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Resonant Laser Ablation: Mechanisms & Applications

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Introduction

Ever since the first report of laser action, it has been recognized that laser ablation (evaporation/volatilization) may provide a useful sampling mechanism for chemical analysis.[1,2] In particular, laser ablation is rapidly gaining popularity as a method of sample introduction for mass spectrometry.[3-5] While most laser ablation/mass spectrometry has been performed with fixed frequency lasers operating at relatively high intensities/fluences ($\geq 10^8$ W/cm^2, ≥ 1 J/cm^2), there has been some recent interest in the use of tunable lasers to enhance the ionization yield of selected components in an analytical sample. This process has been termed resonant laser ablation (RLA),[6-12] and typically relies on irradiation of a sample in a mass spectrometer with modest intensity laser pulses tuned to a one- or two-photon resonant transition in the analyte of interest. Potential advantages of RLA include: 1) simplification of the mass spectrum, by enhancement of signal from the analyte of interest; 2) improvement of the absolute detection limits by improving the ionization efficiency, and 3) improvement in relative sensitivity. The sensitivity enhancement results from reduction of spurious signal, and accompanying noise, in the detection channel. This spurious signal may be due to bleed through from adjacent mass channels, or from isobaric interferences. RLA tends to produce higher mass resolution because of minimal spatial spread in the ion source and small space charge effects. In this manuscript we present a survey of RLA attributes and applications.

Results and Discussion

Analysis

Much of the apparatus has been described previously.[13,14] The optical source consisted of an XeCl excimer laser-pumped dye laser. For most of the experiments described here, the output energy was a few mJ in the blue spectral region (~450 nm), in ~10 nsec pulses, at a repetition rate of 10 Hz to 50 Hz. The dye laser beam was split and attenuated prior to striking the sample, so that typical incident pulse energies were ~10-100 μJ. The ion detector was a channel electron multiplier whose output was amplified, sent to a boxcar averager or digital oscilloscope, and then transferred to a microcomputer. The beam was focused by a 20 cm lens and incident on the surface at an angle of 11°, producing a stripe on the surface that was 0.34 mm by 1.8 mm (0.006 cm^2), measured at the 1/e intensity points of the beam.

Figure 1 shows typical mass spectra obtained from a high purity rhenium sample. Each spectrum corresponds to irradiation of the surface at a different wavelength, corresponding to a "2+1" (photons to resonance + photons to ionize) ionization process for the labeled element: iron, aluminum, copper or chromium. Several features are worth noting. First, signal was obtained with low pulse energies, typically 20 μJ (corresponding to a fluence ~10 mJ/cm^2, or an intensity $<10^6$ W/cm^2). The observation of trace components at very low laser intensities is a significant virtue of this process; this sensitivity is due both to the resonant nature of the ionization process, and to the excellent overlap of the vaporized sample with the ionizing laser beam, as discussed below. Second, virtually no signal due to the bulk material (Re) was observed. In more careful

experiments, we have demonstrated selectivity, δ, in ionization of the target analyte vs. the bulk material of $\delta \geq 10^5$:1. In spite of this, a persistent signal due to sodium and potassium was observed in all of these spectra. These are impurities present in the sample and their presence was perhaps enhanced by excessive manual manipulation. These components are presumably observed because of their high volatility, low ionization potential and presence on the surface as ionic compounds. They are thus easily vaporized, and ionized, by low-order non-resonant multiphoton processes. In addition, we generally observed that the initial pulses of any irradiation sequence produced more signal than subsequent pulses,[15] even though the thermal pulse should decay completely of the time scale of the interpulse interval.
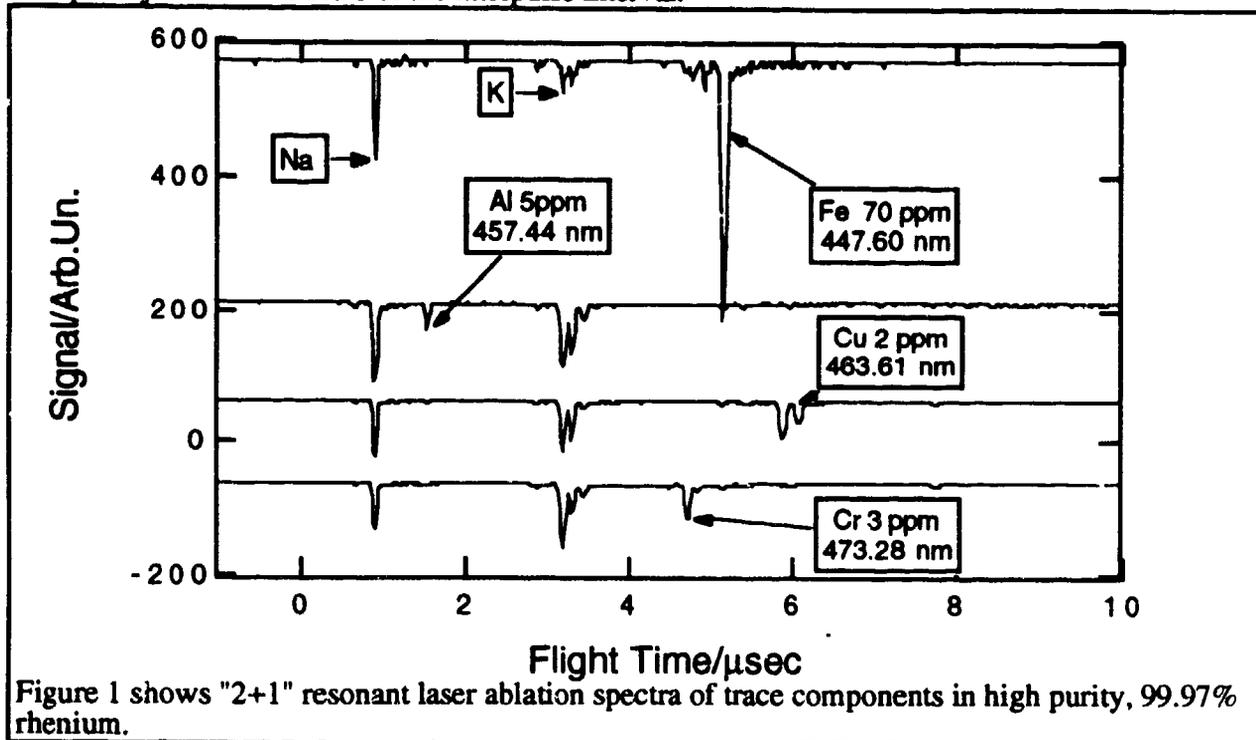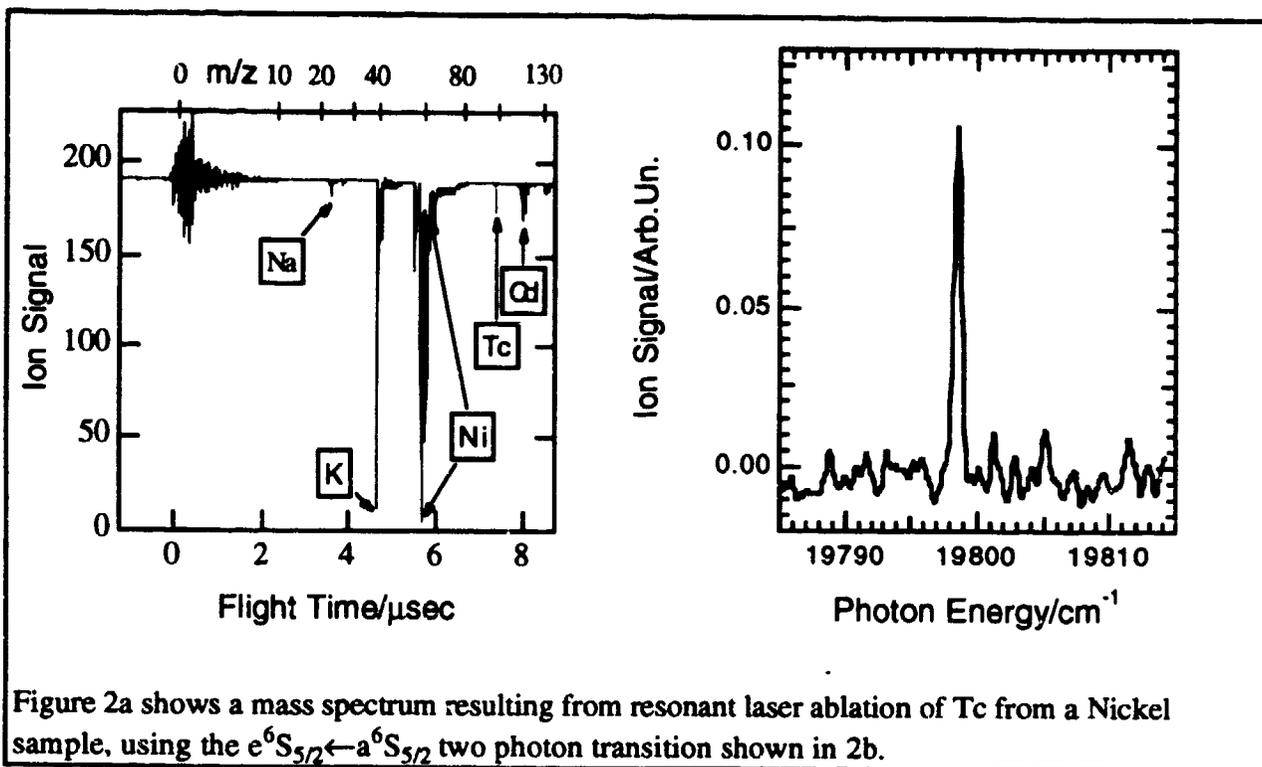

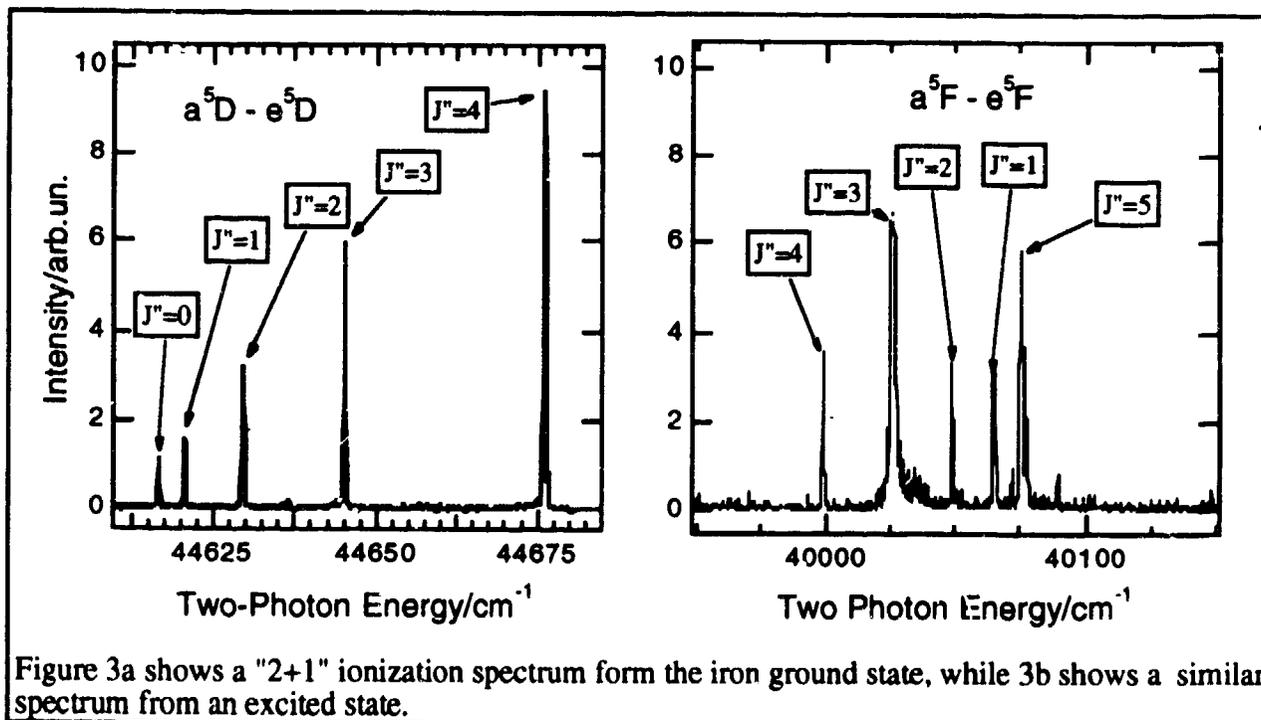Figure 1 shows "2+1" resonant laser ablation spectra of trace components in high purity, 99.97% rhenium.

Several generalizations concerning quantitation can also be made. The results shown above were found to be semiquantitative. All mass spectral traces in Figure 1 were normalized so that the areas corresponding to the sodium signals were equal. Under this constraint, the signals can be seen to scale monotonically with the concentration of the minority species, as was noted previously.[6] In addition, at the low fluences used in these experiments, removal rates were very small; in separate experiments, we estimated ≤ 0.01 monolayer per shot is removed from the sample. This provides the potential for depth profiling of layered or inhomogeneous samples using resonant laser ablation.

The potential of RLA for trace detection is shown in Figure 2a, which depicts a mass spectrum obtained from a nickel sample containing low levels ($\leq$ppb) of technetium. Technetium is an unstable element that does not occur in nature, and is difficult to detect by radiochemical means because of its low specific activity. In our analyses, the laser was tuned to a "2+1" resonant ionization transition for technetium; the optical spectrum is displayed in Figure 2b. While Fig. 2a clearly shows significant non-resonant ionization occurring, it should be noted that the nickel sample had a very rough morphology (the surface appeared black) and the Tc concentration was $\leq$1ppb, illustrating the benefits of significant discrimination for the detection of extremely low levels of analytes.

Figure 2a shows a mass spectrum resulting from resonant laser ablation of Tc from a Nickel sample, using the $e^6S_{5/2} \leftarrow a^6S_{5/2}$ two photon transition shown in 2b.

Spectroscopy

We also show the utility of RLA for spectroscopy and surface studies. This work demonstrates the ease with which high quality atomic spectra can be obtained using RLA. Fig. 3 shows the 2+1 multiphoton ionization spectrum of ^{56}Fe detected by RLA of Re containing 70 ppm Fe.

Figure 3a shows a "2+1" ionization spectrum form the iron ground state, while 3b shows a similar spectrum from an excited state.

We observe the two-photon $\Delta J=0$ transitions from the a^5D ground term to the e^5D excited term near 44640 cm^{-1}; also observed is the $e^5F \leftarrow a^5F$ two-photon transition from the first excited term near ~1 eV. Each of these multiplets spans a wavelength range of <1 nm, yielding essentially constant dye laser power across the multiplet. The $J'=3 \leftarrow J''=3$ and $J'=5 \leftarrow J''=5$ transitions are much stronger than the other lines in the excited state multiplet due to near resonances with the z^5F^o term (detunings of 182 cm^{-1} and 92 cm^{-1}, respectively).

Temperatures can be obtained from these spectra by comparing calculated intensities for a particular temperature with experimental intensities. The agreement between the experiment and calculation is surprisingly good A fit of the experimental intensities to the calculated intensities yielded a straight line (r^2=0.96 to 0.99 for three data sets) for the four lowest lying spin-orbit states in Fe. The observed intensity of the $J''=0 \rightarrow J'=0$ transition is an order of magnitude larger than calculated, possibly due to quantum interferences. We obtain a temperature of 1100 ±200 K for Fe atoms ablated from Re at an intensity of 2±1 x 10^6 W/cm^2. This is in rough agreement with a recent measurement[16] of the temperature of a laser desorbed plume several mm above the surface.

Conclusions.

We have shown that RLA is ideally suited for high sensitivity analyses of complex samples. It requires very modest performance from both laser and mass spectrometer, and is suited for detection of a wide variety of elements. We have also demonstrated that the 2+1 ionization transitions of Fe detected by RLA. Two-photon transition rates for Fe transitions were calculated perturbatively and found to agree semi-quantitatively with experimentally observed intensities.

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