

# Mechanisms and efficient elimination approaches of self-absorption in LIBS

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Received 25 August 2018, revised 11 December 2018

Accepted for publication 13 December 2018

Published 17 January 2019



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## Abstract

Laser-induced breakdown spectroscopy (LIBS) is a promising analytical spectroscopy technology based on spectroscopic analysis of the radiation emitted by laser-produced plasma. However, for quantitative analysis by LIBS, the so-called self-absorption effects on the spectral lines, which affect plasma characteristics, emission line shapes, calibration curves, etc, can no longer be neglected. Hence, understanding and determining the self-absorption effects are of utmost importance to LIBS research. The purpose of this review is to provide a global overview of self-absorption in LIBS on the issues of experimental observations and adverse effects, physical mechanisms, correction or elimination approaches, and utilizations in the past century. We believe that better understanding and effective solving the self-absorption effect will further enhance the development and maturity of LIBS.

Keywords: laser-induced breakdown spectroscopy (LIBS), self-absorption effect, optically thin, elemental analysis

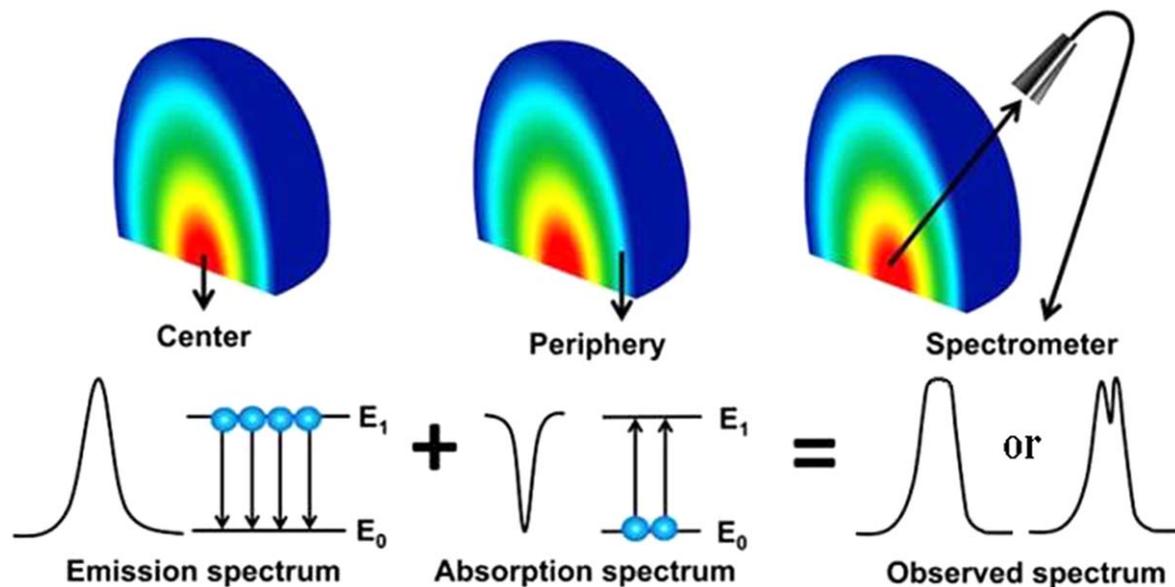
(Some figures may appear in colour only in the online journal)

## 1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a promising spectroscopic analytical technology for quantitative analysis based on atomic emission spectroscopy. It has experienced an increasing popularity in fields such as industrial processing, biomedical research, environmental monitoring, etc, due to its reliability, real time and *in situ*, non-contact optical nature, multi-elemental analysis in any phase and no or little sample preparation [1–9]. In LIBS, the determination of elemental compositions, relative abundance information, and plasma parameters is intrinsically depending on the optically thin

lines. Therefore, the self-absorption effect on emission spectrum, which distorts the spectral line profile, increases the linewidth and reduces the line intensity, need to be taken into account. Self-absorption occurs in any fundamental deduction of the theoretical relationship between the emission and the quantity density of emission/absorption species. This is the result of classical radiation theory. Absorption occurs when light propagates from any light source to the outside due to emission from the same atomic or molecular species in the transmission path. The emission measured outside the source is thus weakened. Fundamentally, only when the radiated light passes through the plasma and escapes without obvious attenuation or scattering, the plasma can be considered as optically thin. In optically thick plasma, the attenuation

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**Figure 1.** The self-absorption process in plasma. Reproduced with permission from [11], ©2015 Optical Society of America.

degree of each spectral line is different, and even the absorption of a single spectral line is a function of wavelength. In some cases, the absorption at the spectral line center may be stronger than those at the sides, that is, the line center is darker than the sides. This phenomenon called self-reversal is one of the extreme cases of self-absorption [10]. The self-absorption process in plasma, including self-absorption and self-reversal, can be illustrated by principle in figure 1 [11]. In fact, the complexity of the interaction between laser and matter, the inhomogeneity of plasma and the instantaneity of plasma evolution make self-absorption a very complicated phenomenon. Till now, reduction of spectral intensity caused by this effect in optical emission spectroscopy has been experimentally observed and studied by numerous papers in order to better interpret its basic physical mechanism and calibrate its adverse impact to improve the performance of LIBS for quantitative analysis.

This paper aims to briefly review the historical evolution of self-absorption in LIBS over the past century from four aspects: the observation and evaluation of self-absorption, the physical mechanisms, the correction or elimination approaches, and several utilizations with the benefit of self-absorption.

## 2. Experimental observations and adverse effects

As early as the 1930s, the phenomenon of self-absorption in the emission spectrum has been observed in experiments. Wood [12] repeatedly observed self-reversal of  $H_{\alpha}$  emission from a spectrum tube with moderate luminosity, and stated that the self-reversal occurred under physical conditions eliminates the difference between the absorption layer and the emission layer. Sibaiya *et al* [13] also encountered the self-absorbed spectral lines in the experiments, which vitiated the

hyperfine structure study. They preliminarily explained this phenomenon on the basis of the classical dispersion theory.

After the LIBS technique was born in the 1960s, the self-absorption phenomenon was also observed in laser-induced plasmas. Its adverse effects on plasma characteristics (such as plasma temperature, electron density, etc), line shape, calibration models, etc were reported as follows.

For plasma characteristics, Leis *et al* [14] found that the measured plasma temperature for steel samples increased due to the self-absorbed Fe I lines, while Surnick *et al* [15] revealed that the electron densities calculated by Stark widths and shifts of self-absorbed neutral aluminum lines and non-self-absorbed ionized nitrogen line were not consistent with that obtained in laser-induced aluminum plasmas. In addition, self-absorption can affect the spectral line shapes, causes them distortions and line-reversals [16–19].

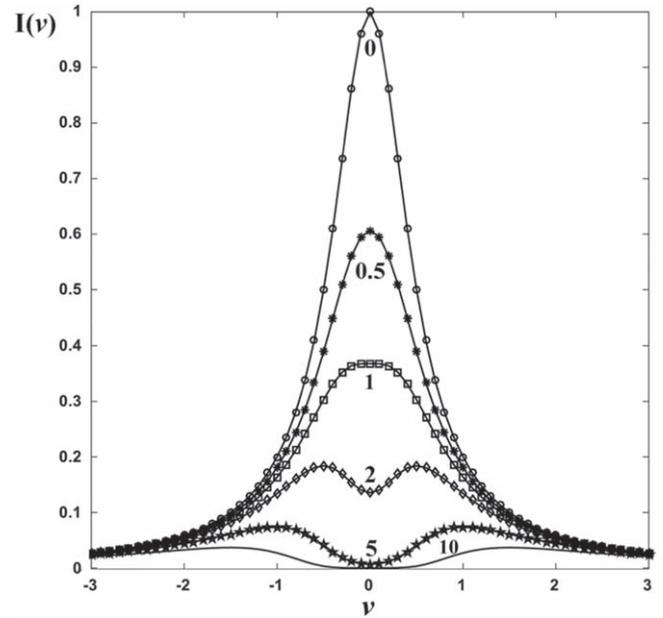
Calibration models usually include univariate and multivariate calibration strategies. For univariate calibration, Grant *et al* [20] found that the calibration curves for aluminum in iron ore were leveling at high aluminum concentrations because of the self-absorbed aluminum resonance line, and suggested that resonance lines are not recommended for quantitative analysis of principle elements because they are more prone to be self-absorbed. Sabsabi *et al* [21] found that the neutral resonance lines of copper at 327.4 nm and magnesium at 285.2 nm had self-absorption at higher concentrations, and suggested that the self-absorption could be reduced by using higher level transition lines or by using time-resolved measurements. Stonge *et al* [22] analyzed the sodium chloride solution using LIBS and concluded that the resonance line with severe self-absorption is very suitable for trace element detection, while the calibration curve by non-resonance line has a wider measurement range. For multivariate calibration, Wang *et al* [23] pointed out that the linear nature of partial least squares makes it unable to satisfactorily

model the nonlinear relationship between the intensity and the elemental concentration caused by self-absorption, and suggested to extract the dominant factor of self-absorption to minimize the prediction errors. Zaytsev *et al* [24] used a multivariate calibration based on principal component regression for the determination of Ni, Cr, Mn, and Si in high-alloyed stainless steels, and experimental results demonstrated that the calibration model containing self-absorbed lines was unstable. Yao *et al* [25] evaluated the self-absorption effect on the multivariate calibration performance, and concluded that self-absorption could significantly reduce the linear regression coefficient of calibration, the quantification sensitivity, as well as the measurement repeatability.

The self-absorption also affects the feasibility of analytical methods in LIBS and consequently reduces the measurement accuracy. The followings are concentrated on discussing the influences of self-absorption on four well-known methods, including the calibration-free LIBS (CF-LIBS), the one-point-calibration, the Csigma method and the CF Inverse. CF-LIBS requires spectral line not to be affected by self-absorption so as to achieve accurate quantitative analysis. However, the plasma radiation is usually affected by self-absorption, and it is critical to select useful emission lines without strong self-absorption. For instance, the Ca II 318.128 nm line was selected for quantitative purpose in steel slag because it has the least self-absorption and the highest upper energy level in all singly ionized calcium lines [26]. The one-point-calibration well reproduces the composition of the analyzed samples, and efficiently compensates for the effect of self-absorption in spite of the element concentration varies substantially [27]. The Csigma method can naturally deal with the moderate self-absorption effect by calculating the optical thickness and the Lorentzian width of the lines. However, since the strongly self-absorbed lines fall beyond the limits of the theoretical model of Csigma method, they should be excluded in the building of the Csigma curve [28, 29]. The CF Inverse cannot work properly when the curves in the Boltzmann plot exhibit strongly non-linear due to the existence of self-absorbed lines. Only after self-absorption correction of the experimental data or removal of the self-absorbed lines from the Boltzmann plot can it work better [27].

### 3. Physical mechanisms

In early studies, scholars interested in the intensities of spectral lines usually selected appropriate experimental conditions to eliminate the self-absorption effects, without having to study the theoretical side of self-absorption in detail. Since the mid-20th century, people have come to realize the importance of studying the physical mechanism of self-absorption. A great deal of detailed research has been undertaken into this topic and achieved a number of significant progresses involved the aspects of theoretical analysis, experimental analysis and environmental impact factors.



**Figure 2.** Line shapes with different degrees of self-absorption represented by the absorption parameter  $p$ .

#### 3.1. Theoretical analysis

Before the emergence of LIBS, Cowan *et al* [10] already carried out a comprehensive study on the self-absorption mechanism and evaluated its effects on the line intensities and line profiles of arcs and sparks. It turned out that the proposed model was sufficient to illustrate the facts encountered in these cases. From the radiation transmission of source and considering the absorption, the radiation intensity at  $r$  can be expressed as:

$$I(v, r) = I_0 P_a(v, r_0) \times \exp \left[ (-h\nu_0 B'/c) \int_{r_0}^r n_a(x) P_a(v, x) dx \right], \quad (1)$$

where  $I_0 P_a(v, r_0)$  is the intensity distribution without absorption,  $r_0$  is the position of the atom which is the source of the energy,  $h$  is the Planck constant,  $B'$  is the total transition probability between all states,  $c$  is the speed of light,  $\nu_0$  is the frequency, and  $n_a(x)$  is the number density of atoms able to absorb the incident radiation. Then, with the introduction of a quantity:

$$p = (h\nu_0 B/c) P_a(\nu_0) \int n_a(x) dx, \quad (2)$$

Equation (1) reduces to:

$$I(v) = I_0 P_a(v) \times \exp \left[ -p \frac{P_a(v)}{P_a(\nu_0)} \right]. \quad (3)$$

Figure 2 presents the reduction amount for various  $p$  values indicated by each trace. For  $p > 1$ , the dip in the center indicates self-reversal. And for  $p = 1$ , the intensity at the

center of the line decreases to  $e^{-1}$ . The shape shown for  $p = 0.5$  has a 40% reduction of intensity in the center and could hardly be distinguished from a non-self-absorbed line ( $p = 0$ ) without precise measurements. Moreover, Cowan *et al* [10] gave a detailed discussion on self-absorption from the point of view of mechanical wave, including the general case of self-absorption, various broadening mechanisms, and the influence of self-absorption on calibration curves for quantitative analysis.

In the decades after the advent of LIBS, a lot of research work has been reported on the theoretical analysis of self-absorption existed in laser-induced plasmas. For the ultraviolet laser-induced plasma in the early phase, Hermann *et al* [30] presented a non-uniform plasma model by considering the self-absorbed spectral lines, which is divided into two homogeneous regions with different electron densities and plasma temperatures. Based on the radiation transfer equation, the radiation  $B$  that emitted by a uniform plasma satisfying the local thermodynamic equilibrium (LTE) condition can be deduced as:

$$B(\lambda, kT_e) = U(\lambda, kT_e)(1 - e^{-\alpha(\lambda, kT_e)L}), \quad (4)$$

where  $U$  is the radiation of blackbody,  $\lambda$  is the irradiation wavelength,  $k$  is the Boltzmann constant,  $L$  is the diameter of plasma observed, and  $\alpha$  is the spectral absorption coefficient given by [31]:

$$\alpha(\lambda) = \pi r_0^2 \chi^2 f_u n_1 P(\lambda_0, \lambda) \times \left[ 1 - \exp\left(-\frac{hc}{\lambda kT_e}\right) \right], \quad (5)$$

where  $r_0$  is the conventional electron radius,  $f_u$  is the absorption oscillator strength,  $n_1$  is the lower energy population density, and  $P(\lambda_0, \lambda)$  is the normalized line profile. For laser-induced high density plasma, the line profile can be approximated to the classical Lorentz shape due to the strong Stark broadening mechanism. Thus, the self-absorbed radiations emitted by a uniform plasma can be judged by the flatness of the line center, of which the radiation is that of a blackbody. This shows that the plasma emission can be combined with blackbody radiation to evaluate the self-absorption level. Hermann *et al* [32] then observed the saturation of the strongest emission lines at the blackbody radiance in time-resolved spectroscopic measurements of the plasma, which was in agreement with the model of a uniform plasma in LTE. Thus the self-absorption degree can be evaluated by adjusting the measured spectrum to the computed radiance.

Su *et al* [33] proposed a simplified radiative hydrodynamic model derived from the basic radiative transfer equation and the conventional fluid dynamic equations. Combining with the steady-state collisional-radiative model, they investigated the dynamic evolution of plasma and spectral radiation characteristics, and successfully simulated the self-absorption properties of spectra of highly ionized tin ions.

Hydrogen lines play a great role in LIBS analysis and have been commonly employed to explore the physical

mechanism of self-absorption. For the population inversions theory, Tallents [34] investigated the Lyman-alpha self-absorption effect in recombining plasmas under quasi-steady state conditions of hydrogen-like ions between the second and the third quantum states. In order to quantify the effect of self-absorbed resonance radiation on population inversion, he extended the conventional treatment of inversions between excited states of hydrogen-like ions including Lyman-alpha self-absorption under optically thin conditions. It was shown that the electron density range of population inversion decreased with the increase of Lyman-alpha self-absorption. Sherbini *et al* [35] demonstrated that the  $H_\alpha$  line was an ideal optically thin independent spectral line with high signal-to-noise ratio and can last for a long time after the laser pulse stops. They also employed the diode laser atomic absorption spectrometry to measure the optical depths of plasmas that correspond to the wavelength of  $H_\alpha$  line under various experimental parameters [36]. Here, the inherent effective absorption coefficient is expressed as:

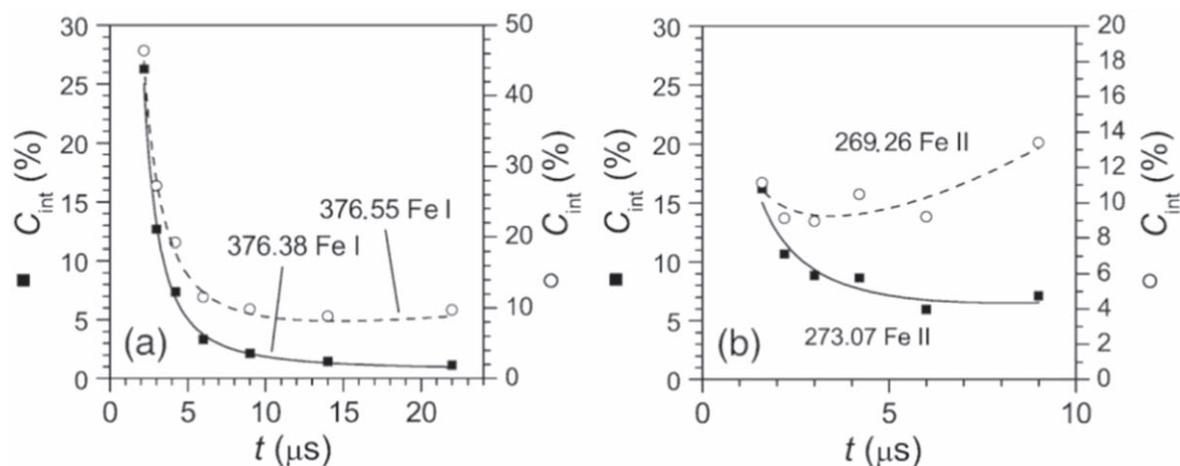
$$k^{\text{ff}}(\text{m}^{-1}) = 3.45 \times 10^{-57} \left( \frac{n_e n_z}{\text{m}^{-3} \text{m}^{-3}} \right) z^2 \times \left( \frac{\lambda}{\text{nm}} \right)^3 \left( \frac{E_R}{k_B T_e} \right) \xi^{\text{ff}}(z, T_e, \lambda), \quad (6)$$

where  $E_R = 13.6$  eV,  $n_e$  and  $n_z$  are, respectively, the electron density and the species density in  $Z$  ionic state, and the Biberman factor  $\xi^{\text{ff}} \sim 1$  at  $k_B T \sim 1$  eV and  $\lambda = 656.36$  nm. The absorption coefficients measured at the initial stage of plasma formation turned out to be consistent with those calculated by the inverse bremsstrahlung theory at the plasma electron density.

### 3.2. Experimental analysis

For better understanding of the changes of self-absorption in laser-induced plasma, several experimental studies emphasized on temporal and spatial distribution and evolution have been carried out. Aguilera *et al* [37] experimentally investigated the change of spectral self-absorption degree in plasma evolution over time. The temporal evolution of the intensity within the optically thin limit and the self-absorbed lines were measured, and the behavior discrepancies between neutral atomic and ionic lines were explained. Although the intensities of neutral atomic lines decreased at the later stage of the plasma evolution, the self-absorption increased strongly. In contrast, the intensities of ionic lines decayed rapidly, but its self-absorption exhibited a relatively small temporal variation. They recommended that the concentration of the intersection of the high and low optical depth asymptotes of the curve-of-growth (COG) can be used to characterize the self-absorption. Figure 3 shows the typical curves of the temporal intersecting concentration for atomic and ionic lines.

Yi *et al* [38] employed the spatially resolved LIBS to reveal the influencing factors of the self-absorption effect by plotting the two-dimensional distributions of intensities and



**Figure 3.** Temporal evolution of the intersecting concentration that characterizes self-absorption for atomic (a) and ionic emission lines (b). Reprinted from [37], Copyright (2008), with permission from Elsevier.

self-absorption coefficients (figure 4) of spectral lines in soil plasmas. Experimental results suggested that the self-absorption effect can be greatly minimized by choosing appropriate collecting regions of the plasmas or by using high energy laser and short delay time to expand the region less affected by self-absorption.

### 3.3. Environmental impact factors

Identification and assessment of environmental impact factors of self-absorption are beneficial to better understand its physical mechanisms and the interactions with environment. Gudimenko *et al* [39] studied the effects of self-absorption on Ar I lines in a reactive ion etching plasma reactor with a series of parameters (laser power, ambient pressure, gas flow rate, etc), and the observed results were in reasonable agreement with the theoretical calculated line ratios. Tang *et al* [40] studied the relationship between self-absorption and the physical conditions involved in energy levels and sample matrix. After the calculation based upon the oscillator strength, the transition probabilities and the Boltzmann equation, they believed that the self-absorption is proportional to the transition probability, elemental concentration, degeneracy of upper level, and wavelength, and is inversely proportional to the lower energy level.

## 4. Correction or elimination approaches

Self-absorption, which is closely tied to the population of lower levels, affects not only the observed intensity of emission line, but also the key assumptions in LIBS, and these in turn, influence the plasma characteristic parameters determination and the quantitative analysis results. In order to weaken even eliminate this undesired effect, novel methods and techniques for self-absorption correction or elimination have become the main direction of many studies, such as the COG method, the self-absorption coefficient method, the

optically thin technique, etc. In the following sections, we will give an overview of these methods and techniques with references to more detailed descriptions.

### 4.1. Curve-of-growth

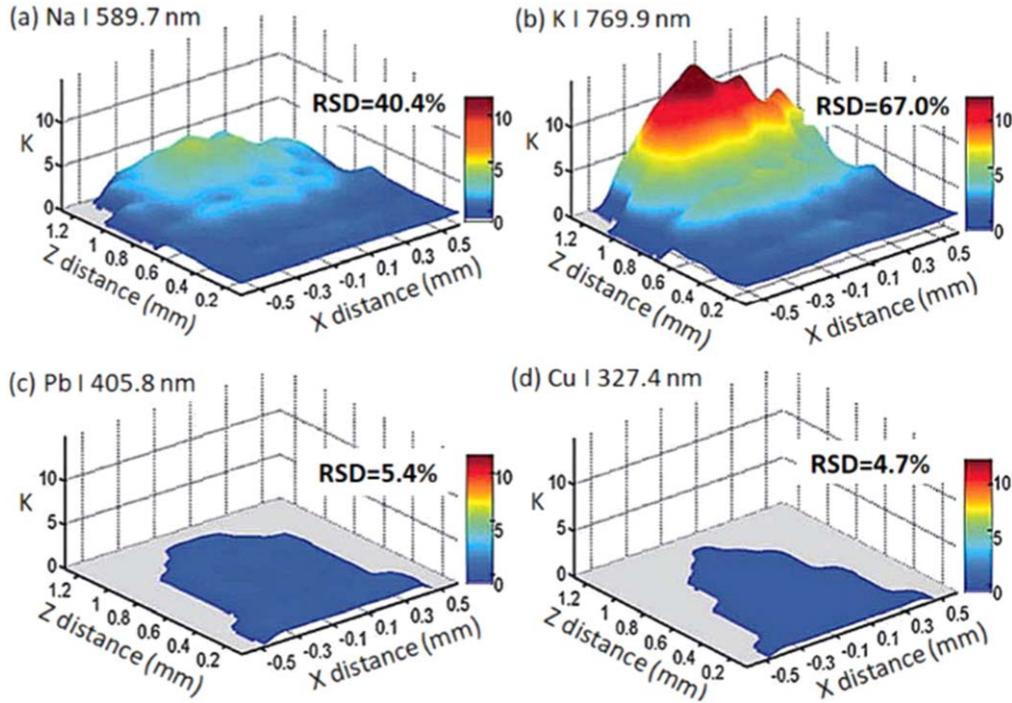
The calibration function characteristics of laser-induced plasma emission spectroscopy generally cover the whole spectrochemical range from optically thin to optically thick behavior. For strong resonance lines, small nonlinearity is usually observed when the element concentration in solid sample is in the order of 0.1%–1%. The application of well-known emission spectroscopy model using the COG concept is almost impossible to be more complex than it is for these plasmas. Although the theory and experiments are complex, it seems useful to study the basic properties of the analytical calibration functions in laser-induced plasmas from the perspective of COG concept for improving the performance of LIBS spectrochemical analysis. In any case, such model can at least be used to determine the limits of linearity and to select the optimal transition lines for quantitative chemical analysis. Gornushkin *et al* [41] carried out the first application of the COG methodology to LIBS measurements, and found that the inflection point between the optically thin and optically thick plasma in the logarithmic–logarithmic calibration curve corresponds to about 0.1% Cr concentration. Next, we will give a brief introduction of the principle of COG.

The COG function can be written as:

$$I = f(n_0), \quad (7)$$

where  $I$  is the integrated intensity of analytical line, and  $n_0$  is the atomic population density of ground state associated with the element content in the sample. The spectral line intensity is expressed by classical theory as follows:

$$I = \alpha' \frac{8\pi hc^2 n_j g_i}{\lambda^3 n_i g_j} \int (1 - e^{-k(\lambda)l}) d\lambda, \quad (8)$$



**Figure 4.** Self-absorption coefficient distributions of spectral lines of Na (a), K (b), Pb (c), and Cu (d) in soil plasmas. Reproduced from [38] with permission of The Royal Society of Chemistry.

where  $\alpha'$  is a constant depending on the parameters of the experimental system,  $n$  is the number density of species,  $g$  is the degeneracy,  $k(\lambda)$  is the absorption coefficient related to wavelength, and  $l$  is the whole length of the absorption path over which the light travels. The optical depth  $k(\lambda)l$  reflects the self-absorption degree of the spectral line, in which the wavelength-dependent absorption coefficient  $k(\lambda)$  can be expressed as:

$$k(\lambda) = \pi \frac{e^2}{mc^2} n_i f \lambda_0^2 L(\lambda), \quad (9)$$

where  $e$  is the electron charge,  $m$  is the electron mass,  $f$  is the transition oscillator strength, and  $L(\lambda)$  is a function of the peak normalized line profile.

The calibration function is directly related to the theoretical COG if the atomic number density in the plasma is assumed to be linear with the corresponding element content in the sample. Other fundamental plasma characteristics such as the plasma temperature and collisional cross-section, the atomic density of ground state can also be obtained from the curves of growth. The theoretical COG correlates the spectral intensity with the optical depth and can well describe the line intensity saturation caused by self-absorption. Power-law calibration curve based on the COG theory can represent the boundary between power-law and linear domains in quantitative LIBS analysis, and has a square-root dependence at high concentrations [42].

Here are some examples of application of the COG methodology to LIBS measurements. Aguilera *et al* [43] employed COG to study the spatial inhomogeneity and

temporal evolution of plasmas, and the self-absorption processes with different degrees causing the COGs saturation have been eliminated at the different plasma domains. Taking advantages of COG, a modified Boltzmann plot method, which was constructed by using the slopes of the low-concentration limits of the COGs, was proposed by Aragon *et al* [44] to perform plasma apparent temperature measurement without systematic error attributed to self-absorption. Alfarraj *et al* [45] also employed COG to estimate the self-absorption degrees and the optical depths of strontium and aluminum lines in LIBS spectra under different experimental conditions.

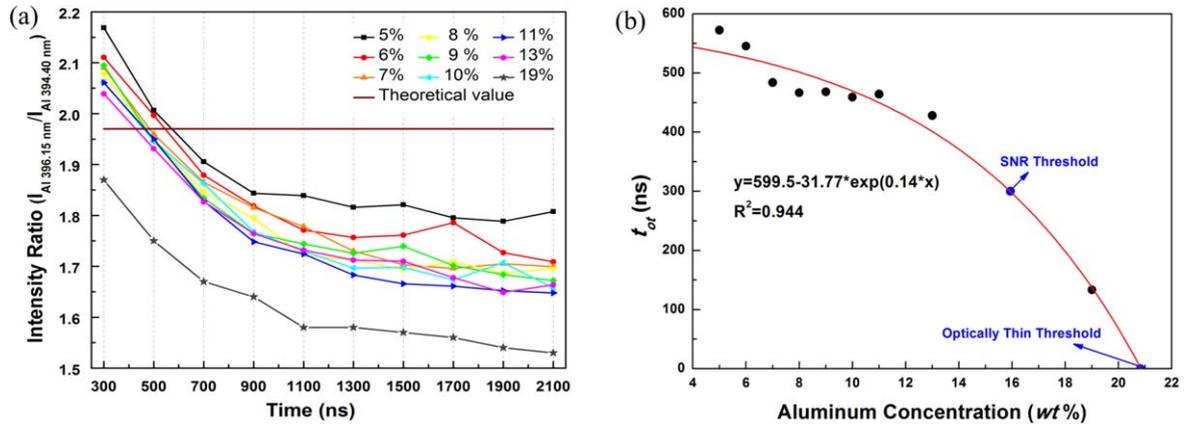
#### 4.2. Self-absorption coefficient

The self-absorption coefficient can indicate the self-absorption degree of laser-produced plasma, and has been widely used to correct either the intensities or the widths of spectral lines. It can be obtained by dividing the measured peak intensity by the expected peak intensity without self-absorption [46, 47]:

$$SA = \frac{I(\lambda_0)}{I_0(\lambda_0)} = \frac{1 - e^{-k(\lambda_0)l}}{k(\lambda_0)l} = \Delta\lambda_0 \frac{(1 - e^{-K/\Delta\lambda_0})}{K}, \quad (10)$$

where  $I$  is the peak intensity,  $\Delta\lambda_0$  is the expected FWHM of the emission line in an optically thin plasma, and

$$K = 2 \frac{e^2}{mc^2} n_i f \lambda_0^2 l. \quad (11)$$



**Figure 5.** Temporal evolution of the intensity ratio of doublet atomic aluminum lines (a) and  $t_{ot}$  at various aluminum concentrations (b). Reproduced with permission from [63], © 2017 Optical Society of America.

The self-absorption coefficient can also be written as:

$$SA = \left( \frac{\Delta\lambda_0}{\Delta\lambda} \right)^\alpha = \left( \frac{\Delta\lambda}{2w_s} \frac{1}{n_e} \right)^{1/\alpha}, \quad (12)$$

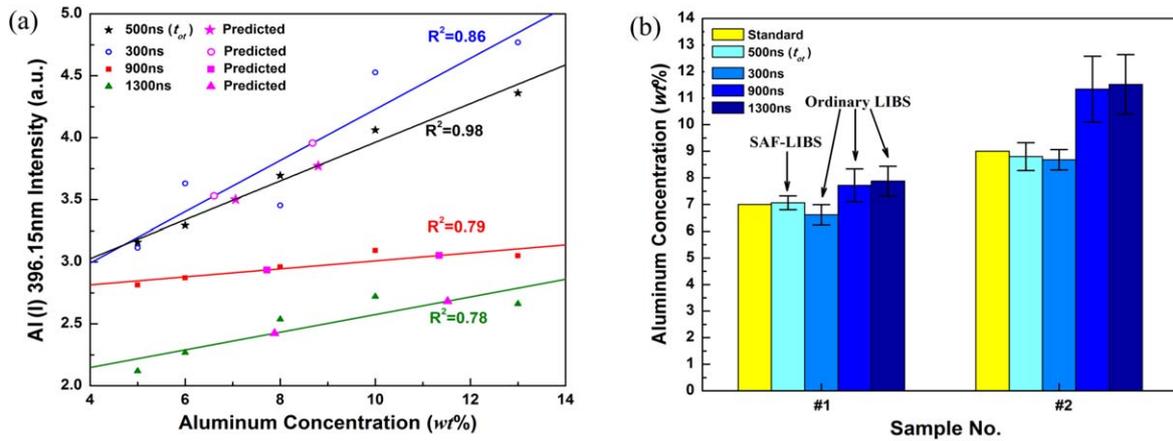
where  $\alpha = -0.54$ ,  $\Delta\lambda$  is the measured FWHM of the line,  $w_s$  is the FWHM Stark width of the line,  $n_e$  is the electron density obtained from the Stark width of  $H_\alpha$  line. The equation derived from the homogeneous plasma model is suitable for the case where the electron density of plasma is known, especially for lines with available Stark broadening parameters. Since this method requires only the electron density and line width that are easily measured experimentally, it seems preferable to others which have to estimate the indirectly measurable parameters such as optical path or atomic number density. Mansour [48] investigated the influences of self-absorption effect on the prediction of electron temperatures. The self-absorption effects on aluminum lines were quantified and corrected through the ratio of the electron density deduced by the analytical lines to that by the optically thin  $H_\alpha$  line. By comparing the deduced electron temperatures from aluminum lines before and after self-absorption correction, it was found that the precision of temperature measurement has been significantly improved.

However, the above method is limited to cases with known electron density and available Stark coefficients, and there is still a great need to put forward more universal approaches. Thus, Bredice *et al* [49] developed an experimental procedure that can evaluate the self-absorption coefficients even if the Stark coefficients are not available. Four years later, they presented another calculation procedure of self-absorption coefficient that merely requires line intensities [50]. Because the procedure mainly involves the measurement of line intensities, it can be used in low spectral resolution experiments and is especially suitable for developing low-cost LIBS instruments. In addition, Pace *et al* [51] proposed another method for obtaining the self-absorption coefficient. This method calculates the optical thickness of spectral lines by deducing the radiative transfer function in homogeneous plasma. Using this method, the self-absorption of magnesium

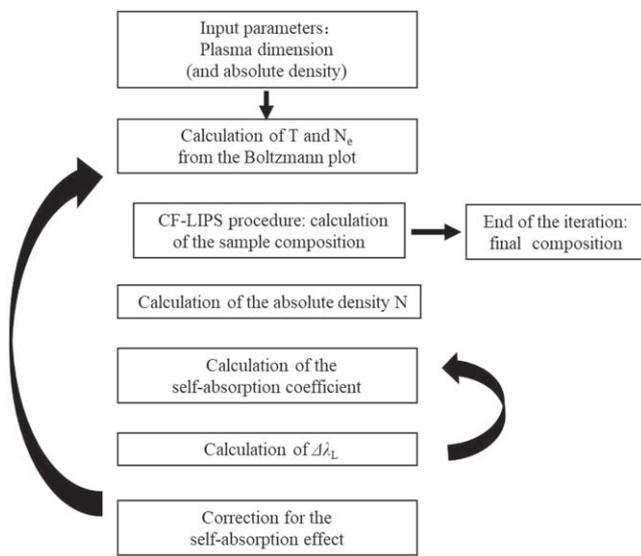
lines induced by various pulse energies on calcium hydroxide substrates was studied and corrected [52].

Another self-absorption coefficient correction method is the well-selected internal reference for self-absorption correction (IRSAC), of which the specific implementation steps can be summarized as: firstly, select an internal reference line for each species, and then estimate the self-absorption degree by comparing other line intensity of the same species with that of the reference line, and finally employ the regression algorithm to complete the optimal correction. Here, because the upper level of the reference line has a high excitation energy, the self-absorption effect is slight and almost negligible. Sun *et al* [53] employed IRSAC to make correction of the self-absorption effect in CF-LIBS, and found that the linearity of all points on the Boltzmann plot was enhanced and the accuracy of the quantitative analysis results was improved. Ramezani *et al* [54] applied IRSAC to predict the surface hardness of ternary metallic alloys, and the correlation coefficient between the intensity ratios of ionic and atomic chromium lines and the surface hardness of alloys significantly increased from 47% to 90%. Borges *et al* [55] performed analysis of frozen aqueous solution samples by using the IRSAC method, and the relative deviation was reduced to be within 3.3%. Shakeel *et al* [56] applied this method to CF-LIBS to analyze the Al-Si alloy, and the reported quantitative analysis results before and after self-absorption correction were 0.6%–6.7% to 0.3%–2.2% deviation from the reference data.

The traditional application of Beer–Lambert law in self-absorption coefficient calculation only considers one-dimensional absorption. However, it tends to be inaccurate for significant absorption effect. Hsu *et al* [57] proposed a modified Beer–Lambert law to correct the raw experimental line intensities so as to perform quantitative LIBS measurement of potassium and sodium that released from lignite and pinewood particles during combustion. As a result, linear responses with respect to alkalis for two modified calibration curves have been obtained.



**Figure 6.** Calibration curves of aluminum at various delay times (a) and comparison on measurement accuracy between SAF-LIBS and traditional LIBS (b). Reproduced with permission from [63], © 2017 Optical Society of America.



**Figure 7.** Flow diagram of the recursive model for self-absorption correction. Reprinted from [71], Copyright (2002), with permission from Elsevier.

### 4.3. Optically thin

For optically thin laser-induced plasma, its emitted radiation can traverse and escape without significant absorption or scattering, also the self-absorption effect can be reasonably ignored. In early studies [58–61], the integrated intensity ratio of the spectral lines of the same element with similar upper energy levels was used as an indicator of the self-absorption degree. The greater the measured intensity ratio deviates from its theoretical value, the more obvious the self-absorption is.

Based on the above methodology, a self-absorption-free LIBS (SAF-LIBS) technique, which is able to collect the optically thin spectrum directly by matching the experimental diatomic line intensity ratios with the theoretical value, was proposed by Hou *et al* [62, 63]. Because the selected doublet lines have close wavelengths and similar energy level configurations, there is a time period in which both lines exhibit

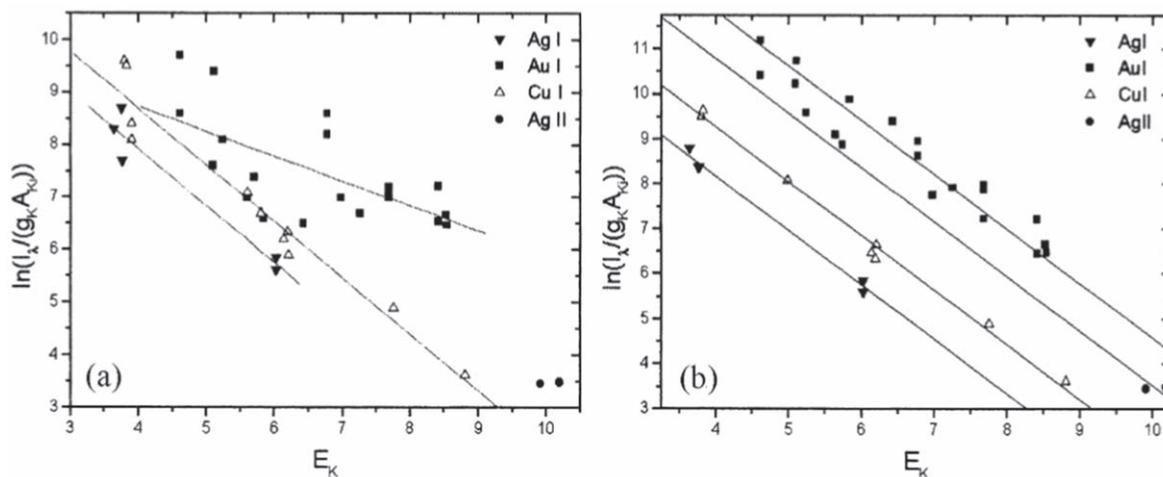
approximate optically thin features. By matching the measured ratios with the theoretical one at various delay times, the exact time period (with delay time of  $t_{ot}$ ) can be found to make the spectral line of plasma as close as possible to the optical thin condition. LIBS is converted to SAF-LIBS as long as the integration and delay time of spectrum acquisition are set to this time period. By comparing the correlation coefficients of Boltzmann curves obtained by this technique with those obtained by traditional self-absorption correction methods, the optical thin condition was verified and the self-absorption coefficients were evaluated. Compared with traditional LIBS, the SAF-LIBS technique not only improves the linear correlation coefficient of calibration curve, but also reduces the error of quantitative analysis, so it can be competent for realization of accurate spectrochemical measurements. Figure 5 presents the temporal evolution curves of the doublet intensity ratio and the optimal delay time values at various aluminum concentrations, while figure 6 shows the calibration curves of Al at various delay times and a comparison on the measurement accuracy between SAF-LIBS and traditional LIBS.

### 4.4. Spectral fitting and plasma modeling

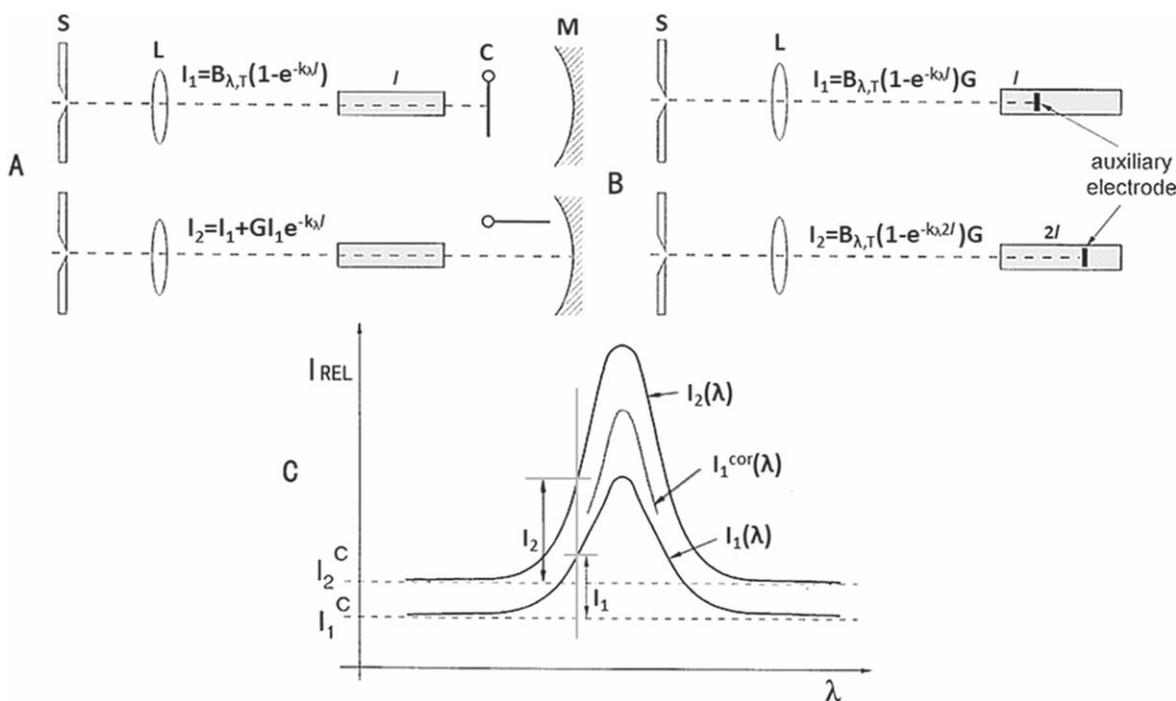
The fitting of spectral lines or modeling of plasma evolution and emission process is also useful tool for self-absorption correction. For the former, the most frequently used nonlinear curve fitting function is [64]:

$$y = a + bc(1 - e^{-x/c}), \quad (13)$$

where  $x$  is the concentration ratio, and  $y$  is the line intensity. This formula can depict the saturation trend of calibration curves vividly. Another fitting method to evaluate self-absorption is to fit the line profiles [65]. It depends on the parameter fitting of the measured self-reversed line profiles to the calculation model of one-dimensional radiative transfer. Note that the self-reversed structure depth is particularly sensitive to the location-dependent populations of upper and lower levels, so it can be used to accurately determine the



**Figure 8.** Boltzmann plots for precious alloy Au917 without (a) and with self-absorption corrections (b). Reprinted from [71], Copyright (2002), with permission from Elsevier.



**Figure 9.** The self-absorption determination set-up based on the doubling mirror technique (A), double the plasma length by the movement of an auxiliary electrode within the discharge process (B) and the recorded line profiles with single and double plasma length (C). Reprinted from [19], Copyright (1999), with permission from Elsevier.

spatial distribution of laser-ablated species in each state. Amamou *et al* [66] proposed another method to obtain the transition probability ratios of homogeneous plasma accords with the LTE condition. The self-absorption was calculated by fitting line profiles with the Simplex algorithm, and the expressions of correcting factors of height, width and surface of spectral lines were then derived.

In addition to the fitting method, various theoretical models have been proposed to minimize the self-absorption effect in spectrochemical LIBS analysis. Gornushkin *et al* [67] established a theoretical model for optically thick and

inhomogeneous plasmas to determine the degrees of self-absorption or self-reversal of emission lines. Considering the reabsorption process, the continuum radiation and the self-absorption coefficient, the model simulates the temporal evolution of continuum and atomic lines of plasma after laser pulse disappears. Aragon *et al* [68] constructed a matrix free self-absorption model for homogeneous plasmas. The model allows prediction of the COGs for given emission lines, beginning with their energy level transition parameters, plasma temperatures and damping constants. Lazic *et al* [69] proposed a model considering the nonlinear relationship

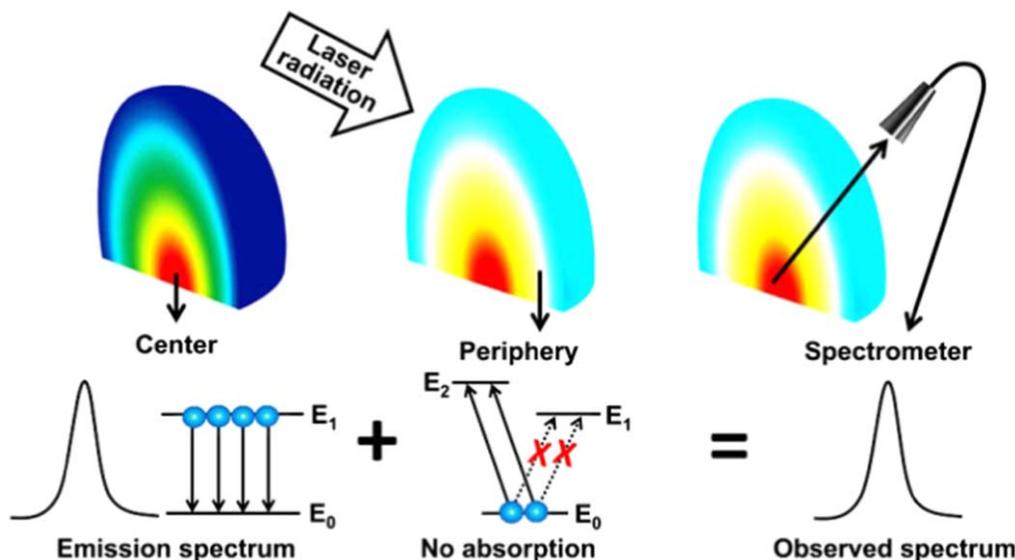


Figure 10. Principle of LSA in a plasma. Reproduced with permission from [11], © 2015 Optical Society of America.

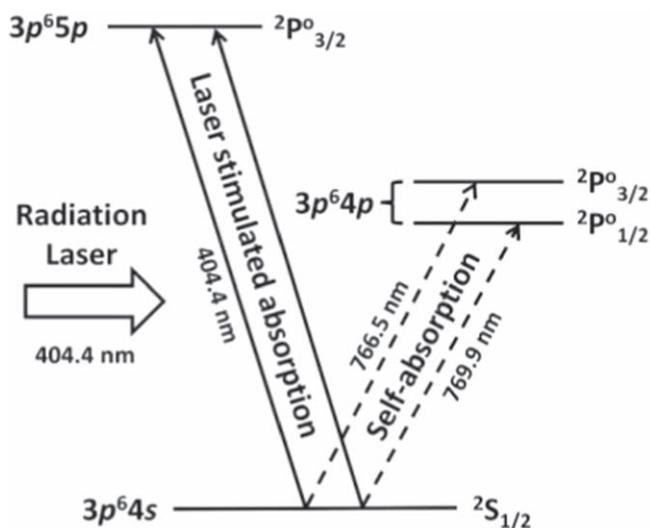


Figure 11. Mechanism of LSA for potassium atoms. Reproduced with permission from [11], © 2015 Optical Society of America.

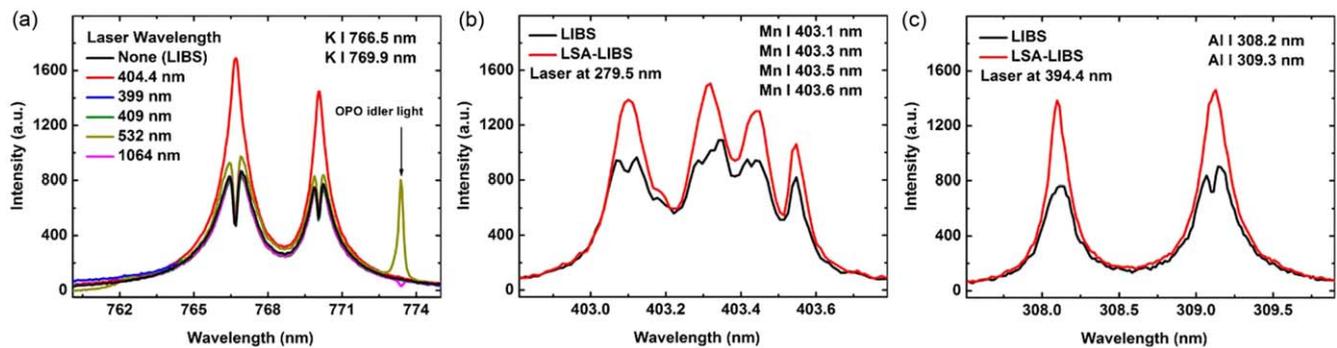
between line intensities and element concentrations. The model takes into account the reabsorption process and the contribution from the spatial regions with different electron densities. The feasibility was verified by analyzing the samples in the range of 15%–40% and calculating the measurement uncertainty. Amamou *et al* [70] established a model of plasma consisted of a hot core and a cold outer layer taking into account the spatial distribution to fit the emission lines of severe deformation due to the self-absorption. The model was applied to aluminum resonance doublet lines at 394.40 nm and 396.15 nm, and the measured ratio of energy level transition probabilities of the two lines was close to the theoretical one. Bulajic *et al* [71] proposed a model of self-absorption with the aim of automatically correcting the self-absorbed lines in CF-LIBS. The flow diagram of the model is presented in figure 7. For validation purpose, three steel samples and three ternary alloys were used to test the model.

The Boltzmann plots for precious alloy with and without self-absorption correction are presented in figure 8. Quantitative results showed that, the precision has been improved by approximately one order of magnitude.

The self-absorption can also be effectively eliminated by utilizing some data processing algorithms. Rezaei *et al* [72] compared the influence of self-absorption correction on LIBS measurement results based on calibration curve and artificial neural network (ANN). Results illustrated that after self-absorption correction, ANN demonstrated a more accurate prediction with a smaller relative error compared to the calibration curve, except for silicon. Dong *et al* [73] utilized the genetic algorithm (GA) to compensate for the effect of self-absorption in CF-LIBS measurements. The superiority of the GA based CF-LIBS method was verified by comparing it with the conventional CF-LIBS method for quantitative analysis of copper alloy. Yang *et al* [74] introduced the particle swarm optimization algorithm into CF-LIBS analysis to minimize the self-absorption effect on analytical lines of various species. Experimental results demonstrated a great improvement in quantitative analysis ability of CF-LIBS, and it processes a broad prospect in industrial on-line measurement.

#### 4.5. Doubling mirror

The doubling mirror technique can be used to check and correct self-absorption by doubling the length of optical path through a concave mirror placed at the double focal length position behind the plasma (see figure 9(A)). Except for transmission loss and reflection, if the signal intensity is also doubled, there is no self-absorption [75]. After then, a modified doubling mirror technique by use of axial uniform pulsed sources has been proposed [76, 77]. An auxiliary movable electrode was introduced between the traditional linear pulsed electrodes (see figure 9(B)). By changing its position, the plasma length could be changed without changing the plasma impedance. By controlling the switch of



**Figure 12.** Comparisons of LIBS and LSA-LIBS emission lines for K (a), Mn (b) and Al (c). Reproduced with permission from [11], © 2015 Optical Society of America.

optical shutter, the recorded profiles of the two lines (see figure 9(C)) can be used for determination of the correction factor  $K_\lambda$ .

This doubling mirror technique has already been introduced into LIBS for self-absorption investigation and correction. Moon *et al* [78] illustrated the application of this technique to characterize the self-absorption degrees of neutral atomic transitions. The technique provides a tool for quick and convenient determination of the optically thin plasma conditions, and improves the linearity of calibration curves and identifies abnormal points in the Saha–Boltzmann plot in temperature measurement. Burger *et al* [79] presented an analytic expression for self-absorption correction of the spectra recorded by the doubling mirror technique. Denote the spectra recorded with and without back mirror as  $F_2$  and  $F_1$ , respectively, and then the corrected spectrum, free of self-absorption, can be expressed as:

$$F_0 = \frac{2F_1}{1 + (F_2 - F_1)/GF_1}, \quad (14)$$

where  $G < 1$  represents the reflectivity of the light, taking in consideration transmittance of the lens, reflectivity of the concave mirror, solid angle of collection, etc.

#### 4.6. Escape factor

The escape factor, which was firstly brought by Irons [80, 81] and Drawin [82], quantifies the amount of radiation emitted from the radiation source and can be used to determine the degree of self-absorption.

Generally, the escape factor can be used to establish the model of radiative transfer of spectral lines by two similar senses. In the first sense, the product of escape factor and the desired spectra of optically thin plasma allows the opacity effect on the spectral lines. In the second sense, the product of escape factor and the energy level transition probability allows the photo-excitation effect on population densities. Hannachi *et al* [83] studied the influences of the self-absorbed oxygen lines on the temperature measurement of laser-induced  $\text{CaCl}_2$ –water plasmas. To take into account the self-absorption effect, the escape factor of the atomic oxygen emission line at 777 nm was computed and the temperature

profile was re-evaluated with the corrected oxygen line intensity. For quantitative analysis, the authors used the escape factor to enhance the linearity of calibration curves by simply multiplying the measured sodium line [84]. Habib *et al* [85] employed the escape factor to predict the self-absorption degrees of the low-level metastable states of atomic nitrogen in  $\text{SF}_6$ – $\text{N}_2$  mixture and pure nitrogen plasmas. The relationship between the resonance escape factors of continuum as well as radiative nitrogen emission lines was drawn graphically.

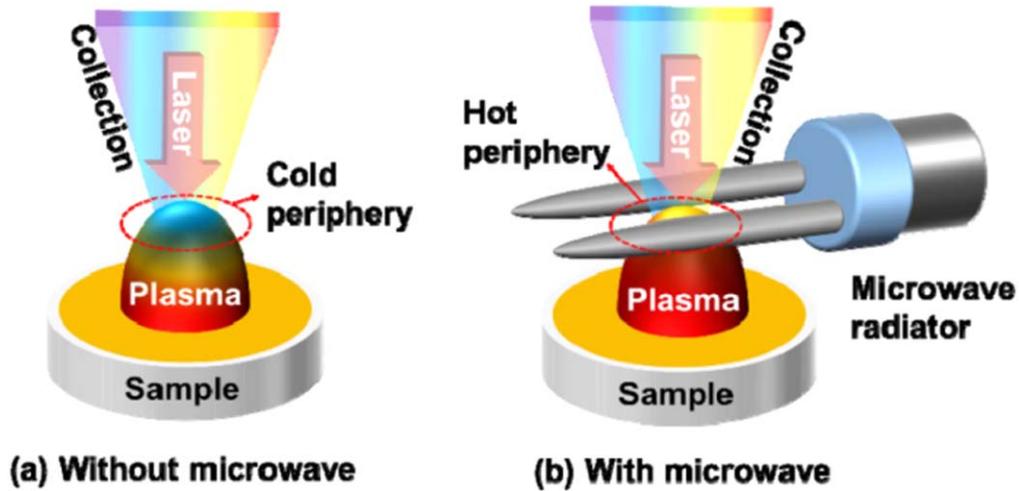
#### 4.7. Other approaches

In addition to the above mentioned methods and techniques, other approaches have also been recently developed to eliminate the self-absorption effect, such as atmospheric pressure control, laser-stimulated absorption (LSA), microwave-assisted excitation (MAE), etc.

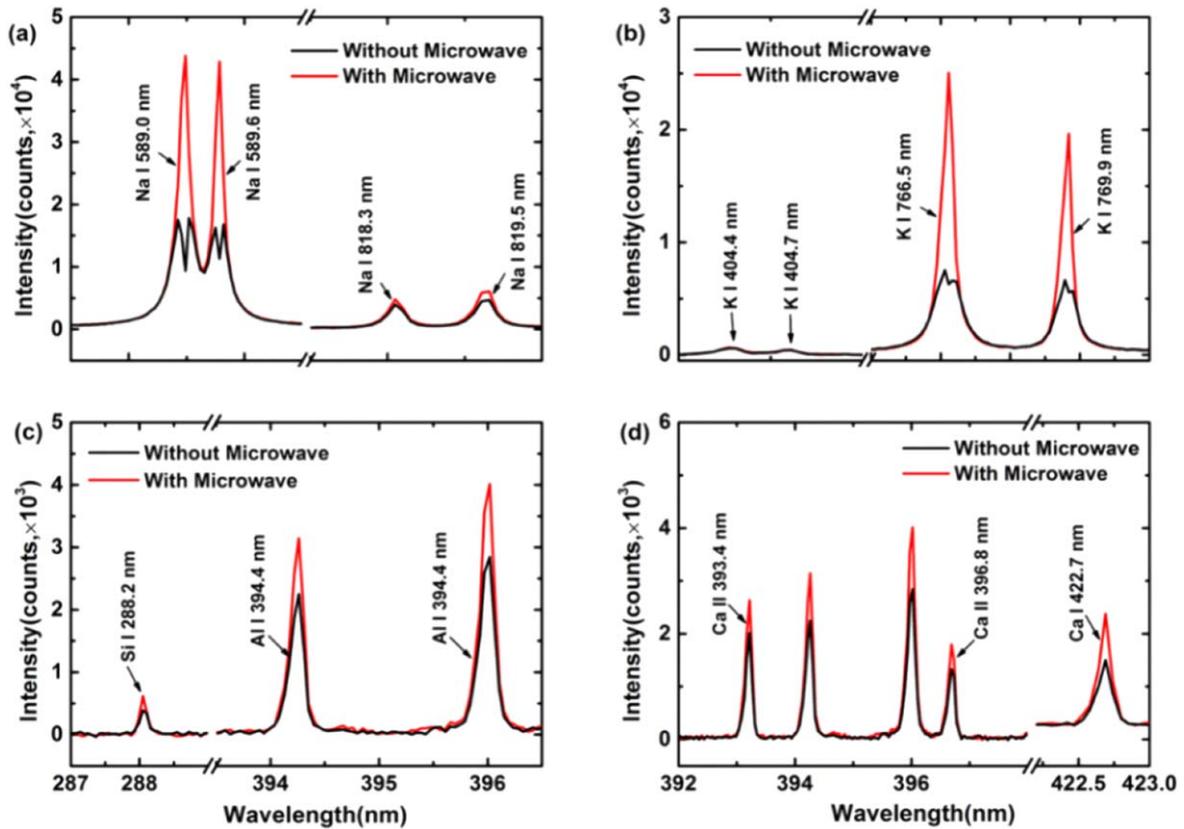
The atmospheric pressure control approach can make the plasma density become low and the self-absorption coefficient close to 1. Hornackova *et al* [86] applied it to zeolites analysis using CF-LIBS. They carried out the measurements at reduced pressure in vacuum chamber and the self-absorption effect on spectral lines was efficiently eliminated. Similarly, in the quantitative experiment performed on steel samples, Hao *et al* [87] found that the nonlinearity of multi-element calibration curves for magnesium and copper caused by the self-absorption effect could be greatly improved if the atmospheric pressure was reduced to 1 kPa.

The LSA assisted LIBS technique proposed by Li *et al* [11] provides another approach for minimizing the self-absorption effect. This technique requires a continuous wavelength tunable laser to re-excite the plasma, promoting the ground-state atoms at the plasma periphery to absorb the photons and transit up to higher energy level state (figures 10 and 11). Figure 12 shows that the FWHMs of Mn, K and Al lines are reduced by 25%, 58% and 52%, respectively, indicating an obvious suppression in self-absorption phenomenon.

The MAE assisted LIBS proposed by Tang *et al* [40] aimed to eliminate the self-absorption effects of laser-induced potassium feldspar plasmas in the 200–900 nm spectral range. The mechanism of MAE-LIBS (figure 13) is similar to that of LAS-LIBS, that is, the ground-state atoms of plasma absorb



**Figure 13.** The self-absorption reduction mechanism of MAE-LIBS. Reproduced with permission from [40], © 2018 Optical Society of America.



**Figure 14.** Comparisons of LIBS and MAE-LIBS emission lines for Na (a), K (b), Si (c) and Ca (d). Reproduced with permission from [40], © 2018 Optical Society of America.

the microwave energy that coupled by near-field radiation and transit up to higher energy level states. As a result, the number density of the ground-state atoms that related to the degree of self-absorption decreases sharply. As can be seen from figure 14, the serious self-absorption effects existed in emission lines are eliminated, and also the FWHMs are reduced by nearly a half.

For better comparison, the advantages and limitations of the above mentioned methods are listed in table 1. As can be seen, all the methods have their own specific advantages and limitations. For instance, the theoretical methods can derive several fundamental plasma characteristics, but the calculation is complex and the applicability tends to be decreased to practical LIBS measurements. The optically thin method can

**Table 1.** Comparison on advantages and limitations of self-absorption correction or elimination methods.

Method	Advantages	Limitations
Curve-of-growth	<ul style="list-style-type: none"> <li>• Can determine the linearity limit and the self-absorption degree.</li> <li>• Can obtain the plasma characteristics (temperature, collisional cross-section, atomic density of ground state, etc).</li> <li>• Can avoid systematic errors caused by self-absorption.</li> </ul>	<ul style="list-style-type: none"> <li>• Needs to calculate many variables (temperature, electron density, Gaussian broadening, Lorentz broadening, optical path length, etc), some of which are difficult to calculate accurately.</li> <li>• Complex and time-consuming.</li> </ul>
Self-absorption coefficient	<ul style="list-style-type: none"> <li>• Can correct the line intensity or line width.</li> <li>• Few parameters are required (line width, electron density, and Stark broadening coefficient).</li> </ul>	<ul style="list-style-type: none"> <li>• Needs to select a line that is not affected by self-absorption.</li> </ul>
Optically thin	<ul style="list-style-type: none"> <li>• Can directly capture the optically thin spectral line.</li> <li>• Can avoid any theoretical errors.</li> </ul>	<ul style="list-style-type: none"> <li>• The spectral detector must be time-resolved.</li> <li>• The elemental content is limited to within a certain range.</li> </ul>
Spectral fitting and plasma modeling	<ul style="list-style-type: none"> <li>• Can derive the correction factors through profile fitting or theoretical modeling.</li> </ul>	<ul style="list-style-type: none"> <li>• Complex and time-consuming</li> <li>• Several approximations and assumptions result in inaccuracy.</li> </ul>
Doubling mirror	<ul style="list-style-type: none"> <li>• Quick and convenient.</li> </ul>	<ul style="list-style-type: none"> <li>• Affected by several experimental factors (transmittance of the lens, reflectivity of the concave mirror, solid angle of collection, etc).</li> </ul>
Escape factor	<ul style="list-style-type: none"> <li>• Can estimate the self-absorption degree.</li> </ul>	<ul style="list-style-type: none"> <li>• Depends on the line profile and thus of all the mechanisms of line broadening.</li> </ul>
Laser or microwave assisted LIBS	<ul style="list-style-type: none"> <li>• Can directly eliminate the self-absorption effect.</li> <li>• Good universality.</li> </ul>	<ul style="list-style-type: none"> <li>• Complicated and high cost.</li> <li>• Unable to quantify the self-absorption degree.</li> </ul>

directly capture the optically thin spectrum, but it requires time-resolved spectral detector (e.g. ICCD) and the elemental content is limited to a certain range. The doubling mirror method is quick and convenient for self-absorption correction, but it is affected by some experimental factors. The laser or microwave assisted LIBS method can directly eliminate the self-absorption effect, but it requires additional device which limits its applications.

## 5. Utilizations

Self-absorption is often seemed as an undesired effect in LIBS measurements. However, the self-absorbed lines that carry hidden information are capable of characterizing plasma characteristics (such as plasma temperature, species density, electron density, LTE, Stark broadening, etc) and even become a precious tool for quantitative LIBS analysis.

Fishman *et al* [88] used asymmetric self-absorbed spectral lines to measure the atom density and several parameters involving the plasma cross-section. They put forward an approach for determination of the electron and atom densities in plasma by measuring the characterization parameters of the self-absorbed or even self-reversed lines.

Gornushkin *et al* [89] proposed a two-line method based on Bartels model of inhomogeneous optically thick plasma to measure the plasma temperature. This method requires the existence of two non-resonance atomic or self-reversed ionic lines in the laser-induced plasma spectrum. Assuming that the temperature distribution along the plasma morphology is parabolic, thus the obtained temperature corresponds to the maximum temperature of plasma core along the line of sight. It was found that the temperature was uniform along the plasma vertical axis. Another work on temperature measurement comes from Karabourniotis *et al* [90], who developed a diagnostic procedure to determine the radial distribution of electron temperature  $T_e$ , excitation temperature  $T_p$ , and

electron density of high electron-density plasma by using a Stark broadened self-reversed spectral line. The great difference between  $T_e$  ( $\geq 13\,500$  K) and  $T_p$  ( $\approx 8900$  K) indicated that it was seriously deviated from the excitation equilibrium.

Sherbini *et al* [91] proposed a method for quantifying the Stark broadening in optically thick plasmas. The method first determines the degrees of self-absorption of a pair of lines from the same species and then rescales the linewidths to make a correction. After that, Bredice *et al* [92] obtained the Stark coefficients of atomic and ionic lines of Mn by measuring the broadening of optically thin plasma, and investigated the effect of self-absorption on line broadening measurements.

In LIBS, the validity of LTE condition is usually examined by the McWhirter/Hey criterion, which is restricted to optically thin plasmas. In fact, the strong self-absorption of resonance transition can reduce the population of ground state, so that the electron number density satisfying the LTE condition is reduced accordingly. Cristoforetti *et al* [93, 94] studied the thermodynamics equilibrium states in laser-produced plasmas and the relationship between self-absorption and LTE. The calculation showed that the threshold of electron density that derived from the McWhirter criterion to ensure LTE could be easily relaxed by one order of magnitude in the case of serious self-absorption of the first resonance line in typical LIBS spectra.

For quantitative analysis, Cristoforetti *et al* [95] proposed an optical depth method to analyze the chemical composition of the laser-induced plasma and characterize the degree of self-absorption. The optical depth of the emission line can be calculated by quantifying the extent of self-absorption, so that the columnar density of each species can be derived under LTE conditions. Then assuming that the plasma is homogeneous, the elemental concentration ratio, the plasma temperature and the absolute number densities of species can be calculated. Hou *et al* [96] also proposed a modified self-absorption quantification method to directly deduce the degrees of self-absorption of emission lines and several plasma characteristics such as concentration ratio, plasma temperature, absolute densities of species, etc. There is no term related to line intensity involved in the algorithm, so the method is not affected by self-absorption effects. Experiments performed on Al–Li alloys verified that this method was capable of semi-quantitative analysis and diagnosis of plasma characteristics.

## 6. Conclusion

As a rapidly developing analytical technique, the quantitative analysis performance of LIBS is inevitably affected by self-absorption. The self-absorption has adverse effects not only on plasma characteristics, but also on spectral line shapes and quantitative analysis results. In this paper, the self-absorption effect involved in LIBS has been comprehensively reviewed from five aspects, including experimental observations and adverse effects, physical mechanisms, correction or elimination approaches, and utilizations. Although it has yielded

substantial results in the physical mechanism research area, however, these theories and models are still proposed based on certain assumptions and approximations. As a result, the applicability of most of these models has been decreased to practical LIBS measurements due to the complexity of laser-target interaction, the fastness of plasma evolution and inhomogeneity of plasma. Similarly, the listed correction or elimination approaches also have their own specific limitations and applicability. For instance, the self-absorption coefficient method requires some fulfilled conditions and additional plasma parameters, the optically thin technique is limited to a fixed elemental content range, some of the fitting and modeling methods tend to be complex and time consuming, the LSA-LIBS and MAE-LIBS require additional device which limits their applications. Therefore, further research should be more devoted to the physical mechanism of self-absorption effect so as to develop more universal and reliable elimination approaches. Fortunately, there are not just disadvantages of self-absorption, and it has now been utilized to characterize plasma or even take quantitative analysis in LIBS.

## Acknowledgments

This work is supported by National Key R&D Program of China (2017YFA0304203), Changjiang Scholars and Innovative Research Team in University of Ministry of Education of China (IRT13076), National Natural Science Foundation of China (NSFC) (Nos. 61475093, 61875108, 61775125), and Major Special Science and Technology Projects in Shanxi Province (MD2016-01).

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