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Lui, S. L.; Cheung, N. H.

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Resonance-enhanced laser-induced plasma spectroscopy for sensitive elemental analysis: Elucidation of enhancement mechanisms

S. L. Lui and N. H. Cheung[a)]
Department of Physics, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

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When performing laser-induced plasma spectroscopy for elemental analysis, the analyte signal-to-noise ratio increased from four to over fifty if the plume was reheated by a dye laser pulse tuned to resonant absorption. Time-resolved studies showed that the enhancement was not due to resonance photoionization. Rather, efficient and controlled rekindling of a larger plume volume was the key mechanism. The signal-to-noise ratio further increased to over a hundred if the atmosphere was replaced by a low-pressure heavy inert gas. The ambient gas helped confine and thermally insulate the expanding vapor. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1532774]

Laser-induced plasma spectroscopy (also known as laser-induced breakdown spectroscopy) is a versatile technique for elemental analysis. It can be performed remotely on practically any sample, and applications ranging from space exploration to art authentication have been demonstrated.[1–3] Unfortunately, laser ignition of plasmas is chaotic and violent. Reproducibility and sensitivity are, therefore, compromised. We recently showed that the sensitivity could be improved if the plume was photoexcited resonantly.[4] For example, we laser ablated a potassium-rich target doped with sodium as a test analyte. The expanding plume was then intercepted by a dye laser pulse (404 nm) to resonantly excite the K atoms ($4\,^2S_{1/2}\rightarrow 5\,^2P_{3/2}$). The Na 589 nm emissions were enhanced. Undoubtedly, the analytical performance of resonance-enhanced laser-induced plasma spectroscopy (RELIPS) can be improved if the underlying processes are better understood. In this letter, we report a study of the RELIPS mechanism and illustrate how the sensitivity could be further enhanced.

Cylindrical pellets of potassium iodate (KIO_3) containing 35 ppm of sodium were used as targets (for details, see Ref. 4). Lithium (55 ppm) was added when the plasma temperature T and electron density n_e were to be measured:[5] T was determined from the intensity ratio of the Li 610.3 and 670.8 nm lines, which was shown to be consistent with that deduced from the more conventional iron lines.[6] n_e was determined from the Stark width of the Li 610.3 nm line, which was shown to agree with estimates based on the linewidths of the H_α and H_β transitions.[6,7] However, n_e deduced from the width of the Li 670.8 nm line, was found to be overestimated, and corrections were necessary. In separate experiments, pellets of sodium bicarbonate ($NaHCO_3$) doped with 50 ppm lithium were used as targets.

The experimental setup, shown schematically in Fig. 1, was similar to the one used previously.[4,8] Briefly, a laser pulse (532 nm, 10 ns, and 10 Hz) from a Nd:YAG laser was apertured and imaged onto the side of the rotating target. 30 ns later, a dye laser pulse (9 ns and 10 Hz) was focused normally onto the same spot. Because near-threshold ablations were studied, the fluence of the 532 nm laser pulse was only about 800 mJ cm^{-2} (Ref. 9). The fluence of the dye laser pulse was about 460 mJ cm^{-2}, which was marginally ablative.

Unless stated otherwise, ablations were done under 1 atm of air although the sample chamber could be filled with different gases to any pressure. Light emissions from the plasma were imaged axially onto the entrance slit of a spectrograph equipped with an intensified charge-coupled device (ICCD). Analyte spectra were captured using a slit width of 300 μm, giving a 0.2 nm resolution. Lithium linewidths were measured with a 100 μm slit at 0.08 nm resolution. Time-integrated spectra were taken with an intensifier gate delay t_d of 40 ns (relative to the onset of the 532 nm pulse) and a 5 μs gate width t_b. For time-resolved studies, t_b was 50 ns while t_d was scanned. The 50 ns t_b was the electronic pulse width. The actual optical gate width was narrower.[10] It was characterized by scanning the gate across the 532 nm light pulse. The resultant pulse width was about 37 ns [full width at half maximum (FWHM)], and the occurrence of the pulse maximum was located to within $\pm$ 5 ns. For that reason, t_d was stepped at 5 ns for time-resolved studies. In all cases,

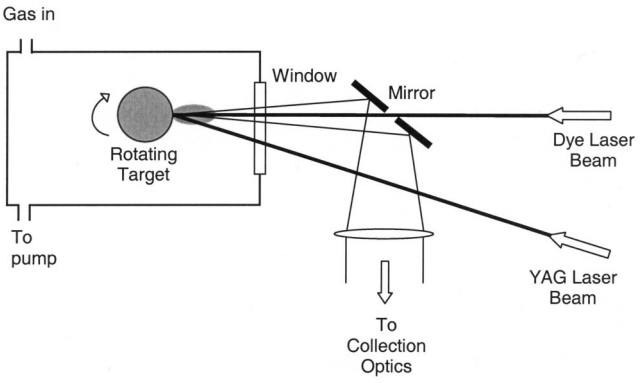

FIG. 1. Schematic diagram of RELIPS setup. A rotating cylindrical pellet of KIO_3 housed in a sample cell was ablated by the second-harmonic (532 nm) output of a Nd:YAG laser pulse of 10 ns width. 30 ns later, the expanding plume was intercepted by a dye laser pulse of 9 ns duration and 0.3 nm linewidth centering on 404.4 nm. The plume emissions were directed onto the entrance slit of a spectrograph equipped with an intensified array detector. The sample cell could be evacuated or filled with various ambient gases to any desired pressure.

a)Author to whom correspondence should be addressed; electronic mail: nhcheung@hkbu.edu.hk

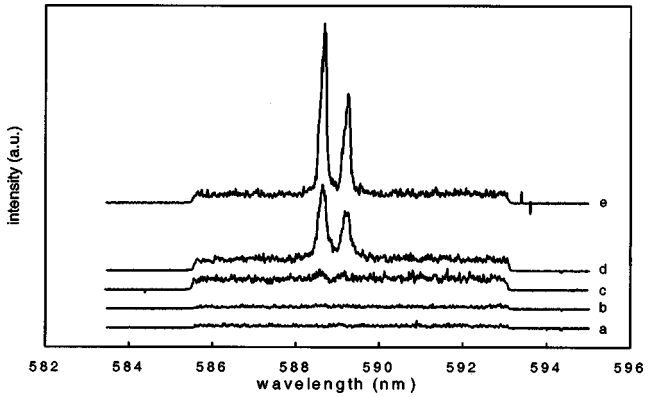

FIG. 2. Plume emission spectra generated by the RELIPS scheme. KIO_3 pellets containing 35 ppm of Na were ablated in air by a 532 nm laser pulse at a fluence of about 800 mJ cm^{-2}. 30 ns later, the expanding plume was intercepted by a minimally ablative dye laser pulse of about 460 mJ cm^{-2}. The plume emissions were time integrated for 5 μs starting 10 ns after the firing of the dye laser. Emission spectra produced by (a) the dye laser alone, (b) the 532 nm laser alone, (c) the 532 nm laser followed by an off-resonance 407 nm dye laser pulse, (d) similar to (c) except with an on-resonance 404 nm dye laser pulse, and (e) similar to (d) except the ambient gas was 13 mbar xenon instead of open air. Since the edge pixels of the charge coupled device (CCD) were not intensified, the spectral trace at the edges served conveniently as baselines in all cases. All spectra were offset vertically for clarity. The SNR for the various traces were about (a) 1, (b) 4, (c) 5, (d) 53, and (e) 110.

300 events were accumulated before the spectrum was stored and processed.

The effectiveness of RELIPS is shown in Fig. 2. Trace (a) was generated with the 404 nm dye laser alone. The edge pixels were not intensified so the two edges served as baselines. Trace (b) was generated with the 532 nm pulse alone. Trace (c) was generated with the 532 nm pulse followed by an off-resonance (407 nm) dye laser pulse. Trace (d) was similar to (c) except with the dye laser tuned to resonance (404 nm). Enhancement is clearly demonstrated. The enhancement may be quantified in terms of the signal-to-noise ratio (SNR). If we define the Na signal as the average intensity under the doublet minus the average background intensity, and noise as the standard deviation of the background, then the SNR of traces (a) through (d) are, respectively, 1, 4, 5, and 53. Trace (e) will be discussed in a later section.

The enhancement mechanism was elucidated by capturing time-resolved spectra. They were taken under conditions identical to that of Fig. 2 (traces c and d) except with a 50 ns gate width and an air pressure of 350 mbar. A lower pressure was selected to ensure a reasonable signal even under nonresonant conditions (see next). The signal and background intensities, as defined earlier, are plotted against time in Figs. 3(a) and 3(b), respectively. The dye laser was tuned to either 404 nm for the on-resonance traces (open circles) or 407 nm for the off-resonance traces (crosses). The time axis t is defined as $t_d + t_b/2$. It marks the center of the time window. Events earlier than 25 ns were not captured because of overwhelming continuum backgrounds. As can be seen, relative to the off-resonance case, 404 nm light induced a small increase in background but a marked enhancement in signal intensity and lifetime.

The evolution of the electron density $n_e(t)$ and plasma temperature $T(t)$ is shown in Figs. 3(c) and 3(d) (darker symbols), respectively. Again, resonant effects are very ap-

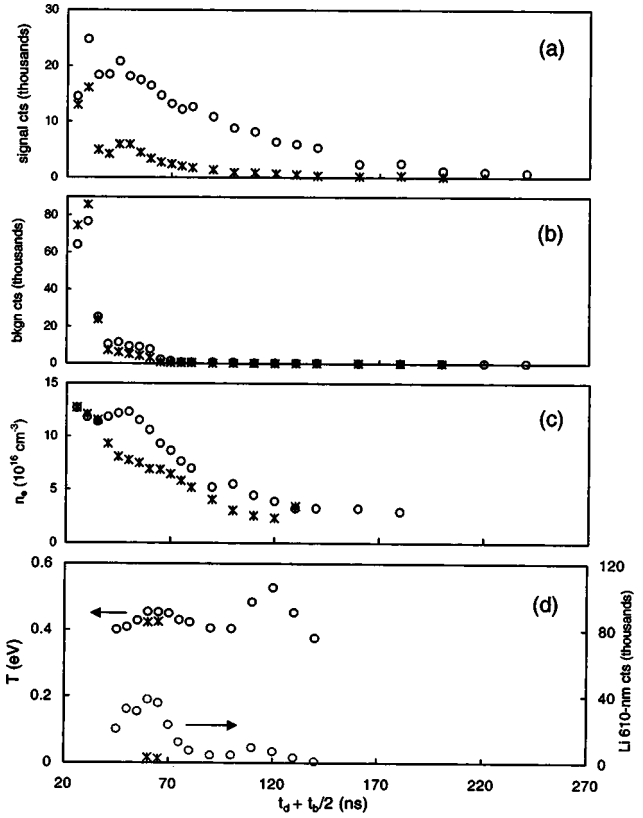

FIG. 3. Time-resolved plume emissions generated under conditions identical to that of traces (c) and (d) in Fig. 2, except the ambient gas was 350 mbar air and the ICCD gate width was 50 ns. The effective optical gate width was about 37 ns. The time axis t was the ICCD gate delay t_d plus half of the gate width t_b. Time t was, therefore, the center of the time window. Both on-resonance (circles) and off-resonance (crosses) behaviors were shown for easy comparison. The four panels are: (a) sodium signal, (b) continuum background, (c) electron density determined from Stark widths of the Li 610.3 and 670.8 nm lines, and (d) plasma temperature determined from the intensity ratio of the same pair of Li lines, together with the Li 610.3 nm line intensity (lighter symbols).

parent. The cyclic variation in T for the 404 nm case was probably due to shock waves.[11] The off-resonance T was only briefly measurable between 60 and 65 ns, when it was found to be about 0.42 eV. At earlier times, the background masked the weak Li 610 nm line. At later times, T dropped below the measurable threshold of 0.35 eV.

In addition to the obvious, three subtle observations may be drawn from Fig. 3 that are no less important. First, n_e remained high (10^{16} and 10^{17} cm^{-3}) during much of the signal lifetime, be it on or off resonance. It guaranteed local thermal equilibrium (LTE) for well-defined plasma temperatures.[12] An unnecessary resonant boost would only contribute to an unwelcome background.

Second, the resonant peaking of n_e occurred at $t = 50$ ns [Fig. 3(c)], which was 20 ns after the 404 nm pulse was fired. This noticeable delay suggests that $1+1$ photoionization,[13]

$$\mathrm{K}(4^2S_{1/2}) + h\nu(404\ \mathrm{nm}) \rightarrow \mathrm{K}(5^2P_{3/2}), \quad (1)$$

$$\mathrm{K}(5^2P_{3/2}) + h\nu(404\ \mathrm{nm}) \rightarrow \mathrm{K}^+ + e^-, \quad (2)$$

could not be the dominant electron production process. Quenching of the excited K ($5p$) atoms via electron–atom superelastic collisions would compete with photoionization (process 2).[14] Given the high n_e, collision deexcitation was

more likely. The suprathermal electrons so produced eventually impact ionized the ambient atoms to raise n_e. At the present dye laser irradiance ($\sim 10^7$ W cm^{-2}) and electron density (10^{16}–10^{17} cm^{-3}), the impact ionization time would be of the order of 10 ns.[16] That is consistent with the 15–20 ns delay (relative to the 404 nm pulse) of the n_e maximum.

Third, even though the on- and off-resonance temperatures were comparable at $t=65$ ns, the 404 nm induced Na 589 nm and Li 610 nm signals were much stronger than the 407 nm case [Figs. 3(a) and 3(d), lighter symbols]. Assuming LTE, the difference in excited state population could not be attributed to the difference in n_e.[15] The only plausible reason was a difference in the mass heated. Since the vapor plume density should be similar in both cases, a much larger volume of the plume was probably heated in the resonance case.

The second observation, concerning the role of $1+1$ photoionization (processes 1 and 2), was further investigated by ablating pellets of $NaHCO_3$ doped with lithium as the analyte. The Na-rich plume was intercepted by a dye laser beam tuned to 589 (594) nm for on (off)-resonance pumping. In this case, ionization was energetically impossible even with the absorption of a second 589 nm photon. Yet, a similar boost in the analyte (Li 670.8 nm) emissions was observed. This unambiguously showed that resonant photoionization is not essential for signal enhancement. The spatial extent (FWHM) of the Li 670.8 nm emissions was also estimated by scanning the plume image vertically across a 50 μm horizontal slit mounted in front of the spectrograph slit. The resonant image was about 400 μm tall while the off-resonance one was about 130 μm. This supports the third observation.

The difference in heated volume may be explained as follows. An off-resonance laser pulse deposits energy in a plasma via inverse Bremsstrahlung absorption. For visible light, that absorption cross section σ is about 10^{-21} cm^2 (Ref. 17). With n_e of 10^{17} cm^{-3}, the absorption coefficient α ($=\sigma n_e$) is only 10^{-4} cm^{-1}. Hotter regions near the beam focus may absorb more light because of higher n_e. So, hot spots become hotter in a positive feedback fashion leading to localized and unpredictable heating.[16] In sharp contrast, a resonant laser pulse deposits energy in the host atoms extremely efficiently. The absorption cross section of the K 404 nm transition is about 2×10^{-16} cm^2. The number density of host atoms is about 10^{18} cm^{-3} (Refs. 16 and 17). The absorption coefficient is therefore $\sim 10^2$ cm^{-1}. Uniform deposition of light energy in an extended volume is possible because local absorption is automatically capped whenever the excited population is saturated.[15] Subsequent superelastic collisions distribute that electronic energy evenly throughout the plasma plume in the form of heat. This sustains an LTE plasma at a temperature favorable for the spectrochemical analysis of sodium or lithium.[18]

Our observations have important practical implications. First, unlike photoionization, superelastic collisions thermalize the absorbed energy without directly generating more unwanted free electrons. A resonant excitation scheme is also simpler to devise than resonant photoionization, as borne out by our 589 nm excitation of Na. An ultraviolet 330 nm $1+1$ scheme or less probable 660 nm $2+1$ transitions would be required to resonantly photoionize Na.[13] Second, resonant absorption, as opposed to inverse Bremsstrahlung heating, offers efficient and controllable energy delivery to targeted atoms. Self-capping prevents local overheating. The more extensive heating means a larger heat reservoir at the optimal temperature, leading to prolonged signals. In other words, maintaining an optimal temperature is the key to analytical sensitivity.

Of course, another effective way to maintain the temperature is to reduce the heat lost from the plasma. A rarefied atmosphere would better insulate the plume and prolong the signal.[19] To test the idea, we reduced the air pressure from one atmosphere to below 0.1 mbar.[20] The analyte signal increased until around 350 mbar and then decreased. At lower pressure, the freer expansion and accelerated thinning of the plume caused a drop in signal and n_e. A heavy inert gas, such as xenon, would confine the plume even at low pressure while hardly conducting heat away. Our study showed that 13 mbar of xenon gave the best SNR. The corresponding RELIPS spectrum is shown in Fig. 2 (trace e). The SNR, as defined earlier, is about 110.

In summary, RELIPS delivered a superior analytical performance because it kept a larger plasma volume at the preferred temperature for a longer time. Interestingly, one may stretch the dye laser pulse to tens or even hundreds of μs, such as with a flash lamp pumped device. The sustained plasma and the extended signal lifetime should enhance the SNR tremendously. RELIPS studies with a long-pulse dye laser are presently underway.

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