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Resonance ionization mass spectrometry for materials analysis and characterization

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Abstract

Resonance ionization mass spectrometry (RIMS) is an analytical tool discovered in the 1970's, developed primarily in the 1980's, and one which will undoubtedly see continued and expanding use through the 1990's. This technique combines laser ionization with mass spectrometric sorting and detection to yield results of unparalleled sensitivity and selectivity. We discuss the application of RIMS to the analysis of conventional analytical samples, as well as the combination of RIMS with laser or particle beam sputtering for the analysis of solids and surfaces with minimal sample preparation.

I. Introduction

It is difficult to foresee the course of science over the time period of a single year, let alone a decade. The rate of change seems to accelerate with each passing year, particularly in the area of instrumentation and technique development. It is safe to predict, however, that optical spectroscopy, particularly as applied to chemical analysis, is destined to occupy a central role in the impending decade of science. The Pimentel Report¹ says of analytical chemistry that "characterization and measurement of atomic and molecular species--qualitative and quantitative analytical chemistry--uniquely contribute to and benefit from the current rapid progress in science." Of optical spectroscopy in particular, the report¹ says "the intellectual opportunities in this field, which introduce a host of valuable analytical techniques, can be illustrated by two notable achievements of the last decade: . . . the detection of single atoms and molecules." The achievement of single-atom detection^{2,3} is based upon the use of laser excitation and ionization combined with detection of the resulting ions; high-sensitivity detection of molecules has been accomplished both by laser ionization⁴ and by condensed-phase laser-induced fluorescence⁵. The application of laser photoionization to atoms or small molecules is often termed resonance ionization, and in combination with mass spectral sorting and detection is called resonance ionization mass spectrometry (RIMS)⁶.

The RIMS technique combines a multistep photoionization process with mass spectral sorting and detection of the resultant ions. Resonance ionization utilizes a light source tuned to a resonant electronic transition in the analyte element(s) of interest to effect a high degree ($\geq 10^6$) of selectivity⁷. Figure 1 illustrates two commonly used resonance ionization schemes. Since high spectral brightness pulsed lasers are typically used to effect ionization, the process is often saturated. That is, all analyte atoms or molecules within the irradiated volume are converted to ions. This leads to extreme sensitivity--with quantification of as little as 10^7 atoms in the sample^{8,9}.

Initial applications of RIMS frequently utilized sample preparation techniques borrowed from conventional thermal ionization mass spectrometry.¹⁰ These techniques included evaporation of (dissolved) aqueous samples onto thin ribbons of refractory metals⁷, electroplating onto metal ribbons¹¹, and adsorption onto resin beads⁸. In all cases, the samples were then subjected to a Langmuir evaporation process,¹⁰ in which the sample and support were heated to produce free gas-phase atoms or small molecules.

Figure 1 depicts schematic energy level diagrams for generic "1+1" (photons to resonance + photons to ionization) and "2+1" ionization processes. Solid lines represent real electronic states, dashed line virtual states and the cross-hatched area the ionization continuum. All photons are absorbed within a single laser pulse (in the case of pulsed laser excitation) or single transit time across the laser beam (in the case of cw laser excitation).

These methods were widely used and very successful in early applications, but exhibited two important limitations: extensive sample preparation was needed in many instances, and the sample was used inefficiently. The former arises from the need to have the sample dissolved in (usually acidic) aqueous solution in order to facilitate handling. The second arises from the common use of pulsed lasers for ionization. The low duty cycle of these lasers, coupled with continuous evaporation of the sample, led to inefficient sample utilization. As an example, consider analyte atoms or molecules moving at a velocity of 5×10^4 cm/sec through a laser beam of 5 mm focal diameter. This yields a turnover rate of sample in the laser beam of $5 \times 10^4 / 0.5 \text{ cm} = 10^5$ Hz. The average pulsed laser, on the other hand, produces pulses at a rate of $\leq 10^3$ Hz, leading to an effective duty cycle of $\sim 10^{-2}$.

Several approaches were applied in a effort to produce more efficient sample utilization. This included the use of cw lasers¹², trapping geometries so that the atoms or molecules made several passes through the laser beam¹³, and pulsed desorption to increase the effective duty cycle. Two approaches to pulsed desorption have received the bulk of attention: particle beam sputtering^{14,15} and laser ablation or desorption.^{16,17} For the remainder of this article the term "laser ablation" will be used to denote any process by which laser-material interactions produce a vapor plume, whether by thermal or non-thermal processes. Laser ablation has a number of additional advantages as well. These include high spatial resolution ($\approx 1 \mu\text{m}$), the evaporation of difficult refractory or tightly bound samples, and the ability to sample directly insulating surfaces. The remainder of this paper will present selected topics in the theory, practice and application of laser-ablation/RIMS.

2. Experimental

Most of the experiments described in this paper utilized a time-of-flight (TOF) mass spectrometer^{16,18} shown in Figure 2. The Q-switch synch-out from the Nd:YAG laser (Quanta Ray/Spectra Physics Model DCR 1A) was used to master the timing sequence. This laser was used as the ablation/desorption source and operated at either the fundamental wavelength ($1.06\ \mu\text{m}$) or one of the harmonics, 3ω or 4ω (355 or 266 nm). The beam spatial and temporal profiles were monitored on a routine basis. For most studies, the laser was equipped with beam-filling optics and produced a near-Gaussian profile. The output pulse was ~ 10 nsec in duration and smooth on the time scale of our detection electronics (~ 2 nsec). The laser output was focused to varying spot sizes on the ablation samples with several different lenses. The residual fundamental and/or other harmonics were removed from the ablation beam by using dichroic mirrors.

Figure 2. Schematic of the experimental apparatus. Beam steering consists of a prism telescope and turning mirror, and beam diagnostics consist of a scanning pinhole and pyroelectric detector.

The mass spectrometer flight tube was 0.4 m long, and was mounted on a stainless steel six-way four-inch cross, with 1.3 inch ports mounted on the diagonals to allow optical access. The targets could be translated and rotated with a high-vacuum feedthrough (Varian Model 1371). The rotation axis of the substrate was displaced from the ablation laser beam axis by ~ 5 mm, thus permitting the interrogation of different substrate sites through substrate rotation. Typical pressures within the source for all experiments were maintained at 10^{-7} Torr by a L-N₂ trapped oil diffusion pump. The extraction field was approximately 110 V/cm, followed by a drift tube at -1000 V. A pair of deflection plates between the

extractor and the flight tube maximized the transmission of ions to the detector and minimized any transmission variation that was due to ion velocity components perpendicular to the flight tube.

Pulses from an excimer-pumped dye laser (Lambda Physik Models 101/2002), propagated in the plane of, and at a 45° angle to, the Nd:YAG laser beam at approximately 2 cm from the target surfaces were used to interrogate the ablated neutral species. Ions produced directly by the ablation laser were strongly discriminated against by the ion optics. Dye-laser pulses (~2 mJ, 10 nsec) produced at a variable delay relative to the ablation laser were spatially filtered and loosely focused through the ionization region.

Detection electronics consisted of a channel electron multiplier, a preamplifier, and a boxcar integrator (PAR 162/164) whose gate delay was set to the flight time of the ion of interest. The boxcar width was adjusted so as to encompass only a few mass units about that of the detected species. For studies involving transient ablation processes, the ion signal was processed with a high-speed waveform recorder (Tektronix 2430 or 2440).

3. RESULTS AND DISCUSSION

3.1 Effects of Laser Ablation.

As noted above, there are similarities in the motivation for pursuing both particle-induced desorption (sputtering) and laser ablation. In both cases, the goal is the production of gas-phase atoms or small molecules in a controlled fashion, so that the sample may be interrogated with the greatest precision and accuracy. However, since there are numerous differences in mechanisms, the temporal and spatial evolution of the sputtered and laser ablated plumes are quite different. Here, only aspects of laser ablation will be considered. For a more detailed discussion of particle sputtering, see reference 13.

For analytical sampling by a laser ablation process, typical pulse energies are 10^{-1} J, delivered to a 1 mm^2 spot in a 10^{-8} sec pulse¹⁶. In the near IR ($1 \mu\text{m}$), this corresponds to a photon fluence of 5×10^{19} photons/cm². It is difficult to estimate precisely the number of ejected particles for the laser ablation, since it is extremely dependent on the material in question as well as the laser temporal and spatial profiles. Pertinent parameters include the absorptivity of the solid at the ablation wavelength, and thermal properties such as the heat capacity and the thermal diffusivity. As a concrete example, for Si¹⁹ an ablation yield of 5×10^{14} atoms per pulse has been reported for a deposited laser energy of 5×10^{-4} J. Such high yields are often encountered in processes involving an energy emission threshold as is the case for laser ablation.

If one assumes that the laser absorption proceeds only in near surface layers, and that the resulting energy distribution is Boltzmann (thermal), then the arrival-time distribution of the resulting gas-phase atoms or molecules is given by:

$$S(t) = K L t^{-4} \exp\{-(L/t)^2/\sigma^2\} \quad (1),$$

where L is the distance between the target surface and ionization region, $S(t)$ is the ionization signal as a function of the flight time (t), σ is the local most probable velocity, $\sqrt{2kT/m}$, and K is a collection of constants related to detection geometry and efficiency.

In real experimental situations, it is often the case that the average rate of material removal exceeds several monolayers per shot. This is large enough that collisional effects must be considered, which may dramatically alter the observed velocity distribution. For a shifted Maxwellian velocity distribution an additional parameter, v_0 , the center of mass velocity, is fit to the signal via equation 2:

$$S(t) = K L t^{-4} \exp(-\{(L/t)-v_0\}^2/\sigma^2) \quad (2)$$

with symbols as defined before, except that v_0 represents the hydrodynamic velocity. Fitting the this observed distribution to equation (2) represents an *ex post facto* rationalization. A more formal accounting of collisions can be obtained through the use of the Knudsen layer model recently developed by Kelly and Dreyfus. This model considers the formation of a Knudsen layer (when particles are no longer adequately described by a Maxwellian velocity distribution) via sputtered particle collisions and parallels shifted Maxwellian distributions. Here, via collisions, ablated species acquire a common center-of-mass velocity rather than a common temperature. Using the formalism of Kelly and Dreyfus, the TOF signal normal to the target surface is described by

$$S(t) = K L t^{-4} \exp\{-\beta_K^2(L-u_K t)^2/t^2\} \quad (3)$$

In this model, u_K represents the center of mass velocity, while β_K is defined in terms of the Knudsen layer temperature, T_K ,

$$\beta_K = \sqrt{m/(2kT_K)} \quad (4)$$

The desorbing surface temperature is related to the Knudsen layer temperature through the heat capacity ratio of the specie in question. A characteristic of this collision-based process is that all components, regardless of mass, should attain the same velocity. This is in contrast to a Maxwellian distribution in which all components will attain the same mean energy. A method to account for the effect on the signal of the finite solid angle subtended by the ionizing laser beam is described in reference 17.

3.2 Analytical applications.

Many applications of laser-desorption/RIMS lie in the area of chemical analysis or isotope ratio measurements. RIMS provides an excellent alternative to more conventional analysis methods because of its high sensitivity and ability to discriminate against isobaric interferences. RIMS analysis of chromium is described in the remainder of this section.

3.2.1 Chromium ionization.

Chromium is laser ionized through a "2+1" process similar to that depicted in Figure 1. In our work, the resonantly excited state ($3d^5 5s^1 \ ^7S_3$) is reached by two-photon excitation ($\lambda = 542.07$ nm) from the ground state ($3d^5 5s^1 \ ^7S_3$). Subsequent absorption of another photon of the same wavelength results in the production of chromium ions, which must lie in their ground state ($3d^5 \ ^6S_{5/2}$) due to the energetics of the process. A small region of the optical spectrum is shown in Figure 3, for a sample which was thermal evaporated from a rhenium filament. It should be noted that this transition is laser-linewidth-limited, $\Delta\nu \sim 0.35$ cm⁻¹. Isotopic distributions determined in this manner fall within the error limits of our measurement for samples of natural chromium.

3.2.2 Chromium detection.

Analytical samples were prepared by dissolution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a mixture of ethanol and water. Twenty microliter aliquots were then spun onto polycarbonate disks, and dried in air. The arrival time distributions were found to be roughly thermal, with a temperature of $\sim 1000\text{K}$, suggesting that the amount of material desorbed is insufficient to cause significant collisional redistribution. A preliminary working curve is displayed in Figure 4, where ion signal is displayed as a function of desorbed sample size. The

detection limit lies near $\sim 10^{-14}$ g, with good linearity over the range 10^{-6} - 10^{-12} g. It should be pointed out that this instrument was optimized for another purpose,²⁰ rather than for maximum sensitivity. Our estimates are that $\ll 1\%$ of the desorbed material passes through the laser focal volume during the time that photons are present. Even with this limitation, however, these results compare favorably with any other method of chromium analysis.

3.3 Sampling of plumes from HTSC targets.

Laser ablation has been shown to be an effective means for producing high-quality epitaxial thin films of high temperature superconductors. Laser ablation from stoichiometric (in the metal components) solid samples produce a partially ionized vapor cloud, which subsequently condenses on an appropriate substrate material to produce the films. Recent experiments in this laboratory^{21,22} have demonstrated the production of $\text{YBa}_2\text{Cu}_3\text{O}_x$ films at rates of up to 15 nm/sec, with transition temperatures $T_c \sim 92\text{K}$, and critical currents $J_c \geq 1 \times 10^6 \text{ A/cm}^2$. Time-resolved RIMS has been used to provide information concerning speciation, and the internal and translational energy distributions of the ablated material.

3.3.1 Ionization processes.

The principal components observed in this laboratory include Y atoms, Cu atoms, Cu_2 dimers, BaO fragments, and a small fraction of so-far unidentified ions²⁰. All neutral species were identified by a combination of optical (resonance) spectra and flight times.

Detection of Cu atoms by RIMS also involved a 2+1 ionization process. A two-photon transition from the ground state ($3d^{10}4s^1 \ ^2S_{1/2}$) to the excited state ($3d^{10}5s^1 \ ^2S_{1/2}$) is followed by absorption of another photon of the same frequency (43137 cm^{-1}) to affect ionization. Other studies in this laboratory indicate that the two-photon transition step is likely saturated,²³ and thus small fluctuations in the laser intensity will have little effect on the signal. Yttrium atom detection paralleled that of copper atom detection. Either one of two ionization schemes was used to detect Y atoms. A two-photon transition from the ground state of yttrium ($4d5s^2 \ ^2D_{3/2,5/2}$) to either the ($5s^25d \ ^2D_{3/2,5/2}$) excited state at $\sim 43000 \text{ cm}^{-1}$ or the ($4d5 \ 6s \ ^2D_{3/2,5/2}$) excited state at $\sim 36500 \text{ cm}^{-1}$ preceded the absorption of an additional photon of the same frequency.

A convenient and sensitive detection scheme for BaO exists via a multiphoton ionization pathway from the $X^1\Sigma$ ground state through the ($v'=4, v''=0$) $A^1\Sigma$ band system. The ionization potential of BaO (6.5 eV) is exceeded via a 1+2 multiphoton transition at this frequency ($\sim 18700 \text{ cm}^{-1}$). Although such transitions are usually inherently weaker than 2+1 transitions, this particular ionization is extremely sensitive. We speculate that absorption of the second photon is enhanced by high-lying electronic states. This transition was particularly convenient, since it allowed Y and BaO detection using the same laser dye.

3.3.2 Velocity distributions.

Arrival-time distributions have been recorded for several neutrals ablated from $\text{YBa}_2\text{Cu}_3\text{O}_x$ at 355 nm. For Cu, this was also compared to distributions observed at an ablation wavelength of 1.06 microns. In each case where 355 nm was used for ablation, the signals peak at approximately the same flight time ($\sim 20\text{--}22 \text{ ms}$), indicating similar velocities for each specie, regardless of the mass. For Cu ablated at 1.06 microns, a thermal Maxwellian velocity distribution provides the best fit, indicating a most probable velocity of $9.8 \times 10^4 \text{ cm/s}$ and temperature of approximately 3680 K. This temperature should be indicative of the surface temperature, since there is no evidence here of post-desorption collisions. At 355 nm, the Cu signal peaks at the same time-of-flight, but possesses a substantially narrower width, although the same approximate ablation laser fluence was used. Here, a center-of-mass velocity of $13 \times 10^4 \text{ cm/s}$ and a thermal width velocity of $4.9 \times 10^4 \text{ cm/s}$ are obtained from a Knudsen-layer analysis. The presence of collisions at 355 nm indicates a greater efficiency of removing material at 355 nm compared to 1.06 μm , as has been observed for many materials. This may be due to a higher effective energy density, resulting from a shallower penetration depth, at 355 nm.

4. Conclusions

RIMS is a powerful diagnostic tool for elemental and transient analysis in studies of laser desorption and laser ablation. The multistep laser photoionization process, when coupled with conventional mass analysis, can provide exceptional detectivity, dynamic range, and discrimination against interfering species. These properties can be used to great advantage both in the analysis of conventional materials and in the interrogation of interfacial phenomena. In this paper, we have briefly reviewed two recent applications of RIMS, both for conventional chemical analysis, and as a diagnostic for other laser-based processes.

In the examination of routine analytical samples, the effective duty cycle can be greatly improved relative to continuous sample evaporation. In addition, these methods allow direct analysis without extensive sample preparation. It is anticipated that RIMS will play an increasingly important role in the study of the laser desorption processes, especially as surface imaging capabilities become coupled to the ionization detection.

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