CHEM 517

Fundamentals And Applications of Laser Induced Breakdown Spectroscopy, LIBS

CHAPTER VII

-Resonance Enhanced LIBS; RE-LIBS

Resonans Enhanced LIBS; RELIBS

✓ A possible complementary approach to resonant laser ablation technique, since1990,

✓ Reheating the plasma plume by a dye laser pulse tuned to resonant absorption of the *abundant host species (matrix atoms of the plasma instead of a particular analyte)* in the vapor plume.

✓ Electrons will then be freed to impact-excite the guest (analyte) atoms at a plasma temperature ideal for emission spectrometry.

✓ The energy absorbed in a selected atomic state is then distributed over all other elements through particle–particle collisions, as in DP-LIBS

✓Two laser pulses are necessary

- ✓the first pulse to ablate and atomize,
- ✓the second pulse to photoionize when the plume has cooled.

✓This is similar to the two-step approach of the so-called resonant laser ablation spectroscopy.

Analysis of Solids by Laser Ablation and Resonance-Enhanced Laser-Induced Plasma Spectroscopy, S. Y. Chan and N. H. Cheung, *Anal. Chem.* 2000, 72, 2087-2092.

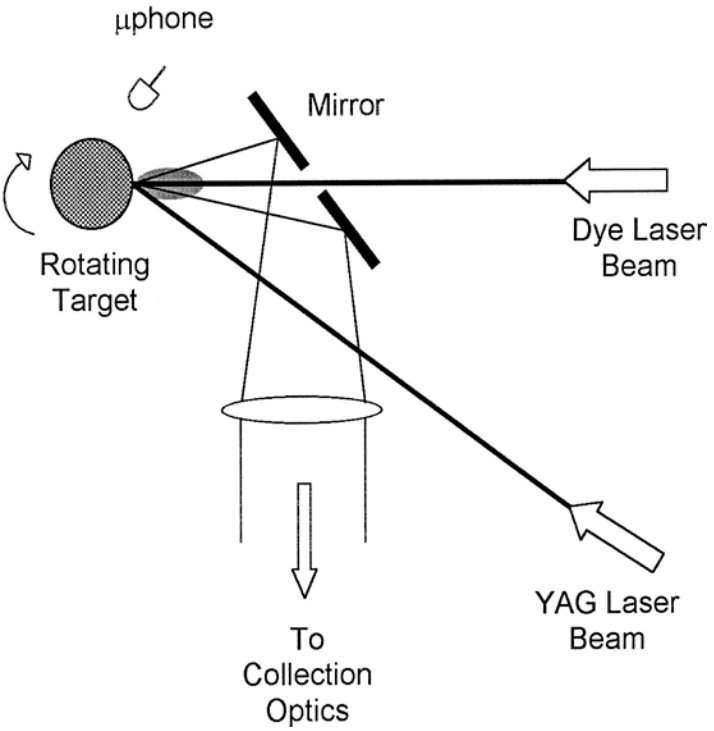


Figure 1 Experimental schematics of the double-pulse scheme are shown. The microphone monitored the photoacoustic signal to help track the amount of mass ablated.

✓ *Detecting Sodium signal in KIO3 pellet...*.

✓A rotating target of cylindrical pellets of KIO_3 was ablated in air by the second harmonic (532 nm) output of a Nd:YAG laser pulse of 5-ns width;

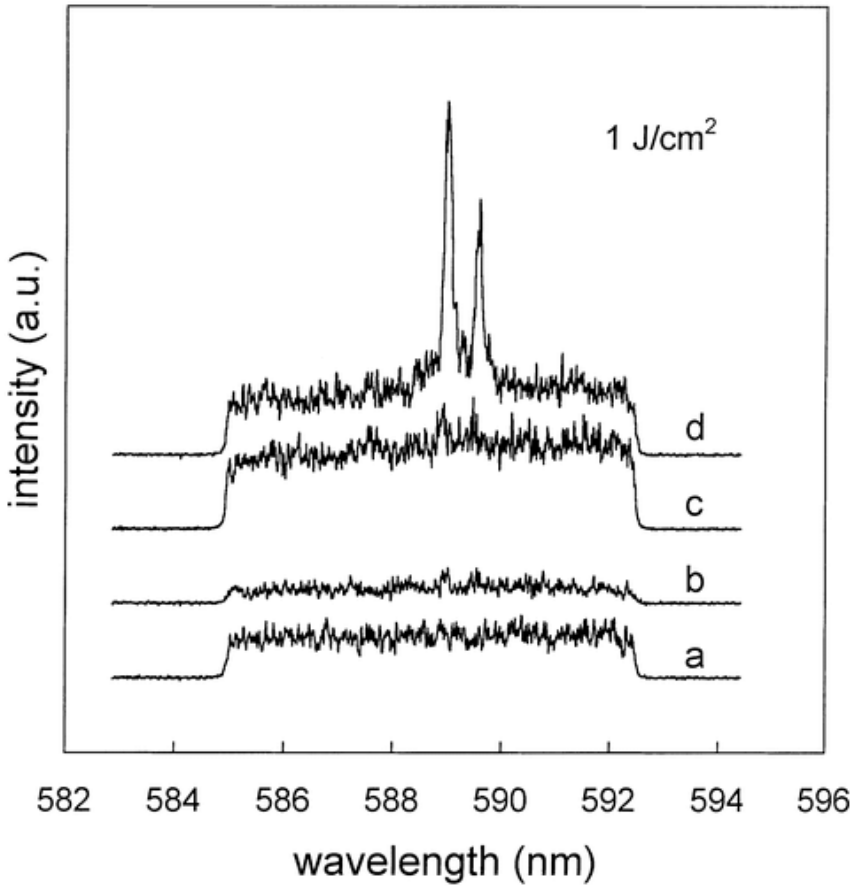
✓ 30 ns later, the expanding plume was intercepted by a dye laser pulse of 5-ns duration and 0.2-nm line width centering on 404.4 nm. to resonantly photoionize the potassium atoms in the vapor plume,

✓ The plume emissions were directed onto the entrance slit of a spectrograph equipped with an intensified array detector.

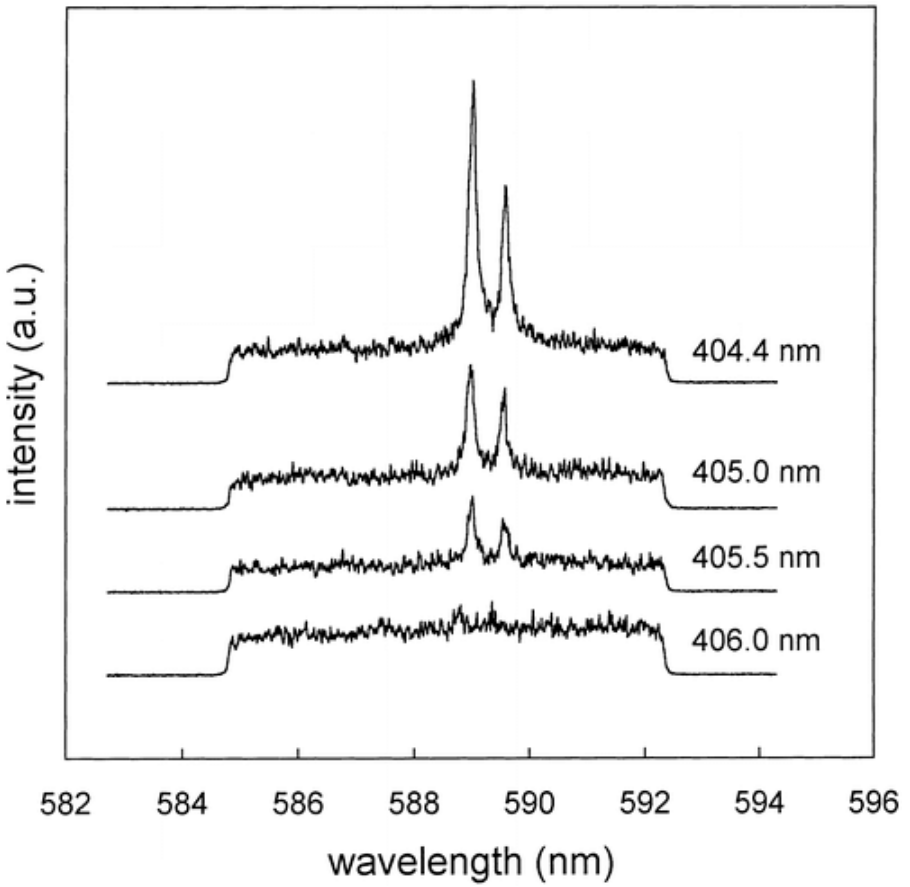
✓The 589-nm emissions of the sodium were found to be significantly enhanced. The enhancement was shown to depend critically on the profile of the 532-nm beam as well as the spatial overlap of the two laser pulses.

✓ Using this double-pulse scheme, the mass detection limit for sodium was estimated to be about 200 pg, which was five times better than that obtained by using the 532-nm laser pulse alone.

S. Y. Chan and N. H. Cheung, *Anal. Chem.* 2000, 72, 2087-2092



Emission spectra produced by
(a) the dye laser alone,
(b) the 532-nm laser alone,
(c) a 532-nm pulse followed by an off-resonance 402-nm pulse, and
(d) a 532-nm pulse followed by an on-resonance 404.4-nm pulse.



Detuning effect of the dye laser in the double-pulse scheme is shown. Spectral traces were obtained under conditions similar to those of trace (d) in the figure except with progressive detuning of the dye laser away from the resonance wavelength of 404.4 and 404.7 nm. Spectral traces were offset vertically for clarity.

Minimally Destructive Analysis of Aluminum Alloys by Resonance-Enhanced Laser-Induced Plasma Spectroscopy,

S. L. Lui and N.H. Cheung, *Anal. Chem. 2005, 77, 2617-2623*

o Nd:YAG laser was directed onto the side of a rotating sample to create a plume.

o After a delay*, a dye laser pulse (9 ns, 10 Hz, Exciton 398 dye pumped at* 355 nm) was focused onto the same spot.

oIt *was controlled* electronically to picoseconds and was adjusted to maximize the analyte signal for each Nd:YAG laser irradiance.

The dye laser was tuned to 396.15 nm to resonantly excite the Al atoms (3 $^2P_{3/2}$ to 4 $^2S_{1/2}$) to rekindle the plasma plume. Emissions from Mg, Cu,Si, and Na were observed.

o The Nd:YAG laser irradiance was varied from 40 MW cm^{-2} to 1 GW cm^{-2} to produce different etch rates.

o The dye laser energy was fixed at 0.1 mJ/pulse. It was focused to a spot size of 600 *microns in* diameter. The dye laser irradiance of 4 MW cm^{-2} was low enough to be non-ablative, as evidenced by electron microscopy.

o Plasma spectral emissions were imaged onto the entrance slit of a spectrograph equipped with an intensified charge-coupled device. The slit width was set to 300 *microns, giving a spectral* resolution of 0.2 nm.

o Time-integrated spectra were taken with the intensifier gate width set to 5 *microns and gate delay* t_d *set to 25 ns* measured from the onset of the dye laser pulse.

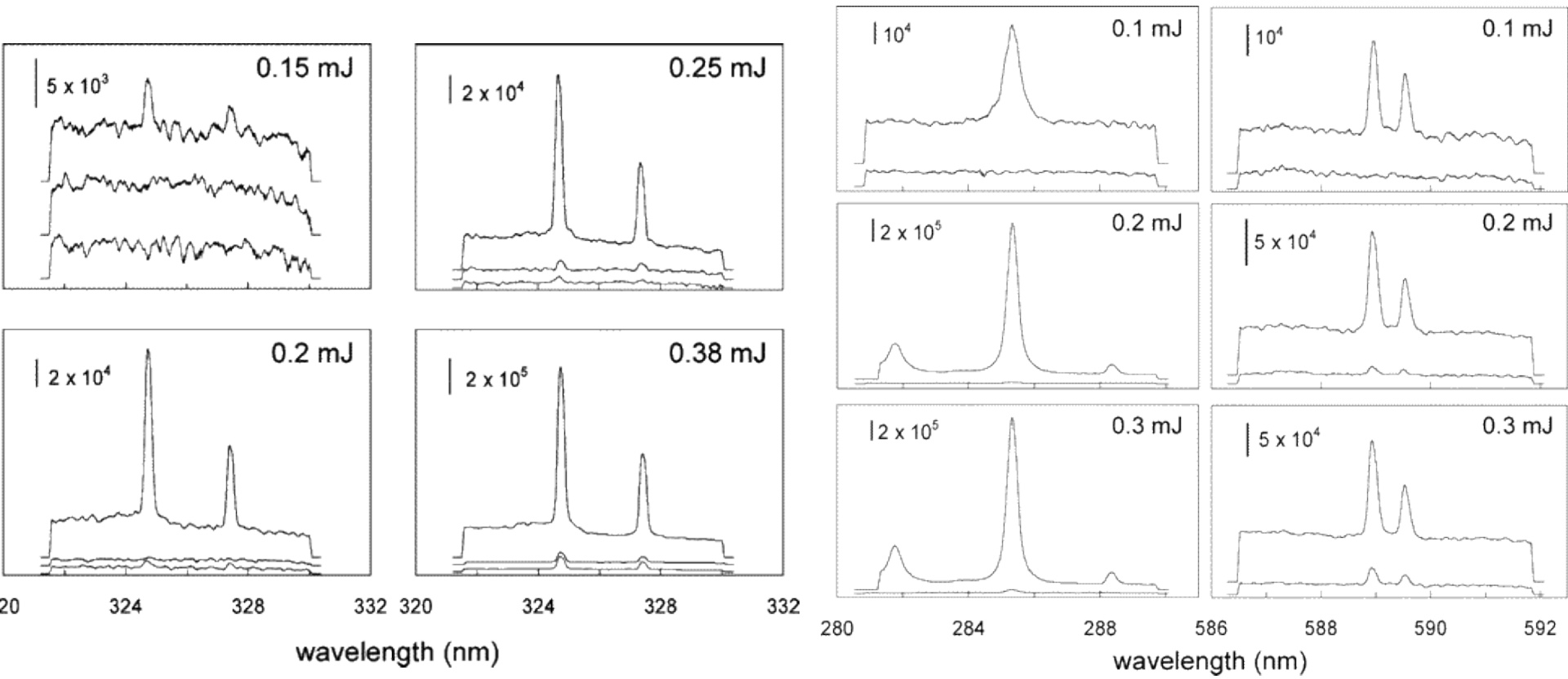


Figure 3. and 4. Analysis of Al 6061 alloys for Cu, Mg, Na by *Nd:YAG laser alone* (bottom lightest trace), followed by an *off-resonance dye laser pulse* (middle grayish trace), or an *on-resonance dye laser pulse* (upper darkest trace), at four Nd:YAG laser pulse energies. Each trace was the accumulation of 300 events and was offset vertically for clarity

Orders of magnitude improvement in SNR was demonstrated if the plasma plume was rekindled resonantly.

Investigation of resonance-enhanced laser-induced breakdown spectroscopy for analysis of aluminium alloys

Christian Goueguel, Stephane Laville, Francois Vidal, Mohamad Sabsabi and Mohamed Chaker, ***J. Anal. At. Spectrom.***, 2010,**25**, 635-644.

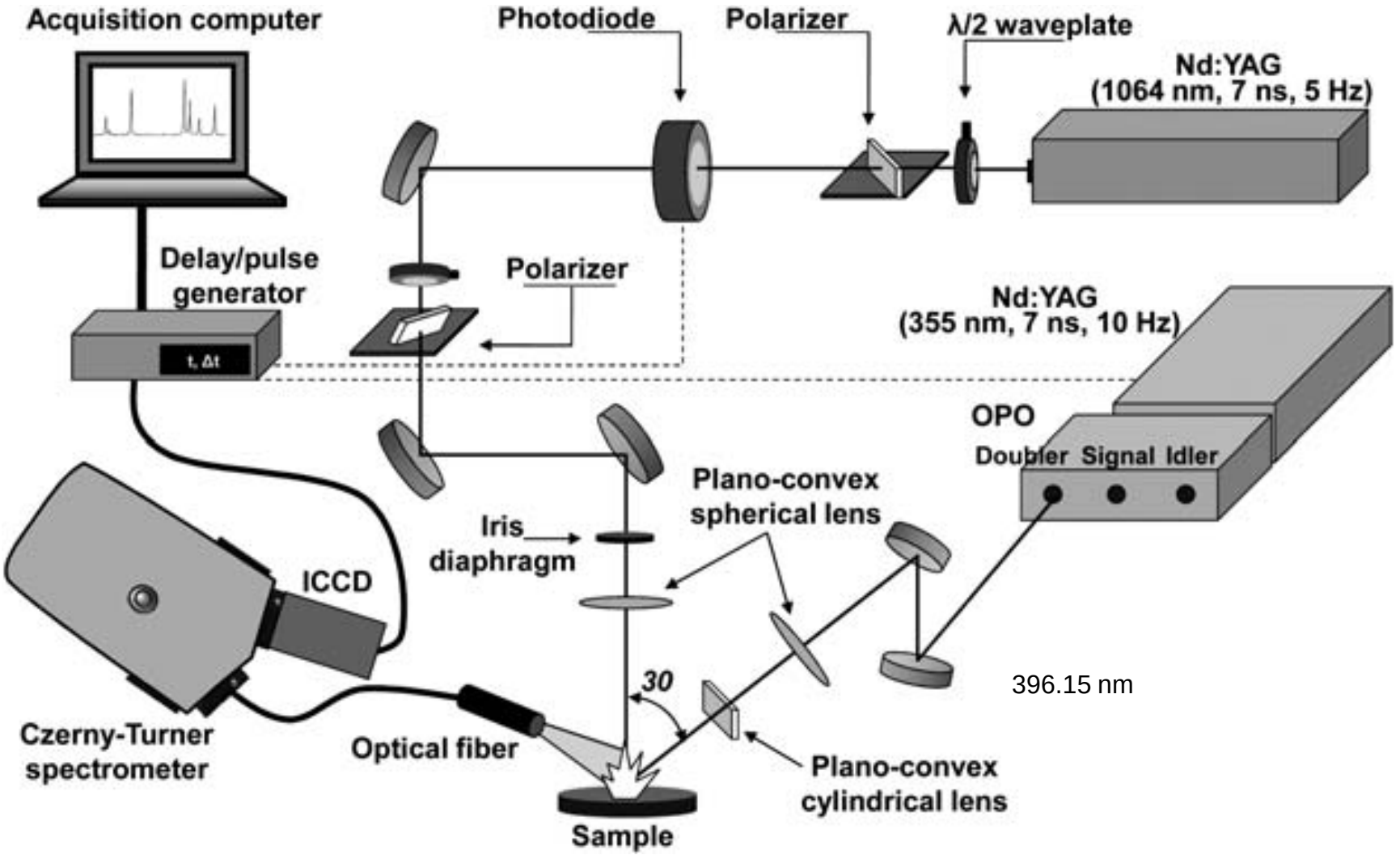
➢ to improve the limit of detection of trace elements in the context of elemental analysis of aluminium alloys.

• the influence of the main experimental parameters
  • the excitation wavelength,
  • the interpulse delay and (30 ns)
  • the ablation and excitation fluences, (3.8 J cm^2 and 1.1 J cm^2.)

on the signal-to-noise ratio for the Mg I 285.21 nm line investigated.

• at low ablation fluences, typically less than a few J/cm^2, the Mg signal at 285.21 nm achieved using RELIBS was significantly enhanced when compared to LIBS using the same ablation fluence.

• At fluences higher than 8 J/cm^2, the effect of the excitation pulse became unnoticeable and similar results were observed for both approaches.



Q-switched Nd:YAG laser pulse (7 ns, 1064 nm) was used for ablation of the samples and followed an Optical Parametric Oscillator (OPO) laser pulse (7 ns), tuned at 396.15 nm, to resonantly excite the aluminum host atoms.

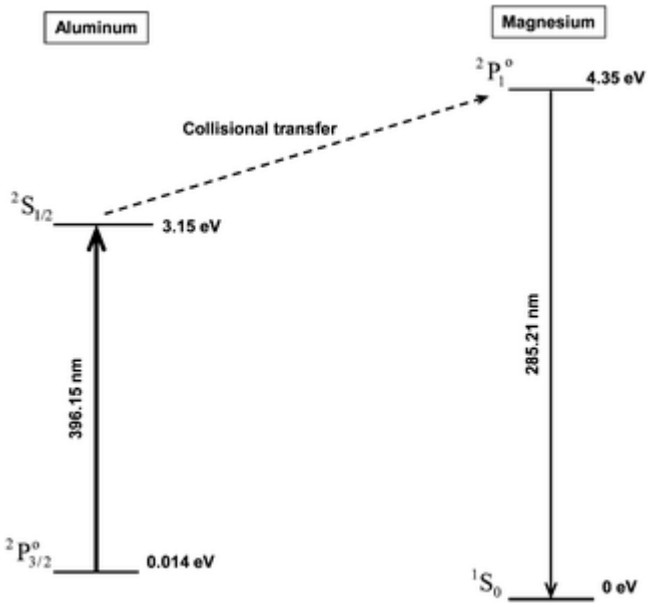


Fig. 2 Partial Grotrian diagram for excitation of magnesium from selective excitation of aluminium atoms.

• The OPO laser, tuned at 396.15 nm, excites the Al neutrals from the state $^2P^o_{3/2}$ to the upper state $^2S_{1/2}$.

• Then, the higher $^2P^o_1$ level of Mg is excited either by free electrons having undergone superelastic collisions with the excited Al neutrals (i.e., collisions in which the incident electrons gain the excitation energy of the excited Al atoms) or by direct collisions of the Mg atoms with the excited Al atoms.

• The 1.2 eV energy gap between the Mg $^2P^o_1$ state and the Al $^2S_{1/2}$ level can be filled for example by particles having undergone multiple superelastic collisions.

•The free electrons mainly come from the plasma produced by the ablation pulse or by the excitation pulse through photoionization or collisional ionization when the laser intensity is high enough.

• Then, Mg atoms decay to their ground state ($^1S_0$) by emitting a fluorescence signal at 285.21 nm. The 396.15 nm line was selected mainly because of its high spontaneous emission probability equal to 9.80×10^7 s^{-1}

Suggested Reading materials:

Investigation of resonance-enhanced laser-induced breakdown spectroscopy for analysis of aluminium alloys, Christian Goueguel,[a] Stéphane Laville,[b] François Vidal,*[a] Mohamad Sabsabi[b] and Mohamed Chaker[a]
J. Anal. At. Spectrom., 2010,25, 635-644

Resonance-enhanced laser-induced plasma spectroscopy for sensitive elemental analysis: Elucidation of enhancement mechanisms
S.L. Lui and N.H. Cheung, Appl. Phys. Lett. 81, 5114 (2002)

S. Y. Chan; N. H. Cheung; *Anal. Chem.* **2000,** 72, 2087-2092.

Laser-Induced Breakdown Spectroscopy: Fundamentals and Applications, W. Miziolek, V. Palleschi, I. Schechter (Eds.), Cambridge University Press, 2006.
Page:516-538 Double Pulse LIBS
Page: 440-476 RELIBS