Observation of exclusively He-induced H emission in cooled laser plasma

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An experiment was performed for the observation of H emission induced in a cooled laser-induced atmospheric pressure gas plasma of He atoms in their metastable excited state. The strong H emission detected clearly established, to the exclusion of other well known major excitation processes, the exclusive contribution of the He-induced excitation (HIE) mechanism. The process is suggested to take place by means of energy transfer from the excited He atoms to the H atoms via Penning collision induced ionization involving electron exchange. The result further shows that this mechanism may also work for elements other than H and thereby strongly suggests the use of ambient He gas to broaden and complement the applications of standard laser-induced breakdown spectroscopy. © *2011 American Institute of Physics*. [doi:10.1063/1.3592351]

I. INTRODUCTION

The employment of ambient helium gas in laser-induced plasma at atmospheric pressure has been shown to result in remarkable reduction of Stark broadening effect[1] along with intensity enhancement[2] effect in the emission spectra of halogen gases and sulfur. This favorable role of ambient helium gas was repeatedly confirmed by a number of recent experiments in laser-induced plasma spectroscopy (LIPS) for hydrogen analysis of zircaloy and other samples with atmospheric pressure ambient He gas.[3,4] It was shown that instead of the very weak H emission line observed with atmospheric ambient air, a very sharp and sustained H emission was detected with ambient He gas at the same pressure. This was considered indicative of the role of the excited He atoms in providing the additional energy for the renewed and delayed excitation of hydrogen at the favorable moment when the plasma was relatively free from the electric charges and thereby reducing the Stark broadening effect and leading to the sharp H emission line. These advantages have further been demonstrated in the achievement of complete resolution of the H and D emission lines in LIPS with ambient He gas.[5,6]

The role of metastable excited He atoms in those favorable effects of He ambient gas has been suggested in works dating back to early 1990s.[7–9] The unusually large energy transfer was later proposed to have taken place in a Penning-like ionization process with some resemblance to the process bearing the same name and well known in the operations of He-Ne and He-Cd lasers. While lacking detailed theoretical elaboration and direct experimental support in the LIPS experimental environment, this collision induced ionization of a number of atoms by metastable He has nevertheless been intensively studied and established since the 1960s, both theoretically and experimentally, mostly in gas discharge and glow discharge experiments.[10–15] Unfortunately similar studies have yet to be performed in the different experimental condition of the hot plasma (~9000 K) generated in LIPS or laser-induced breakdown spectroscopy (LIBS) where thermal excitation is known to be mainly responsible for the emission. In this relatively more complicated condition, the identification of the genuine contribution of the so-called He induced excitation (HIE) mechanism becomes understandably more difficult let alone the difficulty to elucidate the underlying energy transfer mechanism.

In this study, a special experimental setup is devised to enable the observation of the HIE effect without being complicated by the dominant thermal excitation process usually found in the high temperature plasma. With this setup, the contribution of HIE can be exclusively demonstrated by detecting the H_α emission line of H atoms excited from their ground state inside a pre-prepared cooled gas plasma of He atoms in their metastable excited states.

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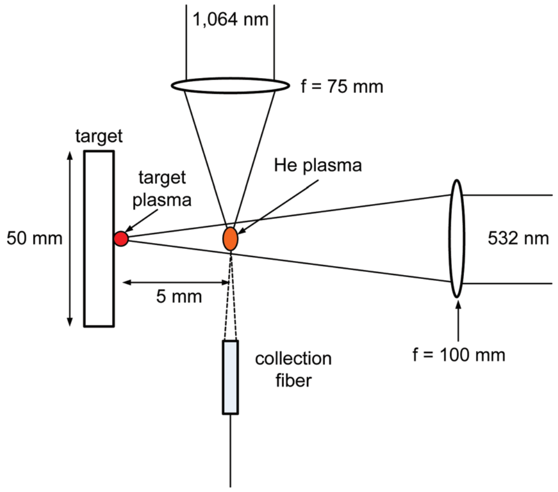

FIG. 1. (Color) Schematic description of the experimental setup.

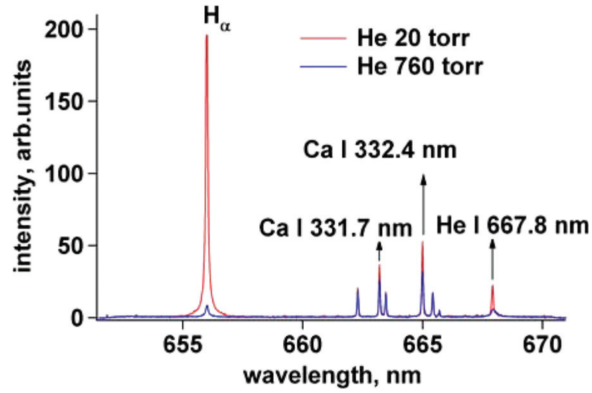

FIG. 2. (Color) Agate spectrum showing H_α, second order Ca I 331.7 nm, Ca I 332.4 nm, and He I 667.8 nm emission lines in the wavelength region from 650 nm to 670 nm detected with 37 mJ laser ablation energy in He gas. The OMA was operated with 100 ns gate delay and 50 μs gate width right after the laser ablation.

II. EXPERIMENTAL PROCEDURES

Figure 1 gives the schematic description of the experimental setup consisting of two Nd-YAG laser systems; both were operated in the Q-switched mode with a repetition rate of 10 Hz and configured to produce the laser beams at mutually perpendicular directions. One of the lasers operating at its fundamental wavelength of 1064 nm and a fixed energy of 110 mJ was focused onto a spot within the ambient He gas in the chamber to generate the He plasma at a point 5 mm in front of the target. The desired pressure of the He gas (Air Liquid, 6 N) was maintained with a constant flow rate of 2 l/min. The second laser was employed at the second harmonic wavelength of 532 nm and a fixed energy of 37 mJ for the ablation of the solid target. This second laser irradiation was started 10 μs after the generation of He plasma by the first laser, thereby allowing the small He plasma (diameter of ~3 mm) sufficient time to cool itself down. The emission spectra of the ablated atoms were collected by an optical fiber with its entrance end fixed inside the chamber at a distance of 2 cm sidewise from the He plasma. The other end of the optical fiber was connected to the detection system consisted of a spectrograph and an optical multichannel analyzer. The emission of ablated atoms outside the detection area was effectively blocked off by a slit placed in front of the entrance end of the fiber. The agate sample used in this study was chosen from among the available solid samples for its strongest H emission, which remained practically unchanged after the 100 repeated laser shots on a fixed spot of the sample surface.

III. RESULTS AND DISCUSSION

In order to ensure that most of the ablated H atoms enter the micro He plasma in their ground state, an initial experiment was performed to verify the suppression of H emission by simply ablating the target with the second laser at atmospheric gas pressure as reported previously.[16] Presented in Fig. 2 are the agate emission spectra in the wavelength region from 655 nm to 670 nm, produced separately at 20 and 760 Torr He gas pressures without generating the He plasma. One observes that while the Ca emission intensity is only slightly reduced upon increasing the gas pressure, the H emission intensity exhibits instead a dramatic decline due to the "time-mismatch" effect on the very light H atom, confirming the expected effect cited in the preceding text. This result implies that direct collision induced excitation of the H atoms is practically ruled out. Meanwhile the extent of intensity reduction in He emission appears to lie between those emission intensities mentioned in the preceding text, which is consistent with the intermediate mass value of the He atom. More importantly, the H atoms were clearly shown to have returned to or largely were left in their ground state as they enter the detection area where the He plasma was to be generated in the following experiment. These H atoms may therefore be used to probe and examine the HIE effect in the cooled plasma of excited He atoms.

The following experiment was performed to ascertain the appropriate time interval between the operations of the two lasers. To this end, the He gas plasma was generated without target ablation, and the time dependent intensity of the detected strong He I 667.8 nm line is shown in Fig. 3. The intensity is seen to reach its maximum in about 5 μs and retain more than half its maximum at 10 μs. Thus the 10 μs delay chosen for the target ablation is appropriate to ensure

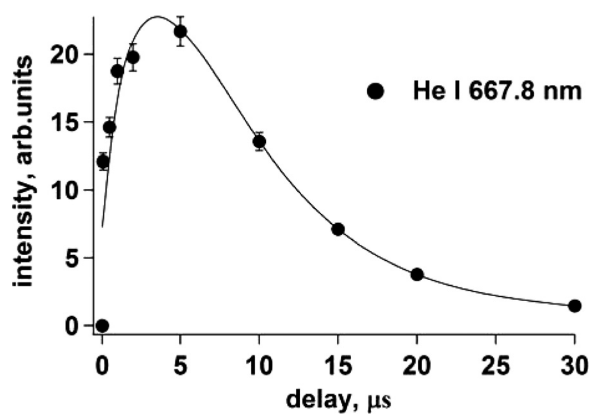

FIG. 3. Time-dependent intensity variation of He I 667.8 nm emission at 760 Torr gas pressure generated by 110 mJ laser at 1064 nm and detected with 100 ns gate width of the OMA system.

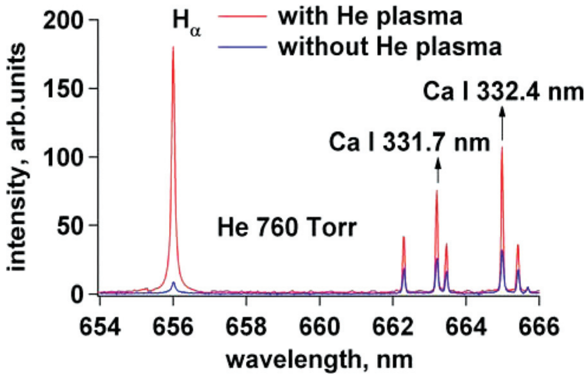

FIG. 4. (Color) Agate spectra showing H_α, second order Ca I 331.7 nm and Ca I 332.4 nm emission lines produced in the presence and absence of the cooled He plasma at 760 Torr detected with the same experimental setting.

that a large number of the He atoms would remain in their metastable excited state while giving the small He plasma sufficient time to cooldown effectively and thereby eliminating the undesired interfering high-temperature effects.

Next, the H and Ca emission lines from the same sample were observed by operating both lasers with the He gas plasma generated 10 μs prior to the ablation process. The emission lines of the ablated atoms detected during their passage through the cooled He plasma are presented in Fig. 4 along with those detected without generating the He plasma. A comparison of these data shows beyond any doubt that the dramatic intensity enhancement effect of H emission is entirely due to the presence of the excited He atoms, which are supposed to serve as temporary energy sources for the subsequent excitation and emission of the H atoms. It is to be added that the resulting spectrum is characterized by a very low background compared to those commonly found in hot plasma emission. Further, the enhancement effect was also found to diminish with increasing time lag of the ablation process; this correlates clearly with the decreasing amount of the excited He atoms in the plasma as shown in Fig. 3.

Having demonstrated the exclusive He-induced H emission effect in the cooled plasma, we shall now proceed with the explanation of the underlying energy transfer mechanism. As mentioned early, this was previously suggested to be mediated by Penninglike ionization process without much elaboration of the underlying physical mechanism. On the other hand, this process was in fact intensively studied in the 1960s on the ionization of noble gas and Hg atoms in glow discharge and gas discharge environment.[3,4] Although it is the H ionization process in the current case, the basic Penning collision induced energy transfer process from He* should remain valid in general. Besides, compared to all the previously observed HIE processes in the laser generated hot plasma, the current experimental condition involving the cooled plasma does resemble more closely the experimental condition of those past experiments except the reversed role of projectile and target played by the He and H atoms.[10–16] We shall therefore suggest and discuss the energy transfer from the metastable He to H induced by the H–He collision, similar to that reported in Refs. 14 and 15 as expressed by the equation:

$$\mathrm{He}^*(1) + \mathrm{H}(2) \rightarrow \mathrm{He}(2) + \mathrm{H}^+ + \mathrm{e}(1) \qquad (1)$$

which involves the electron exchange between the two atoms with the numerals 1 and 2 denoting the electron identities. The mutual tunneling of the two electrons involved in the process is a crucial assumption adopted to allow the description of the actual process as a two-step transitions represented by the radiative decay, He* → He, and the photoionization, H → H^+ + e. As electron exchange is involved in the process, the resonant transition in the He is not forbidden by the dipole selection rule. Under this assumption, both the 2 ^{1}S and 2 ^{3}S metastable states of He may participate with comparable contributions in the energy transfer processes triggered by the atomic collision despite the orders of magnitude difference between their life times. This was experimentally confirmed in previous studies, and in fact, the cross section for H_2 ionization by He projectile, calculated on the basis similar to Eq. (1) and the "billiard ball" model, has yielded the estimated value of 2.6 A^{-2},[15] in close agreement with the experimental result.[14] Thus in this picture, the subsequent H emission is supposed to take place after the rapid recombination of H^+ with e. Admittedly, the individual He* - H collision cross section is likely smaller in this case due to the smaller size of H compared to H_2. However, the H emission intensity in this experiment was detected in the time-integrated mode as indicated by the long gating width of 50 μs. Thus the accumulated emission events are expected to yield the large emission signal observed. In view of its general nature, basically the same mechanism is expected to operate in cases involving atoms other than H.[17] This point is clearly confirmed by the observed intensity enhancement of Ca emission from the same sample as presented in Fig. 4.

IV. CONCLUSION

To conclude, we have demonstrated unambiguously the exclusive role of metastable He in the observed strong emission of H in the cooled He plasma. The associated excitation energy for H is suggested to be transferred from the metastable excited state of He to H via the Penning ionization process discussed in this work. The intensity enhancement and low background reported in this study were also shown to be of rather general nature and may therefore offer an alternative means for complementing and broadening the range of LIBS applications to samples containing elements of large mass differences.

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