Diagnostics of electric fields in plasma using Stark spectroscopy of krypton and xenon atoms

T Jiang\(^1\), M D Bowden\(^2\), E Wagenaars\(^1\), E Stoffels\(^1\) and G M W Kroesen\(^{1,3}\)

\(^1\) Department of Applied Physics, Eindhoven University of Technology, P O Box 513, 5600 MB Eindhoven, The Netherlands
\(^2\) Department of Physics and Astronomy, The Open University, Milton Keynes, MK7 6AA, UK
E-mail: g.m.w.kroesen@tue.nl

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Abstract. We report the development of laser diagnostic techniques based on Stark spectroscopy of xenon and krypton atoms. Measurements of Stark spectra from the sheath regions of glow discharges were performed. Experimental results were compared to theoretical calculation results by solving the Schrödinger equation for xenon and krypton atoms. Good agreement between the calculation results and experimental results for the excitations from 5s to nf for krypton and 6s’ to nf for xenon was achieved. Furthermore we found that energy levels of higher p states of krypton atoms were clearly shifted in the presence of an electric field.

\(^3\) Author to whom any correspondence should be addressed.
1. Introduction

The electric field is one of the most important discharge parameters. In glow discharges, it is the driving force behind many processes at the boundary of the glow region. Many applications that employ discharges depend on the behaviour at the boundary. Furthermore, the electric field is closely connected with other discharge parameters, such as charge densities, fluxes of electrons and ions, and energy distribution functions. It also serves as input data for plasma discharge modelling. However, although it is necessary to understand the spatial distribution of the electric fields in the discharge, electric fields are still difficult to measure.

One well-known way of measuring the electric field in a plasma is by using an electrical probe. However, the main problem for using probes is the perturbation of the plasma by the probe used. The probe tip must be inside the plasma, where it can interact with charged particles. The probe itself will change the electric field in the very region where one wants to measure.

Another way of measuring electric fields is by detecting the plasma emission. The basic idea of this method is that the energy levels of atoms and molecules in an electric field are modified due to the Stark effect. This effect can cause splitting of degenerate energy levels, some normally forbidden transitions can become partially allowed and energy levels can be shifted. The electric field can thus be measured by monitoring the plasma emission related to these energy levels. However, these passive methods can only give reliable results when the electric field strength is more than a few to few hundreds kV cm$^{-1}$ [1, 2], because the transitions observed are often related to levels with small principal quantum numbers, and these energy levels are not very sensitive to the electric field.

An active method to observe the Stark effect is laser spectroscopy. The high energy photons emitted by a laser can excite the target atoms to highly-excited Rydberg states. Because these states are more sensitive to the electric field, the Stark effect can be observed more easily.

Zimmerman et al [3] used laser spectroscopy to investigate the Stark effect in alkali atoms and compared their calculations to experiments. Kelleher and Saloman [4] extended this study to barium, and subsequent investigations applied this method to investigate Stark effects in krypton (Delsart and Keller [5]), in argon (Brevet et al [6]), and in xenon (Ernst et al [7] and Knight and Wang [8]). However, none of these studies considered the Stark effects in a plasma.
Moore et al [9] were the first to use the Stark effect to measure the electric field in a glow discharge in BCl. A similar method was applied to a helium glow discharge by Dougherty and Lawler [10] and Ganguly [11] and to an argon discharge by Gavrilenko et al [12]. Other techniques [13]–[20] were developed for electric field measurements, such as Booth et al [16] using 2 + 1 photon laser Stark spectroscopy for an rf hydrogen discharge, Choi et al [17] in an argon glow discharge using laser-induced fluorescence (LIF) and laser optogalvanic (LOG) spectroscopy, and Czarnetzki et al [18] using LIF dip spectroscopy for a hydrogen rf discharge.

The aims of this research are to examine the Stark effect in xenon and krypton atoms, determine the suitability of this principle as a diagnostic for electric field measurement in a plasma, and to verify the applicability of the theoretical calculation developed for argon atoms by Gavrilenko et al [12]. To do this, we measured the Stark effect in the sheath of a dc glow discharge of xenon and krypton using LOG spectroscopy. The laser excitations are from metastables to nf states of xenon and krypton atoms which orbital quantum number \( l \geq 3 \). The experimental results were compared to the theoretical calculation results to determine the electric field strength.

The structure of this paper is as follows. Section 2 contains a description of the experimental system and the results. In section 3, the method of calculation is described and a short discussion on the calculated results is given. In section 4, we compare the experimental and calculated results. A brief conclusion is given in section 5.

2. Experiment

LOG spectroscopy in a plasma is based on the detection of laser-induced excitation of atomic or molecular energy levels by monitoring the current through the plasma. In this process, atoms or molecules are excited to high-lying Rydberg energy levels, which are easily ionized by collisions. This reduces the plasma resistance and increases the plasma current. By scanning the excitation wavelength, various excited states can be detected.

The spectroscopic scheme used in this work is shown in figure 1. Laser excitation of xenon atoms was performed from the metastable level 6s\( ^1 \)\( 1/2 \)\( _0 \) to nf Rydberg levels. The fact that lower level 6s\( ^1 \)\( 1/2 \)\( _0 \) state is mixed with the 5d\( ^1 \)\( 3/2 \)\( _0 \) state [15], allows excitation from the metastable state to nf Rydberg states. A similar structure in krypton enables laser excitation from the 5s\( ^3 \)\( 2 \) to nf Rydberg states.

2.1. Experimental arrangement

2.1.1. Experimental set-up for xenon. The experimental arrangement is schematically shown in figure 2. The electrodes were round stainless steel plates with a diameter of 4 cm, placed parallel and separated by 10 mm. Pure xenon gas (\( \geq 99.998\% \)) at 24 mbar pressure was used. A dc voltage was applied between the electrodes.

A tunable dye laser (Lambda Physik LPB3002), pumped by an excimer laser, was operated at approx. 480 nm. The laser pulse duration was about 5 ns and the spectral width was approx. 8 pm. A cylindrical lens was used to focus the laser beam into a sheet-like beam with a thickness of about 0.15 mm and a width of about 4 mm. The laser beam was directed through the sheath of the plasma parallel to the electrode surfaces. The excitation pulse energy was near 1 mJ.

The voltage between the electrodes was monitored with a high pass filter which was connected to a data acquisition system. The data acquisition system sampled the voltage signal.
Figure 1. Partial scheme of energy levels of a xenon atom. The arrow indicates laser excitation.

Figure 2. Experimental apparatus for LOG measurements in a dc glow discharge; BD is a laser beam dump, PD is a photodiode and CL is a cylindrical lens.

as a function of time. Measurements were performed by scanning the dye laser wavelength and measuring the plasma current (LOG signal).

2.1.2. Experimental set-up for krypton. The experimental set-up for krypton is similar to that of xenon. The difference in the laser system was that the pumping laser was replaced by a Nd:YAG laser (Continuum Powerlite 8000) working at 532 nm. The dye laser was operated at wavelengths from 611 to 662 nm and its frequency was doubled to generate radiation with a wavelength between 306 to 330 nm. The pulse energy of the excitation laser was about 1 mJ. The vacuum chamber was filled with 99.99% pure krypton gas at a pressure of 7 mbar.
2.2. Experimental results

2.2.1. Experimental results for xenon. Figure 3 shows the LOG spectra obtained in a xenon glow discharge: the sets of spectra resulting from excitation of the 6s' state to 10f and 13f in xenon at different distances from the cathode. The main features of the experimental spectra in figure 3 are:

1. When the laser beam is far from the cathode (d > 2.1 mm) the electric field is low, approaching zero. The LOG spectrum shows a single peak which corresponds to the 6s'[1/2]0 to nf[3/2]1 transition.
2. In the vicinity of the cathode, where the electric field is strongest, the spectra show many peaks, because the Stark effect restructures the energy levels.
3. The number of spectra peaks increases with increasing principal quantum number n (also see the experimental spectra in figures 7 and 12), as expected.
4. The intensity of the LOG signal near the cathode is much larger than far from the cathode, because the charges produced by laser excitation can reach the cathode more easily from there.
5. In the spectra with many peaks, the central peaks are narrower than the outer ones. This is related to the spatial profile of the laser beam. Further discussion of this feature is given in section 5.

2.2.2. Experimental results for krypton. Figure 4 shows the LOG spectra obtained in a krypton glow discharge: (a) is the set of spectra resulting from excitation from the 5s state to 8f and (b) corresponds to excitation to 10f. Both are obtained at different distances from the cathode. Most features of the experimental spectra are similar to the xenon features. However, unlike xenon, the LOG spectra of krypton for zero electric field show two peaks corresponding to the transitions from 5s[3/2]2 (4d[3/2]2) to nf[3/2]2,3 and nf[5/2]1,2.
Figure 4. The LOG spectra obtained in a krypton discharge; (a) and (b) result from excitations from the 5\(s\) state to 8\(f\) and 10\(f\). The different spectra were measured at different positions from the cathode.

3. Theoretical calculation

Stark effect calculations have been discussed in detail in several references [4, 6, 8, 12]. We have performed similar calculations in order to be able to compare them to experimental data. In summary the calculation was done as follows:

1. The \(jK\) coupling scheme was applied for the Rydberg states of krypton and xenon atoms [21, 22]. Using this scheme, energy levels can be described in the form \(|nl(K)\rangle\). A suitable basis set of states was chosen for solving the Schrödinger equation. The corresponding zero-field energies were the diagonal elements of the Hamiltonian \(H_0\). Some of the zero-field energy data was found in references [23]–[26], the remaining data was calculated using the method of Brevet et al [6].

2. The matrix elements of the off-diagonal terms, originating from the Stark Hamiltonian \(H_{\text{Stark}} = -eFz\), were calculated for each value of the electric field \(F\) using a hydrogen-like approximation.

3. The total Hamiltonian \(H = H_0 + H_{\text{Stark}}\) was diagonalized for each \(F\) and \(M\) (the total magnetic quantum number).

4. The energies of the levels in an electric field were the eigenvalues of the Hamiltonian \(H\). The corresponding (relative) excitation intensities were calculated using the eigenfunctions of \(H\). The transition intensities were normalized to the strongest transition at zero electric field.

5. The spectrum which was used to compare to the experimental results was a summation of spectra calculated for each value of \(M\).

We know that the levels with large principal quantum number \(n\) and large \(l\) are very closely spaced. Hence, the Stark coupling of these energy levels has to be considered in the calculation. For instance, in the calculation of the Stark effect in krypton 11\(f\), the zero-field matrix should not only include the energy levels of 11\(f\), but also other levels like 11\(g\), 11\(h\), ..., 11\(l_{n-1}\).
Furthermore, for calculating Stark effects in xenon $13f$ levels, besides the energy levels with orbital quantum number $l \geq 3$, the zero-field matrix also needs to include other adjacent levels, such as $16,17,18s$ $16,17p$, $16,17d$. Figure 5 shows the calculation results in the form of Stark maps, (a) for krypton $11f$ and (b) for xenon $13f$ for various magnitudes of the electric field. The Stark map of krypton $11f$ shows a splitting of the energy levels of $11f$ and of the degenerate levels $11g$, $11h$ and $11l_{n-1}$. The dependence of the $11f$ energy levels on the electric field is quadratic, in contrast to the linear response of the other levels such as $11g$, $11h$, ... etc. This different behaviour can be attributed to the fact that levels with $l > 3$ have almost zero quantum defects (no electron orbit penetrates the core of the atom), but for $11f$ the quantum defect is $0.16$. From the Stark maps in figure 5(b), it is evident that the complexity increases in high electric fields. We can conclude that for the principal quantum number $n \geq 13$, some energy levels of $s$, $p$ and $d$ are closer to the energy levels of $f$, ... , $l_{n-1}$, so the coupling between these energy levels with the $nf$ levels cannot be ignored; hence the Stark components become more complex.

Figure 6 shows theoretical spectra for various magnitudes of the electric field. The distance between the peaks increases with increasing electric field. The calculation shows that the energy level structure of krypton and xenon atoms consist of several equidistant Stark components in high electric fields, and the number of these Stark components is $N = n - 3$, (see figures 7 and 12). Similar results in argon were observed and explained by Gavrilenko et al [12].

4. Comparison of experiment to theoretical calculation

4.1. Comparison for xenon

Figures 7 and 8 show the comparison of the results of the experiments to the theoretical calculations. The following features can be deduced:

1. There is good agreement of peak position for both large $n$ and small $n$. Only for $10f$, peak number 7, is there a discrepancy in peak position between experiments and calculations,
which is probably caused by (minor) inaccuracies in the methods to derive the transition intensities from the calculations.

2. As expected, there are more peaks for larger \( n \). The number of peaks in the experimental spectra is in good agreement with the calculation data for large \( n \) and in poorer agreement for small \( n \) in high field.

3. The calculation is less successful at reproducing the (relative) intensity distribution for small \( n \), but better agreement is obtained for larger \( n \). This is probably due to the relatively simple calculation procedure used to calculate transition intensities from Stark maps. Nevertheless, for the determination of the measured electric field strength using the calculation, only the peak position is needed and the calculation method can accurately describe these peak positions.

4. The Stark manifolds for large \( n \) are more sensitive to the electric field than the ones for smaller \( n \).

5. The peripheral peaks in the experiments are wider than the central peaks. This can be explained by the gradient of the electric field within the cross-section of the laser beam.

6. The experimental spectrum for the 12\( f \) manifold shows an additional (strong) peak around 479.387 nm, superimposed on the Stark manifold. This peak corresponds to the transition \( 6s[3/2]_2 \) to \( 7p[1/2]_1 \). Since LOG spectroscopy detects all transitions in a discharge, additional peaks can be observed experimentally, but these transitions are not included in the calculation.

Because the laser beam width full-width half-maximum (FWHM) is about 0.15 mm and the sheath is only about 1–2 mm, the electric field in the cross-section of the laser beam was inhomogeneous, so the influence of the gradient of the electric field across the laser beam has to be considered. We assume that the intensity distribution of the laser beam in a direction parallel to the electric field is Gaussian, and in the vertical direction is constant. With this simple model,
Figure 7. Experimental LOG spectra compared to calculated spectra for xenon 9, 10, 12 and 13f excitation from 6s’[1/2]0 in the high electric field. Red lines are experimental results and black lines are calculation results.

the corrected theoretical spectra \( I_c(E, \lambda) \) can be:

\[
I_c(E, \lambda) \propto \sum_{\Delta x = -0.075}^{0.075} G \left( \frac{\sqrt{2 \ln 2 \Delta x}}{0.075} \right) I(E + \Delta E, \lambda). \tag{1}
\]

Here, \( I(E + \Delta E, \lambda) = I(0, \lambda) \) when \( E + \Delta E \leq 0 \), and \( \Delta E = k\Delta x \), where \( E \) is electric field strength, \( G(x) \) is the Gaussian distribution, and \( I(E, \lambda) \) is the spectrum without integrating over the electric field distribution of the laser beam. \( k \) is the coefficient of the linear fit of the electric field in the sheath. By integrating over the electric field distribution in the laser beam, the corrected theoretical LOG spectra are obtained and they are presented in the figures 7, 8, 11 and 12.

Figure 9(a) is an uncorrected calculated spectrum compared to an experimental spectrum. The peak positions match well, but the relative intensities of the peaks do not agree. Figure 9(b) shows a corrected calculation compared to an experimental spectrum. It is clear in this figure that a corrected calculation spectrum does reproduce the experimental data more reliably. There is still some difference in the intensities of corrected LOG and the experimental result, which may
be because the laser beam cross-section is not modelled sufficiently well or due to inaccuracies in the calculation method used to calculate transition intensities.

The electric field strength can be determined by directly matching the peak positions of both spectra in the experiment and in the calculation for larger fields ($2000–4000$ V cm$^{-1}$). A very good accuracy, with errors less than $\pm 25$ V cm$^{-1}$ for the excitation to $13f$ can be achieved for these fields. The error increases to $100$ V cm$^{-1}$ at lower fields because the relative LOG signal is smaller and peaks become difficult to distinguish. The accuracy of the method becomes inadequate.

Figure 8. Comparison of experiment and calculation (a) for $13f$ and (b) for $10f$. The red lines are the spectra of the experiments, and the black lines are the theoretical spectra.

Figure 9. Comparison of the uncorrected and corrected calculation spectra to experiment. (a) is the uncorrected calculation (black line), compared to the experimental data (red line) for xenon $10f$ and (b) is the corrected calculation (black line) compared to experiments.
Figure 10. The spatial distribution of the electric field measured in the vicinity of the cathode in a xenon discharge using the results of excitation to 13\(f\).

Figure 11. The comparison of experiment and calculation for krypton (a) for 8\(f\) and (b) for 12\(f\) at different positions from the cathode. The red lines are the spectra of the experiments, and the black lines are the theoretical spectra.

Figure 10 shows the spatial distribution of the electric field measured in the vicinity of the cathode. We can see that the electric field in the sheath is almost linear, as we expect for this kind of discharge. The thickness of the sheath in our case was about 2.1 ± 0.2 mm. By integrating the electric field over the sheath, we can obtain a potential drop over the sheath of 325 ± 20 V. This is about 90% of the voltage of 345 ± 10 V that was applied across the discharge.

4.2. Comparison for krypton

In this subsection, we will present the Stark effect data for krypton atoms. Figures 11 and 12 show a comparison of the results of experiments and theoretical calculations. Similar features as described in subsection 4.1. can be found in these figures: the peaks corresponding to large \(n\) are more sensitive to the electric field than the ones with smaller \(n\). The agreement for high
Figure 12. The comparison of experiment and calculation for krypton, (a) for $9f$, and (b) for $11f$. Both experimental results are obtained at 0.1 mm from the cathode; the calculation results are: $E = 3700$ V cm$^{-1}$ for $9f$ and $E = 3685$ V cm$^{-1}$ for $11f$.

Figure 13. The spatial distribution of the electric field measured in the vicinity of the cathode, using the results of excitation to krypton $12f$.

field and larger $n$ is best, and agreement is poorer at lower fields, even for large $n$. It should be noted that in the experimental spectrum of the $11f$ manifold, an additional peak at 312.34 nm is superimposed on the $11f$ transitions. The position of this peak did not change significantly with electric field, indicating that it is not part of the $11f$ manifold. However, it does obscure peaks number 7 and 8 of the Stark manifold in the experiments.

In zero field conditions there are two fine-structure double transitions, from $5s[3/2]_2$ to $nf[3/2]_{1,2}$ and $nf[5/2]_{1,3}$, and the distance between these two peaks changes in low field (0–800 V cm$^{-1}$). This makes it easier to measure the electric fields at low values, because exact calibration of the peak position is not necessary, as is the case for xenon.

The same method as used for xenon was applied to determine the electric field strength distribution in the sheath of a krypton glow discharge. Figure 13 shows the spatial distribution...
of the electric field measured in the vicinity of the cathode. By integrating the electric field over the sheath, we obtain a potential drop over the sheath of the krypton discharge of 215 V. Similar to xenon, this is about 90% of the voltage of 240 ± 10 V that was applied across the discharge gap.

A remarkable shift of the energy levels of higher $p$ states of krypton in the electric field was demonstrated (see figure 14). The relatively larger LOG signal in the case of $p$ state excitation is interesting from a diagnostics point of view. For some plasma conditions, these $p$-states may be more suitable for observing Stark effects and determining electric fields than $f$ states.

5. Conclusion

A spectroscopic method for the measurement of the electric field in a glow discharge in xenon and krypton was demonstrated. The results show that it is possible to measure Stark effects in the sheath of xenon and krypton glow discharges. Measurement of the electric field in sheaths can be performed using the method of comparing the Stark effect measurements to theoretical calculations. Best accuracy could be obtained for high fields and large principal quantum numbers $n$, since these levels are most sensitive to electric field.

In addition to these $f$ state excitations, we also observed Stark effects of $p$ states, which may be promising for electric field measurements. Further studies of these states are planned.

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