Resonant laser ablation (RLA) is a selective vaporization phenomenon that makes use of tunable laser radiation, to match the ablation wavelength to a resonant gas-phase transition of the analyte of interest. The RLA phenomenon has two main characteristics, which are an increase in the number of atoms ablated from the surface, and a bandwidth of the wavelength dependence of the ablation on the order of 1 nm. These features appear to be virtually identical whether the atoms are detected by use of a microwave-induced plasma with atomic emission detection (lower left), by an inductively coupled plasma with mass spectrometric detection (lower right), or by observation of the number of laser pulses required to penetrate through thin films (top right). Optical images of the craters produced during ablation (top left), and of the laser-induced plasmas (middle right) indicate that enhanced laser–surface, laser–plume, and/or plume–surface interactions possibly occur during resonant ablation. Probably, phenomena such as radiation trapping, and desorption induced by electronic transitions, contribute to the enhanced atomic yields observed for ablation at the resonant line compared to ablation off the transition line. For more information, please see the article “Resonant Laser Ablation of Metals Detected by Atomic Emission in a Microwave Plasma and by Inductively Coupled Plasma Mass Spectrometry”, by Danielle Cleveland, Peter Stchur, Xiandeng Hou, Karl X. Yang, Jack Zhou, and Robert G. Michel.
Resonant Laser Ablation of Metals Detected by Atomic Emission in a Microwave Plasma and by Inductively Coupled Plasma Mass Spectrometry

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It has been shown that an increase in sensitivity and selectivity of detection of an analyte can be achieved by tuning the ablation laser wavelength to match that of a resonant gas-phase transition of that analyte. This has been termed resonant laser ablation (RLA). For a pulsed tunable nanosecond laser, the data presented here illustrate the resonant enhancement effect in pure copper and aluminum samples, chromium oxide thin films, and for trace molybdenum in stainless steel samples, and indicate two main characteristics of the RLA phenomenon. The first is that there is an increase in the number of atoms ablated from the surface. The second is that the bandwidth of the wavelength dependence of the ablation is on the order of 1 nm. The effect was found to be virtually identical whether the atoms were detected by use of a microwave-induced plasma with atomic emission detection, by an inductively coupled plasma with mass spectrometric detection, or by observation of the number of laser pulses required to penetrate through thin films. The data indicate that a distinct ablation laser wavelength dependence exists, probably initiated via resonant radiation trapping, and accompanied by collisional broadening. Desorption contributions through radiation trapping are substantiated by changes in crater morphology as a function of wavelength and by the relatively broad linewidth of the ablation laser wavelength scans, compared to gas-phase excitation spectra. Also, other experiments with thin films demonstrate the existence of a distinct laser-material interaction and suggest that a combination of desorption induced by electronic transition (DIET) with resonant radiation trapping could assist in the enhancement of desorption yields. These results were obtained by a detailed inspection of the effect of the wavelength of the ablation laser over a narrow range of energy densities that lie between the threshold of laser-induced desorption of species and the usual analytical ablation regime. Normal ablation employs high-power lasers in an attempt to create a vapor plume without selective vaporization, and with a stoichiometry that accurately represents the stoichiometry of species in the solid sample. RLA, as a method of selective vaporization, appears to provide an opportunity to exploit selective vaporization in new ways.

Index Headings: Resonant laser ablation; Optical emission spectroscopy; Microwave induced plasma; Inductively coupled plasma mass spectrometry; Trace metal analysis; Atomic spectroscopy.

INTRODUCTION

The use of laser ablation (LA) as a form of sample introduction has gained popularity due to several of its features, which include minimal sample preparation requirements, ability to analyze both conducting and nonconducting materials, capability for localized microanalysis, and surface analysis. The goal is to produce a low-density gaseous plume of material with the same stoichiometric ratios of constituents as found in the solid material. Normally, laser ablation for quantitative elemental analysis involves the use of high power, fixed wavelength, pulsed lasers for ablation of the sample. Various laser wavelengths have been used including 1064 nm from a Nd:YAG laser, or of harmonics of the Nd:YAG, 532 nm, 355 nm, or 266 nm. Also, excimer lasers have allowed ablation deeper into the ultraviolet (UV) down to 193 nm and 157 nm. The advantages of using UV rather than visible or infrared (IR) radiation have been discussed in various papers.

The vaporized material can be detected and quantified in a number of ways. For example, optical emission (OES) in the resultant plasma may be observed as laser-induced breakdown spectroscopy (LIBS) experiments, or the material may be swept with an inert gas directly into a mass spectrometer (MS), or into a subsidiary atom cell, such as an inductively coupled plasma (ICP) or microwave-induced plasma (MIP), for detection.

It has been shown that an increase in sensitivity and selectivity of an analyte can be achieved by tuning the laser wavelength to match that of a resonant gas-phase transition of the analyte. Tuning the ablation laser to such a wavelength has been termed resonant laser ablation (RLA), but only a few papers have studied the phenomenon in a fundamental way.
In general terms, the increase in sensitivity is a result of increased signal size for the element whose resonant transition is targeted. The increase in selectivity of the targeted element results because the signals from other components in an alloy or other bulk sample are less affected by tuning to the ablation wavelength of the target element.\textsuperscript{31-34} The explanations tendered in the literature for this phenomenon have been based primarily on Verdun’s assumption\textsuperscript{29} that the resonant interaction occurs in the gas phase after the material is nonselectively vaporized. Temporally, the first part of a single laser pulse vaporizes the sample, while the remaining part of the pulse can resonantly ionize the resultant gas-phase atoms. This results in more ions, which can be detected by a mass spectrometer. This explanation implies that RLA is another incarnation of resonant ionization spectrometry (RIS). However, this explanation is not so plausible when optical detection of the vaporized atomic species is employed, nor is this explanation likely when ICP-MS detection is used. For optical detection, an increase in atomic signal cannot be rationalized by increased ionization, while in ICP-MS, all species, atoms, and ions are ionized and detected as ions, so an increase in ionization by the laser would not appear as an increased signal. In the present paper, an increase in the size of the signal has been observed and detected by both optical detection (OES) and ICP-MS. To the best of our knowledge, only two papers to date, one by us in 1998,\textsuperscript{25} and a contribution by Pangilinan and Russell in 1999,\textsuperscript{35} have been published for RLA with OES detection, and there is no literature precedent for RLA-ICP-MS.

In the present paper, some mechanisms are postulated for the RLA phenomenon based on the experimental results obtained. Gill et al.\textsuperscript{31} have studied ion production under RLA conditions with direct time-of-flight mass spectrometry (TOF-MS). They suggested enhanced direct photophysical ejection of atoms from the surface via surface plasmon resonance as a possible mechanism for RLA. In light of the experimental evidence and the work of Gill et al., the present authors sought to explore in more detail the increase in the atomic signal, which implies either an increased number of atoms vaporized or generation of more free atoms in the gas phase from the species that have been vaporized from the solid phase.

There have been various reports in the literature concerning RLA. Here a distinction is made between those studies that use two separate lasers, or a split laser beam from a single laser to ablate and then resonantly ionize the sample, and the single-laser single-beam experiments that the present authors refer to as RLA. A complete RLA survey of literature studies done with RLA using single-laser, single-beam experimental arrangements is given in Table I. The following paragraphs give an abbreviated overview of the results reported in the literature of RLA to enable a context for the results reported here.

Aubriet et al.\textsuperscript{34} coupled RLA sample introduction with a Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS) to study trace elements in alloys, cement, and doped glass. Using a tunable dye laser pumped by a 532 nm Nd:YAG laser, the authors ablated nickel–chromium alloys containing 20% chromium and 76% nickel. The alloys were ablated using the chromium resonance wavelength at 357.87 nm, the nickel resonance at 352.45 nm, and off resonance for both elements at 355 nm; the signal was detected with a laser microprobe FTICRMS. The authors found the RLA process to be both wavelength and energy dependent. Enhancements in signal ranged from 1.5 times for nickel to 2.5 times for chromium during on-resonance wavelength ablation, compared to the off-resonance signal. In another experiment the authors observed that as incident laser power was decreased from $4.5 \times 10^{10}$ W cm$^{-2}$ to $1.1 \times 10^8$ W cm$^{-2}$, selectivity for chromium in doped glass increased by a factor of 7. Chromium yields appeared similar on-line and off-line using a laser power density of $4.5 \times 10^{10}$ W cm$^{-2}$, but at $1.1 \times 10^8$ W cm$^{-2}$, the off-line yield nearly disappeared, while the on-line yield only decreased by a factor of 2 from the higher irradiance. The authors also ablated chromium from 200 ppm chromium-doped cement off-line at 355 nm and on-line for chromium at 357.87 nm. Chromium signals during resonant ablation were found to increase by a factor of 3 compared to signals during nonresonant ablation.

Borthwick et al.\textsuperscript{36} demonstrated that an enhanced production of ions resulted if a single ablation laser was scanned through known atomic resonances. The authors used a time-of-flight mass spectrometer (TOF-MS) for the determination of aluminum in NIST stainless steel samples. A single Nd:YAG-pumped dye laser with a pulse width of 10 ns and pulse density of $1 \times 10^7$ W cm$^{-2}$ (corresponding to 1.4 mJ pulse energy) was scanned through known aluminum resonances 308.30 and 309.37 nm and directed at the target with an angle of incidence of six degrees. The ion signals at mass 27 amu were greatly enhanced on-resonance, compared to signals at other masses, and compared to signals at mass 27 amu off-resonance. Spectral features had base-widths of the order of 100 pm and were centered around the aluminum gas-phase transition lines. In another experiment, the ablation laser was directed at the sample while ablation for 500 laser shots at fixed wavelengths, both on- and off-line, 308.3 nm and 307.5 nm, respectively. The on-resonance mass spectrum confirmed that RLA provided significant enhancement of the aluminum signal with an estimated detection limit of 5 ppm. Also, the authors showed that lower laser energies are required to achieve a significant enhancement when the laser is on the resonance line (on-line) compared to that obtained off the resonance line (off-line). As the energy of the laser increased both on- and off-line, the signal ion increased and the signal on- and off-line appeared to be similar at energies exceeding $1.4 \times 10^7$ W cm$^{-2}$ (corresponding to 2 mJ pulse energy). This implies that the normal ablation process was dominant above 2 mJ.

Verdun et al.\textsuperscript{39} explored the utility of RLA for the analysis of cadmium, copper, and molybdenum in thin metal-doped polymers and steel alloy samples by use of a laser microprobe mass analyzer. The authors used a single pulse to achieve both ablation and resonant ionization and compared their results to resonant ionization spectroscopy (RIS). By use of a 10 Hz Nd:YAG pumped dye laser with a 25 ns pulse width and a power density of $10^7$–$10^11$ W cm$^{-2}$, a cadmium-doped polymer was resonantly ablated, which resulted in a factor of five increase in Cd$^+$ signal intensity. The authors noted that particularly broad spectral features, on the order of 400–700 pm, resulted,
which they attributed to plasma pressure broadening during the proposed gas-phase excitation.

Gill et al.\textsuperscript{31} studied the use of low powers for the RLA of copper samples, including bulk copper and thin film samples, using a 10 Hz excimer-pumped dye laser with a pulse width of 12 ns and a power density between $1.4 \times 10^4$ and $5.5 \times 10^6$ W cm$^{-2}$. It was shown that RLA permitted the selective ionization, 1:10$^3$:1, of trace analyte from solid materials using power densities $\leq 2 \times 10^6$ W cm$^{-2}$. In another experiment, the authors measured velocity distributions of particles leaving the surface under copper RLA conditions, but did not look at velocity distributions at nonresonant wavelengths. These velocity distributions closely fitted to Maxwellian curves, which prompted the authors to believe that the desorption process may have a thermal component. However, the high-order dependence of the ion yield on laser intensity ultimately led the authors to speculate that the enhanced ion yields were produced via direct photophysical excitation following absorption by surface plasmons.

Pangalinan and Russell\textsuperscript{35} reported the laser vaporization of aluminum films using an 8 ms flashlamp-pumped dye laser, with a fluence of 17–23 J cm$^{-2}$ and a spot size of 1 mm. The authors scanned the laser from 506–514 nm, through known aluminum oxide molecular resonant transition lines. A rapid scanning imaging spectrograph monitored aluminum emission at 394 and 396 nm, and aluminum oxide bands from 400–570 nm, while a streak camera monitored the emission as a function of time. The authors observed dramatic increases in AlO emission when the laser was tuned to 510, 512, and 514 nm, corresponding to molecular transitions of AlO, compared to emission while the laser was off-line. The enhanced bands disappeared after the aluminum film was burned through, and also disappeared when the laser was shut off. In another experiment, emission signals from aluminum at 394 and 396 nm were observed to have unusually long lifetimes of up to 200 $\mu$s after the laser pulse. Light was observed to be transmitted through the film after 2 $\mu$s of ablation, and this was interpreted as fast expulsion of material, later observed as a hole in the film. The authors hypothesized that the long lifetimes were due to expulsion of Al fragments from the surface of the films, followed by laser vaporization of the solids in air and subsequent ablation plume expansion and re-action with atmospheric oxygen. Increased collisions and increased energy imparted to AlO by the resonant wavelength were believed to facilitate excitation of aluminum in the plume, resulting in aluminum emission and extended emission lifetimes.

Resonant laser ablation experiments have been published for numerous metal species in a variety of matrices, as shown in Table I, and several underlying themes have emerged in the literature concerning the RLA phenomenon. The majority of RLA studies were done with TOF-MS detection, with ablation by a pulsed, tunable dye laser tuned to a one- or two-photon atomic transition for the analyte of interest. Resonant enhancements on the order of 1.5 to 10 times have been observed at the unperturbed gas-phase transition wavelengths for the analyte,\textsuperscript{10,33,37–43} while signals from the bulk matrix have been shown to be limited or nonexistent.\textsuperscript{12,44} Ablation scan peak-widths fall into two regions: 5–20 pm\textsuperscript{45,46} and 100 pm–1 nm at full-width at half-maximum (FWHM).\textsuperscript{47–49} Most authors have attributed the relatively broad spectral features to collisional broadening in the vapor-phase plume,\textsuperscript{30,51} while narrow spectral features imply that RLA occurred in the gas phase without significant collisional broadening. Moderate incident power densities, ranging from $10^6$ to $10^9$ W cm$^{-2}$, have been fruitful in producing resonant enhancements; indeed, laser energy is critical to the RLA phenomenon, as enhancements disappear at larger fluences.\textsuperscript{47,52,53} Resonant experiments have been shown to be more efficient than nonresonant experiments and to require less energy to produce the same yields.\textsuperscript{54,55} The resonant process has been shown to become increasingly efficient relative to the off-line process as energy is continuously decreased.

The majority of authors have attributed the observed enhancements to nonselective ablation followed by resonant ionization in the gas-phase plume, as postulated by Verdun et al.\textsuperscript{29} Few authors have offered alternative explanations for the resonant enhancements observed. Eidem et al.\textsuperscript{32} and Allen et al.\textsuperscript{38} acknowledged that the RLA mechanism is highly nonthermal in nature, confirmed by the high photon order of the RLA process. Gill et al.\textsuperscript{31} felt that increased desorption of species occurs in RLA and postulated that surface plasmon resonances were responsible for such desorption, with possible assistance from a thermal mechanism, but that selectivity occurred by resonant ionization in the plume, as postulated by the Verdun theory.

While the two-step Verdun theory is feasible for particular experimental arrangements that directly observe the ion yield, the mechanism for the single-laser, single-beam RLA arrangement requires further explanation in light of the observations in the present paper, as well as others. In contrast with the ion signal enhancement, well established in the literature, the present authors, along with Pangalinan and Russell,\textsuperscript{33} have demonstrated the enhanced generation of atoms using detection by optical emission spectroscopy.

For direct mass spectral detection, most commonly employed in the literature, an increase in ionization in the vapor state would appear to be the same as an increase in the number of species vaporized from the surface. However, with optical detection, an observation of enhanced atomic emission at an atomic transition line is more likely to be the result of increased numbers of species vaporized from the surface, rather than an increase in ionization above the surface. Furthermore, while increased atomic emission could be a result of increased excitation in the gas phase, this is not true for ICP-MS detection. Here, all species produced are likely to be ionized in the inductively coupled plasma; thus, the signal would be proportional to the number of species vaporized from the surface, rather than those ionized in the vapor-phase ablation plume.\textsuperscript{56}

The implication of the ablation measurements in the present paper lies in the notion that an enhanced gas-phase excitation, as suggested by the Verdun theory, could exhibit high spectral resolution as seen by some authors, while the wider spectral widths, observed here, indicate that not only gas-phase collisional broadening but also solid-state electronic effects could be involved. RLA is explored here using single laser, single beam.
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<sup>a</sup> Tunable dye laser, unless otherwise noted.
high-resolution ablation wavelength scans, detected with both MIP-OES and ICP-MS detection systems. The RLA phenomenon was further demonstrated with thin film penetration data that counted the number of laser pulses required to burn through thin films. Surface characteristics of the observed craters indicate a possible enhanced laser–material interaction, which is not covered in the accepted theory. An explanation for the experimental results reported here, and elsewhere, is postulated to involve the phenomenon of radiation trapping and increased sputtering of the surface by the resultant increased plasma temperatures. In addition, it appears that the desorption induced by electronic transitions (DIET) process is involved in the sputtering process.

EXPERIMENTAL

Two types of spectra can be obtained by RLA. The first can be obtained by scanning the ablation laser wavelength while detecting the emission intensity from vaporized species at a different optical emission wavelength. Likewise, in a mass spectrometer, the detected analyte mass is fixed while scanning the laser wavelength. In this paper these experiments are termed “ablation wavelength scans”. Second, an optical spectrum can be obtained by keeping the ablation laser wavelength fixed at a gas-phase atomic transition and then scanning the detection monochromator to obtain the emission spectrum. Here, this is termed the “emission wavelength scan”. Similarly, a mass spectrum can be obtained by fixing the ablation laser wavelength at a gas-phase atomic transition while scanning the mass spectrometer through the isotopic masses of the analyte of interest. Here, this is termed a “mass scan”.

Atomic Emission Detection. A schematic diagram of the experimental arrangement is shown in Fig. 1 for RLA coupled with MIP atomic emission detection. The ablation chamber is similar to that described by Uebbing et al.\textsuperscript{57} and it was used by us in two previous reports.\textsuperscript{24,25} For this work, some refinements were made. In this apparatus, the Beenakker MIP cavity is water cooled and the plasma is sustained by low-pressure argon gas between 500 mTorr and 2 Torr.\textsuperscript{58} The sample is inserted into the chamber from below and is mounted to a stepper motor. The sample holder is off-centered by 5 mm with respect to the center of the cavity so that it could be rotated to obtain a fresh sample surface. The distance between the sample surface and the bottom of the Beenakker cavity is about 2 to 3 mm. The system was designed so that the sample could be easily replaced without disturbing the MIP; and sufficient vacuum could be obtained quickly after sample replacement. The glass plasma tube with its silica window is inserted into the cavity, and the plasma tube and the glass cell is sealed to the cavity with Viton 70\textdegree O-rings. Ultra high purity argon gas is introduced tangentially into the glass cell to sweep vaporized material into the microwave cavity and to act as the plasma support gas. A mechanical vacuum pump was used to provide a low argon pressure, which was about 800 mTorr for these experiments. A 2.45 GHz microwave power generator (Microtron 200, Electro-medical Supplies, Ltd., Oxfordshire, England, max power 120 watts) powered the microwave field over an operating range from 30 to 50 W. An impedance matching tuner (Model 1878B, Maury Microwave Corporation, Ontario, Canada) was employed to obtain minimum reflected power before the energy was transferred into the Beenakker cavity through a coaxial cable. A microwave power of 45 W was generally used to minimize heating effects and protect the O-rings. The entire ablation chamber was mounted on a vertical rail system to ensure proper focusing of the MIP with respect to the detection system.

The 355 nm output of an injection seeded, Q-switched Nd:YAG laser (10 Hz) (GCR 250, Spectra Physics Laser, Mountain View, CA) was used to pump an optical parametric oscillator (OPO) laser (Quanta-Ray MOPO 730, Spectra Physics Laser, Mountain View, CA). The fundamental output wavelength range of the OPO was 440–1840 nm and, after frequency doubling, this range was extended down to 220 nm. In this range, the output energy was of the order of 1–11 mJ/pulse with a linewidth of the order of 2–5 pm (0.15 cm\textsuperscript{-1}). The OPO laser system has a pulse duration of 6 ns and was previously characterized in Ref. 59. The laser’s output energy was adjusted using an attenuator (Model 935–3, Newport Corporation, Fountain Valley, CA).

The laser beam was first attenuated and then reflected 90\textdegree vertically by use of a right-angle silica prism and passed through the hole in the center of a custom-made ellipsoidal mirror (Aero Research Assoc., Inc., Port Washington, NY) before entering through the silica window of the MIP cavity. A biconvex lens, \(f/9\), was used to focus the beam onto the surface of the sample, resulting in a spot size of 250 \(\mu\)m in diameter. The sample was then ablated and swept into the MIP cavity, where species could be re-excited. The emission from the species within the microwave plasma was collected with the ellipsoidal mirror and focused onto the entrance slit of a monochromator (Model 218, McPherson, Acton, MA; focal length, 1/3 meter; 1200 grooves; bandpass, 0.4 nm; maximum spectral resolution, 0.06 nm). A color glass bandpass filter was used to reduce the scattered and stray laser radiation (Corning CS 7-59; 300–480 nm transmitting; half-width transmittance, 40%; peak transmittance, 380 nm, 85%).
The detection system consisted of a photomultiplier tube (EMI model 9893Q and housing model 0893-492, Products for Research, Inc., Danvers, MA), a preamplifier (Model VV100 BTB, LeCroy Corp., Chestnut Ridge, NY), a boxcar integrator (Model 162 with gated integrator 165, Princeton Applied Research, Princeton, NJ), and a computer for data collection (Model P5-60, Gateway 2000, North Sioux City, SD, with data collection software written in Microsoft Visual Basic). The boxcar integrator was triggered by a laboratory-constructed optical trigger circuit consisting of a fiber-optic cable fitted to a side-on IP28-type PMT (Hamamatsu, Japan) mounted in an LD-R2 housing (CVI Laser Corp., NM) driven at −300 V.

### Inductively Coupled Plasma Mass Spectrometric Detection

A schematic diagram of the experimental arrangement is shown in Fig. 2A for RLA coupled with ICP-MS detection. The mass detection system consisted of a PlasmaQuad II ICP-MS with quadrupole analyzer (Fisons/VG Elemental, Windsford, England, UK), controlled with PQ Vision software running under the IBM OS/2 operating system. Sampling and skimmer cones were made of nickel. The laser beam was first attenuated to the required energy and then reflected 90° vertically by use of a right-angle silica prism and focused with a biconvex lens, f/1.3, resulting in a spot size of about 160 μm. The laboratory-constructed ablation cell, shown in Fig. 2B, was custom-machined from Delrin® and fitted with a half-round, 1.5 mm thick quartz window directly above the sample holder. Argon sweep gas was introduced through a quarter-inch Swagelok fitting, passed through a series of baffles, then through an array of half-inch, 18-gauge, 316 stainless steel hypodermic tubing, arranged in a half circle, before entraining the ablated material. This array of tubing was designed to produce a fairly laminar flow of gas over the sample. The entrained ablated material was then passed through a half-funnel before entering the transport tubing to the ICP-MS. The total volume of the ablation cell, including the half-funnel, was 5 cm³.

The sample cell holder consisted of a sample cup that could accommodate 5/8-in. diameter samples, as used in the RLA-MIP-OES experiments, so that the samples could be used interchangeably between experimental arrangements. The shaft of the sample holder was equipped with a friction-fit O-ring seal to allow for ease of sample replacement. The body of the cell was mounted to a stand and to an optical bench. The cell body was calibrated to accommodate a large range of incidence angles. For these experiments, the cell body was rotated to a 60° angle from the horizontal, to result in a 30° angle between the laser beam and the sample. This angle gave the maximum signal both on and off the resonant line.

The transport tubing was Tygon® (Fisher Scientific, Pittsburgh, PA) and was 2.4 m in length with a 1/4-in. inner diameter and a 3/8-in. outer diameter. An ambient pressure stream of argon flowed through the ablation cell at a rate of 0.7 L min⁻¹ and the transport tube was connected directly to the ICP torch with a laboratory-constructed ground-glass ball joint.

The pulse-to-pulse variation in laser energy was monitored during ablation scans using a laboratory-constructed optical monitoring circuit consisting of a fiber-optic cable fitted to a side-on IP28-type PMT (Hamamatsu, Japan) mounted in an LD-R2 housing (CVI Laser Corp., NM) and driven at −300 V.

### Samples

The samples used were NIST Spectrographic Stainless Steel Standards (D845) and (D839), pure aluminum, pure deoxygenated copper, and chromium oxide deposited by chemical vapor deposition (CVD) on a quartz substrate. The constituents of NIST SSS D845 and SSS D839 are listed in Table II.

### RESULTS AND DISCUSSION

**Crater Morphology and Imaging.** In order to determine whether or not a wavelength-dependent laser–surface interaction existed, craters were formed on a pure, deoxygenated copper sample by ablating for 1000 shots at 0.75 mJ (2.5 × 10⁸ W cm⁻² peak irradiance per pulse) at each of several wavelengths over a 1 nm wavelength range.
range encompassing the resonant gas-phase transition of copper, from 324.254 to 325.254 nm. These craters, 250 μm in diameter, were then imaged using both an optical microscope and a scanning electron microscope (SEM).

From the optical images, shown in Fig. 3A, an outer ring of apparently re-deposited material was formed as the ablation laser wavelength approached that of the resonant transition of copper, 324.754 nm. This ring dissipated as the wavelength of the ablation laser progressed beyond the resonant gas-phase atomic transition. Based on this change, a wavelength-dependent laser-material, or plasma-material, interaction appears to exist.

Upon closer inspection of the center of these craters with SEM (Fig. 3B), distinct changes in morphology were evident as the resonant line of copper was approached. At 500 pm off-line, small beads of copper were observed, appearing more wave-like at 250 pm and 50 pm off-line, and finally, significant melting was observed at the resonant wavelength, 324.754 nm. This may indicate that the RLA phenomenon ultimately has various thermal effects. From both sets of images, it is evident that any discussion of the mechanism of RLA should involve a wavelength-dependent interaction between the laser and the solid sample, or between the resultant laser-induced plasma and the solid surface, in addition to gas-phase processes. This is inconsistent with the Verdun mechanism, which suggests that the resonant excitation might occur exclusively as a gas-phase process.

A line scan SEM image of a crater formed on pure deoxygenated copper using 1000 shots of 0.75 mJ per pulse energy at the resonant wavelength of copper, 324.754 nm (Fig. 4), corroborated the existence of a ring of apparently re-deposited material around the outer crater edges. Here, the line represents the relative crater depth, although the center of the crater cannot be considered to be a true crater, but rather a disruption in the morphology of the sample surface. This is corroborated by observations made by Gill et al. during RLA experiments. Mao et al. noted similar post-ablative surface morphologies during normal ablation experiments on bulk metal targets.

Another view of the RLA process was obtained by looking at craters both on-line and 500 pm off-line under various laser power densities. The optical images in Fig. 5A indicate that at high power densities, using 2 mJ laser energy per pulse, which corresponds to about $6.8 \times 10^8$ W cm$^{-2}$ peak irradiance per laser pulse, the ablation process appears to be roughly similar, with both on-line and

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**Fig. 3.** Crater imaging and morphology. (A) Optical images of craters formed on pure, deoxygenated copper samples. As the laser wavelength approaches that of the resonant atomic gas-phase transition of copper, 324.754 nm, an outer ring of re-deposited copper is observed. (B) SEM images of the centers of the craters shown in panel A reveal changes in surface morphology of the center of the craters at 500 pm off-line (324.254 nm), 250 pm off-line (324.504 nm), 50 pm off-line (324.704 nm), and on-line (324.754 nm).

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Laser-Induced Plasma Imaging. The laser-induced plasma was observed to be larger and brighter as the laser wavelength approached that of the resonant line. This visually observable difference in on-line and off-line ablation is illustrated (see Fig. 6) with video still-frames of the resultant plasma taken with a digital camcorder (Sony DCR-TRV310, Sony, Tokyo, Japan). The exposure on the camera was adjusted to allow only light from the plasma to be observed. The camera was positioned 1.5 inches from the sample surface. The sample used was 99.8% pure copper foil (Alfa Aesar, Ward Hill, MA) with a thickness of 10 μm. Each sample was ablated for 300 laser shots at 3 mJ laser energy (corresponding to 1 × 10^9 W cm^2 per pulse). As seen in Fig. 6, the plasma size and brightness were markedly increased for on-line ablation (324.754 nm) compared to 3 nm off-line (321.754 nm). This difference may indicate that an enhanced laser-material interaction occurs when the laser is tuned to the
resonant gas-phase transition of copper. Also, the larger plasma may be responsible for the re-deposition of material around the edges of the ablation craters via an enhanced plume–material interaction, as described below.

**Delay Time Between the Laser Pulse and Detection by Microwave-Induced Plasma.** A series of delay time experiments produced the results shown in Fig. 7. In Figs. 7A and 7B the atomic emission was observed directly in the laser-induced plasma, with the MIP not operating, under resonant (RLA) and non-resonant (LA) conditions, respectively. In Figs. 7C and 7D, the atomic emission was observed in the MIP under RLA and LA conditions, respectively. Subtraction of the graphs gave the plots labeled 7E (C − A) and 7F (D − B). The laser pulse width was 6 ns, so the time scale of the laser pulse width was not significant compared to the time scale of the processes seen in Fig. 7. For a pure aluminum sample, the resonant line at 308.216 nm was used for resonant laser ablation while the atomic emission was monitored at 396.2 nm across a range of delay times up to 20 μs after the laser pulse, and with a gate width of 30 ns. Figure 7A indicates that the aluminum emission signal was present up to 15 μs after the resonant ablation laser pulse when the MIP was not employed. The emission was then observed approximately 1 nm off the resonant atomic transition of aluminum (307.259 nm). Figure 7B indicates a shorter-lived atomic emission compared to its on-line counterpart (Fig. 7A). Probably, this extended emissive lifetime indicates that plume species were cyclically re-excited in the LIP, during RLA, through resonant radiation trapping, as discussed below. It could be postulated that resonant heating of the plasma might increase the continuum background but that, off resonance, the continuum background would drop. However, any such changes in the level of the continuum and of atomic excitation in the LIP between A and B were dominated by the increased numbers of vaporized atoms detected by the MIP in C and D. This is evidenced by the small signal magnitudes in Figs. 7A and 7B compared to Figs. 7C and 7D, shown by the subtracted Figs. 7E and 7F.

Within the noise of the measurements, the size of the signal in 7E and 7F is about the same at all delay times. Also, a long delay time before detection would measure increased numbers of atoms vaporized, because no laser-induced plasma emission is observed at long delay times (Fig. 7A and 7B). Short delay times would measure the sum of increased excitation in the LIP and increased numbers of atoms vaporized. The optimum delay time was observed to be 120 ns, where maximum signals were produced for both resonant and nonresonant ablation, and this delay time was used during further optical emission experiments reported here. In Figs. 7C and 7D, after RLA and LA, respectively, the vaporized aluminum atoms were re-excited by the MIP and signals were visible at least up to 20 μs. The relative emission after resonant ablation, 7C, was approximately 2 to 3 times greater than for nonresonant ablation, 7D. This same level of enhancement was also observed without re-excitation in the MIP by comparison of Figs. 7A and 7B, where the relative emission intensity in A can be observed to be at least 2 to 3 times greater than that in B. Hence, inspection of Fig. 7 leads to the conclusion that the dominant process in RLA is ablation of more atoms, with secondary processes being an increased excitation of atoms in the plasma, and possible changes in the level of the continuum. The enhancements by factors of 2 to 3 were similar to those found in the ICP-MS measurements discussed below.

**Microwave-Induced Plasma Emission Wavelength Scans. Pure Aluminum.** While the ablation laser was held at a fixed wavelength, the atomic emission signals from the samples discussed below were detected by scanning the monochromator through a 5 nm wavelength range at a rate of 1 nm min⁻¹, encompassing the analyte atomic emission line and possible close-lying emission lines of other constituents. Based on the delay time optimization above, a delay time of 120 ns was employed with a gate width of 30 ns. A monochromator slit width of 15 μm with a PMT voltage of −1600 V gave the highest signal-to-noise ratio. A laser energy of 2 mJ per pulse was used, corresponding to a peak irradiance of \( 6.8 \times 10^8 \text{ W cm}^{-2} \) per pulse, which was focused on the sample, resulting in a 250 μm spot size. Atomic emission scans on a pure aluminum sample were obtained at the aluminum resonance line, 308.216 nm, and 500 pm off-line, at 307.716 nm. For these experiments, the laser was directed normal to the sample surface for each of these wavelengths, while the monochromator was scanned through a five-nanometer range to encompass both emission lines at 394.403 and 396.153 nm. Although the wavelength of the ablation laser differed between the two emission scans by only 500 pm, the resonant enhancement, shown in Fig. 8, was a factor of 5 and 8 for the emission lines at 394.403 and 396.153, respectively. The ratio of the intensity difference between the two emission

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**Fig. 7.** Effect of delay time after laser pulse on emission intensity using (A) resonant ablation with the MIP off; (B) nonresonant ablation with MIP off; (C) RLA with the MIP on; (D) nonresonant ablation with MIP on; (E) RLA with the MIP on, with signal from the laser-induced plasma removed; and (F) nonresonant ablation with MIP on, with signal from laser-induced plasma removed. Gate width was 30 ns. See text for more details.
Fig. 8. Emission scans of pure aluminum sample with optical emission detection in an MIP, while ablating at (A) the resonant gas-phase atomic transition and (B) 500 pm off-line. The inset shows a simplified partial Grotrian diagram of the aluminum atom.

Fig. 9. Emission wavelength scans for molybdenum in a NIST stainless steel sample detected by MIP-OES. (A) Ablation at the molybdenum resonant transition (313.259 nm) reveals several elements in the steel sample, with emission enhanced at the molybdenum wavelength (379.800 nm). (B) The molybdenum enhancement decreased as the ablation laser is tuned 500 pm off-line (313.800 nm), and (C) 1 nm off-line (314.300 nm). (D) No molybdenum enhancement, relative to other species in the steel, is observed during ablation 1.5 nm off-line (314.800 nm). The spectra have been offset here for clarity. The inset shows a simplified partial Grotrian diagram of the molybdenum atom.

Fig. 10. Comparison of emission signal intensities from multiple steel components during resonant and nonresonant ablation, detected by MIP-OES. (A) A signal enhancement for molybdenum, relative to other components, is observed during resonant ablation for molybdenum (313.259 nm). As the ablation laser wavelength is tuned increasingly off-line, the molybdenum emission intensity decreases to match that of the other steel components. However, it appears that the molybdenum signal intensity has been enhanced the most, despite the fact that the other components are present in roughly equal or higher concentrations in the bulk sample compared to molybdenum. The molybdenum emission signal has been enhanced by a factor of 3 on-line, compared to 1.5 nm off-line, while the nickel, niobium, manganese, and iron emission intensities have each been enhanced up to 1.5 times on-line compared to 1.5 nm off-line. It follows then, that in the on-line case, the molybdenum emission has been enhanced by at least a factor of 2 in relation to the emission from other steel components, as illustrated in Fig. 10B, where the ratio between the molybdenum and nickel emission signals obtained at various ablation wavelengths is shown. The emission intensity of molybdenum was obtained at various ablation wavelengths and normalized to the emission intensity of nickel at the same ablation wavelength. As the ablation laser wavelength progressed away from the molybdenum transition to longer ablation wavelengths, the intensities of the molybdenum and nickel emission signals approached one another. Figure 10B demonstrates that ablation at the molybdenum wave-

Trace Molybdenum. The resonant enhancement effect was then investigated by studying the emission signals generated from trace molybdenum in a NIST Spectrographic Stainless Steel Standard sample (D845, 0.92% Mo), rather than the pure metals so far studied. The emission and ablation wavelengths were chosen based on the simplified Grotrian diagram of molybdenum, shown in the inset of Fig. 9. Here, the monochromator was scanned through the range from 377.7 to 382.7 nm, while ablating at a fixed wavelength. During on-line ablation (313.259 nm), as shown in Fig. 9A, several elements in the stainless steel sample are evident in the emission scan, as these elements emit in this wavelength range. As the ablation laser is tuned increasingly off-line, to 313.800 nm, 314.300 nm, and finally 314.800 nm, as shown in Figs. 9B, 9C, and 9D, respectively, the molybdenum emission signal decreased. A comparison of relative emission intensities for each steel component, during ablation at each of the above-mentioned wavelengths (see Fig. 10A), reveals that during on-line ablation for molybdenum, all of the steel components display enhanced emission. However, it appears that the molybdenum signal intensity has been enhanced the most, despite the fact that the other components are present in roughly equal or higher concentrations in the bulk sample compared to molybdenum. The molybdenum emission signal has been enhanced by a factor of 3 on-line, compared to 1.5 nm off-line, while the nickel, niobium, manganese, and iron emission intensities have each been enhanced up to 1.5 times on-line compared to 1.5 nm off-line. It follows then, that in the on-line case, the molybdenum emission has been enhanced by at least a factor of 2 in relation to the emission from other steel components, as illustrated in Fig. 10B, where the ratio between the molybdenum and nickel emission signals obtained at various ablation wavelengths is shown. The emission intensity of molybdenum was obtained at various ablation wavelengths and normalized to the emission intensity of nickel at the same ablation wavelength. As the ablation laser wavelength progressed away from the molybdenum transition to longer ablation wavelengths, the intensities of the molybdenum and nickel emission signals approached one another. Figure 10B demonstrates that ablation at the molybdenum wave-

lines, obtained while ablating on-line, was roughly what would be expected based on the atomic transition probabilities.61
length increases the molybdenum signal relative to nickel. This observation is corroborated by Peng et al., who observed signal enhancements for multiple components, including indium and iron, in a multilayer compound semiconductor during resonant ablation for zinc.

**Copper Mass Scans.** Mass scans were obtained for pure deoxygenated copper by ablating at a fixed laser wavelength while scanning the mass spectrometer through the 62 to 68 mass range, which encompasses the two copper isotopes (Cu-63 and Cu-65). The laser energy was attenuated to 1.9 mJ, corresponding to a peak irradiance of $1.6 \times 10^9$ W cm$^{-2}$ per pulse. The spectrometer was set to uptake for 10 seconds to allow ablated material to traverse the transport tube, and then data were acquired for 15 seconds.

The sample was ablated on-line (324.754 nm), 500 pm off-line (324.254 nm), and 1 nm off-line (323.754 nm). As shown in Fig. 11, the on-line signals were about 1.5 times greater than the off-line signals.

**Molybdenum Mass Scans.** Mass scans were obtained for trace molybdenum in a NIST stainless steel sample (D839, 4.61% Mo) using a fixed laser wavelength while scanning the mass spectrometer through the 93 to 101 amu range, which covers the six molybdenum isotopes. The laser energy was attenuated to 2.5 mJ, corresponding to a power density of $2.1 \times 10^9$ W cm$^{-2}$ per pulse. The instrument was programmed to uptake for 30 seconds to allow ablated material to traverse the transport tube, and then acquire data for 60 seconds.

The sample was ablated on-line at 313.259 nm and 500 pm off-line at 312.759 nm. As shown in Fig. 12, the on-line signals are twice as large as the off-line signals. This enhancement is consistent with the enhancements observed in ICP-MS ablation wavelength scans of molybdenum in stainless steel, as presented below.

**Ablation Wavelength Scans.**

**Molybdenum Ablation Detected by Microwave-Induced Plasma Atomic Emission Spectroscopy.** For a stainless steel sample (D845, 0.92% Mo), ablation wavelength scans were obtained by holding the monochromator at the appropriate fixed emission wavelength and scanning the ablation wavelength through the resonant wavelength of molybdenum over a range of 3 nm. These scans, shown in Figs. 13A–13C, were obtained using 4 mJ, 1.8 mJ, and 1 mJ, respectively, corresponding to power densities of $1.4 \times 10^9$ W cm$^{-2}$, $6.1 \times 10^8$ W cm$^{-2}$, and $3.4 \times 10^8$ W cm$^{-2}$ per pulse, respectively. As the laser energy decreased, the resultant peak became narrower. The FWHM of the ablation wavelength scans was about 1 nm for the 4 mJ pulse energy and narrowed to about 500 pm for the 1.8 mJ pulse energy. As the laser energy was further decreased to 1 mJ, the spectral features were reduced to a series of emission spikes, with the higher density of spikes being centered around the molybdenum resonant wavelength.
Molybdenum Ablation Detected by Inductively Coupled Plasma Mass Spectrometry. Ablation wavelength scans for trace molybdenum in stainless steel (D839, 4.61% Mo) were obtained by holding the mass spectrometer at mass 98, to observe the major Mo isotope, while scanning the ablation wavelength through the resonant wavelength of molybdenum over a 2 nm range. These scans (Fig. 14) were corrected for the variation in laser energy as a function of wavelength, and were obtained at energies of 4 mJ, 2.5 mJ, 1.9 mJ, 1.3 mJ, and 0.7 mJ, corresponding to $3.3 \times 10^9$ W cm$^{-2}$, $2.1 \times 10^9$ W cm$^{-2}$, $1.6 \times 10^9$ W cm$^{-2}$, $1.1 \times 10^9$ W cm$^{-2}$, and $5.8 \times 10^8$ W cm$^{-2}$ per pulse, respectively. As the laser energy decreased, the resultant peak narrowed. The baseline width of the ablation wavelength scan peaks was about 1 nm for the 4 mJ pulse energy and narrowed to about 500 pm for the 2.5 mJ pulse energy. As the laser energy was further decreased to 0.7 mJ, there was no distinguishable difference between a blank scan and the ablation scan, possibly due to sensitivity limitations and losses during material transport. As the incident laser energy was increased above 4 mJ, ablation yields were observed to remain constant regardless of ablation wavelength, in a wavelength-independent process similar to high-energy ablation of thin films, as described later in the present paper. An approximate signal enhancement of a factor of six was observed in ICP-MS for resonant molybdenum ablation at 4 mJ. This was consistent with an enhancement by a factor of 7 for ablation scans by MIP-OES. An enhancement of 3 for molybdenum emission was observed during on-line ablation of stainless steel with 2 mJ pulse energy (Fig. 9), and this was found to be equivalent to the ICP-MS ablation wavelength scans at 1.9 mJ, for which an enhancement factor of 3 was observed.

As the laser energy was increased to 4 mJ, the Mo(II) line at 312.200 nm began to appear, indicating both atoms and ions might be selectively removed from a sample surface if resonant photon energy is provided. Also, as incident laser energy at the resonant wavelength for Mo(II) is increased, molybdenum ions might be created in the plume, allowing a radiation trapping cycle to develop around the Mo(II) wavelength and contribute to enhanced ablation yields, as discussed later.

Copper Ablation Detected by Inductively Coupled Plasma Mass Spectrometry. Similar to the ablation wavelength scans obtained for molybdenum, 2 nm scans were obtained for pure deoxygenated copper samples using ICP-MS detection to observe mass 63 for copper, at 0.7 mJ, 1.3 mJ, and 1.9 mJ, corresponding to $5.8 \times 10^8$ W cm$^{-2}$, $1.1 \times 10^9$ W cm$^{-2}$, and $1.6 \times 10^9$ W cm$^{-2}$, respectively. As the laser approached the resonant gas-phase transition of copper, 324.754 nm, an enhanced signal was observed, as shown in Fig. 15. As the laser energy was decreased from 1.9 mJ to 0.7 mJ, the peak width was found to decrease from 1 nm to 500 pm at the base.

The degree of enhancement observed during the ablation wavelength scan was two to three times larger than the enhancements found for the copper mass scan at 1.9 mJ (Fig. 10). An explanation for this difference has not yet been found.

Thin Film Penetration. In order to further investigate the wavelength dependence of the RLA phenomenon, the number of laser shots required to penetrate a thin film sample was recorded as a function of wavelength. The experimental arrangement is shown in Fig. 16. A thin-film (2 μm) of chromium oxide, deposited on a quartz substrate by chemical vapor deposition (CVD), was ablated with various pulse energies, on-line (320.919 nm), and off-line at various points around the spectral line, using a spot size of 250 μm. As shown in Fig. 17, film penetration at 1.5 mJ (corresponding to $5.1 \times 10^8$ W cm$^{-2}$ peak irradiance per pulse) is four times more efficient when the laser is tuned to the resonant gas-phase transition of chromium, as compared to just 125 pm off-line at 321.044 nm. As the laser energy decreases, the line-length scans obtained for molybdenum, 2 nm scans were obtained for pure deoxygenated copper samples using ICP-MS detection to observe mass 63 for copper, at 0.7 mJ, 1.3 mJ, and 1.9 mJ, corresponding to $5.8 \times 10^8$ W cm$^{-2}$, $1.1 \times 10^9$ W cm$^{-2}$, and $1.6 \times 10^9$ W cm$^{-2}$, respectively. As the laser approached the resonant gas-phase transition of copper, 324.754 nm, an enhanced signal was observed, as shown in Fig. 15. As the laser energy was decreased from 1.9 mJ to 0.7 mJ, the peak width was found to decrease from 1 nm to 500 pm at the base.

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CVD thin film on quartz substrate

Pulsed laser beam

Molecron joulemeter

rail system
width of the ablation process also decreases, from nearly 1 nm at 2.5, 1.9, and 1.7 mJ to 250 pm for 1.1 mJ, and 62 pm for 0.7 mJ. This widening may indicate that normal ablation is occurring at higher energies, while the selective RLA process occurs at the lower energies. A similar linewidth energy-dependence was observed, and discussed earlier, for the ablation wavelength scans of both pure copper and molybdenum in steel detected by the MIP or ICP-MS.

An alternative view of this comparison is presented in Fig. 18. The on-line and off-line penetration data were plotted as a function of incident laser energy. As the ablation laser energy exceeds 1.7 mJ, the ablation yields on-line and off-line become similar. As the energy is reduced to 0.5 mJ, RLA becomes relatively more efficient, requiring fewer laser shots for film penetration compared to the off-line, normal ablation case. On-line ablation with 0.5 mJ of energy is approximately equivalent to off-line ablation with 1.1 mJ energy. Similarly, 0.9 mJ on-line is equivalent to 1.4 mJ off-line, and 1.3 mJ on-line is equivalent to 1.6 mJ off-line. These observations are consistent with the findings of Borthwick et al.66 in their Fig. 7, where RLA of aluminum with mass spectral detection was done.

It should be noted that this experiment was also attempted on annealed chromium oxide CVD films. However, the number of laser pulses required for penetration of these samples was excessive and irreproducible. Annealing annihilates electron-hole pairs and minimizes surface defects. Therefore, this observation may indicate that the RLA mechanism requires surface defects, as discussed later.

**Proposed Resonant Enhancement Mechanism.** The Verdun theory postulates that the resonant enhancement occurs in the gas phase and that it acts first by ablation in the accepted fashion but that, temporally, the second part of the same laser pulse resonantly ionizes atoms to generate an increased number of ions. If this theory were to be applied, to a first approximation, to the use of a single tunable laser pulse, the crater produced with the ablation laser on-line would likely be similar to the crater that would be produced off-line, which is not the case as demonstrated by the data presented here. Also, it is difficult to invoke the Verdun theory to account for an increased atomic emission signal, as opposed to an ion signal, produced when ablating at the resonant atomic gas-phase transition of an element. It is evident that any explanation of the single-laser, single-beam RLA mechanism must be more multifaceted than the present two-step theory. It is likely that a more detailed laser-material and/or plasma-material interaction should be considered in order to account for the changes in crater morphology and the enhanced atom and ion yields that occur as a function of wavelength.

Various phenomena might be invoked to explain some of the observations detailed above. While more work is required to conclusively define the wavelength-dependent enhancement mechanism, it is postulated here that, during the ablation of metals that would generate high atom densities, the thermal effects evident in the SEM images may be a result of radiation trapping effects. During radiation trapping, the increased size and lifetime of the laser-induced plasma observed here, and also by Tsipenyuk and Davydov,62 would lead to increased plasma temperatures, which may result in back heating, or localized heating directed back to the sample surface. Further, the larger resonant plasma might interact more efficiently with the solid surface, compared to a smaller, non-resonant plasma, therefore contributing to enhanced desorption under RLA conditions. Also, radiation trapping would contribute to the increased emission lifetimes observed in the present paper and by Pangilinan and Russell.35

An extended Verdun mechanism for RLA, based on resonant radiation trapping, can be postulated from these observations. In the proposed mechanism, the wavelength-independent formation of the mass plasma, described by Mao et al.,63 is followed by desorption from the surface in a wavelength-independent process. Following collision-induced energy exchanges among electrons and newly desorbed species in the early stages of the plasma, the heavy species begin sputtering the surface, a process that initially occurs regardless of incident wavelength, to supplement the generation of an atom plume in the laser-induced plasma. Here, if the incident radiation is nonresonant, the process proceeds as normal ablation would at low incident energy, resulting in limited desorption of atoms from the surface.

However, during resonant ablation, as the formation of
the high-density atom plume progresses temporally, a resonant radiation trapping cycle develops, in which ground-state gas-phase atoms resonantly absorb incoming laser radiation. These atoms become excited and resonantly emit in the plume, making energy available for neighboring like-atoms to absorb and repeat the cycle, until the photons finally escape the vapor. The cyclic absorption–emission process effectively traps radiation in the plasma, ultimately raising the temperature in the ablation plume, akin to using a larger laser fluence during nonresonant ablation, and causes increased sputtering and increased atom densities. As laser fluence is increased to levels in the normal analytical ablation regime, sufficient laser energy becomes available to generate a higher temperature and higher atom density in the ablation plume, without the presence of resonant radiation trapping, and the wavelength dependence and selectivity of RLA are lost. It can also be considered that in resonant ablation, plasma reflectivity is effectively reduced, and the region near the metal surfaces becomes highly absorbing, such that a more energetic plasma is created, similar to a plasma created with a nonresonant laser pulse of higher incident energy. In nonresonant conditions, a significant fraction of the pulse energy is reflected by the metal itself and by electron density gradients in the plasma.

Further, during resonant ablation, an additional DIET pathway may become available to supplement the selectivity of the resonant radiation trapping cycle. Here, partially desorbed surface atoms may resonantly absorb incoming radiation and contribute directly to the generation of the high-density atom plume.

**Crater Observations.** The radiation-trapping-based mechanism for resonant ablation is substantiated by observations made by Mao et al. during normal, high-power laser ablation experiments, where outer rings of re-deposition were noted around the ablation craters. The large power density used for ablation by Mao et al., which was on the order of 50 GW cm$^{-2}$, probably mimicked the plume temperatures achieved under the influence of resonant radiation trapping during the lower-power RLA process. Therefore, it is reasonable to deduce that both high-power normal ablation and low-power ablation at the resonant gas-phase transition of the analyte will produce the same type of re-deposition around the ablation crater. This is corroborated by the change in crater appearance as a function of incident energy (Fig. 5). Further, this difference in plume temperature, initiated by radiation trapping, explains why, during RLA experiments conducted under the same incident laser power density (Fig. 3A), the re-deposition rings disappeared as the wavelength progressed away from the gas-phase transition line of the analyte.

The observed re-deposition probably arose from surface sputtering and back heating as a direct consequence of an elevated plume temperature generated by radiation trapping during RLA, or as a function of high incident energy in normal analytical ablation. As the size and energy of the plume and the atom density in the plume increased, the amount of surface sputtering probably increased, resulting in enhanced re-deposition and condensation of plume species on the surface. Further, the elevated temperatures induced by radiation trapping may explain the melting phenomena shown in Fig. 3B, and indicates that, for pure metals, the RLA mechanism probably includes a thermal contribution from an increased plasma temperature and an enhanced plasma–surface interaction, in addition to electronic effects.

Consequently, radiation trapping allows RLA to require less energy while still remaining more efficient than nonresonant ablation, and in this way, resonant radiation trapping allows a more efficient coupling to the solid surface. The precise energy dependence and the transition from RLA processes to normal, nonresonant ablation are substantiated by multiple observations in the present paper, as well as those made by Borthwick et al., and Gill et al., and others. Moreover, the present authors hypothesize that as the concentration of a trace analyte decreases, the resonant enhancement will become negligible as the radiation trapping mechanism becomes inoperative, although our current detection techniques are not sensitive enough to confirm this hypothesis.

**Extended Emission Lifetimes and Enhanced Atom Yields.** The proposed resonant radiation trapping mechanism may also be invoked to explain both the enhanced emission lifetimes and the enhanced emission intensities observed during the delay time experiments (Fig. 7). Probably, during resonant ablation, which has been shown to be a high photon order process, radiation trapping increased the energy of the plasma, thereby extending the emission lifetimes beyond those observed for normal ablation. Further, during low-power resonant ablation and resonant radiation trapping, the plume temperature would increase significantly compared to nonresonant ablation at the same fluence. The higher temperatures may have led to cyclically enhanced sputtering of the surface by heavy plasma species, and this, in turn, would have enhanced back heating and the production of more atoms in the plume, thereby both extending the emission lifetime (Fig. 7A compared to Fig. 7B) and increasing the atom yield (Fig. 7E compared to Fig. 7F). During nonresonant ablation, resonant radiation trapping would not occur, thereby limiting surface sputtering and decreasing the subsequent population available for excitation in the plume. Increased surface sputtering, under resonant conditions, may account for the enhanced atom yields observed in the delay time scans (Figs. 7E and 7F), emission wavelength scans (Figs. 8 and 9), mass scans (Figs. 11 and 12), and ablation wavelength scans (Figs. 13, 14, and 15). Additionally, increased sputtering during RLA produces more atoms for re-excitation in the plasma, resulting in a larger relative emission intensity (Fig. 7C), compared to the off-line emission intensity (Fig. 7D). This is substantiated by experiments performed by Burakov and others for the sputtering of aluminum from pure aluminum and aluminum oxide samples using a 308 nm excimer laser, and compared to a 1064 nm Nd:YAG laser. Preferential sputtering at 308 nm was observed by optical emission spectroscopy.

The resonantly enhanced plasma temperature concept is similar to that generated by resonantly reheating the plasma with a second laser beam, such as the arrangement used by Liu and Cheung and Chan and Cheung for resonance-enhanced laser-induced plasma spectroscopy (RELIPS). Those authors use a nominally non-ablative, second dye laser to resonantly reheat the gas-phase plume formed by nonresonant, normal ablation at 532
nm. The authors observed enhancements in emission intensity of trace components when the second laser was tuned to a resonant gas-phase transition of the bulk material. The authors proposed a gas-phase enhancement mechanism, where the use of radiation that is resonant with a gas-phase transition of the bulk ablated material excites a larger volume of the existing plasma more efficiently, resulting in higher plume temperatures. Increased plume temperatures probably then created a more energetic plasma, resulting in detection of enhanced emission from trace elements in the plume. In light of experiments reported in the present paper, it is likely that in some of their experiments, where the dye laser was determined to be marginally ablative, the authors probably observed enhanced desorption contributions due to RLA, in addition to gas-phase excitation processes such as radiation trapping. However, it is not clear that Cheung and co-workers were able to separate gas-phase excitation processes in the plasma from increased vaporization of atoms by the resonant laser, nor did they report spectra that resulted from scanning the ablation laser wavelength. Our delay time experiments (Fig. 7) and laser ablation scans with ICP-MS detection (Figs. 14 and 15) show increased numbers of atoms to be vaporized, which would not be observed if the resonant enhancement occurred solely in the gas phase as a function of excitation temperature as postulated by Cheung and co-workers. Those authors did not look for increased numbers of atoms, nor are there data to indicate whether or not the surface was back-heated to create enhanced desorption of atoms.

Ablation Scan Spectral Widths. The width of the ablation scan spectra may be attributed to collisional broadening in the high-density atom plume via the high plasma temperatures and increased atom densities that set the stage for radiation trapping during resonant laser ablation. Wang et al.,69 suggested that the main contribution to peak width might be inelastic collisional broadening in the high-density plume. Inelastic collisions would broaden the peak but preserve the peak central position at the resonant transition line; this correlates well with the data observed in the present paper and others,29,33,38,54 for which peaks were observed at the unperturbed gas-phase transition values. As previously discussed, plume temperature and atom density increase as a function of increasing resonant laser fluence, broadening the ablation peak width until normal ablative processes dominate. As laser fluence is increased, the population and density of particles in the ablation plume increases; consequently, collision frequency increases, and larger peak widths are observed. This is substantiated here by the relatively flat and broad 2.5 mJ curve in Fig. 17 and the subsequent narrowing trend as incident energy was reduced. Furthermore, the cyclic process of self-absorption is likely to occur at the high atom densities created during resonant laser ablation and radiation trapping, and may also contribute to the ablation scan peak widths. Saturation broadening is a well-known effect in spectroscopy for moderate laser fluences and may also play a significant role in peak widths. Pang and Yeung,51 who observed enhanced ion yields during resonant ablation, attributed peak width to resonant ionization in the gas phase followed by collisional broadening. However, the broad lines observed by Pang and Yeung are consistent with the present authors’ concept of RLA, and therefore, the authors may have been observing RLA that was enhanced further by RIS.

Surface Plasmon Resonances. Surface plasmon resonances had been postulated as a mechanism for enhancements observed during RLA.11 However, although there may exist desorption contributions due to surface plasmon resonances, these are broadly wavelength dependent, on the order of 100–200 nm,70–72 extending over the entire metal surface. Therefore, surface plasmons may have no primary contribution to the RLA phenomenon, where the wavelength dependence and spectral features have line widths typically less than about 1 nm as a function of ablation wavelength.

Surface Defects and Electronic Transitions. Laser ablation phenomena require surface defects to proceed,73 and therefore, as noted in the annealed thin film work, the RLA phenomenon is probably influenced by the presence or absence of surface defects. This observation, together with the wavelength dependence, indicates that the RLA enhancement mechanism may include a contribution from the phenomenon of desorption induced by electronic transitions (DIET). RLA has been shown to be a high photon order process,31,32 which supports the idea that photonic desorption contributes to the phenomenon. While much of the work done on DIET has focused on the mechanism of desorption of alkali halides74–76 or rare condensed gases,77,78 several authors have extended the work to metals.79–83 While the exact DIET mechanism is not agreed upon, a general consensus exists that desorption is caused by an electronic effect and requires localization, either by the presence of self-trapped excitons (STE) in STE-supported materials, or by surface defects in those materials which do not support STE. A possible DIET contribution to the observed RLA enhancements may arise from a Pauli shock-like mechanism, first described by Elango et al.84 An incoming photon may be captured by a localized electron at a defect site, causing a sudden increase in ion radius and a simultaneous rise in repulsive energy. This Pauli repulsion causes desorption from the surface, which may be enhanced by the resonant absorption of partially desorbed surface atoms, and may contribute directly to the generation of the high-density atom plume, as previously described. It is possible that the electronic transitions involved in desorption might occur at wavelengths shifted from gas-phase atomic transitions. While the resonant enhancements were observed at unperturbed gas-phase transition wavelengths in the present paper and others,36,48,50 it is possible that any shift in transition wavelength, from gas-phase atomic transition to bound-atomic transitions, might go undetected since the transition bandwidths were on the order of 1 nm, probably due to collisional broadening. Therefore, it is unclear whether such a shift exists or not, and more work is required to define the role of surface defects and electronic transitions in the RLA phenomenon.

Particle Size Considerations. It was noted during the RLA-ICP-MS experiments that the temporal onset of the ICP-MS transient signal for copper occurred sooner than the onset of the transient signal for molybdenum in the stainless steel samples. Jeong et al.85 have determined that the time required for signal onset in the ICP-MS is particle size dependent. The production of an increased dis-
tribution of large particles during laser ablation was observed to decrease the amount of time required for onset of signal production in ICP-MS. Further, Figg et al. have shown that increased laser power generates increased particle size. However, as previously discussed, radiation trapping may mimic increased incident laser fluence. Accordingly, this observation suggests that increased resonant radiation trapping probably occurred during the ablation of pure materials, such as copper, compared to the ablation of trace materials, such as molybdenum in stainless steel. It is possible then, that this increased radiation trapping results in an increased number of larger-sized particles and clusters desorbing from the copper surface compared to those desorbing from the stainless steel surface.

CONCLUSION

The data presented here support the literature observation that there exists an enhancement in the efficiency of laser desorption of species at the gas-phase resonant transition of an element. This occurs at moderate laser energy densities and disappears at the high laser energy densities generally used in laser ablation. Therefore, it appears that RLA has some characteristics that might provide unique sample introduction capabilities for plasma-based atomic spectrometric measurements. These advantages include increased sensitivity and selectivity for trace metal analysis. The higher sensitivity is evident only at lower energy densities and disappears at the laser energy densities used for traditional laser ablation. The data presented here indicate a distinct laser–plume–material interaction, substantiated by the changing crater morphology as a function of wavelength and the relatively broad linewidth of the ablation laser wavelength scans, compared to gas-phase excitation spectra. The thin film penetration data corroborate the existence of a laser–material interaction because they were also modulated by laser wavelength and energy density.

The wavelength selectivity and energy sensitivity of RLA suggest that the approach is worthy of further study to assess whether or not these features allow advantages to be gained for quantitative laser ablation measurements. There is the possibility of improving sensitivity at low energies, which may allow the use of less powerful and less expensive lasers, while the relative enhancement of the desorption of one element relative to another may be exploited to address matrix interference problems or issues associated with non-stoichiometric vaporization of species. In other words, selective vaporization may be controlled or compensated for by use of RLA. RLA, as a form of enhanced and selective fractionation in the ablation plume, may be desirable in certain applications, despite the fact that fractionation is thought of as the most significant problem of normal LA sampling. Specific applications may include coupling RLA to LIBS, MALDI, and surface analysis techniques, all of which may benefit from the increased sensitivity and selectivity at the lower energies lent by RLA. For example, the thought that the laser wavelength can be modulated to enhance the desorption of specific species has implications for surface mapping of species as well as for quantitative analysis. These results represent a detailed inspection of the effect of the wavelength of the ablation laser over a narrow range of energy densities that lie between the threshold of desorption of species and the usual analytical ablation regime. Normal ablation employs high-energy lasers in an attempt to create a vapor plume without selective vaporization, and with a stoichiometry that accurately represents the stoichiometry of species in the solid sample. RLA, as a method of selective vaporization, appears to provide an opportunity to exploit selective vaporization in new ways.

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REFERENCES
