

Reference lines in the optogalvanic spectra of uranium and thorium in the wavelength range 422 nm to 462 nm

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The spectra of uranium and thorium are convenient sources of reference lines for wavelength calibration at the level of a few parts in 10^8 . We observed these spectra by laser optogalvanic spectroscopy in commercial hollow-cathode lamps using a single-frequency cw dye laser operating over the wavelength range 422 nm to 462 nm. Ten uranium and eight thorium lines were measured with an estimated uncertainty of 0.0003 cm^{-1} by using our Fabry-Pérot wavemeter. The results are compared to previous measurements of these lines and are found to be in good agreement with, and an order of magnitude more accurate than, values determined by Fourier-transform spectroscopy.

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1. INTRODUCTION

Atomic spectral lines in hollow-cathode discharges can be readily observed with tunable lasers by the optogalvanic effect. This effect manifests itself as a change in the discharge current when the discharge is illuminated with light that is resonantly absorbed in the plasma. Spectral lines observed in this way provide a source of reference wavelengths that are particularly convenient for laser spectroscopy [1]. In previous work we measured lines in the optogalvanic spectra of U and Th in the ranges 575 nm to 692 nm [2] and 694 nm to 755 nm [3] and described a simple procedure by which a single-frequency laser can be set on such lines with an accuracy of a few parts in 10^8 .

Some years ago we worked with the laser dye stilbene 3 in the deep blue spectral region. In this region there were no readily observable spectral lines that had been measured with sufficient accuracy to be useful for checking the calibration of high resolution interferometers and wavemeters. Molecular ^{130}Te has a dense absorption spectrum throughout this region. Its spectrum had been recorded and measured using Fourier-transform spectroscopy [4]; however, Doppler-free laser measurements [5] in the region 471 nm to 502 nm had shown that the wave numbers reported in the Te atlas are in error by as much as 0.003 cm^{-1} , more than one part in 10^7 .

In order to address our need for reference lines in the stilbene 3 dye region, we measured selected optogalvanic

lines of U and Th spanning the 422 nm to 462 nm wavelength range using commercially available low current hollow-cathode lamps and our Fabry-Pérot wavemeter. The results were adequate for our use but were not published because we had not accurately characterized the systematic correction stemming from the phase dispersion on reflection from our interferometer plates.

Since then, new interest in Th has arisen because its emission spectrum can provide excellent reference lines for the calibration of astronomical spectrographs. The spectrum is dense, extends over a wide spectral region, and has highly reproducible wavelengths. The spectrum of uranium has similar characteristics and is also under investigation as a source of calibration lines [6]. Improved reference spectra are particularly important for astronomical observations that investigate temporal variation of fundamental constants or attempt to identify extrasolar planets by the radial velocity method [7–9].

The most precise and internally consistent wavelength measurements for complex spectra such as U and Th are obtained by Fourier transform spectroscopy, but accurately known internal reference lines are needed to obtain absolute calibration of the spectra. Our previous optogalvanic measurements of Th in the red and infrared regions have proven to be useful for this application [9]. Lines with similar accuracy are needed at shorter wavelengths.

With this added motivation we have revisited our Th and U optogalvanic data and resolved the phase dispersion problem. In this paper we report measurements for eight Th and ten U lines, each accurate to a few parts in 10^8 , and compare our results to previously published values.

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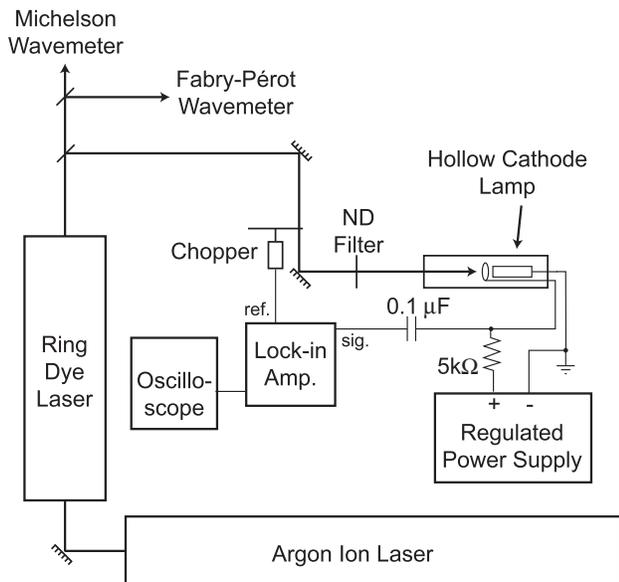


Fig. 1. Schematic diagram of apparatus.

2. EXPERIMENT

Our experimental apparatus is shown schematically in Fig. 1. The experiment will be described only briefly in this report, as full details are given in [3].

The lamps used are hollow cathode discharges with a cathode inner diameter of approximately 3 mm that contain Ne carrier gas at a pressure of approximately 650 Pa (5 Torr) [10]. All measurements were made with a 20 mA lamp current, corresponding to a voltage drop across the discharge and 5 k Ω ballast resistor of approximately 300 V for U and 250 V for Th.

Light in the wavelength range 422 nm to 462 nm was provided by a single-frequency cw ring dye laser with a nominal linewidth of 1.5 MHz. A neutral density filter was used to adjust the laser power incident on the cathode to between 5 mW and 15 mW, the weaker lines requiring higher powers. The photogalvanic signal was detected by chopping the laser beam and monitoring the voltage drop across the 5-k Ω ballast resistor using phase sensitive detection.

The observed linewidths are due primarily to Doppler and collisional broadening which are intrinsic to the hollow-cathode lamp. At the laser power levels used, however, some of the lines are significantly saturated. This contributes slightly to the line width. For purposes of measurement, the additional width is more than compensated by the enhanced signal-to-noise ratio obtained with higher laser powers.

Observations were made by tuning the laser manually to the center of the line profile using the procedure described in [2] and measuring the laser wave number using our Fabry-Pérot wavemeter with a 218 mm spacer [5, 11]. An I₂-stabilized helium-neon laser at 633 nm served as the calibration standard for the wavemeter.

The Fabry-Pérot wavemeter employs an evacuated plane-parallel étalon for which the interference condition

$$[P + \epsilon + \delta(\sigma)]/\sigma = 2t \quad (1)$$

is satisfied. Here P and ϵ are the integer and fractional parts of the order of interference at the center of the spatially resolved fringe pattern, σ is the wave number, and t is the étalon spacing. The quantity $\delta(\sigma)$ is a correction to the order number that accounts for the wavelength dependent phase shift of the light on reflection from the coatings of the Fabry-Pérot plates. By convention we take $\delta(\sigma_r)=0$ at the wave number of the reference laser and understand t to represent the effective spacer length at that wave number.

Our wavemeter produces results under the assumption that $\delta(\sigma)=0$ for all σ . The actual value of $\delta(\sigma)$ for the stilbene 3 region was obtained by observing 38 Doppler-free molecular Te lines for which accurate measurements have been reported by Scholl *et al.* [12]. The phase correction is determined as

$$\delta(\sigma) = 2t(\sigma_u - \sigma_s) \quad (2)$$

where σ_u is the uncorrected result from our wavemeter and σ_s is the published wave number from [12].

This method produces a smoothly varying correction function that is well described by a second degree polynomial (Fig. 2) and that extrapolates smoothly to the phase correction previously determined for longer wavelength regions.

The phase correction is applied to the wavemeter results using the following relation.

$$\sigma = \sigma_u + \delta(\sigma)/2t \quad (3)$$

For our Te observations, the resulting wave numbers agree with the results of [12] with an average deviation of

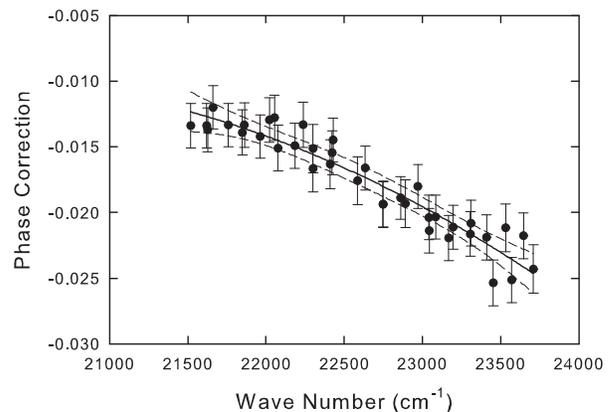


Fig. 2. Phase correction, in dimensionless units of fractional order number, determined using Doppler-free lines of molecular Te. The dashed lines represent the 99 % confidence limit of the polynomial fit.

Table 1. Measured wave numbers (cm^{-1}) for uranium lines.

This Work ^a	Los Alamos [13] U Atlas ^b	Correction to Atlas
23 676.7241	.7259	-0.0018
23 543.5050	.5064	-0.0014
23 178.4523	.4536	-0.0013
22 951.7588	.7604	-0.0016
22 918.5524	.5541	-0.0017
22 754.0580	.0599	-0.0019
22 368.4653	.4671	-0.0018
21 843.9674	.9690	-0.0016
21 637.9637	.9659	-0.0022
21 636.9539	.9558	-0.0019

^aUncertainty: $\pm 0.0003 \text{ cm}^{-1}$.^bUncertainty: $\pm 0.003 \text{ cm}^{-1}$.

$0.000\,000 \text{ cm}^{-1}$ and standard deviation of $0.000\,026 \text{ cm}^{-1}$ (0.78 MHz), well within the $0.000\,037 \text{ cm}^{-1}$ uncertainty reported in [12].

Ten lines of U and eight lines of Th were measured in the wavelength range 422 nm to 462 nm. The lines were selected to provide a broad distribution of lines with good signal-to-noise ratio. Our two longest wavelength U lines are separated by only 1 cm^{-1} . We had originally chosen the line at $21\,637 \text{ cm}^{-1}$ for measurement based on its strength in the emission spectrum, but it proved to be weak in the optogalvanic spectrum. After some measurements had already been made, we discovered that the neighboring line at $21\,636 \text{ cm}^{-1}$ provided a much stronger optogalvanic signal and thus added it to our list of lines. There are many additional lines that could be similarly measured within this region, but this work was not intended to provide a complete description of the U and Th optogalvanic spectra.

Each line was observed in four or five separate measuring sessions. In each of these sessions the laser wave number was measured for ten independent settings on the line, and the ten results were averaged to obtain a single result for the session. The standard error of the mean for these session averages ranged from $0.000\,02 \text{ cm}^{-1}$ to $0.000\,13 \text{ cm}^{-1}$.

3. RESULTS

Our measured wave numbers for U and Th are reported in Tables 1 and 2, respectively. The values reported are the unweighted means of the four or five session averages for each line. The results in Tables 1 and 2 have been corrected to compensate for the phase shift upon reflection from the Fabry-Pérot interferometer plates as described above.

We report a uniform uncertainty of 0.0003 cm^{-1} , corresponding to a 95 % confidence interval, for all of the lines. This value is dominated by random errors and represents twice the standard error of the mean for the line determined with the *least* certainty. The uncertainty as-

sociated with the phase shift correction is more than an order of magnitude smaller. Uncertainties and systematic corrections attributable to the I_2 -stabilized He-Ne laser do not exceed $5 \times 10^{-6} \text{ cm}^{-1}$. The reported uncertainty applies to the experimental conditions of this work. The possibility that the lines may shift in a lamp operated at higher current or with a different carrier gas was not investigated.

In Table 1 our U measurements are compared to previous measurements of the lines made by Palmer, Keller, and Engleman with a Fourier-transform spectrometer (FTS) [13]. These FTS observations were made at the Kitt Peak National Observatory using 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. Our wave numbers are systematically lower than the atlas values by $0.0017 (2) \text{ cm}^{-1}$. This difference is larger than the corrections to the atlas proposed for longer wavelength regions in our earlier work [2, 3]. We note, however, that the Los Alamos atlas is based on spectra recorded for three overlapping wavelength regions. Our earlier measurements were all compared to lines in the longest wavelength region while this work spans the two shorter wavelength regions. The wave numbers that we have measured in all regions are well within the reported uncertainty of the FTS results.

The comparison of our Th measurements with the Los Alamos thorium atlas of Palmer and Engleman [14] is shown in Table 2. The atlas was prepared by observing the emission lines from a similar Th lamp with a discharge current of 75 mA using the same FTS as the one used for the U atlas. The agreement between our measured values and the atlas is well within the stated uncertainty of the atlas. We observe that applying a linear correction to the atlas values brings them into almost perfect agreement with our determinations. The correction $\delta\sigma$ (in cm^{-1}) is given by

$$\delta\sigma = 5.24 \times 10^{-7} \times \sigma - 0.0115 \quad (4)$$

where σ is the wave number (also in cm^{-1}). As in the case of uranium, the Los Alamos FTS results in this region are

Table 2. Measured wave numbers (cm^{-1}) for thorium lines.

This Work ^a	Los Alamos [14] Th Atlas ^b	Correction to Atlas
23 603.5206	.5195	0.0011
23 481.3738	.3730	0.0008
23 210.5392	.5388	0.0004
22 855.2992	.2986	0.0006
22 675.1146	.1142	0.0004
22 425.2819	.2816	0.0003
22 248.9495	.9492	0.0003
21 871.0544	.0544	0.0000

^aUncertainty: $\pm 0.0003 \text{ cm}^{-1}$.^bUncertainty: $\pm 0.002 \text{ cm}^{-1}$.

Table 3. Comparison of measured wave numbers (cm^{-1}) for thorium lines and previous interferometric measurements.

This Work ^a	Littlefield and Wood [15] Wave number ^b	Difference	Goorvitch <i>et al.</i> [16] Wave number ^c	Difference	Meggers and Stanley [17] Wave number ^d	Difference	Giacchetti <i>et al.</i> [18] Wave number ^c	Difference
23 603.5206	.5213	0.0007	.5218	0.0012	.5185	-0.0021	.5224	0.0018
23 481.3738	.3744	0.0006	.3766	0.0028	.3727	-0.0011	.3760	0.0022
23 210.5392	.5367	-0.0025	.5410	0.0018	.5378	-0.0014	.5410	0.0018
22 855.2992	.2993	0.0001	.3003	0.0011	.2956	-0.0036	.2988	-0.0004
22 675.1146	.1174	0.0028			.1143	-0.0003	.1128	-0.0018
22 425.2819	.2827	0.0008	.2837	0.0018	.2801	-0.0018	.2796	-0.0023
22 248.9495	.9486	-0.0009	.9496	0.0001	.9491	-0.0004		
21 871.0544	.0523	-0.0021	.0562	0.0018	.0566	0.0022	.0500	-0.0044

^aUncertainty: $\pm 0.0003 \text{ cm}^{-1}$.

^bUncertainty: $\pm 0.0023 \text{ cm}^{-1}$ estimated from recurring interlevel differences.

^cThere is no clear statement of uncertainty in [16] or [18].

^dUncertainty: $\pm 0.0011 \text{ cm}^{-1}$ estimated from recurring interlevel differences.

derived from a different spectrum than those compared to our earlier laser measurements [2, 3].

In Table 3 our Th results are compared with interferometric measurements of these lines in emission sources. The measurements of Littlefield and Wood [15] were made with a reflecting echelon using a Th hollow-cathode lamp with Kr carrier gas at a pressure of approximately 300 Pa (2 Torr). Hollow-cathode lamps were also used by Goorvitch *et al.* [16] in Fabry-Pérot measurements of the Th spectrum. Meggers and Stanley [17] observed the spectrum using Fabry-Pérot interferometry with an electrodeless discharge lamp containing ThI₄ and He carrier gas, whereas Giacchetti *et al.* [18] used a ThI₄ electrodeless lamp with no carrier gas. Curiously, we note that both sets of electrodeless lamp measurements [17, 18] exhibit deviations from our measurements that vary approximately linearly with wave number but with slopes of opposite sign. The random deviations of all of these measurements from our current results are much larger than those of the Los Alamos atlas.

Giacchetti, Stanley, and Zalubas [19] proposed secondary-standard wavelengths in the thorium spectrum that were widely used for calibrating spectra from high resolution grating spectrographs. Most of their wavelengths were calculated from optimized energy levels based on all interferometric measurements of Th (those listed above and additional measurements in other portions of the spectrum). The difference between the recommended values of [19] and our measurements (Fig. 3) has a linear dependence on wave number similar to that previously noted over a much wider range in the Los Alamos atlas [14].

4. DISCUSSION

Optogalvanic spectroscopy in a commercial hollow-cathode discharge lamp is a simple and convenient technique requiring a minimum of apparatus. Single determination precision of better than 0.0005 cm^{-1} is possible

with lines of U and Th. We have measured ten U and eight Th lines in the wavelength range 422 nm to 462 nm with an uncertainty of 0.0003 cm^{-1} . These lines can be used for wave number calibration at a level of a few parts in 10^8 . Hollow-cathode lamps similar to those used in this work are produced for spectrophotometry by several manufacturers. Our results should be applicable to any U/Ne or Th/Ne lamp of this type.

Our present results are in excellent agreement with the wave numbers from the Los Alamos U and Th atlases fully confirming the 0.003 cm^{-1} and 0.002 cm^{-1} uncertainties reported for the atlases. As we found previously in longer wavelength regions, the deviations between our results and the atlases are highly systematic [2, 3]. An additive correction of -0.0017 cm^{-1} for U and a linear correction given by Eq. 4 for Th bring the atlas results into agreement with our laser measurements to about 0.0005 cm^{-1} throughout the 422 nm to 462 nm region. Based on our experience in this

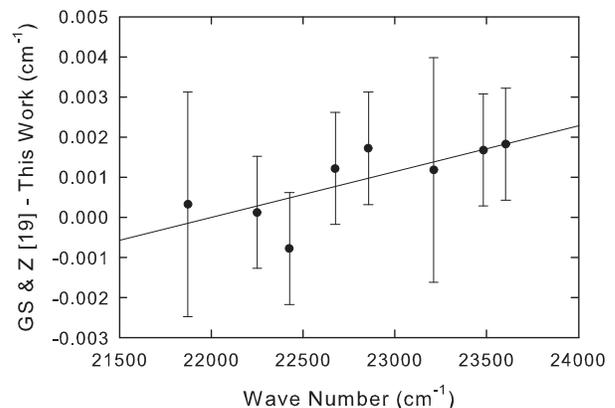


Fig. 3. Difference between the Th recommended secondary standards of [19] and our current measurements.

region, as well as our previous measurements, we believe that other lines from the atlases can be corrected and used for calibration in laser and classical spectroscopy provided the corrections are not used outside the regions of the FTS spectra for which they were determined.

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