Measurement of Echelle Spectrometer Spectral Response in UV

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Abstract. A spectral response of an echelle-type spectrometer (Andor Mechelle ME5000 spectrograph coupled with Andor iStar DH734 camera) in the spectral range 215 to 950 nm is described. In the first step a calibration of a single grating Czerny-Turner spectrometer (Ocean Optics SD2000) in the 210 to 500 nm spectral range was done. The spectrometer's spectral response (used in the first diffraction order only) is simpler than that of echelle-type spectrometer. The UV region calibration was performed by a fitting of measured to simulated emission of NO gamma and N_2 2PS molecular systems emitted from a DC glow discharge. In the VIS region, a tungsten filament lamp was used. The filament temperature was estimated by fitting ratios of the measured and simulated filament emission curves to ratios of measured and simulated intensities of 2PS molecular system. In the next step a calibrated spectrometer was used for the determination of a relative radiation of an uncalibrated deuterium lamp. Finally this deuterium lamp and the tungsten filament lamp with known temperature were used for a calibration of the Mechelle spectrometer.

Introduction

Optical Emission Spectroscopy is important method for investigation of plasma radiation with a possibility to determine its properties. For this purpose a spectrometer, which possibilities are mainly limited by a spectral resolution, a spectral range width and an exposition time, is needed. The focus is on the investigation of plasmas generated by a short laser pulse (LIBS—Laser Induced Breakdown Spectroscopy). Typical plasma formation lasts in order of 1 μs or less, which implies the short exposition time. For the possibility to take more atomics spectral lines per one laser shot, requirement for high spectral range is also needed. The Echelle type of spectrograph coupled with ICCD camera meets these requirements [*Lindblom*, 1999]. LIBS application with the Echelle is presented in [*Floreka*, 2001]. For relative measurements of atomic lines intensities the sensitivity calibration of spectrometer in UV and VIS spectral range is necessary. In the VIS tungsten filament lamp as black body radiator with known temperature is usually applied. For the UV part of spectra a deuterium arc lamp is suitable as a continuous light source. There are not so big requirements for the filament lamp as there are for the deuterium lamp, which certified calibrated version is more expensive. Because of the price calibration of cheap deuterium lamp by fitting vibration and rotation simulation of some diatomic molecules to experimental data was done. Similar principle was used in [*Bibinov*, 2007]. We additionally used another spectrometer to eliminate complicated Echelle spectral response which has a lot of maxima and minima within its whole spectral range due to the simultaneous use of many diffraction orders (Figure 9). This fact results from a construction based on two disperse elements, prism and grating, orthogonal to each other. Therefore the final spectrum is obtained by the whole spectrum reconstruction from a quantity of spectra from different diffraction orders of the grating and so the spectral response curve is strongly influenced.

Figure 1 shows an experimental setup with light sources and spectrometers. As a source of appropriate molecular spectra with the vibration-rotational structure in this range, a DC glow discharge is used [*Bogaerts*, 1998]. The discharge was maintained in the air under pressure ≈ 2.5 Torr. In the discharge the radiation of NO gamma and Second positive system (2PS) was dominant and used for a calibration. As the filament lamp a small bulb lamp was used, powered by 8 V and 4 A with nominal lamp voltage 6 V. The deuterium lamp was 30 minutes turned on and stabilized before measurement. Ocean Optics SD2000 as Czerny-Turner spectrometer was used with a spectral range 200–520 nm and a resolution of ≈ 0.6 nm. The goal of presented paper is a description of sensitivity

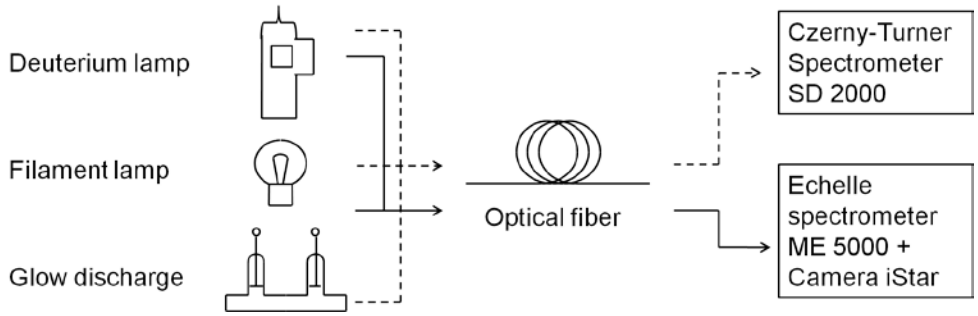

Figure 1. Scheme of apparatus.

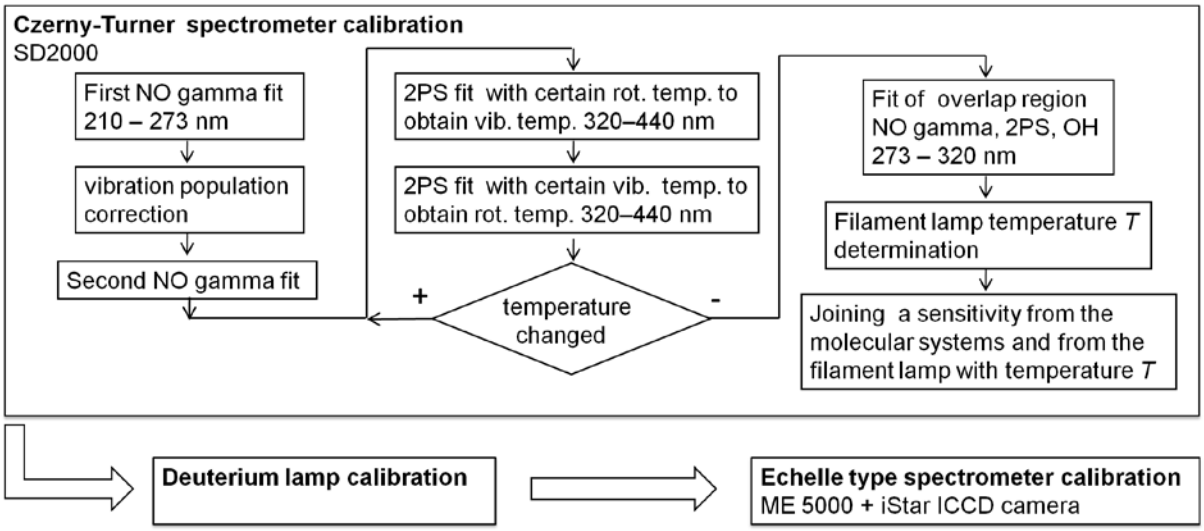

Figure 2. Block diagram for the calibration procedure. Spectral response of Czerny-Turner spectrometer was determined fist. Relative radiation of the deuterium lamp was found and then the sensitivity calibration of Echelle spectrometer was done.

calibration of a spectrograph Andor ME 5000 equipped with an Andor iStar ICCD camera cooled to – 15 ˚C.

The procedure of the calibration is shown in the block diagram in Figure 2.

Czerny-Turner calibration process

For the purpose of SD2000 spectrometer calibration a spectra region 210–440 of glow discharge in the air was measured and simulated. The simulation was fitted to the measured data and spectral response curve reconstructed. For this purpose the NO gamma and 2PS systems were used.

NO gamma fit

Emission spectrum of NO gamma is described by transition NO($A^2\sum^+ \rightarrow X^2\Pi_r$), more detail described in [*Bibinov*, 2007]. Simulation of the system was performed by [*LIFBASE*]. For different rotation temperatures with step of 100 K, 5 separated vibration bands were generated. The simulated spectra were convoluted with instrumental function, which was taken from measurement of Hg/Ar low pressure discharge lamp. Hg atomic line was chosen from position 253.65 nm. Fit was performed in three steps. In the first step fit of rotation temperature, vibration distribution and spectral response curve in region 210–273 nm was done. Previously simulated LIFBASE spectra were interpolated with respect to a rotational temperature and spectral response curve was fitted by four points spline curve (Figure 4). Because the higher vibration states did not fit well (Figure 3 left), a correction under assumption of Boltzmann distribution of the vibration states was applied as the second step. The distribution of the vibration states with the corrections is shown in Figure 3 right. In the third step new fit of NO gamma was applied. The vibration temperature was fixed to 3400 K. The spectral response

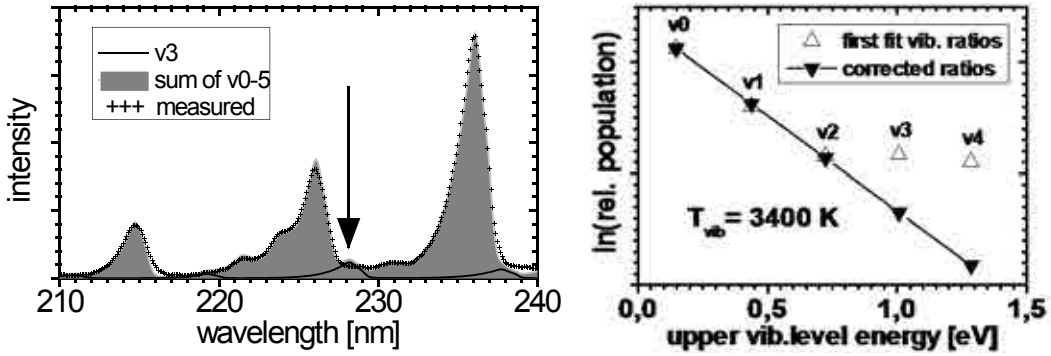

Figure 3. Sum of first six simulated vibrations bands (v0–v5) is shown and a bad fit of 3rd vibration band (v3) is marked in the left panel. It is overrated because its intensity is comparable with background and undefined peaks. The Boltzmann plot for corrections of higher vibration level populations (v3 and v4) is shown in the right panel.

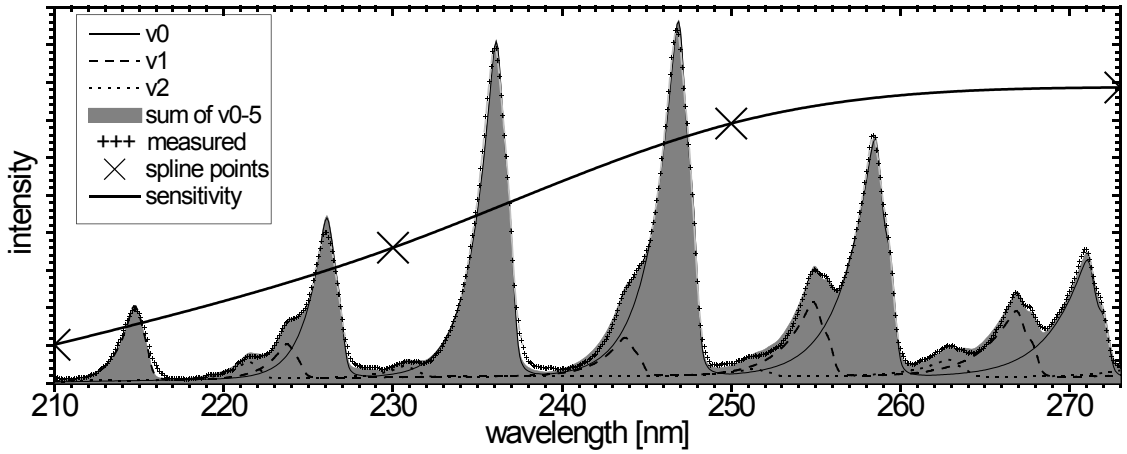

Figure 4. Fit of simulation to measurement of NO gamma. First three (v0–v2) separately and sum of first six (v0–v5) vibration bands are shown. Sensitivity correction is fitted by four spline points.

curve from fit and the first three vibration bands are shown in Figure 4. Rotation temperature was determined by fit to value 2140 K. The difference in vibration and rotation temperatures is common for some of types of discharges even they can be described by one temperature separately [*Britun*, 2007; *Popa*, 1996].

N_2 Second positive system fit

Emission spectrum of 2PS is described by transition $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$ [*Britun*, 2007]. It was simulated by [*Specair*] without possibility of the vibration bands separation. As it is drawn in the middle part of the Figure 2, a spectra was fitted in the loop. In all iteration the vibration or the rotation temperature was fixed and a new simulation was generated alternately until their stabilization.
The simulated spectra were convoluted with instrumental function which was taken from the measurement of low pressure HgAr discharge lamp. Hg atomic line was chosen from position 404.66 nm. The rotation and vibration temperatures were stabilized to value 800 K and 5260 K respectively. Final simulation with fitted sensitivity correction is shown in Figure 5.

Fit of overlap region

The overlap region of NO gamma and 2PS was fitted with fixed rotation and vibration temperatures, determined previously. The intensity ratio between the NO gamma and 2PS is defined by the fit in this region so implementation of the simulation and fit of OH system was performed to improve its quality. OH was simulated by [*LIFBASE*] in the same way as NO gamma. A convolution with an instrument function was also performed. Figure 6 shows the result of the fit.

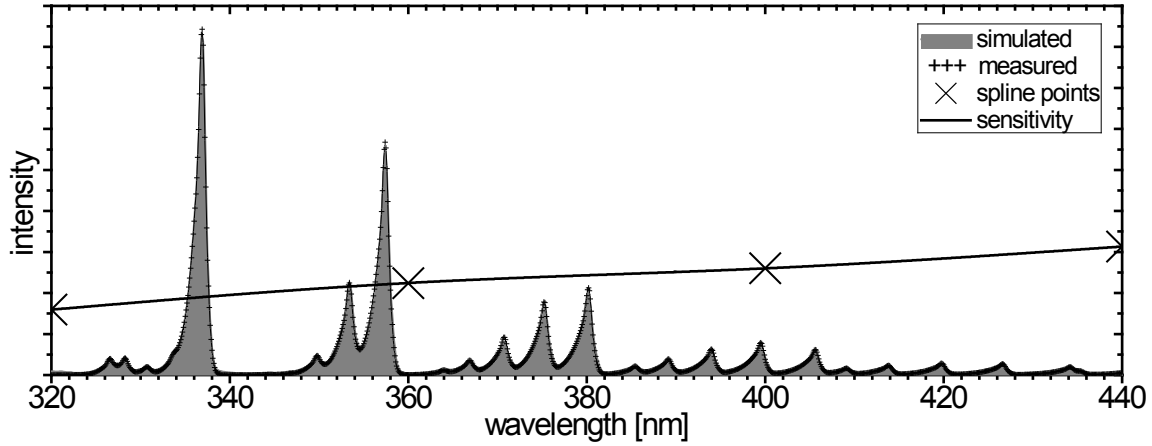

Figure 5. Fit of simulation to measure of 2PS. Sensitivity correction is fitted by four spline points.

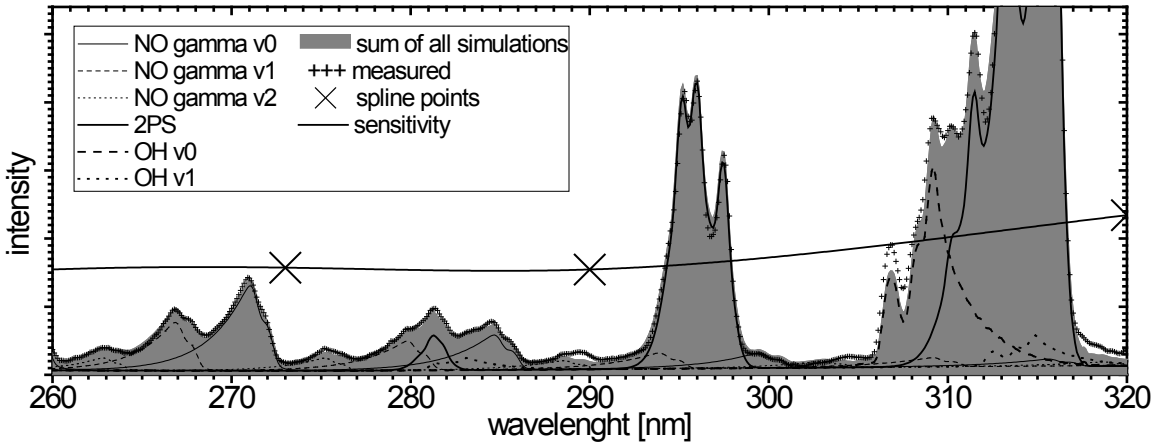

Figure 6. Fit of simulation to measure of NO gamma, 2PS and OH. First three (NO gamma v0–v2) and first two (OH v0–v1) vibration bands of NO gamma and OH system respectively were shown. In the case of second positive system (2PS) vibration bands were not separated. In fitting process rotation and vibration temperature of NO gamma and 2PS were fixed. Sensitivity correction is fitted by three spline points.

Filament temperature determination

A temperature of the filament of the tungsten filament lamp was determined for reconstruction of VIS part of the spectral response. Ratios of simulated to measured intensities (averaged around the maximum of vibration band head) of the first three vibration bands were scaled independently to fit them to ratio of simulated to measured filament radiation with certain temperature, which was also fitted. That's mean that in process of fitting vibration transitions from same upper vibration state was scaled by one coefficient and then ratio to measured intensities were done. The ratios were fitted to ratios determined from measured and simulated black body radiator with certain temperature which was also fitted to find best temperature. The filament radiation was simulated by Plank's law of black body radiator [*MacIsaac*, 1999]. Only transitions above 340 nm were taken for the fit, because of a strong bulb glass absorption starting from ≈ 340 nm to shorter wavelengths. The temperature of the filament was determined to a value 2900 K (Figure 7).

Final spectral response of SD2000

With UV and VIS sensitivity parts it is possible to create a spectral response of the SD2000 spectrometer in its whole spectral range. The connection of the parts was done at wavelength ≈360 nm (Figure 8 left). Consequently by using the obtained spectral response, relative radiation of the deuterium lamp was determined. Difference before and after correction can be seen in Figure 8 right.

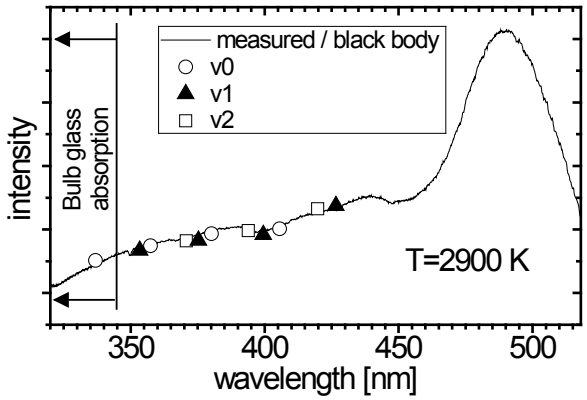

Figure 7. Filament temperature determination. Ratios of measured to simulated of first three vibration bands (v0–v2) of 2PS were scaled to fit them to sensitivity derived from filament radiation with simulated temperature also fitted.

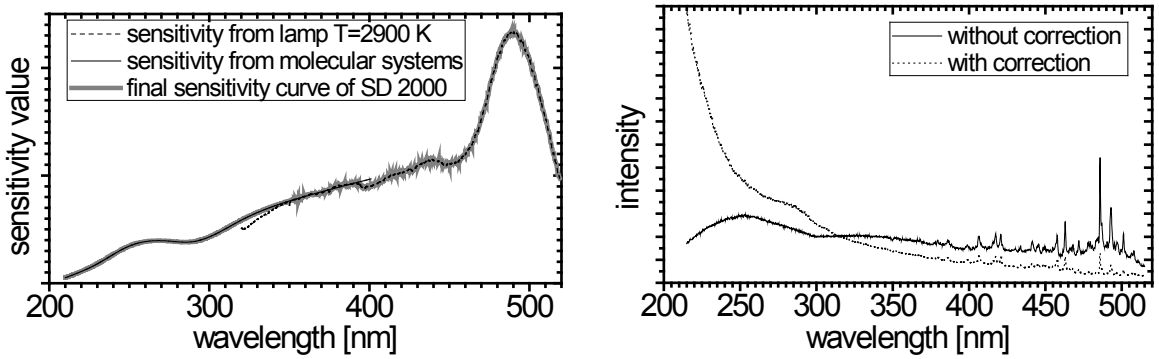

Figure 8. There are spectral response curves in the left panel. The final one is composed in VIS part of sensitivity derived from a tungsten filament lamp and in UV region of sensitivity determined by NO gamma and 2PS simulation. In the right panel the spectrum of a deuterium lamp radiation is shown.

Echelle calibration

Radiation from the filament and deuterium lamp was measured with spectrograph ME 5000 equipped with iStar ICCD camera. A previous calibration of lamps was used to calibrate the Echelle spectrometer in two separate parts. Those parts were joined to create one spectral response curve for the whole spectrometer spectral range 215–950 nm. Zoomed overlap region of both spectral responses is shown in the left top corner of Figure 9. Joining point is ≈ 360 nm. Notice decrease of spectral response derived from filament lamp below 340 nm caused by bulb glass absorption.

Discussion

The calibration of an Echelle type of spectrograph coupled with ICCD camera was presented. Quality of final spectral response curve is dependent on a quality of SD2000 spectrometer calibration and filament temperature determination. The simulation and the fit of vibration-rotation spectra were separated in three regions. Quality of fit in all parts of spectra was affected by background and emission bands from undefined transitions. Critical part for the fit is the overlapped one, because it determines ratio between the remaining two parts. Additional simulation and fit of OH system was performed to improve fit of this part. Because of the comparable width of instrumental function to vibration transition peaks widths they are strongly influenced by it. Shape and width of the instrumental function is different for different spectra region, so two different instrumental functions for convolution with simulation were used to improve fit. In the case of filament temperature valuation, the used method was limited by bulb glass absorption.

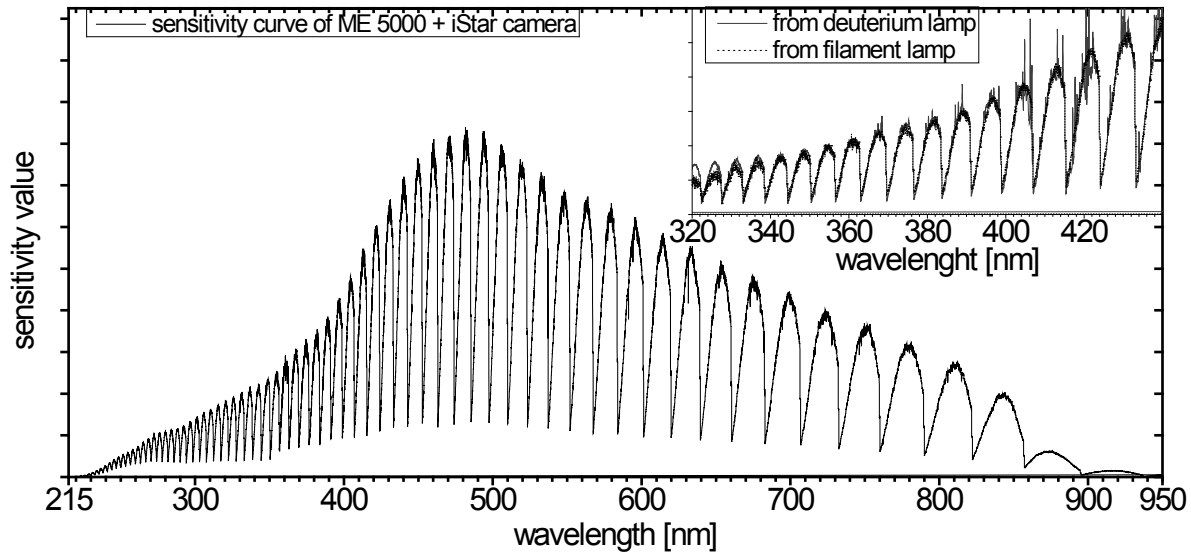

Figure 9. Spectral response curve of ME 5000 coupled with iStar ICCD camera composed from two parts. In the left top corner, a connection region of two spectral response curves is shown.

Conclusion

Correction to spectral response of spectrometer is important for the relative intensity measurement of atomic lines in LIBS experiments. By presented calibration process we avoided the usage of an expensive calibrated UV radiation source. Less than 10 % error was reached in the region 215–273 nm. An error in the whole spectra range is higher, mainly because of uncertainty in fit of the overlapped part of NO gamma and 2PS and it is less than 30 %. This precision is satisfactory for many LIBS applications. For example to determine electron states population consider up to 30 % error coming from Einstein's spontaneous emission coefficients. Additional improvement can be done by better radiation sources.

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