Measurement of excited species in discharges using Laser Absorption spectroscopy

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<Abstract>

The population density of excited species in dc, rf and laser ablation plume plasmas has been measured using laser absorption spectroscopy. It was shown that, when the plasma was modulated by on and off with, the sensitivity and signal to noise (S/N) ratio became high. For example, the atomic $O(3^5S^o_2)$ population density, N_{O^*} in O_2/He mixtures was obtained by the highest S/N ratio at a frequency of 2.7kHz. In a 20Torr room air, the lowest N_{O^*} level to be detectable was shown to be an order of 10^7 cm^{-3}. The population densities of resonance $Ar(1S_2)$ and $Xe(1S_4)$ levels were also measured in barrier discharges and laser ablation plasmas.

Key Words : plasma discharge, laser ablation plume, plasma modulation laser absorption spectroscopy (PMLAS), classical laser absorption spectroscopy(CLAS)

1. Introduction

It is well known that excited particles play an important role in various plasmas related technologies, e.g. oxidation and ozone production, remedy of air and water pollution, for atomic oxygen, laser reactions and radiation for rare gas excimers, etching and deposition of semiconductor industry for radicals, etc. In these applications, it is important to know the population density of these species. Recently, for measurement of excited state population using a laser absorption technique, a new method of modulation of continuous plasma by *on* and *off* has been proposed [1]. This method reveals clearly that the profile of the absorption signal is high spectral selectivity, which offers information of isotopic shifts and hyperfine structure of atomic oxygen as indicated in Ref.[2,3]. In this article, a plasma modulation laser absorption spectroscopy(PMLAS) technique is shown along with a classical laser absorption spectroscopy (CLAS) technique, which is obtained to chop the laser light by *on* and *off* synchronizing with the reference frequency of a lock-in-amplifier.

The population density N_{O^*} of $O(3^5S^o_2)$ in O_2/He mixtures and room air discharges, and excited rare gas atoms are measured using a PMLAS coupled with CLAS.

2. Experimental set-up and procedure

Figure 1 shows a schematic diagram of the present measurement system of the population density N_{X^*} using PMLAS and CLAS. A diode laser and its temperature are driven and controlled by a power supply (Melles-Griot 06DLD203).

The laser light is collimated, at the light source, to a fine parallel beam of ~300mm using a 10X microscope objective. The intensity of the laser beam is adjusted using neutral density filters (NF).

The laser wavelength tuned to the energy between the lower and upper transition is monitored by a wavelength meter (Burleigh WA-1000) adopting a part of the main beam split by BS_2. The wavelength of the laser light is scanned in a 20 GHz range changing the current of the diode using a triangular wave generator with 100 mHz frequency. The laser beam after passing through the plasma is detected by a photo-diode. The photo-diode signal is amplified by a lock-in amplifier, and is simultaneously recorded to a computer through a GPIB interface.

In a PMLAS system, the plasma is modulated by *on* and *off* with frequencies (f_{PM}) between 50 Hz and 3kHz. f_{PM} is varied by a signal generator built in the current sink. The CLAS system the laser beam is chopped at a frequency of 1 kHz by a mechanical shutter at the inlet of the beam to the discharge chamber. In the discharge chamber, there are electrodes the distance between which is movable. In the case for laser ablation experiment, this chamber is replaced to the chamber in which the ablation plume is sustained.

3. Absorption signals

Figure 2 shows a example of waveforms of the discharge current and the photo-diode signal in O_2/He plasma at a f_{PM} of 2.7 kHz. In order to obtain high S/N value, it is preferable to operate a lock-in amplifier with the same reference frequency as f_{PM}. Figure 3 shows a PMLAS absorption signal obtained by transition of $O(3^5S^o_2 \rightarrow 3^5P_1;\ l_{01}=777.753$ nm) along with the interference fringes of the Fabry-Perot etalon. The spectrum is broadened due to Doppler and collisional effects. The area of the spectrum corresponds to N_{O^*} [2].

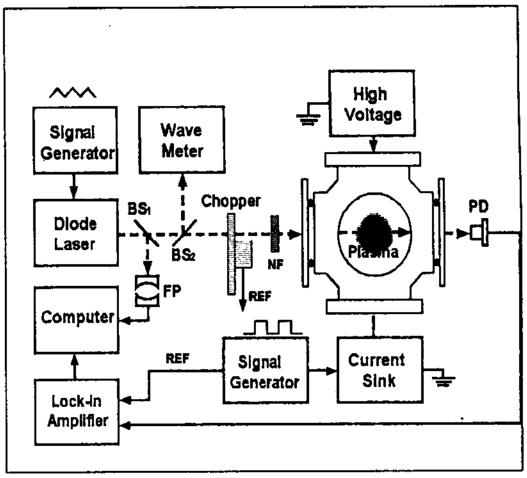

Fig. 1. Experimental set-up

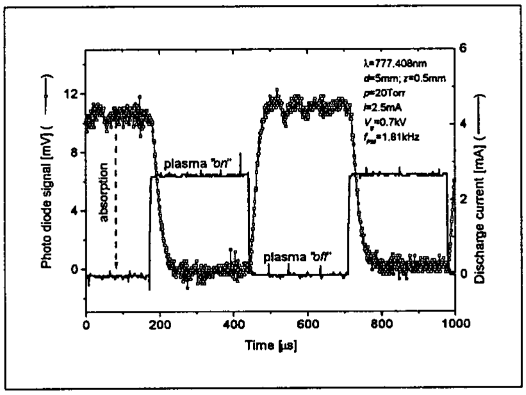

Fig. 2. Discharge current and photo-diode response of absorption signal in PMLAS system

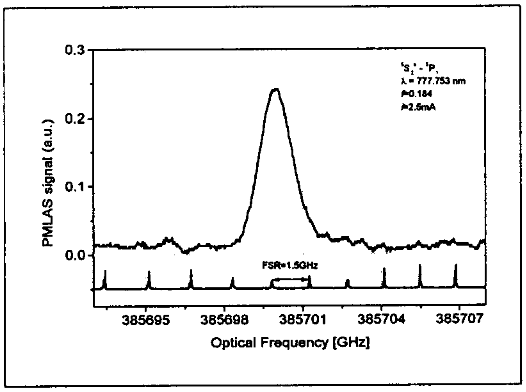

Fig. 3. Absorption spectrum along with Fabry-Perot etalon interference fringes

4. Theory to obtain excited species x* population

In the PMLAS system, the absorption signal I_{PM} is given as,

$$I_{PM} = I_O - I \qquad (1)$$

where I_O is the signal detected by a photo diode when plasma is *off* and I is the signal when plasma is *on*. The value of I_{PM} is directly proportional to the population N_{X^*} of excited species along the light path. Then, N_{X^*} is given as:

$$N_{X^*} = \beta \cdot I_{PM} \qquad (2)$$

where *b* is a constant (calibration factor).

To determine *b* value, generally we take the absorption coefficient *a(n)* at a frequency *n* as [2]

$$\alpha(\nu) = \frac{1}{L} \cdot \ln[1 - \frac{I(\nu)}{I_O(\nu)}] \qquad (3)$$

where *L* is the absorption length for the light beam, $I_O(n)$ and $I(n)$ are the beam intensities at the inlet and outlet of the beam to the plasma, respectively. The value of N_{X^*} may be given integrating equation (2) for all over the n range, where the laser beam is absorbed, as $S = \int[1 - I(\nu)/I_O(\nu)]d\nu$ then N_{O^*} is given as

$$N_{X^*} = \frac{g_l}{g_u} \cdot \frac{8\pi \cdot \nu_0^2}{c^2 \cdot A_{ul} \cdot L} \cdot S \qquad (4)$$

where n_0 is the resonance frequency (= c / l_0). g_l and g_u are the statistical weights of the lower and the upper levels, respectively. A_{ul} is the Einsteins coefficient for spontaneous emission. Combining equations (1) and (3), a calibration factor *b* in cm^{-3}/mV is given as

$$\beta = \frac{g_l}{g_u} \cdot \frac{8\pi \cdot \nu_0^2 \cdot S}{c^2 \cdot A_{ul} \cdot L \cdot I_{PM}} \qquad (5)$$

5. Results and discussion

5.1 Dependence of *No** on O2 mol fraction in O$_2$/He mixtures

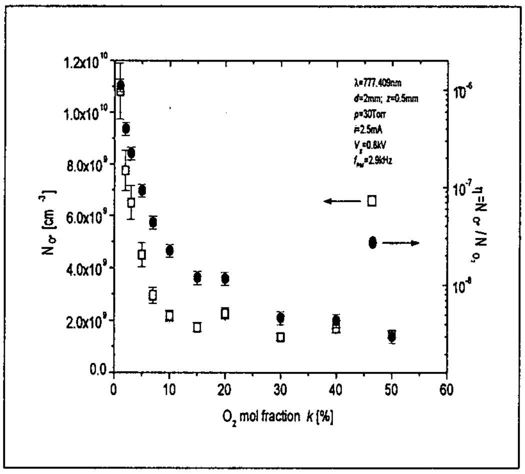

Fig. 4. Dependence of N_{O^*} and efficiency h on k in glow type discharge at the plane electrode in O$_2$/He at d=2mm, p=30Torr, i=2.5 mA, Vg=0.8kV and positive needle.

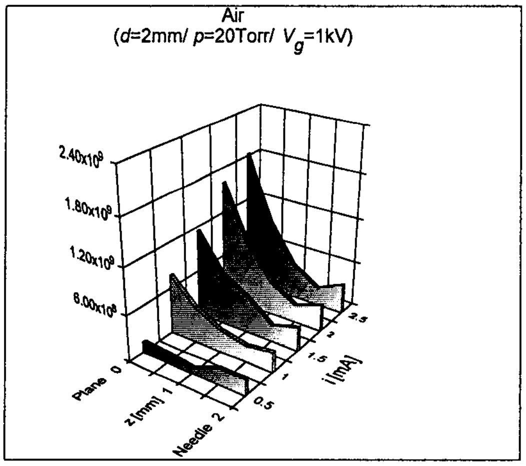

Fig. 5. Spatial distribution of N_{O^*} in 20 Torr room air for i between 0.5 and 2.5 mA, d=2mm, Vg=1kV

Figure 4 shows that the N_{O^*} at the distance, 0.5mm, from the grounded electrode, where the glow type discharge is sustained, decreases monotonously from about 1.2 10^{10} cm^{-3} at $k\sim$ 0.01% to 10^9 cm^{-3} with increasing *k*. The current is fixed to be *i*=2.5mA.

A noticeable feature of N_{O^*} on *k* is the significant increase in N_{O^*} with decreasing *k* for *k*<1%.

The efficiency *h* defined as the ratio of the O(35So2) to O2 population is from 10^{-9} to 10^{-6}. Among the present experimental conditions, the maximum *h* was ~ 3.7x10^{-4} at $k\sim$ 0.01%. In the present PMLAS system, $O(3^5S^O{}_2)$ could be detected for *k*<50%.

5.2 $O(3^5S^O{}_2)$ population in air

The spatial distributions of $N_{O^*}(z)$ in the gap for *i* between 0.5 and 2.5mA are shown in Fig. 5. The N_{O^*} is obtained to be about 2x10^9 cm^{-3} near the plane electrode (grounded one).

The results shows that the spatial gradient of $N_{O^*}(z)$ is smaller that in the case of O_2/He mixtures.

5.3 $Ar(1s_2)$ population in a carbon ablation plume

The absorption signal of the resonance state of $Ar(1s_2)$ is shown in Figure 6, which was measured in a carbon plume plasma generated in a buffer Ar gas with pressures *p* between 0.05 and 20Torr by irradiation of ArF excimer laser with fluence of 5 Jcm^{-2} to a graphite target. The $Ar(1s_2)$ population corresponds to the area of the waveform.

The signal increased with increasing the *p* for *p* <5Torr due to frequent excitation collisions, but decreased with *p* for *p*>5Torr due to energy loss by collision with buffer gas. The $Ar(1s_2)$ population density was estimated to be ~10^{10} cm^{-3} at *p* =5Torr. The residence time of $Ar(1s_2)$ was found to be ~80msec.

The decay rate of the $Ar(1s_2)$ population decreased from 110msec to 20msec with increasing *p* in the present Ar *p* range. This result may indicate that energetic electrons, which can produce $Ar(1s_2)$, are present in the laser ablated plume.

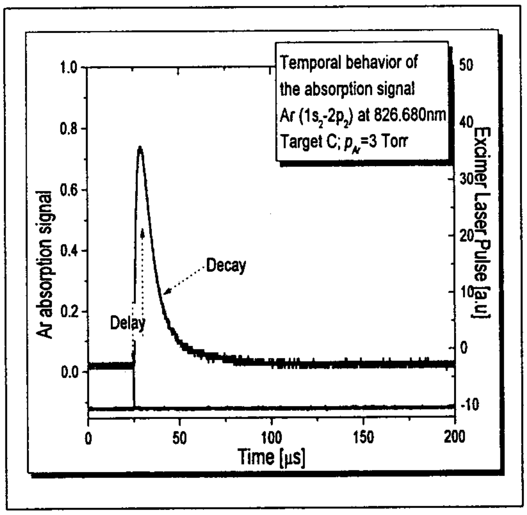

Fig. 6. Waveform of an absorbed signal by $Ar(1s_2)$ of buffer gas in a carbon plume

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