5 Conclusions

In this work a collisional–radiative model has been developed in order to use it as a plasma diagnostics tool. Challenges were discovered when comparing the modelling results to experimental data especially at low pressure. Several aspects have therefore been considered and modified to improve the modelling:

**Number of modelled states**

The number of modelled states has been increased by adding the $3d$ and $5s$ states to a former version of the model, which only consisted of the $4s$ and $4p$ states. 30 states are therefore included and the cascades from the $3d$ and $5s$ states have been found to play a role for the $4p$ states. The extension was thus necessary, but did not improve the agreement with the experimental data.

**Gas temperature**

Rotational spectroscopy using CH bands has been applied in an attempt to determine the gas temperature. However, the states seem to not have thermalized and no temperature could be extracted. The gas temperature was therefore chosen according to diode laser absorption spectroscopy performed in a previous work for the GEC cell discharges. For the industrial CCP the temperature of the heated electrodes was used.

**Diffusion of metastables**

The modelling of the diffusion of metastables was extended to cover the case of very low neutral gas densities, which might occur due to the electron pressure. A numerical calculation of the mean distance to the wall for a cylindrical plasma was used to describe the empty–vessel movement of the particles, which was included in the diffusion rate coefficient.

**Electron energy distribution function**

The impact of the shape of the EEDF on the derived plasma parameters was demonstrated. The discharge pressure has a significant influence on the EEDF due to the depletion of the high–energetic tail, which is most important for the excitation kinetics. A
parameterized form of the EEDF is suggested, which should be fitted to EEDFs obtained by Langmuir probe measurements, simulations or Boltzmann solvers (if applicable) to be able to include a proper EEDF in the calculations.

**Einstein coefficients**

Measured and calculated Einstein coefficients were discussed and tested. Using the measured data of the NIST database [79] is preferred, but the data set has to be completed using calculated data e.g. by Bartschat et al. [81,91] as it lacks some important transitions.

**Radiation trapping**

Radiation trapping was found to be one of the most crucial processes in CR modelling. Various escape factors provided by the literature were tested and found to yield different results. Besides, none of these is capable of describing a finite plasma volume with spatial gradients nor do they allow for a distinction between a volume averaged escape factor for the rate equations and a line–of–sight integrated escape factor for the calculation of line intensities. A numerical calculation has therefore been carried out in this work including these aspects. The result is found to be closest to the empirical formula of Mewe [114]. This formula might be used as a first attempt, but should be exchanged by this work’s escape factor for more precise results. As a second improvement the line of sight is fitted using the ratio of the spectral lines at 763.5 nm and 800.6 nm. As they originate from the same upper state, their ratio only depends on the escape factor and thus on the line of sight. Introducing this fitting routine was the major improvement made to the CRM.

**Electron impact excitation**

The extensive set of cross sections by Bartschat and Zatsarinny [80,81] built the basis of this work’s CRM. The energy range and energy resolution of these cross sections are found to be suitable for the conditions investigated here. As the modelled intensities showed deviations to the measurements especially at low pressure, the set of cross sections has been modified in several ways. A subset of the calculated cross sections was rescaled using measured Einstein coefficients. The effect was found to be negligible. Replacing some of the cross sections by measured data (e.g. by Lin et al. [88]) turned out to yield some improvement. However, while some of the spectral lines are modelled more accurately by one set of cross sections, another set is more suitable for other lines. At low pressure no good agreement was found between the modeling results and the measured spectra for
none of the tested sets of cross sections. For the high–pressure gas mixtures the cross sections of Lin et al. [88] were found to be most suitable.

**Gas mixture discharges**

Gas mixture discharges were investigated by adding argon as a trace gas. Different regimes exist for the gas mixture CRM. At low pressures, an extension of the pure argon model is suitable, while at higher pressures a corona–like model with additional quenching term applies. While this is easier in terms of mathematical treatment, it comes along with the disadvantage that the line–ratio technique is not applicable in this case. An absolute calibration of the spectral lines is then mandatory and a method was suggested to circumvent the difficulties involved. The functionality of this method and the high–quenching CRM have been demonstrated for a high pressure hydrogen–silane–argon discharge.

All in all, many different aspects of the collisional–radiative modelling were investigated in this work. However, deviations are still found between calculation and measurement. They manifest most clearly in the two spectral lines at 706.7 nm and 738.4 nm (both originating from the state $4p_3$), which are about a factor of 2 off compared to the other spectral lines.

Radiation trapping was found to be a crucial process and its treatment was improved significantly. It was, however, also found to not be responsible for the deviations of these spectral lines. As radiation trapping occurs on the 706.7 nm transition but does not on the 738.4 nm transition (at low pressure), their relative deviation compared to each other is a measure of the quality of the radiation trapping modelling. As the lines deviate equally strong, radiation trapping is not the cause of the deviation. In addition, the agreement of calculation and measurement does not correlate with the importance of radiation trapping for a state or spectral line.

The number of states is also important and the extension to 30 states has shown some difference. Cascades from the higher lying $3d$ and $5s$ states are a non-negligible excitation mechanism for many $4p$ states under the conditions investigated in this work. A missing cascade contribution from an even higher lying state might in principle be an explanation for the deviations seen in the $4p_3$ density. The next higher states ($5p$), however, do not have allowed radiative transitions to the $4p$ states. They might have an effect on the metastable states, but this is not as selective as to increase the $4p_3$ number density while leaving the other $4p$ states unaffected. Even higher states ($> 5p$) have optically allowed transitions to $4p_3$, but as they lie at even higher energies their contribution is expected to
not be significant. An increase in the number of states is therefore not believed to yield an improvement in the modelling.

As the CRM is zero–dimensional, spatial gradients are not included in the model. This is expected to have an effect on the absolute values of the number densities and line intensities, but is not expected to introduce state selective changes by up to a factor of 2. It would, however, allow for a better modelling of some of the processes such as radiation trapping and the spatial variation of the EEDF.

It has been searched for correlations between the deviation of the ratio of a spectral line from the common mean value and certain plasma parameters such as electron density, electron temperature, the shape of the EEDF, metastable and resonant \(4s\) densities, strength of excitation from the ground state or the \(4s\) states, strength of cascade contributions, escape factor and absorption coefficient, position within the spectrometers and strength of the line’s intensity. None of these seemed to determine whether the lines were over– or underestimated in the model.

These arguments suggest that the cross sections are the source of the modelling restrictions. This would explain the missing correlation with plasma parameters as the cross section data are calculated independently of any plasma application. Additionally, the cross sections are individually calculated for every state and might therefore fit for some of the states while they do not fit for others for no discernible plasma related reason. A further argument is the difficulty in modelling the state \(4p_1\), which is very simple in terms of plasma kinetics: at low pressure it is almost entirely excited by electron collisions from the ground state and de-excited by trapping free radiation (750.4 nm) to a resonant \(4s\) state. The resulting weak dependence on the electron density can be proved experimentally. Despite the simplicity of this state’s kinetics, large deviations have been found in the modelling, which effectively only depends on the excitation process. A manual manipulation of the cross sections has been tried, but a more extensive investigation is needed. Monte Carlo calculations including Bayesian Probability Theory have been shown to be a suitable tool [63, 119]. This goes beyond the scope of this work. Nevertheless, the basic idea and method for such future investigations are described in appendix G. To allow the reproduction of this works calculations, appendix H explicitly shows results of three well–defined conditions, which might be used for comparison for other CRM codes.