CONF-960391--2

LA-UR- 95-3888

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Submitted to: Optical Society of America, March 18-22, 1996, Orlando, FL

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Resonant Laser Ablation Ion Trap Mass Spectrometry - Recent Applications for Chemical Analysis

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Abstract

Resonant Laser Ablation is a useful ionization mechanism for quadrupole ion trap mass spectrometry. Presented are: selective ionization for attogram range analytes, metal ion chemistry, and M^+ CI for chemical analysis.

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Introduction

Resonant Laser Ablation (RLA) is a useful ionization process for selectively producing gas phase ions from a solid sample. Recent use of RLA for mass spectrometry by this group [1] and by others [2] has produced a wealth of knowledge and useful analytical techniques. The method relies upon the focusing of modest intensity laser pulses ($\leq 10^7$ W·cm^{-2}) upon a sample surface. A small quantity of material is vaporized, and atoms of desired analyte are subsequently ionized by (n+m) photon processes in the gas phase (where n = # of photons to a resonant transition and m = # of photons to exceed the ionization limit). We have been using (2+1) resonant ionization schemes for this work; a comprehensive list of (2+1) transitions used by this and other research groups has been published elsewhere [3].

Quadrupole ion trap mass spectrometry is realizing a very prominent role in current mass spectrometric research. Ion traps are versatile, powerful and extremely sensitive mass spectrometers, capable of a variety of ionization modes, MS^n type experiments, high mass ranges and high resolution, all for a fraction of the cost of other instrumentation with similar capabilities. Quadrupole ion traps are ideally suited to pulsed ionization sources such as laser ionization methods, since their normal operational method (Mass Selective Instability [4]) relies upon the storage of ions from a finite ionization period followed by ejection and detection of these ions based upon their mass to charge ratios.

2. Selective Ionization for Trace Atomic Analysis

As with all ion storage mass spectrometric methods, the effects of space charge are experienced when too many ions are created and subsequently stored by the mass analyzer. The effects of space charge upon ion traps include severely degraded resolution and even a total loss of meaningful analytical signal. For trace analysis, it is desirable to either store selected analytes, or to use a selective ionization scheme (i.e. RLA) for the desired analyte. Application of either or both of these methods allows elimination of unwanted matrix species ions from the ion storage volume, eliminating the effects of space charge. The selective nature of RLA is presented: no signal is observed for modest laser plulse energies(~20 μJ/pulse) unless the laser is tuned to a resonant transition for a component in the sample. The etch rate for RLA was determined (using 100 Å Copper films on Silicon wafers) to be 0.33 pg/shot. The RLA Pb(2+1) mass spectra for lead (26.5 ppm) in NIST sample # 494 (unalloyed copper) was readily obtained with significant ion signal for all naturally ocurring lead isotopes. Assuming that the etch rate is similar for thin film copper and bulk copper, this results in an absolute detection limit of ~9 attograms. This is a conservative value, since the signals observed for lead were much larger than the standard 3σ from the background typically used to calculate detection limits.

3. Selective Reagent Ion Source for Ion Chemistry Investigations

Mass spectrometric investigations of the gas phase chemistry of metal ions have been conducted as early as the 1970's. These early studies involved metal ion affinity investigations for simple compounds. This early work used thermionic emitters for metal ion production and FT-ICR mass spectrometers for reaction and product analysis. A recent review of gas phase metal ion chemistry [5] is given to which readers can refer for additional information.

The use of quadrupole ion trap mass spectrometers for metal ion chemistry can be traced back to Cooks and co-workers [6] who examined the chemistry of gold ions with benzene. Recent quadrupole ion trap research by Brodbelt et.al.[7] used laser desorption to generate a variety of metal ions for gas phase ligand complexation investigations.

A variety of metal ion sources have been used for gas phase ion chemistry studies. Alkali metals are readily generated via thermionic emission sources, and various metal carbonyls can be reduced by electron impact to yield naked metal ions. An alternate mode for creating gas phase metal ions is through laser ablation of pure metal and mixed metal samples within the mass spectrometer. A potential deficiency of any of these methods arises when the researcher wants to compare reactivities of different metal ions with the same chemical system(s). Previous work with pure metal ion sources required that the metal source be changed; this often involving in the temporary corruption of the high vacuum environment, and leading to altered though similar conditions after the change. Alternately, if a mixed metal source was used, the reactions due to the various reactants had to be sorted out simultaneously, potentially leading to very complex chemistry.

Research in this laboratory has been directed at using Resonant Laser Ablation (RLA) as a means of selectively creating different types of ions from a multicomponent sample. This work demonstrates an alternative strategy for the investigation of the gas phase ion chemistry of a variety of metal ions under identical chemical conditions, since all ions investigated can be created selectively from the same sample by simply tuning the ablation (dye) laser to the appropriate "2+1" transition for the desired metal ion. This method is not only simple to implement, but allows rapid changes between different types of metal ions without disruption of the vacuum environment or altering sample geometry.

For a test system, we chose the reaction of several first-row transition elements (Cr^+, Fe^+, Ni^+ and Cu^+) with acetone. This reaction system, and similar reactions with other aldehydes and ketones, has been studied previously,[8] and serves as a convenient test to benchmark this technique. Figure 2 shows the observed trends for the various metal ions reactivity with acetone.

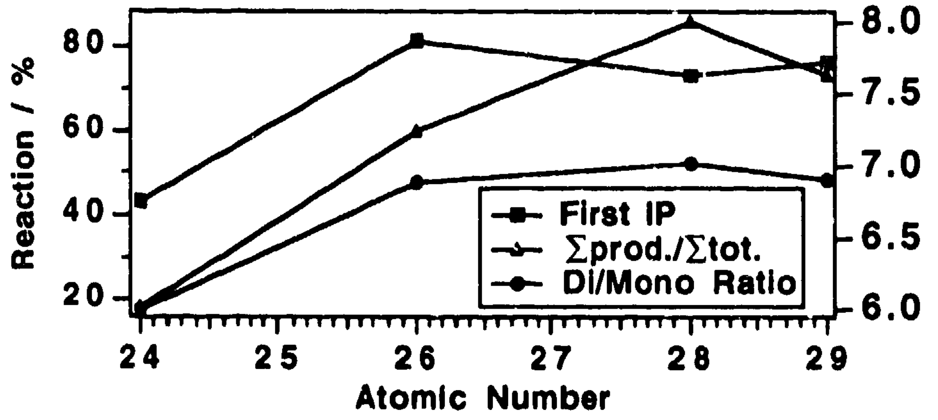

Figure 2: Reactivity trends for first row transition metals with acetone.

The results of this study show an increase in reactivity (ΣProducts / ΣTotal) as the ionization potential of the specific metal reagent ion increases, for both mono- and bi-adduct formation. This observation is consistent with the findings of other researchers [9], who conclude that the IP of gas phase metal ions is directly related to their observed gas phase reactivity.

4. Transition Metal CI for "difficult" Environmental Contaminants

The structure of certain chemical compounds makes "fingerprint" analysis difficult. The tri-butyl ester of phosphoric acid (TBP), is used as both a plasticizing agent and as a metal complexation agent for actinide chemistry. Environmental contamination by TBP is difficult to diagnose: TBP has low volatility, is thermally unstable, does not absorb in the visible spectrum, and gives predominately low mass fragments by electron impact ionization. In efforts to alleviate the difficulties associated with TBP analysis, it's gas phase ion chemistry with first row transition metal ions (Cr^+, Fe^+, Ni^+, Cu^+) was examined. Both iron and nickel ions yield TBP adducts that lose 2 hydrogens, whereas chromium and copper form direct condensation products. Similar results have been reported for metal ion reactions with ketones, the differing reaction products explained by d electron configurations. The metal ion CI mass spectra are relatively simple, with large ion signals observed for the parent adduct species. The characteristic isotopic patterns for the metal ions in question confirm that the observed adduct species are indeed metal containing products.

Further investigations involving trace quantities of TBP upon a sample insertion probe for RLA/LD type experiments proved difficult: the TBP adduct signals rapidly decay upon probe insertion into the mass spectrometer. It is assumed that the TBP simply evaporates from the probe, with no direct laser desorption observed. To solve the volatility problem, a modified zeolite sample (containing silver) was prepared. This material was head space equilibrated with a small amount of TBP (gas phase interaction); subsequent analysis of the zeolite by using Ag(2+1) RLA @ 469.84 nm resulted in a mass spectrum (Figure 2), which shows ion signals for $Ag(TBP)^+$, as well as the loss of one, two and three butyl groups.

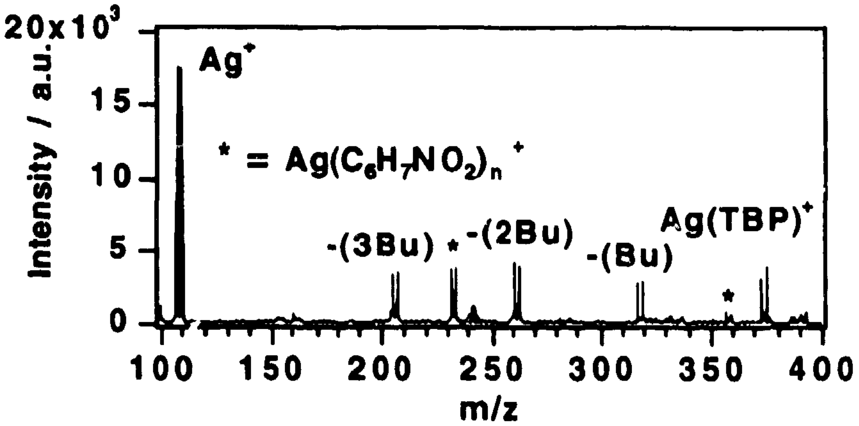

Figure 2: The Ag(2+1) RLA mass spectrum for a silver modified zeolite equilibrated with TBP headspace vapors. The zeolite was mounted on a type 304L Stainless steel probe with Ethyl-Cyanoacrylate Glue.

The characteristic doublet isotopic distribution for silver ($^{107}Ag = 0.5184$, $^{109}Ag = 0.4816$) is observed for all the TBP condensation products, as well as for adducts that originate from the ethyl-cyanoacrylate (super glue) used to mount the zeolites to the probe. The origins of the fragmentation of the TBP are under investigation, as they may be from catalytic cracking by the zeolite or from decomposition during the RLA process. Current research includes the use of these modified zeolite sorbents for environmental measurements, as well as direct approaches to the analysis of TBP in environmental samples.

5. References

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