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Detection of Single Atoms by Resonance Ionization Spectroscopy [and Discussion]

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Detection of single atoms by resonance ionization spectroscopy

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Rutherford's idea for counting individual atoms can, in principle, be implemented for nearly any type of atom, whether stable or radioactive, by using methods of resonance ionization. With the technique of resonance ionization spectroscopy (RIS), a laser is tuned to a wavelength that will promote a valence electron in a *Z*-selected atom to an excited level. Additional resonance or non-resonance photoabsorption steps are used to achieve nearly 100% ionization efficiencies. Hence, the RIS process can be saturated for the *Z*-selected atoms: and because detectors are available for counting either single electrons or positive ions, one-atom detection is possible.

Some examples of one-atom detection are given, including that of the noble gases, to show complementarity with accelerator mass spectrometry AMS methods. For instance, the detection of ^{81}Kr by using RIS has interesting applications for solar-neutrino research, ice-cap dating, and groundwater dating.

1. Introduction and scope

The physical process known as resonance ionization spectroscopy (RIS) was discovered in 1975 when it was used as a method to measure the population of the He(2^1S) state following the interaction of radiation with helium gas (Hurst *et al.* 1975). Nearly all applications of the method have involved atoms in their ground state, because the need to count individual atoms has overwhelmed the application of RIS to radiation physics problems. The applications of the technique up to 1984 have been summarized in Hurst & Payne (1984).

Resonance ionization spectroscopy is used to ionize atoms (or molecules) selectively, based on known spectroscopy of the species. When using the process, a laser is tuned to a wavelength that will promote a valence electron in a *Z*-selected atom from its ground state to an excited state. Additional resonance or non-resonance steps are used to achieve nearly 100% ionization efficiencies. Hence, the process can be saturated for the *Z*-selected atoms. One-atom detection is accomplished by using detectors for counting either a single electron or a single positive ion.

In this article, the RIS principle will be discussed briefly and the status of the technology associated with practical use of atom counting will be summarized. Some examples of the application of one-atom detection will be given to show complementarity with AMS methods. For instance, the detection of ^{81}Kr with RIS has a range of interesting uses, including solar-neutrino research, ice-cap dating, and groundwater dating.

2. The RIS principle

Each atom contains electrons that orbit around a nucleus with positive charge. Normally, these electrons are packed near the nucleus in a configuration of orbits determined from quantum mechanics. An atom in its ground state can be excited by the absorption of a photon of the proper energy (wavelength). Each type of atom has its own unique ground states and set of excited states, and one can take advantage of this to detect only those atoms of a given kind.

Now suppose that the atom of a preferred type has been excited, i.e. an electron was promoted from its ground state to some excited state because of the absorption of a photon from a laser beam that was tuned to the exact wavelength acceptable by the type of atom to be detected. An atom in its excited state can also absorb photons and be excited to a higher discrete state. Or, if the photon carries enough energy, the excited electron in the atom can be totally removed from the atom. We now need to stress the most important feature of RIS. If a laser is tuned to a wavelength such that direct ionization cannot occur from the ground state, and if the wavelength is precisely tuned so that excitation can occur, then resonance ionization can occur provided the sum of the energy carried by the two photons is greater than the ionization potential (I) of the atom. In other words, only the photons having a narrow range of energies will ionize an atom, and this was called resonance ionization spectroscopy (RIS) (Hurst *et al.* 1975).

Modern laser technology provides means for using many colours in the same beam; thus, more than one resonance excitation step can be employed. This makes it possible to achieve resonance ionization with atoms having the larger values of I, e.g. hydrogen and the noble gases. In figure 1, we show that by using various RIS schemes it is possible to achieve selective ionization of nearly every element in the periodic table. The noble gases helium and neon are the most difficult because lasers are not yet available for promoting the first transition from the ground state to first excited state.

If a laser provides enough photons in a single pulse, a truly remarkable process is possible. Suppose a real sample is composed of free atoms of several types. A tuned laser can be pulsed once to ionize all of the atoms of a selected type, yet will leave undisturbed all of the other types of atoms. This is known as saturation of the RIS process. It has been shown (Hurst *et al.* 1979) that the saturated RIS process can be achieved for nearly all of the elements as shown in figure 1. However, the effective ionization volume depends very much on the type of atom. This is because of several factors. First, lasers can be used to generate photons in certain wavelength regions more easily than in others. Generally, it is easy to saturate the discrete transition from the ground state but more difficult to saturate the photoionization step where cross sections are typically 10^{-17} cm^2. However, because the cross section for photoionization of an excited state depends on photon wavelength and the quantum-mechanical description of the level in question, some types of atoms are more easily ionized than are others. At one extreme, with the caesium atom, a laser producing 1 J per pulse at 4555 Å† would saturate an area of several square centimetres; and, because the laser beam has a low divergence, effective volumes could be several litres! On the other hand, for RIS of krypton it is difficult to produce more than about 1 μJ per pulse at the vacuum ultraviolet (VUV) wavelength needed to excite the first (one-photon allowed) level in krypton (Hurst *et al.* 1985). Consequently, the first step is the limiting step and effective volumes are only about 10^{-3} cm^3. Furthermore, the effective ionization volume that can actually be utilized depends also on the type of sensitive ionization detector used.

The enormous potential for sensitive analyses based on RIS principles cannot be realized until technology is available for counting individual atoms. One-atom detection has been clearly

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† 1 Å = 10^{-10} m = 10^{-1} nm.

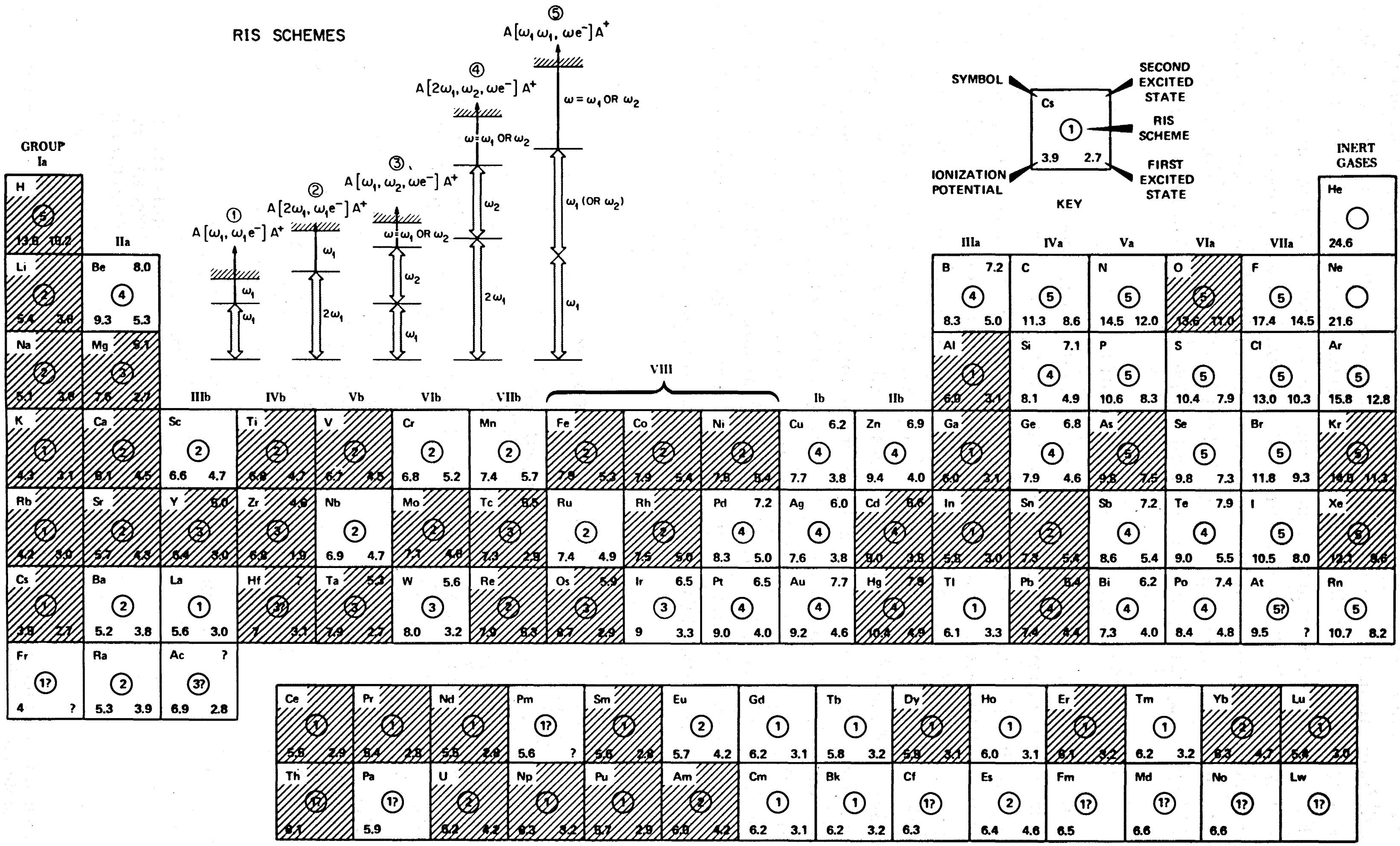

FIGURE 1. With modern pulsed lasers it is possible to saturate the RIS process for nearly all of the elements. At saturation, any atom in the effective volume has a probability of resonance ionization approaching 100%. However, the size of the effective volume varies greatly from atom to atom (see text).

demonstrated in three fundamental ways. It was shown (Hurst *et al.* 1977) that individual caesium atoms diffusing from a metal source could be counted. Furthermore, caesium atoms were detected (Grossman *et al.* 1977) following their dissociation from molecules of CsI. Finally, it was shown (Kramer *et al.* 1978) that caesium atoms could be detected at the instant of their birth from the fission decay of ^{252}Cf. All of these basic demonstrations used proportional counters to detect single electrons created from the RIS process on individual atoms. These interesting demonstrations do not, however, constitute proof that sensitive analyses can be done in practical applications. Widespread applications for routine analytical problems require some additional steps.

3. Maxwell's sorting demon

Noble-gas atoms do not bond with each other or with other materials. Thus, they are free atoms, already in a state ready for RIS detection. However, these atoms owe their chemical inertness to the fact that their ionization potentials and other energy levels are greater than for other atoms, making the RIS process more difficult. For this reason, rather special methods based on a process called four-wave mixing (Payne *et al.* 1984) had to be developed for RIS of the noble gases (Kramer 1984). Even with these elaborate techniques, it is not possible to ionize an atom in a large volume of free spaces; volumes of 10^{-4} cm^3 are typical. The apparatus illustrated in figure 2 is known as the Maxwell demon because it sorts individual atoms (Hurst *et al.* 1985). An 'atom buncher' was incorporated to increase the probability that an atom would be ionized in the RIS process. After an atom is selected for Z, it is then mass selected with a small quadrupole filter. Following both Z and A selection, an atom is accelerated and implanted into a target where it is counted and stored until all like atoms have been counted. Figure 3 shows some results in which 1000 atoms of ^{81}Kr were counted in about 2 h.

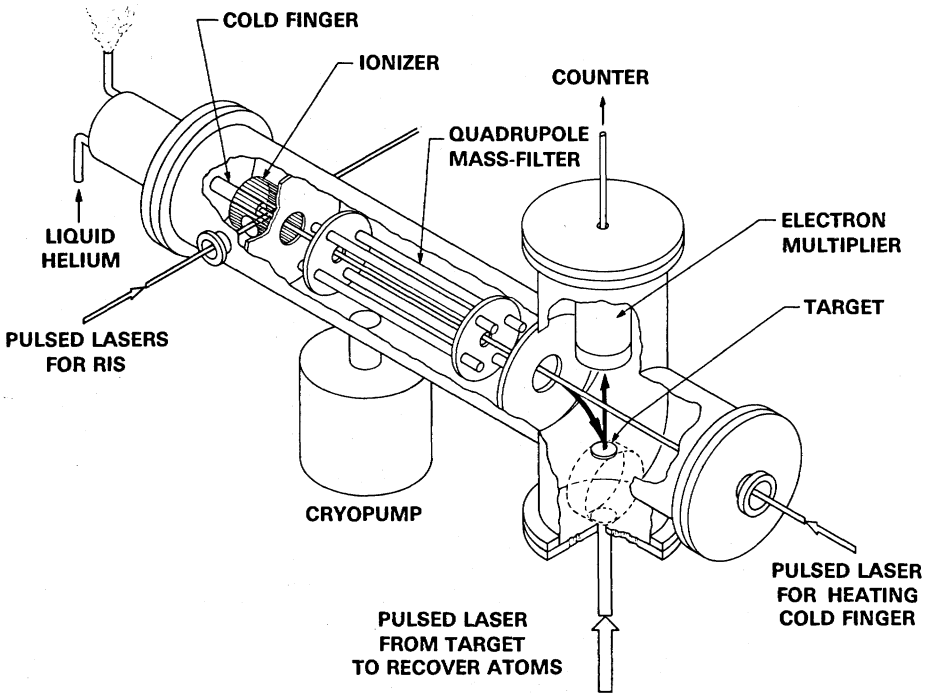

Figure 2. Illustration of a device that can be used to count each atom of a noble gas with isotopic selectivity. The principle of operation is the same as that of Maxwell's sorting 'demon'.

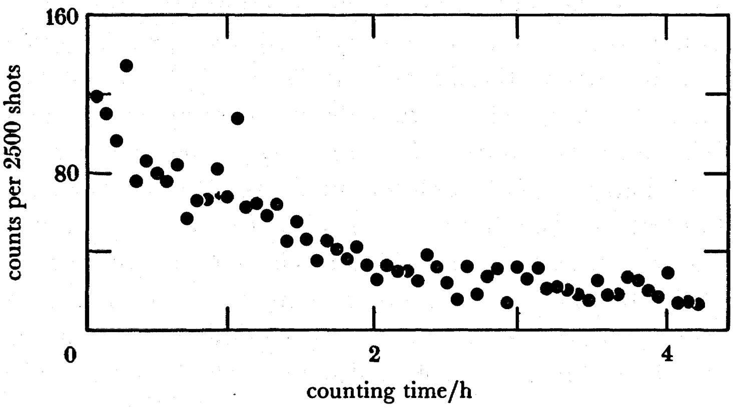

Figure 3. Illustration of the use of Maxwell's demon to count 1000 atoms of ^{81}Kr in an atmosphere of other isotopes of krypton.

A new-generation device is now being developed at Atom Sciences, Inc. by N. Thonnard and associates (Thonnard *et al.* 1984) that first uses a time-of-flight principle for isotopic enrichment, then for atom counting. Furthermore, major improvements have been made in the atom buncher and in the laser method for RIS. We can anticipate that commercial services will be available for counting krypton and xenon with isotopic selectivity in the near future. But the method will continue to be a difficult one, requiring elaborate apparatus and skilled personnel for a few years to come. Some examples of the use of Maxwell's demon are given in §5.

4. Analysis of solids

The analysis of trace elements in solids requires an 'atomization' step before RIS methods are applicable. The desired objective of the atomization step is the liberation of neutral atoms representative of the atomic composition of the solid. After atomization, RIS is used for Z-selective ionization and therefore inherently discriminates against isobars. Even when the analysis does not require isotopic selection, it can be important to include a mass spectrometer to reduce backgrounds due to non-resonant multiphoton ionization (MPI). Even with Z-selection and mass selection, it is still possible to have molecular ions that interfere with the detection of a specified type of atom. The best way to avoid these interferences is by control of the power level of the RIS lasers and the use of RIS schemes that avoid photons of short wavelength. Several methods have been used to atomize a sample, including thermal, laser ablation, and ion sputtering.

Laser ablation holds much potential, but to date certain fundamental problems such as plasma processes near the sample that can interfere with ion optics have not been solved. When thermal methods are used with RIS, they are usually called resonance-ionization mass spectrometry (RIMS) (Donohue *et al.* 1984; Young *et al.* 1984; Travis *et al.* 1984; Clark *et al.* 1984; Nogar *et al.* 1984; Harrison *et al.* 1984). Finally, when sputtering is employed to initiate the RIS process, it can be referred to as SIRIS (Parks *et al.* 1983, 1984). Early work on the use of sputtering to atomize samples for RIS analyses was advanced by Winograd and his collaborators (Kimock *et al.* 1984) for bulk materials and by the Atom Sciences group (Parks *et al.* 1983, 1984) for trace element analyses.

Because the sputtering process has been characterized in detail and is understood as a simple first-order process, it is reasonable to believe that SIRIS is almost independent of matrix effects. To elaborate, with secondary-ion mass spectrometry (SIMS), the signal is caused by secondary ions released from the solid when a primary ion (e.g. 10 keV Ar^+) strikes. The yield of these ions (per neutral atom of the trace element originally in the sample to be analysed) depends substantially on the host material (matrix). But this may be because of complex chemistry involving ions; and if so, matrix effects should be much less when the signal is derived from neutral atoms ejected during the sputtering process. However, some recent results cast doubt on this optimism; and as a result, SIRIS analyses will also have to be calibrated with standards. It is too early to know how often such calibrations are required. There is also a large advantage to the extra sensitivity of SIRIS compared with SIMS. A schematic diagram of SIRIS as developed by Atoms Sciences, Inc., is shown in figure 4, and figure 5 shows some representative data.

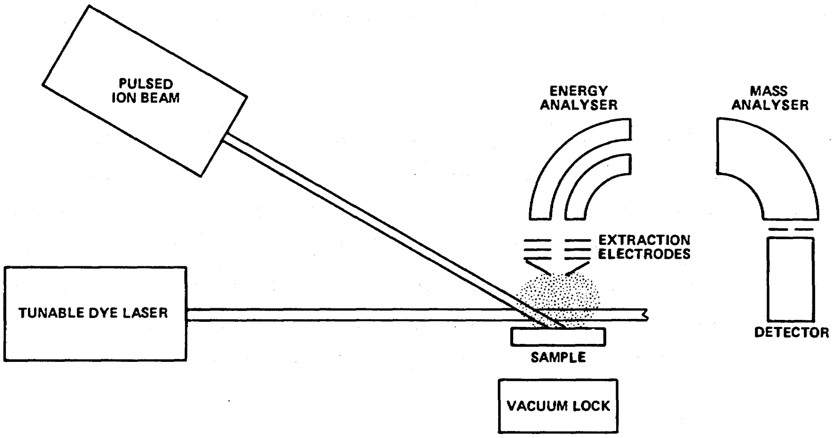

FIGURE 4. Diagram of a device known as sputter-initiated RIS (SIRIS) as developed by Atom Sciences, Inc., for the analysis of impurities in solids.

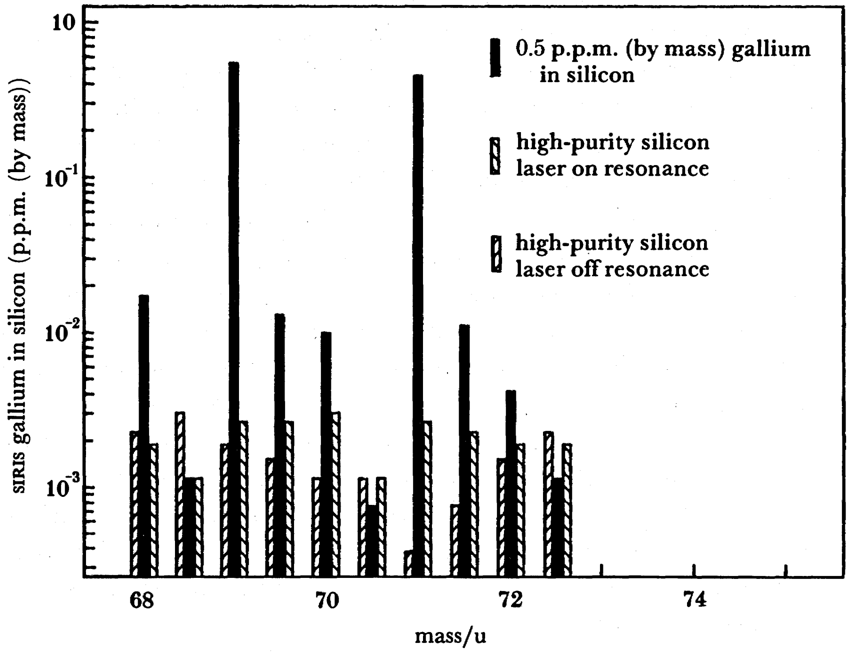

FIGURE 5. Data illustrating the use of SIRIS to detect impurities of gallium atoms in electronics-grade silicon. The data acquisition system creates channels on intervals of 0.5 u.

Note that the full potential of SIRIS would be about 10 to 100 times that shown in figure 5. Thus, it is hoped that analyses of the order of parts per billion† (by mass) will be routine with only moderate matrix effects. Applications of the SIRIS method (Parks *et al.* 1983, 1984) range from measurement of impurity levels in electronics-grade semiconducting materials to the detection of trace elements in the blood of prenatal children.

5. THE ^{81}Br(ν, e^-) ^{81}Kr SOLAR-NEUTRINO DETECTOR

It is believed that the Sun and its internal energy source are understood well enough to make an accurate prediction of solar-neutrino production. However, a careful experiment has been done (see below) and the result is a neutrino flux that is significantly lower than predicted. Because of this problem, the calculations by Bahcall and associates, as well as experimental refinements by Davis and associates, have continued but have not resolved the problem. The origin of the discrepancy is still unknown; it may be because of a flaw in the standard astronomical model, or it could be caused by a lack of knowledge in neutrino physics.

A review by Bahcall *et al.* (1982) gives a critical evaluation of uncertainties in predicting capture rates in solar-neutrino detectors, by using standard solar models (Bahcall 1978, 1979). The results of folding nuclear-reaction cross sections, the solar constant, elemental abundance, mean opacity, equation of state, and solar age into the standard solar model are shown in figure 6, based on a presentation by Burks (1983). According to the currently accepted solar model of Bahcall, the fraction of energy produced by the p–p chain is 0.985 and only 0.015 for the C–N–O cycle.

The only solar-neutrino flux measurement to date was made in the landmark experiment by Ray Davis, Jr. and his associates, from the reaction ^{37}Cl(ν, e^-) ^{37}Ar. For a very interesting history of this classic experiment, see the account by Bahcall & Davis (1982). This difficult experiment has been done, refined, and repeated over the last two decades; for recent reviews, see Davis *et al.* (1983) or Cleveland *et al.* (1984). Table 1 shows some results of typical runs of the Cl experiment, where it is seen that the total rate of ^{37}Ar production is just 0.38 atoms per day. After background correction, the 0.30 ± 0.08 atoms per day corresponds to 1.6 ± 0.4 SNU‡. Thus, the solar-neutrino problem; the measured flux is a factor of 3.6 smaller than the value calculated from the standard model. These low values persisted in a series of experiments from 1971 until 1983.

The large discrepancy between predictions of the standard model and experimental results from the Cl experiment has set the stage for a number of interesting speculations. In very general terms, the problem must be in the standard model or in neutrino physics. In the standard model it is possible that some astrophysics or nuclear-physics facts are missing, or that some uncertainties come into the transport calculations. In the area of neutrino physics, perhaps all types of neutrinos have rest mass. A difference in mass among ν_e, ν_μ, and ν_τ could lead to oscillations between neutrino types. New theories involving the concept of resonance scattering of neutrinos in the high-density matter have been put forth (Bethe 1986) in an attempt to solve the solar-neutrino problem.

It is not surprising that a number of new experiments have been seriously considered and proposed to try to resolve the solar-neutrino mystery. Other radiochemical experiments,

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† In this paper, 1 billion is used to represent 10^9.
‡ 1 solar-neutrino unit (SNU) = 10^{-36} captures per target atom per second.

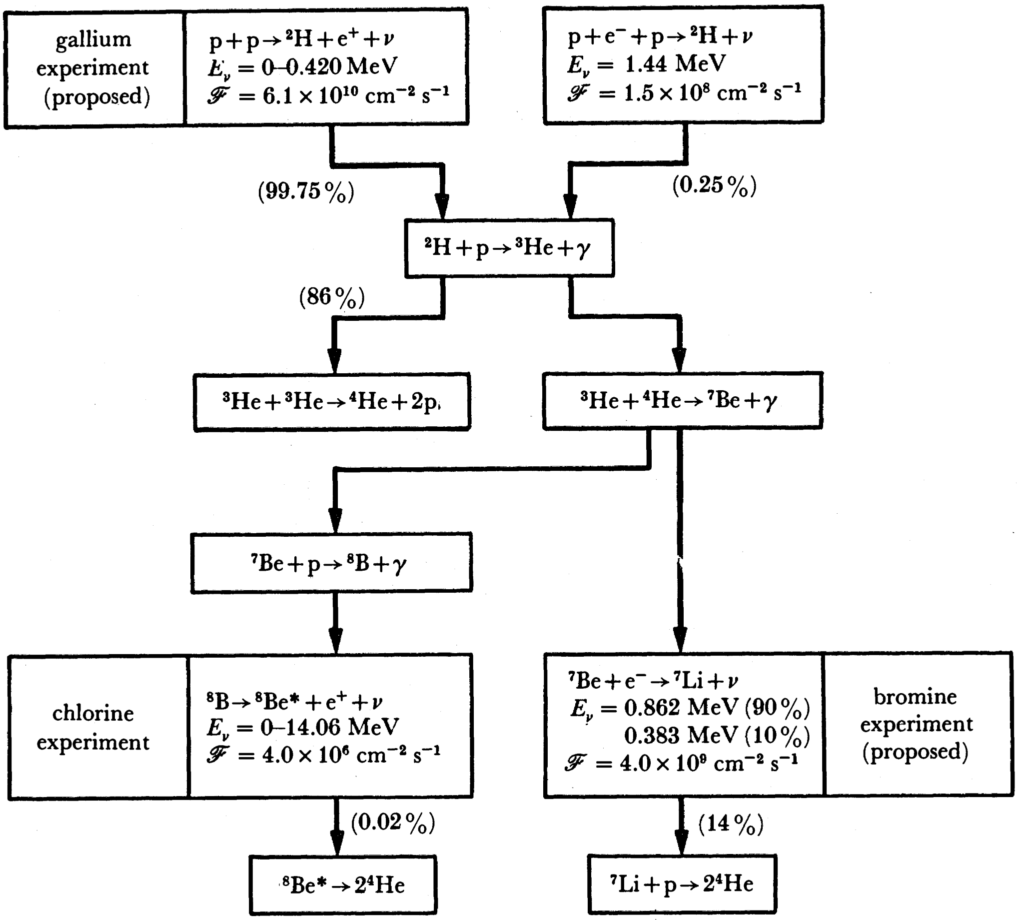

FIGURE 6. Calculated flux, $\mathscr{F}$, of solar-neutrinos on the Earth, according to the standard stellar model of Bahcall (1985).

TABLE 1. SUMMARY OF RESULTS

	production rate (^{37}Ar per day)	
run nos	most likely value	68 % confidence range
18→39	0.38	0.31–0.46
40→47	0.39	0.27–0.50
18→47	0.38	0.33–0.45

average ^{37}Ar production rate (18→47) = 0.38 ± 0.07
cosmic-ray background (muons and ν_μ) = 0.08 ± 0.03

rate above known backgrounds = 0.30 ± 0.08

Possible solar-neutrino rate = 5.24 × (0.30 ± 0.08) = 1.6 ± 0.4 SNU.

following the original chlorine experiment, are the gallium and the bromine experiments. With gallium, low-energy neutrinos could be measured because the interaction ^{71}Ga$(\nu, e^-)\,{}^{71}$Ge has a threshold at 233 keV. The inverse decay, by electron capture, occurs with a half-life of 11.4 days; thus, detection of ^{71}Ge decay is a measure of the neutrino flux provided cross sections are well known. This experiment was first developed at Brookhaven National Laboratory (see Davis *et al.* 1983) with theoretical support by Bahcall (see Bahcall 1978; Bahcall *et al.* 1982).

Currently, an experiment is planned in West Germany (Kirsten 1984; Hampel 1985) and in the U.S.S.R. (Barabanov *et al.* 1985).

The bromine experiment would utilize the reaction ^{81}Br(ν, e$^-$) ^{81}Kr, which has a threshold at 470 keV and would measure the neutrinos of intermediate energy, primarily the ^{7}Be source in the Sun. Because ^{81}Kr has a half-life of 2.1×10^5, a solar-neutrino experiment with this reaction cannot be done by decay counting. Because it appears that RIS is the only feasible way to count small numbers of ^{81}Kr atoms, we will discuss this important experiment in more detail (Hurst *et al.* 1984). Scott (1976) first suggested the use of bromine as a geophysical experiment; here we are discussing a Davis-type radiochemical solar-neutrino detector.

Combining the cross sections in table 2 with the fluxes of the standard and chlorine-consistent solar models yields capture rates for the Br detector. Approximately 65% of the total signal in both of these models is assigned to the ^{7}Be neutrinos. Fortunately, the bromine experiment is dominated by a single solar-neutrino-flux component even if higher excited states contribute to the capture rate. The gallium experiment, in contrast, is dominated by the p–p neutrinos if excited states are neglected, but becomes increasingly sensitive to the ^{7}Be neutrinos as the effect of excited states increases. Results from a bromine experiment may thus be essential to interpret a gallium experiment.

TABLE 2. CALCULATED ^{81}Br NEUTRINO-CAPTURE RATES FOR THE MAJOR SOLAR-NUCLEAR REACTIONS

source and energy MeV		neutrino flux 10^6 cm^{-2} s^{-1} standard model	consistent model	^{81}Br cross section 10^{-46} cm^2 Bahcall	Haxton	^{81}Br capture rate/SNU standard model	consistent model
p–p	(0–0.42)	61000	64000	0	0	0	0
pep	(1.44)	150	150	78	85	1.3	1.3
^{7}Be	(0.862)	4300	1800	25	27	11.8	4.9
^{8}B	(0–14)	5.6	1.1	1700	5400	3.0	0.6
^{13}N	(0–1.20)	500	160	19	20	1.0	0.3
^{16}O	(0–1.73)	400	130	41	44	1.7	0.6
	totals					**18.8**	**7.7**

The chlorine-consistent model predicts a capture rate for the bromine experiment of 8 SNU; and the standard model, assuming that neutrino oscillations are responsible for the low result of the chlorine experiment, predicts a result in the range of 4.5 to 6.0 SNU. With a detector size comparable to that of the present chlorine experiment, the rate of production of ^{81}Kr is about two atoms per day for the bromine compounds $CHBr_3$, CH_2, Br_2, $C_2H_2Br_4$, and $C_2H_2Br_2$. Each run of six months to a year will then contain several hundred atoms. Extraction of ^{81}Kr from a bromine-containing compound can be performed by using a helium purge system like that used for extracting ^{37}Ar from C_2Cl_4. The entire krypton extraction process with the 380 m^3 tank of C_2Cl_4 at Homestake has been demonstrated by R. Davis & B. T. Cleveland (unpublished data) (see figure 7).

Background effects have to be considered for any proposed solar-neutrino experiment (Rowley *et al.* 1980). These arise from the penetrating cosmic-ray muons, from α-decay in the target itself, and from neutrons generated by fission decay or (α, n) reactions in surrounding rock. Cosmic-ray muons can create protons by the photonuclear process and the reaction

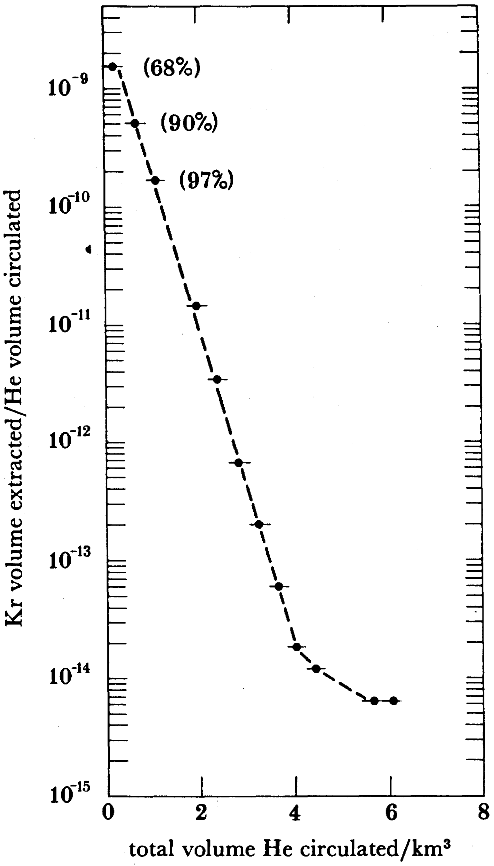

FIGURE 7. Extraction of krypton from the C_2Cl_4 tank at Homestake. An initial volume of 1 cm³ of krypton was added to the 380 m³ tank, and the extracted volume of krypton was measured for 15 solar-neutrino runs. The horizontal bar indicates helium flow of each run. Accumulated percentage of krypton recovered is indicated for the first three runs (unpublished data from B. T. Cleveland & R. Davis, Jr).

^{81}Br(p, n) ^{81}Kr leads to a background. At the depth of the Homestake mine (410 kg cm^{-2} or 4100 hg cm^{-2}) this background is reduced to about 0.07 atom of ^{81}Kr per day, with the assumption of a volume of 380 m³ for the bromine-rich organic solution. Alpha particles from the decay of uranium or thorium in the target would initiate ^{81}Br(α, p) ^{84}Kr followed by ^{81}Br(p, n) ^{81}Kr. Furthermore, the α-process ^{78}Se(α, n) ^{81}Kr leads to background if ^{78}Se is an impurity. The total α-induced background is about 0.03 atom of ^{81}Kr per day, assuming impurity levels to be the same as in the chlorine solution. Similarly, ^{81}Br(n, p) ^{81}Se followed by ^{81}Br(p, n) ^{81}Kr is a neutron-induced background. And ^{84}Sr(n, α) ^{81}Kr leads to ^{81}Kr if ^{84}Sr is an impurity (unlikely). These neutron-induced reactions would produce about 0.1 atom of ^{81}Kr per day in the target; however, the neutron flux can be easily reduced by a water shield around the tank. Thus, we are left with a total background rate of about 0.1 atom per day, considerably less than the expected rate of about 2.0 per day from solar neutrinos. The reaction ^{79}Br(p, n) ^{79}Kr could provide a monitor of (p, n)-associated backgrounds. More frequent recovery of krypton atoms, followed by decay counting of ^{79}Kr (electron capture, $T_{\frac{1}{2}} = 35$ h) could confirm that the (p, n) background is negligible.

Any krypton from air leaks will contain the atmospheric abundance of ^{81}Kr, namely 1.6×10^7 atoms of ^{81}Kr per cubic centimetre of krypton (Loosli & Oeschger 1969; Barabanov *et al.* 1973). The measurements made of krypton extraction from the 380 m^3 C_2Cl_4 tank give an upper limit of 10^{-6} cm^3, and that will not be a serious source of background. Excessive ^{82}Kr could interfere with the RIS detection of ^{81}Kr; thus, one step of isotopic enrichment could be necessary to reduce the number of ^{82}Kr atoms due to air contamination before doing the RIS counting.

6. AN ^{81}Kr DATING METHOD FOR ICE CAPS

It has long been recognized that ^{81}Kr could be used for dating groundwater or polar ice-core samples in the range 50 ka to 1 Ma. A ^{81}Kr-based technique would considerably extend the range that is accessible to ^{14}C dating and is expected to have definite advantages over other dating methods because of (1) the inert chemical character of krypton, (2) the fact that the atmosphere is the main reservoir with a concentration that has probably been constant for a long time, and (3) the expectation that underground production should be small (Davis & Bentley 1981).

With a solubility of krypton in groundwater of 9.2×10^{-5} cm^3 of krypton per litre of water (10 °C) and a Kr:^{81}Kr ratio of 1.9×10^{12}, we expect to find only 1300 atoms of ^{81}Kr in 1 l of modern water. Because of this very low concentration, it has been impossible to use this isotope in geophysical studies. Even the best low-level decay counting techniques would require hundreds of tons of water. Furthermore, contamination with as little as 0.1% of modern air would add enough ^{85}Kr activity to completely mask the ^{81}Kr signal (Lehmann & Loosli 1984).

Obviously, it would be very desirable to have a technique for counting ^{81}Kr atoms directly rather than having to wait for their decay. The recently developed accelerator-based atom-counting systems have successfully been used for several cosmic-ray-produced radioisotopes, such as ^{14}C, ^{10}Be, and ^{36}Cl in geophysical studies (Suter *et al.* 1985; Beer *et al.* 1984; Finkel *et al.* 1980). They cannot be used, however, for ^{81}Kr analyses because krypton does not easily form negative ions for use in a tandem accelerator. Cyclotron machines operating with Kr^+ ions could, in principle, be used for noble-gas work, but the current estimates for sample size are again in the range of several hundred thousand litres of water (Davis & Bentley 1981).

Lehmann *et al.* (1985), using RIS, demonstrated for the first time that ^{81}Kr atoms originating from a groundwater sample of only a few litres can be detected. The complete chain of sample processing, including sampling and degassing of water, separation and purification of noble gases, two cycles of isotope enrichment, and the final detection of ^{81}Kr atoms, has been successfully completed. The procedure does not allow for any direct monitoring of ^{81}Kr until the final counting step. The fact that we were able to detect 1200 (±300) atoms of ^{81}Kr from an initial calculated level of 1500 atoms proves that losses in the two isotope-enrichment cycles, where ions are implanted into and recovered from different targets, can be kept reasonably small. Because these losses are not yet quantified and because the overall accuracy was not very high in this first demonstration, it is too early to assign an 'age' to our ^{81}Kr determination. We might, at best, estimate a rough upper limit for the age of this sample or get a preliminary indication that ^{81}Kr underground production in this sandstone aquifer is small.

To make the step from a first demonstration of the technique to a ^{81}Kr dating method, the effort directed by N. Thonnard of Atom Sciences, Inc. now concentrates on the following aspects. (1) Because the enrichment procedure used for this first demonstration is certainly inadequate for more-routine measurements, a new facility has gone into operation for the first enrichment cycle by using a commercial isotope enricher (Colutron) with a plasma ion source and a velocity filter to reduce all unwanted krypton isotopes by a factor of at least 10000. The second cycle of enrichment is now performed in a separate quadrupole system, which is never used at high krypton pressures. The overall enrichment factor will be at least 10 times larger than in this first demonstration and will enable us to completely separate the ^{81}Kr signal from ^{82}Kr interferences in the counting step. (2) Relative calibration will be achieved by using ^{78}Kr as an internal standard. The initial modern ^{78}Kr:^{81}Kr ratio of 6.0×10^9 will be reduced by a factor of 200 in each enrichment step by simply switching for short time intervals from a channel 81 to channel 78. A total of about 10^8 atoms of ^{78}Kr, together with 1000 atoms of ^{81}Kr, will be introduced to the counting system. A measurement of a ^{78}Kr:^{81}Kr ratio will then be the basis for dating applications where only isotope ratios are needed.

With an improved calibration and with the capability of processing samples in a more-routine procedure, we will investigate the potential of this new isotope for dating polar ice core and groundwater samples in the range 50 ka to 1 Ma. Deep polar ice-cores from the Greenland and Antarctic ice shields contain an invaluable record of past climatic conditions, probably extending several hundred thousand years into the past. Establishing a chronology for these ice cores is clearly of great scientific importance, but a reliable dating technique for the deepest parts of such cores, where the ice is older than about 10 ka, does not exist (Patterson & Waddington 1984). Because 1 kg of modern ice contains roughly the same amount of krypton as 1 l of modern groundwater, the sample processing for ^{81}Kr analysis for ice is analogous to the one outlined for groundwater.

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Discussion

W. KUTSCHERA (*Argonne National Laboratory, Illinois, U.S.A.*). I would like to ask Dr Hurst three questions. In the decay curve of ^{81}Kr, the measurements stop at the point where there was still a rate above zero. If he had gone on measuring, what would be the total time to get all the atoms, and have there been further improvements? Secondly, what is the current limit for an isotopic ratio? Thirdly, this is a very beautiful technique for measuring a few atoms, but during the course of this meeting we have heard many times that when one has got very small samples, one begins to get into more and more problems with background and decontamination in the chemical procedure, and I would just wonder what Dr Hurst's point of view is on that.

G. S. Hurst. The decay curves taken on krypton were not intended to be complete. We were showing the slope of that decay, and it is not necessary to run the experiment to completion. From the slope one can integrate the curve to get the total number of atoms. The second point was concerning isotopic selectivity. In the quadrupole mass filter that is not outstanding, but we have an abundance sensitivity of about 10^5. That means that if the mass spectrometer is timed to mass 81, then mass 82 will be attenuated by a factor of 10^5. The way we have dealt with limited abundance sensitivity was to develop isotopic enrichment with another machine, in which atoms were implanted into a silicon target and then recycled. A machine having an abundance sensitivity of 10^5 would give 10^{10} in two cycles and so on. I showed the Kr peak that had actually gone through many of those cycles. Dr Kutschera's third point was about contamination. That certainly is a real problem, although many people think there would be no memory effects with noble gases. However, these effects do exist and they come in mainly when something very disruptive or violent happens inside the system, e.g. sputtering. But one of the advantages of the resonance-ionization step with lasers is that one does not have hot filaments or materials of any sort in the final step. Laser ionization is very clean; the atoms that happen to be out there in free space are ionized free from surfaces. But you are certainly right that there are memory effects, and one has to build machines that get around them the best way one can.

H. Oeschger. I think that once in Oak Ridge Dr Hurst and I discussed the possibility of measuring ^{14}C by cooling down CO to the ground state and then exciting the molecules. Did Dr Hurst's group follow up this technique or try to develop it?

G. S. Hurst. No, we did not. The idea was developed by my colleague Marvin Payne and he liked the technique and thought it had lots of selectivity, but it was very expensive to try it. We did not have the funds to try it out, and he also looked at what the AMS people were doing and felt the competition was really very tough.

G. Korschinck (*Technical University, Munich, F.R.G.*). What percentage of atoms are ionized, and what happens to the other neutrals?

G. S. Hurst. The neutrals evaporated from the target of the atom buncher have about a 10% probability of being in the laser beam at the right time, and they have about a 10% probability of being ionized. That is only 1% yield, but what happens is that the atoms that are not ionized are returned to the cold surface. The laser beam finds all the atoms eventually and puts them in the target. The curve that you saw is the composite representing all of these processes, and it would have required one thousand times longer had we not used the atom buncher.

D. S. Donahue (*University of Arizona, Arizona, U.S.A.*). Dr Hurst mentioned seeing impurities in silicon to one part in 10^{10}, I believe.

G. S. Hurst. I mentioned that we would like to see that level, but we have not achieved it yet.

D. S. Donahue. Does Dr Hurst have some data on that?

G. S. Hurst. The Atom Sciences Laboratory can do about one part in 10^9 at the present time. There are many kinds of impurities in silicon, and analysis involves running the sample for about five minutes.

A. E. Litherland. Is it true that AMS is already at about the level of one part in 10^9? I think that Professor Donahue has published some work along those lines.

D. S. Donahue. For some elements it is one part in 10^9.

A. E. Litherland. I was just a little puzzled about Dr Hurst's discussion on molecular discrimination. The molecular spectra of molecules are very complicated and one would expect there to be resonant states. Is Dr Hurst saying that one can always find a window where one can ionize only the atoms and so discriminate against the molecules? How does one do it?

G. S. Hurst. Molecular ionization can be a background when using lasers because multiphoton ionization occurs when the laser beam is too intense. Many photons can be absorbed at the same time, leading to non-resonance and non-selectivity and ionization. Most of the molecular background is caused by non-resonant multiphoton ionization.

A. E. Litherland. Is it possible to be quantitative about it? It seems that there will always be some molecular ionization, but maybe the discrimination factor is very large. Can Dr Hurst give us a number or any typical case?

This is also one of the main problems in AMS, and there by a great stroke of luck the molecules are completely disassociated in the terminal stripper of the tandem.

G. S. Hurst. What does Professor Litherland mean by 'complete'? Is it down to one part in a million or more?

A. E. Litherland. In all probability they are not completely dissociated, but what we mean is that one can detect C^{14} at one part in 10^{15}, ^{36}Cl and one part in 10^{15} and that the molecular species do not interfere at that level, so it is a very big discrimination factor.

G. S. Hurst. If I go back to the first experiment we did with Cs atoms, it may be recalled that in the proportional counter there were argon and methane, and yet we could see one atom of Cs even when there were 10^{19} atoms of argon in the laser beam and 10^{18} molecules of methane. So we could claim in that case that we were discriminating against molecules by a factor of 10^{18}.

K. Ledingham (*Glasgow University, Glasgow, U.K.*). Perhaps I can answer Professor Litherland's question on laser-ionization spectroscopy and molecules. Dr Hurst showed us how sensitive the technique is, and it is a beautiful and sensitive technique especially with atoms. Indeed, one can detect Cs in about one part in 10^{16} or better. In answer to Professor Litherland's question, the molecular ionization efficiency depends on the laser wavelength. If one is operating at 466 nm, indeed one gets the sensitivity that Dr Hurst claims. If one uses wavelengths that are closer to the UV things get worse as molecules have got resonances below 300 nm. So what happens with molecules is that the background is going to go up by perhaps four orders of magnitude roughly, but of course it depends on the resonant cross sections.

A. E. LITHERLAND. That helps to answer my question but I understand, and Dr Hurst knows, that one can find regions where the molecule is actually transparent to the radiation. I am incredibly impressed by the fact that ^{14}C is detected at 10^{-12} by laser absorption. It can only be done at the right kind of wavelength and one has to know the molecular-absorption spectrum. So I think that one has to search for the appropriate wavelength where there is a good signal-to-noise for the detection of particular isobars. There may be some wavelengths that are better than others.

W. KUTSCHERA. Dr Hurst describes the beautiful bromine experiment that could be performed in Davis's tank. What is the status of that experiment and what is the likelihood that Dr Hurst will run it?

G. S. HURST. The status of the experimentation is that all support for solar-neutrino experiment has been withdrawn.

If we can just start the bromine experiment we can do some background studies as a part of the chlorine experiment now continuing with U.S.F. support at Homestake but eventually we need to find a new location. Either we have to make a decision to stop the chlorine experiments and trade it for bromine or we have to find a new place for it. Funding is at a very low ebb for these kinds of experiment at the present time.

W. HENNING. I want to make a comment that Dr Hurst should only take half seriously that has to do with the disassociation of molecules. We all have been to many AMS meetings where it is always pointed out that one of the great advantages of AMS is that molecules get disassociated and consequently lost, and we all know strictly that is not true. Note the experiments by Gemmell at Argonne with the Dynamitron where one finds molecules going through stripper gas and going through foils at levels of 10^{-6}. That would be disastrous to AMS. The real point is that even if the molecules make it through the stripper, they would never make it through the subsequent beam-analysis system.