Determination of atomic oxygen state densities in a double inductively coupled plasma using optical emission and absorption spectroscopy and probe measurements

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Abstract

A collisional radiative model for fast estimation and monitoring of atomic oxygen ground and excited state densities and fluxes in varying Ar:O₂ mixtures is developed and applied in a double inductively coupled plasma source at a pressure of 5 Pa and incident power of 500 W. The model takes into account measured line intensities of 130.4 nm, 135.6 nm, 557.7 nm, and 777.5 nm, the electron densities and electron energy distribution functions determined using a Langmuir probe and multipole resonance probe as well as the state densities of the first four excited states of argon measured with the branching fraction method and compared to tunable diode laser absorption spectroscopy. The influence of cascading and self absorption is included and the validity of the used cross sections and reaction rates is discussed in detail. The determined atomic oxygen state densities are discussed for their plausibility, sources of error, and compared to other measurements. Furthermore, the results of the model are analyzed to identify the application regimes of much simpler models, which could be used more easily for process control, e.g. actinometry.

Keywords: atomic oxygen, optical emission spectroscopy, collisional radiative model, Langmuir probe, multipole resonance probe, process control

1. Introduction

Oxygen containing plasma are widely used in industry for etching [1, 2], cleaning [3], or layer deposition processes [4–7], but are also a topic in recent scientific developments, e.g. plasma sterilization [8–10]. Due to its high reactivity atomic oxygen is of major interested in all these applications but the reliable measurement of atomic oxygen densities and fluxes is still a challenge especially if used for process control. Different techniques have been successfully applied to measure atomic oxygen, e.g. actinometry [11, 12], laser-induced fluorescence (LIF) [13, 14], VUV absorption [15, 16], cavity enhanced absorption spectroscopy (CEAS) [17], or optical emission spectroscopy (OES) [18, 19]. However, all of these methods cannot be applied without great technical and/or theoretical effort as well as taking special care regarding their drawbacks and applicable regime. Therefore, the improvement and benchmarking of these methods is important to be able to understand plasma surface and volume processes and the role of atomic densities. In the case of OES, the technical challenges are rather simple as spectrometers and detectors...
from the VUV to the NIR are achievable with convenient control software [20, 21]. Furthermore, the non-invasive measurement does not influence the plasma itself and thereby the atomic oxygen density which is possible in actinometry, LIF or VUV absorption when applied incorrectly or in the wrong regime. However, this advantage is dearly bought with the challenge to develop a correct collisional radiative model (CRM) to reproduce the excitation and relaxation processes yielding the atomic oxygen density in the end (e.g. in [18]). In general, these models need several plasma parameters as input, e.g. the electron density \( n_e \), electron energy distribution function (EEDF), or gas temperature \( T_g \). In a few regimes, it is possible to apply simple models. These are based on line ratios which often cancel out the need for \( n_e \) or the EEDF, like in actinometry, determine the plasma parameters from the emission [19, 22], or calculate densities using the corona model [20]. However, the validity of these approaches has to be checked precisely as many effects can change the populations of an atomic level due to electron impact excitation and quenching, or self absorption in case of emitting transitions. Unfortunately, the majority of cross sections, reaction rates, diffusion constants, and surface coefficients necessary to describe the collisional radiative processes is only determined theoretically (if at all) or in single experiments with unknown reproducibility. Therefore, applying OES in combination with collisional radiative models acquires critical review of the plasma processes as well as of the used data. However, if applied correctly the CRM has the great advantage of physically coupling all determined states and parameters by reasonable relations and building a correct hierarchy of the state densities. This way, unjustified statements or conclusions can be avoided which might be necessary in other direct measurement techniques like TALIF.

In this work, a collisional radiative model is presented for fast estimation of the volume averaged atomic oxygen ground and excited state densities and fluxes in Ar:O\(_2\) mixtures. The model deals with the population of the first seven states of atomic oxygen and can be used for optimizing the setup for the ground state and a specific excited state density or flux yielding the possibility of process control. However, as will be shown, this would imply a parallel measurement of all necessary plasma parameters for a wide range of applications or can only be used for fine tuning of the density by measuring line intensities and applying plasma parameters determined in advance. The CRM is applied in a double inductively coupled plasma system (DICP) used for analyzing the inactivation mechanisms during plasma sterilization [23] and is investigated for photon [24] as well as particle fluxes. The model takes into account several measured plasma parameters obtained with a Langmuir probe (LP), multipole resonance probe (MRP), tunable diode laser absorption spectroscopy (TDLAS), and optical emission spectroscopy, as well as self absorption of emission lines, cascading, diffusion of particles to the walls, and quenching of Ar metastable and resonant states. The handling of the self absorption is discussed in detail. Available cross sections and reaction rates are reviewed regarding their plausibility and reproducibility. The results of the CRM are analyzed for plausibility and possible sources of error as well as for regimes to determine the atomic oxygen density with simplified models.

2. Experimental Setup

The CRM is applied in the double inductively coupled plasma system depicted in figure 1. It consists of a stainless steel vessel (diameter: 400 mm, height: 200 mm) with several diagnostic flanges at the half height of the system aligned to the center of the discharge. The top and bottom are sealed with quartz plates with an ICP coil mounted outside the vacuum chamber, respectively. Therefore, the system is powered from two sides and yields a homogeneous plasma zone in the central region of the vessel. All data used in the CRM are obtained from measurements at a pressure of \( p = 5 \text{ Pa} \), generator power of \( P = 500 \text{ W} \), Ar flow rate of 100 sccm, and O\(_2\) flow rate of 2.5 sccm, 5 sccm, 7.5 sccm, 10 sccm, and 20 sccm. A data set in pure oxygen with a flow...
rate of 20 sccm is used as well. The setup is described in detail in [26].

Several plasma parameters have been determined and are used in the CRM. The electron density in the center of the discharge was measured using the MRP as well as the LP [26]. The electron energy distribution functions of the different Ar:O₂ mixtures was analyzed using the LP [26]. TDLAS determined the volume averaged state density of the Ar 1s₅ metastable state as well as the Doppler width of the transition yielding the gas temperature Tₑ in the Ar plasmas. The state density measurements were compared with the branching fraction method which utilizes several Ar lines from the 2p₃ states (3p⁵4p manifold) to the 1s₅ states (3p⁵4s manifold) to determine the state densities of the 1s₅ resonant and metastable states [27]. Two spectrometers (VUV and UV/VIS/NIR) were used to determine the volume averaged emissivity in photons cm⁻³ s⁻¹ of the discharges in the range from 116 nm to 860 nm yielding the intensities of the 130.4 nm, 135.6 nm, 557.7 nm and 777.5 nm emission lines of atomic oxygen. The details of the spectrometers and their response calibration are described in [24]. The uncertainties of the input parameters used for the model are given at the end of the following section.

3. Collisional radiative model

The presented CRM is based on the idea to minimize uncertainties in the state density estimation by including measured parameters from different complementary diagnostics. The possibility to implement absolute line intensities offers the potential to calculate certain state densities in advance which reduces the number of variables in the model calculation and, thus, sources of error due to unknown or insufficient reaction rates. Furthermore, cascading and self absorption are taken into account as they can have a significant effect on the state populations.

### Table 1. Atomic oxygen states taken into account in the collisional radiative model [28].

| Atomic level          | Energy/eV |
|-----------------------|-----------|
| 2s²2p(1S)3p          | 10.99     |
| 2s²2p(1S)3p(3P³/₂)    | 10.74     |
| 2s²2p(1S)3s(3S¹)      | 9.52      |
| 2s²2p(1S)3s(3P³/₂)    | 9.15      |
| 2s²2p(1S)3s(1S⁰)      | 4.19      |
| 2s²2p(1S)3p(1D₂)      | 1.97      |
| 2s²2p(3P³/₂)P₂,1,0    | 0.00      |

### 3.1. Atomic oxygen states, excitation, and transitions

The energy diagram of atomic oxygen is depicted in figure 2 (left). The CRM takes into account the first seven states of atomic oxygen listed in table 1 with their respective energy. The optical transitions included in the model, the statistical weight of the upper level, Einstein coefficient Aₕk, and if absolute line intensities are available, are given in table 2. Furthermore, the multiplet structure of the transitions is shown which has to be taken into account for self absorption and will be handled in detail in the section of the escape factor calculation. However, due to the resolution of the VUV spectrometer and to keep the model simple, multiplet levels are summarized to one level and their average wavelength in the rest of the model. Arrows in green in figure 2 show transitions with low transition probabilities (135 nm, 557 nm). Therefore, the effect of self absorption can be neglected for these levels as will be shown later. The transitions marked in red exhibit high Einstein coefficients (130.4 nm, 777.5 nm, 844.6 nm) and the effect of self absorption has to be considered.

The excitation and deexcitation of the levels can be influenced by electron impact, quenching, spontaneous emission, and self absorption. The electron impact excitation of atomic oxygen from the ground state, higher lying states as well as through dissociative excitation of O₂ is considered if reliable cross sections are available. The collision of Ar 1s₅ with atomic oxygen in the ground state can lead to the
Table 2. Transitions of atomic oxygen included in the CRM with their respective statistical weight of the upper level \( g_p \) and lower level \( g_s \), Einstein coefficient \( A_{\text{pk}} \), and wavelength \( \lambda_{\text{pk}} \) [28]. In the CRM, multiplet lines are handled as one transition with their averaged wavelength.

| Transition | \( g_p \) \( g_s \) | \( A_{\text{pk}}/\text{s}^{-1} \) | \( \lambda_{\text{pk}}/\text{nm} \) | Measured |
|------------|----------------|-------------------------------|--------------------------|----------|
| \( 2p^4^{1}S_0 \rightarrow 2p^4^{1}D_2 \) | 1, 5            | 1.26 × 10^7                  | 557.7         | x        |
| \( 3s^3S^1 \rightarrow 2p^4^{3}P_2 \) | 5, 5            | 4.2 × 10^3                  | 135.6         | x        |
| \( 2p^4^{3}P_1 \) | 5, 3            | 1.4 × 10^3                  | 135.9         | x        |
| \( 3s^3S^1 \rightarrow 2p^4^{3}P_2 \) | 3, 5            | 3.4 × 10^8                  | 130.2         | x        |
| \( 2p^4^{3}P_1 \) | 3, 3            | 2.0 × 10^8                  | 130.5         | x        |
| \( 2p^4^{3}P_0 \) | 3, 1            | 6.8 × 10^7                  | 130.6         | x        |
| \( 3p^5P_4 \rightarrow 3s^3S^1 \) | 7, 5            | 3.7 × 10^7                  | 777.7         | x        |
| \( 3p^5P_2 \) | 5, 5            | 3.7 × 10^7                  | 777.4         | x        |
| \( 3p^5P_1 \) | 3, 5            | 3.7 × 10^7                  | 777.5         | x        |
| \( 3p^5P_0 \rightarrow 3s^3S^1 \) | 1, 3            | 9.2 × 10^7                  | 844.6         |         |
| \( 3p^5P_2 \) | 5, 5            | 9.2 × 10^7                  | 844.6         |         |
| \( 3p^5P_1 \) | 3, 3            | 9.2 × 10^7                  | 844.7         |         |

The model consists of a simplification of the generation and loss terms yielding the rate equations at steady-state conditions for the state densities at steady-state conditions is depicted in table 3. The detailed processes and their rate coefficients are listed in the respective sections. The left hand-side represents the loss terms of the respective level due to electron impact excitation, quenching at the wall or with other particles, or radiative transitions. The right hand-side are the generation terms to the considered level from other levels by electron impact, quenching or emission. Because the densities of \( O(2p^4^{1}S, 3s^3S, 3p^5P) \) are determined previously the model simplifies to five rate equations of the remaining levels \( O(2p^4^{1}P, 2p^4^{1}D, 3s^3S, 3p^5P), \) and \( O_2 \). The details of the cascading and self absorption as well as the discussion of and comments on the used cross sections and rate coefficients will be given in the following paragraphs.

3.2. Solution of the rate equations at steady-state conditions

The model consists of five rate equations at steady-state conditions with the loss terms on the left and the generation terms on the right hand-side (see table 3). If all input parameters, like densities, line intensities, and rate coefficients would be precisely known an exact solution of the rate equations would be possible. However, as all input parameters are based on measurements or simulations only an approximate solution (regression) which minimizes the residuals of loss and generation term in each rate equation can be achieved. The variables in the model are the densities of the excited state of the \( O(3p^3P) \) level [29]. Furthermore, a collision with molecular oxygen results in dissociation into one ground state atom and either a second ground state atom or excitation to \( O(2p^4^{1}D) \) or \( O(2p^4^{1}S) \) [30, 31]. Because \( O(2p^4^{1}D) \) and \( O(2p^4^{1}S) \) are metastable states, their quenching due to collision with ground state atomic oxygen, \( O_2 \), or \( Ar \) to the ground state is taken into account. At the walls, recombination of ground state atomic oxygen and quenching of the ground state is taken into account. At the walls, recombination of ground state atomic oxygen and quenching of the outer layer is considered. Where possible, the population rate or depopulation rate of a state due to radiative transitions is replaced by the measured line intensity minimizing the influence of cross sections or quenching rates on the calculation. If self absorption influences the transition the lifetime is increased to the effective lifetime using the escape factor \( \gamma \), which depends on the lower state density.

The state densities of \( O(2p^4^{1}S) \) and \( O(3s^3S) \) can be determined from the absolute line intensities prior to the solution of the rate equations. The reason is the low Einstein coefficient of 1.26 s\(^{-1}\) and 5.6 × 10\(^{11}\) s\(^{-1}\), respectively, of the radiative transitions. Therefore, self absorption is only relevant for very high state densities of the lower levels which is typically not the case in the low pressure regime except for metastable states. Thus, the state densities calculated from the measured line intensities include all effects influencing the population like quenching or excitation to higher levels as this would lower the transition intensity. The densities of \( O(2p^4^{1}S) \) and \( O(3s^3S) \) are given by

\[
[O(2p^4^{1}S)] = \frac{I_{7777.7\ nm}}{A_{7777.7\ nm}},
\]

\[
[O(3s^3S)] = \frac{I_{135.6\ nm}}{A_{135.6\ nm}}.
\]

with the respective atomic state density in square brackets and the respective line intensity \( I \). Here, \( A_{135.6\ nm} \) is the sum of the Einstein coefficients of the two transitions at 135.6 nm as they originate from the same upper level to two multiplet levels of the ground state (see table 2).

The 777.5 nm transition from \( O(3p^3P) \) to \( O(3s^3S) \) is possibly influenced by self absorption due to the high Einstein coefficient of \( A_{777.5\ nm} = 3.7 \times 10^7\ \text{s}^{-1} \). However, the density of \( O(3s^3S) \) is calculated from the 135.6 nm emission and can be used to determine the escape factor of the transition. Thus, the density of the \( O(3p^3P) \) can be determined as well to

\[
[O(3p^3P)] = \frac{I_{7777.5\ nm}}{\gamma([O(3s^3S)]) \cdot A_{7777.5\ nm}}.
\]

The details of the escape factor and Einstein coefficient handling due to the presence of the multiplet structure is given in the escape factor section. For a quick overview of the model, a simplified representation of the generation and loss terms yielding the rate equations at steady-state conditions for the state densities at steady-state conditions is depicted in table 3. The detailed processes and their rate coefficients are listed in the respective sections. The left hand-side represents the loss terms of the respective level due to electron impact excitation, quenching at the wall or with other particles, or radiative transitions. The right hand-side are the generation terms to the considered level from other levels by electron impact, quenching or emission. Because the densities of \( O(2p^4^{1}S, 3s^3S, 3p^5P) \) are determined previously the model simplifies to five rate equations of the remaining levels \( O(2p^4^{1}P, 2p^4^{1}D, 3s^3S, 3p^5P), \) and \( O_2 \). The details of the cascading and self absorption as well as the discussion of and comments on the used cross sections and rate coefficients will be given in the following paragraphs.
states O(2p$^4$ 3P), O(2p$^4$ 1D), O(3s 3S), O(3p 3P), and O$_2$ which all could not be determined in advance from the absolute line intensities. Because of quenching processes between different atomic oxygen levels and the calculation of the escape factor the rate equations are nonlinear. Therefore, to determine the approximate solution with the lowest error the nonlinear least-squares solver lsqnonlin in Matlab is used. However, the convergence of the solver was only possible for a fixed O$_2$ density. Thus, the O$_2$ density was recalculated after each run by subtracting the atomic O density of the model from the O$_2$ density determined by the ideal gas law and used as new fixed parameter in the next run. This procedure was repeated until the O$_2$ density change was less than 1%.

### 3.3. Cascading

The effect of cascading is illustrated in figure 2. Besides the direct excitation of an excited state via electron impact the level density is also influenced by higher lying levels which deexcite to the respective state. This effect is called cascading and can significantly influence the transition intensity depending on the excitation rates into the higher states and the following cascading to the observed level. For atomic oxygen a detailed analysis of the cascading pathways has been performed by Julienne and Davis [32]. In general, the restriction of a multiplet change for spontaneous emission in the LS-coupling yields a dominant contribution of the triplet states to the O(3p 3P) level whereas the quintet states mainly contribute to the O(3p 3P) level. O(3p 3P) is connected to O(3s 3S) via the 844.6 nm transition and O(3p 3P) to O(3s 3S) via emission at 777.5 nm. Therefore, the cascading from high energy states directly to O(3s 3S) and O(3s 3S) can be neglected as most of the contribution is via O(3p 3P) and O(3p 3P).

To account for the effect of cascading in the CRM the electron impact excitation rates to the O(3p 3P) state (direct and dissociative) are increased by the excitation rates to all triplet states above O(3p 3P) from the respective levels using a cascading factor. The cascading factor is determined by the ratio of the excitation rate to O(3p 3P) and the excitation rates to levels above. This approach assumes that relaxation in the states above O(3p 3P) is only via radiative processes and is not influenced by e.g. quenching. The influence on the O(3p 3P) level through cascading is already included due to the state density determination using the absolute line intensity. Therefore, the cascading factor is only used to increase the excitation rates from states below O(3p 3P) to take
Table 4. Electron impact excitation processes. The rate coefficients were calculated assuming a Maxwellian electron energy distribution and are fitted over an energy range of $T_e = 1.5$–$4$ eV.

| Reactions | Rate coefficients m$^{-3}$s$^{-1}$ | references |
|-----------|-------------------------------------|-------------|
| O(2p$^4$P) + e $\rightarrow$ O(2p$^4$D) + e | $6.1 \times 10^{-9} - 8.2 \times 10^{-9}$, $\exp(-T_e/2.4)$ | [33] |
| O(2p$^4$P) + e $\rightarrow$ O(2p$^4$S) + e | $9.8 \times 10^{-11} - T_e - 9.5 \times 10^{-11}$ | |
| O(2p$^4$P) + e $\rightarrow$ O(3s$^5$S) + e | $-9.0 \times 10^{-11} + 5.4 \times 10^{-11}$, $\exp(T_e/2.4)$ | [33] |
| O(2p$^4$P) + e $\rightarrow$ O(3s$^5$S) + e | $-9.4 \times 10^{-11} + 3.9 \times 10^{-11}$, $\exp(T_e/1.5)$ | [33] |
| O(2p$^4$P) + e $\rightarrow$ O(3p$^3$P) + e | $-2.8 \times 10^{-11} + 1.2 \times 10^{-11}$, $\exp(T_e/1.5)$ | [33] |
| O(2p$^4$P) + e $\rightarrow$ O(3p$^3$P) + e | $-4.6 \times 10^{-11} + 1.6 \times 10^{-11}$, $\exp(T_e/1.3)$ | [33] |
| O(2p$^4$P) + e $\rightarrow$ triplet states $>$O(3p$^3$P) + e | $-6.3 \times 10^{-11} + 1.4 \times 10^{-11}$, $\exp(T_e/1.0)$ | [33] |
| O(2p$^4$D) + e $\rightarrow$ O(2p$^4$S) + e | $1.4 \times 10^{-9} - 1.7 \times 10^{-9}$, $\exp(-T_e/2.7)$ | [33] |
| O(2p$^4$D) + e $\rightarrow$ O(3s$^5$S) + e | $-1.1 \times 10^{-12} + 5.8 \times 10^{-13}$, $\exp(T_e/2.0)$ | |
| O(2p$^4$D) + e $\rightarrow$ O(3p$^3$P) + e | $-4.0 \times 10^{-12} + 1.9 \times 10^{-12}$, $\exp(T_e/1.8)$ | [33] |
| O(2p$^4$D) + e $\rightarrow$ triplet states $>$O(3p$^3$P) + e | $-4.0 \times 10^{-11} + 1.5 \times 10^{-11}$, $\exp(T_e/1.4)$ | [33] |
| O(2p$^4$D) + e $\rightarrow$ O$^+$ + e + e | $-1.2 \times 10^{-10} + 2.4 \times 10^{-11}$, $\exp(T_e/1.0)$ | [18] |
| O(2p$^4$S) + e $\rightarrow$ O(3p$^3$P) + e | $-1.5 \times 10^{-11} + 1.2 \times 10^{-11}$, $\exp(T_e/4.7)$ | [33] |
| O(3s$^5$S) + e $\rightarrow$ O(3p$^3$P) + e | $-1.8 \times 10^{-8} + 4.2 \times 10^{-8}$, $T_e - 1.9 \times 10^{-8}$, $T_e^2$ | [34] |
| O(3s$^5$S) + e $\rightarrow$ O(3p$^3$P) + e | $+3.7 \times 10^{-10}$, $T_e^2 - 2.8 \times 10^{-10}$, $T_e^2$ | [34] |
| O(3p$^3$P) + e $\rightarrow$ O(3p$^3$P) + e | $-1.1 \times 10^{-7} + 3.6 \times 10^{-7}$, $T_e - 1.5 \times 10^{-7}$, $T_e^2$ | [34] |
| O(3p$^3$P) + e $\rightarrow$ O(3p$^3$P) + e | $+3.0 \times 10^{-8}$, $T_e^3 - 2.2 \times 10^{-9}$, $T_e^3$ | [34] |
| O(3p$^3$P) + e $\rightarrow$ O(3p$^3$P) + e | $4.5 \times 10^{-8} + 4.9 \times 10^{-8}$, $T_e - 3.5 \times 10^{-8}$, $T_e^2$ | [34] |
| O(3p$^3$P) + e $\rightarrow$ O(3p$^3$P) + e | $+8.5 \times 10^{-9}$, $T_e^3 - 7.3 \times 10^{-10}$, $T_e^3$ | [34] |
| O(3p$^3$P) + e $\rightarrow$ O(3p$^3$P) + e | $5.1 \times 10^{-9}$, $\exp(-7.3/T_e)$ | [18] |
| O(3p$^3$P) + e $\rightarrow$ O(3p$^3$P) + e | $9.4 \times 10^{-9}$, $\exp(-10.0/T_e)$ | [18] |
| O(3p$^3$P) + e $\rightarrow$ O(3p$^3$P) + e | $-7.1 \times 10^{-13} + 8.9 \times 10^{-14}$, $\exp(T_e/0.8)$ | [35] |

into account the excitation to the cascading states. For the 130.4 nm, 135.6 nm, 777.5 nm, and 844.6 nm lines emission cross sections are available which already include the cascading contribution from higher levels. In the case of dissociative electron impact excitation of O(3s$^5$S) and O(3s$^5$S), only emission cross sections are available. Therefore, the excitation rate for 130.4 nm and 135.6 nm are lowered by the emission cross section of 844.6 nm and 777.5 nm, respectively, to determine only the direct electron impact excitation to the O(3s$^5$S) and O(3s$^5$S) levels. This is necessary as the cascading to these levels is already included in the model via the emission of 777.5 nm and 844.6 nm.

3.4. Cross section, reaction rates, and diffusion

The analysis and selection of cross sections is of particular interest as unreliable data significantly falsifies the resulting level densities. Itikawa and Ichimura [36] and Laher and Gilmore [37] summarized and evaluated the known cross section more than 25 years ago. Unfortunately, many cross sections lack a number of experiments to verify the data and the measured values often deviate significantly by a factor of 2 or more, especially for higher lying levels. This situation has not changed much to the present day regarding experimental data. Therefore, a critical evaluation of the cross sections, measured and calculated, is necessary to achieve reliable results.

The processes taken into account and their cross sections are listed in tables 4 and 5. Most of the atomic data is based on more recent calculations by Zastarinny and Tayal [33] performed with the B-Spline R-Matrix approach. Their calculations are in good agreement to recommended cross sections summarized by Laher and Gilmore [37]. Therefore, excitation cross section from the metastable levels O(2p$^4$D) and O(2p$^4$S) are expected to be most reliable from them. Excitation from O(3s$^5$S, 3s$^5$S, 3p$^3$P) to higher levels are taken from Barklem [34]. His calculations from the metastable levels are in excellent agreement with Zastarinny and Tayal. Dissociative reaction rates resulting either in two atoms in the ground state or in one ground state and one O(2p$^4$D) atom are taken from Fuller et al [18]. They determined reaction rates for both processes based on recommended cross sections of Itikawa et al [38] and measurements of Cosby [39]. The dissociative process resulting in one ground state and one O(2p$^4$S) atom is taken from McConkey et al [35]. Several emission cross sections were determined in the literature especially regarding the dissociative excitation of molecular oxygen. These cross sections are useful to determine the influence of cascading on the atomic state densities and are taken from recent reviews of Itikawa [40] and McConkey et al [35]. The ionization cross section of atomic oxygen is taken from Laher and Gilmore [37]. Although the included data was critically evaluated continuous comparison with other data is necessary. For example, the dissociative cross sections of Itikawa and Cosby vary from data of Phelps [41–43] in the low energy range by up to one order of magnitude. Furthermore, Zastarinny and Tayal recently published updated calculations for atomic oxygen cross sections. [44]. Thus, even if a set of cross sections yields reasonable results it is possible that two imprecise cross sections only compensate each other. Therefore, for improving and validating the CRM, extensive
sensitivity analysis of the influence of the different cross sections and comparison with other diagnostics will be necessary. However, this is out of the scope of this publication.

Besides electron impact excitation, quenching processes significantly influence the state densities. The quenching rates of the first four excited states of Ar 1s, 1s\textsubscript{A}, 1s\textsubscript{B}, and 1s\textsubscript{2} by molecular oxygen were reviewed by Velasco \textit{et al} [30].

The quenching leads to dissociation of the molecule yielding one oxygen atom in the O(2p\textsuperscript{3}P) ground state as well as a second in the O(2p\textsuperscript{3}P), O(2p\textsuperscript{1}D), or O(2p\textsuperscript{1}S) state. The ratio of O(2p\textsuperscript{3}P), O(2p\textsuperscript{1}D), and O(2p\textsuperscript{1}S) production was determined by Balamuta and Golde [31] to 0.46, 0.52, and 0.02 for Ar 1s\textsubscript{A} and Ar 1s\textsubscript{B}. The same ratio is also assumed for Ar 1s\textsubscript{A} and Ar 1s\textsubscript{2}. The rate coefficients for quenching of excited argon and other processes considered in the CRM are listed in table 6. Quenching rates only available at room temperature are weighted by the ratio \( \frac{\sqrt{T_e}}{2.87K} \) to account for the influence of the thermal velocity of the particles and increasing frequency of collisions.

The determination of the diffusion rates is of particular interest due to the low pressure regime. Here, the diffusion rates are high and possible deexcitation or recombination at the chamber walls contributes to the state densities of the different levels. After Morgan and Schiff [45], the diffusion coefficients \( D \) of atomic oxygen in argon and atomic oxygen in molecular oxygen at 1 Pa and 300 K are \( 2.88 \times 10^8 \text{ m}^2 \text{ s}^{-1} \) and \( 3.06 \times 10^8 \text{ m}^2 \text{ s}^{-1} \), respectively. The rate coefficient for diffusion of atomic oxygen to the walls \( k_{\text{diff}} \) in a cylindrical vessel can be determined with

\[
k_{\text{diff}} = \left( \frac{\Lambda_0^2}{D} + \frac{2V_{\text{DIPC}}(2 - \alpha_{\text{wall}})}{\Lambda_{\text{DIPC}} \cdot \tau \cdot \alpha_{\text{wall}}} \right)^{-1},
\]

\[
\Lambda_0^{-1} = \sqrt{\left( \frac{\pi}{L_{\text{DIPC}}} \right)^2 + \left( \frac{2.405}{\tau_{\text{DIPC}}} \right)^2},
\]

where \( \Lambda_0 \) is the diffusion length, \( V_{\text{DIPC}} \) the volume of the vessel, \( \Lambda_{\text{DIPC}} \) the surface area of the vessel, \( \alpha_{\text{wall}} \) the sticking or
recombination coefficient, \( L_{\text{DCCP}} \), the height of the cylindrical vessel, and \( r_{\text{DCCP}} \) the radius [11, 46, 47]. \( D \) is determined for each Ar\( \text{O}_2 \) gas mixture by weighting the diffusion coefficients by the feed gas ratio. The recombination coefficient on stainless steel is based on Gudmundsson and Thorsteinsson [47] who reviewed known data and is in the range of \( \sigma_{\text{Stainless steel}} = 0.15 \) for the used regime. However, half of the reactor is made of quartz with a much lower recombination coefficient of around \( \sigma_{\text{quartz}} = 1 \times 10^{-2} \) [48, 49]. Therefore, an effective coefficient of \( \sigma_{\text{wall}} = 0.1 \) is assumed. In case of metastable atomic oxygen, \( \sigma_{\text{wall}} \) is set to unity, as the energy is lost at the chamber walls. In both cases, the exact value of \( \sigma_{\text{wall}} \) is not known as it also depends on the wall material, temperature, and morphology and the state of the colliding particle. But due to the lack of data this simple assumptions are used.

3.5. Self absorption

The effect of self absorption can drastically effect the state densities of the involved states as well as the measured intensity of the emission line. It occurs especially for atoms in their ground state as it is often the state with the highest density. However, it is also possible for highly populated excited states, e.g. metastable states. Radiation emitted during the transition from a higher level \( p \) to the ground state \( k \) is called ‘resonance emission’, which is easily reabsorbed by ground state atoms of the same species to the upper level \( p \). In consequence, this process reduces the number of photons measured outside the plasma and is taken into account by adding a correction called escape factor \( \gamma_{pk}(n_k) \) depending on the density of the absorbing level \( n_k \)

\[
I_{pk} = n_p \gamma_{pk}(n_k) A_{pk}. \tag{6}
\]

Calculating the escape factor is a complex task as it depends on the geometry of the system, density profiles of the emitting and absorbing species and spectral line profiles [54–59]. Therefore, an empirical formula determined by Mewe [60] is often used [27, 61–63] assuming a homogeneous density profile in both involved states

\[
\gamma_{pk}(n_k) = \frac{2 - \exp(-10^{-6} \kappa_{pk}(n_k) L_{pd})}{1 + \kappa_{pk}(n_k) L_{pd}} \tag{7}
\]

with \( L_{pd} \) the thickness of the observed plasma volume and the absorption coefficient \( \kappa_{pk}(n_k) \) defined as

\[
\kappa_{pk}(n_k) = \frac{\lambda_{pk}^2}{8\pi} \frac{g_p}{g_k} n_k \gamma_{pk} A_{pk}, \tag{8}
\]

where \( \lambda_{pk} \) is the wavelength of the transition, \( g_p \) and \( g_k \) the statistical weights of the two energy levels and \( P_{pk} \) the spectral line profile. \( \kappa_{pk}(n_k) \) strongly scales with the Einstein coefficient and transitions with low emission probabilities, like 3s \( ^2S - 2p \) \( ^3P \) (135.6 nm) and \( 2p \) \( ^3S - 2p \) \( ^1D \) (577.7 nm), are not affected by self absorption.

To handle the calculation of the escape factors correctly, the multiplet components of the transitions have to be taken into account. Due to the low resolution of the VUV spectrometer, it is not possible to separate the 130.4 nm line into its three multiplet components at 130.2 nm, 130.5 nm, and 130.6 nm. Because each of the three lines has its own Einstein coefficient their escape factors have to be calculated separately as well. The same effect applies for the 777.5 nm and 844.6 nm transitions. In the case of the 130.4 nm line, the ground state consists of three multiplet components and the upper level of one component (see table 2). Thus, the emission intensity of all three multiplet lines \( I \) is given as

\[
I = I_1 + I_2 + I_3 = n_p [\gamma_1(n_{k1}) A_{p1} + n_p \gamma_2(n_{k2}) A_{p2} + n_p \gamma_3(n_{k3}) A_{p3}], \tag{9}
\]

where \( I_1, I_2, I_3 \) are the intensities of the three multiplet lines, \( n_p \) is the upper state density, \( \gamma_i(n_{ki}) \) is the escape factor of the emission line to the lower level \( k \) multiplet component \( i \), \( n_{ki} \) is the density of the lower level \( k \) multiplet component \( i \), and \( A_{pki} \) is the Einstein coefficient from the upper level \( p \) to the lower level \( k \) multiplet component \( i \). The sum of all \( n_{ki} \) components is the total lower state density \( n_k \). However, due to the low spectrometer resolution \( n_k \) cannot be determined. Therefore, the statistical weights of the multiplet components \( g_i \) are used to estimate the density distribution in the multiplet and using only the density of the total multiplet of the lower level \( n_k \) yielding

\[
I = n_p [\gamma_1 \left( \frac{g_1}{\sum g_i} n_k \right) A_{p1} + \gamma_2 \left( \frac{g_2}{\sum g_i} n_k \right) A_{p2}] + \gamma_3 \left( \frac{g_3}{\sum g_i} n_k \right) A_{p3}] \tag{10}
\]

This way, the correct handling of the escape factors is possible using only the total state density of the lower level \( k \), here, the ground state \( p \) \( ^3P \). In case of the 777.5 nm and 844.6 nm transitions the lower level consists only of one multiplet component and the upper level of three components (see table 2). Therefore, the intensity of the transition is

\[
I = I_1 + I_2 + I_3 = n_p [\gamma_1(n_{k1}) A_{p1} + n_p \gamma_2(n_{k2}) A_{p2} + n_p \gamma_3(n_{k3}) A_{p3}] \tag{11}
\]

and the escape factors depend on the same lower state density. However, the upper state density is split into three multiplet components \( (n_{ki}) \) and the statistical weights are used again to estimate the density distribution in the upper state. In case of both transitions (777.5 nm and 844.6 nm) the Einstein coefficients are identical in each multiplet \( A_{p1} = A_{p2} = A_{p3} = A_{p} \) simplifying the description to

\[
I = n A_p \left( \frac{g_1}{\sum g_i} \gamma_1(n_k) + \frac{g_2}{\sum g_i} \gamma_2(n_k) + \frac{g_3}{\sum g_i} \gamma_3(n_k) \right). \tag{12}
\]

In addition to only using the statistical weights to estimate the multiplet distribution, the Boltzmann factor can be taken into account to calculate the equilibrium distribution. However, for the \( 2p \) \( ^3P \) level, the difference of the statistical weights \( (0.56, 0.33, 0.11) \) and the equilibrium at 700 K \((0.64, 0.28, 0.08)\) is not too severe. For the \( 3p \) \( ^3P \) and \( 3p \) \( ^1P \) multiplets the equilibrium distribution is nearly identical to the statistical weight due to the tiny energy difference of the levels. Furthermore, the existence of an equilibrium distribution of the ground state and especially of the excited states is unknown as it is related to the number of collisions of atomic oxygen atoms and can be strongly
influenced by different processes (e.g. dissociation of O₂, electron impact excitation of 2p⁴-⁵P). Thus, only the statistical weights are used in the approximation for estimating the multiplet distribution of the levels and future investigations are necessary to check the applicability of this assumption. In total, this procedure enables the use of the low resolution spectra as well as keeping the CRM simple because the multiplet densities do not have to be taken into account.

Because of its simplicity equation (7) is very useful to be included in CRMs in the low pressure rf plasma regime where the dominant line broadening mechanism is Doppler-broadening which depends on the gas temperature. However, the correctness of the empirical approach has to be considered. Sushkov et al [64] and Siepa [65] evaluated the approximation of Mewe and compared it with complex calculations. Both found good agreement between the empirical formula as long as the spatial density profiles of the upper and lower level are similar. This assumption is prone to error especially in the case of resonance emission to the ground state as the ground state level O(2p⁴-⁵P) and the excited state O(3s⁵S) are affected differently. For example, the excitation to the excited state is reduced near the chamber walls due to low electron densities and temperatures. Furthermore, collisions with the wall can also lead to quenching to the ground state increasing the ground state density near the chamber wall while the excited state is less populated. On the other hand, the low pressure regime leads to a fast diffusion of particles and a homogenization of the densities and profiles. Sushkov et al [64] calculated the worst case scenario where the excited state is localized at the center of the discharge while the lower level is spatially uniform. In this case, the empirical formula used in this study is approximately a factor of 2–3 off to the correct escape factor. However, this case is physically unrealistic and due to the size of the used chamber similar profiles should be present in the most part of the observed volume. The same holds for the gas temperature which is probably slightly reduced near the chamber wall but should be quite uniform in most of the observed plasma. Therefore, we assume the correctness of the empirical formula to be in the range of a factor of 2.

3.6 Input parameters

The CRM is based on several measured parameters listed in table 8:

| Gas     | Average line ratio |
|---------|--------------------|
| 100:7.5 | 0.84               |
| 100:10  | 1.27               |
| 100:20  | 2.9                |

Table 7. Averaged ratios of the calculated to measured line intensities for direct excitation of the Ar lines at 727.3 nm, 794.8 nm, 826.5 nm, and 852.1 nm.

s spectrometers: a VUV monochromator (Jobin-Yvon AS50, 116 nm–320 nm) and an echelle spectrometer (LLA Instruments ESA4000, 200 nm–860 nm). The spectrometer were calibrated by two calibrated standards: a D₂ lamp (Hamamatsu X2D2 L9841) calibrated from 116 nm–400 nm at the electron storage ring BESSY II of the Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany, and a tungsten ribbon lamp (OSRAM WI 17/G) calibrated from 350 nm–2500 nm at the manufacturer. During the continuous DICP operation the experimental error is determined by the inaccuracy of the calibration and the performed measurements. The calibration accuracy of the standards is 14% at 116.0 nm–120.4 nm, 36% at 120.6 nm–122.6 nm, 14% at 122.8 nm–170 nm, 7% at 172 nm–350 nm, 2.3% at 380 nm, 1.6% at 600 nm, and 2.3% at 780 nm. The intensity deviation of the measured spectra was less than 10% [24].

The correct measurement of the 557.7 nm dipole-forbidden transition is a possible source of error. In general, great effort is necessary to construct sources which emit the 557.7 nm line while suppressing other intense lines to correctly measure its intensity [66–68]. Figure 3 shows the spectrum of the discharge at a gas mixture of Ar:O₂ 100:7.5 sccm with a zoom to the 557.7 nm emission. The intensity is just above the noise level of the spectrometer and is roughly 3.5 orders of magnitude lower than the 777.5 nm emission. The possibility to measure this intensity difference is connected to the sensitivity of the spectrometer which has its maximum around 550 nm and low sensitivity around 800 nm. Thus, as the very intense argon and oxygen lines are in the insensitive infrared range, high exposure times are necessary for a sufficient signal which in parallel allows to measure weak signals in the 550 nm range. Furthermore, the line is also not influenced by the O₂ first negative system with band heads of the (2-1) and (3-2) transitions located at 559.8 nm and 556.7 nm, respectively, [69] which are not visible in the spectrum. Therefore, the correct measurement of the 557.7 nm line is assumed.
Electron densities and EEDFs

The electron density was determined using a multipole resonance probe (MRP) and was compared to a Langmuir probe (LP) which also measured the EEDF [26]. The results indicated that the determination of the electron density measurement of the LP was disturbed by the etching of the tungsten wire in oxygen containing plasmas while the shape of the EEDF was not affected. Therefore, the electron density values determined by the MRP are used in this study. For the Ar:O2 mixtures the EEDFs showed a Maxwellian shape in the measurement range of the LP from 0 eV–15 eV. In pure oxygen the low energetic part was disturbed by insufficient rf floating potential compensation. However, extrapolating a Maxwell distribution from the high energy range, the same electron density as measured with the MRP could be determined yielding the indication that a Maxwell distribution is valid in the low energy range.

To estimate the validity of the Maxwell distribution above 15 eV, the line intensities of the Ar lines at 727.3 nm, 739 nm, 754 nm, and 852.1 nm are calculated for direct excitation and compared to the measured line intensities. The intensity $I_{\text{Ar}}$ is given by

$$I_{\text{Ar}} = n_{\text{Ar}} \cdot n_e \cdot \gamma_{\text{Ar}} \cdot k_{\text{Ar}}^{\text{em}}(T_e)$$

with $n_{\text{Ar}}$ the argon density, $\gamma_{\text{Ar}}$ the escape factor of the respective line determined using the known $1_s\text{Ar}$ states densities (see below), and $k_{\text{Ar}}^{\text{em}}(T_e)$ the emission rate coefficient for excitation from the ground state [70]. To estimate the influence of step-wise excitation from the $1_s\text{Ar}$ states [71] the rate coefficients are compared using the known $1_s\text{Ar}$ densities and the Ar ground state density. If step excitation is less than 10%, direct excitation is assumed to be the dominant mechanism which applies for the Ar:O2 mixtures of 100:7.5 sccm, 100:10 sccm, and 100:20 sccm. Unfortunately, the cross sections for excitation from the $1_s\text{Ar}$ states are not well known. Therefore, the procedure is only applied to the Ar:O2 mixtures where direct excitation strongly dominates. Table 7 shows the averaged ratios of the calculated to measured line intensities for direct excitation. At 100:7.5 sccm and 100:10 sccm the difference is less than 30% indicating a Maxwellian EEDF above 15 eV. At 100:20 sccm the measured and calculated values differ significantly suggesting that because of inelastic collisions with molecular oxygen the EEDF is deviating from the Maxwellian shape. Thus, the results of the model have to be discussed regarding a possible non-Maxwellian EEDF in the case of Ar:O2 100:20 sccm.

**Argon state density and gas temperature**

The first four excited states of argon with two metastable ($1s_g, 1s_x$) and two resonance levels ($1s_x, 1s_2$) were determined using the branching fraction method and checked for correctness using laser absorption spectroscopy (LAS) of the $1s_g$ level at 772 nm [27]. Additionally, the Doppler profile of the argon absorption was used to determine the gas temperature in the argon mixtures. Regarding the state densities both measurement techniques yield the same trend and result in a maximum deviation of 40% of the $1s_g$ state. The gas temperature in pure oxygen could not be determined and is assumed to be 700 K based on rotational temperature measurements in H2 and N2 in the same system at 5 Pa and 500 W.

**Molecular oxygen density**

In the pure oxygen discharge it was possible to measure the molecular oxygen ground state density in absorption at 154 nm where absorption of O$_2$(^3Δ) is negligible. For this, a D$_2$ lamp (Hamamatsu X2D2 L9841) was flanged on the opposite side of the vessel to the VUV spectrometer and the signal was measured with and without plasma. For calculating

| Table 8. Input parameters of the CRM: argon resonant and metastable states [27], electron density and temperature [26], gas temperature [27], and absolute line intensities [24]. |
|----------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Gas sccm | Ar(1s$_g$) | Ar(1s$_x$) | Ar(1s$_2$) | Ar(1s$_2$) | n_e | $T_e$ eV | $T_g$ K | $I_{130}$ 10$^{18}$ photons s$^{-1}$ m$^{-3}$ | $I_{115}$ 10$^{18}$ photons s$^{-1}$ m$^{-3}$ | $I_{557}$ | $I_{777}$ |
|----------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 100:2.5 | 2.20 | 0.68 | 0.23 | 0.55 | 52.10 | 1.9 | 622 | 4500 | 29.00 | 0.16 | 520.00 |
| 100:5 | 2.80 | 0.82 | 0.28 | 0.67 | 33.00 | 2.2 | 683 | 5100 | 37.00 | 0.19 | 570.00 |
| 100:7.5 | 2.40 | 0.61 | 0.16 | 0.47 | 21.23 | 2.5 | 717 | 4600 | 40.00 | 0.10 | 470.00 |
| 100:10 | 1.90 | 0.46 | 0.08 | 0.32 | 16.29 | 2.6 | 739 | 4000 | 35.00 | 0.09 | 340.00 |
| 100:20 | 0.31 | 0.07 | 0.01 | 0.05 | 10.84 | 2.7 | 787 | 2600 | 18.00 | 0.07 | 150.00 |
| 0:20 | 5.18 | 2 | 700 | 8200 | 1.30 | 0.01 | 32.00 |
the density from the relative measurement the absorption cross section of [72] was used. The determined O2 density is used to check the result of the model in the pure molecular discharge.

4. Results

Using the plasma parameters determined with the LP, MRP, OES, and TDLAS, the state densities of the first seven states of atomic oxygen are calculated. The results are shown in figure 4 amended by the overall atomic density as well as the molecular oxygen density. At low oxygen concentrations (2.5 sccm) the atomic oxygen density is determined by the ground state O(2p^3P) and the first metastable state O(2p^41D), both yielding around 4 × 10^{18} m^{-3}. For higher oxygen content the ground state density increases and peaks in the pure molecular case at 3 × 10^{19} m^{-3} while the O(2p^41D) density drops by more than one order of magnitude to 2 × 10^{17} m^{-3}. In general, all excited states O(2p^41S, 3s^2S, 3s^2P, 3p^3P) show a density maximum at 5 sccm or 7.5 sccm O2 flux and decline afterwards. The lowest density is given for the highest energy level O(3p^3P) and the densities ascend with decreasing energy gap to the ground state. However, this is not true for the 3p^3P level which exhibits even higher densities than 3s^3S for Ar:O2 mixtures up to 100:10 sccm. This effect is most-likely induced by the high 3s^3S density and the resulting self absorption of the 3p^3P → 3s^3S transition increasing the 3p^3P density.

Figure 5 depicts on the left side the atomic and molecular oxygen density, the measured molecular oxygen density in the pure molecular discharge as well as the degree of dissociation \( \alpha_{\text{diss}} \).

\[
\alpha_{\text{diss}} = \frac{0.5 n_O}{n_{O_2} + 0.5 n_O}. \tag{14}
\]

Although the atomic oxygen density increases with higher oxygen concentrations, the degree of dissociation decreases considerably from around 30% to 3% in the pure molecular case due to the drop of the electron temperature at high oxygen flow rates and the rise of the O2 density. The right side of figure 5 shows the atomic oxygen flux on a substrate surface in the plasma. Left: Atomic oxygen density is not true for the 3s^3S to 2s^3S transition increasing the 3s^3S density than 3s^3S. In general, all excited states O(2p^41S, 3s^2S, 3s^2P, 3p^3P) show a density maximum at 5 sccm or 7.5 sccm O2 flux and decline afterwards. The lowest density is given for the highest energy level O(3p^3P) and the densities ascend with decreasing energy gap to the ground state. However, this is not true for the 3p^3P level which exhibits even higher densities than 3s^3S for Ar:O2 mixtures up to 100:10 sccm. This effect is most-likely induced by the high 3s^3S density and the resulting self absorption of the 3p^3P → 3s^3S transition increasing the 3p^3P density.

5. Discussion

To evaluate the results of the collisional radiative model, the discussion will be structured into three parts. First, the quality of the result of the least-squares solver is analyzed by calculating and comparing the loss and generation terms of each atomic state using the state densities determined by the model. In the ideal case, generation and loss terms should be identical and deviations yield possible hints which processes need to be adjusted. Second, the escape factors as well as selected states are analyzed to investigate the excitation pathways and changes in the excitation mechanisms with varying gas mixture. This analysis helps to identify the relevant processes to simplify the model and reduce the number of lines that need to be measured. Furthermore, the range of applicability of relative emission intensity diagnostics like actinometry can be investigated. Third, additional possible sources of error are discussed which could significantly influence the model, like the formation of ArO(1D) excimers during Ar and O(2p^41D) interaction, collisions of atomic oxygen excited in higher states, and the shape of the EEDF.

Least-squares results/solution of the rate equations

Using the measured 135.6 nm, 557.7 nm, and 777.5 nm line intensities, the densities of O(2p^3S), O(3s^3S), and O(3p^3P) are determined in advance and reduce the complexity of the system of rate equations at steady-state conditions. In case of correct measurements and Einstein
### Table 9. Results of the atomic oxygen CRM. $T_g$ is taken from the TDLAS measurement in Ar:O$_2$ and estimated in the pure oxygen discharge.

| Ar:O$_2$ sccm | O($2p^4\,^3P$) $10^{15}$ m$^{-3}$ | O($2p^4\,^1D$) $10^{17}$ m$^{-3}$ | O($2p^4\,^1S$) $10^{15}$ m$^{-3}$ | O($3s^2\,^3S$) $10^{15}$ m$^{-3}$ | O($3s^2\,^3P$) $10^{13}$ m$^{-3}$ | O($3p^2\,^3P$) $10^{12}$ m$^{-3}$ | $n_O$ $10^{19}$ m$^{-3}$ | $n_{O_2}$ $10^{20}$ m$^{-3}$ | $\alpha_{\text{diss}}$ % | $T_g$ K | $\Gamma_O$ $10^{21}$ m$^{-2}$ s$^{-1}$ |
|----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------------|-----------------|----------------|-------------|----------------|
| 100:2.5        | 4.10                            | 4.10                            | 1.30                            | 5.20                            | 0.60                            | 2.90                            | 4.70             | 0.83             | 0.10             | 29.5          | 623             | 1.89            |
| 100:5          | 9.30                            | 6.10                            | 1.50                            | 6.70                            | 1.40                            | 3.50                            | 6.90             | 1.55             | 0.17             | 30.8          | 683             | 3.70            |
| 100:7.5        | 14.00                           | 5.90                            | 0.79                            | 7.20                            | 1.70                            | 3.00                            | 9.00             | 2.00             | 0.25             | 28.3          | 718             | 4.87            |
| 100:10         | 17.00                           | 5.20                            | 0.73                            | 6.30                            | 1.80                            | 2.00                            | 9.20             | 2.23             | 0.33             | 25.1          | 740             | 5.51            |
| 100:20         | 23.00                           | 3.10                            | 0.54                            | 3.20                            | 1.50                            | 0.65                            | 7.20             | 2.62             | 0.64             | 17.1          | 788             | 6.68            |
| 0:20           | 31.50                           | 0.23                            | 0.11                            | 0.23                            | 0.66                            | 0.09                            | 1.10             | 3.17             | 5.02             | 3.1           | 700             | 7.64            |
coefficients, these densities are most reliable as they are not affected by the validity of several cross sections and other plasma parameters and are introduced as fixed densities in the model. The remaining densities of O(2p$^3$P, 2p$^1$D, 3s$^3$S, 3p$^1$P), and O$_2$ are the variables in the set of rate equations and are determined by minimizing the error in each rate equation by varying the densities using a least-squares solver. To evaluate how well the determined state densities solve the rate equations, figure 6 depicts the ratio of the loss term to the generation term of each rate equation.

In case of the ground state O(2p$^3$P), the rate equation is solved nearly perfectly in the argon mixtures with a maximum deviation of loss and generation rate of 4%. In pure oxygen the generation term is 14% larger than the loss term. With increasing oxygen content, the main loss mechanism of the O(2p$^3$P) state changes from electron impact excitation to diffusion and recombination at the chamber walls. As the recombination coefficient is only poorly known, this effect might cause the lesser consistency of the generation and loss term. Furthermore, the dominant generation mechanism of O(2p$^3$P) changes to dissociation of O$_2$ (see figure 7). As mentioned in the discussion of the cross sections, the used rate coefficient might be erroneous in the threshold region and causes the increase of the generation term.

A similar trend is visible for the O(2p$^1$D) state rate equation. The agreement of the generation and loss terms are very good for the argon mixtures with a maximum deviation of 6%, but around 35% higher generation in the pure oxygen discharge. The main generation process of the O(2p$^1$D) state is the electron impact excitation from the ground state O(2p$^3$P). With increasing oxygen content the dissociative excitation from O$_2$ gets more important and is responsible for up to 28% of the O(2p$^1$D) state population. The dominant loss mechanism of the O(2p$^1$D) state shifts completely from electron impact and quenching at the walls, by O(2p$^3$P), Ar, and O$_2$ to quenching by O$_2$ (see figure 7). Because the dissociative excitation process gets more important with increasing oxygen content, again the problem of an incorrect cross section in the threshold region might be responsible for the increasing error as was also discussed for the O(2p$^3$P) state.

The ratios of the generation and loss rates of O(3s$^3$S) and O(3p$^1$P) always match perfectly because of the weak coupling to any of the other state densities. The O(3s$^3$S) density is determined by matching its value to the measured line intensity of the 130.4 nm emission (see table 3). Here, the only coupling is due to the escape factor of the 130.4 nm transition. Thus, if the escape factor decreases the O(3s$^3$S) density increases to compensate the change in self absorption. In case of the O(3p$^1$P) level many processes contribute to its generation. However, the dominant loss mechanism is spontaneous emission to O(3s$^3$S) and the quenching by Ar can be neglected. Thus, because the loss process is not coupled to other levels the O(3p$^1$P) density is matched in a way that the loss term compensates the generation term.

The rate equation of O$_2$ shows an increase of the generation term compared to the loss term with increasing oxygen content from −17% to 32%, thus, the loss term is larger in the first place but afterwards the generation term dominates. The only generation term is the recombination at the chamber walls and around 85%–97% of the loss is due to electron impact dissociation depending on the gas mixtures. Based on the clear trend with increasing oxygen content either the recombination coefficient is too low at high oxygen concentrations or is changed in the presence of high argon concentration.

In general, the strongest divergence of the rate equations is present in the pure oxygen discharge as well as in the Ar:O$_2$ 100:20 sccm mixture. In both cases the existence of a Maxwellian EEDF above 15 eV is highly questionable as mentioned in the sections of the input parameters. Therefore, the insufficient solution of the rate equations at high oxygen content might also be attributed to false reaction rates because of insufficient knowledge of the EEDF shape.

To check the plausibility of the results, the degree of dissociation in the pure oxygen discharge is compared to measurements in other ICP discharges with metal (or stainless steel) walls. At similar power densities (40 W l$^{-1}$–50 W l$^{-1}$) and pressures (1.3 Pa–7.65 Pa) [18, 73, 74], degrees of dissociation of 1%–2% are measured compared to 3% determined by the CRM. All discharges only have one ICP coil at the top in contrast to the setup used in this study which exhibits a second coil at the bottom. Furthermore, the largest volume is also given in the DICP setup. Thus, the higher dissociation rate is possibly connected to the reduced loss rates to the walls because of the different volume to surface ratio as well as to the second electron heating zone. However, significantly higher dissociation rates have been reported (e.g. 16% in [17] using a set of 128 high flux magnets to confine the plasma) which can be connected to a different plasma generation or larger glass surface with significantly reduced recombination coefficients. Furthermore, the O$_2$ density measured with VUV absorption fits exactly the density predicted by the model. As the atomic oxygen density only slightly influences the O$_2$ density due to the low degree of dissociation, the consistency indicates the application of the correct gas temperature of 700 K which could only be
assumed from measurements in pure H₂ and N₂ under the same conditions.

Escape Factors and Excitation Pathways

The escape factors of the potentially self absorbing transitions at 130.4 nm, 777.5 nm, and 844.5 nm are depicted in figure 8. The escape factor of the 130.4 nm resonance line is inversely connected to the ground state density and decreases with increasing O₂ and O(2p⁴3P) density from 12% down to 2%. Thus, 88%–98% of the emitted photons are reabsorbed and the determination of the ground state density without taking into account self absorption would be falsified by up to a factor of 50. Interestingly, although the O(3s 3S) density is significantly increased by the self absorption effect of the 130.4 nm line, the escape factor of the 844.6 nm line, which deexcites to O(3s 1S), is constantly 1 and no reabsorption of the photons is present. However, due to the metastable level O(3s 3P) which exhibits significantly higher densities than the O(3s 3S) level, the 777.5 nm transition is affected by self absorption. In the Ar:O₂ mixtures the escape factor is in the range of 42%–63% and is nearly negligible in the pure oxygen discharge with 95%.

The problem of the validity of the empirical escape factor used in this study has already been discussed. However, its reasonable applicability for excited states has been demonstrated in the case of the branching fraction method to determine the Ar(1s) states in different systems [62, 64] and also in the used setup [27]. Because the empirical formula fits well to more complex calculations if the spatial distribution of the upper and lower level is the same [64, 65], the escape factors of the 777.5 nm and 844.6 nm transitions are most likely correct. This is the case as both upper and lower level are excited levels which are probably equally influenced by electron densities and temperatures as well as quenching processes at the walls. For the same reason the escape factor of the 130.4 nm line is prone to error. Here, the lower level is the ground state to which excited states get quenched at the walls and which is less depopulated in the case of decreasing electron densities and temperatures near the walls during the H-mode of the DICP [75]. As demonstrated by Sushkov et al [64] the maximum error is in the range of a factor of 3 if the upper state is only present in the center of the discharge and the lower level is evenly distributed. Thus, the error of the 130.4 nm transition is likely in the range of a factor of 1–3 depending on the spatial density profiles. Nevertheless, the very low escape factors clearly demonstrate the necessity to include the effect of self absorption in CRM for determining atomic densities, especially for resonance lines but also sometimes for transitions in excited state.

The analysis of the excitation of the O(3p 3P) level yields the possibility to simplify the determination of the ground state O(2p⁴3P) density. Figure 8 shows the change of the excitation pathways depending on the gas mixture. In the pure oxygen discharge more than 98% of the excitation of the O(3p 3P) level is from direct excitation from the ground state or from dissociative excitation. Furthermore, the effect of self absorption can be neglected for the 844.6 nm transition (3P 1P – 3S 1S) under the presented discharge conditions. Thus, the ground state density in the pure oxygen discharge could be monitored just by one single emission line if the electron density and temperature are known. An even more robust approach might be the use of actinometry. Here, only relative intensities of an Ar line excited from the ground state as well as the 844.6 nm line of atomic oxygen are necessary. Figure 8 reveals that for small admixtures of Ar to O₂ the excitation mechanisms of the O(3s 3S) level do not change. Thus, because the ratio of the line intensities cancel out the electron density and temperature, the ground state atomic oxygen density could also be monitored with a relative measurement and without knowledge of the electron parameters.

Further sources of error

Three other possibilities exist which can falsify the results and need to be discussed. First, the shortening of the O(2p⁴3S) lifetime due to collisions with Ar. During the collision of O(2p⁴3S) and Ar both atoms form a ArO(3S) excimer. In case of ArO the potential curves of ArO(3S) and

![Figure 7](https://example.com/figure7.png) Analysis of the excitation pathways of O(2p⁴3P) and losses of O(2p⁴3D) depending on the gas mixture at 5 Pa and 500 W. Only processes with a minimum share of 5% in the total generation or loss are shown.
ArO(1D) are very similar [76]. Therefore, the wavelengths of the transitions O(2p41S → O(2p41D) and ArO(1S) → ArO(1D) are nearly identical. As the lifetime of the transition is significantly shortened during the interaction with Ar (from 1.26 s to 1 × 10−5 – 1 × 10−7 s) [77] it is possible that most of the 557 nm emission originates from ArO(1S) excimers and not from atomic oxygen, thus falsifying the O(2p41S) density determination. To estimate the influence of the process, its share on the overall emission is calculated. The collision cross section of Ar and O(2p41S) is estimated using the hard-sphere model [78] to σ_{ArO} = 5.4 × 10−20 m². The collision frequency is therefore ν_{ArO} = n_Arσ_{ArO}ν_{Ar,therm} = 2.6 × 10^4 s⁻¹ using the gas temperature for the thermal velocity and Ar gas density n_{Ar} in Ar:O₂ 100:5. As the increased transition probability is only valid during the interaction of Ar and O, the interaction time τ_{int} is determined with the width of the potential well (τ_{ArO} ≈ 0.4nm) and the thermal velocity of atomic oxygen (τ_{O} = 950 m s⁻¹) to τ_{int} = 2τ_{ArO}τ_{O} = 8 × 10−13 s. By comparing the Einstein coefficient of atomic oxygen to ArO weighted by the time the excimer exists (A_{O(1S)/ν_{ArO}ν_{Ar,therm}A_{ArO}}), the O(2p41S) → O(2p41D) transition is roughly 60 times more likely than emission of the 557 nm line by ArO(1S) → ArO(1D). Thus, the calculation of the 1S density from the 557 nm line is not influenced by ArO excimers at the given experimental conditions.

Second, the high energetic states above O(3p3P) might be influenced by collisions with other oxygen atoms. Similar to ArO, two oxygen atoms form a collisional complex, i.e. molecular oxygen, with a potential curve depending on the atomic states of both atoms. During the reduction of the intermolecular distance a predissociative point can be reached and the molecule can dissociate to different atomic states than at the beginning of the process (e.g.: O(2p43P) + O(2p43D) → O²⁺ [5] → O(2p43P) + O(2p43P)). The first level above 3p3P is 4s5S with an energy of 11.83 eV [37]. Comparing the potential curves of molecular oxygen given in [69], the potential curve of O(2p43P) + O(4s5S) would need an energy of roughly 17 eV.

In this range, only ionic states of O₂ exist, thus, this process is not possible for oxygen atoms in states >O(3p3P) and a possible influence on the cascading must not be taken into account.

Third, besides incorrect cross section, quenching rates or missing processes, the increasing inaccuracy of the loss and generation terms at high oxygen concentrations of the O(2p43P), 2p41D) and O₂ rate equations might also be the result of the deviation of the EEDF from a Maxwellian shape. The comparison of the calculated and measured intensities of four different Ar lines supports this assumption for the high energy range above 15 eV. Furthermore, in the pure oxygen discharge the LP characteristic is distorted by uncompensated rf oscillations and prevents measurement of the correct shape in the low energy range. Although the distortion is not too severe and the comparison with the MRP suggests the presence of a Maxwellian distribution in this range (see above), the error would directly affect the excitation of the O(2p41D) level as its energy gap to the ground state is only 1.97 eV. Therefore, different diagnostics need to be applied to perform meaningful sensitivity analysis in the future and benchmark and improve the presented CRM.

6. Conclusion

The presented collisional radiative model for Ar:O₂ mixtures in low-pressure plasmas estimates the state densities and fluxes of the first seven states of atomic oxygen using measurements from several diagnostics as input parameters. The model takes into account cascading from higher levels as well as self absorption of transitions with large Einstein coefficients and diffusing processes. The used cross sections and reaction rates are critical evaluated to minimize potential sources of error and include as many processes as possible. The measurements of absolute intensities are used to determine and fix the state densities of O(2p41S), 3p5S, 3p3P in advance. The variables of the set of rate equations at steady-state conditions are the

Figure 8. Left: Analysis of the excitation pathways of O(3p3P) depending on the gas mixture at 5 Pa and 500 W. Only processes with a minimum share of 5% in the total generation are shown. Right: Escape factors of atomic oxygen transitions possibly affected by self absorption.
remaining states O(2p^3P, 2p^3D, 3s^3S, 3p^3P), and O_2 which are estimated by minimizing the error in each rate equation using a least-squares algorithm (regression). The previous determination of state densities significantly reduces the complexity of the model as less rate equations have to be solved with several reaction rates unknown or of poor quality. The plausibility of the model is analyzed by evaluating the deviation of the generation and loss terms of each level using the determined state densities, discussing the dominant excitation and loss processes and escape factors as well as comparing the results to the VUV absorption of O_2 and other measurements from the literature. The determined atomic oxygen state densities show a reasonable trend and realistic quantitative values. With small admixtures of oxygen in argon, the dissociation of the molecules is significant (approx. 30%) due to the high electron density dominating the dissociation by electron impact compared to dissociation by Ar metastables. With increasing oxygen content, the dissociation degree is reduced to roughly 3% in the pure oxygen discharge, which is a typical value for molecular plasmas in chambers with metal (or stainless steel) walls. Furthermore, the analysis shows the possibility of determining and monitor the ground state density with a much simplified model under a specific condition determining and monitoring the ground state density with a much reduced degree of dissociation which all can be used for surface process diagnostics, e.g. TALIF, to identify missing processes or imprecise reaction rates.

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