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TITLE MEASUREMENT OF TRACE ISOTOPES BY PHOTON BURST MASS SPECTROMETRY

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Measurement of trace isotopes by photon burst mass spectrometry

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ABSTRACT

Progress is reported on the development of a new laser- and mass spectrometer-based technique for measurement of trace levels of radioisotopes. Significant results to date include the demonstration of high efficiency and throughput in a mass spectrometer, efficient production of metastable atoms from Ar^+ and Kr^+ beams, a demonstration of the photon burst detector principle with Mg^+ ions, and the verification of zero background in a two-detector system.

1. BACKGROUND

Radioactive isotopes are widely used in dating, tracer, and monitoring applications. Traditionally, isotopic abundances are determined by radioactive decay methods. However, the percentage of atoms detected in a decay measurement is small when the lifetime exceeds 10 years. In such cases it is preferable to directly count the rare atoms. Atom counting is possible in conventional mass spectrometry, but background interferences due to molecular isobars or neighboring isotopes generally limit the sensitivity to about the 10^{-6} level. Many applications require a sensitivity five-to-ten orders of magnitude below this. Accelerator mass spectrometers have been able to overcome this limitation through the use of nuclear mass- and charge-selective detection methods and are now widely used for dating with ^{14}C and several other isotopes. In this paper we report progress on the development of a detector for mass spectrometers which has very high isotopic and isobaric selectivity. It is based on detecting a burst of fluorescence photons absorbed and emitted by a selected single atom or ion as it passes through a resonant laser beam.^{1,2} The basic principles of this new technique called Photon Burst Mass Spectrometry (PBMS) have been outlined elsewhere.³⁻⁵ It is expected that PBMS, once developed, may be used to measure isotopes of about half the elements of the periodic table at abundances in the 10^{-11} to 10^{-16} range. At present the research is centered on the noble gas isotopes ^{39}Ar , ^{81}Kr and ^{85}Kr due to important applications in oceanography, groundwater dating, and nuclear monitoring and because accelerator mass spectrometry, at least with tandem accelerators, is incapable of measuring these isotopes.

Figure 1. Photon Burst Mass Spectrometry apparatus for noble gas measurements.

2. MASS SPECTROMETER PROGRESS

Isotope ratio measurements at the 10^{-11} to 10^{-16} level require both extremely high selectivity and high throughput. A photon burst detector alone has great selectivity but cannot tolerate the current which is needed in order to have a reasonable measurement time. The main features required of the mass spectrometer in the PBMS method are (1) a high ($\geq 10\%$) ionization efficiency in the ion source, a high transmission ($\sim 100\%$) for the desired isotope and a relatively high (10^6) reduction in the flux of stable isotopes. The photon burst detector on the output of the mass spectrometer provides an additional selectivity of $\geq 10^{10}$ against the residual isotopes and isobars which exit the mass spectrometer along with the desired species.

The instrument which is being developed for the first full demonstration of PBMS at Los Alamos National Laboratory is illustrated in Fig. 1. It consists of a microwave ion source, 126° magnetic sector of radius of 1.5m,⁶ decelerator to slow the exiting ions from 50 keV to 100-1000 eV energy, charge exchange cell to convert Kr or Ar ions to metastable atoms, and photon burst detector assembly consisting of 10-20 light collectors and photomultiplier tubes, with atomic excitation provided by a tunable diode laser at 811nm. The mass spectrometer, ion source and decelerator are now in place on this system. The charge exchange cell and photon burst detector are being tested and developed at Colorado State University.

Some of the required features of the mass spectrometer are illustrated in the mass spectrum for krypton gas shown in Fig. 2. The overall transmitted krypton current is about 3.5 μ A and the demonstrated instrumental abundance sensitivity is 5×10^4 . The small peaks at mass 79, 81, 85 and 87 are due to KrH, which was formed in the source at the 0.1% level. It is expected that further developments will reduce the tails of the abundant isotopes and that cleanliness measures (e.g., bakeout and gas purification) will suppress hydride formation in the source by several orders of magnitude. The current stability of the present source is 0.2%.

Figure 2. Kr mass spectrum from the Los Alamos mass separator.

The small peaks at mass 79, 81, 85 and 87 are due to KrH, which was formed in the source at the 0.1% level. It is expected that further developments will reduce the tails of the abundant isotopes and that cleanliness measures (e.g., bakeout and gas purification) will suppress hydride formation in the source by several orders of magnitude. The current stability of the present source is 0.2%.

Tests to determine the ionization and transport efficiency of the system are in progress. Preliminary measurements in which a calibrated leak of krypton gas was seeded into a flow of argon support gas yielded 5% total efficiency for krypton. This is already close to the desired range. The decelerator for the system was designed by computer ion trajectory calculations. It has been constructed and installed, but no testing has yet been done.

3. CHARGE EXCHANGE STUDIES

Charge exchange collisions of ground state np^5 noble gas ions with alkali metal atoms result in the formation of $np^5(n+1)s$ atoms and ground state alkali ions, e.g.:

Theoretical calculations indicate that at low energies (< 1000 eV) this process is quite resonant and that the use of different alkalis leads to the selective population of different fine structure states.⁷ In the case of Kr^+ and Cs vapor, the two $J=1$ states are preferentially populated in low energy collisions, whereas the $J=0$ and 2 states selectively receive the population from the $2P_{1/2}$ and $2P_{3/2}$ ion states, respectively, in Rb vapor.

Figure 3. Charge exchange test apparatus.

The apparatus being used to study the charge exchange process is illustrated in Fig. 3. It consists of a Balzers PIQ102 ion source, focussing and deflection optics, a recirculating charge exchange cell, Faraday cup detectors mounted on a precision manipulator, and a single photon burst light collector with a 27mm long photodiode detector. The large Faraday cup is used to compare the total transmitted ion current before the Cs cell is heated up and after it reaches operating temperature. The small Faraday cup is used to obtain spatial profiles of the charged and neutral beam components. Changing the bias on the cup allows a separation of these two species. The goals of the charge exchange studies are to demonstrate that efficient (80-100%) neutralization can be achieved with minimal perturbation of the angular and longitudinal velocity distribution of the beam and to measure the fraction of atoms formed in the desired atomic state (e.g., for ^{85}Kr the $4p^5 5s [3/2]_2^o F=13/2$ hyperfine structure state).

It has been found that 80-90% neutralization of Ar and Kr can be achieved routinely at a modest pressure of Cs vapor and that a single 25g charge of Cs can be used indefinitely. Accurate beam profile measurements have been difficult to make due to beam wander and thermal expansion problems during the time the cell heats up to its operating temperature. However, all results indicate only a small broadening of the beam, as is shown in one set of data presented in Fig. 4. We conclude that most angular deviations in the charge exchange collisions are <1 mrad.

The metastable $4p^5 5s [3/2]_2^o$ state population of the neutral Kr beam has been probed by collinear laser spectroscopy with a diode laser operating at 811nm. A recent spectrum taken at 620eV beam energy is shown in Fig. 5. Features due to the abundant even isotopes ^{82}Kr , ^{84}Kr and ^{86}Kr are seen along with a weak broad background due to the 15 hyperfine

Figure 4. Position scan of ion (no cesium) and neutral beams (at 90% neutralization with cesium).

Figure 5. Fluorescence spectrum of metastable Kr beam showing ^{82}Kr , ^{84}Kr and ^{86}Kr peaks.

structure lines of ^{83}Kr . The Doppler width in this spectrum is quite large, corresponding to a longitudinal energy spread of about 20 eV. This large value can be understood by considering the conditions of ionization in the source. The Kr ions are formed at various potentials within a 70V well, in which a beam of electrons is reflected back and forth. The other two sources used in our experiments (the microwave and the Colutron sources) are expected to have one- to two- orders of magnitude smaller energy spread. Thus there should be very good resolution of the various isotopic and hyperfine structure lines with those sources. Roughly estimating the light collection efficiency of the system, we calculate that on the order of 10% ($\pm$ factors of two or so) of the Kr atoms are in the desired $4p^5 5s [3/2]_2^o$ state. This is consistent with the theoretical predictions of somewhat less than statistical ($5/12 = 42\%$) population of this state when Cs is used.⁶

4. PHOTON BURST STUDIES

The detection of single Mg^+ ions by the photon burst method has been presented elsewhere.² In those studies an isotopic selectivity of 10^3 was demonstrated. The major limitation was a background burst rate of 1-4 bursts per second which arose from comparable contributions of stray laser light, ion source light and bursts from cosmic rays striking the photocathode.

Since then stray laser light reaching the detectors has been reduced by two orders of magnitude by more effective use of apertures and the ion source light has been eliminated by the introduction of a 10° electrostatic bend. It was expected that cosmic ray background could be eliminated by requiring time delayed coincidences in two collinear photon burst detectors. A test with an on-line digital cross correlator showed zero coincidences of ≥ 4 count bursts in 16 hours in 24 different time delay bins. For a single delay time this is equivalent to zero background in 384 hours. These tests were done at a stray light level of $\sim 35,000$ counts per second in each detector. This is good evidence for the original prediction that background-free atom counting can be done by PBMS over many hours of operation.^{4,5}

5. SUMMARY

As of this date, most of the original PBMS assumptions⁴ concerning the ion source current and efficiency, mass spectrometer abundance sensitivity, charge exchange properties, and photon burst statistics have been verified in experimental studies. Remaining work includes measurement of the ion beam spot size and divergence after deceleration, more detailed investigation of Doppler widths and tails by collinear laser spectroscopy for specific ion sources of interest, construction of a 10-detector system, observation of photon bursts from Kr^+ , and finally a full test of the method with real Kr and Ar samples. On the basis of the successful results obtained to date, we remain confident that the original expectation for the PBMS method, i.e., isotope analysis at the 10^{-11} to 10^{-15} level, can be achieved in the near future.

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