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Time-resolved measurement of atomic emission enhancement by fs–ns dual-pulsed laser-induced breakdown spectroscopy*

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Time-resolved measurement of atomic emission enhancement is performed by using a 500-fs KrF laser pulse incident upon a high density supersonic O_2 gas jet, synchronized with an orthogonal ns frequency-doubled Nd:YAG laser pulse. The ultra-short pulse serves as an igniter of the gas jet, and the subsequent ns-laser pulse significantly enhances the atomic emission. Analysis shows that the contributions to the enhancement effect are made mainly by the bremsstrahlung radiation and cascade ionization.

Keywords: time-resolved measurement, atomic emission enhancement, dual-pulse LIBS
PACC: 0765, 4260, 5250J, 9575F

1. Introduction

When irradiated by a focused high-power pulsed laser, a material in a focal region breaks down, forming a plasma whose emitting spectrum betrays the elemental compositions in the material. Measurements including the integration of the emitting signals from spectral lines over a certain time interval can be used to identify the atom species present in the material. The element content can be determined by constructing a calibration curve of signal intensity *vs* concentration, with samples of known compositions introduced into the source. Such a technique is known as laser-induced breakdown spectroscopy (LIBS), and now it has become a prevailing method of identifying elemental compositions[1−5] due to its own numerous advantages. LIBS possesses the ability to simultaneously monitor all elements in the plasma as long as their concentrations sufficiently high. The microplasma formed by focusing the optical pulse upon the sample can facilitate an *in situ* and spatially resolved analysis. In addition, LIBS is suitable for remote and on-line measurement in which contamination of the sample and human intervention can both be avoided.

Though LIBS is convenient in use due to its above-mentioned advantages, it would be restricted when the elemental concentration is rather lower than the detector sensitivity. The situation has become relaxed since the dual-pulse LIBS was introduced by Uebbing's group.[6] Atomic emission enhancement was observed when a second laser pulse was used to reheat the material ablated by the first pulse.[7−9] Dong *et al*[10] found that double fs pulses could be used to prolong the lifetime of plasma channels in air. Most recently, in a pump-probe experiment, fs–ns dual laser pulses focused upon a high-density supersonic O_2 gas jet, aiming to create a relativistic ionization front,[11,12] was surprisingly found to be able to enhance the atomic emission fortyfold,[13] so this experiment is suitable for LIBS research. A possible interpretation for the enhanced effect was also made. The present article demonstrates further the temporal behaviours of the atomic emission enhancement and briefly discusses some measurements.

2. Experiment

The experimental diagram is shown in Fig.1. A 248 nm/500 fs/10 mJ UV pulse from a dye/excimer hybrid laser system (A) and a 532 nm/8 ns/15 mJ

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green pulse from an Nd:YAG laser (B) are simultaneously directed towards the vacuum chamber (F) by 45° HR mirrors (M_{1-4}) and focused upon a high density pulsed O_2 gas jet, whose density is measured to be $5\times10^{19}\mathrm{cm}^{-3}$ by other means, from a supersonic nozzle[14]by L_1 ($f/3$) and L_2 ($f/5$) lens with focal lengths of 150 mm and 200 mm respectively. The spark formed by laser-induced breakdown is imaged on the inlet of the ICCD-equipped optical multichannel analyser (OMA, E) through a band-stop filter (stop/pass ratio 10^6 at 532 nm, 9nm FWHM) and lens L_3. Two long-focal-length microscopes (not shown in the figure) are orthogonally mounted to monitor the laser focal spots near the nozzle outlet in the vacuum chamber. The timing of the lasers and the spectrometer is controlled by a delay/pulse generator (D, DG535). Due to the ns-scale jitter of the laser systems, a fast diode detector (G, rising time 200 ps) attached to an oscilloscope (C) is fixed at the place that is suitable for monitoring the pulse timing and energy. Their typical waveforms are shown in Fig.2, where the delay between the two pulses is set to be 0 ns. Integration time of OMA is set to be 9 ns, slightly longer than the duration of the ns laser pulse. Grating used in the experiment is 150 g/mm, and centred at 460 nm.

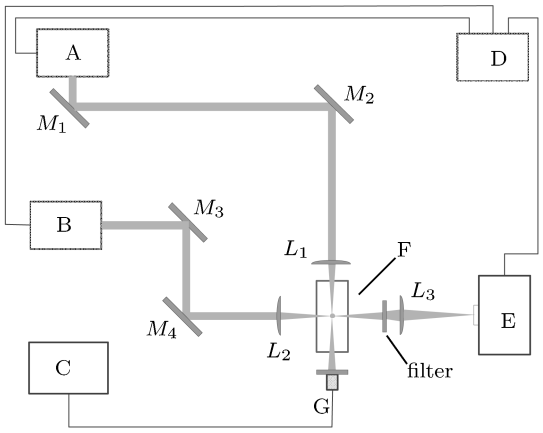


Fig.1. Schematic of fs–ns dual-pulse LIBS setup.

The diameter of the focal spot is measured by one of the microscopes to be less than 50 μm for the fs pulse, and leading laser intensity to be over $10^{15}\,\mathrm{W/cm}^{-2}$, beyond the threshold to strongly ionize the gas in the focal region. For the ns laser pulse the corresponding values are 100μm and $2\times10^{10}\,\mathrm{W/cm}^2$. No visible spark is observed while the fs laser beam is blocked, which implies that the intensity of the ns laser is not high enough to achieve considerable ionization of the gas. But when the ns laser pulse is delayed from 0 to tens of ns with respect to fs laser pulse, a very bright spark appears in the focal region. This is a direct evidence of atomic emission enhancement induced by dual pulsed lasers.

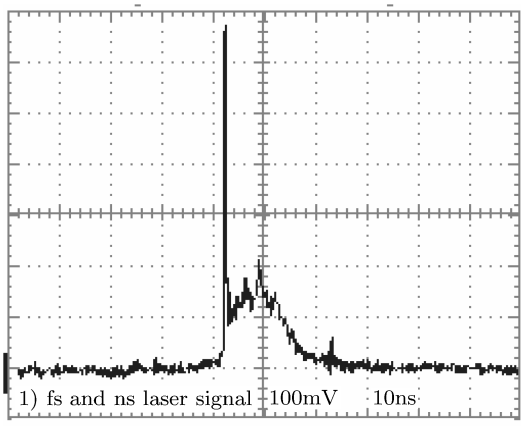


Fig.2. Typical waveforms of fs and ns pulses measured by fast diode detector. Delay between the two pulses is 0 ns.

To measure the temporal behaviour of the enhancement effect, the delay (denoted by τ_1) of the fs laser pulse with respect to the leading edge of the ns laser pulse is set to be 0 ns for each shot as shown in Fig.2, and the delay (denoted by τ_2) between the ns laser pulse and the OMA integration gate varies from 0 ns to 300 ns. For each τ_2, spectra are recorded by OMA for five shots. In the experiment, for τ_1=0 ns, we select τ_2=0ns, 5 ns, 10 ns, 15 ns, 20 ns, 25 ns, 30 ns, 35 ns, 40 ns, 50 ns, 60 ns, 70 ns, 80 ns, 100 ns, 130 ns, 180 ns, 300 ns. For τ_1=10 ns, 20 ns, and 30 ns, we select τ_2=0 ns, 10 ns, 20 ns, 30 ns, 80 ns, 180 ns, 300 ns.

3. Results and discussion

Measurements show that the significant atomic emission enhancement happens for each delay τ_1, and the emission becomes weaker as τ_1 increases. For τ_1=0 ns, three measured spectra are depicted in Fig.3 in which τ_2=0 ns, 30 ns, 130 ns respectively. This shows that the strongest emission takes place when delay τ_2=0 ns, which means that the greatest emission enhancement occurs when the ns laser pulse passes through the gas jet immediately after the fs pulse. At the beginning of the emission, under a series of characteristic spectral lines there lies a large continuous area that predominantly contributes to the enhancement. It gradually diminishes with time passing and

disappears after $\tau_2 = 20$ ns, the time right when the ns laser pulse entirely transmits through the gas jet. After that, contributions to the emission are made only by the characteristic spectral lines of singly ionized oxygen atoms. This implies that the continuous composition in the spectrum is produced mainly by the bremsstrahlung radiation of free electrons in the ns laser fields, while characteristic lines originate from the cascade ionization of oxygen atoms by energetic free electrons. Maximal laser energy absorbed or scattered by the gas jet is calibrated to be about 30% of the total pulse energy obtained by fast diode detector as shown in Fig.2.

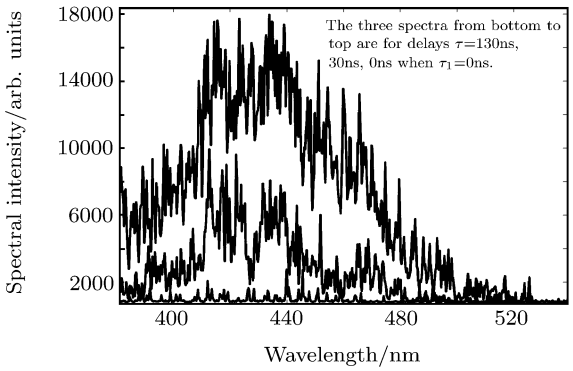


Fig.3. Spectral intensity of dual-pulse laser enhanced atomic emission, measured by OMA with various delays. The delay between fs pulse and ns pulse is set to be 0 ns.

For each delay τ_2, the emission intensity between 380 nm and 540 nm is integrated to display the temporal evolution of the enhancement shown in Fig.4. Three fitted curves are depicted for delay τ_1=0 ns, 10 ns, 20 ns respectively which show that the emission enhancement gradually becomes less significant as τ_1 increases. This can be attributed to a reduction in the initial free electrons in the focal region due to their diffusion or absorption. For each τ_1, the integrated emission intensity decreases exponentially and dies away at time t=200 ns, 150 ns and 120 ns for τ_1=0 ns, 10 ns and 20 ns respectively. Lifetime of the enhanced emission with a longer delay between ns laser pulse and fs pulse is shortened. The measurements further show that considerable enhancement can still be achieved even the delay extends to 50 ns. What is vital in the LIBS application is to use well synchronized (τ_1=0 ns) fs–ns dual pulse to efficiently enhance the atomic emission and appropriately control the time delay of measuring the emission spectrum to eliminate the continuous emission in our case.

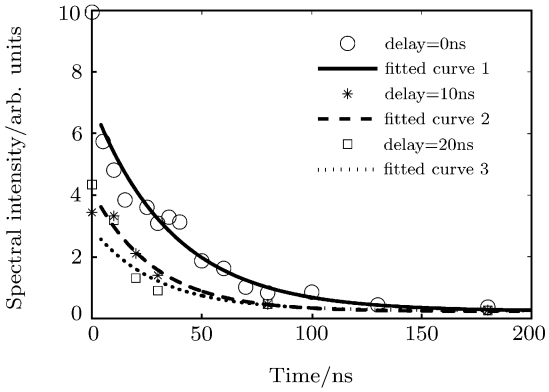


Fig.4. Integral spectral intensity of dual-pulse laser-induced atomic emission enhancement measured by OMA with various delays.

4. Conclusion

Time-resolved measurement of atomic emission enhancement shows that the contributions to the enhancement effect are made mainly by the bremsstrahlung radiation and partially by the cascade ionization of the gas jet plasma. The fs laser intensity is so high that gases in the focal region can be highly ionized into high-valence oxygen ions. When the fs laser pulse is applied prior to the ns pulse, the initial free electrons provided by the fs laser via multi-photon ionization can be cascade-ionized by the ns laser pulse. Consequently, the ultra-short pulse serves as an igniter of the gas jet while the ns laser pulse applied later is responsible for significantly enhancing the atomic emission.

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