CONF-840449--7

For presentation by G. S. Hurst at the Second International Symposium on Resonance Ionization Spectroscopy and Its Applications Knoxville, Tennessee - April 16-20, 1984

CONF-840449--7

DE84 011654

Historical Survey of Resoance Ionization Spectroscopy

G. S. Hurst

Chemical Physics Section

Health and Safety Research Division

Oak Ridge National Laboratory

Oak Ridge, Tennessee 37830

April 1984

Historical Survey of Resonance Ionization Spectroscopy

G. S. Hurst

Chemical Physics Section, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

1. Introduction

We have recently celebrated the 10th birthday of Resonance Ionization Spectroscopy (RIS), and this seems an appropriate time to review the history of its development. While the history of the atom itself might be a far more interesting topic, an examination of developments in RIS during the past decade will help to introduce our program for the next few days.

The speaker who will follow me has contributed substantially to the development of this subject, particularly to the conceptual and theoretical aspects, and he will be reviewing in greater depth the physics of this process. Basically, RIS is a photophysics process (Hurst et al 1975, 1979; Payne et al 1975a) in which tunable light sources are used to remove a valence electron from an atom of selected atomic number, Z. If appropriate lasers are used as the light source, one electron can be removed from each atom of the selected Z in the laser pulse. This implies that RIS can be a very efficient, as well as selective, ionization process. In what we normally call RIS, laser schemes are employed which preserve both of these features. In contrast, multiphoton ionization (MPI) (Morrelick et al 1982; Parker 1982) is more general, although not necessarily Z selective or very efficient because resonances are often not used. Early research (Ambartsumyan and Letokhov 1972), completed in the USSR and described as selective two-step photoionization, employed resonances to ionize the rubidium atom and served to guide work on laser isotope separation. Examples of the incorporation of isotopic selectivity in the Z-selective RIS process can be found in the work of Bushaw and Whitaker (1976) for krypton isotopes and in new proposals by T. Lucatorto and his colleagues at the National Bureau of Standards (see these proceedings).

2. The He(2^1S) RIS Experiment

My first awareness of a resonance ionization process came in January of 1974, when we conceived of a way to use lasers to measure the population of singlet metastable helium, He(2^1S), created by a beam of energetic protons (Hurst et al 1975). This indeed was an old problem which first arose from the field of radioactivity. In 1913, Taylor had measured the ionization created in various gases by alpha particles. His values for the ionization in helium appeared too large to Neils Bohr (1915) who suggested that the effects could be due to impurities in the helium which was used. These effects were studied extensively in the 1950's by W. P. Jesse (1955), and they became known as the Jesse effect, in recognition of the excellent work done at the Argonne National Laboratory. The Jesse effect (or Penning ionization), as explained by U. Fano, Robert L. Platzman, and M. Inokuti, is as follows: When an alpha particle interacts with helium gas, many excited states, some bound and some in the ionization continuum, are produced directly by the electric dipole interaction. Some of the excited states remain in the gas long enough to collide with impurities; and if these have ionization potentials less than the energy of the metastable state, some additional ionization (of the impurity) is produced. Thus, our first RIS experiment was indeed embedded in the study of radioactivity, since we were looking for details on which of the metastable states of helium were excited and what type of collision process could be responsible for the Jesse effect.

Our first RIS experiment is shown schematically in Fig. 1. A beam of protons from a small Van de Graaff accelerator (Judish 1975) was pulsed into a cell containing helium gas. As soon as the protons passed through the gas cell, direct ionization was produced. When the laser was pulsed after a short time delay, a second ionization pulse was observed, but only if the laser was tuned to 5015 Å radiation. At this wavelength a photon can ionize the singlet metastable state $He(2^1S)$ by

$$He(2^1S) + \omega_1 \rightarrow He(3^1P)$$

$$He(3^1P) + \omega_1 \rightarrow He^+ + e^-$$

as shown schematically in Fig. 1. Thus we called the process resonance ionization spectroscopy to distinguish it from the more familiar but nonselective ionization produced by the proton beam. The experiment provided the information needed to clarify which states were created by charged particles in helium and how the singlet metastable state transfers energy to impurities. Both the magnitude of the $He(2^1S)$ population and the lifetime of the state, determined by collisions at a given gas pressure, were obtained, and these verified an energy pathways model (Payne et al 1975b) for the excited states.

We are not aware of any additional work where RIS has been used to obtain populations of metastable species. Currently, there is a plan (Wunderlich 1984) to study the helium triplet metastable, $He(2^3S)$, as a possible detector of magnetic monopoles, since it has been shown by Professors Drell and Kroll (1983), with their colleagues at SLAC, that a magnetic monopole would excite the $He(2^3P)$ level exclusively. Thus, detection of $He(2^3P)$ using RIS could give a unique signature to a monopole track. Some additional speculations of this type will be discussed later in this symposium.

3. One-Atom Detection

The first RIS experiment proved that an excited state of an atom could be selectively ionized at nearly 100% efficiency. Almost simultaneously, with the concept of RIS, it was realized (Hurst et al 1976) that single atoms could be counted if the process were carried out for an atom in its ground state and if done in a proportional counter where one electron could be detected. Cesium atoms were chosen for this

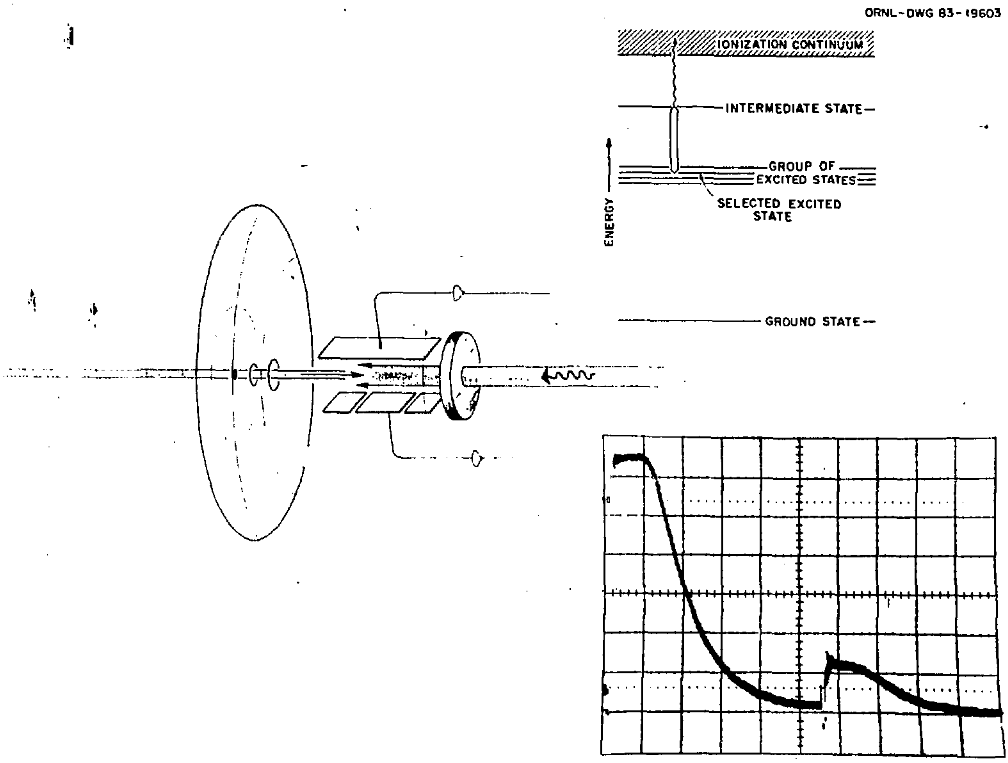

Fig. 1 Original RIS experiment for measuring a population of quantum selected states first excited by a beam of charged particles. Protons were pulsed into a parallel plate ionization chamber filled with helium gas, producing a large pulse of direct ionization. When the laser was tuned to promote the process shown schematically in the upper right, an additional smaller pulse was produced. In the geometry where the laser was coaxial with the proton beam, all of the singlet metastable states surviving at the time the laser was fired were measured.

first experiment (Hurst et al 1977a) on one-atom detection (see Fig. 2), since from the ground state, the RIS process requires only one photon. For example, at 4593 Å, the transition $Cs(6^2S_{1/2} \rightarrow 7^2P_{1/2})$ has a terminal state which can be ionized by another photon of the same wavelength.

The experiment was simply a demonstration that selectivity and sensitivity could both be maintained in a measurement of atomic populations. It was shown that one atom of cesium could be detected even if there were 10^{19} atoms of argon and 10^{18} atoms of CH_4 in the same laser beam. This implies, of course, that possible background effects due to photoelectric effects from walls or nonresonant MPI of the gas could be dealt with. The key to control of background when using a proportional counter, sensitive to single electrons, is to keep laser beams off walls, to use field tubes to eliminate electrons from laser windows, and to use low power (i.e., long duration) laser pulses to keep the MPI at a low level.

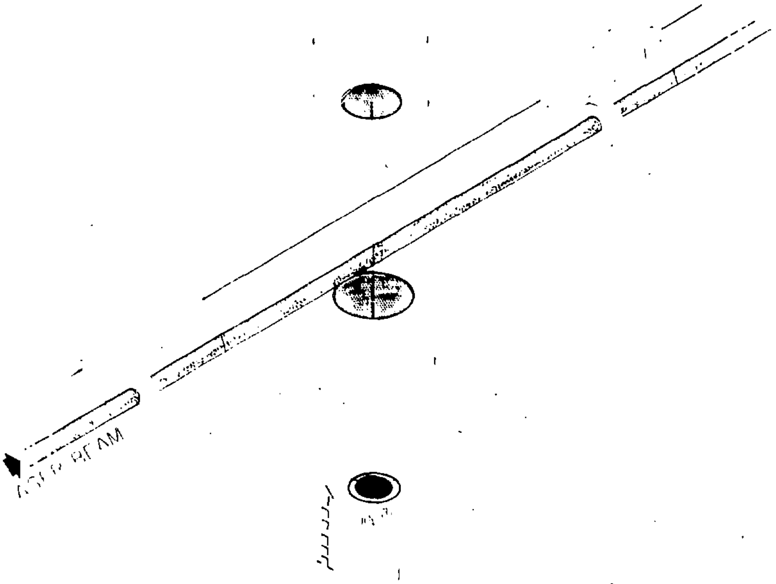

Fig. 2 Experimental arrangement used to count individual atoms of cesium. A very low concentration of cesium atoms could diffuse into the active region of a proportional counter containing P-10 gas (90% Ar, 10% CH_4). A pulsed laser beam tuned to 4593 Å excited cesium from the ground state ($6^2S_{1/2}$) to ($7^2P_{1/2}$) which is rather efficiently ionized by a second photon in the same laser pulse. A proportional counter was used to count single electrons and hence single cesium atoms in the saturated RIS beam.

In a very real sense the ORNL experiment on one-atom detection was the completion of a concept set forth by Rutherford (see the illustration in Fig. 3). The Rutherford archives, at the University of Cambridge, contain notes on Rutherford's speculation that atoms, if they are real, could be counted. With Geiger, he invented the proportional counter (Rutherford and Geiger 1908). Rutherford's idea could not be completed so that stable atoms, as well as radioactive ones, could be counted until the tunable laser was developed.

Another interesting experiment was done with cesium atoms that were created in the fission decay of ^{252}Cf. The experiment, illustrated in Fig. 4, proved that a single daughter atom could be counted in time coincidence with the nuclear decay of a parent atom. This involved counting the ^{252}Cf atom by decay counting, which was originated by Rutherford, in coincidence with direct counting of the cesium atom by using RIS. Unfortunately, this method has not advanced because of one very basic problem. In the case of the cesium daughter atoms arising from the fission decay, the initial charge state is Cs^{n+} which quickly converts to Cs^+. Even Cs^0 can be created in argon or CH_4 having a higher ionization potential than cesium without violation of energy conservation. Thus, the recoil energy left in Cs^+ drives the neutralization process. In a typical case where the method would be

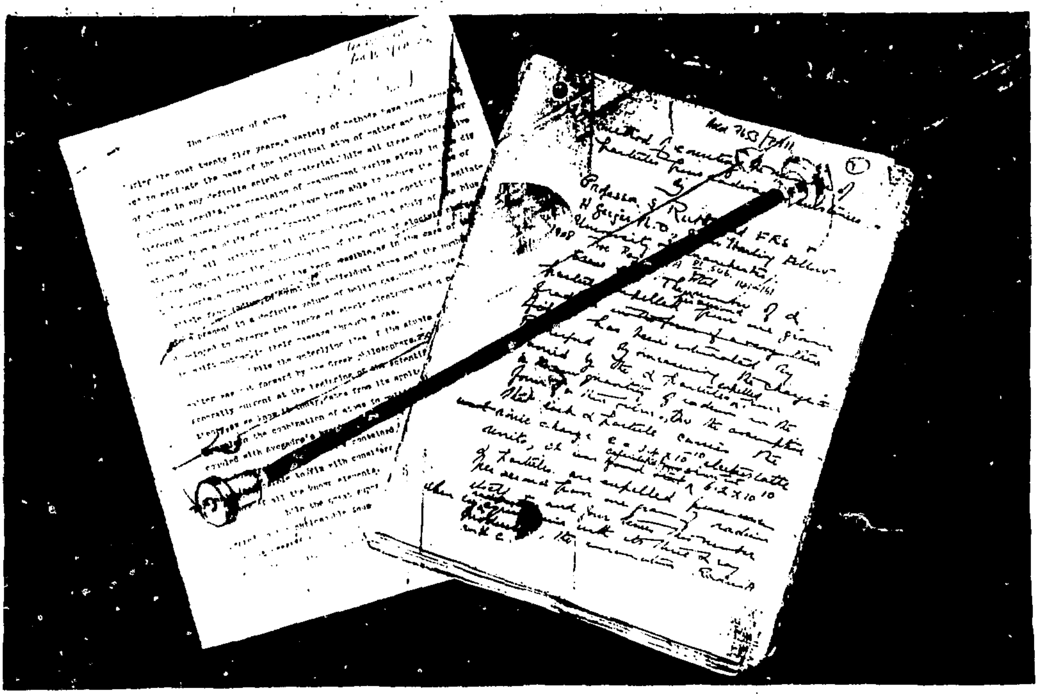

Fig. 3 Rutherford had the complete idea for counting single atoms and with Geiger initiated the development of the proportional counter. Only the tunable pulsed laser was needed to complete the idea. We are indebted to the University of Cambridge for access to the Rutherford archives and for the University's permission to use this material.

most useful, i.e., beta decay, the daughter atom is not only in the n+ charge state but also cannot advance from 1+ to 0 because it has a low recoil energy (on the order of 1 eV). Rapid neutralization of daughter atoms remains a challenging problem. Studies of charge transfer and the solution of this problem would add the dimension of radioactivity to RIS.

Generalization of RIS to the elements of the periodic table in the neutral charge state has been very successful. In an early review article (Hurst et al 1979) it was shown that it should be possible to use RIS on all elements except helium and neon in their ground states by using commercially available lasers. In Fig. 5, we show the periodic table with an indication of the atoms that have now been demonstrated with experiments. Additions are being made at such a rapid rate that it is not feasible to give all of the references here. Individual papers in these Proceedings will contain most of them. Atomic energy levels, oscillator strengths, and other spectroscopic data are good enough to ensure us that the RIS process can be carried out for all of the atoms for which laser wavelengths are available. Currently, this includes all atoms except helium and neon in their ground states.

4. Photophysics, Chemical Kinetics, and Statistical Mechanics

Photodissociation of diatomic molecules, combined with resonance ionization spectroscopy ionization of a product atom, provides a new

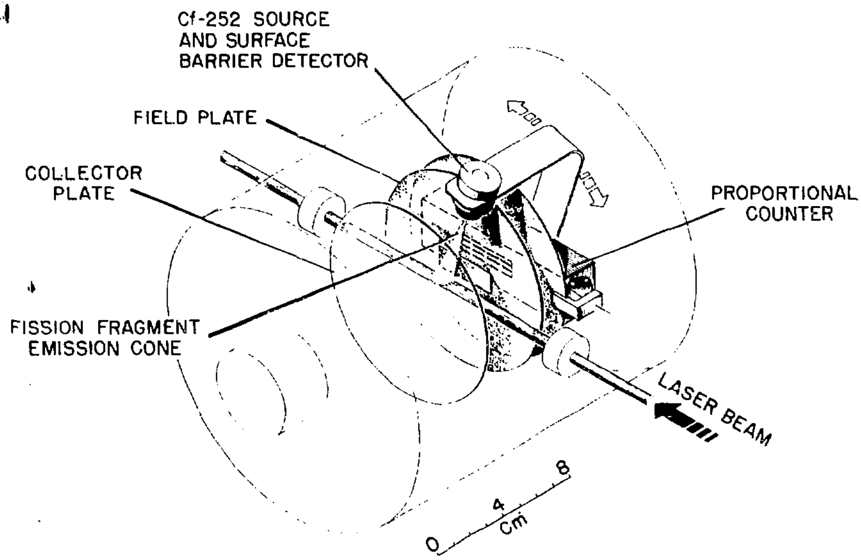

Fig. 4 Schematic of an experiment demonstrating that daughter atoms of cesium could be counted in time coincidence with the fission decay of ^{252}Cf atoms. A parallel plate chamber was first pulsed to remove the familiar nonselective ionization (about 10^6 ion pairs) before a laser was pulsed to create just one ion pair by the selective RIS process. This one electron was drifted into a proportional counter for detection.

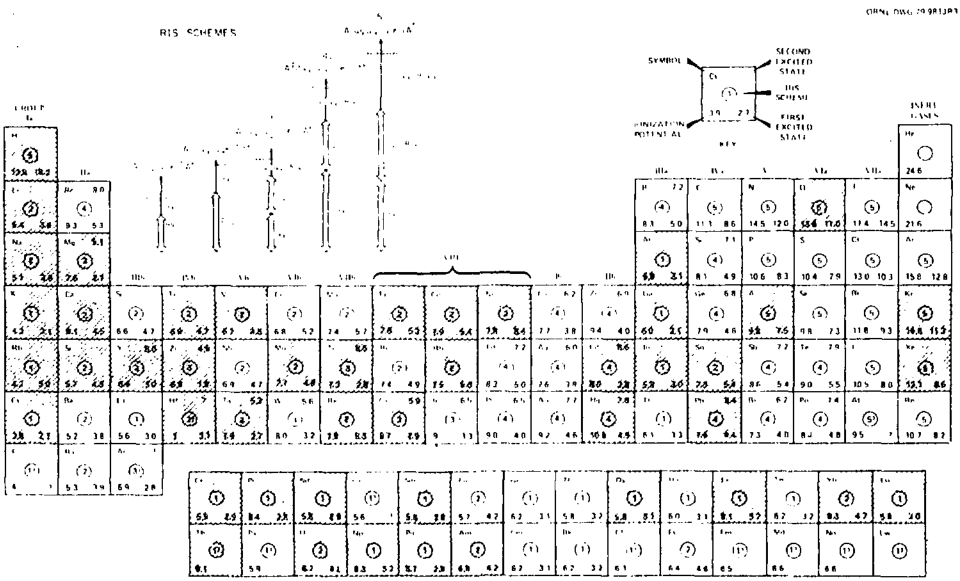

Fig. 5 Periodic table of elements with applicable RIS schemes according to the predictions of Bushaw and Whitaker (1976). Shaded areas indicate atoms for which RIS has been proved by experiment.

approach to the study of several problems in photophysics, chemical kinetics, and statistical mechanics. The basic idea behind the method is illutrated in Fig. 6. One laser is used to dissociate a molecule, e.g., CsI, and a second laser is used to detect atoms (e.g., cesium).

As shown in the figure, the source laser beam and the detector laser beam can be coaxial or parallel, and can be directed through either a parallel plate ionization chamber (to count down to several thousand atoms in one pulse) or a proportional counter (to count down to single atoms). Finally, the detector laser can be time delayed by an arbitrary amount with respect to the source laser.

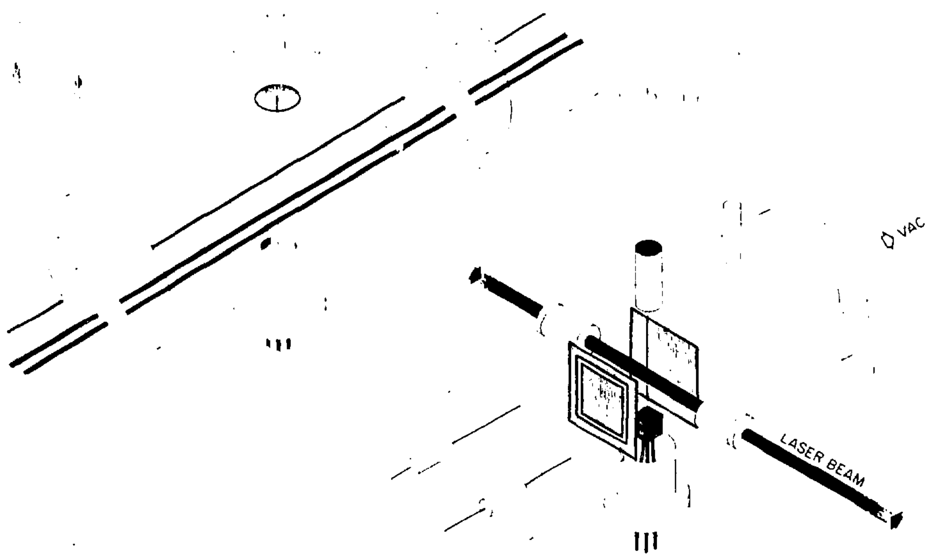

Fig. 6 Generalized schematic of experiments which can be done when one laser dissociates molecules to make time-resolved sources of atoms and a second laser is used to detect free atoms. Source lasers and detector lasers can be colinear or parallel. Ionization detectors can be parallel plates on proportional counters.

The first work using these methods was that of Grossman et al (1977a, 1977b), in which he used a coaxial geometry in a parallel plate ionization chamber to study photodissociation of CsI. With the detector (of cesium atoms) laser providing enough photons to detect all cesium atoms, and the source laser dissociating nearly all CsI molecules in the beam, essentially the concentration of CsI in argon gas could be measured. Then, by decreasing the energy per pulse of the source laser to the linear region, the absolute cross section for photodissociation was measured (Grossman et al 1977a). By time delaying the detector laser, it was found that the signal due to cesium atoms decreased due to diffusion out of the detector beam (Grossman et al 1977b). If impurities, such as O_2, were present, cesium reactions with O_2 occurred more rapidly than diffusion losses, and chemical reaction rate constants could be estimated from the single component exponential decays (Grossman et al 1977b).

The coaxial beam is not an accurate way to determine diffusion coefficients, due to the sensitivity of the time decay curves to chemical reaction. Thus, in the work of Hurst et al (1978), the parallel beam geometry was introduced. By taking data at several time delays and at two separations, chemical reactions can be eliminated and

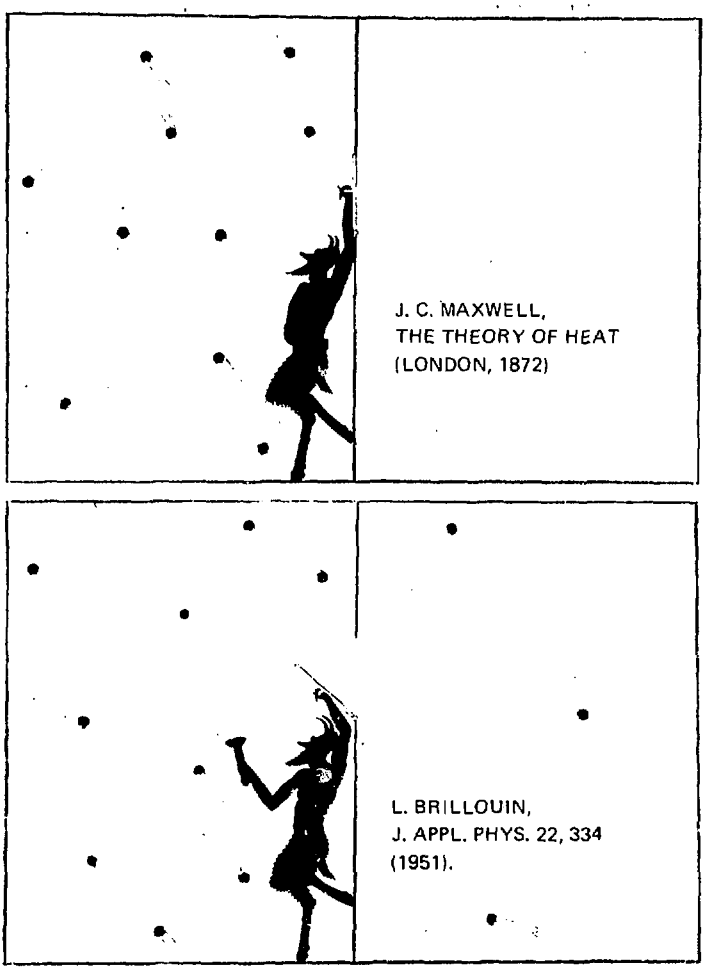

Fig. 7 James Clerk Maxwell first described his demon in a letter to P. G. Tait on the 11th of December 1867 [quoted in C. G. Knott (1911)] and later in his book entitled Theory of Heat (Maxwell 1872). Maxwell's creature was first called a *demon* by W. Thomson (1889). L. Brillouin proved that a demon does not violate the entropy principle when he showed that a light source must be used to "see" atoms.

6. Resonance Ionization Mass Spectrometry (RIMS)

We have already indicated how Z selectivity can be added to mass spectrometers to have both Z and A selectivity in the same measurement. During the past two years, very significant work has been done with a technique now called RIMS. Lasers can be integrated into magnetic, quadrupole, or time-of-flight mass spectrometers to provide resonance ionization sources in all of these analytical facilities. With these sources, more efficient, as well as more selective ionization is produced. In particular, Z selectivity can help to remove interferences from molecules and to resolve isobars.

In the case of solid samples it is necessary to free atoms from the solid before resonance ionization can be carried out. Several types of "atomizers" have been used, including hot filaments to evaporate atoms

Fig. 8 Artist's conception of the modern Maxwell demon along with some applications of atom counting. Illustrations show the solar neutrino tank in the Homestake Mines in South Dakota (courtesy of Raymond Davis, Jr., Brookhaven National Laboratory), ^{39}Ar sampling in ocean water (courtesy of Harmon Craig, Scripps Institution of Oceanography), polar ice cap sampling (courtesy of Hans Oeschger and J. Loosli, University of Bern, Switzerland), and tanks of radioactive waste (courtesy of M. Cates, formerly with Los Alamos National Laboratory).

(see Session III for exciting developments from Los Alamos National Laboratory, National Bureau of Standards, and the ORNL Analytical Chemistry Division). In particular, sputtering by charged particles may be one of the most direct ways of freeing atoms with populations characteristic of the solid. Thus, sputter-initiated RIS, or SIRIS, looks promising for analysis of materials for low levels of impurities (see the paper by Winograd and Parks in Session IV). Finally, we point out that the SIRIS method, along with Maxwell's demon, is involved in many of the weak-interaction and particle physics applications discussed in Session VI.

7. Weak-Interactions and Particle Physics

Weak-interaction and particle physics are particularly fertile ground for the use of RIS methods. Solar neutrino flux measurements, ββ-decay rate measurements, quark (superheavy atom), and magnetic monopole searches are examples of the applications to be discussed at this meeting. The organizers of this symposium are very pleased to have prominent scientists from many disciplines accept their invitations to speak. The last day, on weak interactions and particle physics, will be a special treat for all of us.

To conclude on a historical note, we recall that Prof. J. J. Thomson developed the first mass spectrometer and his student Ernest Rutherford developed the first electrical counter. In a very real sense, the laser has given new capability to both of these basic ionization detectors. At this conference, we will have the pleasure of discussing the many fruitful combinations of lasers and ionization detectors for applications ranging from particle physics to important practical matters such as groundwater and ice cap dating and semiconductor analyses (McGuire et al 1983).

Acknowledgment

This research was sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

References

Ambartsumyan R V and Letokhov V S 1972 Appl. Opt. 11 354

Bohr N 1915 Philos. Mag. 30 581

Bushaw B A and Whitaker T J 1976 Proc. 20th Annual Technical Symposium of the Society of Photo-Optical Instrumentation Engineers (Bellingham, Washington: SPIE Publications) Vol. 82 pp 92-94

Chen C H, Kramer S D, Allman S L, and Hurst G S 1984 Appl. Phys. Lett. (in press)

Drell Sidney D, Kroll Norman M, Mueller Mark T, Parke Stephen J, and Ruderman Malvin A 1983 Phys. Rev. Lett. 50 644

Grossman L G, Hurst G S, Payne M G, and Allman S L 1977a Chem. Phys. Lett. 50 70

Grossman L G, Hurst G S, Kramer S D, Payne M G, and Young J P 1977b Chem. Phys. Lett. 50 207

Hurst, G S, Payne M G, Nayfeh M H, Judish J P, and Wagner E B 1975 Phys. Rev. Lett. 35 82

Hurst G S, Payne M G, and Wagner E B 1976 United States Patent No. 3,987,302, "Resonance Ionization for Analytical Spectroscopy"

Hurst G S, Nayfeh M H, and Young J P 1977a Appl. Phys. Lett. 30 229

Hurst G S, Nayfeh M H, and Young J P 1977b Phys. Rev. A 15 2283

Hurst G S, Allman S L, Payne M G, and Whitaker T J 1978 Chem. Phys. Lett. 60 150

Hurst G S, Payne M G, Kramer S D, and Young J P 1979 Rev. Mod. Phys. 51 767

Jesse W P and Sadauskis J 1955 Phys. Rev. 100 1755

Judish John P 1975. Special thanks for his excellent work on the accelerator physics

Knott C G 1911 (Letter from Maxwell to Tait, December 11, 1867) Life and Scientific Work of Peter Guthrie Tait (Cambridge) pp 213-214

Kramer S D, Young J P, Hurst G S, and Payne M G 1979 Opt. Comm. 30, 47

Letokhov V S 1976 International Conference on Tunable Lasers and Applications, Leon, Nordfjord, Norway

Maxwell James Clerk 1872 Theory of Heat (New York: Appleton) pp 308-09

Morrelick J, Normand D, and Petite G 1982 in Advances in Atomic and Molecular Physics (New York: Academic) Vol 18 pp 97-164

Parker David H 1982 Ultrasensitive Laser Spectroscopy ed Davis S. Kliger (New York: Academic) Chapter 4 pp 233-309

Payne, M G, Hurst G S, Nayfeh M H, Judish J P, Chen C H, Wagner E B, and Young J P 1975a Phys. Rev. Lett. 35 1154

Payne M G, Klots C E, and Hurst G S 1975b J. Chem. Phys. 63 1422

Poisson S D 1837 Dissertation: Recherches sur la Probabilite des Jugements en Matiere Criminelle et en Matiere Civile (Paris) p 206

Rutherford E and Geiger H 1908 Proc. Roy. Soc. Lond. A 81 141

Taylor T S 1913 Philos. Mag. 26 402

Thomson W 1889 Popular Lectures and Addresses (London) Vol I, pp 137-41

Walther H 1984, these Proceedings

Wunderlich R K E 1984 Guest at ORNL and sponsored by the Max-Planck Institut fur Kernphysik, Heidelberg