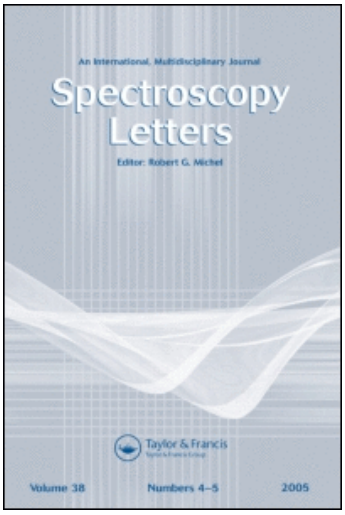

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Application of Diode Lasers to Determine Excitation Temperature in Hollow Cathode Discharges by Optogalvanic Spectroscopy

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APPLICATION OF DIODE LASERS TO DETERMINE EXCITATION TEMPERATURE IN HOLLOW CATHODE DISCHARGES BY OPTOGALVANIC SPECTROSCOPY

Key Words: Diode laser, Excitation temperature, Hollow cathode discharge, Optogalvanic spectroscopy, Emission spectroscopy

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ABSTRACT

The excitation temperatures of sputtered gadolinium and uranium atoms in an argon hollow cathode discharge have been determined by diode laser-excited optogalvanic spectroscopy. These results have been compared to those determined by conventional emission spectroscopy. It was found that the temperatures derived from each method do not differ very much, but the optogalvanic method revealed a better standard deviation uncertainty due to the good signal-to-background ratios and excellent spectral resolutions. Temperature variations with discharge currents ranging from 15 to 50 mA have been examined.

INTRODUCTION

Hollow cathode discharge (HCD) tubes have long been used for spectroscopic and analytical applications.[1] For the maximum realization of the potentials of discharge sources, reliable diagnostics of the plasma parameters are required.[2] One of the important parameters is the atomic excitation temperature. Atomic emission spectroscopy has hitherto been mainly used to measure excitation temperature.[3-8] Although this method is well established, it was found in our experiment that unavoidable background in emission intensities gave ambiguous results when determining excitation temperatures. The background occured not only due to the dark current of the photomultiplier but also to the background radiation of the discharge tube. Furthermore, the emission spectra of lanthanide or actinide species showed very dense spectral lines and sometimes the limited instrumental resolution interrupted to obtain correct intensities, excluding the background.

In this work, optogalvanic (OG) spectroscopy was adopted to determine excitation temperatures. OG spectroscopy[9,10] has been extensively investigated in plasma diagnostics,[11-14] because of its simple experimental setup and capability of yielding rich information with high spectral and spatial resolution. The use of the OG method in the measurement of excitation temperature has been introduced in a HCD tube.[15] However, no further investigations to show the usefulness of this method have been reported. Therefore, it is of interest to apply OG spectra obtained by diode lasers for sputtered Gd and U atoms to determine excitation temperatures, as an alternative to the emission method. We found that the results agreed well with those measured by emission intensities which were corrected with background subtraction. The merit of the OG method associated with good signal-to-background characteristics and spectral resolutions was demonstrated. Dependence of the excitation temperature upon discharge current was also examined.

EXPERIMENTAL

Two commercial HCD tubes (Cathodeon Inc., model 3QQAY/Gd and 3QQAY/U) with cylindrical (inner diameter of 2 mm and length of 20 mm for both elements) hollow electrodes were used. Both tubes contained argon buffer gas at a pressure of about 6 mbar. The electrodes were connected to a stabilized dc power supply (Bertan Associate Inc., model 105-01R) with a voltage of 100-400 V at a current of 10-50 mA. The OG signals were detected with a lock-in amplifier (EG&G, model 5210) by blocking the dc voltage using a coupling capacitor of 0.01 μF.

An external cavity diode laser (New Focus Inc., model 6200 controller with 6226 laser head) having a center wavelength of 785 nm was used. An achromatic anamorphic prism pair (New Focus Inc., model 5411) was used for transforming the elliptical shape of the laser beam into a circular one. The diameter of the laser beam was adjusted by iris diaphragms of 0.5 mm diameter. The spatial distribution of the laser beam intensity showed a nearly Gaussian curve with a full width at half maximum of about 0.3 mm at the front of the HCD tube. The laser beam at the constant power of 0.6 mW was carefully adjusted to pass through the center of the negative glow region. A small part of the laser beam was split off by a thin glass plate and sent to a wavemeter (Burleigh Inc., model WA-4500) or confocal Fabry-Perot etalon (Tec Optics, model SA-300) having a free spectral range of 0.01 cm^{-1}.

The emission of the HCD plasma was projected onto the input slit of a monochromator (Acton Research Corp. model SpectraPro-500) with the aid of two lenses (focal length of 125 mm and diameter of 50.8 mm). The slit width was 0.2 mm. An intensified charge-coupled device (Oriel Instruments, Instaspec V model 77193-5) attached to the output slit served as a detector. The detector was operated at -10 °C to reduce the dark current background.

RESULTS AND DISCUSSION

Usually the excitation temperature, T_{EX}, is obtained by measuring the intensities of a number of emitted lines, I_{EMI}, of the same thermometric species and using a Boltzmann plot.[5-7,16] For conventional emission spectrometry, plotting

$$\ln (I_{EMI} \cdot \lambda_{21} / g_2 \cdot A_{21}) = C - (E_2 / kT_{EX}) \quad (1)$$

gives a line with a slope equal to $(-1/kT_{EX})$. In this equation, g_2 and E_2 are the statistical weight and energy level of the upper state, respectively, A_{21} is the transition probability of the transition, C is the constant containing units and scale factor, k is the Boltzmann constant.

Two mechanisms, a change in ionization probability following the excitation of atoms to a energy level closer to the ionization potential and a change in electron temperature resulting from superelastic collisions between electrons and laser-excited atoms, are most often used to explain the OG effect.[9,10,17] On the basis of the latter mechanism,[18,19] the OG signals of sputtered atoms have been applied to the derivation of the excitation temperature as:[15]

$$\ln (I_{OG} / I_L \cdot \lambda_{12} \cdot g_1 \cdot f_{12}) = C - (E_1 / kT_{EX}), \quad (2)$$

where I_{OG} is the OG signal magnitude at the laser power of I_L, f_{12} is the oscillator strength of the transition, g_1 and E_1 are the statistical weight and energy level of the lower state. In the Equation (2), $\lambda_{12} \cdot f_{12}$ is proportional to the cross section of peak absorption.

The spectral lines for Gd and U atoms measured in this work are given in TABLE 1, TABLE 2 and TABLE 3, respectively.[20,21] The measured OG signal magnitudes at the current of 30 mA are listed in the last column of TABLE 1, 2 as representatives among the data sets for different discharge currents. The gf values have been taken from the work

TABLE 1

Spectral lines used for both optogalvanic and emission measurements of Gd atom.[20]

Wavelength (nm)	Lower energy level (cm^{-1})	Upper energy level (cm^{-1})	gf	gA (10^8/sec)	OG signal at 30 mA (mV)
771.766	7480	20434	0.0098	0.011	0.087
773.350	999	13926	0.0161	0.018	1.68
774.930	533	13434	0.0056	0.0062	0.883
783.446	10884	23644	0.050	0.055	0.085
784.487	10360	23104	0.058	0.063	0.107
784.580	19165	31907	0.61	0.66	0.038
785.693	6976	19701	0.070	0.075	0.384
786.972	11297	24000	0.094	0.10	0.117
788.439	7480	20160	0.0096	0.010	0.058

of Corliss and Bozman[20] for Gd and Palmer et al.[21] for U. The relative values of gf from each atlas have estimated errors of about 30% for Gd and 8% for U.

The Boltzmann plot using Equation (1) is shown in FIG. 1(a) for Gd. The fitted solid line by least-square regression shows a linear-correlation coefficient r=0.956. The slope of this line yields an excitation temperature of 3381 ± 396 K. Relative emission intensities corrected with background subtractions were determined as average values of five times measurements. The estimated uncertainty of excitation temperature was derived from the standard deviation error of the slope in the least-square program. The result of OG measurement by Equation (2) is shown in FIG. 1(b). The slope of the solid line with a correlation coefficient of 0.996 yields an excitation temperature of 3436 ± 123 K.

Regardless of the well-agreed temperature values within the standard deviation uncertainties, we have to note that the estimated uncertainty by

TABLE 2

Spectral lines used for optogalvanic measurement of U atom.[21]

Wavelength (nm)	Lower energy level (cm^{-1})	Upper energy level (cm^{-1})	*gf*	*gA* (10^8/sec)	OG signal at 30 mA (mV)
774.819	10640	28943	0.6831	0.7591	0.055
775.988	7645	20528	0.0473	0.0524	0.105
776.185	7005	19885	0.0608	0.0673	0.154
778.416	620	13463	0.0903	0.0994	2.210
781.633	13127	25918	0.2847	0.3109	0.060
783.574	5991	18749	0.0193	0.0210	0.088
784.472	16040	28784	0.5382	0.5834	0.041
786.874	78641	20569	0.0313	0.0337	0.067
786.879	3800	16505	0.0281	0.0302	0.260
787.539	11308	24002	0.2608	0.2805	0.140
788.194	6249	18932	0.4770	0.5122	1.140
789.603	13127	25789	0.1472	0.1575	0.035
790.043	4275	16929	0.0220	0.0235	0.160
790.429	8118	20766	0.0638	0.0681	0.099
790.798	7005	19647	0.0206	0.0220	0.075
791.882	4275	16900	0.0280	0.0297	0.203

the OG method is about three times less than that by the emission method. Non-linearity in the Boltzmann plots is usually due to uncertainties in either the *gf* values or the line intensities or deviation from thermal equilibrium. Among these, the scattering of the emission data in FIG. 1(a) was mainly caused by misreading line intensities due to the overlapped spectral line shapes. A comparison of a typical emission with an OG spectrum is shown in FIG. 2. All transition lines in TABLE 1 are fully resolved without overlapping in the OG spectrum, as shown in FIG. 2(a). Moreover, no background signals were found. The spectral resolution in OG spectrum depends only on the translational temperature of the species in the discharge. In the present experimental conditions, the full

TABLE 3

Spectral lines used for emission measurement of U atom.[21]

Wavelength (nm)	Lower energy level (cm^{-1})	Upper energy level (cm^{-1})	gA (10^8/sec)
566.944	620	18253	0.0526
568.037	6249	23848	0.0601
568.521	4453	22038	0.0828
570.949	7103	24613	0.1262
571.688	4453	21941	0.1118
576.538	8118	25458	0.0792
576.745	5991	23325	0.0545
578.059	6249	23544	0.5369
580.211	8118	25348	0.2771
580.519	5991	23212	0.1007
583.602	10347	27477	0.6532
585.200	4453	21536	0.0935
589.878	6249	23197	0.1397
590.249	3868	20805	0.0892
591.539	0	16900	0.4454
592.546	7645	24517	0.2027
593.382	620	17468	0.0330
595.686	3868	20651	0.0666
597.150	620	17362	0.1172
597.632	3800	20528	0.4269
598.610	3868	20569	0.1991
599.941	3801	20464	0.0713
601.086	10347	26979	0.2452
601.919	4453	21062	0.0625
602.812	3868	20452	0.0788
603.555	7191	23755	0.0835
603.962	8118	24671	0.1974
606.231	4275	20766	0.0922

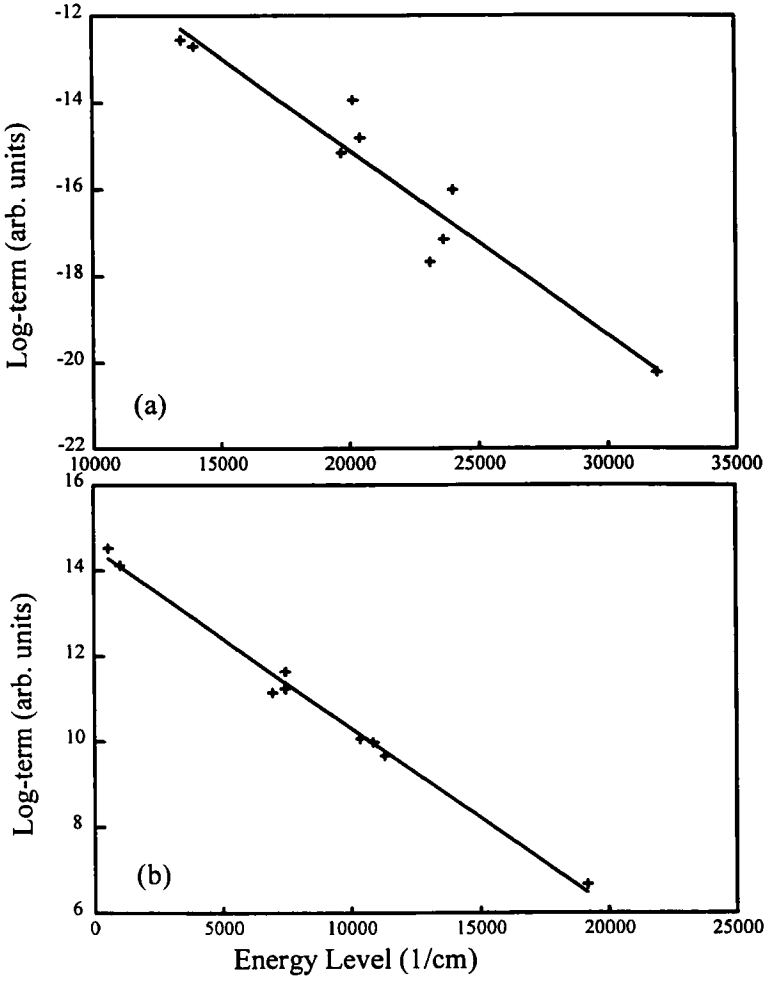

FIG. 1. Boltzmann plot for Gd lines at the discharge current of 30 mA. The slope of the line determined by least square fit is $(-1/kT_{EX})$. (a) $\ln(I_{EMI} \cdot \lambda_{21} / g_2 \cdot A_{21})$ vs E_2. The slope of the line yields an excitation temperature of 3381 ± 396 K with a correlation coefficient of 0.956. (b) $\ln(I_{OG} / I_L \cdot \lambda_{12} \cdot g_1 \cdot f_{12})$ vs E_1. The slope of the line yields an excitation temperature of 3436 ± 123 K with a correlation coefficient of 0.996.

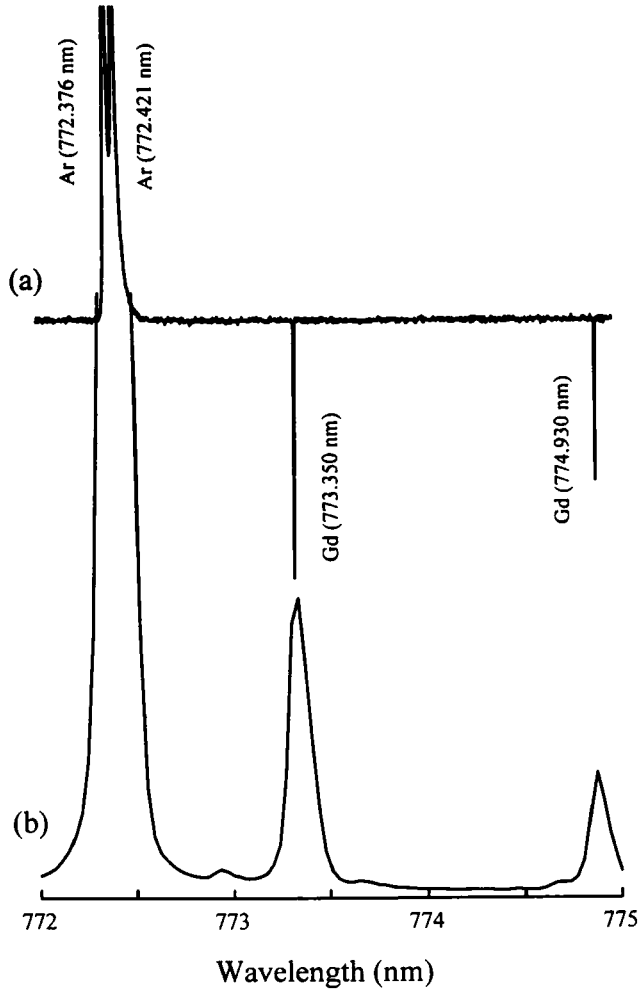

FIG. 2. Gd and Ar transitions observed on the same discharge condition. (a) Optogalvanic spectrum, (b) Emission spectrum. Optogalvanic spectrum shows better resolutions without any background.

width at half maximum of Doppler linewidth for a Gd atom was less than 0.03 cm^{-1}. Although seven Gd isotopes exist, the linewidths of all structures were observed to be less than 0.1 cm^{-1} for all spectral lines in TABLE 1 except for one line, 785.693 nm. The lines from the seven isotopes are spread in the range of about 0.2 cm^{-1} for 785.693 nm. On the contrary, however, the linewidth of the emission spectrum depends on the instrumental resolution. It was about ten times larger than the linewidth of the OG spectrum, as shown in FIG. 2(b).

The Boltzmann plots of emission and the OG signals for the U atom are shown in FIG. 3(a) and (b), respectively. The slope of the solid line in FIG. 3(a) yields an excitation temperature of 3828 ± 82 K with a correlation coefficient of 0.994. The use of more spectral lines having stronger emission intensities results in smaller uncertainty in estimated temperature than that of the Gd atom. The result of the OG experiment in FIG. 3(b) gives an estimated temperature of 3755 ± 95 K with a linear correlation coefficient of 0.996. The uncertainty and linear correlation coefficient are almost comparable to those of Gd.

FIG. 4(a) shows part of an emission spectrum which was used to estimate the excitation temperature for U atom at the current of 20 mA. Even though well resolved spectral lines were chosen, we found the unavoidable background gave an ambiguous temperature value. The background was caused 85-90% by the dark current of the photodetector and 10-15% by the background radiation of discharge tube. The importance of the background correction in the emission intensities is demonstrated in FIG. 4(b). The lower and upper line represent the result with and without background subtraction, respectively. The former yields a temperature of 3625 ± 81 K, while the latter yields 4167 ± 135 K. The difference is about five times larger than the estimated uncertainty. The temperature of 3600 ± 101 K is estimated using the OG spectrum at the same discharge condition. All results of temperature measurement for various discharge currents are summarized in TABLE 4. The emission results with background corrections agree well with the OG results within the standard

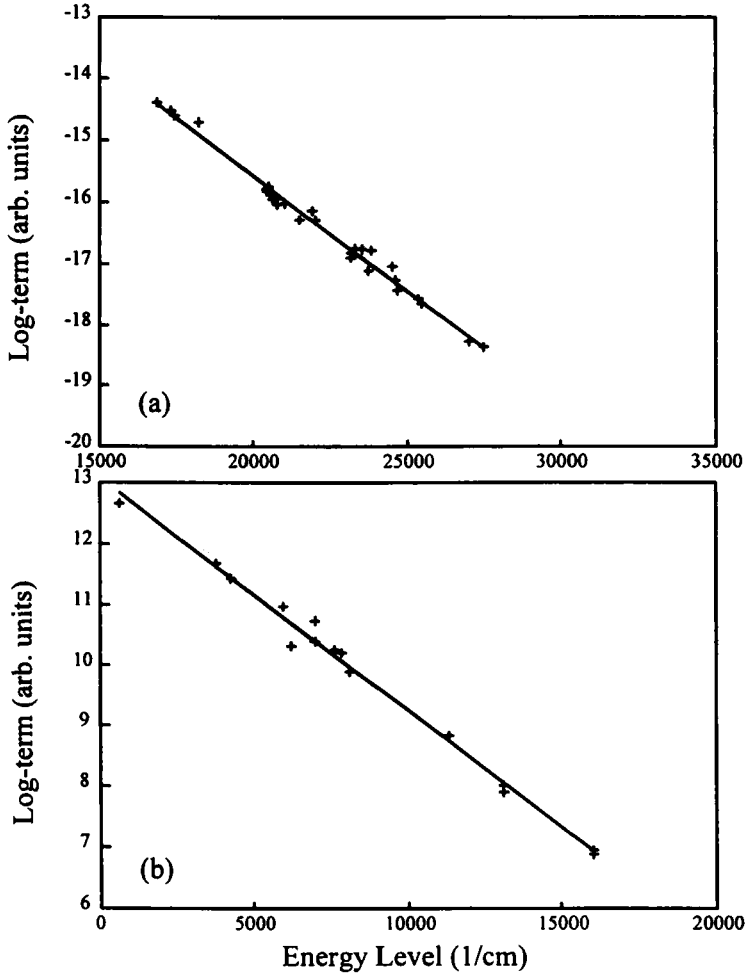

FIG. 3. Boltzmann plot for U lines at the discharge current of 30 mA. The slope of the line determined by least square fit is $(-1/kT_{EX})$. (a) $\ln(I_{EMI} \cdot \lambda_{21} / g_2 \cdot A_{21})$ vs E_2. The slope of the line yields an excitation temperature of 3828 ± 82 K with a correlation coefficient of 0.994. (b) $\ln(I_{OG} / I_L \cdot \lambda_{12} \cdot g_1 \cdot f_{12})$ vs E_1. The slope of the line yields an excitation temperature of 3755 ± 95 K with a correlation coefficient of 0.996.

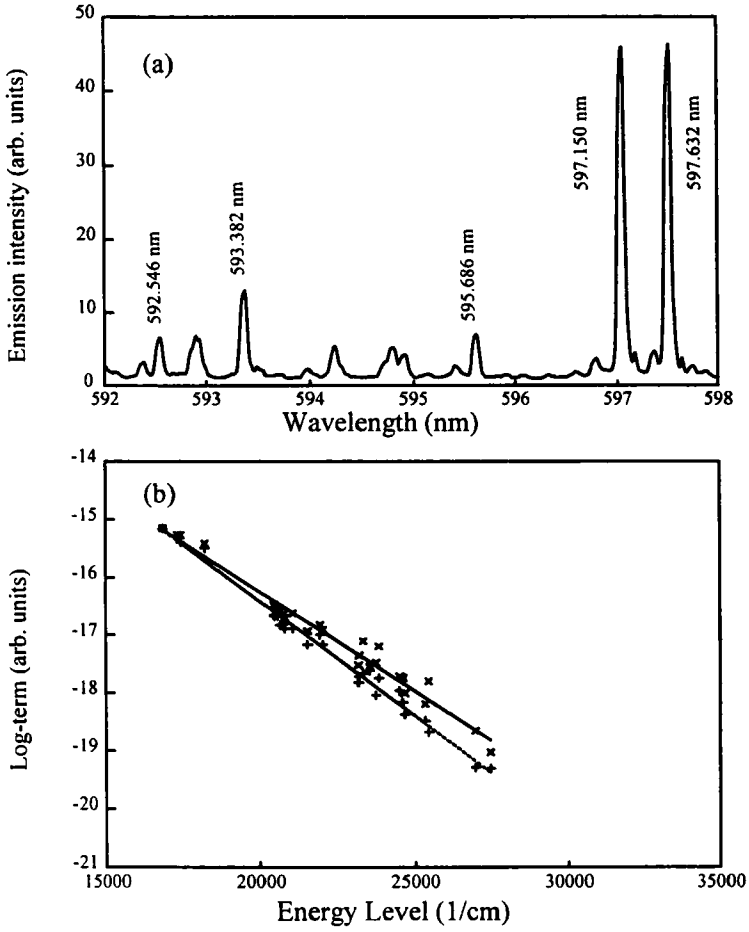

FIG. 4. (a) Emission spectrum of U atom at the discharge current of 20 mA. Background signal is shown. (b) Comparison of Boltzmann plots with and without background subtraction. The former result yields the temperature of 3625 ± 81 K with a correlation coefficient of 0.994 and the latter one yields the temperature of 4167 ± 135 K with a coefficient of 0.987. At the same discharge condition, the result of optogalvanic measurement yields the temperature of 3600 ± 101 K with correlation coefficient of 0.995.

TABLE 4

Temperature variations with discharge currents.

Current (mA)	Excitation temperature (degrees Kelvin)					
	Gd			U		
	OG method	Emission method[a]	Emission method[b]	OG method	Emission method[a]	Emission method[b]
15	3364 ± 138 (r=0.994)	3268 ± 359 (r=0.960)	3823 ± 375 (r=0.968)	3478 ± 105 (r=0.994)	3543 ± 84 (r=0.994)	4815 ± 329 (r=0.944)
20	3460 ± 131 (r=0.995)	3361 ± 382 (r=0.958)	3756 ± 382 (r=0.966)	3600 ± 101 (r=0.995)	3625 ± 81 (r=0.994)	4167 ± 135 (r=0.987)
30	3436 ± 123 (r=0.996)	3381 ± 396 (r=0.955)	3659 ± 398 (r=0.961)	3755 ± 95 (r=0.996)	3828 ± 82 (r=0.994)	4221 ± 123 (r=0.989)
40	3383 ± 102 (r=0.997)	3382 ± 414 (r=0.951)	3624 ± 415 (r=0.957)	3866 ± 92 (r=0.996)	3995 ± 96 (r=0.993)	4368 ± 134 (r=0.988)
50	3332 ± 108 (r=0.997)	3400 ± 416 (r=0.951)	3650 ± 420 (r=0.957)	3891 ± 92 (r=0.996)	4142 ± 114 (r=0.991)	4429 ± 154 (r=0.985)

[a]The result with background correction

[b]The result without background correction

deviation errors for both Gd and U atoms. The comparisons of each value make us convinced on the usefulness of the OG method associated with high signal-to-background ratios, in addition to high spectral resolutions.

CONCLUSION

Diode laser-excited OG spectra in the wavelength region of 770-790 nm were used to determine excitation temperatures for sputtered Gd and U atoms in HCD. These spectra include a possible reduction in background signals because of their ability to generate an electrical signal directly without the need of an opto-electrical detector. The narrow linewidths of the OG spectra prevent the scattering of data points in the Boltzmann plot, especially for lanthanide or actinide atoms having very dense spectral lines. With these advantages, OG measurement can be adopted as an alternative spectroscopic method to determine excitation temperatures. The other point

of this work is that measured atomic lines having good OG signals can be used for either wavelength calibrations or frequency stabilization in the near-infrared wavelength region.

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