Laser and Emission Spectroscopy in H₂ and H₂-N₂ dc Discharges

J. Amorim (*), G. Baravian, S. Bockel (**), A. Ricard (***) and G. Sultan

Laboratoire de Physique des Gaz et des Plasmas (****), bâtiment 212 Université Paris XI,
91405 Orsay, France

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Abstract. — Two-photon Laser Induced Fluorescence (LIF) was used for the determination of H atom concentrations in H₂ and N₂-H₂ dc discharges. A model was developed which takes into account the absorption of two photons by ground state atoms, ionization by absorption of a third photon, induced fluorescence, stimulated emission, and collisional quenching. The H-atom LIF profile analysis, associated with PhotoFragment Translational Spectroscopy (PFTS) was used to measure the concentration of ammonia synthesized in N₂-H₂ dc discharges, as a function of % H₂ in the mixture.

1. Introduction

Reactive plasmas are playing an increasing role in the processing of novel materials. Large quantities of atomic and radical species are produced in the bulk of the plasma through electron impact dissociation in molecular gas discharges, so that, the measurement of absolute atom and radical concentrations is of great interest. In this context laser-based techniques are convenient diagnostic tools because of their nonintrusive nature and their good spatio-temporal resolution.

The first part of this work is devoted to the study of the interaction between the laser field and the H atoms. Rate balance equations of the three lower levels of H atom and H⁺ ion populations, coupled with the photon transport equation were solved in one-dimension model [1]. We took into account the absorption of 2 photons, subsequent ionization by a third photon, induced fluorescence, stimulated emission and collisional quenching. The results obtained are compared to experiments. Then a two-dimension model is presented to illustrate the spatio-temporal evolution of the involved level populations.

In the second part, the H₂-N₂ gas mixture dc discharge is analyzed. H₂-N₂ discharges which are used in iron surface nitriding, have been recently studied in detail both experimentally [2,3] and theoretically [4,5]. The absolute concentration of ammonia produced in such discharges is obtained as a function of H₂ concentration by the analysis based on PFTS of the H atom LIF profile. This technique allows us to determine the value of the dissociation energy of ammonia.

(*) *Present address:* Instituto de Estudos Avançados-Centro Técnico Aeroespacial, 12237-900 São José dos Campos, Brazil

(**) *Present address:* Laboratoire de Science et Génie des Matériaux Métalliques (****), École des Mines de Nancy, 54042 Nancy, France

(***) Author for correspondence

(****) URA CNRS

2. Experiment

The experimental apparatus was already described in details elsewhere [1,2]. Briefly, the gas flows through a Pyrex discharge tube, with tungsten electrodes, of 1.6 cm *i.d.* at a gas pressure ranging from 0.2 to 5.0 Torr and discharge current between 1 and 50 mA. Because studies in the post-discharge region are also possible with this configuration, the discharge tube was connected to a steel cylindrical chamber of diameter 20 cm. The laser probe beam passes through lateral quartz windows at Brewster angle. By means of two 2.2 mm diameter holes in the discharge tube, the laser beam crosses the positive column. The LIF diagnostic is performed by using a tunable (10 Hz repetition rate, 7 ns duration) pulsed laser, Datachrom 5000 from Quantel. The Nd:Yag laser emission at 1064 nm (900 mJ) is frequency doubled (400 mJ at 532 nm) into a KDP crystal to pump the dye part. The laser operates in a mixture of rhodamine 640 and DCM dyes to produce the 615 nm wavelength. In the next step, the dye laser frequency is first doubled in a KDP crystal and after a phase matching in a $\lambda/4$ waveplate, mixed with the resulting beam in a BBO crystal to give emission at 205 nm. An intracavity beam expander narrows the dye laser linewidth to 0.08 cm^{-1} . The U.V. laser beam with energy around 1 mJ is focused through a 35 cm focal length lens into the steel chamber.

The detection of LIF is by imaging the interaction region onto the entrance slit of a Jobin-Yvon HR 640 monochromator, associated with a Hamamatsu R928 photomultiplier tube and a EG&G 4400 boxcar triggered by the laser pulse. This apparatus is also used for emission spectroscopy. In atom LIF detection, two laser photons at 205 nm pump the $1s^2 \text{ S}_{1/2} - 3d^2 \text{ D}_j$ transition of hydrogen atom. The fluorescence radiation is observed in the $3d^2 \text{ D}_j - 2p^2 \text{ P}$ transition at 656 nm. The Laser Induced Stimulated Emission (LISE) is concerned by the same atomic transition as LIF and is detected in the forward direction of the laser beam. An optical filter stops the laser radiation and transmits the LISE beam which is collected by a photodiode. The resulting electric signal is analyzed in the second channel of the boxcar.

3. Laser-Atom Interaction. Hydrogen Discharge

A d.c. positive column in hydrogen was employed in order to test the validity of the model developed to describe LIF, LISE, and MultiPhoton Ionization (MPI) phenomena. A rate equation approach is utilized in the analysis of the interaction of the laser field with H atoms. The laser beam ($D = 0.5 \text{ cm}$ diameter), with a divergence $\theta = 5 \times 10^{-4} \text{ rad}$ is focused with a 35 cm focal lens (f) in the plasma. It is assumed a Gaussian distribution for the laser power density as a function of both the radius and the time. The interaction region is a stretched pseudo-hyperboloid of cylindrical symmetry. The length $2f^2\theta/D$, is 2.45 cm and the diameter $f\theta$, $1.75 \times 10^{-2} \text{ cm}$. The volume is divided in small slices longitudinally, where the following coupled set of rate equations was solved,

$$\begin{aligned} \frac{dN_1}{dt} &= - \left(N_1 - \frac{g_1}{g_3} N_3 \right) \frac{\alpha_{1,3} \Phi_1^2}{h\nu_1} + N_2 A_{2,1} \\ \frac{dN_2}{dt} &= N_3 A_{3,2} - N_2 A_{2,1} + \frac{B_{3,2} I_{se}}{c} g_D(\nu) \left(N_3 - \frac{g_3}{g_2} N_2 \right) \\ \frac{dN_3}{dt} &= \left(N_1 - \frac{g_1}{g_3} N_3 \right) \frac{\alpha_{1,3} \Phi_1^2}{h\nu_1} - N_3 \left(\frac{\sigma_{3,1} \Phi_1}{h\nu_1} + Q_3 + A_{3,2} \right) - \frac{B_{3,2} I_{se}}{c} g_D(\nu) \left(N_3 - \frac{g_3}{g_2} N_2 \right) \\ \frac{dN_i}{dt} &= N_3 \frac{\sigma_{3,i} \Phi_1}{h\nu_1} \end{aligned}$$

Fig. 1. — Laser induced stimulated emission as a function of the discharge current. Solid lines - model. (●, ■) Experimental points.

In these equations N_j ($j = 1, 2, 3$) is the concentration of the appropriate level, N_i is the H⁺ concentration, Φ_1 is the probe laser irradiance, $h\nu_1$ the laser photon energy, and $h\nu$ the LIF photon energy, $\alpha_{1,3}$ is the two-photon excitation cross section and $\sigma_{3,i}$ the ionization cross section, g_j is the statistical weight of the level j , A_{ij} the spontaneous emission rate coefficient for a transition from the level i to the level j , Q_3 is the quenching rate coefficient of level 3 and $B_{3,2}$ the Einstein stimulated emission coefficient, $g_D(\nu)$ is a Doppler line shape factor.

To take into account the propagation of the LISE, the photon transport equations in the forward and backward directions were solved simultaneously with the rate equations, in each specific slice, considering the photon flux coming from adjacent cells.

$$\begin{aligned} \frac{dI_{sef}}{dx} &= \left(N_3 - \frac{g_3}{g_2} N_2 \right) \frac{B_{3,2} I_{sef}}{c} g_D(\nu) h\nu + A_{3,2} N_3 \Delta\Omega g_D(\nu) h\nu \\ \frac{dI_{seb}}{dx} &= - \left[\left(N_3 - \frac{g_3}{g_2} N_2 \right) \frac{B_{3,2} I_{seb}}{c} g_D(\nu) h\nu + A_{3,2} N_3 \Delta\Omega' g_D(\nu) h\nu \right] \\ I_{se} &= I_{sef} + I_{seb} \end{aligned}$$

I_{sef} and I_{seb} are the LISE intensity in the forward and backward directions, respectively, $\Delta\Omega$ and $\Delta\Omega'$ are the fraction of the isotropic spontaneous emission that contributes to the LISE in both directions. The system of equations presented above were solved initially considering only one dimension in space. Figure 1 shows the calculated and measured intensities of the LISE, in the H₂ positive column, as a function of the discharge current. The input values of ground state atom density to the model were obtained from absorption of the L α (121 nm) line, coupled to LIF measurements of the H α line. Good agreement between the experimental points and the model results is obtained. We can distinguish three regions when the discharge current

Fig. 2. — Simulation results of the concentrations of the hydrogen excited state N_3 level as a function of the ground state H atom concentration N_1 , both with and without LISE terms included in the model.

is varied. The first one, when there is no LISE, for discharge current values ranging from 1 to 3 mA, and pressure of 2.0 Torr. An exponential growth of the LISE signal is observed for currents ranging from 3.2 until 9 mA. A pseudo-saturation is obtained for discharge currents greater than 9 mA. For a pressure of 0.5 Torr the same behavior can be seen, but the threshold for LISE is at 3.9 mA. Figure 2 shows the influence of LISE on LIF. As pointed out above, the LISE influences the LIF only when the gain for stimulated emission is in the exponential region. In order to illustrate the spatio-temporal evolution of the level populations and the LISE, the set of rate equations coupled to the photon transport equations were solved in two dimensions in space, as is shown in Figure 3. We can observe the depletion of the ground state by absorption of two photons (Fig. 3a). The excited state profile (Fig. 3b), is depleted in the center due to the absorption of a third photon that ionizes the atom. The spatial evolution of the ions formed and the LISE profile are given respectively in Figures 3c and 3d, where the effect of the absorption of the third photon is responsible for the depletion of LISE signal in the center of the interaction region.

4. H_2 - N_2 Discharge

The ammonia radicals synthesized in N_2 - H_2 mixture dc discharges are detected by the analysis of the LIF spectral lineshapes of ground state H atoms. In this experiment we observe the same phenomenon as discussed by Dunlop *et al.* [6], *i.e.*, a leak in the vacuum system produced an enlargement of the H atom LIF spectral profile (which in pure H_2 or in H_2 -Ar mixtures is of Gaussian shape) by the appearance of wings. These wings are the result of N_2 introduction,

Fig. 3. — Simulation results of the spatio-temporal evolution of: a) ground state level, b) excited level, c) ions generated and d) LISE in the forward direction. Time of 10 ns, laser energy of 1.0 mJ. The coordinates length and radius are relative to the dimensions along the laser beam axis and transverse to it respectively, in the interaction region.

into the vacuum system, which participates in the synthesis of ammonia. During the laser-gas interaction, to probe the ground state H atoms, the 205 nm photons used have enough energy to photodissociate or photolysis the ammonia radicals, producing hot H atoms that were subsequently detected in the same laser pulse. This mechanism was used to study the synthesis of ammonia in N₂-H₂ mixture discharges. As we can see in Figure 4, when a 205 nm photon is absorbed by the ground state NH₃ ($\tilde{X}^1A_1$), the molecule will be excited to the ($\tilde{A}^1A_2''$), which is a predissociative state. The ($\tilde{A}^1A_2''$) state, dissociates into NH₂ ($\tilde{X}^2B_1$) + H ($^2S_{1/2}$), with a probability near unity [7]. Although the lifetimes of the lower vibrational levels of the ($\tilde{A}^1A_2''$) state are short (some ps), they correspond to many vibrations of the molecules, and a statistical distribution of energy among the internal degrees of freedom of the molecules is observed [8]. After the photodissociation, the nascent H atoms can have, from the conservation of momentum law, a maximum energy of 94% of the total translational energy $E_T = E(H) + E(NH_2)$ released by the excess between the photon ($h\nu_{\text{laser}}$) and the dissociation (D_0) energies. We have $D_0 = h\nu_{\text{laser}} - E_T = h\nu_{\text{laser}} - 1.06E(H)$ with $E(H) = 1/2m_Hc^2(\Delta\lambda/\lambda)^2$, where $\Delta\lambda$ is the maximum wavelength shift. It corresponds to the extremum value of the wings width relatively to λ .

In the laser-plasma interaction region, two populations of ground state H atoms may exist. The resulting H LIF spectral profile (Fig. 5) reflects this particular situation and the spectral shape may be described as a relatively narrow peak with wings. A mathematical analysis of this profile shows that it is composed by the addition of two Gaussian shape profiles, the

Fig. 4. — Scheme for photofragment translational spectroscopy associated with laser induced fluorescence in the detection of NH_3 .

narrow one is attributed to the “cold” atoms produced in the discharge as the result of H_2 dissociation in the bulk of the plasma by electronic impact, the wider one to the “hot” atoms arising from the photolysis of NH_3 . By measuring the maximum kinetic energy of the nascent H atoms, the dissociation energy can be evaluated. The H — NH_2 bond dissociation energy is determined by the “leading edge” of the Doppler profile with a very good accuracy (150 experimental points for each profile) and was found to be 4.34 ± 0.07 eV, value which is in agreement with previous results [9]. In Figure 5, the areas under the curves are representative of the H atom density produced by the discharge itself and from the concentration of H atoms produced in the NH_3 photolysis. As each ammonia molecule photodissociated produces one hydrogen atom, the measurement of hot H atom density leads to the density determination of NH_3 .

The calibration of H atom LIF measurement done in a pure H_2 discharge, allows the determination of the absolute concentration of ammonia in N_2 - H_2 discharge. The calibration procedure is based on a VUV absorption spectroscopy on the L_α line at 121 nm. Briefly, the calibration apparatus included a microwave discharge lamp that generates the 121 nm resonance line, which emission spectral broadness was previously measured, for absorption measurements of ground state H atoms. The radiation generated by the microwave lamp was transmitted through a MgF_2 window and absorbed in the positive column of a pure H_2 (2 Torr) discharge over a 10 cm length. A Jobin-Yvon VUV spectrometer of 50 cm focal length was employed in order to select the desired line. The 121 nm wavelength was detected by using a sodium salicylate scintillator and a photomultiplier tube. To improve the signal to noise ratio, lock-in amplifier detection was used. It should be mentioned that the calibration of the LIF signal was done in a pure H_2 discharge, for which, the quenching of the $\text{H}(3d\ ^2D_j)$ state is only due to H_2 molecules. The use of this calibration, for H LIF signals obtained in N_2 - H_2 mixture discharges, seems to us also valid, because the quenching rates of the $\text{H}(3d\ ^2D_j)$ state by N_2 and H_2 [10, 11] are approximately the same. The H atom temperature in the positive column

Fig. 5. — Profile of the LIF spectral line obtained by the dye laser wavelength scan around 6 150 Å. Contributions of H atoms formed in the discharge and in the photolysis of NH_3 .

was determined from the Doppler spectral LIF profile. This temperature value was included in the determination of absolute H atom density in order to obtain realistic values.

By exploring the profiles as a function of the % of H_2 in the mixture, we determined NH_3 and H atom absolute densities as a function of the discharge parameters. Figure 6 shows a continuous growth of the H atom density with the % of H_2 , and a maximum density of ammonia for a 75% H_2 -25% N_2 mixture, that corresponds to the stoichiometric composition of H_2 and N_2 for ammonia formation. The same maximum of NH_3 relative density was observed in a H_2-N_2 microwave discharge in a Pyrex tube by Uyama and Matsumoto [12], and in an ac discharge by Eremin *et al.* [13]. As we can observe in Figure 6, very large amounts of ammonia are synthesized in H_2-N_2 mixture discharges. For a 75% H_2 -25% N_2 mixture (discharge pressure of 2 Torr and dc current of 50 mA) a NH_3 density of about $8 \times 10^{12} \text{ cm}^{-3}$ was measured.

5. Conclusion

A model for the interaction of photon laser field with H atoms in their ground state was developed. This was obtained by solving a set of rate equations for the involved levels coupled to photon transport equation in one-dimension, taking into account the main processes occurring during the laser-atom interaction. A two-dimension model is proposed to elucidate the ion production, depletion of ground state and evolution of stimulated emission. An application to hydrogen dc glow discharge shows a good agreement between the model predictions and the experimental LISE intensity, in the measurement of ground state H-atom density, *versus* discharge current intensity.

Fig. 6. — H and NH₃ concentrations as a function of the % of H₂ in the mixture. Discharge pressure of 2 Torr and current of 50 mA.

The main information obtained from the analysis of the LIF spectral profiles of H atoms in a N₂-H₂ mixture discharge is the following:

- i) the experimental profile is, with a high degree of accuracy, the sum of two Gaussian shape profiles, iso-centered, with two different widths;
- ii) the area of the narrow one is proportional to the H atom population created by the discharge and its FWHM gives the atom temperature, which is found to be between 500 K and 1200 K, for a range of dc discharge currents from 1 to 50 mA and pressure of 2 Torr; the area of the wide one is proportional to the population of NH₃ synthesized in the discharge, its FWHM gives a temperature of about 8 000 K, and the Gaussian shape is well explained by the photolysis through excitation of the predissociative ($\tilde{A}^1A_2''$) state;
- iii) the extreme values are related to the dissociation energy of NH₃, 4.34 ± 0.07 eV;
- iv) NH₃ molecules are produced in large quantities and maximum amount is obtained for stoichiometric conditions. This high density value shows that NH₃ molecules, as well as NH radicals which are also present in the discharge [2], must be taken into account in the discharge modeling, to better understand the role of active species in metallic surfaces nitriding;
- v) PFTS associated with LIF may be a powerful diagnostic technique for radical detection in reactive plasmas; in the case of ammonia, the same wavelength photon is used to dissociate the radical and to probe the H atom emitted photofragment, during the same laser pulse.

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