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Direct evidence of mismatching effect on H emission in laser-induced atmospheric helium gas plasma

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A time-resolved orthogonal double pulse laser-induced breakdown spectroscopy (LIBS) with helium surrounding gas is developed for the explicit demonstration of time mismatch between the passage of fast moving impurity hydrogen atoms and the formation of thermal shock wave plasma generated by the relatively slow moving major host atoms of much greater masses ablated from the same sample. Although this so-called “mismatching effect” has been consistently shown to be responsible for the gas pressure induced intensity diminution of hydrogen emission in a number of LIBS measurements using different ambient gases, its explicit demonstration has yet to be reported. The previously reported helium assisted excitation process has made possible the use of surrounding helium gas in our experimental set-up for showing that the ablated hydrogen atoms indeed move faster than the simultaneously ablated much heavier major host atoms as signaled by the earlier H emission in the helium plasma generated by a separate laser prior to the laser ablation. This conclusion is further substantiated by the observed dominant distribution of H atoms in the forward cone-shaped target plasma. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4789817]

INTRODUCTION

Hydrogen analysis is greatly needed in many fields of application such as the detection of hydrogen trapped in zircaloy pipe in nuclear power plant and hydrogen impurity in titanium for industrial and medical applications.1,2 As we noted in our previous work regarding H analysis using laser induced plasma spectroscopic method,3 the intensity of hydrogen emission is largely reduced when the surrounding gas pressure was increased to atmospheric-pressure. This unfavorable pressure effect was explained on the basis of shock wave excitation model. Namely, it was assumed that there was a time lag between the passage of the hydrogen atoms and the formation of shock wave induced by the propelling atoms of the much heavier target’s host elements. This time lag was supposed to increase with increasing pressure, which slows down the propelling host atoms and hence delays the formation of the shock wave. We called this phenomenon as “mismatching effect.” It was further shown that the ablated atoms were generally excited in the limited area just behind the shock front. Thus, only a small part of the ablated hydrogen atoms can be excited by the shock wave and thereby lowering the hydrogen emission efficiency. This has come to be known as one of the weaknesses of the celebrated in-situ laser-induced breakdown spectroscopy (LIBS) technique. For in-situ hydrogen analysis in nuclear power station, the use of atmospheric-pressure surrounding gas is mandatory, since the zircaloy tube was submerged in the water. To overcome this problem, we have offered several

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alternative techniques such as the double pulse laser irradiation, and introducing the use of helium surrounding gas allowing the metastable excited helium atoms to provide the excitation energy for the hydrogen atoms at atmospheric pressures instead of relying on the conventional shock wave excitation mechanism. This technique was shown to yield the much desired strong and sharp hydrogen emission turning the so called “mismatching effect” to its advantage. However, direct experimental evidence of the mismatching effect itself has yet to be demonstrated.

In order to provide the direct evidence of this effect, one needs to determine the relative speeds of the ablated atoms and the relative times of excitation from their respective ground states. For the determination of an atom in its ground state, the laser-induced fluorescence (LIF) spectroscopic method is commonly employed. Unfortunately, the tunable laser required for the case of H having the resonance wavelength of 121.5 nm is hard to come by. In an effort to overcome this obstacle, we came across the idea of utilizing the experimental observation mentioned earlier which shows that atoms can be effectively excited in a cooled helium gas plasma containing a large number of metastable excited helium atoms. In those experiments, the helium plasma was generated well ahead of the second laser irradiation performed on the target with a suitable delay to assure that the helium gas plasma had already been sufficiently cooled down. When the ablated atoms enter the cooled helium gas plasma, they are not expected to be thermally excited. Instead, the detected strong, sharp, and low background hydrogen emission spectra can only be the result of excitation with the energy released from the large amount of metastable excited helium atoms remaining in the plasma. It is further confirmed that almost all the ablated atoms of the sample used in those studies can be excited from their ground state in this cooled helium gas plasma. It thus occurred to us that this technique can be employed as “metastable excited helium probing technique.” This technique is applied to study the “mismatching effect” of hydrogen atoms in the atmospheric-pressure plasma. It should be stressed that this technique is different from the double pulse laser irradiation technique in which the second laser is activated after, instead of prior to the target ablation by the first laser for the enhancement of the emission intensity.

**EXPERIMENTAL PROCEDURES**

Fig. 1 shows the experimental set-up used in this work. A Q-switched nano-second Nd:YAG laser (Quanta Ray, LAB SERIES, 450 mJ, 8 ns) was operated at its fundamental wavelength of 1064 nm with a repetition rate of 10 Hz. The laser beam of a fixed energy of 110 mJ is focused onto a spot in the chamber through a quartz window. The chamber is equipped with an inlet and outlet ports for the helium gas flow and two other quartz windows for the observation of plasma emission. The high purity helium gas (6N) is flown at a constant rate of 3 l/min to maintain the 760 Torr gas pressure. The gas plasma produced in this set-up exhibits a thin and vertically elongated shape featuring white emission at its center with an outer shell of strong orange color.

For the experimental study, laser ablation was carried out by focusing the second laser (Nd:YAG, Quanta Ray, LAB SERIES, 532 nm, maximum energy of 225 mJ, 6 ns) onto the solid agate sample, and the ablated atoms were rapidly propelled into the helium gas plasma region as clearly shown in Fig. 1. This laser irradiation was conducted at two different energies, 37 mJ and 75 mJ for different measurements as explained later. The time interval between irradiations of the two lasers is controlled by means of a digital delay generator (Stanford Research System, model DG-535). The resulted emission spectra of the ablated atoms in the helium plasma are detected by using an optical fiber inserted into the interaction chamber at a distance of 2 cm in front of the helium plasma. At this position, the fiber is expected to collect the emitted light entering the fiber end within 27° of solid angle. A mask is placed in front of the detector to cut off the emission from the target plasma. The other end of the optical fiber is connected to the entrance slit of the spectrograph (McPherson model 2061 with 1000 mm focal length, 1800 g/mm grating and f/8.6 Czerny Turner configuration) with its exit slit attached to an optical multichannel analyzer (OMA system, Andor iStar intensified CCD 1024 × 256 pixels).

The agate sample used in this study was chosen from the available solid samples for its strongest H emission, which remained practically unchanged after 100 repeated laser
shots on a fixed spot of the sample surface. The repeated 100 laser shots are performed on a different near-by spot by simply rotating the sample. The resulted intensities are averaged to yield the data presented in this report.

RESULTS AND DISCUSSION

In the first part of our experiment, the emission spectra of agate sample are measured by means of the conventional LIBS method, using a single laser for sample ablation. The effects of both radiation energy and surrounding gas pressure are examined in this part of the experiment.

Fig. 2 shows the emission spectra taken from the agate sample in the wavelength region between 650 nm and 670 nm at laser ablation energy of 75 mJ, and two different gas pressures, 20 Torr and 760 Torr. The gate delay and width of the OMA system are set at 1 μs and 50 μs, respectively, right after the target ablation. It should be noted that only second laser for target ablation is used in this experiment. The figure clearly shows the greatly reduced hydrogen emission intensity at helium 760 Torr compared to that detected at 20 Torr. Meanwhile, the other emission lines such as those from calcium and helium exhibit remarkably smaller pressure effect.

This pressure effect on the silicon and oxygen emission intensities are also investigated by similar measurement smaller laser energy 37 mJ for the more abundant host atoms. The resulted spectra are presented in Fig. 3 for (a) silicon emission and (b) oxygen emission, at both 20 Torr and 760 Torr helium gas pressures. It is clearly seen from Fig. 3(a) that the emission intensity of silicon line is almost unaffected by the gas pressure. Remarkably, similar result is shown in Fig. 3(b) for oxygen emission regardless of the fact that oxygen has nearly the same excitation energy (10.25 eV) with hydrogen (12.75 eV). The only perceptible difference is the more severe spectral broadening effect at higher gas pressure.

As we reported previously using slide glass sample,24 hydrogen intensity reduction was much more serious in the case of nitrogen surrounding gas. Presented in Fig. 4 are the spectra measured with 37 mJ laser energy from agate sample in the wavelength region from 650 nm to 670 nm in surrounding nitrogen gas at 2 Torr and 760 Torr. One notes that virtually no hydrogen emission is observed at nitrogen gas pressure of 760 Torr. Meanwhile, the reduction of calcium

![FIG. 2. Agate spectrum showing H I 656.2 nm, Ca I 332.4 nm, and He I 667.8 nm emission lines in the wavelength region from 650 nm to 670 nm detected in the different surrounding helium gas pressure of 20 Torr and 760 Torr, as measured with laser energy at 75 mJ, and with the OMA operated at 1 μs gate delay and 50 μs gate width right after the laser ablation.](image)

![FIG. 3. Agate spectrum showing separately (a) Si I 288.2 nm and (b) O I 777.1 nm emission lines obtained with 37 mJ laser ablation energy in helium gas with different surrounding gas pressure of 20 Torr and 760 Torr. The OMA is operated with the same time setting as in Fig. 2.](image)

![FIG. 4. Agate spectrum showing H I 656.2 nm and Ca I 332.4 nm lines in the wavelength region from 650 nm till 670 nm obtained at laser energy of 37 mJ. Nitrogen surrounding gas is used in this experiment with the same OMA setting.](image)
emission intensity is much less pronounced. It should be noted that the strong and sharp hydrogen emission at 2 Torr nitrogen gas is practically free from the mismatching effect and is hence mainly due to shock excitation as reported previously.\(^3\) This result has thus confirmed the unbiguity of the proposed mismatching effect.

In order to demonstrate explicitly the “mismatching effect,” it is necessary to show the relative speeds at which hydrogen and other host elements in their ground states move in the target plasma. For this purpose, we introduce a novel technique employing two laser set-up described in Fig. 1. In this set-up, the helium gas plasma is produced in front of the sample surface by focusing the fundamental Nd:YAG laser of 110 mJ. Subsequently, the sample is irradiated by the 532 nm laser of 75 mJ with a delay of 10 \(\mu s\) to send the ablated atoms to the sufficiently cooled helium gas plasma containing the metastable excited helium atoms with its excitation energy level diagram including the metastable triplet and singlet energy levels given in Fig. 5. The relatively long delay is also chosen to assure that the ablated atoms will return to their ground states before entering the helium gas plasma. The collisions of these atoms with the metastable excited helium atoms remaining in the plasma resulted in the Penning like energy transfer process\(^{11,12}\) leading to the excitation and the subsequent emission of those ablated atoms. Fig. 6 shows how the H I 656.2 nm, O I 777.1 nm, and Ca I 422.6 nm emission intensities vary with time. We recall that a special mask is properly placed near the optical fiber entrance end as shown in Fig. 1 in order to allow the detection of emission coming solely from the region of helium gas plasma. The 50 ns gate width of the OMA system was set to yield the desired time-resolved spectra. The gate signal was synchronized with the initiation of the second laser for target ablation. It is observed that hydrogen emission peak already appear at 100 ns, implying that the hydrogen atoms have travelled a distance of 5 mm (see Fig. 1) within 100 ns, which corresponds to a speed of 50 km/s. The hydrogen emission also decays very rapidly with time, corresponding to the short time spent by hydrogen atoms during their passage through the helium gas plasma where they are excited by the metastable excited helium atoms. As a comparison, the figure also shows the time profiles of oxygen and calcium emission intensities. It is seen that for the same figure, the oxygen emission reaches its maximum at 500 ns, while the maximum of calcium emission appears at 2 \(\mu s\). This is consistent with the previously proposed scenario envisioning the ablated atoms of lesser masses move at higher speeds and thereby arriving sooner at the probing region containing the cooled helium plasma. In other words, the ablated calcium of atomic mass 40 is thus implied to arrive at the helium plasma later than the simultaneously ablated oxygen of atomic mass 16.

The result described above can be further corroborated by measuring the time profiles of emission intensities from the target plasma in the ordinary LIBS fashion. To this end, the blocking mask is removed and the fiber entrance end is positioned near the target surface. The time profiles of detected emission intensities without generating the helium plasma are presented in Fig. 7. It is clearly seen that both silicon and oxygen emission intensities are detected, and they attain their peak values at around the same time (700 ns) followed by similar slow decays as the shock wave plasma cools down.\(^3\) It means that the shock excitation becomes most effective at around 700 ns. By then most of

![FIG. 5. Energy level diagram of helium atom associated with the commonly observed spectrum including the metastable excited energy levels.](image)

![FIG. 6. Time profiles of hydrogen, oxygen, and calcium emission intensities from the same agate sample obtained with the first laser operated at 110 mJ and fired 10 \(\mu s\) before the second laser irradiation. The second laser ablation energy is fixed at 37 mJ. The gate width of the OMA system is set at 50 ns with the He flow rate kept at 3 l/min to maintain the atmospheric gas pressure.](image)

![FIG. 7. Time profile of oxygen and silicon emission intensities from the target plasma generated by the second laser with ablation energy of 37 mJ without activating the other laser. The OMA system is operated with a gate width of 50 ns.](image)
the hydrogen atoms have long left the plasma behind them, missing the prime excitation process. As explained earlier on the basis of Fig. 6, most of the hydrogen atoms are expected to have reached a distance of about 5 mm beyond the plasma. That is why no hydrogen emission is observed in Fig. 7. These results have thus explicitly and directly demonstrated the mismatching effect proposed in a number of previous experiments and manifested also the pressure induced intensity diminution effect of hydrogen emission.\(^3\)

The same experiment giving the result shown in Fig. 6 is repeated by operating the ablation (second) laser at 75 mJ and the result is presented in Fig. 8. One observes the strong helium emission consisting of a fast component and a slow component in succession, accompanied by hydrogen emission of qualitatively similar trend with much lower intensity. This is in contrary to the previous experiment shown in Fig. 6 where no helium emission is observed due to the much smaller ablation energy used in the corresponding experiment. This fast component of helium emission signal is probably due to the fact that metastable excited helium atoms are ionized by collisions with high speed hydrogen atoms. Thereafter, the helium emission takes place through the recombination process with the electrons.\(^26\) In the meantime, the hydrogen atoms are also excited and leading to the emission observed. The slow component of the helium emission on the other hand is probably due to the fact that helium in its metastable excited state is re-excited by interaction with the strong shock wave plasma. On the other hand, the time profiles of calcium and oxygen emission intensities show the typical contribution of the thermal shock wave excitation process.

Finally, one would expect the fast moving hydrogen atoms to be found mostly distributed in the forward direction. In order to provide the desired experimental evidence, the spatial distribution of hydrogen atoms is exhibited by imaging with a lens the helium gas plasma on the image plane of the vertical elongated helium gas plasma. For this measurement, the ablation laser is operated at 37 mJ with a flow rate of 3 l/min. The gate delay and width of the OMA system was set at 50 ns and 500 ns, respectively. The result is presented in Fig. 9. It is shown in the figure that the hydrogen atoms are more forwardly distributed resulting in a cone shape plasma. On the other hand, a host element such as calcium is seen to have a more spread out spatial distribution.

**CONCLUSION**

This experiment has demonstrated the gas pressure induced intensity diminution of hydrogen emission in the conventional LIBS set-up with helium as well as nitrogen surrounding gas, confirming the same phenomenon observed previously in similar experimental environment using different samples and other surrounding gases. This study goes on to probe the time mismatch effect proposed to explain the peculiar observation employing a novel time-resolved double-pulse LIBS set-up specially developed by modifying the previous double-pulse technique for the study of the so-called helium assisted excitation mechanism. The measurements obtained by this special technique has succeeded to present the direct and explicit experimental evidence of mass-dependent speeds of the ablated atoms, showing the higher speed of hydrogen compared to those of the much more massive major host atoms from the ablated sample, thereby explicitly demonstrates the time mismatch between the passage of the fast moving hydrogen atom and the shock wave formation by the relatively slow moving major host atoms. This result is further corroborated by the measured spatial distributions of emission intensities of the target plasma exhibiting the dominant presence of the emitting hydrogen atoms in the forward cone shape plasma compared to the more spread out plasma of the ablated major host atoms.

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