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

George Laity, Andrew Fierro, James Dickens, Andreas Neuber, and Klaus Frank

Citation: Appl. Phys. Lett. 102, 184104 (2013); doi: 10.1063/1.4804369
View online: http://dx.doi.org/10.1063/1.4804369
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i18
Published by the American Institute of Physics.

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors
Simultaneous measurement of nitrogen and hydrogen dissociation from vacuum ultraviolet self-absorption spectroscopy in a developing low temperature plasma at atmospheric pressure

George Lality,1 Andrew Fierro,1 James Dickens,1 Andreas Neuber,1 and Klaus Frank2
1Center for Pulsed Power and Power Electronics, Department of Electrical and Computer Engineering and Department of Physics, Texas Tech University, Lubbock, Texas 79409, USA
2Erlangen Centre for Astroparticle Physics, Department of Physics, Friedrich-Alexander University at Erlangen - Nürnberg, 91058 Erlangen, Germany

(Received 12 April 2013; accepted 23 April 2013; published online 9 May 2013)

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 surfaces1,2 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 atmospherics. However, VUV radiation has been shown5 to dramatically increase electron production rates from photo-ionization, and recent studies6 have investigated the density of H radiation to N radiation at 124.3 nm, in addition to the 2s22p33s transition has been measured previously7 to determine 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.

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 (Tg)

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

and

\[ \delta v_G = 2 \sqrt{\ln(2)} \frac{v_0}{c} \sqrt{\frac{2k_B T_g}{m_A}}, \tag{2} \]

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.

Fast plasma formation across dielectric surfaces1,2 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 atmospherics. However, VUV radiation has been shown5 to dramatically increase electron production rates from photo-ionization, and recent studies6 have investigated the density of H radiation to N radiation at 124.3 nm, in addition to the 2s22p33s transition has been measured previously7 to determine 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.

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 (Tg)

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

and

\[ \delta v_G = 2 \sqrt{\ln(2)} \frac{v_0}{c} \sqrt{\frac{2k_B T_g}{m_A}}, \tag{2} \]

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 ($\delta L$) 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 estimates 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

$$I_L(v) = \frac{(\delta L)^2}{(v-v_0)^2 + \left(\frac{\delta L}{2}\right)^2},$$

where the total Lorentz width is the sum of pressure broadening, the Lorentz component of instrumental broadening, 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 ($\kappa$) 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

$$\kappa = \frac{q^2 n f_{ij} I_r}{4\pi\varepsilon_0 m_e c},$$

where $q$ is the charge of the electron, $n_i$ is the density of absorbing atoms in the ground state, $\varepsilon_0$ is the permittivity of free space, and $m_e$ is the mass of the electron. The oscillator strength ($f_{ij}$) is given by

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

where $A_{ji}$ is the Einstein coefficient for spontaneous emission given in $s^{-1}$, $\lambda$ is the transition wavelength given in nm, and $g_i$ and $g_j$ 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 ($\eta$)

$$n_i = 2\eta n_0 \frac{g_i}{Z(T_e)} e^{-\frac{E_i}{k_BT_e}},$$

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 $n_i$ is determined for each species as a function of $N_2/H_2$ mixture, while $\eta$ is assumed to be species dependent.

Other spark discharge studies have shown 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 ($dI_i$) 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

$$dI_i = A_{ji} n_i(r) \cdot (I_V \ast I_R) \exp \left[-\kappa(r)dr\right].$$

where $dr$ is the discrete numerical thickness of each plasma slab and $n_i$ 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 experiment consists of an 8.0 mm needle discharge gap in 80%/20% $N_2/H_2$ mixture at atmospheric pressure, triggered via $\sim 100$ 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 $\sim 180$ ns after field collapse is nearly 20 A. Previous measurements 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 $\sim 1.0$ 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 $\eta$ and $n_0$ 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
The Stark broadening is estimated\textsuperscript{19} by quasi-contiguous approximation\textsuperscript{20} 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-$\alpha$ 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 $2.65 \times 10^{19}$ cm$^{-3}$, which is above the estimated\textsuperscript{21} minimum value of $\sim 10^{17}$ 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 groups\textsuperscript{22} have observed the highest luminosity near the plasma edge of spark discharges with higher currents ($>100$ 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 $\mu$m and 375 $\mu$m, each falling to 1% of the peak density value within 125 $\mu$m. The resulting total profile is 500 $\mu$m 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 $3.73 \times 10^{17}$ cm$^{-3}$, while the N atom density must be increased to $7.62 \times 10^{17}$ 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%.

This work was supported by the U.S. Air Force Office of Scientific Research (AFOSR) grant on the “Basic Physics of Distributed Plasma Discharge.” G. Laity was under fellowship support from the Directed Energy Professional Society and the Directed Energy Scholar program at the U.S. Air Force Research Laboratory (AFRL). A. Fierro was under fellowship support from the National Physical Science Consortium in partnership with Sandia National Laboratories. The authors would like to thank the National Institute of Standards and Technology (NIST) for the Atomic Spectra Database (ASD) available online.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.pdf}
\caption{Comparison of measured (blue) and calculated (red) profiles for N and HI 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 instrumental resolution are 0.097 nm and 0.097 nm, respectively.}
\end{figure}