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RESONANCE IONIZATION SPECTROSCOPY: COUNTING NOBLE-GAS ATOMS¹

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1. Introduction

From its beginning, Resonance Ionization Spectroscopy (RIS) [1] has been recognized as a method for the ionization of matter which is spectroscopically selective and has one-atom sensitivity. Prior to the development of RIS for sensitive analytical purposes, similar laser ionization schemes were proposed [2] for the separation of isotopes. Two-step selective photoionization of Rb atoms was reported [3] by AMBARTSUMYAN, KALININ, and LETOKHOV in 1971. For further information on the history of RIS and the use of various laser methods for sensitive detection of atoms, the reader is referred to recent reviews [4-6].

With five simple laser schemes [5,6], RIS can be used to selectively ionize each element in the periodic table except He and Ne. Most of the work reported thus far on one-atom detection has involved the detection of single electrons created by a laser in a proportional counter. For example, the first such experiment [1] detected single atoms which diffused from a warm Cs metal and migrated by chance into a region of the space of a proportional counter where a laser could be pulsed. In another case [7], Cs atoms were detected following their photodissociation from the chemically stable CsI molecule. Single atoms of Cs have also been found [8] in individual ionization tracks created by the fission decay of ²⁵²Cf. Recently [9] a practical application of RIS was made by using laser beams in proportional counters to detect Na impurity atom in electronics grade Si.

The purpose of this paper is to describe new work on the counting of noble gas atoms, using lasers for the selective ionization and detectors for counting individual particles (electrons or positive ions). When positive ions are counted, various kinds of mass analyzers (magnetic, quadrupole, or time-of-flight) can be incorporated to provide A selectivity. We show that a

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variety of interesting and important applications can be made with atom-counting techniques which are both atomic number (Z) and mass number (A) selective.

2. RIS of Noble Gases (Z Selection)

A laser scheme to demonstrate [10] RIS of Xe is the following. A Nd-Yag laser beam was frequency doubled and used to pump a red dye to obtain tunable light between 645 and 675 nm with a pulse duration of 5 ns. The dye laser output was doubled and then mixed with $1.06\ \mu\text{m}$ to yield tunable light from 246 to 258 nm. At a two-photon resonance in Xe (i.e., 252.6 or 249.6 nm), the energy per pulse was $\sim 1\ \text{mJ}$ and the bandwidth was estimated to be $\sim 0.1\ \text{\AA}$. During the experiment the laser beam was focused down to $0.1\ \text{mm}$ at the center of an ionization chamber which contained Xe at pressures ranging from 10^{-8} to 10^{-6} Torr.

The ionization line shape for the three-photon ionization of Xe near the two-photon resonances with $\text{Xe}[1/2]_0(5p^56p)$ and $\text{Xe}[3/2]_2(5p^56p)$ states is shown in Fig.1. We observed that the two-photon transition occurred at a rate of $2 \times 10^{-9}\ \text{I}^2\ (\text{sec}^{-1})$ when I is W/cm^2 and could be saturated for laser power densities higher than $6 \times 10^8\ \text{W}/\text{cm}^2$. The ratio of background ions from residual gases to the saturated resonance ionization signal is $\sim 10^{-2}$ when the Xe pressure is 1×10^{-6} Torr. When a quadrupole mass filter was introduced, the background was reduced to such a low value that the detection of single Xe atoms of a selected isotope was possible.

Fig.1 Tuning curve for Xe atoms involving two-photon excitation followed with one-photon ionization at the two indicated wavelengths

Following the experimental demonstration of RIS with Xe, calculations [11] were made to show how to generalize the results to the other noble gases with commercial lasers (Kr and Ar). We describe here estimates of volumes of ionization, ΔV , for RIS beginning with the following two-photon resonance excitation schemes:

The lasers assumed here are the ArF excimer laser (1933 Å), the F₂ laser (1576.3 Å), and other laser outputs that can be generated with commercial dye laser systems pumped by harmonics of the Nd-Yag. Thus far, the use of the F₂ laser has been limited due to the fact that no major effort has been devoted to developing a F₂ laser with good beam quality and with gas mixtures having long lifetimes.

The effective volume for ionization, ΔV , was calculated by using a rate analysis and assuming a Gaussian radial intensity profile. The two-photon excitation rates were calculated [11] with reasonable self-consistency by several approximation schemes, and the photoionization rates for the upper state were based on the results of DUZY and HYMAN [12]. Numerical values for the effective ionization volumes were obtained for a beam divergence of 10⁻³ rad and assuming a lens of 10-cm focal length. If the F₂ laser can be made to work reliably, ΔV can be at least 3 x 10⁻⁴ cm³ for Ar, Kr, or Xe.

Recently, there have been important advances in the development of tunable light sources in the vacuum ultraviolet spectral region where Ar and Kr have strong, one-photon allowed transitions [13]. Using a two-photon resonance, four-wave mixing process in Hg vapor, ~1 kW of peak power in a bandwidth of 0.04 cm⁻¹ was generated at the Kr transition line at 1235.8 Å [14]. By frequency tripling a dye laser in Xe gas, ZAPKA [15] obtained tunable output with a maximum peak power of almost a watt in the range from 1061 to 1068 Å. Using a more powerful dye laser, a peak power of 100 W at the 1066.7 Å Ar transition is possible. Doppler-free, two-photon RIS with isotopic selectivity has been demonstrated in both Xe and Kr [16]. This method is particularly useful in achieving separation between even isotopes and those odd isotopes that have large hyperfine shifts; however, these separations are too small for use in the technique described here.

3. Laser-Mass Spectrometer Techniques for Noble Gas Detection

While a substantial amount of work on RIS has been done with proportional counters, it is clear that evacuated particle detectors also have unique applications with RIS. Proportional counters are excellent analogue devices and can be used to count just one electron (or one atom using RIS), however they require gases of selected properties for their operation. Fortunately, other particle detectors are available which can be used to count individual charged particles (electrons, negative ions, or positive ions) with nearly 100% efficiency; and they work at pressures below 10⁻⁵ Torr. Positive ion detectors can be substituted for electron detectors, which eliminates any

noise problems associated with photoelectrons produced by laser interactions with window materials.

Detection of positive ions also makes possible mass analysis (A selectivity) prior to counting. The combination of Z selection (made possible by the laser) and A selection (with a mass spectrometer) can be put to great advantage in practical applications. In particular, it is a natural combination for the isotopically selective counting of individual noble gas atoms as discussed below. More generally, however, all of the standard forms of mass spectrometers play their own special roles when combined with RIS. Magnetic deflection offers both a high transmission (approaching 100% of the ions) and good resolution ($> 10^6$ discrimination between A and $A + 1$). Time-of-flight mass spectrometers have much less resolution but retain high transmission and offer the advantage of simultaneous recording of a range of A values. Quadrupole mass filters have low transmission and medium resolution, but they have the unique feature that the ions being analyzed are kept at a very low energy. In the experiment of CHEN et al. [10] a simple version of a quadrupole mass filter was used to selectively detect Xe atoms. With the laser linewidth greater than isotopic splittings, it was found that Xe isotopes were detected by amounts according to their normal abundances.

4. Maxwell's Sorting Demon

4.1 The Concept

In 1871, JAMES CLERK MAXWELL visualized a demon which could see and identify atoms and open and close doors to sort atoms into well-defined compartments. We consider the system shown in Fig.2 to be a practical realization of Maxwell's demon for noble gases. The ultraviolet laser ionizes all noble gas atoms of a particular type (Z selection) in a small volume; the quadrupole mass filter separates ions of a particular isotope (A selection), which are then implanted into a CuBe target. The electron multiplier counts secondary electrons emitted from the activated CuBe surface.

4.2 The Atom Buncher

Since the effective volume of the high-vacuum chamber is rather large (~ 2.5 liters) and the volumes that can be saturated in a two-photon process are quite small (3×10^{-4} cm³), it is necessary in a practical application of the demon concept to find a way to increase the chance of a noble gas atom being in the beam at the time the laser is fired. In our case, the sample will be frozen onto the liquid helium cold finger. When the light of a pulsed CO₂ laser strikes the cold finger, the noble gas atoms will be released instantly and travel a few millimeters before the time-delayed ultraviolet laser is pulsed just above the cold finger and ionizes a significant fraction of the sample. The ionization probability for a single atom of a selected isotope can be adjusted to approximately 10% in order to achieve true digital counting.

4.3 Implantation and Counting of Single Ions

Ions of 10-keV energy have been implanted at an average depth of ~ 100 Å in Al or glass [17]. The diffusion of atoms in solids at room temperature is extremely slow; thus, ions which are implanted into a metal foil such as CuBe remain stored in the foil for months without significant escape:

Fig.2 Artist's conception of "Maxwell's sorting demon" which utilizes pulsed lasers and a quadrupole mass spectrometer to count Z- and A-selected noble gas atoms.

The ability to sort Xe atoms in a small volume by means of selective laser ionization and ion implantation was demonstrated in our laboratory [10]. Fig.3 shows the depletion of Xe atoms in volumes of 50 and 15 cm³ [curves (a) and (b), respectively], using a pulsed Nd-Yag laser to produce Xe⁺ ions followed by implantation of the ions into a channeltron detector. The measured Xe pump-out rates were consistent with an implantation probability of nearly 100%, in agreement with measurements by KORNELSEN [18]. When ions are implanted, they can be detected by observing secondary electron emission (see Fig.3). BAUMHÄKEL [19] measured electron yields from activated CuBe surfaces bombarded with noble gas ions. For 3-keV Ar⁺, Kr⁺, and Xe⁺ ions, the electron yields are 2 to 3.5 secondary electrons per incident ion. For ion energies of 10 keV, electron yields of 6 to 8 electrons per ion are expected.

4.5 Recovery of Implanted Atoms, Recycling

Since the abundance ratio of the quadrupole mass spectrometer is only 10³, many atoms of neighboring isotopes will be implanted even for samples where the selected isotope occurs only in a very small fraction of the sample, e.g., 1:10¹⁵ (see ³⁹Ar applications, section 5.2). The system, therefore, is designed to allow for a target to be heated or melted inside the high vacuum

Fig.3 Selective pumping of Xe atoms using a pulsed laser in the RIS process in gas volumes of 50 cm³ (curve a) and 15 cm³ (curve b)

in order to release the implanted atoms, which will then be collected again on the liquid He cold finger. After a small number, n , of these cycles, an enrichment of 10^{3n} will be achieved and the selected atoms will be counted by implantation into the final fresh CuBe target.

Some of these pre-enrichment cycles may be done without lasers by using the electron ionizer of the quadrupole. In a 2.5-liter system, with the mass spectrometer tuned to mass 84 and operating with a throughput efficiency of 2 mA/Torr, the time required to reduce the ratio of ^{84}Kr to total Kr concentration by one e-fold was found [10] to be 82 min.

4.6 Summary of Expected Characteristics of the Machine

The laser/mass spectrometer realization of Maxwell's demon should enable one to count small numbers (i.e., 100–1000) of atoms of any selected isotope of Ar, Kr, Xe, or Rn in isotopic backgrounds of up to 10^{15} .

The final counting, after any necessary pre-enrichment steps, should only take a few minutes, so that interferences with noble gas atoms degassing from the walls of the vacuum system can be minimized.

5. Application of Noble Gas Counting

5.1 Solar Neutrinos

Many very timely problems in physics can now be considered seriously for the first time because Maxwell's demon for counting noble gas atoms is becoming available. One of these applications involves the work of RAY DAVIS and his group at Brookhaven National Laboratory. In a 100,000-gallon tank filled with perchloroethylene, the enormous flux of neutrinos from the sun that pass through the earth can convert a few atoms of ^{37}Cl to ^{37}Ar via the process $^{37}\text{Cl}(\nu, e^-)^{37}\text{Ar}$. After exposure to neutrinos from the sun for about 6 months, the 100 or so ^{37}Ar atoms are removed and counted as they decay in a proportional counter. Another interesting measurement could be made by using $^{81}\text{Br}(\nu, e^-)^{81}\text{Kr}$. Here the "direct" counting of ^{81}Kr atoms with Maxwell's demon is essential because more than 10^5 yr are required for the 100 atoms of ^{81}Kr to decay in a proportional counter! The very new idea in weak interaction physics that neutrinos could have a finite rest mass and hence

oscillate between neutrinos of different types (e.g., electron, muon, and tau neutrinos) can also be tested by using these new detectors.

Another interesting test of weak interaction physics involves the measurement of double beta ($\beta\beta$) decay. For example,

can occur even though ^{82}Se is stable against β^- decay. The $\beta^-\beta^-$ half-life is uncertain by more than an order of magnitude but is about 10^{19} or 10^{20} yr. Direct measurement of ^{82}Kr with a RIS technique is quite feasible and is the basis of a collaboration between ORNL, BNL, and JACK ULLMAN of the Herbert H. Lehman College in New York. PETER ROSEN and WICK HAXTON at Purdue University are interested in extending these studies to the $\beta\beta$ decay of Te to Xe.

5.2 Oceanography

The radioisotope ^{39}Ar , produced by cosmic rays in the upper atmosphere and dispersed through the oceans by oceanic transport processes, is potentially one of the most valuable tracers available for studying the pattern and rates of circulation in the deep ocean and the processes by which the ocean is internally mixed. The half-life of ^{39}Ar (270 yr) is ideally matched to the characteristic time scales of ocean mixing and circulation, while the inert nature of ^{39}Ar ensures that its distribution in the oceans is determined only by advection, mixing, and radioactive decay.

The application of ^{39}Ar to ocean studies has been thwarted by the extremely low ^{39}Ar activities expected in the ocean (0.01 to 0.1 dpm/liter). Such low levels presently necessitate the collection and processing of at least 2000 liters of ocean water per sample for conventional decay counting. This requirement is absolutely prohibitive for routine application. With Maxwell's sorting demon, however, the sample size requirement will be reduced to only 10 liters, thus enabling our collaborators at the Scripps Institution of Oceanography to routinely make use of this powerful and long-awaited tracer.

5.3 Other Applications

Other applications of direct counting of noble gases which have been considered in some detail are cosmic-ray histories (^{39}Ar and ^{81}Kr), radon transport (^{222}Rn), polar ice cap dating (^{31}Kr), aquifer ages (^{81}Kr), earthquake prediction (noble gases), transuranic waste isolation (Xe fission product), diagnoses of bone diseases (^{37}Ar), and neutron dosimetry (^{37}Ar).

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