# Reference lines in the optogalvanic spectra of uranium and thorium over the wavelength range 694–755 nm

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The optogalvanic spectra of uranium and thorium are convenient sources of lines with which to calibrate wavemeters for high-resolution laser spectroscopy. We used hollow-cathode lamps for both uranium and thorium to observe the spectra, using a single-frequency cw dye laser operating over the wavelength range 694–755 nm. Eight uranium and seven thorium lines were measured with an accuracy of a few parts in $10^8$ with our Fabry–Perot wavemeter. The estimated uncertainty of the measurements is 0.0002 $cm^{-1}$ for both species. The results were compared with several previous measurements of these lines and were found to be in good agreement with values determined by Fourier-transform spectroscopy.

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## 1. INTRODUCTION

There is often a need for reproducible, high-accuracy wave number standards not only for classical spectroscopic techniques but for laser-based techniques as well. As an example, with our Fabry–Perot wavemeter at the National Institute of Standards and Technology we often make measurements by using several spacers of different lengths to determine the correction that must be made for dispersion of the phase change on reflection at the interferometer plates. Each time the spacer is changed, the length of the new spacer must be determined with an accuracy of approximately 0.2 $\mu$m to enable the integer order of interference in the Fabry–Perot interferometer to be determined unambiguously. For this length determination, several reference lines whose wave numbers are known to a few parts in $10^8$ are needed.

For a reference standard to be useful, it must satisfy several criteria. First, its spectrum should be easy to observe. Second, the lines need to be highly reproducible under well-defined experimental conditions. Third, the wave numbers of the lines must be measured with respect to an internationally accepted standard. Finally, the source should provide a broad and well-spaced distribution of reference lines.

Over the years a number of sources of reference lines have been developed. Of these, the best known is the molecular-iodine vapor cell.[1] This is a particularly convenient source because a dense comb of lines covering the green to red regions of the spectrum can be observed at room temperature. Accuracy is limited to $\sim$1 part in $10^7$ because of the asymmetry of the Doppler-broadened lines, which reflects the underlying hyperfine structure. Doppler-free observations, which have been reported for more than 100 lines, permit measurements at 1 part in $10^9$ or better.[2–5] Thousands of additional $I_2$ transitions, which are also observable with Doppler-free techniques, can be calculated to better than 1 part in $10^8$ from molecular constants optimized by use of these precise measurements.[3–5]

The situation in the near infrared is much less satisfactory. A few measurements of Doppler-free $I_2$ lines have been reported,[6] but these lines are inconvenient for use as standards because the $I_2$ vapor cell must be heated to approximately 600 °C to populate the lower states of the transitions. Two-photon transitions in the alkali metals can also provide useful calibrations in the near infrared,[6,7] but these lines require relatively high laser powers and are best observed in cells or heat pipes with thermionic detector systems that are not readily available in most laboratories.

For many applications, optogalvanic spectra of commercially available hollow-cathode lamps provide an attractive alternative source of reference lines.[8] Many lines that cover a broad spectral range can easily be observed with a simple optical setup and detection method. Lines of heavy monoisotopic elements with zero nuclear spin are particularly suitable because of their narrow symmetric profiles. In earlier studies at the National Institute of Standards and Technology a number of lines of U and Th in the range 575–692 (Ref. 9) and near 744 nm (Ref. 10) were measured and shown to be useful as reference lines at the level of a few parts in $10^8$.

Recently we extended the uranium and thorium measurements into the range 694–755 nm. This region is of particular interest because there are no easily accessible transitions in $I_2$ at room temperature here. We report measurements of 15 lines in this range, each accurate to a few parts in $10^8$, and compare our results with previously published values.

## 2. EXPERIMENT

A schematic diagram of the experiment is shown in Fig. 1. Output from the ring dye laser is directed coaxially into the cathode of a hollow-cathode lamp. Neutral-density filters attenuate the laser beam and reduce the incident power to a few milliwatts. The laser beam is modulated with an optical chopper, and the voltage drop across a ballast resistor is monitored with a lock-in amplifier as the laser scans.

The lamps that we use in this research are commercial hollow cathodes with a 2.5-mm-diameter bores containing approximately 650 Pa (5 Torr) of neon carrier gas.[11] A 5-k$\Omega$ resistor is used for ballast, and the optogalvanic signal is coupled to the lock-in amplifier through a 0.1-$\mu$F capacitor, as shown in Fig. 1. The lamps are electrically quiet and have good signal-to-noise ratio performance over the range of wavelengths that we observed. All measurements are made with a nominal 20-mA lamp current, corresponding to voltage drops across the discharge and ballast of 300 V for U and of 250 V for Th.

The laser used in this experiment is a single-frequency cw ring dye laser with Pyridine 2 dye, permitting measurements over the wavelength range 695–755 nm. The laser cavity is actively stabilized to yield an output linewidth of 1–2 MHz. The peak single-frequency power is 300 mW. A portion of the output is directed to a fringe-counting Michelson wavemeter to measure the wave number of the output light with a precision of 0.002 $cm^{-1}$. This wavemeter allows us to find the desired transition and provides the initial wave-number value that we need to calculate the integer order number of the Fabry–Perot wavemeter. We also direct another small portion of the laser output to the Fabry–Perot wavemeter, as shown in Fig. 1.

The main laser beam passes through the optical chopper (700–750 Hz) and the variable neutral-density (ND) filter before entering the cathode (see Fig. 1). The beam is not collimated, focused, or otherwise shaped. When it enters the cathode the beam diameter is approximately 3 mm. We adjust the neutral-density filter to set the laser power incident upon the cathode to 3–15 mW; the weaker lines require higher powers.

The observed linewidths range from 650 to 750 MHz. The primary line broadening mechanisms are Doppler and collision broadening, but power broadening accounts

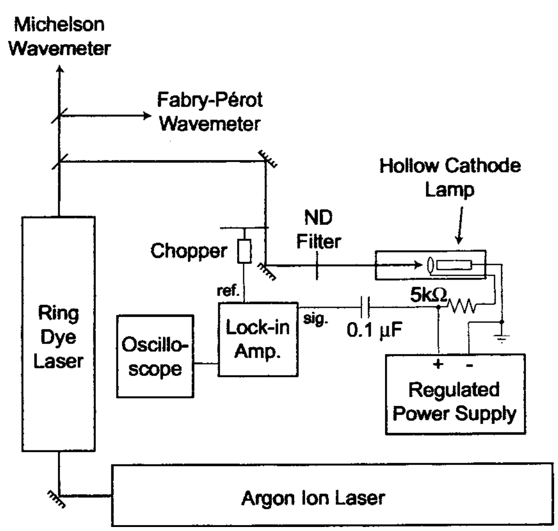


Fig. 1. Schematic diagram of the apparatus.

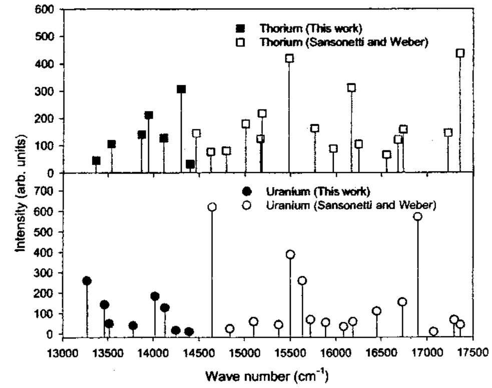


Fig. 2. Distribution of lines of uranium and thorium measured by optogalvanic spectroscopy. Intensities are from Refs. 14 and 15.

for up to 10% of the linewidth for the highest intensities. This saturation broadening is more than compensated for by the enhanced signal-to-noise ratio of the weak lines. As expected for such moderate laser intensities, wave-number shifts in the lines as a function of laser intensity have not been observed.

The tops of the broad peaks of the Doppler- and saturation-broadened lines are relatively flat. We identify the line center by tuning the laser to the average of the tuning voltages measured at equal signal intensities on the steep sides of the line.[9] Use of this method is justified because U and Th exhibit symmetric line shapes, as there is no hyperfine or isotope structure. Earlier measurements in which the method outlined above was compared with direct setting to the estimated line center found the reproducibility increased by a factor of 2 when this method was used.[9]

After setting the laser to a line center, we determine its wave number by using our high-precision Fabry–Perot wavemeter. The Fabry–Perot wavemeter uses the same interferometer as in the earlier optogalvanic work[9] but has been upgraded with a diode detection array and computerized fringe analysis.[2,12,13] The wavemeter uses an $I_2$-stabilized He–Ne laser as a calibration standard. With a 21.82-cm spacer, the ultimate resolution of the wavemeter is a few parts in $10^9$.

We made measurements of the transitions by using Fabry–Perot spacers of lengths 21.82 and 0.70 cm. The correction for phase change on reflection from the interferometer plates was determined from the difference in the measured wave numbers.[13]

We measured eight lines of U and seven lines of Th in the wavelength range 694–755 nm. The lines were selected to provide a broad distribution of lines with good signal-to-noise ratio. Figure 2 shows the distribution of lines for this study as well as for the earlier one of Sansonetti and Weber.[9] There are many additional lines within this region, but this study was not intended to serve as a complete analysis of the U and Th optogalvanic spectra.

## 3. RESULTS

The measured wave numbers of eight U lines are listed in Table 1. Seven to fifteen independent determinations of the transition wave number were made for each line by use of the 21.82-cm spacer. The reported values are the unweighted averages of the individual determinations. The standard deviations for the individual transitions range from 0.000 10 to 0.000 18 $cm^{-1}$.

Table 2 summarizes the results for the seven measured Th lines. For these measurements, data were collected in the same way: 7 to 15 independent determinations with the 21.82-cm spacer were analyzed. The standard deviation for the individual lines ranges from 0.000 11 to 0.000 23 $cm^{-1}$.

The reported uncertainty of 0.0002 $cm^{-1}$ for the entire set of lines is twice the standard error of the mean, corresponding to approximately a 95% confidence interval, of the line determined with the *least* certainty for each of the two elements. Measurements of the individual lines with each spacer indicate that any phase-dispersion correction is negligible at the level of setting precision that is possible for these Doppler-broadened lines. Higher-accuracy measurements of the $2\,^2S_{1/2} \rightarrow 3\,^2S_{1/2}$ two-photon transition in atomic lithium at 13 605 $cm^{-1}$ suggest that the correction is not greater than $5 \times 10^{-5}$ $cm^{-1}$, well below the setting uncertainty for these lines. Uncertainties and systematic corrections attributable to the $I_2$-stabilized He–Ne laser that serves as a calibration standard for the Fabry–Perot wavemeter do not exceed $3 \times 10^{-6}$ $cm^{-1}$. The reported uncertainty represents only random errors under these experimental conditions. The effect of higher lamp current or different carrier gas on the transitions was not investigated in the study reported here.

In Table 1 the measurements for the U lines are compared with previous measurements of the lines made with a Fourier-transform spectrometer (FTS).[14] The FTS measurements were made at Kitt Peak National Observatory with a similar hollow-cathode lamp at a current of 75 mA, and the results are reported in an atlas prepared by Los Alamos National Laboratory.[14] The measured lines exhibit a systematic offset from the atlas value of −0.000 84 (7) $cm^{-1}$, comparable to the −0.001 09 (3) $cm^{-1}$ correction proposed by Sansonetti and Weber[9] for the 575–692-nm range. The offsets, which are within the reported uncertainty of the FTS results, are strikingly constant in value.

The U line at 13 463.3919 $cm^{-1}$ was previously measured in our laboratory by Scholl *et al.*,[10] who recorded the signal at a number of points over the feature and fitted a Voigt profile to extract the center value. The re-

**Table 1. Measured Wave Numbers ($cm^{-1}$) for Uranium Lines**

| Measured Wave Number[a] | Los Alamos Atlas Wave Number[b] | Atlas Correction |
|---|---|---|
| 14 391.9782 | 0.9789 | −0.0007 |
| 14 249.8333 | 0.8341 | −0.0008 |
| 14 130.8129 | 0.8139 | −0.0010 |
| 14 023.5431 | 0.5439 | −0.0008 |
| 13 780.8367 | 0.8375 | −0.0008 |
| 13 515.3017 | 0.3027 | −0.0010 |
| 13 463.3919 | 0.3924 | −0.0005 |
| 13 269.6376 | 0.6387 | −0.0011 |
| Average correction | | −0.00084 |
| Standard deviation | | 0.00021 |
| Standard error of mean | | 0.00007 |

[a] Uncertainty, ±0.0002 $cm^{-1}$.
[b] Ref. 14; uncertainty, ±0.003 $cm^{-1}$.

**Table 2. Measured Wave Numbers ($cm^{-1}$) for Thorium Lines**

| Measured Wave Number[a] | Los Alamos Atlas Wave Number[b] | Atlas Correction |
|---|---|---|
| 14 397.7581 | 0.7579 | 0.0002 |
| 14 302.9127 | 0.9125 | 0.0002 |
| 14 112.0912 | 0.0908 | 0.0004 |
| 13 945.3075 | 0.3070 | 0.0005 |
| 13 869.6397 | 0.6392 | 0.0005 |
| 13 536.3153 | 0.3149 | 0.0004 |
| 13 362.8838 | 0.8836 | 0.0002 |
| Average correction | | 0.00034 |
| Standard deviation | | 0.00015 |
| Standard error of mean | | 0.00006 |

[a] Uncertainty, ±0.0002 $cm^{-1}$.
[b] Ref. 15; uncertainty, ±0.003 $cm^{-1}$.

**Table 3. Comparison of Measured Wave Numbers ($cm^{-1}$) for Thorium Lines and Previous Interferometric Measurements[a]**

| | Littlefield and Wood[c] | | Meggers and Stanley[d] | | Giacchetti *et al.*[e] | |
|---|---|---|---|---|---|---|
| Measured Wave Number[b] | Wave Number | Difference | Wave Number | Difference | Wave Number | Difference |
| 14 397.7581 | 0.7545 | −0.0036 | 0.7566 | −0.0015 | 0.7570 | −0.0011 |
| 14 302.9127 | 0.9088 | −0.0039 | 0.9107 | −0.0020 | 0.9103 | −0.0024 |
| 14 112.0912 | 0.0870 | −0.0042 | | | 0.0870 | −0.0042 |
| 13 945.3075 | 0.3046 | −0.0029 | | | 0.3046 | −0.0029 |
| 13 869.6397 | 0.6363 | −0.0034 | | | 0.6390 | −0.0007 |
| 13 536.3153 | 0.3092 | −0.0061 | | | 0.3138 | −0.0015 |

[a] We are unaware of any earlier interferometric measurements of the 13 362-$cm^{-1}$ line.
[b] Uncertainty, ±0.0002 $cm^{-1}$.
[c] Ref. 16.
[d] Ref. 17.
[e] Ref. 18.

ported result, a value of 13 463.391 62 (4) $cm^{-1}$, deviates by 0.0003 $cm^{-1}$ from our current value. We have no explanation for the difference between the results, but we do note that the present measurement of this line has a smaller correction to the Los Alamos atlas than the other lines that we measured. The earlier value has a correction that is in closer agreement with the rest of the lines.

The comparison of our Th measurements with the Los Alamos atlas[15] of Th emission lines of a similar lamp with a discharge current of 75 mA is shown in Table 2. The spectrum was recorded with the same FTS as the one used for the U atlas. The agreement between the measured values is good, although a small correction to the atlas values of 0.000 34 (6) $cm^{-1}$ shifts the values into better agreement. The differences between the optogalvanic measurements and the FTS emission measurements are similar to those observed in the 575–692-nm range.[9]

In Table 3 our results are compared with previously reported values. The values of Littlefield and Wood[16] were measured with a reflecting echelon and a Th hollow-cathode lamp with Kr carrier gas at a pressure near 300 Pa (2 Torr). Meggers and Stanley[17] observed the spectrum by using Fabry–Perot interferometry with an electrodeless discharge lamp containing $ThI_4$ and helium. The values of Giacchetti *et al.*[18] were proposed and widely used as secondary standards for calibrating spectra from high-resolution grating spectrographs. They were calculated from optimized energy levels based on all interferometric measurements of Th. The deviations between our results and these three sources are larger and have much greater scatter than our deviations from the Los Alamos atlas.

## 4. DISCUSSION

Optogalvanic spectroscopy in a commercial hollow-cathode discharge lamp is a simple technique that requires a minimum of equipment and easy setup. Single-shot precision of better than 0.0005 $cm^{-1}$ is possible with U and Th. We have measured eight U and seven Th lines in the wavelength range 694–755 nm with an uncertainty of 0.0002 $cm^{-1}$. These lines can be used for wave-number calibration at a level of a few parts in $10^8$. Hollow-cathode lamps for spectrophotometry are available from several manufacturers. All are similar in construction and gas fill. Our results should be applicable to any commercial U–Ne or Th–Ne lamp of this type.

The spectra of U and Th may be useful as sources of reference lines at higher precision if they are observed by Doppler-free intermodulated optogalvanic spectroscopy in see-through hollow-cathode lamps.[19,20] Laser setting accuracy on narrow Doppler-free lines would probably be an order of magnitude better than in the Doppler-limited case. To evaluate this possibility it would be necessary to make extensive tests of the wave-number reproducibility from lamp to lamp and as a function of lamp age. Shifts owing to variation in carrier gas pressure and changes in discharge characteristics as the cathode hole erodes with age may set a fundamental limit on the reproducibility of standards of this type.

Comparisons of our current results with the wave numbers from the Los Alamos U and Th atlases reveal the same constant deviation that was found by Sansonetti and Weber at shorter wavelengths.[9] Additive corrections of $-0.0010$ $cm^{-1}$ for U and $+0.0003$ $cm^{-1}$ for Th bring the atlas results into agreement with the laser measurements throughout the 575–755-nm region. This agreement gives added confidence that other lines from the atlases, both within and outside the region of laser observations, can be corrected for these constant offsets and used for calibration in laser spectroscopy.

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