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Resonant multiphoton ionization for the detection of technetium

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Introduction

The occurrence of isobaric (same mass) interferences presents a persistent problem to the precise experimental determination of isotope ratios.¹ The problem is particularly acute when large isotope ratios must be measured, and in the determination of extremely small samples, where counting statistics will make subtraction of a background signal rather inaccurate. While there exist classical techniques for reducing background interferences, the application of resonance ionization mass spectrometry (RIMS) currently seems most likely to provide an optimal solution to this problem.²⁻⁵ We present here a preliminary report on the application of RIMS to the selective detection of technetium.

Technetium is an extremely rare element exhibiting no stable isotopes; it is nearly undetectable in normal crustal samples. Because of its scarcity it is particularly useful as a tracer in hydrologic and geologic studies. Another potential application results from the fact that technetium can be used as an indicator for the passage of solar neutrinos. It has been proposed⁶ to measure technetium isotope ratios in molybdenite ore in order to gain a measure of the integrated boron-8 solar neutrino flux averaged over the past several million years. Since the technetium is to be extracted from molybdenite ore, it is anticipated that isobaric interferences from molybdenum may present a serious problem for the determination of technetium isotope ratios. The application of RIMS to this problem is clearly indicated. Our immediate goals are twofold: to determine optimum wavelengths for the selective ionization of Tc, and to estimate the ultimate sensitivity obtainable for RIMS detection of Tc in real samples.

Experimental

The experiments were carried out using a thermal atom source, pulsed laser, and time-of-flight mass spectrometer, as shown in Fig. 1. Light pulses were generated by frequency doubling (Inrad Autotracker) the output of a Nd³⁺:YAG (Quanta Ray DCR 14) pumped dye laser (Quanta Ray PDL) operated with Exciton DCM dye. Output consisted of 10-ns pulses ranging in energy from ~0.2-2.5 mJ, at 10 Hz. The 1-cm diameter pulses were directed, without focusing, into the source region of 1-m time-of-flight mass spectrometer.¹⁰ Ionization took place in a constant field (7 V/cm) region surrounded by a L-N₂ cooled cryotrap. The ions were accelerated in two stages to 125 V for flight through the drift tube. Ion flight times were typically 35 μ s. Ions were detected with a channel electron multiplier biased at -2500 V. The signal was preamplified (PARC 115) and passed to a gated integrator (PARC 164/162) and x-y recorder. A gate width of ~4 μ s and a time constant of 1 s were routinely used. The mass resolution of the system was ~3-4 amu.

Samples were prepared by electroplating Tc onto rhenium filaments. Typical samples contained 1-2 μ g of material and were deposited at 2-7 V from an H₂SO₄/HF/H₂O₂ solution. The electrodeposition process promotes the production of atomic technetium and inhibits the formation of molecular species. Technetium atoms were volatilized in the source region of the mass spectrometer by resistively heating the Re filaments. These filaments typically produced stable Tc signals for 6-8 hours at a current of ~3 A (1300°C).

Results and Discussion

Technetium ions were generated via a simple 1+1 photoionization scheme utilizing two photons of the same frequency and a real intermediate state. We examined only the spectral region for which the sum of the photon energies was near (~0.2 eV) the Tc ionization limit (58730 cm⁻¹, 7.28 eV). This was done for two reasons: first, the probability of background ionization tends to increase with increasing photon energy, and second, the frequency region just to the high energy side of 58730/2 cm⁻¹ is a particularly favorable region for the generation of tunable radiation. Figures 2 and 3 display ionization signal as a function of excitation wavelength over the spectral range where photoionization was observed. The one photon absorption resonances generated ionization signals at the wavelengths shown.

TIME-OF-FLIGHT MASS SPECTROMETER

Fig. 1. Schematic of experimental apparatus.

Fig. 2. Wavelength dependence of photoionization signal.

Fig. 3. Wavelength dependence of photoionization signal.

These wavelengths are gathered in Table 1, along with tentative assignments based on published¹¹ Tc spectra.

The power dependence of the ion signal at 3183 Å was also examined, and is displayed in Fig. 4. The straight line drawn through the dots is simply a linear regression for the data shown, and is not meant to suggest any theoretical justification for a linear fit. In fact, at very high pulse intensities, the curve should turn over as the ionization saturates,¹³ while at low intensities, the power dependence should be greater than first order. The graph suggests that the first transition is saturated, while the excited state to continuum transitions is not saturated. However, over the range of intensities used in these experiments, the linear scaling shown provides a convenient means of normalizing the ion signals to laser power. This method has been used to generate the relative intensities shown in Table 1. These relative intensities are thus simply the ion signal divided by the average pulse energy at that wavelength. Although no determinations were made for the last four entries in Table 1 because of difficulties in obtaining stable laser output, the results shown in Fig. 3 suggest that at least the 3099 Å and 3098 Å lines may be analytically useful.

The analytical problem for the detection of solar neutrinos is defined as follows:^{8,14} the accurate determination of the technetium isotope ratio for a sample which contains $\sim 10^8$ $^{98,99}\text{Tc}$ atoms, $\sim 10^{11}$ ^{98}Tc atoms and as many as 10^{15} $^{92-100}\text{Mo}$ atoms. Previous experience indicates^{2,3,10} that if the analytical line is ≥ 25 Å from the nearest resonance in an isobaric interference that discrimination against the interference is complete ($\geq 10^3$).³ Since there are a number of Tc analysis lines to choose from, and only a handful of interfering Mo resonances, the Mo interference is unlikely to pose a significant problem [Table 1]. Further, since these experiments will eventually be conducted on a magnetic mass spectrometer capable of measuring isotope ratios $\geq 10^5$, the measurement of the $^{98}\text{Tc}/^{99}\text{Tc}$ ratios is feasible. The primary question remaining is: can a sufficient number of $^{98,99}\text{Tc}$ ions be generated from a sample containing 10^8 atoms to insure good counting statistics.

First of all, we will assume that ion production can be saturated over a beam diameter of 0.5 cm. This may be possible for a number of the transitions listed in Table 1. If we assume that the 1500°C Tc atoms are moving at a velocity of 4×10^5 cm/s, they will traverse the beam diameter in $\sim 10^{-8}$ s. Thus the population of atoms in the laser volume will be renewed 10^8 s⁻¹. Since the laser operates at 10 Hz, the effective duty cycle will be

Fig. 4. Low energy power dependence of the photoionization signal

10^{-4} . Previous experience indicates that geometric factors, ion collection and transmission, and counting inefficiencies will reduce the potential ion signal by 100. Thus, a 10^8 atom sample will be expected to produce $\sim 10^8(10^{-4})(10^{-2}) = 10^2$ ion counts if atomization is 100% efficient. Since the detection of 100 ions is only marginally sufficient to ensure adequate counting statistics, alternatives should be explored.

At least three alternatives suggest themselves. A higher repetition rate laser might be used. There exist coincidences between the output of a KrF laser and a weak Tc line at $\lambda = 2484.6$ Å transition, and between the Raman-shifted output (second Stokes, H_2) of a KrF laser and a strong Tc transition at $\lambda = 3123$ Å. The former of these appears to be free of molybdenum interferences. Since excimer lasers are now commercially available with repetition rates ≥ 10 Hz, and will soon be available up to 10^3 Hz, there is the possibility of gaining 10^2 in the efficiency of ion production simply by changing photon sources. This possibility will be investigated in the near future. The use of cw lasers for RIMS has also been suggested,¹⁵ and recently demonstrated.³ In preliminary experiments the rate of ion production using cw laser excitation was $>10^4$ that observed using pulsed lasers. The generation of substantial quantities of uv light with cw lasers is still a difficult problem, however.^{16,17} The most reasonable application of cw lasers to the Tc problem would lie in a three-photon, two-color, double-resonance scheme, presumably using the 4238.2 Å resonance for the first step. We are currently exploring this possibility.

Table 1. Observed Tc Resonance Photoionization Transitions and Potential Molybdenum Interferences

Observed λ (Å)	Assignment ^a	I (Relative)	Mo	Lines ^b
3183	$Y^6P_{5/2}^o$	2.5	3194	S
3182	$Y^6P_{7/2}^o$	1.8		
3173	$Y^6P_{3/2}^o$	3.0	3170	S
3163	$Z^4F_{7/2}^o$	0.8	3158	S
3131	$Z^4P_{5/2}^o$	1.6	3132	S
3123	$Z^4F_{5/2}^o$	2.0	3112	M
3099	$Z^4F_{3/2}^o$	ND ^c		
3098	$Z^4P_{3/2}^o$	ND		
3064	$Z^4D_{7/2}^o$	ND		
3021	$Z^4D_{5/2}^o$	ND		

^aAll observed transitions originated in the ground state ($4d^55s^2\ ^6S_{5/2}$) the final state configuration in all cases is $4d^6(a\ ^5D)\ 5p$; assignment indicates the designation of the final level.

^bThe listed lines are those originating in ground state Mo that lie close to a Tc transition: S-strong, M-medium. From Ref. 12.

^cNo determination.

Lastly, more clever utilization of the sample may well provide the most dramatic improvement, as well as the mostly generally useful. Methods which utilize either pulsed sample volatilization,^{18,19} or trapping²⁰ of a continuously volatilized sample could easily increase the effective duty cycle for pulsed lasers by several orders of magnitude. In addition, trapping schemes may assist greatly in reducing sample loss from the optical field of view (geometric loss). These problems deserve serious consideration if RIMS is to become a practical analytical tool.

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