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TITLE HIGH-FIDELITY IN ISOTOPE RATIO MEASUREMENTS FOR RESONANCE
IONIZATION MASS SPECTROMETRY

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High-Fidelity in Isotope Ratio Measurements for Resonance Ionization Mass Spectrometry

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ABSTRACT: Calculations are performed to gauge the effect of the convolution of atomic spectral characteristics with laser sources upon isotope ratio measurements by Resonance Ionization Mass Spectrometry (RIMS). Comparison with experimental data is included.

1. INTRODUCTION

Atomic transitions, such as those used for resonance ionization schemes, are often thought of as single lines at a particular wavelength. Often this is a gross oversimplification of the complex atomic hyperfine structure, which itself may vary from one isotope to another. Isotope shifts also may challenge the assumption of a single wavelength for a particular element. In addition, the resonant laser has a finite frequency spread and distinct mode pattern which must be considered. As the precision of isotope ratio measurement by RIMS increases, the effects of hyperfine structure, isotope shifts, and laser spectral properties upon the accuracy of the measurements become visible.

This paper presents the results of calculations designed to gauge the magnitude of the effect of spectral parameters on isotope ratio measurements by RIMS. A comparison with experimental results for the $^{176}\text{Lu}/^{175}\text{Lu}$ isotope ratio is also made.

2. EXPERIMENTAL

Experiments were performed in a manner similar to Miller and Nogar (1983b). Briefly, a continuous wave dye laser operating at 452 nm was tuned to excite the $^2D_{3/2}^0 \leftarrow ^2D_{3/2}$ lutetium transition; absorption of a second photon caused ionization. The dye laser bandwidth was specified to be 1.3 cm^{-1} . The laser frequency was adjusted by means of a micrometer connected to a three-plate birefringent filter. A lever action was employed to increase the resolution and reproducibility with which the wavelength could be set. Samples consisted of lutetium and uranium evaporated onto rhenium filaments. A 12 inch, 90 degree magnetic mass spectrometer with pulse counting electronics was used to disperse and detect the individual isotopes.

Isotope ratios for $^{176}\text{Lu}/^{175}\text{Lu}$ were taken at intervals of approximately 0.040 cm^{-1} . Multiple ratio sets were obtained to give precisions greater than 1% relative.

2. CALCULATIONS

In essence, our calculations represent a convolution of a laser frequency profile with the hyperfine structure of the resonance transition for the isotope of interest. The calculation essentially scans the laser pattern and hyperfine pattern relative to one another and produces a response function of ionization signal versus wavelength

for each isotope. The ratio of two such response functions for different isotopes (properly normalized) yields the isotope ratio as a function of wavelength. For our purposes, the dye laser was taken to have a Lorentzian profile, while the atomic lineshapes were assumed to have a Doppler-broadened Gaussian profile. Hyperfine and isotope shift data for lutetium were taken from Miller *et al* (1985). No account was made for optical saturation of the resonance transition, although this is known to perturb relative intensities of hyperfine components when narrowband lasers are employed (Engleman *et al* 1985) and certainly occurs when pulsed lasers are employed. Similarly, differences in ionization efficiency and ion collection efficiency throughout the ion source were ignored: a simple one-dimensional geometry was assumed. This latter assumption has been shown to be reasonable (Miller and Nogar 1983a, and Apel *et al* 1987).

3. RESULTS

Figure 1 displays the results of a sample calculation for an atom with no hyperfine structure. Assumed are a transition frequency of $25,000 \text{ cm}^{-1}$, a mass of 100, and a temperature of 1000 K. A laser width of 1 cm^{-1} is used. The response function of two isotopes is shown, with a relative isotope shift of 0.1 cm^{-1} . As expected, these responses appear as slightly shifted Lorentzian-like functions. Also displayed is the ratio of the two functions, i.e., the isotope ratio as a function of wavelength. It is readily apparent that even a small difference in the optical spectroscopy of isotopes can significantly affect isotope ratio measurements.

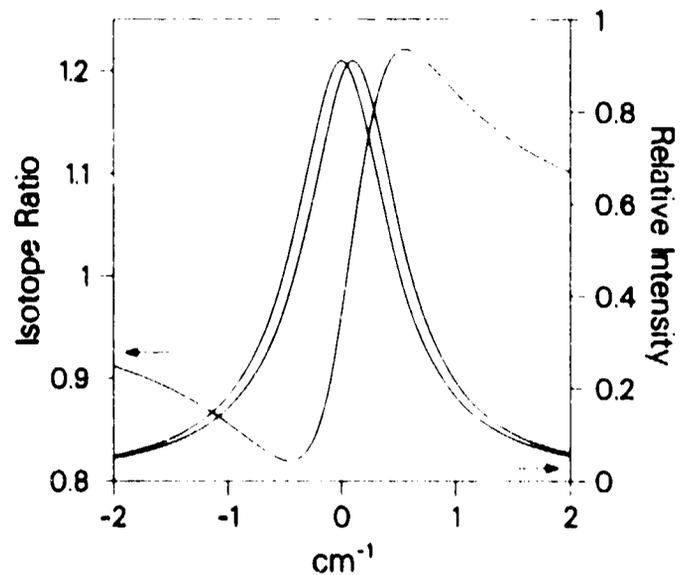


Fig. 1. Sample calculation of two imaginary isotopes' responses to 1 cm^{-1} laser width (Lorentzian-like curves). Also shown is the calculated isotope ratio as a function of wavelength. Frequency is relative to line center.

Calculations of this type reveal that the correct isotope ratio is obtained only at the exact midpoint between the line centers of the two isotopes. This point has the twin disadvantages of lowered response from both isotopes and a large sensitivity to the exact wavelength. A change of $\sim 0.012 \text{ cm}^{-1}$ in frequency will result in a one percent change in the observed isotope ratio. In contrast, for measurement of the ion signal at the peak of the response, a $\sim 0.035 \text{ cm}^{-1}$ frequency change produces only a 1/2 percent signal change. Thus, the isotope ratio measurement is much less sensitive to wavelength shifts when the peak of each isotope is addressed individually by the laser.

As one considers hyperfine structure and isotope shifts, the optical spectrum rapidly becomes complicated. Figure 2 illustrates this for ^{175}Lu . This isotope has nine individual hyperfine components with non-zero intensity. At high resolution (small laser width), several of these components are resolved. As the laser bandwidth is increased, the spectral structure gradually decreases, until a single broad spectral feature remains. This broad line is not identical to the simple case discussed above, however, but includes contributions of the several hyperfine components. Similar effects also occur for the other lutetium isotopes, with their apparent resolution

and line positions depending upon the individual hyperfine splittings and isotope shifts. As with the simple calculation of Figure 1 above, sensitivity of isotope ratios to laser wavelength changes is minimized at the peak of each isotopes' response. Obviously, the optimal choice of laser bandwidth and frequency depends upon the actual magnitude and shape of the particular response function.

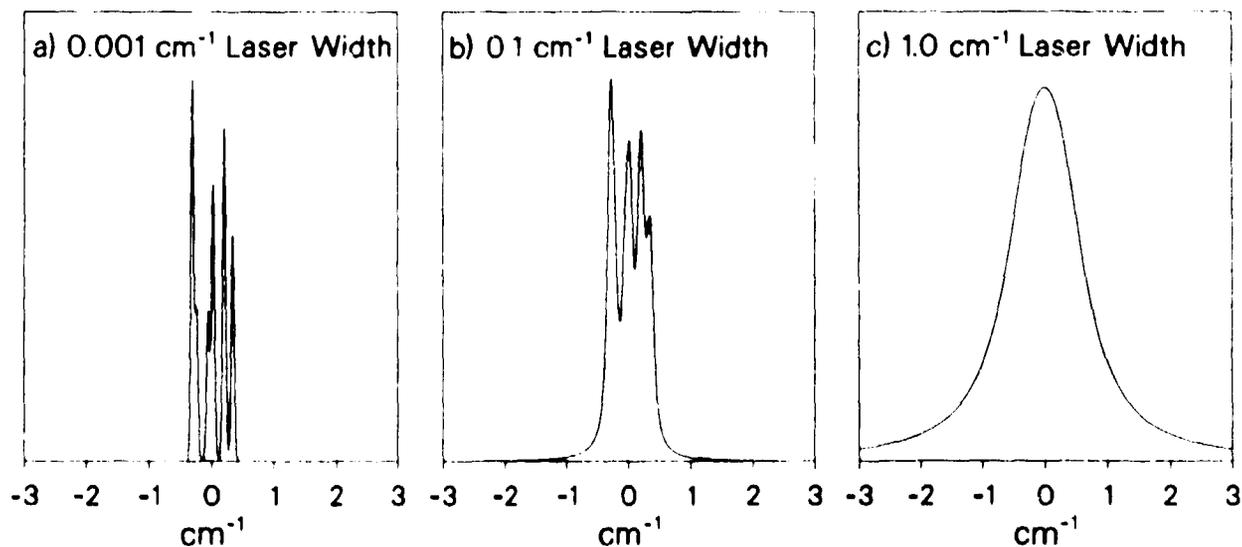


Fig. 2. Calculated hyperfine pattern for the ${}^2D_{3/2}^0 \leftarrow {}^2D_{3/2}$ transition at 452 nm of ${}^{175}\text{Lu}$. A 1500 K sample temperature is assumed; laser widths are as indicated. Frequencies are relative to the ${}^{175}\text{Lu}$ line center.

Figure 3 shows a comparison between the calculated and experimentally observed ${}^{176}\text{Lu}/{}^{175}\text{Lu}$ isotope ratio as a function of laser position relative to the ${}^{175}\text{Lu}$ line origin. Calculations were done assuming the specified laser line-width of 1.3 cm^{-1} ; experimental values were scaled to the natural isotopic abundances (0.0265, De Bievre and Barnes 1985). No other scaling was performed. The agreement between calculation and experiment is quite good, given the simple assumptions of the model. Note that at the ${}^{175}\text{Lu}$ line center artificially low ratios are observed. For this laser line-width, this effect is due to the somewhat greater width of the ${}^{176}\text{Lu}$ hyperfine pattern, which places a larger fraction of the isotopes' transition in the low power wings of the laser bandwidth.

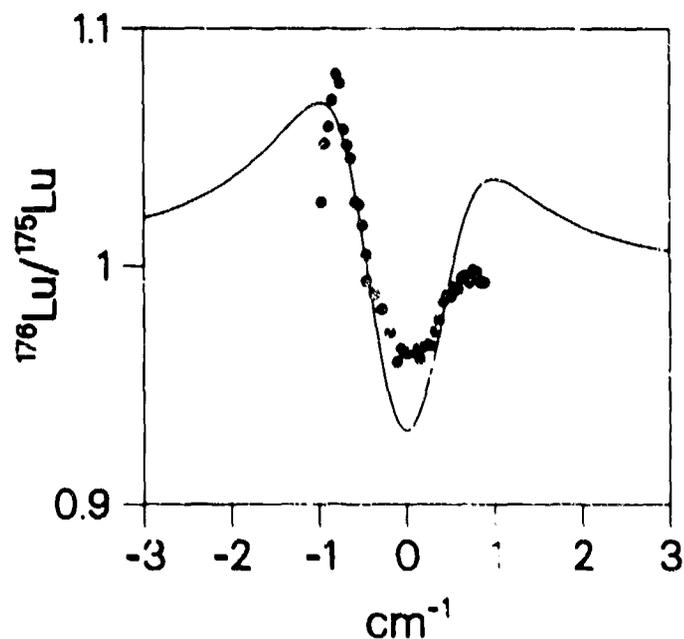


Fig. 3. Comparison of calculation (solid line) and experiment (closed circles) for the ${}^{176}\text{Lu}/{}^{175}\text{Lu}$ isotope ratio.

A further complication arises from the detailed spectral properties of the laser. We have observed a complicated mode structure in broadband dye lasers through Fourier transform spectrometry. This structure depends on factors such as alignment, tuning, time, and temperature, and has been previously observed (Nieuwesteeg *et al* 1986). The effect of such variables on the laser output spectrum, and in turn on the response functions of the isotopes of interest, must be understood.

4. DISCUSSION

From the calculational and experimental results discussed above, it is obvious that detailed spectroscopic information is necessary for a complete understanding of the resonance ionization process. This includes both the laser source and the isotopes under investigation. Fortunately, RIMS itself may be the source of some of this information (Miller *et al* 1985). With such information, appropriate strategies may be derived to insure the highest possible fidelity in isotope ratio measurement with RIMS.

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