Isotopically selective atom counting using photon burst detection

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(Received 4 March 1996)

Photon burst detection is used to count Mg^+ ions in a 500-eV beam with high optical isotopic selectivity. Background rates of less than 1 count in 2 h have been achieved corresponding to an optical abundance sensitivity of 2×10^{-8}. [S1050-2947(96)00611-7]

PACS number(s): 42.62.Fi

Isotopic measurements for radiochemical dating and environmental monitoring often require the determination of abundances in the 10^{-10}–10^{-15} range. Photon burst mass spectrometry (PBMS) is an atom-counting method which has been proposed for such measurements [1,2]. In PBMS, the isotopic selectivity of a mass spectrometer (10^3–10^5) and that of an optical single-atom detector, based on the photon burst method (10^8–10^{10}), are combined to achieve the required level. Application of PBMS to half the elements of the periodic table may be possible [2]. The noble gas isotopes ^{39}Ar, ^{81}Kr, and ^{85}Kr are of special interest because important applications exist and because these isotopes cannot be measured in samples of useful size by other methods without extreme isotopic enrichment procedures [3,4].

In our initial experiments using a simple PBMS apparatus with one photon burst detector, an optical isotopic selectivity of $>10^3$ for single Mg^+ ions was achieved [5]. The fundamental limitation in those experiments was background photon bursts due to stray laser light and cosmic rays, at the rate of ~1 sec^{-1}. In this paper a high isotopic selectivity of 5×10^7 is demonstrated using two photon burst detectors in delayed coincidence. A comparison of experimental and simulated burst distributions provides support for the projected application of PBMS in low-level isotope measurements [2,3].

The apparatus used in these experiments is shown in Fig. 1. Magnesium ions produced in a Colutron ion source are accelerated to 2 kV, mass selected when needed by a 15-cm-long Wien ($\mathbf{E}\times\mathbf{B}$) filter, and brought into collinear alignment with the laser beam by a 10° electrostatic bend. The ion beam is then decelerated to 500 eV and refocused to a parallel beam of ~3 mm diameter in the photon burst detection region.

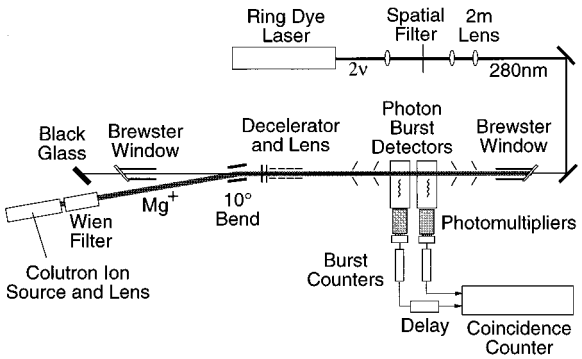

FIG. 1. Schematic diagram of the experimental apparatus.

The photon burst transition in Mg^+ is the $^2S_{1/2}$ to $^2P_{3/2}$ transition at 279.5 nm. Laser light at this wavelength is generated by intercavity doubling with a potassium dihydrogen phosphate (KDP) crystal in a Coherent 699 ring dye laser [6]. The laser beam is focused with a lens of 2-m focal length to a waist radius of 250 μm inside the photon burst detectors. The typical laser power in the interaction region is 0.5 mW, resulting in a maximum intensity equal to the saturation intensity for the transition. To minimize stray laser light, the laser beam is spatially filtered, Brewster-angle windows are used for the entrance and exit to the vacuum manifold, apertures are positioned along the laser beam path, and the beam is terminated using black glass placed at Brewster's angle. The apertures also ensure that the laser and ion beam paths are collinear to a few milliradians.

Each photon burst detector has a light collector consisting of an elliptical cylinder, 48 mm long, with reflecting end plates. The laser and ion beams coincide with one line focus of the ellipse, and a slit and photomultiplier (Thorn EMI 9954) are placed at the other focus. The measured quantum efficiencies of the photomultipliers are 10.5% and 11.5%. The reflectivity of the surface coating of MgF_2 over Al is 83% at 280 nm. Photons emitted near the center of a detector are collected with a calculated collection efficiency of 49%.

The collection efficiency was checked experimentally by filling the vacuum system with nitrogen and measuring the amount of Rayleigh scattered light. Using a total Rayleigh scattering cross section of 6.8×10^{-26} cm^2, scaled by λ^{-4} from experimental measurements [7] at 694.3 nm, the peak collection efficiencies were determined to be 49% and 43% for the two detectors, in good agreement with the predicted value.

The output of each photomultiplier is connected to a discriminator and then to a burst counter, which puts out a pulse if the number of detected photons during an ion transit time reaches or exceeds a preset level, called the clip level. Parallel outputs for clip levels from 1 to 20 allow the accumulation of statistics for various burst sizes. The burst signal from the first detector is delayed by an ion transit time, then checked for coincidence with the burst signal from the second detector.

The optical isotopic selectivity of the photon burst method is determined experimentally by measuring the rate of coincident bursts from single ions, with the laser tuned to resonance, for an isotope of known abundance and comparing it

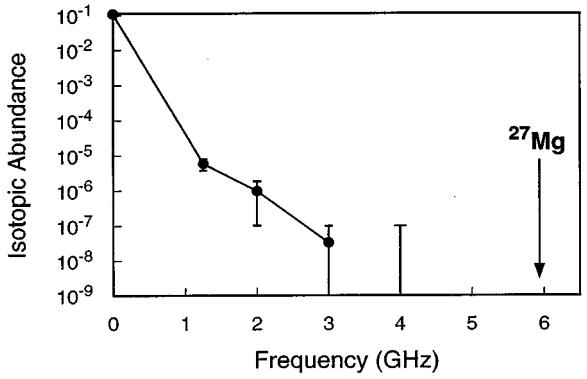

FIG. 2. Isotopic abundance sensitivity as a function of detuning from the $^{26}Mg^+$ resonance. The vertical axis represents the background coincidence rate at clip level 4, measured at different detunings from the $^{26}Mg^+$ resonance, normalized to the on-resonance signal and scaled by the abundance of ^{26}Mg.

to the background coincidence rate in the region of the resonances of radioactive isotopes. Results for a 500-eV Mg^+ beam are shown in Fig. 2. Each point represents the measured coincidence rate for bursts of ≥ 4 counts in each detector at a particular laser frequency divided by the measured value on resonance for $^{26}Mg^+$, and multiplied by the abundance of $^{26}Mg^+$. Thus the ordinate intercept is the abundance of $^{26}Mg^+$ and other points represent abundance limits as a function of frequency detuning. It is seen in Fig. 2 that the abundance limit falls to $<10^{-7}$ by half the frequency shift of the nearest radioactive isotope, $^{27}Mg^+$, which is estimated to be ~ 5.9 GHz for this beam energy. A second set of data was also taken at 200 eV (~ 4.4 GHz shift for $^{27}Mg^+$) with 4-GHz detuning. The results were similar. Both experiments were done with the Wien filter off, so that all Mg^+ isotopes passed through the apparatus together.

In the two sets of data, only one background coincidence was recorded for detunings of ≥ 3 GHz in over 2 h of operation. From the measured on-resonance signals, the total number of detectable Mg^+ ions in this time is 5×10^7. Thus the derived isotopic abundance limit is $\leq 2\times10^{-8}$.

The only important systematic error in these experiments is the effect of variations in the Mg^+ ion current. Slow variations (minutes to hours) in the current were compensated by averaging $^{26}Mg^+$ on-resonance coincidence rates recorded before and after each off-resonance measurement. Rapid current fluctuations ($\ll 1$ sec) were a potentially greater problem because of the possibility of extra bursts in the on-resonance signal due to multiple ions during short periods of much higher current. (On average, the current was set low enough to ensure negligible contribution of multiple ion bursts.) To check for a multiple ion component, on-resonance data were also recorded with the output signals of the two photomultipliers interchanged, so that the coincidence electronics looked for a burst in the second detector followed by a burst in the first detector. No single ions should have been recorded in this mode, only random bursts from multiple ions and background counts. In most of the measurements, this random contribution was less than 5%, and on the order of that expected from the average burst rate in each detector. In the worst cases, when the total photon count rate in each

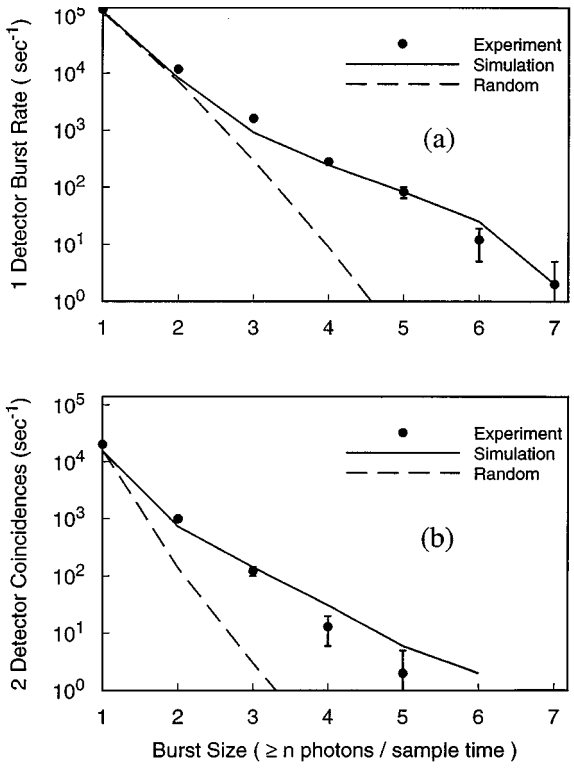

FIG. 3. Experimental and theoretical burst and coincidence distributions on the $^{26}Mg^+$ resonance: (a) burst signal from a single detector and (b) delayed coincidence signal using two detectors. The random statistics line (dashed) in (a) is a Poisson distribution using the average count rate, while in (b), it is the expected rate of random coincidences based on the measured rate of bursts in each detector.

detector was high ($>3\times10^5$ counts/sec or 0.26 photons/sample time), the random contribution was up to four times the expected rate. For each on-resonance measurement, the random component was subtracted from the total coincidence rate. The maximum correction was 22%.

The implications of this demonstration for PBMS measurements with these and other isotopes rely, for the moment, on simulations of the method. The validity of the rough [2,3] and more detailed Monte Carlo simulations [8] of the photon burst detectors can be tested by studying the burst statistics for one detector and for two detectors in delayed coincidence. Results are presented in Fig. 3. The solid line represents the predictions of the Monte Carlo simulation. The agreement between experiment and the Monte Carlo simulations is excellent. The dashed line represents the distribution expected if the measured count rate consisted of photons arriving at random times (e.g., from multiple atoms and stray light). For clip levels ≥ 4, the random component is small, and detected events are almost exclusively single $^{26}Mg^+$ ions.

All but one of the parameters and distribution functions used in the Monte Carlo simulation were measured quantities or the results of straightforward calculations, e.g., detector quantum efficiency, collection efficiency as a function of position, ion and laser beam spatial profiles, and ion beam energy distribution. Effects due to multiple ions in the detector, stray laser light, the random arrival of ions, and photon pres-

sure were also included. The $^{26}Mg^{+}$ ion current density, 7.6 pA/cm^2 in this case, was the only model parameter adjusted to fit the experimental data. The results of rough simulations [2,3], which treat the various distribution functions in an average way, agreed reasonably well with those from experiment and Monte Carlo simulations [8] for clip level >2.

An important concern in the extrapolation of the results of this work to isotopes of practical interest, with abundances in the 10^{-11}–10^{-15} range, is the total throughput of the PBMS instrument. A realistic instrument is expected to have a source current in the μA range. Assuming a mass spectrometer abundance sensitivity of $\sim 10^5$, the output at the rare isotope mass will be in the pA range. Abundance measurements are expected to be made in 10^3–10^4 sec. It is noteworthy that the total current ($\sim$2 pA) and measurement time (7690 sec) in this work are comparable to those in plans for a practical PBMS system [2,3]. Thus the optical abundance sensitivity demonstrated in this work is very relevant to expectations for future PBMS systems.

A full PBMS instrument with up to 20-μA source current and 10^5 abundance sensitivity has been constructed by our group and is being tested with ^{85}Kr. We plan to report measurements of artificial samples with an ^{85}Kr abundance of 6×10^{-9} elsewhere. When the full benefit of the high optical abundance selectivity of the photon burst method is implemented in that system in the near future, isotope ratio measurements of ^{85}Kr and ^{81}Kr at ambient atmospheric levels (1×10^{-11} and 5×10^{-13}, respectively) can be expected.

In summary, the high optical isotopic selectivity (5×10^7) and low background (<1 event/h) demonstrated in these experiments represent an important verification of the fundamental principles of photon burst mass spectrometry. Experimental burst statistics also confirm PBMS models. When combined with up to 10^6 selectivity provided by a conventional mass spectrometer, direct measurements of isotopic abundances in the 10^{-11}–10^{-15} range should be possible in the future with this method.

The authors are grateful to R. A. Keller, B. F. Fearey, E. P. Chamberlin, and H. Oona for helpful discussions. This work was supported by the U. S. Department of Energy under Contract No. W-7405-ENG-36.

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