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Ne I spectral line shapes in Grimm type glow discharge

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We report the results of five Ne I line shapes study in an abnormal Grimm type glow discharge operating in neon. The spectral lines were observed along the axis of a cylindrical glow discharge parallel (side-on) and perpendicular (end-on) to the cathode surface. The side-on spectra show spectral line shifting and sometimes simultaneous shifting and splitting in the cathode fall region of the glow discharge. The results of the measured line shift with available data for the *dc* Stark effect are used for estimate electric field strength in the cathode fall region of the glow discharge. The end-on recorded line profiles show up to 30% larger half-widths than the side-on recorded line profiles from the negative glow. This effect is a result of the superposition of line emission in the cathode fall region under the influence of the *dc* Stark effect on the line profile from the negative glow. In addition, wavy features at the far wing in the direction of *dc* Stark shift are detected. All observed phenomena related to end-on line shapes in Grimm discharge are related quantitatively to *dc* Stark effect in the cathode fall region and plasma line broadening in negative glow region.

1. Introduction

With the growing number of applications of Optical Emission Spectroscopy (OES) of Glow Discharge Sources (GDS)[1,2] it became evident that reliable wavelength tables of Glow Discharge (GD) spectra are needed. Since there are great variety of GDs whose spectra excitation depends upon large number of parameters like cathode shape and material, operating pressure, voltage, current *etc*. the universal wavelength and line intensity tables is almost impossible to establish. Fortunately, most of GDS applications is based on original GDS Grimm design [3] and this narrows considerably the spectrum of wavelengths and line intensities. On the other hand, large number of applications increases the field of interest and formation of wavelength tables remains an extraordinary difficult and time consuming task in particular if data compilation is carried out in several laboratories equipped with different spectrometers, see *e.g.* [4]. One of primary tasks in the compilation of line wavelengths and their intensities is the analysis and characterization of spectra belonging to the gas used to operate GDS. Low intensity lines or some not completely understood spectral features are of particular importance for the trace elemental analysis when minor changes in line intensity influence considerably final result.

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Recently, Ar I and Ne I lines much broader than instrumental profile have been detected [5]. An attempt was made to explain this phenomenon and some features at the far wing that follow line broadening are detected [6]. It was found that broadened profiles and "distorted" far line wings were related to *dc* Stark effect in the Cathode Fall (CF) region. In addition to the influence of *dc* Stark effect for some lines plasma broadening in Negative Glow (NG) region of GDS plays certain role in description of end-on (usual direction of GDS observation of spectra) recorded line profile as well. Thus, by changing operating GDS conditions (pressure, voltage *i.e.* CF electric field) one can influence the degree of line shape distortion but the presence of line shape distortion can't be avoided completely. Fortunately, only transitions with close perturbing level (or levels) with large *dc* Stark effect generate spectral lines with large measurable *dc* Stark shift in CF of GDS where electric field strength is typically below 20kV/cm [6-9].
Since, neon is one of gases used for GDS operation, in this work we extended the study of Ne I line profiles started in Ref. 6. An attempt will be made also to estimate electric field strength distribution in CF region of neon GDS with iron cathode using Stark shift measurements of Ne I 511.368 nm and 534.109 nm lines.

2. Experimental

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The discharge source, a modified Grimm GDS, was laboratory made after a Ferreira *et al.* design [10] and it was described in detail elsewhere [11]. Here, for completeness, minimum details will be given. A hollow anode 30 mm long with inner diameter 8 mm has a longitudinal slot (16 mm long and 1.5 mm wide) for side-on observations along the discharge axis, see figure 1. The water-cooled cathode holder has an exchangeable iron electrode, 18 mm long and 7.60 mm in diameter, which screws tightly into its holder to ensure good cooling.

All experiments were carried out with neon (purity 99.999%). The continuous flow of about 300 cm^3/min of neon (at room temperature and atmospheric pressure) was sustained in the pressure range 5-10 mbar by means of needle valve and two two-stage mechanical vacuum pumps. The reported results for gas pressure represent an average between gas inlet and outlet pressure measurements.

To run the discharge a current-stabilized *dc* power supply (0-2 kV, 0-100 mA) is used. A ballast resistor of 5.3 kΩ is placed in series with the discharge and the power supply.

Spectroscopic observations of Grimm GD were performed end-on, while for axial intensity distribution of side-on radiation observed through the anode slot, the discharge tube was translated in ≈ 0.125 mm steps. The light from the discharge was focused with an achromatic lens (focal length 75.8 mm) with 1:1 magnification onto the 20 μm entrance slit (height restriction 2 mm) of 2 m focal length Ebert type spectrometer with 651 g/mm reflection grating blazed at 1050 nm. For the line shape measurements the reciprocal dispersion of 0.37 nm/mm is used throughout this experiment. All spectral measurements were performed with an instrumental profile very close to Gaussian form with measured full width at half maximum (FWHM) of 0.0082 nm. Signals from CCD detector (29.1 mm length, 3648 pixels, 1 pixel ≈ 0.00278 nm) are A/D converted, collected and processed by PC.

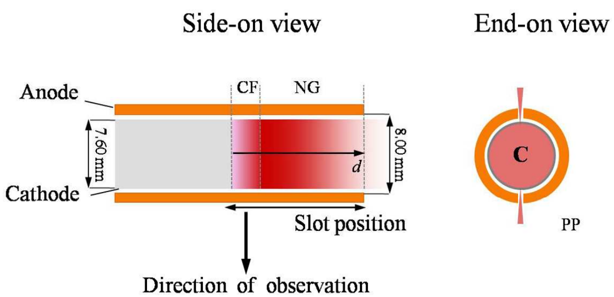

Figure 1. Schematic diagram of the central part of the Grimm GD for side-on and end-on observations. Symbols: CF – cathode fall region, NG – negative glow region, PP – protruding plasma, C – cathode.

3. Electric field effect

Before we discuss the importance of *dc* Stark effect in CF region and the influence of plasma micro-field in NG of GDS let us present the list of studied Ne I lines with relevant spectroscopic data, see table 1.

Table 1. The list of studied Ne I lines. The lines denoted by an asterisk were studied in Ref. 13.

Wavelength (nm)	Lower Level	Upper Level
508.038	$2s^22p^5(^2P^\circ_{3/2})\ 3p\ ^2[^5/_2]$	$2s^22p^5(^2P^\circ_{3/2})\ 5d\ ^2[^7/_2]^\circ$
511.367*	$2s^22p^5(^2P^\circ_{3/2})\ 3p\ ^2[^1/_2]$	$2s^22p^5(^2P^\circ_{1/2})\ 4d'\ ^2[^3/_2]^\circ$
515.443	$2s^22p^5(^2P^\circ_{3/2})\ 3p\ ^2[^3/_2]$	$2s^22p^5(^2P^\circ_{3/2})\ 5d\ ^2[^3/_2]^\circ$
520.886	$2s^22p^5(^2P^\circ_{3/2})\ 3p\ ^2[^3/_2]$	$2s^22p^5(^2P^\circ_{3/2})\ 5d\ ^2[^3/_2]^\circ$
534.109*	$2s^22p^5(^2P^\circ_{3/2})\ 3p\ ^2[^1/_2]$	$2s^22p^5(^2P^\circ_{3/2})\ 4d\ ^2[^1/_2]^\circ$

3.1 *dc* Stark effect

The line shifting of hundred and forty one Ne I lines in *dc* electric field was studied in Ref. 13. Unfortunately, relevant data required for Stark shift evaluation were reported only for two lines, see lines denoted with an asterisk in table 1. Using data from table 2, Stark shifts of non-degenerate upper levels *4d'* (Ne I 511.367 nm) and *4d* (Ne I 534.109 nm) can be evaluated in function of electric field strength F from an approximate formula [13]:

$$\Delta\sigma = \Delta\sigma_1 + \Delta\sigma_2 \qquad F = \sqrt{\frac{\Delta\sigma(A_2 - \Delta\sigma_1)}{A_1 + A_2A_3 - \Delta\sigma_1 A_3}} \quad (1)$$
$$\Delta\sigma_1 = (A_1F^2)/(A_2 - \Delta\sigma_1); \Delta\sigma_2 = A_3F^2$$

where: $\Delta\sigma$ represents the change of wave number of level (cm^{-1}); F – field strength ($kVcm^{-1}$); A_1, A_2, A_3 – algebraic coefficients for studied energy levels taken from table II in Ref. 13. The data required for evaluation of Stark shifts of the 511.367 nm and the 534.109 nm lines in table 2 were used with equation (1) to calculate *dc* Stark shifts. The Stark shift dependence versus electric field strength F for the 511.367 nm and the 534.109 nm lines are given in figures 2a and 2b, respectively.

Table 2. Wavelengths and Stark effect coefficients for studied Ne I lines [13].

Wavelength (nm)	*Comp. No.*	A_1 (kV^{-2})	A_2 (cm^{-1})	A_3 ($cm\ kV^{-2}$)
511.367	1	- 6.111e-02	2.783e 1	- 4.700e-05
	2	- 8.889e-02	5.165e 1	- 1.370e-04
	3	-1.416e-01	4.707e 1	- 6.700e-15
534.109	1	- 7.935e-02	7.138e 1	- 1.470e-04
	2	- 2.330e-01	1.883e 2	- 5.200e-05

Unfortunately, two Ne I lines in figure 2 have small Stark shifts, which with available spectroscopic equipment, can't be used for reliable electric field strength measurements in CF region of neon GDS. Other studied Ne I lines, see table 1, have much larger Stark shifts, but there is no experimental data *i.e.* algebraic coefficients for electric field strength F evaluation.

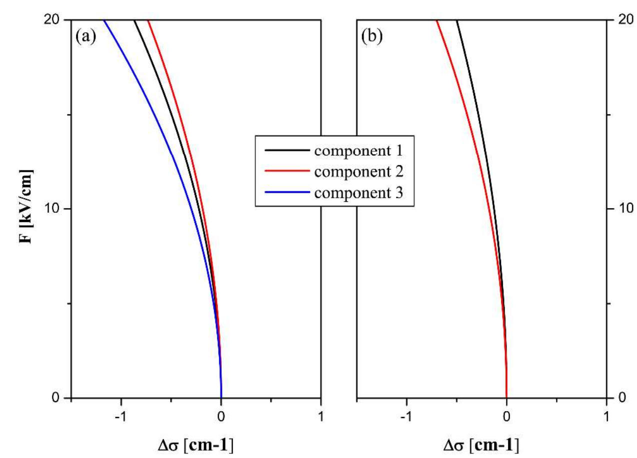

Figure. 2. Behaviour of terms group 4d' and 4d: (a) Ne I 511.367 nm and (b) Ne I 534.109 nm in a Stark field calculated from equation (1) using data from Table 2 in Ref. 13.

Apart from small shift, splitting of the lines 511.367 nm and 534.109 nm to three components or two components, respectively, occur apparently above 10 kV/cm, see figure 2.

The line splitting illustrated by figure 2 can't be detected in CF region of our GDS and the average value of three components (511.367 nm) or two components (534.109 nm) is used for estimation of the field strength. The uncertainty of electric field value calculated by means of different sets of coefficients, see table 2 and figure 2, does not exceed 10%.

3.2 Plasma micro-field effect

To the authors' knowledge Stark broadening parameters of studied lines, see table 1, are not available. An attempt to use simple approximate formula by Freudenstein and Cooper [14] to evaluate Stark broadening parameters of Ne I lines failed [6]. This disables the use of plasma broadening for electron number density N_e diagnostics of NG region of our GDS. Nevertheless, the profiles of Ne I lines from NG region are recorded and their FWHM reported, see table 3 below.

4. Results and discussions

As pointed out already the Ne I line profiles were studied side-on along the axis of discharge through the anode slot as well as end-on perpendicular to the cathode surface. The dc Stark effect was studied side-on only. In its essence for Stark shift study in the CF region of the GDS, the Lo Surdo technique was applied, see *e.g.* Ref. 15. The Stark broadening induced by the plasma micro-field was studied side-on in the NG region. During end-on GDS observations line shapes induced by both effects were observed simultaneously. The overall shape of the spectral line recorded during end-on observation is determined not only by dominant strong line radiation from the NG region, but also by shifted radiation from the CF region. The side-on line shapes from the CF region will be analyzed first.

4.1. CF region and the *dc* Stark effect

In accordance with figure 2(*a*), Ne I 511.368 nm line shifts are toward larger wavelengths (smaller wave numbers). Here, we point out that in figure 3, where the first two spectra recordings (figures 3(*a*) and (b)) depict spectral line shapes at two axial positions of the GDS starting from the vicinity of the cathode surface and the third and fourth one, figure 3(*c*) and *(d)*, show the line shape from NG region and end-on profile, respectively. The detector sensitivity and geometrical factors of the optical system are identical in figures 3(*a*)–(*c*), while for figure 3(*d*) the discharge is set up for end-on observations and the sensitivity scale is incomparable with the preceding three. The same remark is valid for similar figures that follow.

Within recorded spectra, see figure 3(*a*), the line from the discharge protruding through the anode slot, see figure 1, always appears. This line radiation emitted from the discharge protruding outside of the electric field region has unshifted wavelength, with Gaussian line shape and instrumental profile FWHM. This phenomenon was noticed earlier in the study of He I lines in a Grimm discharge of the same type [8]. This unshifted profile appears in all side-on spectra recordings and was successfully used for line shift measurements induced by an electric field. The line shapes along the electric field, see figures 3(*a*) and (*b*), are fitted with Gaussian profiles to determine the peak position as precise as possible within the emitted feature. The width of the fitting profiles is the same along the discharge

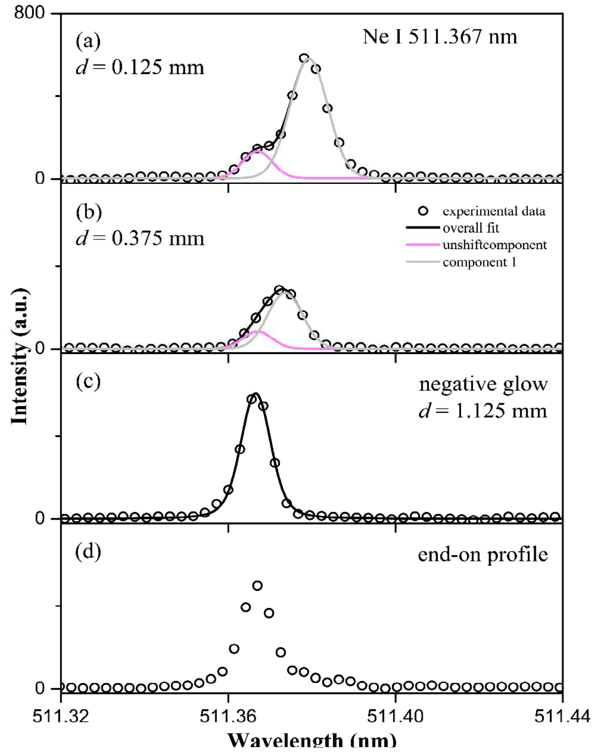

Figure. 3. (Color online) Spectral line shapes and best fits of Ne I 511.367 nm at different axial positions from cathode: (*a*), (*b*) and (*c*); and end-on experimental profile: (*d*) Discharge conditions: iron cathode, $p = 6.5$mbar; $I = 12$ mA; $U = 600$ V.

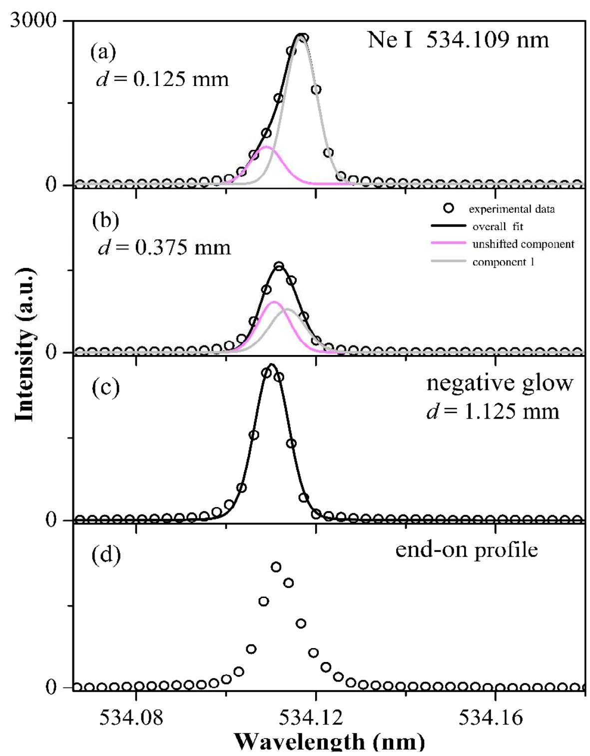

Figure. 4. (Color online) Same as figure 3, but for Ne I 534.109 nm line.

axis: the unshifted component always has an instrumental line shape with Gaussian profile, while the shifted component is supposed to be again Gaussian, but with two instrumental half-widths. The exceptions of the Gaussian fitting procedure are profiles recorded from the NG region, which were fitted with a Voigt function. The end-profile in figure 3(d) and in all similar figures was not fitted and the line width was measured only. The very same methodology applies to the line Ne I 534.109 nm, see figure 4. Using the results of line shift coefficients in table 2 for lines Ne I 511.368 nm and Ne I 534.109 nm and applying equation (1) it is possible to determine the electric field strength distribution in the CF region of the GDS. Since the Stark shift for these lines is small, see Section 3.1, only estimate of maximum electric field strength ~ 15 kV/cm (close to the cathode surface) and CF length of about 0,9 mm is achieved. The voltage across the CF region calculated by integrating the measured field strength distribution *vs.* axial coordinate agrees within 15% with the applied discharge voltage.

For other studied Ne I lines, the dc Stark effect is large, see figures 5–7 and in some cases more than one component appear. Another phenomenon is noticeable from figures 3-7, line intensity closer to the cathode surface are stronger then at further position what is in contradiction with standard picture of CF region.

4.2 NG region and plasma line broadening

In an abnormal glow discharge such as Grimm GDS the largest plasma broadening mainly induced by electron collisions with emitter in the NG region, see *e.g.* [6, 11]. By measuring plasma broadened line profile it is possible to determine *N*e if data of theoretical calculations are available. .

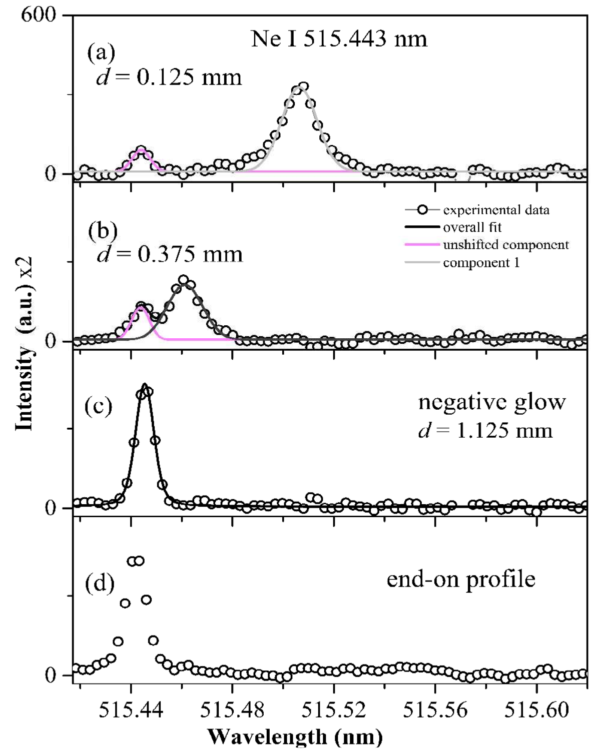

Figure. 6. (Color online) Same as figure 3, but for Ne I 515.443 nm line.

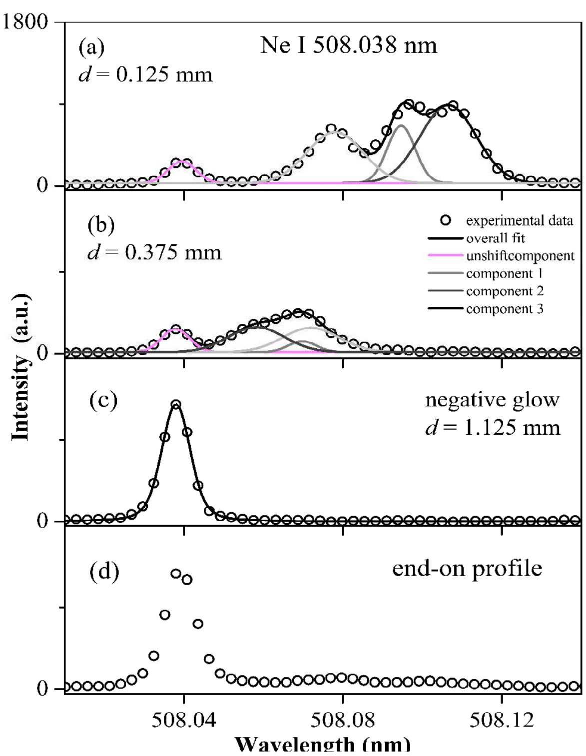

Figure. 5. (Color online) Same as figure 3, but for Ne I 508.038 nm line.

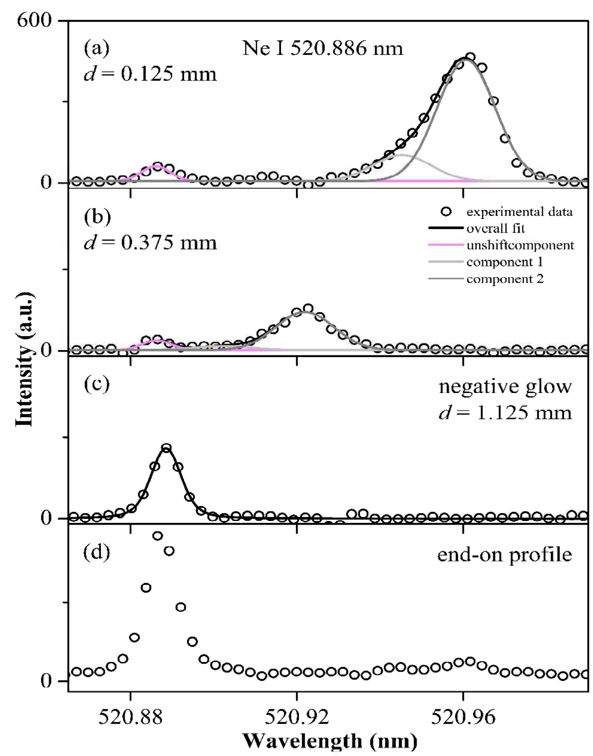

Figure. 7. (Color online) Same as figure 3, but for Ne I 520.886 nm line.

Since this is not the case with studied Ne I lines we performed line shape analysis in NG in the region of largest line broadening, which is usually characterized also with the largest line intensity. This is of importance for the analysis of end-on line profiles.

Thus, to determine side-on Ne I line profile we observed NG side-on and line shape is recorded when largest line width is detected. Line shapes are recorded using same detector sensitivity and the spatial angle of GDS observation. The NG line profiles, see figures 3-7 under (c), are then fitted with Voigt function and the results for the half width are given in table 3.

Table 3. Comparison of measured half widths of side-on measurements w_V from NG region and end-on $w_{end\text{-}on}$.

Wavelength (nm)	w_v (10^{-3} nm)	$w_{end\text{-}on}$ (10^{-3} nm)
508.038	8.5	10
511.367	8.5	10
515.443	8.5	10
520.886	8.5	10
534.109	8.5	11

For all these best fit Voigt profiles the instrumental profile with Gaussian shape with FWHM = 0.0082 nm dominates but nevertheless, Ne I line profiles are always slightly broader indicating plasma broadening is not negligible.

4.3 End-on line shapes

The end-on profiles are asymmetric and sometimes with wavy line wing in wavelength direction of *dc* Stark shift. Therefore, the end-on line profiles were not fitted and only profile FWHM was measured and reported in table 3, see last column. The end-on line widths are systematically larger than from NG and this is an indication that *dc* Stark effect in CF region influences also end-on line width. The wavy nature of the end on line wing may be only result of *dc* Stark effect in CF and its magnitude depends upon discharge conditions in this region of GD.

5. Conclusions

Spectral line profiles of five visible Ne I lines were recorded side-on and end–on from a laboratory made Grimm type glow discharge. The side-on recordings of line shapes offer good prospective for the study of cathode fall and negative glow region of discharge. In the case of line with large *dc* Stark effect in electric field of cathode fall region, the observed line profile is shifted and sometimes split to several components. This line behavior enables electric field measurement in cathode fall region of an abnormal glow discharge. In negative glow region plasma broadening contributes to the line profile resulting in an increase of the line width. The end-on Grimm glow discharge line profile is result of integral radiation coming from cathode surface to the far end of negative glow. The end-on line profile is broadened due to electric field in cathode fall region and plasma broadening in negative glow. In addition wavy features at the far wing in the direction of *dc* Stark shift may appear.

The described line shape phenomena related to dc Stark effect and plasmas line broadening is characteristic for transitions with close dipole allowed perturbing levels. These cases are relatively rare but possible as demonstrated in this work. These lines are from one side potential candidates for low electron density diagnostics and from the other side precautions in sample trace analysis in vicinity of these lines have to be taken.

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