous discharge experiments,^{18,19} which include external imaging, revealed that the radial plasma depth ranges between 480 and 560 μ m during the spark phase, and so an average plasma depth of 500 μ m is assumed. In first approximation, the plasma density is assumed to fall to 1% of the peak (core) value at the channel edge, leading to a Gaussian density taper of 10^{-2} . The instrumental profile is determined to be 0.097 nm for both the Lorentzian and rectangular components.

FIG. 2. Comparison of measured (blue) and calculated (red) profiles for OI and NI emission observed from the early spark phase of plasma formation in atmospheric pressure air (exposure time = 100 ns). The Lorentzian and rectangular components due to instrumentation are 0.097 nm and 0.097 nm, respectively.

An interesting note for modeling the radiation self-absorption of air discharges arises as a consequence of the lower energy levels of O atoms for 130.49/130.60 nm radiation. These transitions are able to be thermally populated by collisions with gas molecules, atoms, or ions in the bulk discharge plasma, and so re-absorption of radiation emitted from these transitions is especially likely. The emission line at 129.85 nm is due to excitation of anode material, and therefore not included in the plasma radiative model. The number density of O atoms in the discharge is estimated by the ratio of emission lines at 130.22/130.49/130.60 nm which are all absorbed by different amounts, and the resulting peak O atom density in the plasma core is $8.5 \times 10^{17} \text{ cm}^{-3}$. This results in a peak O₂ dissociation percentage of 8.10%, while the average dissociation in the Gaussian volume is 3.32%. The number density of N atoms in the discharge is then estimated by increasing the N atom density until the intensity ratio between NI and OI emission lines matches the measured spectrum, which results in a peak N atom density of $9.9 \times 10^{17} \text{ cm}^{-3}$. This results in a peak N₂ dissociation percentage of 2.50%, while the average dissociation in the volume is 1.03%. Note that this value is close to the 0.43% dissociated N atom density recently estimated⁹ by calculating the collisional quenching of N atoms in pure N₂ discharges with the same electrode geometry. The estimated dissociation of N₂ molecules is higher in air discharges most likely as a result of the overlap in certain cross species photo-dissociative processes between N₂ and O₂ molecules (for example,²⁰ the Birge-Hopfield and Carroll-Yoshino bands in the $\sim 12 \text{ eV}$ range) which is believed²¹ to be a decisive element in the development of spark discharge plasmas in air. The overall higher O₂ dissociation percentage compared to the N₂ dissociation percentage is due to the lower dissociation energy of the O₂ molecule (5.17 eV) compared to the N₂ molecule (9.79 eV).

The normalized RMS error between the measured and simulated emission profiles in this range is roughly 4.2%, which indicates that the profile is matched within good agreement. The statistical deviation of the estimated atom densities is less than 15% over the number of discharges generated. It is observed during the calculations that an uncertainty in the Boltzmann electronic temperature of $\pm 10\%$ results in a change in the estimated atom densities by about $\pm 30\%$. Note that previous studies¹² investigated the effect of assuming a non-Gaussian plasma channel geometry in the estimation of atom densities. For example, in the extreme case of a relatively hollow plasma geometry with peak plasma densities near the channel edge (such geometries correspond to energetic shockwaves which result from very high current discharges²²), it is observed that the estimated atom densities change by a factor of about 2–3. However, assuming that the Gaussian radial geometry is in good approximation for plasma formation in low discharge currents, the total estimated uncertainty for application of the VUV-SAS technique in this plasma geometry is estimated to be less than 50%.

IV. CONCLUSIONS

In conclusion, the vacuum ultraviolet self-absorption spectroscopy diagnostic is capable of passively measuring O

and N atom densities in transient plasma structures, without the use of potentially invasive optical diagnostic techniques currently in widespread practice. For an 8.0 mm spark discharge between needle electrodes at atmospheric pressure, typical peak O atom densities of $8.5 \times 10^{17} \text{ cm}^{-3}$ and peak N atom densities of $9.9 \times 10^{17} \text{ cm}^{-3}$ are observed within the first $\sim 1.0 \text{ mm}$ of plasma near the anode tip by analyzing the OI and NI transitions in the 130.0–132.0 nm band of the vacuum ultraviolet spectrum. As a result, the VUV-SAS method should prove useful for a variety of future plasma experiments in pulsed power laboratories and traditional high voltage environments.

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