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Volume 426

Laser-based Ultrasensitive Spectroscopy and Detection V

Richard A. Keller
Chairman/Editor

Cooperating Organizations
Los Alamos National Laboratory
Oak Ridge National Laboratory

August 23-24, 1983
San Diego, California

Proceedings of SPIE—The International Society for Optical Engineering

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LASER-BASED ULTRASENSITIVE SPECTROSCOPY AND DETECTION V

Volume 426

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Session 1—Resonance Ionization Mass Spectrometry (RIMS)

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Session 2—Fluorescence Detection of Single Atoms and Molecules

William Fairbank, Jr., Colorado State University

Session 3—Advanced Concepts in Absorption Measurements

James Snyder, National Bureau of Standards

Session 4—Applications of Laser-Based Analytical Techniques

Edward S. Yeung, Iowa State University

INTRODUCTION

The major purpose of this conference was to bring scientists specializing in developing laser techniques capable of the highest sensitivity and selectivity together with scientists interested in applying these techniques to important practical problems. The conference divided into four sessions: 1) Resonance Ionization Mass Spectrometry (RIMS), 2) Fluorescence Detection at the Single Atom or Molecule Level, 3) Advanced Concepts in Absorption Measurements, 4) Applications of Laser Based Analytical Techniques.

It is clear from the talks presented in the first session that RIMS is rapidly becoming a practical technique for the removal of isobaric interferences in atomic analysis with important applications in uranium and plutonium analysis, weapons diagnostics, and trace detection for geochemistry and basic physics. The second session concentrated on techniques and problems associated with the detection of single atoms, ions, and molecules as they transit a laser beam. The most practical problems in this area are associated with the spectroscopy and detection of atoms and ions in a beam exiting a mass separator. New methods of measuring changes in optical transmission at the level of 1 part in 10^7 to 1 part in 10^8 were discussed in the third session. This sensitivity results from the fact that laser amplitude fluctuations fall below the shot noise in the emitted photons if the laser is modulated at frequencies higher than 1-10 MHz. It was demonstrated that this technique is capable of quantitative detection of ~ 1000 atoms in the laser beam. It appears that this method possesses considerable potential for certain analysis problems. The final session was devoted to the application of sensitive and selective laser-based techniques to problems in chromatography, mass spectrometry of molecules, combustion, and Raman spectroscopy. It is clear from these talks that significant progress is being made and that the prognosis for future improvements is excellent.

From the lively discussion following each of the talks and comments made to me following the conference, it appeared that the goal of improving communication between scientists interested in ultrasensitive detection was successful. The real test of success in this endeavor is to see if new experiments result from the interactions developed at this meeting.

Richard A. Keller
Los Alamos National Laboratory

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Session 1

Resonance Ionization Mass Spectrometry (RIMS)

Chairman

G. Samuel Hurst

Oak Ridge National Laboratory

Noble Gas Detection Using Resonance Ionization Spectroscopy and a Quadrupole Mass Spectrometer

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Abstract

The technique of Resonance Ionization Spectroscopy (RIS) is being extended to develop a means for counting individual atoms of a selected isotope of a noble gas. In this method, lasers are used for RIS to obtain atomic species (Z) selectivity and a small quadrupole mass spectrometer provides isotopic (A) selectivity. A progress report on the objective of counting each atom of a particular isotope of a noble gas is given.

Resonance ionization spectroscopy and its use for the detection of single atoms has been reviewed.¹ More recently, our efforts at ORNL have turned to the problem of direct counting of noble gas atoms^{2,3,4} as an alternative to decay counting of particular isotopes of noble gas species. For broader applications, the ORNL group is trying to develop a facility for counting a few rare gas atoms of a given isotopic variety in a sample. The detection of a small number of ^{81}Kr atoms (<1000) is very important for groundwater dating, polar ice-cap dating, and nuclear waste disposal applications, and solar neutrino research. The ultimate goal is to count a small number (e.g., 100 to 1,000) of selected atoms having mass number A, even when mixed with 10^{12} or more atoms having mass number $A \pm 1$.

The experimental schematic is shown in Figure 1. The concept for counting noble gas atoms with isotopic selectivity is to utilize a laser for ionizing atoms of a selected atomic

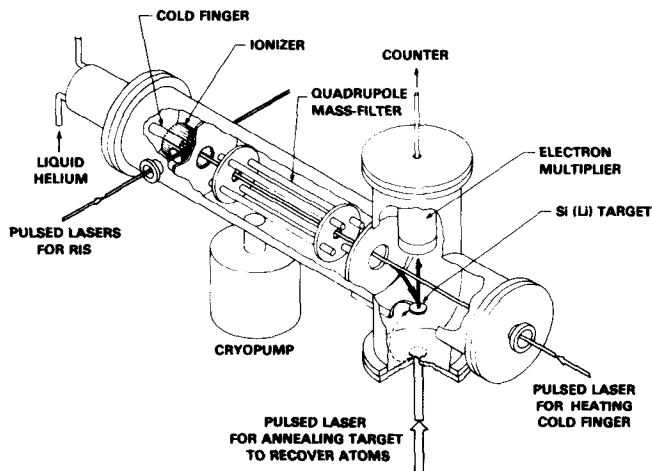


Figure 1. Experimental schematic for counting noble gas atoms with isotopic selectivity (a device referred to locally as "Maxwell's demon").

number (Z) and a mass spectrometer for atomic mass (A) selection. After atoms have been Z and A selected, the ions are accelerated to a few kilovolts onto a target where they are implanted. Suitable targets will emit a pulse of several electrons each time that the selected ions are implanted. An electron multiplier is used with sufficient gain to count each implanted ion from the electrons emitted by the target. In a small quadrupole mass spectrometer the rejection ratio for neighboring masses is only about 10^4 . Thus, the krypton atoms implanted in the target must be released and passed through the mass filter again. For example, a sample containing 10^8 krypton atoms of all isotopes and 1000 ^{81}Kr atoms will have to be cycled twice through the quadrupole filter. The first time through, 10^7 atoms of ^{80}Kr will give 10^3 counts which is comparable to the number of counts

from ^{81}Kr . If the gaseous part of the sample is pumped and the implanted krypton atoms are released, there will be 1000 ^{81}Kr atoms and 1000 ^{82}Kr atoms in the chamber. On the next cycle of this process the chances are good that not a single atom of ^{82}Kr will be counted.

There are no commercially available lasers for the efficient and selective excitation of krypton. A four-wave mixing scheme was used to generate a 116.5-nm laser beam with energies of 500 nJ/pulse. Thus, krypton atoms could be efficiently excited by resonance radiation and subsequently ionized. Finally, an "atom buncher" is needed to enhance the probability that krypton atoms will be in the ionization laser beam at the time of the laser pulse. In brief, the major requirements for counting a few isotopically selected atoms include (1) an atom buncher to put krypton in the ionization laser beam, (2) the appropriate laser beams for achieving excitation and ionization of krypton, (3) a method for implanting the isotopically selected krypton atoms into a metal target with efficiency approaching 100%, (4) an electron multiplier with efficiency near 100% for counting the pulses of secondary electrons released during ion implantation, and (5) a method for the total release of the implanted krypton atoms so that the counting sequence can be repeated. In addition to the above requirements, the experimental facility must be maintained under high vacuum without pumping, the outgassing rate of krypton from the chamber must be low ($<10^5/\text{min}$), and the surfaces of the chamber must be clean to prevent krypton from sticking to the walls of the chamber.

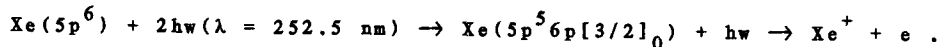
The stay times of krypton and xenon on various metal surfaces have been measured by Wilmoth and Fisher.⁵ The stay time of rare gases on clean metal surfaces can be estimated as

$$\tau = \tau_0 [\exp(\epsilon/kT_s)] ,$$

where τ = stay time, ϵ = heat of adsorption, and T_s = temperature of the metal. For most metals, τ_0 is less than 10^{-15} s and ϵ_0 is less than 8 kcal/mole. Thus, the stay time of rare gases on the surface of a clean metal chamber should be less than 1 ns. With a clean chamber surface, it is unlikely that rare gas atoms will be lost by sticking to the wall of the chamber. The experimental chamber was electropolished to reduce the outgassing rate and to prevent the sticking of rare gases to the walls. Radioactive ^{85}Kr was put in the chamber to determine the loss of krypton. No loss due to sticking to the surface was observed.

In order to keep the chamber surface clean, no pumps containing oil were used. The experimental chamber was roughed down to a few microns by a liquid nitrogen cryosorption pump. A compressed helium cryopump was used to achieve ultrahigh vacuum. The chamber was baked and pumped for two days before introducing a sample to reduce the outgassing rate. A titanium-zirconium getter pump was used to getter outgassed molecules without pumping rare gases. The typical chamber pressure was 10^{-10} Torr before a sample was introduced. The pressure of the chamber can be kept below 10^{-8} Torr for several weeks after the cryopump is valved off.

Excitation processes for rare gas atoms can involve either two-photon absorption or one VUV-photon absorption. Two-photon resonance excitation of xenon followed by photon ionization was demonstrated in 1980.⁶ These excitation and ionization processes were



The two-photon transition rate was found to be $2 \times 10^{-9} \text{ s}^{-1} \text{ w}^{-2} \text{ cm}^4$ when using a laser bandwidth of 0.01 nm. The ionization cross section of $\text{Xe}(5p^5 6p)$ was $3 \times 10^{-18} \text{ cm}^2$ at the 252.5-nm wavelength. The effective volume for ionization of xenon by two-photon excitation was estimated to be $\sim 1 \times 10^{-4} \text{ cm}^3$ when the laser power density was $2 \times 10^9 \text{ w/cm}^2$. It is much more difficult to achieve two-photon excitation of krypton atoms. The effective volume for two-photon excitation of krypton will be orders of magnitude less than the process for xenon when using a commercially available Nd-YAG laser. Since it is always necessary to focus the laser beam for a two-photon excitation process, the ionization of background gases can be significant due to multiphoton processes.

The probability of ionization¹ well away from any resonance is $P_i = F\tau\sigma_n$, where F = photon flux, τ = laser pulse duration, and σ_n is the cross section for the n -photon ionization process. The cross section is approximately

$$\sigma_n \approx 3 \times 10^{-18} \left[\frac{1.5n \times 10^{-14}}{E_1 \sqrt{\lambda}} \right]^{2(n-1)} ,$$

where E_1 is the energy of the first excited state in units of eV and λ is the wavelength in nanometers. With $I \sim 10^9 \text{ w/cm}^2$, $E_1 \sim 12 \text{ eV}$, $\lambda = 252.5 \text{ nm}$, and $\tau = 4 \times 10^{-9} \text{ s}$, the probability of ionization is $\sim 10^{-9}$. Since large molecules have a very dense excited state, the probability of multiphoton ionization can be several orders of magnitude higher than

this value. With a background pressure of 10^{-8} Torr, multiphoton excitation of molecules may cause a large background of other atoms, making the counting of a few thousand isotopically selected rare gas atoms very difficult.

Since two-photon excitation of rare gases not only causes multiphoton ionization of background gases but also gives a small effective ionization volume, it is obvious that single VUV photon excitation of rare gas atoms is preferred. The most difficult step is the generation of vacuum ultraviolet radiation at 116.5 nm to excite $\text{Kr}(5s[1/2]J=1)$. However, coherent radiation at this wavelength was recently produced by four-wave mixing in xenon gas.⁷ The laser scheme is shown in Figure 2. The sum process $2w_1 + w_2$, with w_1

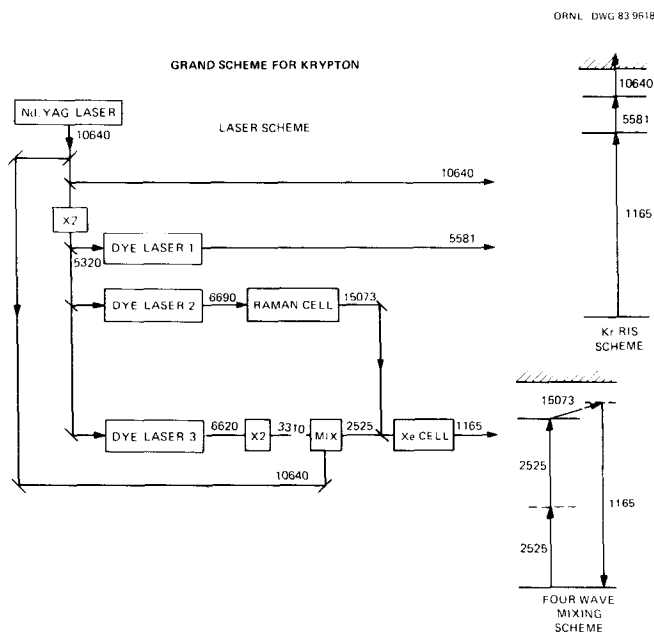


Figure 2. Laser schemes suitable for RIS of krypton atoms.

corresponding to 252.5 nm for two-photon excitation of xenon and w_2 corresponding to 1.51 μm , produced 116.5 nm radiation near the $7s$ level in xenon. With a xenon pressure of 90 Torr and argon pressure of 835 Torr (to produce phase matching for constructive interference) the energy per pulse for the VUV around 116.5 nm was found to be ~ 500 nJ, using commercially available Nd-YAG pumped dye lasers. After krypton was excited by the VUV laser beam, another dye laser was used to promote krypton to the $6p[1/2]_0$ state which was ionized by a 1.06- μ infrared laser. By putting a known amount of krypton into the mass spectrometer chamber and calibrating the detection efficiency of a Johnston multiplier, the effective ionization volume, which includes the transmission of a quadrupole filter, was found to be $1 \times 10^{-4} \text{ cm}^3$. With a mass spectrometer volume of three liters, the probability is 3×10^{-8} that an atom moving at random will be ionized in one laser pulse. With a laser repetition rate of 10 Hz, 1000 hours are required to count all the isotopically selected atoms. Thus, an atom buncher⁸ was designed to reduce the time required to count krypton atoms.

It is known that rare gas atoms sitting on a cold metal surface can be released by a fast laser pulse. For instance, Ready⁹ calculated the time required for release of a gas after a laser pulse. For a Q-switched fast laser pulse, a gas leaves the surface in less than a few hundred nanoseconds. The atom buncher was designed so that rare gas atoms could be trapped on a cold surface and subsequently released at any desired time by the application of a laser pulse. With the correct time synchronization between the laser pulse releasing the gas and the ionization laser beam, the probability of putting rare gas atoms in the ionization laser beam can be enhanced dramatically. The atom buncher⁸ consists of a cold finger held at low temperature by means of liquid helium in contact with a copper conductor that connects onto a thin stainless steel disk which terminates in a heat sink. In this way, a temperature gradient is established so that a 2-mm diameter spot is held at about 15 K. The temperature outside the 2-mm diameter disk can be kept above 80 K such that krypton can only condense on the cold spot. When light from a flashtlamp-pumped dye laser is absorbed on the metal surface, all atoms leave quickly (< 200 ns) and travel about 1 mm

before encountering the slightly time-delayed RIS laser pulse. After a thin layer of the buncher disk is heated to about 80 K to release krypton atoms, it cools back to 15 K in several microseconds; thus, the krypton atoms that were not ionized by the laser beams return with a characteristic recurrence time. The entire atom buncher was tested by using ^{85}Kr and a Geiger-Mueller (G-M) tube to count ^{85}Kr . All atoms were released when a 0.1 J/cm^2 dye laser pulse struck the cold spot. The recurrence time in a 1-liter chamber was $\sim 15 \text{ s}$. The experimental data are shown in Figure 3. With the atom buncher, 10% of krypton atoms from the buncher can be put into the RIS laser beam. Only 20 to 30 minutes are required to count 1000 isotopically selected krypton atoms.

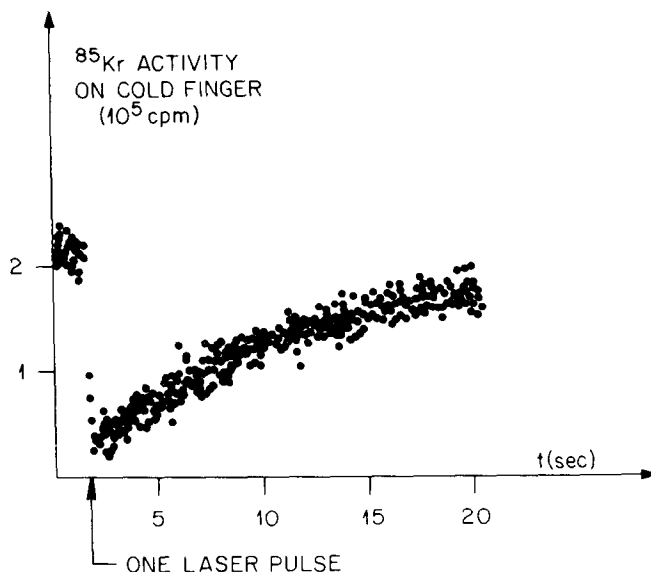


Figure 3. Demonstration of the atom buncher. The recurrence time was found to be 15 s for a 1-liter system.

After krypton atoms are ionized by the laser beams, the isotopically selected krypton ions pass through a quadrupole mass filter with high transmission efficiency ($>90\%$ for a 2-mm aperture). Ions not passing through the mass filter impinge on the quadrupole rods or the chamber wall and are neutralized. Since the ion energy is kept low ($<20 \text{ eV}$) through the quadrupole filter, ion implantation causing the loss of krypton atoms can be neglected. The population ratio of $^{84}\text{Kr}/^{86}\text{Kr}$ remained the same for several hours when the high voltage on the detector was off. Thus, the possible loss due to ion implantation onto quadrupole rods was ruled out.

After passing through the quadrupole filter, the krypton ions were accelerated to 10 keV and implanted in a metal target. Using radioactive ^{85}Kr , we found the sticking probability of krypton on aluminum at 10-keV energy to be almost 100%. The ion implantation of xenon in stainless steel was also demonstrated by RIS.¹⁰ The implantation depth for 10-keV krypton in metal is about 10 nm. The stay time of rare gas atoms in metal depends on the diffusion process of rare gases in metals. The diffusion rate depends on the activation energy and the temperature of the metal:

$$D = D_0 \exp(-E_a/kT).$$

For most metals at room temperature, weeks to years are required for krypton atoms trapped at 10 nm to diffuse out of the metal.

When high-energy krypton ions strike a metal target, secondary electrons are emitted from the metal. The numbers of secondary electrons (γ) produced from aluminum and beryllium copper for one 10-keV krypton ion are three and six, respectively. A Johnston electron multiplier was used to detect the secondary electrons and produce a pulse for counting krypton ions. With $\gamma = 6$ and $\delta = 1$ (δ is the number of secondary electrons produced from the front surface of the Johnston multiplier by one incident 10-keV electron), the counting efficiency is close to 100%. If aluminum foil is used as a target, the counting efficiency is less than 100%. An "electron preamplifier" containing two MgO plates can be used to

give six electrons at low energy for each high-energy (10 keV) electron. Thus, the counting efficiency can be increased to ~100%.

With a sample containing small numbers of isotopically selected krypton atoms, but having more than five orders of magnitude of other krypton isotopes, the isotopically selected krypton atoms cannot be counted accurately without preenrichment since the abundance ratio of the quadrupole mass filter is only about 10^4 . After implanting all isotopically selected krypton atoms and 10^{-4} of undesired other krypton isotopes, the residual krypton in space will be pumped out. By implanting ^{85}Kr in aluminum foil at 10 keV, all ^{85}Kr atoms can be released by rf heating to vaporize the aluminum foil.¹⁰ Rare gas releases from solids can also be achieved by laser annealing.¹¹ The detailed mechanism is currently under study at ORNL.

Since the abundance ratio of a small quadrupole mass spectrometer is only 10^4 , the outgassing rate of krypton should be kept low to achieve accurate counting. The rate of outgassing of krypton from our apparatus was measured to be $\sim 1 \times 10^5$ atoms/min. If the time required to count a sample is ~ 20 min and the rejection ratio of the mass filter is 10^4 , the outgassing of krypton will not contribute appreciably to the counting rate in mass ^{81}Kr .

If the sample has more than 10^{12} krypton atoms, preenrichment of isotopically selected krypton is impractical using the RIS-laser method because of space charge limits. Thus, an electron impact ionizer for the mass spectrometer is needed to achieve preenrichment. Experimental data in Figure 4 indicate that three orders of magnitude of isotopic enrichment can be achieved by such a scheme, but a loss of a part of the sample can also occur due to

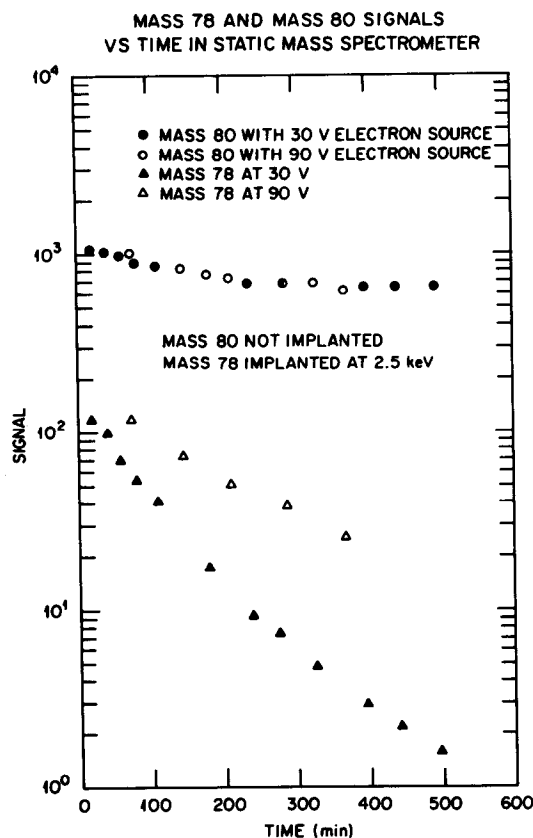


Figure 4. Enrichment of ^{80}Kr in the gas phase by implanting ^{78}Kr in a stainless steel plate biased at -2.5 kV. The spectrometer throughputs for krypton were 5.7 mA/Torr and 1.6 mA/Torr, respectively. The volume of the mass spectrometer was about 2 liters.

implantation. For most applications, only the ratio between two isotopes is required; groundwater dating is an example. In such an application the loss of a minor part (25%) of the sample does not limit the experimental accuracy.

In conclusion, we have successfully tested all the major parts of an experiment to count a few thousand isotopically selected krypton atoms. We are in the process of putting these separate parts together for the first demonstrations using real samples.

Acknowledgments

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References

1. G. S. Hurst, M. G. Payne, S. D. Kramer, and J. P. Young, "Resonance Ionization Spectroscopy and One-Atom Detection," Rev. Mod. Phys., Vol. 51, pp. 767-819. 1979.
2. G. S. Hurst, M. G. Payne, S. D. Kramer, and C. H. Chen, "Counting the Atoms," Phys. Today, Vol. 33, No. 9, pp. 24-29. 1980.
3. C. H. Chen, G. S. Hurst, and M. G. Payne, "Resonance Ionization Spectroscopy: Inert Atom Detection," in Progress in Atomic Spectroscopy, Part C, edited by H. F. Beyer and H. Kleinpoppen (Plenum Publishing Co., New York), in press.
4. G. S. Hurst, C. H. Chen, S. D. Kramer, M. G. Payne, and R. D. Willis, "A Radiochemical Solar Neutrino Experiment Using $^{81}\text{Br}(\nu, e^-)^{81}\text{Kr}$," in Science Underground, edited by Michael Martin Nieto, W. C. Haxton, C. M. Hoffman, E. W. Kolb, V. D. Sandberg, and J. W. Toevs, AIP Conference Proceedings No. 96 (American Institute of Physics, New York, 1983), pp. 96-104.
5. R. G. Wilmoth and S. S. Fisher, "Steady Time Measurements for Xe, Kr, and CO₂ Physisorbing on Ni and Cu Surfaces," Surface Sci., Vol. 72, pp. 693-708. 1978.
6. C. H. Chen, G. S. Hurst, and M. G. Payne, "Direct Counting of Xe Atoms," Chem. Phys. Lett., Vol. 75, pp. 473-477. 1980.
7. S. D. Kramer, C. H. Chen, M. G. Payne, G. S. Hurst, B. E. Lehmann, and R. D. Willis, "Two-Photon Resonant, Four-Wave Mixing in Xenon-Argon Gas Mixtures," in Proceedings Sixth International Conference on Laser Spectroscopy (Interlaken, Switzerland, June 27-July 1, 1983), in press.
8. G. S. Hurst, M. G. Payne, R. C. Phillips, J.W.T. Dabbs, and B. E. Lehmann, "Development of an Atom Buncher," submitted for publication.
9. J. F. Ready, "Effects Due to Absorption of Laser Radiation," J. Appl. Phys., Vol. 36, pp. 462-468. 1965.
10. R. D. Willis, S. L. Allman, C. H. Chen, G. D. Alton, and G. S. Hurst, "Pumping of Inert Gases by Electron-Impact Ionization Sources and Associated Memory Effects," submitted for publication.
11. B. R. Appleton (Solid State Division, Oak Ridge National Laboratory), private communication. See, for example, E. M. Lawson, M. D. Scott, and A. Rose, "Annealing of Ar Sputter-Etch-Damaged Si by a Q-Switched Ruby Laser," J. Vac. Sci., Vol. B114, pp. 5-36. 1983.

Selective laser ionization for mass spectral isotopic analysis

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Introduction

The mass spectrometric determination of accurate atomic isotope ratios is a task greatly complicated by the presence of isobaric (same mass) interferences. While there exist classical techniques for reducing such interferences, such as ultrahigh resolution mass spectrometry, these solutions often break down in the face of particular technical difficulties, such as the determination of very large isotope ratios or very small samples.

Resonance ionization mass spectrometry (RIMS) has been suggested as a potential solution for these difficulties.¹⁻⁵ Resonant enhancement of the ionization process can provide a high degree of elemental selectivity, thus eliminating or drastically reducing the interference problem. In addition, extension of this method to isotopically selective ionization has the potential for greatly increasing the range of isotope ratios that can be determined experimentally. This gain can be realized by reducing or eliminating the tailing of the signal from the high abundance isotope into that of the low abundance isotope, augmenting the dispersion of the mass spectrometer.

Most analytical applications of RIMS have relied on thermal atomization followed by pulsed laser ionization. Relatively poor sensitivities¹⁻³ have often resulted because of the poor temporal overlap associated with the match of continuous sample evaporation and low repetition rate (< 30 Hz) pulsed lasers. There are several methods of addressing this problem. One potential solution is simply to use very high (> kHz) repetition rate lasers for the photoionization process. This should be possible using copper vapor- or excimer-pumped dye lasers. Another possibility is to match the laser and sample duty cycles by pulse-evaporating the sample via laser ablation^{6,7} or ion sputtering.⁸ Lastly, laser and sample duty cycle may be matched by using a continuous wave (cw) laser source.⁹ This last possibility is particularly appealing for several reasons. First, the sample preparation technique (thermal evaporation) is well known, and reasonably well understood.⁹ Second, the necessary laser hardware is reasonably mature and reliable. And lastly, the use of cw lasers for ionization allows the use of pulse counting electronics, with its potential advantages in sensitivity and additional dynamic range.

In the remainder of this paper, we briefly discuss the hardware and techniques used in both our pulsed and cw RIMS experiments. Results are presented for both cw ionization experiments on Lu/Yb mixtures, and spectroscopic studies of multicolor RIMS of Tc. Lastly, we discuss practical limits of cw RIMS analysis in terms of detection limits and measurable isotope ratios.

Experimental

Two sets of equipment were used to produce the results presented here. For survey work and basic spectroscopy, a time-of-flight (TOF) mass spectrometer system in conjunction with two excimer laser-pumped dye lasers was utilized. Although of limited resolution and sensitivity, this system provided a rapid and convenient means to obtain appropriate wavelengths for future analytical measurements. The latter were done on a 12", 68° magnetic sector mass spectrometer¹⁰ using a broadband cw dye laser pumped by an ultraviolet-output argon-ion laser. High sensitivity and mass resolution were thus available for measuring high dynamic range isotope ratios.

In the TOF system, two dye laser heads were pumped by a single excimer laser, providing roughly synchronized pulses (± 10 nsec) at two different wavelengths. These laser beams (1-5 mJ each) were counterpropagated through the TOF source region, with loose collimation to prevent striking interior surfaces. Technetium samples, prepared through electrodeposition of 1-2 micrograms of metal, were introduced to the source at right angles to the laser beams and ion flight path. Photoions were accelerated down the flight tube in two stages, impacting a channeltron detector after traveling approximately 40 cm. Pulses from the channeltron were amplified, then monitored with a boxcar integrator connected to a stripchart recorder. Associated electronics made it possible to scan either laser wavelength or the detection gate, producing optical or TOF spectra.

In experiments with cw ionization, the single dye laser output was focussed between the side filaments of a triple-filament thermal ionization source.¹¹ Lutetium samples were prepared by evaporation from HCl solution, and contained approximately 1 μ g each of Lu, U¹² and in some cases, Yb. After a preliminary degas step in which the filaments were heated to 1400 C in the source, then cooled to room temperature, analytical measurements were performed at 900 C. Ions were detected in one of the two ways after mass analysis: with an electron multiplier or, for count rates > 250000 Hz, a faraday cup. Isotope ratio determinations were performed by alternate mass measurements, with 30 seconds dwell time at each repetition.

Results

Lutetium

Radiochemical weapons diagnostics applications for resonance ionization mass spectrometry require the capability to measure large dynamic range isotope ratios, typically 10^{-3} to 10^{-5} , as well as isobaric selectivity. This in turn requires high ionization rates, to insure reasonable counting statistics, and provides the rationale for cw ionization. Having previously demonstrated that cw lasers do indeed yield large numbers of ions,⁴ the current experiments were designed to demonstrate the ability to measure large isotope ratios, approaching those necessary for practical application to diagnostics.

Table 1 shows the composition of a typical mixed Lu/Yb sample where large isotope ratios must be determined in the presence of isobaric impurities. Figure 1 shows a comparison between conventional thermal ionization and cw resonance ionization at 451.9 nm for this sample. Quite clearly, thermal ionization does not have the ability to provide a meaningful ¹⁷⁵Lu/¹⁷⁶Lu ratio. Resonance ionization, via cw laser, however, does provide elemental selectivity while maintaining sufficient ion yields (10^6 - 10^7 cps) for long periods of time (> 1 hour). Typical accuracies of the RIMS measurement are 10% on a ¹⁷⁵Lu/¹⁷⁶Lu ratio of 3.6×10^{-3} . The primary source of this error is wavelength drift in the dye laser system coupled with the Lu isotope shift. The use of stabilized single-frequency dye lasers is expected to reduce the magnitude of this error. This improvement should also allow the use of lower sample temperatures through greater ionization efficiency, eliminating the residual Yb thermal ionization visible in the baseline of Figure 1b.

Table 1. Isotope Amounts

<u>Lu</u>	<u>Mass</u>	<u>Yb</u>
310 pg	173	320 ng
59 pg	174	630 ng
1.75 μ g	175	--
47 ng	176	250 ng

Technetium

Technetium is an extremely rare element exhibiting no stable isotopes. Because of its scarcity it is particularly useful as a tracer in hydrologic and geologic studies. Another potential application arises from the fact that the production of technetium can serve as an indicator for the passage of solar neutrinos.¹³ We have previously reported¹⁴ on the use of pulsed lasers for single color, two photon ionization on Tc in the wavelength range $300 \text{ nm} < \lambda < 320 \text{ nm}$. Since analysis of that data suggested that the pulsed laser source would be inadequate for the analytical problem,¹⁵ we are currently exploring multicolor ionization schemes using visible wavelengths that can be generated with a cw dye laser.

Initial experiments involved absorption of a violet photon, $420 \text{ nm} < \lambda_1 < 430 \text{ nm}$, to excite one of the ⁶P_{1/2} {4d⁵5s(a'S)5p} levels, followed by absorption of a blue photon, $450 < \lambda_2 < 475$, to excite one of the ⁶D_{3/2} {4d⁵5s(a'S)5d} or ⁶D_{5/2} {4d⁵(a'D)6s} levels.¹⁵ These levels are all sufficiently high in energy that another photon of either color could effect the ionization. Figure 2 shows a representative spectrum in which ionization signal is monitored as a function of λ_2 following excitation of the ⁶P_{1/2} level ($\lambda_1 = 423.8 \text{ nm}$). The wavelengths displayed are taken from a reading of the dye laser dial, which had been previously calibrated using uranium optogalvanic signals,¹⁶ and are accurate to 0.1 nm. Several features should be noted. First, the abundance of resonances available from this single excited state suggest that spectral overlap from isobaric interferences should not be a significant problem. If interferences occur at one wavelength, one simply chooses another resonance. Secondly, the relative intensities observed here show virtually no correlation with the published arc and spark spectra,¹⁵ in

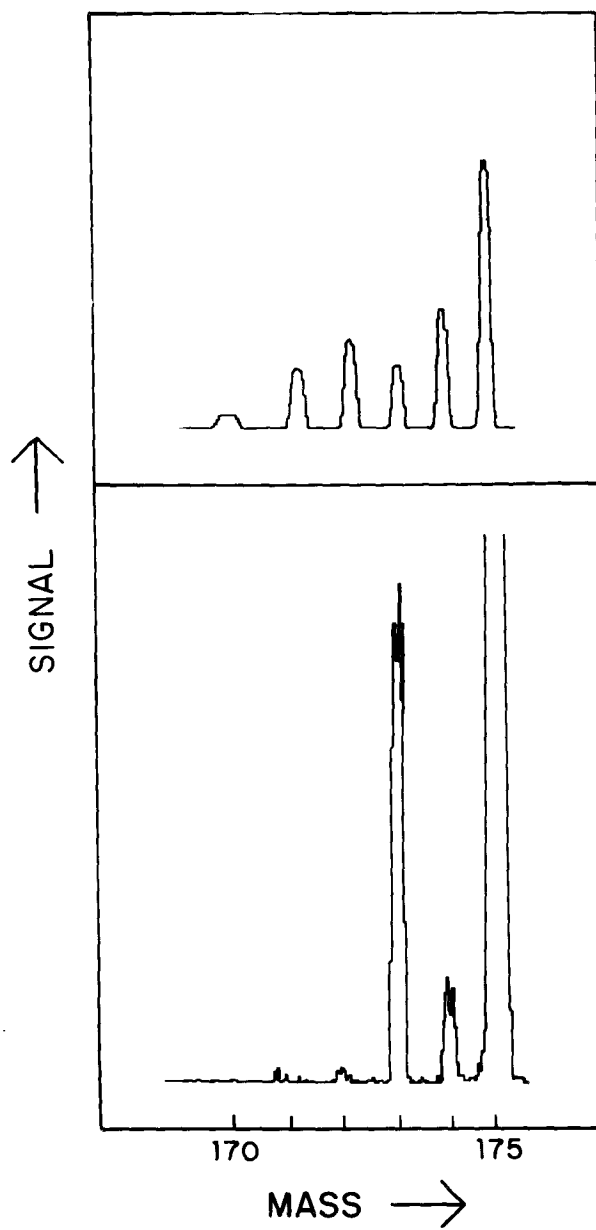


Figure 1. (a) Thermal ionization of a Lu/Yb mixture. The signal represents 1.9×10^7 counts per second at mass 175. (b) Cw laser resonance ionization of the same sample. Full scale is 300 counts per second, while the mass 175 signal is 1.1×10^6 counts per second.

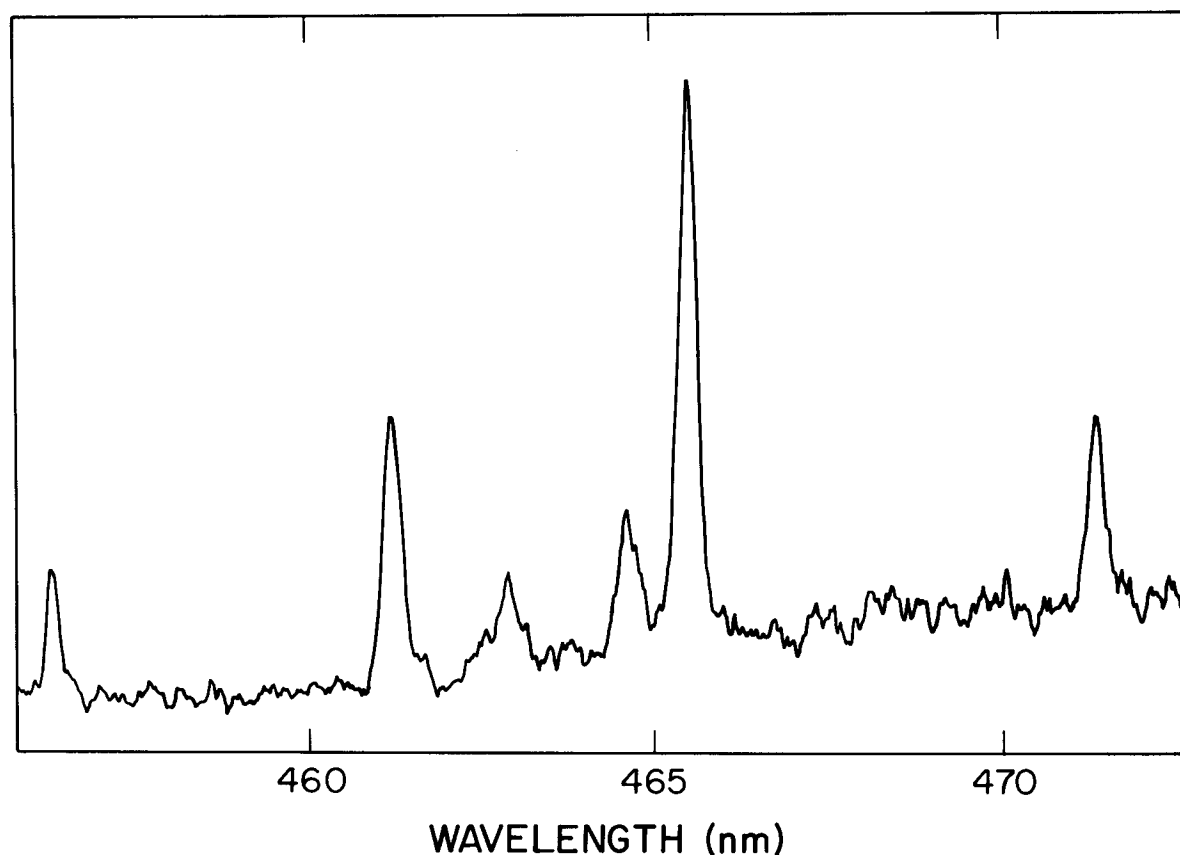


Figure 2. Wavelength dependence (λ_2) of Tc ionization signal following excitation ($\lambda_1 = 423.8$ nm) to the $^6P_{3/2}$ state.

agreement with previous observations.² Lastly, the structure observed between atomic resonances does not represent baseline noise or drift. It is due to a molecular absorption which produces both Tc^+ and electronically excited Tc atoms.¹⁷ This "non-resonant" production of Tc^+ requires the presence of both λ_1 and λ_2 and shows a nonlinear dependence on laser pulse energy.

Discussion

The results presented here for lutetium cw resonance ionization confirm the viability of this technique for measuring large dynamic range isotope ratios, especially in the presence of isobaric interferences. Although the ionization efficiency for each atom must be lower for cw than pulsed laser irradiation, the duty cycle is much greater, producing higher ion yields as the final result. These high ionization rates thus allow the measurement of greater isotope ratios. Elemental selectivity is maintained as well. In fact, cw RIMS may be superior in this respect, in that the probability of interfering multiphoton events drops dramatically with laser intensity.

The high ionization rates demonstrated here, in combination with large isotope ratios, illuminate the problem of incomplete mass spectrometer resolution. This places a fundamental limit on the range of isotope ratios that can be measured. Improvements in mass spectrometer dispersion (i.e., multi-stage machines) can only extend the range marginally. Single-frequency cw dye lasers appear to offer the capacity to overcome mass resolution difficulties through isotopically selective ionization; thus, the natural isotope shift of the element of interest can be used to augment the resolution of the mass spectrometer. Additionally, increased ionization efficiency can be expected through a more efficient matching of the dye laser output to the atomic line profile, allowing saturation of the resonant transition.