Laser ablation of Ag in water and in nitrogen gas atmosphere: Shift and broadening of emission line profile of ablated Ag atoms

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Abstract. Laser ablation of Ag in water, and in N₂ gas atmosphere for comparison, has been studied by emission spectroscopy. A self-reversed dip in the emission line of Ag (I) appearing at around 338 nm was investigated. Shift of the wavelength of the self-reversed dip was observed. The shift was larger in water than in N₂ gas atmosphere. The relation between the density and self-reversed dip was investigated.

1. Introduction

Recently, laser ablation of solid targets submerged in liquid is attracting increasing attention [1] – [4], because of its potential application of nanoparticle formation directly in liquid. A major difference between the liquid-phase and gas-phase laser ablation is the pressure and density of the plume, i.e., they are very high in liquid because of a strong confinement effect.

We have studied the laser ablation both in liquids and gases by emission spectroscopy [5] – [8]. In the emission spectra the self-reversed dip is often observed. When the self-reversed dip appears, information about the spatial distribution of ground- and excited-state species can be obtained by comparing with a theoretical calculation [6]. The self-reversed dip results from the re-absorption of the emission by ground-state species abundant especially in the peripheral region of the plume. In the present work we found that the wavelength of the self-reversed dip shifts from the original position with time. It is probable that the plasma is quenched in the peripheral region of the plume due to the effect of the water or the gaseous ambient, and therefore, the Stark shift is not likely to be dominant in this region. Also, the Doppler shift is not expected because of the frequent collisions in high pressure gas or in liquid. Thus, we attributed the shift of the dip wavelength to molecular collisions. Then, the shift gives information on the density at the periphery of the plume. In the present work, we focused on the laser ablation plume in water. We also investigated the plume in N₂ gas atmosphere for comparison, because it gives a larger plume than in water, and hence, space resolved measurement can be performed.

2. Experimental

For the gas phase laser ablation, a target was set in a vacuum chamber equipped with a rotary pump for evacuation, a line for gas introduction, and a quartz window for laser irradiation. An Ag plate (99.98% Nilaco Co.) was used as a target and N₂ gas was used as an ambient gas. The chamber was filled with N₂ gas up to a pressure of 1520 Torr after evacuation. The pressure was measured by a
capacitance-type pressure gauge (MKS Baratron 722A). The Nd:YAG laser beam (1064 nm) was focused on the target through a 70 mm focal length lens. The full width at half maximum (FWHM) of the pulse was 20 ns and the pulse energy was ca. 90 mJ. The incidence angle of the ablation laser was normal to the target surface.

For the liquid phase ablation, Nd:YAG laser beam (1064 nm) was focused on the target through a 32.7 mm focal length lens. The target was immersed in de-ionized water (Millipore Milli-Q System) in a quartz glass cell. The other laser parameters were the same as in the gas phase ablation.

Emission from the plume was collected and focused on the entrance slit of a spectrograph (Ritsu Oyo Kogaku, MC100N) equipped with two 1800-grooves/mm diffraction gratings. In order to cover the Ag (I) $^2S_{1/2}$-$^2P_{1/2}$ (338.289 nm) line profile, the spectral range from 337 to 340 nm was observed. The intensified charge coupled device (ICCD) (Princeton Instruments, ICCD-1024MTDGE/1) gated by a high-speed pulse generator (Princeton Instruments, PG-200) was used as a detector. The timing between the laser pulse and the detector was based on the triggering signal obtained by taking a portion of the excitation laser pulse and the delay generated by the pulse generator. The exposure time was also controlled by the pulse generator. The ICCD read-out was taken into a personal computer.

In the case of laser ablation in N$_2$ gas atmosphere, the emission line spectra were measured as a function of the distance from the target. The observation position was changed by 0.05 mm. The nearest position to the target surface where the emission was detectable was assigned to be 0 mm from the surface. On the other hand, in the case of laser ablation in water, the emission is weaker and the plume is smaller than that in a gas phase. Therefore, the position of the measurement was fixed at the most brightest part of the plume.

3. Results and Discussion

A typical emission spectrum of Ag atoms observed in N$_2$ gas atmosphere is shown in Fig. 1. The emission spectrum has a self-reversed dip in the middle of the whole emission line profile.

![Figure 1. Typical emission spectrum of Ag atoms in N$_2$ gas atmosphere. The self-reversed dip is indicated by an arrow.](image)

In Fig. 2 the shift of the self-reversed dip from its original position is plotted as a function of the distance from the target surface. The shift increased until a certain distance and stayed constant in the farther region. As mentioned above, the shift of the self-reversed dip is most likely due to the molecular collisions. Therefore, the results should carry the information on the density. We examined the delay time of 21 ns (Fig. 2(a)) and 500 ns (Fig. 2(b)) at various ambient pressures. The results at 21 ns show a clear pressure effects, i.e., a higher ambient pressure gives a larger shift. This is explained by an efficient confinement effect for the plume by high ambient pressure. On the other hand we do not see any pressure effects in the case of the delay time of 500 ns. The initial explosive expansion of the plume finishes well before 500 ns. These results suggest that the density is high and rather constant in the region more distant than 0.6 mm irrespective of the delay time and the ambient...
Figure 2. Shift of the self-reversed dip plotted as a function of the distance from the target surface at the delay time of (a) 21 ns and (b) 500 ns in the case of laser ablation of Ag in N\textsubscript{2} gas atmosphere.

The distribution of the shift is consistent with the density distribution expected by the time-resolved plume imaging study \cite{9}. Thus, we conclude that the shift of the self-reversed dip is correlated with the density. Outside the plotted region in Fig. 2, we could not observe the self-reversed dip but the continuous emission or an emission line without the self-reversed structure.

In Fig. 3 the shift of the self-reversed dip wavelength is plotted as a function of the delay time. Open circles indicate the plume in water environment, while closed circles indicate the high density region of the plume at around 0.8 mm from the target surface produced in 1520 Torr of the N\textsubscript{2} gas atmosphere. The ablation plume in water is so small that we did not perform a spatially resolved measurement. The shift of the self-reversed dip observed in water is clearly much larger than the maximum shift observed in the N\textsubscript{2} gas atmosphere. This large shift observed in water decreases with delay time and finally reaches the value similar to that in N\textsubscript{2} gas.

As shown in Fig. 4 the spectral feature observed in water is considerably different from that in the gas phase (N\textsubscript{2}, 1520 Torr). The self-reversed dip is extremely broadened and the bottom of the dip is round. Since the broadening is due to molecular collisions, the broad dip, as well as the spectral shift, also suggests a high density of the ground state Ag atoms in the plume periphery. This is consistent with the concept of the confinement effect in water, since the confinement effect as well as the cooling
of the periphery due to the presence of dense water gives high density of the ablation species in the peripheral region. The spectrum in water at the delay time of 500 ns, however, becomes closer to the spectral feature observed in a gas phase at the delay time of 21 ns. This indicates that the density of the plume in water at this time range becomes comparable to that in N₂ gas atmosphere at 21 ns.

![Figure 4](image)

**Figure 4.** Typical spectral profiles obtained by the laser ablation of Ag in water with different delay times. A spectrum obtained in N₂ gas atmosphere (1520 Torr) is also shown for comparison.

4. Conclusion

Spectral profile of Ag (I) \(^{2}S_{1/2} \rightarrow ^{2}P_{1/2}\) (338.289 nm) line was investigated for the emission from the laser ablation plume produced in water environment as well as in N₂ gas atmosphere. The shift of the wavelength of the self-reversed dip was observed. In the case of laser ablation in water, the shift was larger than that in N₂ gas atmosphere. This indicates the high density of the peripheral region of the plume in water, which is consistent with the previous study. Consequently, it is suggested that spectral shift of the self-reversed dip can be an indicator of the density in the peripheral region of the plume.

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