Laser spectroscopic electric field measurement in krypton

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Abstract. A laser spectroscopic method for sensitive electric field measurements using krypton has been developed. The Stark effect of high Rydberg states of the krypton autoionizing series can be measured by a technique called fluorescence dip spectroscopy (FDS) with high spatial and temporal resolution. Calibration measurements have been performed in a reference cell with known electric field and they agree very well with numerical solutions of Schrödinger’s equation for \( jl \)-coupled states. The application of this method has been demonstrated in the sheath region of a capacitively coupled radiofrequency (RF) discharge. The laser spectroscopic method allows us to add krypton as a small admixture to various low temperature plasmas.

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1. Introduction

Electric fields play a key role for the motion and spatial distribution of charged particles in low temperature plasmas [1]. Especially in the sheaths of capacitively coupled RF discharges, electric fields induce strong heating and transport processes. The nonlinear behaviour in this region can excite collective resonances and wave phenomena. For the development of a consistent model of the sheath and its dynamic interaction with the plasma bulk, sensitive space and phase resolved electric field measurement methods are required. These methods should be independent of existing models of the investigated processes and non-invasive, as their influence on the discharge physics should be negligible.

Laser spectroscopic measurement methods for electric fields in plasmas based on the Stark effect of molecules and neutral atoms have already been developed. Some examples are: BCl [2], NaK [3], CS [4], helium [5]–[7], hydrogen [8, 9], argon [10]–[13] and recently krypton and xenon [14, 15]. For discharges in those gases, one would prefer to use the respective gases also for the electric field measurements. However, it would be problematic to add molecular gases like hydrogen to another discharge. Due to the relative low dissociation degree in low temperature, low power plasmas, a relative large amount of gas is needed in order to get a sufficient neutral atom density. Furthermore, the vibrational and rotational levels in molecular gases can absorb a substantial amount of electron energy by inelastic collisions and thereby the electron energy distribution function can be strongly affected. On the other hand, rare gases can be admixed in relative small amounts as atomic probes for the electric field measurements. Calibration can easily be made without a plasma if the excitation occurs from the electronic ground state. In helium and argon, excitation out of the ground state can only be done by using vacuum UV wavelengths, thus for practical reasons it is necessary to excite out of the metastable state. In helium, a sensitivity of 50 V cm$^{-1}$ has been reached [7]. Argon provides a much higher sensitivity of 3 V cm$^{-1}$ [12]. Unlike atoms in the ground state, metastables have to be created in a discharge and can also be quenched easily at higher pressures. In contrast to xenon, the excitation wavelength of krypton is close to that of atomic hydrogen (205 nm), which enabled us to use our existing laser
system. Former investigations of the Stark effect in krypton have been performed at relatively high field strengths (few 100 to several 1000 V cm\(^{-1}\)) [14, 16] by means of laser optogalvanic spectroscopy, which limits the measurement to a line-integrated one. Furthermore, it seems not to be applicable to RF discharges.

Here, we describe the development of a more sensitive, purely optical method using krypton as a probe gas. The aim is to study the dynamics in the sheaths of radiofrequency discharges. Therefore, electric field distributions have to be measured with high spatial and temporal resolution. Fluorescence dip spectroscopy (FDS) fulfils these requirements when a pulsed laser system is used and the fluorescence is imaged onto a CCD camera. Due to the complex atomic structure, the basic data of the Stark effect have to be obtained at known electric field strengths before it can be applied as a technique for electric field measurement. In addition to the reference measurements under defined conditions, the Stark effect is calculated numerically. These calculations require, inevitably, certain assumptions and simplifications. However, combining experiment and simulation allows a verification and provides a deeper insight in the underlying relevant physical mechanisms.

In the next section, the theory of the Stark effect and the algorithm of the numerical calculation are described. Then, the spectroscopic scheme and the laser spectroscopic technique are discussed. Section 4 gives some information about the experimental set-up of the laser system, the calibration cell and the modified Gaseous Electronics Conference (GEC) reference cell. The main part of the study is presented in section 5, where detailed investigations of the Stark effect in krypton are compared to the theoretical results. In section 6, the applicability of the novel scheme in the sheath of a capacitively coupled RF plasma discharge (CCP) plasma is demonstrated. Finally, we draw conclusions and give a short outlook.

2. Numerical calculation of the Stark effect

The theoretical calculation of the Stark effect in krypton, that is described in the following section, is based on the calculation for argon atoms developed by Gavrilenko et al [11]. For the exact computation of the Stark effect, Schrödinger’s equation for the perturbed system with the Hamiltonian \( \hat{H} = \hat{H}^0 + \hat{H}^S \) has to be solved, where \( \hat{H}^0 \) is the Hamiltonian of the unperturbed system and \( \hat{H}^S = e\mathbf{r} \cdot \mathbf{E} = eE_z \) is the perturbation by the electric field. Furthermore, the solution of the unperturbed system is known:

\[
\hat{H}^0 |\varphi_n\rangle = \epsilon_n^0 |\varphi_n\rangle. \tag{1}
\]

For the solution of the perturbed system, we use an expression in which we express it as a linear combination of the eigenstates of the unperturbed system:

\[
|\psi_i\rangle = \sum_{n=1}^{N} a_{in} |\varphi_n\rangle. \tag{2}
\]

This leads us to the following eigenvalue equation, which can also be expressed in terms of a matrix equation:

\[
\sum_{n=1}^{N} a_{in} (\epsilon_n^0 \delta_{mn} + \langle \varphi_m | \hat{H}^S | \varphi_n \rangle) = \epsilon_i a_{im}, \tag{3}
\]
where $H_{mn}^S = \langle \varphi_m | H^S | \varphi_n \rangle$ is the matrix element of the unperturbed states with the perturbation operator. From the diagonalization of the matrix in (4), one obtains the new eigenvalues $\varepsilon_n$, describing the energy level shifts, and the coefficients $a_{in}$, quantifying the mixture of the states. For the calculation of the matrix elements $H_{mn}^S$, we have to consider the $ji$-coupling scheme in heavy rare gases [17]. When an electron from the closed outer shell is excited, the spin of the remaining, unpaired electron can have two possible orientations relative to its orbital angular momentum: $j_c = l_0 + s$. This strongest interaction leads to two separated ionization limits (In krypton, the difference is: $\Delta \tilde{v} = 5370 \text{ cm}^{-1}$). The second strongest interaction is the spin-independent part of the Coulomb interaction between the excited electron and the core electrons. The angular momentum of the core $j_c$ couples to the orbital angular momentum of the excited electron: $K = j_c + l$. Finally, there is a weak Coulomb-exchange and spin–orbit interaction: $J = K + s$, where $s$ is the spin of the excited electron. $J$ can have $(2J + 1)$ possible orientations relative to the quantization axis, expressed by the magnetic quantum number $M$, where $-J \leq M \leq J$. Energy levels are denoted by the Racah notation $nl'[K]_J$ if $j_c = 1/2$ (primed system) and $nl[K]_J$ if $j_c = 3/2$ (unprimed system).

Applying the Wigner–Eckart theorem and decoupling the angular momenta using $6j$ symbols [17], one can derive the matrix element for the component of the dipole operator $D_q$. The special case which is important here is $D_{q=0} = z$. When the atomic states are being identified by the set of quantum numbers $|\psi\rangle = |nl_jKsJM\rangle$, one can express the dipole matrix elements as follows:

$$
|\psi\rangle D_q |\psi\rangle = (-1)^J - M + K + s + j_c + K'\begin{pmatrix} J & 1 & J' \\ M & q & M' \end{pmatrix} \times \delta_{ss'} \sqrt{(2J + 1)(2J' + 1)} \begin{pmatrix} K & J & s \\ J' & K' & 1 \end{pmatrix} \times \delta_{j'j_c} \sqrt{(2K + 1)(2K' + 1)} \begin{pmatrix} l & K & j_c \\ K' & l' & 1 \end{pmatrix} \langle nl||D||n'\rangle,
$$

where $\langle nl||D||n'\rangle$ denotes the reduced matrix element, which can be fractionized into a geometrical and a radial factor

$$
\langle nl||D||n'\rangle = \left\{ \begin{array}{ll}
-\sqrt{I + 1} \langle nl|r|n', l + 1 \rangle, & l' = l + 1, \\
\sqrt{I} \langle nl|r|n', l - 1 \rangle, & l' = l - 1.
\end{array} \right.
$$

Although for high $l$-values, the hydrogen-like formula $\langle n, l + 1|r|nl \rangle = 3/2a_0 n \sqrt{n^2 - (l + 1)^2}$, where $a_0$ is the Bohr radius, is a good approximation [11, 18], the general case can be calculated by a 4-point-Lagrange interpolation [19] of the tabulated values in [20].

For allowed dipole transitions, the matrix element has to have a nonzero value. From this condition, one can obtain the following selection rules for the Stark effect (electric field in $z$-direction) and for excitation with parallel to the $z$-axis linearly polarized light, respectively

$$
\Delta l = \pm 1.
$$
Figure 1. Excitation scheme in krypton. The intermediate state $5p'[3/2]_2$ is excited by two photons out of the ground state. The fluorescence light from the transition to $5s'[1/2]_1$ is depleted when the second step excitation is resonant with a (Stark-split) Rydberg state.

$$\Delta j_c = 0.$$  \hfill (8)

$$\Delta K = 0, \pm 1,$$  \hfill (9)

$$\Delta s = 0,$$  \hfill (10)

$$\Delta J = \begin{cases} 
\pm 1, & \text{if } M = 0 \\
0, \pm 1 & \text{if } M \neq 0
\end{cases} \quad (0 \leftrightarrow 0) \text{ forbidden},$$  \hfill (11)

$$\Delta M = 0.$$  \hfill (12)

From the Russell–Saunders (LS)-coupled ground state $4p^6 1S_0$ in krypton, the $5p'[3/2]_2$ intermediate state can be accessed by a two photon excitation, involving the $ns'[1/2]_1$ ($n \geq 5$) and $nd'[3/2]_1$ ($n \geq 4$) intermediate states \cite{21}. When the excitation is done by a single, linearly polarized laser beam, the magnetic quantum number $M = 0$ of the ground state will be maintained \cite{22}. Due to the selection rules only the $ns'[1/2]_1$, $nd'[3/2]_{1,2}$ and $nd'[5/2]_{2,3}$ Rydberg states can be accessed in the case of zero electric field (figure 1). Line strengths are proportional to the squares of the absolute values of the corresponding transition matrix elements. Thus in the case of the $nd'$ levels the relative line strengths of the four fine structure components can be
Table 1. Relative line strengths of the \( nd' \)-levels when excited from \( 5p'[3/2]_2 \) \((M = 0)\).

| Series  | \( \Delta M = 0 \) | \( \Delta M = \pm 1 \) |
|---------|-------------------|-------------------|
| \( nd'[3/2]_1 \) | 1/63              | 1/144             |
| \( nd'[3/2]_2 \) | 0                 | 3/16              |
| \( nd'[5/2]_1 \) | 0                 | 1/8               |
| \( nd'[5/2]_2 \) | 1                 | 1                 |

easily calculated, normalized to the strongest transition (table 1). The ratios of the line strengths depend on the change of the magnetic quantum number, thus on the polarization of the laser beams. The correlation of the polarization with the spectra of \( nd' \) levels will be discussed later in subsection 5.2.4.

For the computation of the Stark effect, the exact knowledge of the energies \( \varepsilon_n \) of the unperturbed states is essential. Rydberg states with large principal quantum numbers \( n \) can be approximated very well by a quantum defect formula: From the viewpoint of the excited electron that is predominantly far away from the core, the nucleus with charge \( Ze \) is screened by \((Z - 1)\) electrons, resulting in an effective charge \( q \approx e \) ‘felt’ by the electron. Thus the Rydberg formula can be used \([23]\)

\[
\varepsilon_{nlKJ} = \varepsilon_i - \frac{R}{(n^*)^2} = \varepsilon_i - \frac{R}{(n - \delta_{lKJ})^2}.
\]

(13)

Here, \( n^* \) denotes the effective quantum number and \( \delta_{lKJ} \) the quantum defect, which depends primarily on the orbital angular momentum quantum number \( l \), since for small \( l \)-values the shape of the electron’s orbit becomes more elliptical, with a higher residence probability near the nucleus. On the other hand, quantum defects for \( l \geq 3 \) can be neglected for our purposes. Values for quantum defects could be experimentally measured for both \( ns'[1/2]_1 \) and \( nd'[5/2]_3 \) Rydberg series, others were taken or derived from the literature. The values used in the calculation are listed in table 2.

Of course, the calculation can only include a finite number of states \( N \), corresponding to a \((N \times N)\)-matrix in (4). The interaction of two different states decreases with their energetic distance; therefore, we can consider a limited number of energetic proximate states, with a similar effective principal quantum number \( n^* \). In this study, the \( nd' \) and \( np' \) levels are of prime interest due to their visibility in the zero and nonzero field case, respectively. Thus the set of states listed in table 3 has been used for the calculation.

When the matrix for each electric field strength has been constructed from the energy values given by (13), and the matrix elements (5), the *Jacobi method* \([25]\) has been applied for the diagonalization. The results of the calculations are shown and discussed in connection with the experimental results in section 5.

3. Spectroscopic scheme

For the spectroscopic investigation of the Stark splitting of Rydberg states of atoms which are usually in the ground state, one has to master two basic challenges: the first is to overcome
Table 2. Quantum defects (dimensionless numbers) used in the numerical calculation.

| Series          | δ_{lKJ} | References |
|-----------------|---------|------------|
| ns'[1/2]_{l=0}  | 3.104   | [16]       |
| ns'[1/2]_{l=1}  | 3.095   | This work^a |
| np'[1/2]_{l=0}  | 2.55    | This work^b |
| np'[1/2]_{l=1}  | 2.61    | This work^b |
| np'[3/2]_{l=1}  | 2.62    | This work^b |
| np'[3/2]_{l=2}  | 2.605   | This work^b |
| nd'[3/2]_{l=1}  | 1.21    | [25]^c     |
| nd'[3/2]_{l=2}  | 1.36    | [16]       |
| nd'[5/2]_{l=2}  | 1.36    | [16]       |
| nd'[5/2]_{l=3}  | 1.335   | This work^a |
| nl'[K]_{J, l ≥ 3}| 0       | -          |

^aQuantum defect formula fit at \(E = 0\) (section 5).
^bFitted values at \(E \neq 0\).
^cValid for \(n = 17 \ldots 25\).

Table 3. The set of states used in the numerical calculation of the Stark shift of the \(np'\), \(nd'\) levels and the linear Stark effect. The integer \(\nu\) has to be chosen in order to incorporate particular states into the calculation. For instance, if the Stark shifts of the 19\(d'\) and the 20\(p'\) states are of interest, one has to choose \(\nu = 18\).

| \(n\) | \(l\) | \(\delta_{lKJ}\) | \(\nu^{*}\) |
|-------|-------|-----------------|-------------|
| \(\nu\) | \(f', g', \ldots\) | 0.0 | \(\nu\) |
| \(\nu + 3\) | \(s'\) | 3.1 | \(\nu - 0.1\) |
| \(\nu + 1\) | \(d'\) | 1.3 | \(\nu - 0.3\) |
| \(\nu + 2\) | \(p'\) | 2.6 | \(\nu - 0.6\) |
| \(\nu - 1\) | \(f', g', \ldots\) | 0.0 | \(\nu - 1.0\) |
| \(\nu + 2\) | \(s'\) | 3.1 | \(\nu - 1.1\) |

the huge energy difference between the ground state and the Rydberg states; the second is the detection of the transition, because fluorescence photons emitted from the Rydberg states are very hard to detect due to their long lifetime and probability for autoionization in the case of \(j_c = 1/2\) (primed system).

Therefore, a technique called FDS is applied that has been developed initially for measurements in hydrogen [9]. It is based on a two-photon (UV) excitation into a short-living intermediate state from which the strong fluorescence in the visible wavelength range can easily be detected. High Rydberg states can be excited from this intermediate state by a one-photon excitation in the visible to NIR wavelength range. When the second excitation occurs instantaneously with the two-photon step, the population density of the intermediate level is being depleted before it can decay radiatively. Thus the fluorescence signal is lowered. Spectra are taken at a fixed UV wavelength by scanning the fundamental wavelength \(\lambda_2\) of the second laser, while the fluorescence from the intermediate state is observed. When the excitation is in resonance with a Rydberg state, one observes a dip in the fluorescence intensity. The quantity recorded in the
spectra is the relative decrease of fluorescence: $\delta F \equiv (I_F^0 - I_F^F)/I_F^0$. If the saturation phenomena in the second step is negligible, $\delta F$ is proportional to the excitation cross-section $\sigma(\omega_2)$ and the energy $W_2$ of the second laser, but independent of the population density of the intermediate level:

$$\delta F(\omega_2) = \sigma(\omega_2) \frac{W_2}{\hbar \omega_2} g(\Delta \omega).$$

(14)

The cross-section is related to the matrix element: $\sigma = e^2 \omega_2 |\langle \psi_R | r \cdot e | \psi_b \rangle|^2 / (2c\epsilon_0 \hbar)$.

The excitation scheme in krypton is shown in figure 1. It is based on the two-photon absorption laser-induced fluorescence spectroscopy in krypton which has initially been developed for sensitive measurements of absolute neutral densities [21]. The two-photon excitation is carried out from the $4p^6 1S_0$ ground state to the $5p^4 [3/2]_2 (\tau \approx 34\,\text{ns})$ intermediate state by the first laser pulse at a wavelength of 204.13 nm. Fluorescence to $5s^2 [1/2]_1$ at $\lambda_F = 826.3\,\text{nm}$ is being detected.

For the FDS, one excites to the Rydberg states of the primed system by a second laser pulse. The sensitivity for electric fields increases with the principal quantum number $n$. From [16], one can estimate a sensitivity of approximately 1000 V cm for the $15d'$ levels. Thus lower states where $n < 15$ are not well suited for our purpose. Therefore an interval of $491.5\,\text{nm} \leq \lambda_{\text{exc}} \leq 506.2\,\text{nm}$ for the second step excitation can be specified.

4. Experimental set-up

There are two set-ups connected with the dye laser system. The first one is a calibration cell for the investigation of the Stark effect at known electric fields and the second one is for space and time resolved electric field measurements in a modified GEC reference cell [26].

4.1. Laser system

The experimental set-up is shown in figure 2. The frequency-doubled output beam (532 nm) of a seeded Nd:YAG laser (Continuum, 9020), having a pulse width of 7 ns and pulse energy of 900 mJ at a repetition rate of 20 Hz, is split by a ratio of 2:1 to pump two tunable double-grating dye lasers (Radiant Dyes, Narrow Scan). The first one emits a fundamental wavelength of 612.4 nm, which is frequency-tripled for the two-photon excitation (204.13 nm, 3 mJ). The oscillator of this laser has been modified compared to the original design for improving the spectral purity and stability. A $\lambda/2$ plate is inserted between the dye cell and the prism beam expander and an output mirror of reflectivity $R = 30\%$ instead of 10% is used.

The fundamental of the second dye laser (615–645 nm) is focused into a tube filled with 10 bar H$_2$ gas, converting it into the desired wavelength range of 490–509 nm by stimulated anti-Stokes Raman scattering (SARS) at approximately 150 $\mu$J. A filter and dielectric mirrors block both the fundamental and Stokes component. For more sensitive measurements of changes in the fluorescence signal, an electro-mechanical shutter enables to switch the second laser beam on and off, so that drifts of the intensity (on the timescale of seconds) can be compensated. Both beams can be guided collinearly into either the calibration cell or the GEC reference cell. The laser system was calibrated by optogalvanic spectroscopy of neon lines and the absolute reproducibility of the frequency is around 0.3 cm$^{-1}$.
4.2. Calibration cell

The calibration cell is a vacuum chamber filled with krypton, where measurements with known electric field strength are performed. It contains a two parallel-plate electrodes structure ($d = 9.8$ mm) providing a homogeneous DC electric field up to $3 \text{kV cm}^{-1}$ without electrical breakdown. The laser beams pass the cell in the middle between the electrodes through quartz windows on opposite sides. The fluorescence light can leave the chamber perpendicular to the beams through a standard BK7-window and is detected by a red-sensitive photomultiplier (Hamamatsu, R943-02). An interference filter blocks scattered light from the visible laser beam.

4.3. Set-up with GEC reference cell

For phase and space resolved measurements in the sheath of a CCP, the calibration cell was replaced by a modified GEC reference cell (a standard hybride capacitively/inductively coupled plasma source introduced in 1995 [26]). The modification was a replacement of the metal cylinder surrounding the antenna (for inductive coupling) and the dielectric window by a monolithic quartz housing (figure 3). Here, only the lower electrode is driven and the whole chamber acts as grounded electrode. Therefore, the CCP is highly asymmetric and the entire voltage drops across the sheath at the powered electrode. The voltage is measured by a high voltage probe.

The Q-switch of the Nd:YAG pump laser has been synchronized with the RF generator ($f = 13.56$ MHz) via frequency divider ($f_{\text{out}} = 20$ Hz) and a delay generator (Stanford, DG535). The variable delay allowed us to measure at different phases within the RF cycle. The gate of an image intensified CCD camera (Princeton Instruments) was synchronized with the laser pulse passing the GEC cell through quartz windows. The unfocused UV laser beam covers approximately 2 mm of the sheath height, and therefore excites only a fraction of $10^{-4}$ of the atoms, thus saturation of the two photon excitation is negligible. The imaging system provides a spatial resolution of about $50 \mu$m. The fluorescence light was accumulated on the CCD for
Figure 3. Scheme of the modified GEC reference cell used for space and phase resolved electric field measurements in the sheath of a CCP. The laser pulse is synchronized with the RF voltage and the gated ICCD camera images the fluorescence light with high spatial resolution.

4 s (80 shots) at each wavelength and the shutter being in both opened and closed position. A difference image was calculated every time in order to determine the fluorescence decrease. Pixels in the horizontal direction were binned in order to reduce the noise.

5. Measurements in the calibration cell

5.1. Rydberg series without electric field

The strong nd′[5/2]3 autoionizing Rydberg series in the zero field case has been measured for principal quantum numbers 15 \(\leq n \leq 50\), and the weaker ns′[1/2]1 lines have been observed for 21 \(\leq n \leq 33\). The spectrum is shown in figure 4(a). The fluorescence decrease is around 60% at \(n = 15\), thus the transitions at lower \(n\) are almost saturated. Additional, relative broad lines have been detected at \(n \approx 18.4, 23.7, 35.0\). They are probably transitions to lower levels which are excited by the small fraction of the fundamental laser beam that still passes the dielectric mirrors and the filter. The energy levels obtained from the spectrum are listed in table 4. They have been fitted by the quantum defect formula (figure 4(b)); thus the ionization energy (table 5) and quantum defects (table 6) could be determined.

The width of the resonance lines shows nearly the expected \(a/(n^*)^3\) dependence [16] (figure 5(a)). The exponent has been determined to be \(-2.6 \pm 0.1\).

5.1.1. Dependence of line strengths on polarization. The dependence of the line strengths in the zero field case on the relative polarization of the two laser beams can be qualitatively seen in figure 5(b). The ns′[1/2]1 lines are much stronger in the case of parallel polarization (\(\Delta M = 0\)
Figure 4. (a) Spectrum of the Rydberg series in krypton. The fluorescence decrease $\delta F$ is plotted versus the principal quantum number $n$ of the $nd'[5/2]_3$ levels, given by the inversion of the quantum defect formula (13). (b) Quantum defect formula fittings (——) of the $ns'[1/2]_1$ (■) and $nd'[5/2]_3$ (●) Rydberg series.

than in the perpendicular case ($\Delta M \pm 1$), where the weaker $nd'[3/2]_2$ and $nd'[5/2]_2$ levels, which cannot be separated from each other, appear like a ‘shoulder’ at the long wavelength side of the relative broad $nd'[5/2]_3$ line. The $nd'[3/2]_1$ levels have not been observed at all. This agrees with the calculated relative line strengths of the fine structure components in table 1 and the assumption, that the Rydberg states are excited from the $M = 0$ component of $5p'[3/2]_2$.

5.2. Stark effect

In the following sections, spectra of Rydberg states have been investigated at different electric field strengths. For all conditions we examined, the UV laser beam was polarized perpendicular and the VIS laser beam was polarized parallel to the electric field.

5.2.1. Overview. The most prominent features of the Stark effect in krypton can be discussed on the basis of a two-dimensional map of the fluorescence decrease (figure 6(a)). It consists of eleven spectra which were obtained at field strengths between zero and about 1000 V cm$^{-1}$. The wavelength range covers the interval between the $19d'$ and $21d'$ levels in the zero field case. For comparison, a map of the calculated line positions is shown in part (b) of the figure. In order to keep the figure clear, the field dependent line strengths are not shown.

At the left edge, one can only recognize the strong $nd'$ and the much weaker $ns'$ levels. With increasing field strength, they are slightly shifted to the longer wavelengths and disappear. Especially the $nd'$ levels disappear very rapidly at around 500 V cm$^{-1}$. On the other hand, the ‘forbidden’ $np'$ levels become visible at around 200 V cm$^{-1}$, shifting with increasing field strength very strongly and getting brighter at the same time. A manifold of the higher, quasi-degenerated states with $l \geq 3$ appears above 500 V cm$^{-1}$ between the $nd'$ and $(n + 2)p'$ states.
Table 4. Energies (in cm$^{-1}$) of $ns'[1/2]_1$, $nd'[5/2]_3$ Rydberg series in krypton, excited from $5p'[3/2]_2$. The uncertainty is around 0.3 cm$^{-1}$. The values from [25] (excitation out of the ground state) are listed, for comparison.

| $n$ | $ns'[1/2]_1$       | $nd'[5/2]_3$      |
|-----|--------------------|--------------------|
| 15  | 117510.5           | 117696.7           |
| 16  | 117625.8           | 117774.3           |
| 17  | 117717.0           | 117837.6           |
| 18  | 117790.6           | 117889.5           |
| 19  | 117850.6           | 117933.4           |
| 20  | 117900.5           | 117969.7           |
| 21  | 117942.5           | 117942.1           |
| 22  | 117977.7           | 117977.3           |
| 23  | 118007.6           | 118007.2           |
| 24  | 118033.4           | 118033.2$^a$       |
| 25  | 118055.7           | 118055.4$^a$       |
| 26  | 118075.4           | 118074.9$^a$       |
| 27  | 118092.4           | 118091.9$^a$       |
| 28  | 118107.8           | 118106.9$^a$       |
| 29  | 118121.1           | 118120.5$^a$       |
| 30  | 118133.1           | 118132.4$^a$       |
| 31  | 118144.0           | 118159.7           |
| 32  | 118153.3           | 118168.0           |
| 33  | 118161.9           | 118175.0           |
| 34  |                   | 118181.7           |
| 35  |                   | 118187.4           |
| 36  |                   | 118193.3           |
| 37  |                   | 118198.2           |
| 38  |                   | 118203.1           |
| 39  |                   | 118207.3           |
| 40  |                   | 118211.1           |
| 41  |                   | 118214.9           |
| 42  |                   | 118218.3           |
| 43  |                   | 118221.3           |
| 44  |                   | 118224.1           |
| 45  |                   | 118227.1           |
| 46  |                   | 118229.8           |
| 47  |                   | 118232.2           |
| 48  |                   | 118234.0           |
| 49  |                   | 118236.5           |
| 50  |                   | 118238.4           |

$^a$ The line is partially blended with a member of the $nd'[3/2]_1$ series [25].
Table 5. Ionization energy of the primed system in Kr.

| Reference                  | $\varepsilon_i$ (cm$^{-1}$) |
|----------------------------|------------------------------|
| This work                  | 118284.6 ± 0.3               |
| Yoshino et al (1978) [25]  | 118284.6 ± 0.2               |
| Moore (1970) [27]          | 118285.5                     |
| Moore (1952) [28]          | 118284.7                     |

Table 6. Quantum defects of the two observed series at $E = 0$.

| References | $ns'[1/2]_1$ | $nd'[5/2]_3$ |
|------------|--------------|--------------|
| This work  | 3.095 ± 0.002| 1.335 ± 0.002|
| Yoshino et al [23] | 3.094 | - |

Figure 5. (a) Lorentz width of the $nd'[5/2]_3$ Rydberg states. The experimental data (■) can be fit well by a function $a/(n^*)^3$ (——). (b) Spectra taken at parallel (----) and perpendicular (——) relative polarization of the two laser beams. $\lambda_2$ denotes the fundamental wavelength of the second laser.

5.2.2. $ns'$ levels. The measurement of the shifts of $ns'$ levels turned out to be difficult due to their relative low line strength and their energetic vicinity to the higher $l$ quantum number states having $(n - 3)$, thus definite identification may be impossible at higher field strengths. The $32s'[1/2]_1$ level shows a quadratic dependence on the electric field strength: $\lambda_c$(nm) = $(622.786 ± 0.001) + (2.68 ± 0.16) \times 10^{-6} (E(V\text{cm}^{-1}))^2$. A further, more systematic investigation of the Stark effect of the $ns'$ levels could be interesting in the case of parallel polarization of the two laser beams ($\Delta M = 0$), where visibility would be much better (subsubsection 5.1.1).

5.2.3. $np'$ levels, quadratic Stark effect. The $np'$ states become visible when an electric field is applied, because they get admixtures of the $ns'$ and $nd'$ states due to the Stark effect. In each spectrum, the position of maximum intensity has been measured. As already shown in the numerical simulation, the levels avoid a levelcrossing with the Stark manifold, but the intensity maximum keeps running through it. The shift can be described very well by a simple quadratic function $\varepsilon_{np'}(E) = \varepsilon_{np'}^0 - 1/2\alpha_{np'} E^2$, as shown in figure 7. Similarly to
Figure 6. (a) Measured Stark map in krypton in the range $19d' \ldots 21d'$. The fluorescence decrease is indicated by grey scales (brighter $\equiv$ higher $\delta_F$). The straight line at $\lambda_2 \approx 630.8$ nm is an artefact. (b) Result of the numerical calculation of the same region, but with disregard of the line strengths. The map is composed of two different calculations, therefore the avoided levelcrossing of $22p'$ and $19f', g', h' \ldots$ is not shown.

Figure 7. Quadratic Stark shift of $np'$ levels. The energy differences $\Delta \varepsilon$ between the observed shifted lines and the associated, extrapolated zero field energies have been plotted versus the square of the electric field $E$.

the other unperturbed states, the extrapolated zero-field energy $\varepsilon^{(0)}_{np'}$ can be expressed by the quantum defect formula (13), where $\delta_{np'} = 2.616 \pm 0.001$. It turned out that the polarizability $\alpha_{np'}$ is proportional to $(n^*)^{6.86 \pm 0.06}$, also very close to the hydrogen-like case where $\alpha \propto n^7$ [29] (figure 8). Comparison with the numerical calculation is shown in figure 9(a). In order to compare energy shifts, the extrapolated zero-field energies from the measurement have been identified with the calculated ones. Therefore, the measured energies had to be shifted upwards by $0.3 \text{ cm}^{-1}$. This systematic error is within the range of the reproducibility of the laser frequency (subsection 4.1.) and the scatter of the literature values for the intermediate $5p'[3/2]_2$ state. A detailed numerical calculation for an interval where the first anticrossing occurs is shown.
Figure 8. Polarizability of $np'$ levels. Measured data points (■) can be fitted very well by a $(n^*)^7$–function (——), as in the hydrogen-like case.

Figure 9. (a) Comparison of experimental data (■) and numerical calculation (· · · · · ·) for the $21p'$ level. The calculated line strengths are indicated by grey circles of different size. (b) Detailed numerical calculation of the electric field interval where the first anticrossing of the $21p'$ level with the Stark manifold of $n = 19$ occurs. The calculated line strength is indicated by the size of the black dots.

in figure 9(b). Although the crossing of the $21p'$ level with the Stark manifold is avoided, the line seems to cross due to the change in intensity. Because the energy gap is smaller than the line width, it is not possible to resolve the anticrossing and therefore the quadratic line shift is maintained. Considering the electric field interval where each $np'$ level could be clearly detected, a dependence of $E_{\text{max}} \propto (n^*)^{-4.3\pm0.3}$ and $E_{\text{min}} \propto (n^*)^{-4.5\pm0.6}$ has been observed for the upper and the lower limit, respectively (figure 12).
5.2.4. \( nd' \) levels. The most intensive lines at zero electric field are the \( nd'[5/2] \) levels. The spectra of \( 20d' \) at perpendicular polarization and different electric field strengths are shown in figure 10. One can clearly observe the highly nonlinear wavelength shift and the decrease in intensity at the same time. The measured energy shift is shown in comparison with the numerical calculation for four different levels in figure 11. As in the case of the \( np' \) levels (subsubsection 5.2.3.), the measured energies were shifted upwards by 0.3 cm\(^{-1} \) in order to correct the systematic error. However, in the cases of \( 16d' \), \( 18d' \) and \( 20d' \) there is a good agreement with the theory, but deviations can be identified for \( 26d' \). A close inspection showed that the calculations of the shifts of the \( nd'[5/2] \) levels are very sensitive to variations of the quantum defects, probably due to the nearby Stark manifolds that repel the \( nd' \) states. In contrast to the \( np' \) levels, their shift cannot be described by a simple, quadratic function. It seems that below a ‘threshold’ electric field strength the shift is hardly measurable. Beyond that, the shift increases rapidly and the line strength decreases at the same time. When about twice the threshold field was reached, the \( nd' \) levels could not be detected any more. The dependence of the upper electric field limit on the effective principle quantum number \( n^* \) can be expressed by a power function \( E_{\text{max}} \propto (n^*)^{-4.7\pm0.2} \), similarly to the upper and lower limits of the \( np' \) levels (figure 12). Within the statistical uncertainties, one can probably assume a \( E_{\text{min/max}} \propto (n^*)^{-4.5} \) dependence for the electric field measurement ranges. Despite their highly nonlinear behaviour, the \( nd'[5/2] \) levels are useful for electric field measurements due to their line strength and visibility in the zero field case, which allows a simple measurement of the Stark shift.

5.2.5. Higher \( nl' \) levels, linear Stark effect. The quantum defects of the \( nl' \) levels with \( l \geq 3 \) can be neglected, therefore they are practically degenerated. In the presence of an external electric field, they exhibit a linear splitting into \( n-3 \) equidistant lines. The fine structure components of each angular momentum state could not be resolved further due to the line width. Examples of measured spectra at \( n = 19 \) are shown in figure 13. The line comb appears at field strengths
Figure 11. Measured energy shifts (■) of four $nd'[5/2]_3$ levels in comparison with the numerical calculation (······). The calculated intensities are indicated by grey circles of different size.

beyond approximately 500 V cm$^{-1}$, when the nearby $20d'[5/2]_3$ level ($n^* \approx 18.7$) disappears. This observation agrees also with numerical calculations of the line strengths.

The average line separation has been determined for different field strengths by fitting Lorentz profiles to all observed lines. Energy values which have been calculated from the centre wavelengths were numbered and plotted versus this number. The average line separation $\Delta \sigma$ is given by the slope of the linear regression. In figure 14(a), the linear splitting for four different values of $n$ is compared with the theory. In first approximation, the splitting is proportional to the electric field $\Delta \sigma = p_n E$, where $p_n$ depends almost linearly on the principal quantum number $n$ (figure 14(b)). This is comparable to the linear Stark effect in hydrogen, where the separation between two adjacent lines is proportional to $n$ [18]. A weaker dependence seems to exist for values $n \leq 15$: Delsart and Keller observed a $n^{0.7}$ dependence for $8 \leq n \leq 15$ [16]. Considering electric field measurements, the linear Stark effect promises to be the easiest and most accurate sensor, when measuring relative high electric fields and having a good signal to noise ratio of the spectra. As only energy differences have to be measured, an absolute calibration of the laser system is not necessary.
Figure 12. Electric field ranges in which different angular momentum states in krypton can be accessed in this specific spectroscopic scheme. The upper (●) and lower (○) electric field values, where the np′ states appear, and the upper limits of nd′ (■) that can also be considered as lower limits for the nf′, g′ . . . states, have been measured. The straight lines (——), which represent power functions that fit to the measurements, divide the area into four different regions: (1) only nd′ states visible, (2) np′ and nd′ states, (3) np′ and nf′, g′ . . . states and (4) nf′, g′ . . . only.

Figure 13. Measured spectra of the linear Stark effect for n = 19.
Figure 14. Measured linear Stark splittings (a) and splitting constants $p_n$ (b) for different $n$, in comparison with the numerical calculation (——).

Figure 15. (a) Space and phase resolved electric field measurements in a pure Kr, 10 Pa, 8 W CCP at 13.56 MHz. The solid lines (——) are the result of a three-point adjacent averaging of the data points and serve as a guide to the eye. (b) Comparison of the integrated sheath voltages (■) with the electrode potential measured by a high voltage probe (○). The dashed line (----) is a sinusoidal fit to the probe measurements.

6. Electric field measurements in a CCP

Our motivation for the investigation of the Stark effect in krypton was to provide the basic data for a diagnostic of electric field distributions in the sheath regions of various RF discharges. A capacitively coupled pure Kr discharge in a so-called GEC reference cell was used in order to demonstrate the applicability of the technique under realistic conditions.

First space and phase resolved electric field measurements were performed in a pure Kr discharge at a pressure of 10 Pa and a power of 8 W. The shift of several $n^d[5/2]_3$ levels ($n = 15 \ldots 26$) were measured and compared with the experimental database, if available, otherwise with the numerical calculation. Figure 15(a) shows the experimental results of the electric field measurement diagnostic. Sheath voltages have been determined by integration of the electric field distributions. For these purposes, the measured fields have been extrapolated.
linearly towards the powered electrode, because an approximately constant ion density and a negligible electron density can be assumed in this region.

In figure 15(b), the results of the integration are compared with values taken with a high voltage probe. The agreement is very good and shows that there are no substantial systematic errors in the measurement method. Numerical sheath models that can explain the specific field distributions are still the subject of current research.

7. Conclusions and outlook

A laser spectroscopic method for sensitive electric field measurements in radiofrequency discharges using krypton has been developed. The autoionizing Rydberg series has been measured and the Stark effect for different angular momentum states has been investigated in detail. The measurements have been compared with numerical calculations. The applicability of the method to problems in plasma physics has been demonstrated in a RF discharge.

At zero electric field, the $ns'[1/2]_1 (n = 21 \ldots 33)$ and the $nd'[5/2]_3 (n = 15 \ldots 50)$ levels have been identified and the energies have been measured, most of them for the first time. They could be described very well by a quantum defect formula. The quantum defects and the ionization energy have been determined. The $(n^*)^{-3}$ dependence of the line width has been verified.

When an electric field was applied, a quadratic Stark effect could be observed for the $np'$ levels ($n = 17 \ldots 32$). The most intensive $nd' (n = 16 \ldots 26)$ states show a much more nonlinear behaviour, and the higher angular momentum states ($l \geq 3, n = 15 \ldots 27$) exhibit a linear Stark effect. The polarizability and the dipole moment of high, autoionizing Rydberg states in krypton is very hydrogen-like, as reported already in [16]. A sensitivity of approximately 25 V cm$^{-1}$ has been reached.

There is very good agreement of the experimental results and the numerical calculations. In combination with the experimental results, the model has been improved, so that even states which have not been calibrated experimentally could be used for electric field measurement.

The applicability of the method to plasma physics has been successfully demonstrated in the sheath region of a capacitively coupled RF discharge, and high spatial and temporal resolution has been obtained. Sheath voltages which have been obtained by integrating the measured electric field distributions compare very well to measurements done by a high voltage probe. This also proves indirectly that the calibration has been performed successfully.

When the sensitivity of the detection system at the fluorescence wavelength is sufficient, krypton can be added in relatively small amounts below 0.1 Pa to various discharges and serves as a universal probe gas for electric field measurement. Heating processes, wave phenomena as well as ion dynamics can be studied.

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