SDI Review Form 1.6

Journal Name:	**Physical Review & Research International**
Manuscript Number:	**2013_PRRI_6986**
Title of the Manuscript:	**Measurements of absolute atomic oxygen density by two-photon absorption laser-induced fluorescence spectroscopy in hot air plasma generated by microwave resonant cavity**
Type of the Article	**Research Paper**

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This journal's peer review policy states that **NO** manuscript should be rejected only on the basis of '**lack of Novelty'**, provided the manuscript is scientifically robust and technically sound.
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PART 1: **Review Comments**

	Reviewer's comment	**Author's comment** *(if agreed with reviewer, correct the manuscript and highlight that part in the manuscript. It is mandatory that authors should write his/her feedback here)*
Compulsory REVISION comments		The authors are grateful to the referee for careful reading of the manuscript and constructive suggestions aimed to improving the text. The reply is given hereafter and the text amendments are green highlighted in the manuscript.
	1. Line 35: Should include recent work that involves direct laser absorption spectrometry to quantify ground-state oxygen atom densities: **a. http://dx.doi.org/10.1063/1.2408655**	1. It is right, this absorption spectroscopy method to measure atomic oxygen density is interesting to notice for the reader (Please see lines 54-57 and ref 6)
	2. Please refine the manuscript's English. There are several awkward sentence and phrase constructions that make the manuscript more difficult to read. For example, use "gas conditioning cell" instead of "cell of gas conditioning". This applies throughout the manuscript.	2. The English was improved (please see some green and also yellow highlighted texts of the revised version). The change "gas conditioning cell" is also considered.
	3. Please describe the pumping system and gas flow rates.	3. Further information are given on the pumping system (please see page 3, lines 86-87 and 93-99)
	4. Lines 108 – 109, please provide the spectral resolution of the spectrophotometers. This is especially relevant in determining the linewide of the laser, which may be heavily convoluted with the spectrophotometer resolution.	4.The two gratings of 1800 grooves.mm^{-1} and 2400 grooves.mm^{-1} provide a spectral resolution of the spectrophotometer close to respectively 0,02 nm and 0,015 nm (this is added in the text). The spectral linewidth of the laser beam was not measured with the spectrophotometer. It's a specification of Sirah Cobra Stech dye laser function of the tuning element. Our specific

		configuration (two grating of 1800 grooves.mm^{-1}) allows a beam linewidth equal to 1.7 pm and 2 pm after the frequency doubling.
	5. Lines 113 – 122, please provide laser power for each wavelength regime.	5.The characteristics of the dye laser beam are added in the text (please see page 4).
	6. Lines 197 – 198. The authors show the fine structure of the TALIF spectrum; however, there is no discussion about this fine structure. Please add a paragraph describing this structure and, ideally, showing that it fits model results (or matches expectations).	6.Unfortunately, the fine structure of the Talif spectrum and specially the components corresponding to the excitation of the tree levels 3p $3P_0$, 3p $3P_1$ and 3p $3P_2$ cannot be clearly resolved due to the very low energy interval of these levels (max 0.7 cm^{-1}). This corresponds to an excitation laser wavelength interval up to 0.6 pm. The Gaussian profile of the laser beam (FWHM = 2pm) do not allow us to separate the different components of the fine structure. (Comments are added in the text, page 7lines 215-220)
	7. Figure 7: The point of this figure is to show that the FWHM is independent of pressure. Thus, please list the FWHM of the 2 profiles. Also discuss the shift of the line position.	7.The FWHM of the two-photon excitation spectra of the 2 p^4 $^3P_2$ is about 3 pm in the pressure range between 100 mbar and 600 mbar and the profile line is better fitted by a Gaussian profile. This indicates negligible broadening due to the background gas. The discrepancy between the FWHM of laser beam (about 2 pm) and the FWHM measured is weak and probably due to the fine structure of the excitation spectrum. Thus, the fluorescence intensity spectrally integrated corresponds to the excitation of the upper three sub-levels. The shift of the line position cannot be evaluated with enough accuracy. The wavelength reproducibility of the dye laser beam is up to 5

		pm. The line shift of the O(2p4 3P2 → 3p 3PJ) resonance cannot be inferred from our results in view of the uncertainty of the wavelength calibration (these comments are added in the revised version: page 8, lines 237-244)
	8. Calculation of the ground-state oxygen density. This is the most significant issues with this paper. **a. The authors assume that the linear relationship between laser pulse energy and fluorescence signal (Figure 8) suggests that there is negligible collisional depletion and photo-ionization. While the latter is correct, the former is not. The linear relationship suggests that collisional depletion due to 2 excited state oxygen atoms colliding is negligible. However, it does NOT indicate that a ground-state oxygen atom (or other gas constituent) cannot collisionally-deactivate an excited state oxygen atom. Thus, collisional deactivation may lead to a very significant decrease is fluorescence and estimated ground-state oxygen atom population.**	8.The referee is right. The ground state oxygen atoms or other gas constituents can collisionally deactivate the 3p ^3P_J state oxygen atoms. This leads to a decrease of the TALIF signal if the collision decay of the excited state competes with the radiative decay of this state and if the collisional reaction time is close to the lifetime of the excited state. The quenching of excited O atoms by ground state O atoms is neglected if the atomic oxygen is supposed to be a minority species. Anyway, the upper limit of value of the quenching rate constant was estimated to be $0.82.10^{-11}$ cm^3s^{-1} in an oxygen plasma jet having a sufficiently high and controllable degree of dissociation (G Dilecce, M Vigliotti1 and S De Benedictis J. Phys. D: Appl. Phys. 33 No 6 (21 March 2000) L53-L56 "A TALIF calibration method for quantitative oxygen atom density measurement in plasma jets"). Thus, in our case, the radiative time decay of reaction remains shorter than the collisional time decay reaction.
	b. Alternatively, the xenon calibration accounts for this deactivation issue. But, the xenon work is done at much higher pressures (1 – 10 torr versus < 1 torr), and it the xenon-xenon collisional deactivation is not comparable to the oxygen atom deactivation.	b. Figure 10 shows that the TALIF signal is proportional to the xenon density up to $3.3.10^{17}$ cm^{-3} (10 Torr at 295 K). In that density range, the collisional deactivation of excited states of xenon can be neglected. Note that the density range of xenon is close to

	c. Also, it seems that the collisional deactivation rate would be heavily dependent on the gas temperature, yet this is not discussed or taken into account.	the measured density of atomic oxygen. c-We have assumed that radiative decays of oxygen and xenon excited atoms are predominant. So the collisional constant rates are not taken into account for density calculations. Furthermore the temperature dependence of the collision reaction rate of oxygen atoms is not known in the literature.
	d. Thus, this reviewer does NOT understand how TALIF provides an accurate measurement of ground-state oxygen density. It is clear that TALIF provides a good relative measurement of ground-state oxygen density at a given pressure.	d-In our case, the best technique available for determination of the oxygen density is the two-photon absorption laser induced fluorescence (TALIF) which couples high sensitivity and high spatial resolution. The reviewer is right, absolute calibration of the TALIF technique is, nevertheless, a hard task and involves some approximations concerning the decay of excited species.
	9. Lines 263 – 264. Are the filter transmission percentages measured or taken from data sheets?	9.The filter transmission percentages are taken from data sheets. (it is added in the revised version)
	10. The plasma temperature was determined by adding H2 to the gas flow and measuring the fluorescence spectra of the OH radical. There are several issues with this technique that need to be addressed: **a. Adding a small amount of hydrogen (how much was added?) changes the plasma characteristics, including the temperature. How is this taken into account or shown to be negligible?**	10a.3% of H2 has been added in the air to better see the OH spectra. The referee is right because it is important to know how the air plasma characteristics can be affected by the addition of H2 admixture because H2 has thermal conductivity 6 times higher than the air one and the thermal diffusion of H2 is faster than the air one. In fact from measurements of NOγ bands not shown in the manuscript (well representative of O2 and N2 dissociation in our air plasma), we have shown that the NOγ spectra with and without H2 admixture are very close. This is why we assumed that a small amount of

		H2 does not affect significantly the air plasma characteristics. Figure 12 displaying NOg bands with and without H2 is added in the revised version with some comments (please see pages 10- 11, lines 330-341)
	b. As noted in the text, the OH temperature measurement assumes ro-translational equilibrium. Is there any evidence to suggest that, at the low pressured in this plasma (< 1 torr), that ro-translational equilibrium exists?	b. Under our pressure conditions (600mbars or about 450 Torr), the collision frequency is high and the ro-translationnel equilibrium is reached in a very short time scale (lower than ns).
	11. Table 1: Please add uncertainties to the listed values, using a proper convolution of measurement and listed uncertainties.	11. uncertainties are added in table 1
Minor REVISION comments	The English should be revised to make the manuscript more readable.	The English was improved (please see some green and also yellow highlighted texts of the revised version)
Optional/General comments		Thank you again for your careful reading of the manuscript and your constructive suggestions