Self-absorption influence on the optical spectroscopy of zinc oxide laser produced plasma

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Abstract. Optical spectroscopy is used to study the laser ablation process of ZnO targets. It is demonstrated that even if Partial Local Thermal Equilibrium is present, self absorption process leads to a decrease of recorded lines emission intensities and have to be taken into account to obtain correct values of such parameters. It is presented a method that combines results of both Langmuir probe technique and Anisimov model to obtain correct values of plasma parameters.

1. Introduction
Optical Spectroscopy is one of the key techniques to characterize plasmas, as it offers several methods to extract densities and temperatures of species that form the plasma. Laser produced plasmas (LPP) are characterized by their intrinsic density and temperature gradient, which may induce strong self-absorption of emission from the core of the plasma, by less excited species on the edge of it. As a result, intensities of recorded self-absorbed emission lines are lower than they really are. The latter misleads plasma temperature and density values, calculated using intensity based spectroscopic methods. In order to correct such errors it is needed to take absorption into account.

In this paper it is analyzed LPP from a zinc oxide target. It is demonstrated that for the used laser pulse energy fluence, recorded emission lines suffer a strong self-absorption. In order to extract proper plasma parameters it is presented a method that fits recorded spectra accounting for self-absorption and other plasma related phenomena like line shifting and broadening. Furthermore, calculus procedure uses Anisimov’s model [1] to up bound values of calculated plasma parameters.

2. Experimental setup
The work was carried out in a stainless steel chamber with a base pressure of 8x10⁻⁶ mbar using a Pfeiffer-Balzers TSH 050 turbo molecular system (50 l/s). When working in a background gas, 5.0 grade oxygen (Air Products) was fed through a Whitey needle-valve into the chamber. A Balzers Penning was used as pressure gauge for the 10⁻⁵ to10⁻³ mbar range. For the region of 0.2-1 mbar an Edwards Pirani gauge was used. The latter was calibrated using a Hastings HPM-2002-OBE wide range gauge, which consists of a dual sensor unit containing a piezoresistive direct force sensor and a thin film Pirani type sensor.

A KrF (248 nm, 26 ns) excimer laser was used for ablation. The laser pulses were focused on the rotating target using a 50 cm focal length lens obtaining a rectangular spot of (0.6 x 0.1) cm dimensions obtaining a fluence of 1 J/cm². The laser pulse was incident at an angle of 45° to the
normal of the target. The average energy per pulse (0.06 J) was measured using a Scientech thermopile joulemeter.

A 25 cm focal length Oriel Imaging Spectrometer coupled to an Andor ICCD camera was used to record emission spectra. The spectrometer focal length together with both a 1200 lines/mm grating and 50 μm slit ensured a spectral resolution of 0.175 nm. The spectra were recorded in both time and space resolved mode over a distance of (0-35) mm from the target surface. A Stanford delay generator, with a time resolution of 5 ps, was used to trigger the ICCD. All measurements were performed with a time window of 18 ns on the image intensifier and the counts on 8 pixels were binned together and summed over 100 laser shots at each wavelength. The ICCD detector was cooled to 0 °C.

A 0.053 cm² planar Langmuir probe, biased at -30 V, and the Koopman circuit [2] were used to record ions current.

3. Results and discussion

3.1. Langmuir probe and Anisimov model

Ionic currents detected by using the Langmuir probe can be associated to the ion number density in a plasma [3]. Figure 1 shows the ion number density obtained from the measured ion currents, at different positions from the target surface, while figure 2 shows the peak ion densities as a function of the distance from the target surface. The measurements were performed in vacuum.

![Figure 1](image1.png)

**Figure 1.** Ion signals and densities measured in vacuum at different distances from the target surface.
Figure 2. Peak ion densities as extracted from ion signals measurements in vacuum.

The ionic currents can be combined with Anisimov model to calculate the plasma dimensions as a function of time. Figure 3 shows the result of such calculation. Detailed explanation of this procedure can be found in [4].

Figure 3. The time dependence of the Z/X, Z/Y and Y/X values.
3.2. Emission spectroscopy

Figure 4 shows an example of the recorded spectra after ablating a ZnO ceramic target. All spectra were recorded at 0.5 cm from the target surface and 290 ns after laser pulse interacts with the target.

![Emission spectra recorded after the laser ablation of a ceramic ZnO target.](image)

There was no evidence of lines associated to ionized species, red arrows in the figure indicates where transitions belonging to ionized zinc should appear.

It can be observed that most emission lines come from common or closely spaced levels, these are triplet $4s4d \ ^3D$ and $4s5s \ ^3S$. If the plasma is optically thin the relative radiance within the multiplets should remain constant and be determined by the line strength ($S$).
Table 1 shows values of fundamental properties of the levels involved in the studied transitions. Different colours were used to group transition from the same multiplet.

Table 1. Values of fundamental properties of the levels involved in the studied transitions. In the table $S$ is the line strength in atomic units and $A_{21}$ is the transition probability.

| Wavelength (nm) | $E_2$ (eV) | $A_{21}$ (s$^{-1}$) | $g_1$ | $g_2$ | $f_{12}$ | $f_{21}$ | $S$ (a.u.) | $\lambda^2 \cdot f_{12} \cdot g_1$ (10$^{-13}$ m$^2$) |
|-----------------|------------|---------------------|-------|-------|----------|----------|-----------|---------------------------------|
| 213.857         | 5.796      | 7.039E+08           | 1     | 3     | 1.4390   | 0.4797   | 10.19     | 0.658                          |
| 301.836         | 8.113      | 3.583E+06           | 1     | 3     | 0.0146   | 0.0049   | 0.15      | 0.013                          |
| 303.578         | 8.113      | 1.057E+07           | 3     | 3     | 0.0145   | 0.0145   | 0.44      | 0.040                          |
| 307.206         | 8.113      | 1.702E+07           | 5     | 3     | 0.0144   | 0.0239   | 0.73      | 0.068                          |
| 328.233         | 7.783      | 8.657E+07           | 1     | 3     | 0.4169   | 0.1390   | 4.53      | 0.449                          |
| 330.258         | 7.783      | 1.072E+08           | 3     | 5     | 0.2904   | 0.1742   | 9.53      | 0.950                          |
| 330.294         | 7.783      | 5.956E+07           | 3     | 3     | 0.0968   | 0.0968   | 3.18      | 0.317                          |
| 334.502         | 7.784      | 1.500E+08           | 5     | 7     | 0.3501   | 0.2501   | 19.40     | 1.959                          |
| 334.557         | 7.783      | 3.749E+07           | 5     | 5     | 0.0625   | 0.0625   | 3.46      | 0.350                          |
| 334.594         | 7.783      | 4.166E+06           | 5     | 3     | 0.0042   | 0.0069   | 0.23      | 0.023                          |
| 462.981         | 8.473      | 1.492E+06           | 3     | 5     | 0.0079   | 0.0048   | 0.37      | 0.051                          |
| 468.013         | 6.655      | 1.553E+07           | 1     | 3     | 0.1521   | 0.0507   | 2.36      | 0.333                          |
| 472.215         | 6.655      | 4.576E+07           | 3     | 3     | 0.1520   | 0.1520   | 7.13      | 1.017                          |
| 481.053         | 6.655      | 7.004E+07           | 5     | 3     | 0.1449   | 0.2415   | 11.54     | 1.677                          |
| 636.234         | 7.744      | 4.652E+07           | 3     | 5     | 0.4676   | 0.2806   | 29.57     | 5.679                          |

Using $S$ values in table 1 lines within triplet $4s4d \ ^3D$ would have ratios of 1.8, 5 and 2.8. However it can be observed in figure 5, where temporal behavior of normalized intensities is shown, that such ratios are not met. Similar problem can be observed for the triplet $4s5s \ ^3S$.

Figure 5. Left hand side shows the time behaviour of the intensity of the lines in the triplet $4s5s \ ^3S$ and $4s4d \ ^3D$. Right hand side shows evolution of the relative intensities of the lines in the triplet and in the legend the theoretical relative intensity is presented.
From figure 5 it can be observed as well that the transitions reach their maximum at different times which seems unreasonable since they belong to the same triplet. This behaviour suggests that a self absorption process is present, and therefore, the plasma is optically thick for some transitions.

In order to correct for such a process it is necessary to know if and to what extent each line is self absorbed. The self absorption coefficient \( \kappa_{\text{abs}}(\lambda, T) \) is defined by:

\[
\kappa_{\text{abs}}(\lambda, T) = \pi r^2_0 \lambda^2 f_{12} P(\lambda, \lambda_0) \left[ 1 - e^{-\frac{hc}{2kT}} \right]
\]

(1)

where \( r_0 = 2.82 \times 10^{-15} \) m is the classical electron radius, \( n_1 \) is the population of the lower level in the transition and \( f_{12}, P(\lambda, \lambda_0) \) are the absorption oscillator strength, the wavelength and the profile of the transition line [5]. As a first approximation a comparison of the absorption among lines of the same multiplet can be performed by looking at the product \( \lambda^2 f_{12} n_1 \). Assuming LTE, an estimate of the relative level population can be made from their statistical weight \( g_1 \).

From the values in the last column of the table 1 is to be expected that within their respective multiplet the lines 307.206 nm, 334.502 nm and 481.053 nm are the most self absorbed. This is in agreement with the pattern of the relative intensities showed in figure 5 and is more clearly observed in figure 6, where an evolution in time of the emission from the multiplet \( 4s5s \ ^3S \) is shown.

![Vacuum at 0.5 cm from target](image)

**Figure 6.** Evolution in time of transitions from the triplet \( 4s5s \ ^3S \). The line 481.053 nm shows a greater self absorption.
3.2.1. **Correction for self-absorption.** For a complete estimate of the absorption coefficient (equation (1)) it is necessary to know both the line profile and population of the lower level involved in the transition.

The line profile used to do the radiation transport calculation will be Gaussian or Lorentzian if Doppler or pressure broadening can be neglected, respectively. If both are taken into account a Voigt profile is obtained. It should be noted that the recorded spectral line can be modulated by the spectrometer response function. This is the case if the FWHM of the response function is comparable to or greater than the resultant FWHM of the line due to all the broadening mechanisms. The recorded spectra will be a convolution of the line profile with the spectrometer response function, which is closely reproduced by a Gaussian profile.

Doppler broadening is usually determined by the thermal velocity, relative to the observer, of the emitting species and is characterized by a Gaussian distribution. For heavy atomic and ionic species this velocity is small and the Doppler broadening can be neglected in comparison with pressure broadening. In laser produced plasmas, depending on whether the process takes place in vacuum or in presence of gas background, the expansion velocity could be greater than the thermal and the former determines the Doppler broadening. It should be noticed that in such case the profile is not necessarily Gaussian as the relevant one-dimensional velocity distribution function may not be Gaussian.

A full discussion of this aspect is out of the scope of this work and it will be treated in a future paper. It will be assumed that pressure mechanisms are predominant and a Lorentzian profile should be used. This is a common practice for laser produced plasmas [6-8].

A Lorentzian line profile [6] can be defined by:

\[
P(\lambda, \lambda_0) = \frac{1}{2\pi} \frac{\Delta\lambda}{(\lambda - \lambda_0 - \delta\lambda)^2 + \left(\frac{\Delta\lambda}{2}\right)^2}
\]

\[
\Delta\lambda = \Delta\lambda_{\text{res}} + \Delta\lambda_{\text{vw}} + \Delta\lambda_{\text{st}}
\]

\[
\delta\lambda = 0.36\Delta\lambda_{\text{vw}} + 0.86\Delta\lambda_{\text{st}}
\]

where \(\lambda_0\) is the transition wavelength, \(\Delta\lambda\) is the total width of the line and \(\delta\lambda\) is the line shift, while \(\Delta\lambda_{\text{res}}, \Delta\lambda_{\text{vw}}, \Delta\lambda_{\text{st}}\) are the resonance, van der Waals and stark broadening, respectively. These broadenings are defined by the following expressions [6]:

\[
\Delta\lambda_{\text{res}} = \frac{\lambda_0^2}{c} \pi C_{\text{res}} n_{\text{rad}}
\]

\[
\Delta\lambda_{\text{vw}} = \frac{\lambda_0^2}{2\pi c} 8.08 \left(\frac{8kT}{\pi}\right)^{0.3} \sum_p \left(\frac{1}{\mu_{\text{rad},p}}\right)^{0.3} C_{\text{vw}}^0 n_p
\]

\[
\mu_{\text{em},p} = \frac{m_{\text{rad},p}}{m_{\text{rad}} + m_p}
\]

\[
\Delta\lambda_{\text{st}} = \frac{\lambda_0^2}{2\pi c} 11.37 \left(\frac{8kT}{\pi m_e}\right)^{1.7} C_{\text{st}}^{1/2} n_e
\]

The summation is performed over the total number of neutral perturbers denoted by index \((p)\), \(m_{\text{rad}}\), \(m_p\) are the mass of the radiating and the perturber species and \(n_{\text{rad}}, n_e\) are the density of radiating species and electrons. The constants \(C_{\text{res}}, C_{\text{vw}}, C_{\text{st}}\) are the coefficients for resonance, van der Waals and Stark broadening respectively.

Griem [9] stated that PLTE can exist between certain level with respect to the ground state of the next higher ionization stage. The criteria is defined by:
where \( n \) is the level for which the criteria is applied. \( E_z \) is defined as:

\[
E_z = \frac{z^2 e^2}{2a_0}
\]

\( z \) is the effective charge, equal to 1 for atomic species, 2 for single ionized and so on.

For levels with \( n \geq 3 \) electron number density should be or the order of \( 10^{14} \) cm\(^{-3} \), which in our experiments is fulfilled at distances equal or lower than 0.5 cm (see figure 2).

If a PLTE exists, the number density of atoms in state \( j \) \((naj)\) is related to the electron \((ne)\) and ion \((ni)\) number densities by [5]:

\[
n_{aj} = \frac{2\left(\frac{2\pi mkT}{\hbar^3}\right)^{\frac{3}{2}} g_{aj} Z_{aj}(T)}{g_{e} Z_{e}(T)} \exp\left(-\frac{E_{aj}}{kT}\right)
\]

where \( g_{e}, g_{aj} \) are the statistical weights and \( Z_{e}(T), Z_{a}(T) \) the ion and atom partition functions. Since the oxygen ionization energy is greater than that of zinc, it was assumed that all ionic species are single ionised Zn atoms. Equation (3.7) can be expressed as:

\[
n_{aj} = \frac{2\left(\frac{2\pi mkT}{\hbar^3}\right)^{\frac{3}{2}} g_{aj} Z_{aj}(T)}{g_{e} Z_{e}(T)} \exp\left(-\frac{E_{aj}}{kT}\right)
\]

Combining equations (1), (3) and (6), the absorption coefficient is completely defined by the principal properties of the plasma such as both electron and atom number density and plasma electron temperature. Therefore it is possible to have a complete estimation of self absorption effects over the different transitions providing we know the plasma properties. On the other hand these are, indeed, the parameters which need to be determined. In order to obtain these parameters synthetic spectra for different values of the plasma parameters were generated and fitted until the experimental recorded spectra is matched.

3.2.2. Spectra calculation. The radiance \( L(\lambda, T) \) emitted by a transition from the upper level \( n_2 \) to a lower \( n_1 \) is defined by [5]:

\[
L(\lambda, T) = \frac{2\hbar c^2 g_{n_2}}{\lambda^5 g_{n_1}}
\]

and accounting for self-absorption:

\[
L(\lambda, T) = \frac{2\hbar c^2 g_{n_2}}{\lambda^5 g_{n_1}} \left(1 - e^{-\kappa(\lambda, T)l}\right)
\]

where \( \kappa(\lambda, T) \) is the absorption coefficient as defined in equation (1) and \( l \) is the length of line of sight in the measurement.

As highlighted earlier the recorded spectra are a result of a convolution of the line profile and the spectrometer response function. The spectrometer response function was assumed to be Gaussian with a FWHM determined by the greatest of the used slits \((W_{slit})\), the instrument magnification in the horizontal axis \((1.1)\) and the instrument linear dispersion \((LD)\), that is:

\[
FWHM_{spect} = 1.1 \times W_{slit} \times LD
\]
From equation (8) with $W_{\text{slit}} = 50\mu\text{m}$ and a $LD = 3.2\mathrm{nm/m}$ the $FWHM_{\text{spect}} = 0.176\mathrm{nm}$.

For the calculations a small code was developed using the LabTalk programming tool within Origin software. The general algorithm is as follows:

- First a set of values for the plasma parameter is introduced and using the above defined set of equations the radiance of a defined spectral region is calculated. The reason for calculating separately the different spectral regions is due to the fact that each of them was recorded with different wavelength calibration, so the wavelength step was different.
- The second step was to convolve the calculated spectrum with a normalized Gaussian distribution with $FWHM_{\text{spect}} = 0.176\mathrm{nm}$.

Finally the convolved spectrum is compared to that obtained experimentally.

The following constraints are used during the calculation:

- The value for the line of sight ($l$) is obtained using the Anisimov model. Knowing the position of the plasma front at the time the spectrum was recorded, the dimension of the line crossing the plasma at the measuring position can be calculated.
- Although the atom number density has little effect in the calculation, which follows from the negligible effect of both resonance and van der Waals broadening in the lines profile, its value is obtained too (see procedure in [10]).
- The electron number density, which is assumed to be equal to the ion number density, is upper bounded by the ion number density extracted using Langmuir probe.

Figure 7 shows the result of such a calculation.

**Figure 7.** The figure shows a comparison of the recorded and calculated spectra of the transitions from triplet 4s4d $^3\mathrm{D}$ and triplet 4s5s $^3\mathrm{S}$. In the calculation both lower levels populations and upper level population of triplet 4s5s $^3\mathrm{S}$ were let to adjust to the best values.
The result of the calculation is in reasonable agreement with the recorded spectra. For all cases the relative lines intensities are well reproduced. The major discrepancies are in the line profiles with greater deviation for the transitions from the triplet $4s5s^3S$. Such a discrepancy can be explained if the accuracy of the broadening coefficients ($\sim 20\%$) is taken into account [11].

4. Conclusions
It was demonstrated that in order to extract proper plasma parameters using emission spectroscopy it is needed to select lines that are little or not affected by self-absorption. If this is not possible recorded spectra should be corrected taking into account such process. It was presented a simple calculus method that allows obtaining plasma parameters by comparing synthetic spectra and experimental measured ones.

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