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Simultaneous measurement of nitrogen and hydrogen dissociation from vacuum ultraviolet self-absorption spectroscopy in a developing low temperature plasma at atmospheric pressure

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We demonstrate a method for determining the dissociation density of N and H atoms present in a developing low temperature plasma, based on the emission and self-absorption of vacuum ultraviolet radiation produced from the plasma. Spark plasmas are produced via pulsed discharge in N₂/H₂ mixtures at atmospheric pressure, where information on the dissociated densities of the constituent gas molecules is desired without employing invasive diagnostic techniques. By analyzing the self-absorption line profile of 121.5 nm Lyman- α H radiation emitted within the first ~ 1.0 mm of plasma near the anode tip, a peak dissociated H atom concentration of $5.6 \times 10^{17} \text{ cm}^{-3}$ was observed ~ 100 ns into spark formation, with an estimated electron density of $2.65 \times 10^{18} \text{ cm}^{-3}$ determined from Stark broadening. Similarly, simultaneous line fitting of the N 120.0/124.3 nm emission profiles revealed a peak dissociated N atom concentration of $3.8 \times 10^{17} \text{ cm}^{-3}$ during the same discharge period. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4804369>]

Fast plasma formation across dielectric surfaces^{1,2} is a severe limiting factor in the engineering of high power microwave and pulsed power modulators, especially in environments where UV radiation is prevalent for seeding higher background electron densities.³ Recent studies⁴ of the effects of UV radiation on fast plasma formation have been focused on wavelengths longer than 200 nm, due to the complexity of measuring vacuum ultraviolet (VUV) radiation at atmospheric pressures. However, VUV radiation has been shown⁵ to dramatically increase electron production rates from photo-ionization, and recent studies⁶ have investigated the temporal relationship of VUV emission during the early stages of spark plasma formation. Furthermore, it is desired to measure the dissociated gas density from these surface flashover plasmas without the need for potentially invasive optical techniques such as two-photon absorption laser induced fluorescence (TALIF) spectroscopy.^{7,8}

We demonstrate a method for determining the dissociated density of H atoms in H₂ plasmas by measuring the absorption characteristics of the $2p \rightarrow 1s$ Lyman- α transition of H at 121.57 nm. This transition has been measured previously to determine dissociated gas density,⁹ but only at the expense of using an invasive radiation source, such as a micro-discharge hollow cathode lamp, to provide external photons for absorption in the plasma medium. This approach has the drawback of introducing a large flux of high energy VUV radiation into the plasma environment, which has the ability to directly dissociate molecules via single photon absorption.¹⁰ The method presented in this paper instead uses the intrinsic self-radiation released from the plasma spark, which undergoes partial radiation trapping as it leaves the plasma medium. Sufficient levels of self-emission at 121.5 nm are detected, leading to a treatment of H self-absorption as an estimate of dissociated gas density. The

plasma state is preserved without alteration by external radiation sources in the experiment, and the H emission has the added benefit of providing information on the electron density derived from measuring the Stark broadened¹¹ line profile. If a N₂/H₂ mixture is used, the self-absorption approach can be extended¹² to simultaneously provide information on the density of N atoms by comparing the absolute intensity of H radiation to N radiation at 124.3 nm, in addition to measuring the approximate absorption characteristics of the $2s^2 2p^2 3s \rightarrow 2s^2 2p^3$ transition(s) of ground state N at 119.96 nm, 120.02 nm, and 120.07 nm (collectively referred to in this paper as “120.0 nm”). It is worth noting that the self-absorption treatment could also be used to determine dissociated O density of air plasmas in the future, by using the $2s^2 2p^3 3s \rightarrow 2s^2 2p^4$ transition of O.¹³

The general treatment¹⁴ of the mechanisms leading to line broadening is well understood, and only a brief overview is presented here. The recorded line profiles consist of a Gaussian and Lorentzian component, where the resulting Voigt profile is additionally convolved with the spectral apparatus profile. The normalized Gaussian profile is given by the Doppler broadening of radiation released from the plasma, which is a function of the gas temperature (T_g)

$$I_G(v) = \exp \left[-4 \ln(2) \frac{(v_0 - v)^2}{\delta v_G^2} \right], \quad (1)$$

$$\delta v_G = 2 \sqrt{\ln(2)} \frac{v_0}{c} \sqrt{\frac{2k_B T_g}{m_A}}, \quad (2)$$

where v_0 is the transition frequency, c is the speed of light, k_B is Boltzmann's constant, and m_A is the mass of the radiating atom.

The Lorentzian profile is generally considered to be a consequence of pressure broadening, while for this experiment the H transition at 121.57 nm is considered to also be Stark broadened by the local electron density within the Debye radius of the emitter. Note that the spectral apparatus profile is accounted for in the following spectral analysis. That is, depending on the spectral instrumentation used, the apparatus profile will make a contribution to the recorded Lorentzian profile (primarily from detector pixel cross-talk) as well as add a rectangular profile (primarily from spectrograph entrance slit) to the overall convolution.

The value of the Lorentz full-width at half maximum (δ_L) for the N emission is of little interest by itself, although the difference in Lorentz widths between the N and H emission profiles is approximately the magnitude of Stark broadening present in the H emission profile if the pressure broadening from collisions with neutral particles is minimal. This condition is assumed for the following analysis, where estimates¹⁵ of pressure broadening due to resonance or Van der Waals collisions with constituent species yield line widths on the order of <1% of the total line width due to the Stark effect and instrumentation. The normalized Lorentzian distribution is given by

$$I_L(v) = \frac{\left(\frac{\delta_L}{2}\right)^2}{(v - v_0)^2 + \left(\frac{\delta_L}{2}\right)^2}, \quad (3)$$

where the total Lorentz width is the sum of pressure broadening, the Lorentz component of instrumental profile, and Stark broadening (for H). The normalized Voigt profile (I_V) is then generated by numerical convolution of the Gaussian and Lorentzian profiles for each line (see the Appendix in Ref. 6).

The absorption coefficient (κ) for the self-absorbed emission lines is generated by a similar Voigt distribution, assumed to have the same line width (i.e., distribution of energy perturbation) as the emission profile. The absorption coefficient is then given by

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

where q is the charge of the electron, n_i is the density of absorbing atoms in the ground state, ϵ_0 is the permittivity of free space, and m_e is the mass of the electron. The oscillator strength (f_{ij}) is given by

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

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

The density of atoms in each energy level is assumed to be Boltzmann distributed in local thermodynamic equilibrium (LTE) condition, as a function of electron temperature (T_e). The atom density of each species is then given by the background number density of molecules (n_0) and the dissociation percentage (η)

$$n_i = 2\eta n_0 \frac{g_i}{Z(T_e)} \exp\left[-\frac{E_i}{k_B T_e}\right], \quad (6)$$

where E_i is the energy level and $Z(T_e)$ is the partition function for each species as a function of electron temperature. Note that n_0 is determined for each species as a function of N_2/H_2 mixture, while η is assumed to be species dependent.

Other spark discharge studies have shown¹⁶ that the highest luminosity is present in the center of the plasma column, and in first approximation the plasma is assumed to be of Gaussian cylindrical shape with the plasma density falling to 1% of the peak core ($r=0$) density at a defined radius. The local relative emission intensity (dI_ℓ) for each line is assumed to be primarily from spontaneous de-excitation of the excited state given by the local plasma density, while subsequently this emission packet passes through an inhomogeneous series of plasma slabs which each absorb due to the Beer-Lambert law

$$dI_\ell = A_{ji} n_j(r) \cdot (I_V * I_R) \exp\left[-\int \kappa(r) dr\right], \quad (7)$$

where dr is the discrete numerical thickness of each plasma slab and n_j is the density of radiating atoms in the excited state. The simulation integrates (in 1D) over time the radiation which leaves the plasma in a single direction, where radiation which originates from a location farther from the detector edge passes through more plasma slabs and is more heavily absorbed. Evaluation of the plasma integration and spectral fitting calculations are executed in the MATLAB® environment and are accelerated via graphics processing unit (GPU) resources using the NVIDIA® CUDA™ architecture. The transition probabilities, statistical degeneracies, and energy levels for N and H species are available online at NIST.

The experiment¹⁷ consists of an 8.0 mm needle discharge gap in 80%/20% N_2/H_2 mixture at atmospheric pressure, triggered via ~ 100 ns rise-time high voltage pulse. The peak voltage prior to breakdown is 10–15 kV while the peak current observed in the spark phase ~ 180 ns after field collapse is nearly 20 A. Previous measurements⁶ of the N spectrum in the 130–150 nm range estimate an electron temperature of 3.0 eV in the LTE condition during the spark phase after breakdown. The discharge is located near a MgF_2 dielectric surface, forming the interface into a vacuum spectrograph with an intensified CCD (ICCD) as the detector. The discharge is positioned so only radiation from the ~ 1.0 mm of plasma nearest to the anode needle tip is detected, for a 100 ns ICCD exposure recorded 100–200 ns into the spark phase.

The measured and calculated intensity profiles in the wavelength range 119–125 nm are shown in Fig. 1. The calculated spectrum is generated to best fit the entire profile, normalized to the N emission line at 124.3 nm which is not strongly self-absorbed. The calculated spectrum is corrected for the attenuation of the spectrograph optics, diffraction grating efficiency, and quantum efficiency of the detector. Variations are estimated for the fit values of η and n_e by recording the emission for five sets of ten averaged measurements and finding the standard deviation. Due to the short timescales of the experiment it is reasonable to assume a

FIG. 1. Comparison of measured (blue) and calculated (red) profiles for N and H α emission observed from the early spark phase of plasma formation in 80%/20% N $_2$ /H $_2$ mixture by volume at atmospheric pressure (exposure time = 100 ns). The Lorentzian and rectangular components due to instrumentation are 0.097 nm and 0.097 nm, respectively.

kinetic gas temperature of 300 K. The radial plasma depth is observed from imaging^{17,18} to range between 480 and 560 μm , therefore the Gaussian column diameter is estimated to be 500 μm in first approximation. The instrumental profile is measured to be 0.097 nm for both the rectangular and Lorentzian components.

The amount of simulated peak H atom density in the plasma core required to balance the relative emission and absorption magnitudes for proper matching of the measured self-absorption profile is $5.6 \times 10^{17} \text{ cm}^{-3}$, which represents a peak H $_2$ dissociation percentage (in this mixture) of roughly 5.60%. If the peak dissociation is averaged over the area of the Gaussian radial profile, the resulting average H $_2$ dissociation percentage becomes 2.30%. Once the H atom density is known, the N atom density can be estimated by increasing the N density until the relative line strengths between the H and N lines are matched. The resulting estimation of the N atom density near the anode is $3.8 \times 10^{17} \text{ cm}^{-3}$, which represents a peak N $_2$ dissociation percentage (in this mixture) of roughly 0.90%. The simulated profile does not completely reconstruct the N triplet at 120.0 nm, most likely due to a combination of discharge statistics and the uncertainty in the absolute attenuation of the spectral instruments in this area, where the transmission attenuation of MgF $_2$ is steep. However, the calculated normalized RMS error between simulation and measurement is better than 4.59% in this range, which implies that the profiles are generally matched to a good degree. The average N $_2$ dissociation over the Gaussian profile is 0.39%, which is very close to the 0.43% average dissociation estimated recently⁶ from calculating the de-excitation rate by collisional quenching of N atoms in the discharge. In addition, the percentage of dissociated H $_2$ molecules is greater than the percentage of dissociated N $_2$ molecules by a factor of about six, primarily a consequence of the much lower dissociation energy of H $_2$ (4.52 eV) compared to N $_2$ (9.79 eV).

The Stark broadening is estimated¹⁹ by quasi-contiguous approximation²⁰ of the Holtsmark micro-field from the local electrons within the Debye radius, where the electron density is estimated by matching the quasi-contiguous Stark width of the Lyman- α emission line from H atoms. A smaller electron density corresponds to a smaller Stark width, which results in narrower wings in the emission line profile and a sharper characteristic absorption dip in the center of the profile. The estimated electron density near the anode of the plasma discharge is $2.65 \times 10^{18} \text{ cm}^{-3}$, which is above the estimated²¹ minimum value of $\sim 10^{17} \text{ cm}^{-3}$ needed at 3.0 eV to validate the LTE approximation for H spectroscopy. The statistical deviation of the estimated atom and electron densities over the number of discharges generated is less than 15%. In simulation, it is observed that an electron temperature uncertainty of $\pm 10\%$ will change the estimated atom densities by about $\pm 30\%$.

Note that other groups²² have observed the highest luminosity near the plasma edge of spark discharges with higher currents ($> 100 \text{ A}$), and it has been proposed that this is due to the radial shockwave of energy which propagates out of the core of the plasma channel. It is desired to determine the relative change of estimated atom density due to uncertainty in predicting the actual radial plasma profile due to this shockwave. For example in the extreme case, the plasma profile can be approximated in 1D as a pair of Gaussian profiles with density peaks at 125 μm and 375 μm , each falling to 1% of the peak density value within 125 μm . The resulting total profile is 500 μm in diameter and approximates a cylindrical shockwave which has evacuated the core of the plasma channel and propagated halfway to the plasma edge. In order to produce a simulated emission profile similar to Fig. 1 with the shockwave geometry, the peak H atom density must be reduced to $3.73 \times 10^{17} \text{ cm}^{-3}$, while the N atom density must be increased to $7.62 \times 10^{17} \text{ cm}^{-3}$. Therefore, the atom densities can be determined by this method within a factor of two, given reasonable estimates on plasma radial geometry. However assuming the Gaussian radial profile is a good approximation for low discharge currents, the total measurement uncertainty from application of this technique is less than 50%.

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