Diode-laser-based resonance ionization mass spectrometry of the long-lived radionuclide $^{41}$Ca with $<10^{-12}$ sensitivity

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There are a number of applications requiring measurement of the long-lived radionuclide $^{41}$Ca at isotopic abundance, relative to $^{40}$Ca, in the range of $10^8$ to $10^{10}$. The long lifetime and electron-capture decay mode make radioanalytical measurements impractical and conventional mass spectrometric methods can not overcome isotopic interferences such as $^{41}$K or $^{40}$Ca$^+$ at these levels. We approach this problem by combining laser-based resonance ionization spectroscopy with mass spectrometry. Using high-resolution single-mode lasers for resonant excitation and an intense non-resonant laser for ionization of the selectively created excited-state atoms, it is possible to essentially eliminate interference from isotopes and to obtain additional optical isotopic selectivity, which can be combined with that of the mass spectrometer. Single-, double-, and triple-resonance excitation schemes have been investigated experimentally and theoretically, and it is found that performance with respect to both selectivity and sensitivity increases dramatically with each additional resonance step. Thus far, triple-resonance measurements have demonstrated minimum detectable isotopic abundance of $2 \times 10^{-12}$ with detection limits of $2 \times 10^6$ atoms.

Introduction

Despite the fact that calcium is a major component of the earth's crust, there are a number of applications that require highly sensitive and selective measurement of specific calcium isotopes. These include integrated cosmic-ray flux determinations,$^{1}$ radiochemical age-dating,$^{1,2}$ medical isotope tracer studies,$^{3,4}$ neutron dosimetry,$^{5}$ and cosmochemical studies of nucleosynthetic models based on the measurement of isotope ratio anomalies.$^6$ Particularly difficult is the determination of the long-lived radionuclide $^{41}$Ca ($T_{1/2} = 1.04 \times 10^5$ a)$^7$ which requires abundance sensitivities of $\approx 10^{-10}$ for medical tracer applications and $\approx 10^{-14}$ for age dating. Radioactive decay counting methods are not practical because of both the long half-life and the electron capture decay mode. Similarly, conventional mass spectrometric methods do not appear to be feasible because of unavoidable isotopic interference from species such as $^{41}$K and $^{40}$Ca$^+$. Currently, accelerator mass spectrometry (AMS), which has been used for most of the studies cited above, is the only method capable of measuring $^{41}$Ca at these low levels. However, these measurements are very expensive and can be performed only at a few large AMS facilities around the world. Thus, the development of more compact instrumentation with the capability for rapid analyses would be desirable. This might be accomplished with high-resolution resonance ionization mass spectrometry (RIMS), which combines laser-based optical isotopic selectivity with the mass discrimination of a conventional mass spectrometer to achieve the required overall abundance sensitivity.$^8-10$ Generally, highly selective methods must also exhibit high efficiency to be of practical value in analytical applications. Fortunately, the cw lasers suited for isotope-selective optical excitation are not limited by the duty-cycle constraints encountered with conventional pulsed lasers, and detection limits on the order of $10^4$ atoms have been demonstrated with discrete samples.$^{10}$

To reach the extremely high selectivity needed for $^{41}$Ca applications, we have been developing triple-resonance ionization of Ca for several years.$^{11}$ Where additional optical isotopic selectivity can be attained in each of the resonance excitation steps. The excitation schemes studied are shown in Fig. 1. As necessary precursors to the complete implementation of the triple-resonance excitation, the isotope shifts (IS) and hyperfine structure (HFS) for all stable Ca isotopes and $^{41}$Ca have been precisely measured in the first two resonance transitions.$^{12}$ Isotopic selectivity depends not only on the isotope shifts, but also on the details of the spectroscopic line shape function. These have been studied in the double-resonance excitation of Ca and a theoretical model using the density matrix equations of motion, integrated over atomic angular-velocity distributions and laser intensity profiles, has been found to provide an accurate description of the complex lineshapes that are observed experimentally.$^{13}$

The double-resonance excitation has now been extended to the full triple-resonance implementation. The requisite IS and HFS in the $\text{4snp } ^1P_1$ and the $\text{4snp } ^1F_3$ Rydberg series have been measured, and the odd isotopes $^{41,43}$Ca were found to exhibit anomalously large isotope shifts, which could be accurately described in terms of hyperfine-induced singlet-triplet mixing.$^{14}$ Furthermore, extensive studies on lineshapes in triple-resonance ionization have been carried out and, as in the double-resonance case, good agreement is found between theory and experiment.$^{15}$

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In this work we restrict the discussion to triple-resonance excitation (C in Fig. 1) to a specific, optimal target Rydberg level, the 4s15pF3 state, and concentrate on other factors relevant to analytical implementation. These include the consequences of triple-resonance line shapes for selectivity optimization, the attained isotopic selectivity and detection efficiency, and test measurements with low-level synthetic 41Ca samples.

Experimental

The experimental arrangement used for the measurements reported in this work has been described in detail previously \(^{12,16}\) and is only briefly reviewed here. Calcium samples, either metallic or aqueous nitrate solutions are atomized from a small electrothermally heated graphite crucible. In the case of aqueous nitrate samples, the crucible was lined with titanium, which was found to increase atomization yields by about a factor of 3. A cw ring dye laser (Coherent 699-21) and a titanium-sapphire ring laser (Coherent 899-21) were used for the first and second-resonance excitations in most studies reported here. However, it should be noted that diode-laser-based systems can also be used to pump these two transitions\(^{11}\). The third transition, from the 4s4p1D2 second excited state to Rydberg states, was pumped by an extended-cavity diode laser (ECDL, EOSI model 2010) operating in the range of 840–880 nm. To reach the 4s15pF3 state targeted in this work, the operating wavelength was 868.5 nm. To increase excitation efficiency, a high power ECDL (SDL model 8550), which was modified to act as a single pass amplifier, was used to increase the diode laser power from ~20 mW up to ~400 mW. All three of the resonance lasers have jiter limited bandwidths of <1 MHz. Long-term drift correction (<3 MHz/dry) and frequency tuning (<300 kHz RMS accuracy) is provided simultaneously for all three lasers by computer controlled fringe-off setting to a stabilized single-frequency He:Ne laser in a 150 MHz free-spectral-range confocal interferometer.\(^{17,18}\) After triple-resonance excitation to the Rydberg state, efficient photoionization is accomplished with a 20 W cw carbon dioxide laser (Synrad model 48-2). The photoions produced are then analyzed with a quadrupole mass spectrometer (ABB Extrel) fitted with an off-axis channeltron detector for low background ion counting.

Results and Discussion

Optical isotope selectivity

As mentioned above, the combination of isotope shifts with the details of the lineshape function will determine the optical isotopic selectivity that can be achieved in a cw-RIMS excitation scheme. Figure 2 shows a spectroscopic determination of the optical selectivity that can be expected when analyzing for 41Ca in the presence of the stable natural isotopes. To cover the necessary dynamic range, this determination was performed in two steps, as follows: The first- and second-step lasers were tuned to resonance for the major stable isotope 40Ca (97% abundance) and the third-step laser was scanned over the respective resonance for 40Ca. This results in a ‘reference’ resonance signal, denoted (a) in the figure, and corresponds to the response of a desired, targeted isotope. The crucible temperature was adjusted to yield an ion count rate of ~2 MHz on this resonance. Then the first two lasers were detuned to the position of the 41Ca resonance in the first two excitation steps, 155.5 and 443.4 MHz, respectively. The third-step laser was tuned a corresponding ~598.9 MHz, such that the sum frequency for all three lasers is still in resonance for the 40Ca Rydberg state, even though the individual transitions are detuned. This corresponds to the resonance marked at position (b) in Fig. 2. At this point, the observed ion count rate from 40Ca was measured and found to be ~4 orders of magnitude lower than the “true-resonance” rate at (a) and gives a cross-reference for subsequent measurements. The crucible temperature was then increased to again give a count rate of ~1 MHz at (b), for an effective dynamic range of ~10 orders of magnitude. Finally, a second spectrum, the lower trace in Fig. 2, was recorded at this elevated atomization rate with the first two lasers fixed on resonance for 41Ca. Also, the resolution of the mass spectrometer was reduced to allow the transmission of all Ca isotopes. In this spectrum (f) is the 42Ca equivalent of (b), while the weak features (c-e) are from 40Ca and result from quantum electrodynamical interaction of the atomic states with the laser light fields.