NON-ANALYTICAL APPLICATIONS OF LASER-INDUCED BREAKDOWN SPECTROMETRY

Timur A. Labutin[1]*, **Andrey M. Popov**[1]

[1]Department of Laser Chemistry, Lomonosov Moscow State University
119234 Moscow, Leninskie gory 1b3, Russia
**e-mail: timurla@laser.chem.msu.ru*

1. Introduction

In laser-induced breakdown spectrometry (LIBS) a pulsed laser generates a plasma that vaporizes a small amount of a solid, gaseous or liquid sample. The emission spectrum of the excited species in the laser-induced plasma usually used for qualitative or quantitative analysis of the sample. The last 20 years witnessed a sharp growth of the number of publications devoted to the application of LIBS for analytical purposes. Indeed, LIBS started to be used for determining the elemental composition of various samples from molten steels [Noll 2001] to zooplankton [Sushkov 2020]. LIBS instruments were successfully implemented for on-line control of the raw materials [Gaft 2007], steel or sludge during production as well as finished products on the conveyor belt [Legnaioli 2020]. An interesting application of this method is elemental mapping, which was performed for minerals, plant tissues and histological examination of animal organs [Jolivet 2019].

Protocols and instrumentations for analysis of samples located in a harsh environment were designed and developed to perform measurements on the bottom of a sea up to 3000 m deep [Thornton 2015], to examine underwater garbage in the nuclear reactor core [Saeki 2014], and to study the Martian surface by means of the ChemCam and SuperCam [Meslin 2013, Nelson 2020]. Numerous papers are devoted to applications of LIBS for solving analytical problems like biomedical research, pharmaceutical products [Gaudiuso 2018], food [Markiewicz-K. 2017], analysis of aerosols [Diaz 2020], cultural heritage objects [Botto 2019] and so on. Several handheld LIBS instruments appeared on the market in recent years aiming at providing fast sorting of scrap, plastics or geological samples [Senesi 2021]. Thus, LIBS instruments with pulsed solid state ns-lasers became a “work horse” in various analytical applications. Besides this, there are other application areas where the emission of laser-induced plasma can be employed to solve specific, mostly theoretical tasks. We aim to focus on such non-analytical applications, namely the fundamental studies of laser ablation itself, determination of atomic line parameters (mostly Stark broadening parameters) and imitation of radiation from cosmic objects.

2. RESULTS AND DISCUSSION

The model of the evolution of a laser plasma is based on numerical simulation of ongoing processes [Shabanov 2014], relying on data obtained by optical tomography of plasma. Spectra of laser-induced plasma is also used to support the modeling of the processes occurring during laser–solid interaction [Bogaerts 2005]. This model was then applied to study the influence of laser irradiance, pulse duration and wavelength on laser ablation. In case of fs-plasma the competing processes lead to formation of several fractions in plasma plume. The LIBS helps to distinguish three different velocity populations during the plasma expansion: ions with high kinetic energy, neutrals with a velocity comparable to the nanosecond regime, and lastly by nanoscale clusters.

The next possibility is the determination of transition probabilities in the laser-induced plasma. In this case, branching ratios are determined by measuring the relative emission-line intensities for lines arising from the same upper levels in an optically thin laser-produced plasma. Following these relative values of transition probabilities are put on an absolute scale [Ferrero 1997]. Laser-induced plasmas are also quite extensively used for the determination of Stark parameters [Konjević 2002, Popov 2016], relatively easy to work with, have considerable electron number density and allow selecting different working conditions merely by changing temporal parameters of signal acquisition. Generating of a long plasma ("long spark") instead of a spherical plasma can provide the following advantages for Stark parameter measurements: *i)* illumination of the whole available focal plane of spectrograph, thus increasing the vertical dimension of plasma image on the detector 5–7-fold, which leads to an enhancement of signal-to-noise ratio; *ii)* a long spark is more homogeneous than a spherical one, as we demonstrated earlier, resulting in lesser optical thickness and lower experimental errors (<10%). This allowed us to accurately estimate an impact of hyperfine splitting on the profile shapes of the copper lines taking also into account the isotope shifts. We have shown that both effects considerably influence shift and width of Cu I line at 510.554 nm, and shifts of Cu I lines at 515.324 and 521.820 nm. Hyperfine structure and isotope shift additionally broad and shift the profile of the Cu I 510.554 nm line. This observation helps to resolve observed discrepancies between existing theoretical results and experimental data.

Last, we consider the time-evolution of the spectra of laser-induced plasma of high-purity iron in air, which is used to mimic the FeO pseudo-continuum emission. The iron oxide "orange arc" bands are unambiguously detected in persistent meteor trains, meteor wakes, and clouds, as well as in the terrestrial airglow. In contrast to the majority of other astronomically important diatomic molecules, theoretical simulation of the FeO rovibronic spectra is not feasible due to the extremely condensed and strongly perturbed multiplet structure of its excited states. The LIBS spectra were convolved with Gaussian profile with the FWHM equal to 0.38 nm which is provided a good agreement between the observed profiles of the Fe I isolated line at 537.15 nm in LIBS and Benesov meteor spectra. For comparison, the bolide spectrum at 39 km altitude was chosen, since it contains both persistent Fe I lines and FeO peaks. The significant variations of the intensity of the band at 625 nm should be noted. Such strong variations cannot be explained by changes in the level population due to changes in temperature. At the same time, this can be easily explained if one assumes a significant contribution to the 625 nm band from FeO_2 emissions as the laser plume cools, which is confirmed by the thermodynamic calculations. Although current experiments have been performed in air at atmospheric pressure, they provide high resolution spectra, which are similar to bolide spectra. Moreover, it seems possible to complete a simultaneous fit for both atomic and molecular emissions of meteor spectra in order to avoid errors due to the erroneous exclusion of atomic lines. The environment of FeO airglow emission looks to be quite different from that of meteor events and laser experiments. Considering that the cold FeO molecules in the upper Earth's atmosphere are excited by solar radiation during the day, while FeO molecules produced during bolide events and laser experiments are hot, LIBS experiments seem to be more suitable for modeling FeO emission in meteor spectra at low altitudes.

3. References

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