Resonance ionization mass spectrometry for spectra of rare isotopes

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Resonance ionization mass spectrometry (RIMS) is becoming a useful tool for isotopic analysis, especially in cases when isobaric (same-mass) interferences from other elements can perturb results. In RIMS, one or more dye lasers are tuned to match atomic transitions (resonances) of atoms of the element of interest in the sample chamber of a mass spectrometer. This causes step-wise excitation of the atoms through the resonant energy levels to the ionization continuum, resulting in a positive ion and an electron. The positive ion is then mass analyzed by the mass spectrometer.

Selectivity derives from the unique pattern of resonances for each element, while sensitivity results from the high ionization efficiencies attainable with laser irradiation as well as the sensitivity of the mass spectrometer for ion detection. Indeed, elemental discrimination levels of at least $10^6$ have been demonstrated\(^1\), with significantly higher levels postulated, and detection limits of $10^3$ atoms have been reported\(^2\). Note that without mass-resolved detec-
tion, resonance ionization is capable of single-atom detection. One of our particular interests in RIMS is its application to the measurement of high dynamic range isotope ratios. In such cases, minor isotopes account for only a few parts per million of a given element's composition. At this level, isobaric impurities, which are difficult to remove by chemical purification, can present significant obstacles to the analysis, and the discrimination of resonance ionization against the isobaric impurities can be particularly useful. In one example, a 60-ng sample of the rare-earth element lutetium was analyzed, yielding a $^{172}\text{Lu}/^{175}\text{Lu}$ ratio of $4.4 \times 10^{-7}$, with ionization/collection efficiency of $10^{-4.4}$. Only $10^8$ atoms of $^{173}\text{Lu}$ were present in this sample, along with approximately a thousand times greater amount of $^{172}\text{Yb}$. This analysis would have been extremely difficult without selective photoionization.

To increase the range of feasible isotope ratio measurements, it will be necessary to increase our ability to distinguish between isotopes of a given element, such that the tailings from major isotopes do not obscure the signals from the minor isotopes. One way to do this is to increase the resolution of the mass spectrometer; however, this approach has a practical limit and may result in less overall sensitivity. An alternative approach is the use of isotopically selective-photoionization, in which the laser is used to preferentially ionize individual isotopes.

To do this, it is necessary to have detailed knowledge about the hyperfine structure and isotope shifts in the element of interest, such that appropriately selective transitions can be chosen. In general, this information is difficult to obtain, particularly for rare and/or radioactive isotopes. However, RIMS itself may be used to provide the needed data, using the selectivity and sensitivity that led to its use as an analytical technique. We have chosen the lutetium system to demonstrate the feasibility of RIMS for determining the spectroscopy of rare isotopes. Analytically, this element is interesting because of practical problems of our laboratory, associated with the mechanisms of nuclear reactions. Spectroscopically, the lutetium isotopes are of interest primarily because of the previously uncertain nuclear spin of $^{174}\text{Lu}$. The photoionization scheme for Lu is attractive for spectroscopic studies (see Fig. 1): a single photon at approximately 452 nm will promote the Lu atom to a resonant intermediate state that is more than halfway to the ionization potential.

A second photon takes the atom to ionization, in a region that previous studies have shown to be free of autoionization structure. This

**FIGURE 1.** Diagram of the resonance ionization process for lutetium. At the left is shown the coarse atomic energy level structure, with the ground state, resonant intermediate state, and ionization continuum. Absorption of two 452-nm photons leads to the creation of a positive ion and an electron. At the right, the hyperfine structure of the resonant levels is shown schematically.
means that spectra observed in resonance ionization will be characteristic of the resonant transition alone, considerably simplifying the analysis of results. (Autoionization structure can be useful, however, in increasing the overall sensitivity of the RIMS process.)

Resonance ionization spectra of the lutetium isotopes were obtained using a scannable, single-frequency, ring-dye laser and a magnetic-sector mass spectrometer. Samples of mixed lutetium isotopes, totaling about 1μg were evaporated from solution onto rhenium filaments and installed in the spectrometer. Resistive heating of the filament evaporated atoms of Lu into the source region of the spectrometer, where they intersected the focused output of the dye laser. As the laser was scanned across the resonant transition, ions were generated, accelerated out of the source, mass resolved, detected with pulse counting electronics, and recorded digitally.

Spectra of individual isotopes were obtained by setting the mass spectrometer to pass only the mass of interest to the detector. Although 174Lu was present to only 30 parts per million in the sample (and with a total amount of 30 picograms), its spectra could be observed without interference from the 97% abundant 175Lu or the presence of 0.3% 174Yb. In this manner, the individual spectra of 173Lu through 176Lu shown in Fig. 2 were obtained.

The data were analyzed by using a least-squares procedure to match the observed spectra to theoretical predictions. The resulting fit yielded hyperfine splitting constants and isotope shifts. The analysis was complicated by the presence of Doppler (velocity) and Lorentz (power) broadening of the observed lines, as well as the effects of differing optical saturation for each hyperfine component. In the case of 174Lu, the nuclear spin was determined by elimination: for values other than unity, no reasonable set of hyperfine splitting constants would produce a spectrum at all resembling the one observed. The complete results for lutetium, as well as a complete description of the experiment, modeling, and data reduction processes, may be found in Refs. 5 and 6.

The experiments described above demonstrate that RIMS is a useful and sensitive technique for high-resolution spectroscopy of rare isotopes. Several fundamental nuclear constants were obtained through interpretation of the spectra. However, it was also observed that in the present case, the presence of Doppler and Lorentz
broadening precluded isotopically-selective RIMS with any analytically useful selectivity. Doppler-broadening may be reduced through the proper selection of the excitation process and the use of counterpropagating lasers to cancel velocity effects. Lorentz broadening may be reduced through the use of low-power excitation schemes in the resonant steps, followed by a high-power laser to ionize from the highest level. We are presently exploring these and other alternative RIMS schemes to alleviate the broadening problems, leading to the eventual goal of ultra-high resolution optical spectroscopy and isotopically-selective RIMS for high dynamic range isotope ratio measurements approaching 1 part in \(10^{10}\).

References