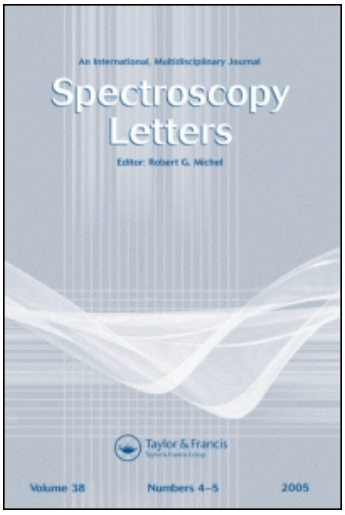

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Diode Laser-Excited Optogalvanic and Absorption Measurements of Uranium in a Hollow Cathode Discharge

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ABSTRACT

Optogalvanic spectra for fifty two transition lines of uranium in the wavelength ranges of 662–683, 774–792, and 834–862 nm were measured by using external-cavity diode lasers. Among these transitions, 860.795 nm and 682.691 nm were chosen for a detailed investigation of the detection limit for uranium by wavelength modulation spectroscopy due to its stronger signal magnitudes. A detection limit of about 2×10^{-5} absorbance achieved at 860.795 nm is more sensitive than that obtained at 682.691 nm, but the absorption spectrum at 682.691 nm is preferable to determine the isotope ratio due to the narrower hyperfine structure as

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well as the larger isotope shift. A preliminary result for an isotope ratio determination in a depleted sample is presented.

Key Words: External-cavity diode laser; Uranium; Wavelength modulation spectroscopy; Optogalvanic spectroscopy; Hollow cathode discharge; Isotope shifts.

INTRODUCTION

The demand for highly sensitive laser spectroscopy has considerably increased during recent years. Wavelength modulation spectroscopy and optogalvanic (OG) spectroscopy are known as sensitive trace detection technologies for atoms and molecules.[1–4] On the other hand, it is of interest to make the spectroscopic detection system as small as possible to use for the trace detection at contaminated sites. In order to develop compact and highly sensitive analytical systems, a spectroscopic detection system consisting of a hollow cathode glow discharge atomizer and tunable diode lasers can be a reasonable choice. Considerable research in the field of analytical atomic spectroscopy with diode lasers has been reported. Niemax et al. have demonstrated the feasibility of diode laser-based absorption spectroscopic systems for trace analysis.[5–7] Shaw et al. successfully demonstrated isotope detection of uranium atoms by using OG spectroscopy with a diode laser in a hollow cathode discharge at 776.19 and 778.42 nm.[3,4] Diode lasers offer an important advantage for the measurement of the background signal, when small samples are atomized, because of its rapid wavelength tunability.[7]

Recently, we reported on the identification of sixteen OG spectra for uranium in the near-IR wavelength region by using an external-cavity diode laser with a center wavelength of 785 nm.[8] In the present paper, thirty six transitions of uranium in the wavelength region of 662–683 and 834–862 nm were investigated as additional aspects of the previous work. As a consequence, OG signal magnitudes for fifty two transition lines have been tabulated.

This study is focused on the atomic spectra of the transitions at 682.691 nm and 860.795 nm due not only to stronger signal magnitudes but also to the relatively large isotope shifts. Both wavelength modulation and OG spectroscopy were performed. As a result, we present the optimum conditions such as modulation frequency, modulation amplitude, and laser power for acquisition of a strong signal magnitude in wavelength modulation spectroscopy. The minimum detectable absorbances of about

2×10^{-5} and 4×10^{-5} were achieved by the $2f$ detection scheme with a modulation frequency of a few hundred Hz at 860.795 nm and 682.691 nm. These absorbances are sensitive enough to detect an atomic concentration of $4 \times 10^{7}/\text{cm}^3$.

In addition, we report preliminary isotopic abundance ratio measurement. Highly-resolved atomic spectrum of a minor isotope could be recorded at 682.691 nm due to its narrower hyperfine splitting as well as its larger isotope shift. The spectra recorded by wavelength modulation method are compared with those obtained by the OG detection method.

EXPERIMENTAL

The experimental setup is shown in Figure 1. The equipment used, including external-cavity diode lasers (New Focus Inc., model 6200 for 785 nm and 850 nm, Newport Inc., model 2010 for 680 nm), hollow cathode discharge cell, and the OG detection circuit have already been described in a previous work.[8] Here, only the wavelength modulation detection technique is briefly explained. The sinusoidal waveform at the frequency of a few hundred Hz is added to the saw-tooth waveform at the

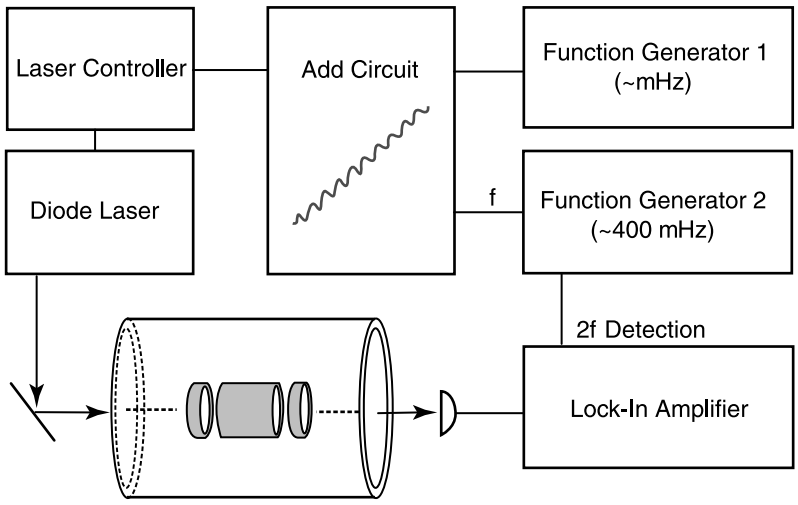

Figure 1. Experimental arrangement for wavelength modulation spectroscopy, by use of a hollow cathode discharge cell and an external-cavity diode laser.

Table 1. Spectroscopic parameters of the transitions studied in this work. Wavelengths, oscillator strength (gf), optogalvanic (OG) signal, isotope shift (IS) values are tabulated.

Wavelength (nm)	gf[9]	Relative OG signal (a.u.)[a]	IS (GHz)[10]	Wavelength (nm)	gf[9]	Relative OG signal (a.u.)[a]	IS (GHz)[10]
662.52957	0.0315	0.022	− 3.6	790.42933	0.0638	0.023	16.5
664.77929	0.0108	0.013	4.5	790.79822	0.0206	0.017	− 7.5
665.68188	0.0065	0.030	5.7	791.88150	0.0280	0.046	− 9.2
668.33848	0.0333	0.046	3.9	834.67576	0.0545	0.046	2.4
672.79721	0.0251	0.022	5.0	835.70605	0.0135	0.025	11.6
673.68046	0.0068	0.050	− 11.4	838.18709	0.1308	0.071	− 7.8
674.13641	0.1012	0.055	13.4	838.72018	0.0205	0.035	–
676.86418	0.0414	0.014	5.7	838.75677	0.0234	0.013	1.4
678.25998	0.0230	0.014	–	838.91689	0.0504	0.047	2.7
678.28570	0.0172	0.016	− 11.4	839.92437	0.0191	0.024	0.3
679.03029	0.1295	0.038	− 5.9	842.67471	0.0065	0.014	9.5
682.07693	0.0520	0.065	− 8.3	844.12048	0.1426	0.063	6.8

682.69133*	0.6810	0.903	− 11.4	844.53826	0.1322	0.242	5.4
774.81903	0.6831	0.013	5.6	845.00312	0.1000	0.187	8.7
775.98806	0.0473	0.024	− 6.3	849.60939	0.1449	0.039	3.5
776.18507	0.0608	0.035	− 12.6	850.45510	0.2753	0.025	14.1
778.41587	0.0903	0.504	3	854.01846	0.0937	0.094	6.5
781.63278	0.2847	0.014	2	854.23313	0.1050	0.019	1.1
783.57385	0.0193	0.020	8.4	855.73309	0.1866	0.028	1.1
784.47200	0.5382	0.009	2.7	856.69409	0.0735	0.013	2.4
786.87396	0.0313	0.015	− 11	856.77189	0.0264	0.043	− 4.7
786.87878	0.0281	0.059	5.4	857.05168	0.2634	0.084	14.7
787.53929	0.2608	0.032	− 7.5	857.46051	0.0572	0.042	20.3
788.19441	0.4770	0.260	9.5	860.79503*	0.1240	1	5.1
789.60320	0.1472	0.008	13.7	861.27765	0.0196	0.024	7.7
790.04339	0.0220	0.037	0.6	861.84599	0.0168	0.019	− 5.6

[a]The signal magnitudes measured in this study. Two stronger transition lines adopted in wavelength modulation spectroscopy are denoted by asterisk.

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frequency of a few mHz, as shown in Figure 1. For the wavelength modulation, the resulting waveform is applied to the laser controller to dither the piezoelectric transducer attached to the tuning mirror of the external-cavity.

The detected signal is processed by a lock-in amplifier (EG&G Inc., Model 5302). Typical time constant of 100 ms is applied for the measurement. Second harmonic detection at a frequency of $2f$, where f is the modulation frequency, is adopted. In the $2f$ operation scheme there is no signal contribution from the periodic, linear change of the laser power.

RESULTS AND DISCUSSION

Identification of Transition Lines and Signal Magnitudes

The magnitudes of the OG signals are listed in Table 1 for the selected set of fifty two transitions. All the experimental conditions were controlled precisely in order to compare the relative signal magnitudes of the observed spectra. The discharge current was maintained at a constant current of 30 mA. A laser power of 0.6 mW, with a laser beam diameter of 1 mm, was also maintained constantly while the wavelength of the laser was changed. More transition lines could be measured in these wavelength regions, but all of the unlisted lines showed very weak signal magnitude and no additional effort was made to detect them. Table 1 also lists oscillator strengths (usually reported as gf values, where g is the statistical weight of the lower state and f is the oscillator strength of the transition) and isotope shifts. These values have been taken from the work of Palmer et al.[9,10]

Determination of Detection Limit

The experiments to investigate the detection limit of the technique has focused on two transitions, 682.691 nm and 860.795 nm, which showed the stronger OG signal magnitudes denoted by asterisk in Table 1. Figure 2 shows the magnitudes of $2f$ signals as a function of the modulation frequency. A typical $2f$ spectrum is shown as the inset of Figure 2. The magnitude of the $2f$ signal is defined as the difference between the maxima at the line center and the minima near the line wing as shown in the figure. A sine-function generator, which modulated the wavelength through the external input of the laser controller, was set to a peak-to-peak amplitude of 160 mV for 860.795 nm and 270 mV for 682.691 nm, respectively, in this

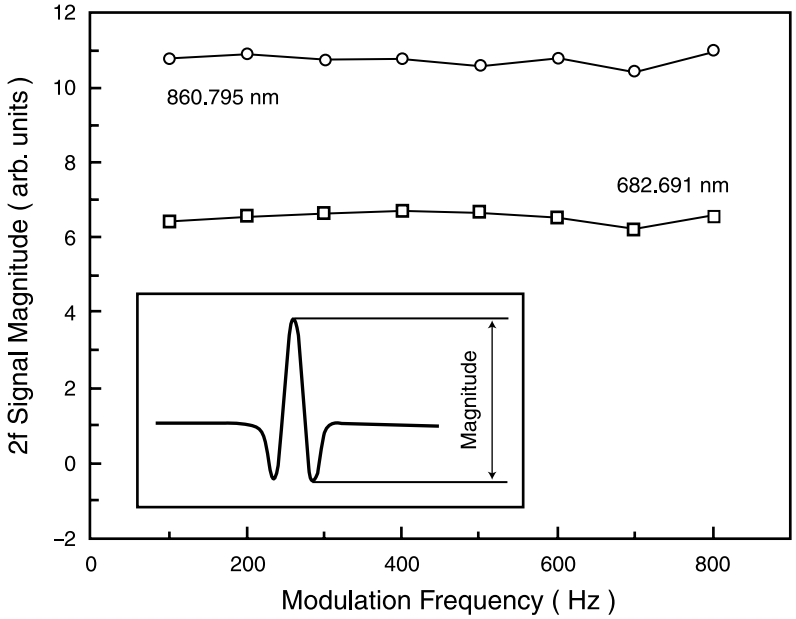

Figure 2. Dependence of the 2*f* signal magnitudes as a function of the wavelength modulation frequency. The peak-to-peak modulation amplitudes were 160 mV for 860.795 nm and 270 mV for 682.691 nm. The inset shows a typical 2*f* spectrum. The signal magnitude is defined as the distance between the maxima and the minima.

measurement. The 2*f* signal magnitudes are almost constant in the modulation frequency range of a few hundred Hz. We could not use higher modulation frequencies ($\sim$kHz) due to a limit in the bandwidth of the frequency input (about 2 kHz with 3 dB drop) for the mechanically dithering the mirror.[11,12]

Figure 3 shows the dependence of 2*f* signal magnitude on the wavelength modulation amplitude (peak-to-peak). The data were taken with a modulation frequency of 400 Hz. The biggest signal magnitudes were observed at the amplitudes of 130 mV for 860.795 nm and 270 mV for 682.691 nm, respectively. These amplitudes are related to the line-width of the absorption spectrum, as this reflects the horizontal distance of the maxima at the line center from the minima near the line wing in the 2*f* spectrum. The input gains of the modulation amplitude are 22 for 860.795 nm (New Focus Inc., model 6200 controller) and 10 for 682.691 nm

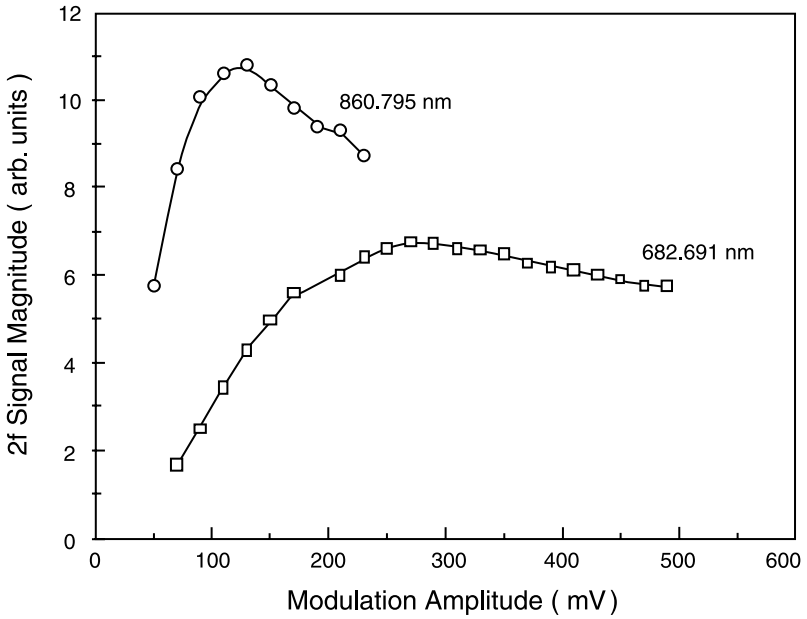

Figure 3. Dependence of the 2*f* signal magnitudes as a function of the wavelength modulation amplitude (peak-to-peak) at the modulation frequency of 400 Hz. Laser power was 100 μW. Discharge current was 10 mA.

(Newport Inc., model 2010 controller). Thus, about two times the difference in modulation amplitudes means these two absorption spectra have similar line-widths.

The dependence of the 2*f* signal magnitude at 860.795 nm on the laser power is shown in Figure 4. The data were taken with a modulation frequency of 400 Hz and a modulation amplitude of 130 mV, respectively. The discharge current of 10 mA was maintained. The signal increases linearly with laser power up to about 80 μW. When the laser power increases further, a saturation behavior in the signals is observed. The saturation in the 2*f* signal seems to be related to the saturation power. We measured the saturation power of about 70 μW at the a discharge current of 10 mA by using a classical absorption measurement. Similar behavior was also found at 682.691 nm.

The calibration curve for various atomic densities of uranium measured by 2*f* detection is shown in Figure 5. Each datum was taken with the optimum modulation frequency and modulation amplitude, as shown in

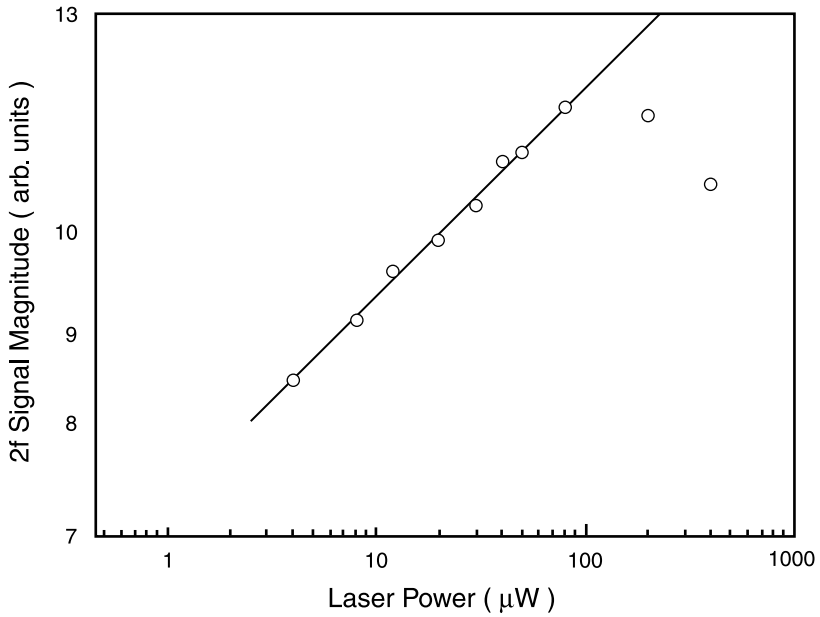

Figure 4. Dependence of the 2*f* signal magnitudes as a function of the laser power at the modulation frequency of 400 Hz and modulation amplitude of 130 mV. Discharge current was 10 mA.

Figures 2 and 3. The laser power of 30 μW was maintained. The atomic density was varied by changing the discharge current. Both the direct absorption spectrum and the 2*f* spectrum were recorded for comparison purposes. The atomic densities were estimated from the direct absorption spectrum by the following equations:[13]

$$[N] = \frac{8\pi}{\lambda^2} \cdot \frac{g_1}{g_2 A} \cdot \int a_v dv \tag{1}$$

$$a_v = -\frac{1}{L} \cdot \ln\left(\frac{I}{I_0}\right) \tag{2}$$

where, α_v is an absorption coefficient, I is the intensity of the transmitted laser beam, and I_o is the intensity of the incident beam, and L is the path length. In this measurement the path length was 2 cm, which corresponds to the length of the cylindrical cathode. The solid lines in Figure 5 show the

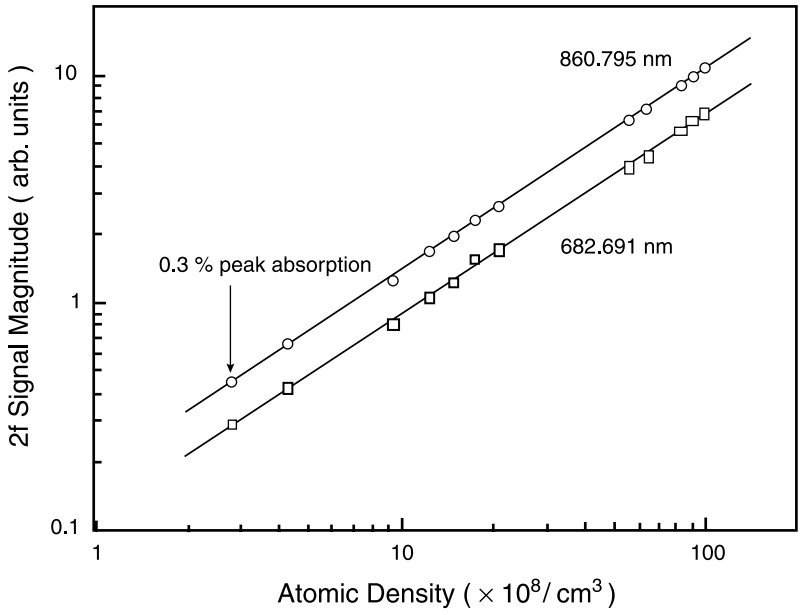

Figure 5. Dependence of the 2*f* signal magnitudes as a function of the atomic density.

linear regression for the data, with a correlation coefficient of 0.999. Deviations of the data points from the straight lines are not found. All data points in Figure 5 were obtained in the discharge current range from 2 mA to 10 mA. The current of 2 mA is the lowest current to maintain the discharge in the adopted cell. If the discharge is decreased below 2 mA, no discharge is observed.

The datum designated by an arrow in Figure 5 was measured at the discharge current of 2 mA. The peak absorption of 0.3% was observed in the direct absorption spectrum, as shown in Figure 6(a). We compare the 2*f* spectrum measured at the same discharge condition with the direct absorption spectrum in Figure 6(b). The strong 2*f* signal, with a high signal to noise ratio, as well as a flat baseline is clearly shown. The noise is defined as 3σ where σ is the standard deviation of the base line. The signal to noise ratio is about 70 in the 2*f* spectrum. Thus, the absorbance at the detection limit is about 2×10^{-5} which corresponds to an atomic density of $4 \times 10^7/\text{cm}^3$. Meanwhile, the signal to noise ratio is about 5 in the direct absorption spectrum. This means that the absorbance is about 2.6×10^{-4} at the detection limit.

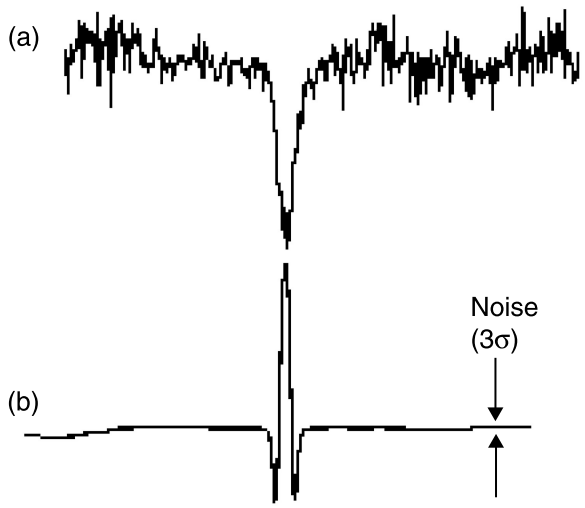

Figure 6. Comparison of the direct absorption spectrum and the wavelength modulated 2*f* spectrum at the peak absorption of 0.3%. (a) Direct absorption spectrum, (b) wavelength modulated 2*f* spectrum. The discharge current was 2 mA.

With this successful demonstration of the detection sensitivity, detection of the minor isotope (^{235}U) of uranium sample has been performed. Figure 7(a) and (b) show both OG (bottom traces) and wavelength modulation (top traces) spectra at 860.795 nm and 682.691 nm, respectively. The origin in the horizontal axis means the spectral position of the major isotope. The positive direction in the horizontal axis corresponds to the longer wavelength direction. The Arabic numbers indicated by arrows in the figure mean the gain factors for the spectra of the minor isotope. The 2*f* spectrum of the minor isotope at 860.795 nm is severely distorted due to the overlap with the wing of the major isotope, as shown in Figure 7(a). Moreover, the broader hyperfine structure is also observed. Meanwhile, a distinctive 2*f* spectrum of the minor isotope is observed at 682.691 nm, as shown in Figure 7(b). The isotopic abundance of about 0.134% (±0.009%) for the minor isotope was estimated by comparing the 2*f* signal magnitude between the minor- and major isotopes. This value was obtained by averaging eight measurements at different discharge currents ranging from 10 mA to 45 mA. The error means the standard deviation. The signal to noise ratio is about 7 in the 2*f* spectrum of the minor isotope. Thus, the minimum abundance of the minor isotope is about 0.02%.

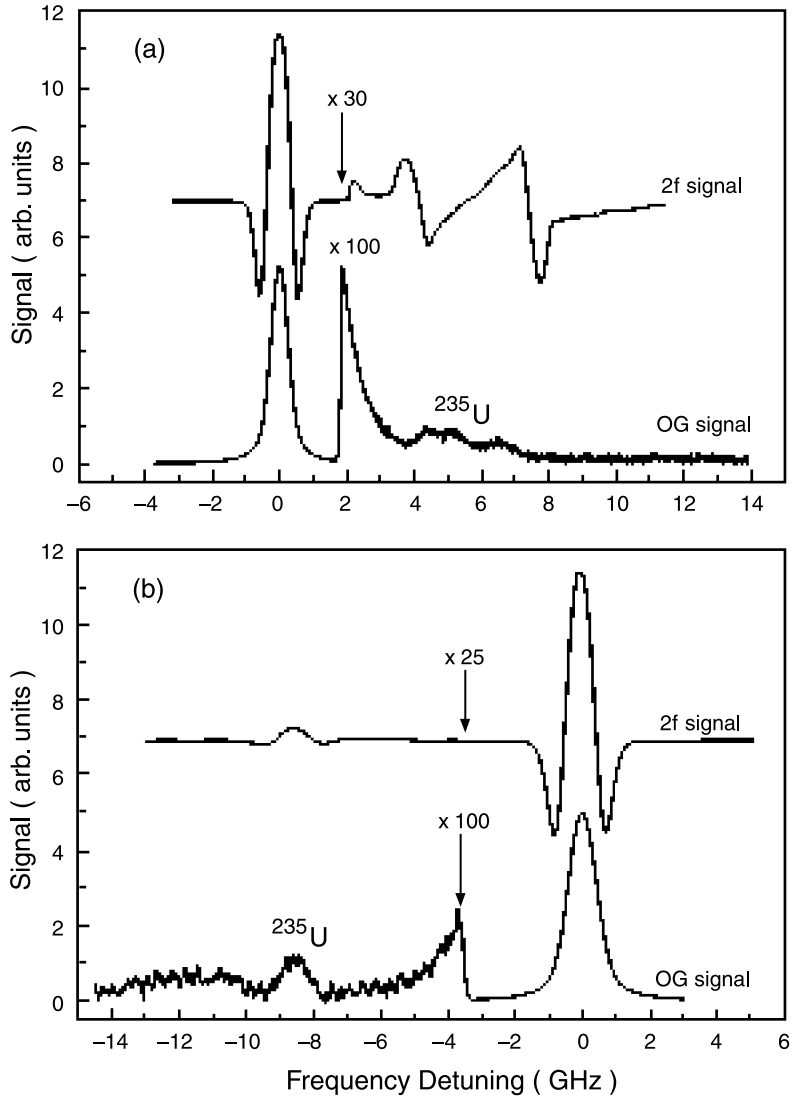

Figure 7. Comparison of the 2*f* spectrum with the OG spectrum for minor isotope detection. (a) The OG spectrum was recorded at 860.795 nm with a laser power of 8 mW. (b) The OG spectrum was recorded at 682.691 nm with a laser power of 4 mW. Both 2*f* spectra were recorded at a laser power of 30 μW with the optimum modulation frequencies and modulation amplitudes. The discharge current was 30 mA. A positive number in the X-axis corresponds to the longer wavelength direction.

CONCLUSIONS

Optogalvanic spectra and wavelength modulated absorption spectra were measured for a uranium sample in order to determine optimum transition lines as well as the detection limit of the adopted techniques. Amongst the observed transition lines, 860.795 nm showed the highest signal magnitude, while the line at 682.691 nm showed a wider isotope shift. This result indicates that 682.691 nm can be the best transition for the analysis of isotope abundances for uranium. Results on the isotope analysis in a hollow cathode glow discharge (HC-GD) cell for a rubidium sample have already been published by the authors.[14] The HC-GD cell adopted in the rubidium study was designed to use a few micro-liter of solution samples and could be used for the determination of the isotopic abundances for the uranium trace by using information and techniques described in this paper. This study is in progress.

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