Lam Research Corporation:

Recombination and detachment in oxygen discharges: The role of metastables

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Introduction

- We report on a volume averaged global model calculation of a low pressure oxygen discharge
- This work has been made in collaboration with
  - Prof. Michael A. Lieberman

  and is based on the work of
  - Chris Lee (Lee, 1995)
  - Kedar K. Patel (Patel, 1998)

  and started as an experimental work on oxygen discharges together with
  - Alexei M. Marakhtanov

Introduction

- Oxygen discharges have been applied to numerous applications
  - ashing of photoresist
  - removing polymer films
  - oxidation or deposition of thin film oxides
  - sterilization
- Oxygen is a diatomic gas that has been particularly well studied
- The presence of negative ions alters the overall discharge phenomena with additional volume recombination loss

Introduction

- The main idea of a global model is to neglect the complexity which arises with spatial variations
- The model can include a large number of reactions in order to model a processing plasma with a limited computing power
- The model does not describe spatial distribution but captures scalings of plasma parameters with control parameters
- The global model is an ideal tool to investigate the plasma chemistry
- The methods and assumptions of the model are discussed in several publications (Lee et al., 1994; Lee and Lieberman, 1995; Patel, 1998; Gudmundsson et al., 2000, 2001)

Assumptions

- Steady state is assumed
- All densities are assumed to be volume averaged
  - The electron density is assumed to be uniform except near the sheath edge
  - The negative ion density drops to zero at the sheath edge
- All particles are assumed to be created uniformly throughout the discharge volume
- Electrons are assumed to have a Maxwellian energy distribution in the range 1 – 7 eV
- The gas and ion temperature are assumed to be 600 K
- A cylindrical discharge with dimensions $L = 7.6$ cm and $R = 15.24$ cm is assumed

Assumptions

- The model includes thirteen species
  - electrons,
  - molecular oxygen in ground state $O_2(^3\Sigma_g^-)$, metastable molecular oxygen $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ and the Herzberg states $O_2(A^3\Sigma_u^+, A'^3\Delta_u, c^1\Sigma_u^-)$,
  - atomic oxygen in ground state $O(^3P)$, metastable atomic oxygen $O(^1D)$ and ozone O_3,
  - the positive ions O^+ and O_2^+
  - the negative ions O^-, O_2^- and O_3^-
- The reaction rate coefficients have been revised from earlier work (Gudmundsson et al., 2001; Guðmundsson, 2004)

Motivation

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COMMENT

Is oxygen a detachment-dominated gas or not?

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Abstract. The apparent contradiction between treatments of discharges in oxygen at low pressures is highlighted, and the question asked why in radio-frequency generated plasmas it is permissible to ignore detachment due to collisions between metastables and negative oxygen ions whereas in dc discharges the consensus is that this process is dominant.

A recent paper (Gudmundsson *et al* 2000) was concerned with giving an experimental and theoretical description of a low-pressure discharge in oxygen, excited inductively at 13.56 MHz. A notable feature was the extent to which the authors sought to include all the atomic and molecular processes relevant to such a discharge in oxygen. The purpose of this communication is to indicate a fundamental difference between their treatment and the body of literature in dc discharges, where it has been clear for some time that there was an agreement that detachment by collisions with metastables and atoms is the significant loss process for the negative oxygen ions. A representative, but not exhaustive, list with corresponding values of pL (pressure × plasma dimension) is Thompson (1961) 50–250 mTorr cm, Edgley and von Engel (1980) 10–1000 mTorr cm, Ferreira *et al* (1988) 160–4000 mTorr cm, Gousset *et al* (1991) 16–4000 mTorr cm, Ivanov *et al* (1999) 90–600 mTorr cm—these compare with 10–135 mTorr cm for the rf excited plasma.

Generally, it is assumed that the processes are similar in dc and rf discharges, while it is recognized that different mechanisms set the electron temperature and even the distribution of charged particles. For this reason, I believe that it is incumbent on the authors to explain why, in an rf discharge, it is possible to ignore detachment other than by electron impact as a loss process. It is apposite to quote from Ivanov *et al* (1999) 'Detachment processes on $O(^3P)$ atoms and $O_2(a^1\Delta_g)$ molecules strongly influence the discharge electrodynamics and determine the electric field in a wide range of the pL parameter'.

Interestingly, a recent paper by Kaganovich *et al* (2000), albeit in an afterglow situation, indicates the importance of detachment in an oxygen plasma in a comparable range of pL.

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Gudmundsson T, Marakhtanov A M, Patel K K, Gopinath V P and Lieberman M A 2000 *J. Phys. D: Appl. Phys.* **33** 1323–31
Ivanov V V, Klopovsky K S, Lopaev D V, Rakhimov A T and Rakhimova T V 1999 *IEEE Trans. Plasma Sci.* **27** 1279–87
Kaganovich I D, Ramamurthi B N and Economou D J 2000 *Appl. Phys. Lett.* **76** 2844–6
Thompson J B 1961 *Proc. R. Soc.* A **262** 503–18

Motivation

- The metastable oxygen atom $O(^1D)$ has a threshold energy of 1.96 eV and a lifetime of 147.1 s
- The metastable oxygen molecule $O_2(a^1\Delta_g)$ has a threshold energy of 0.98 eV and a lifetime of 4400 s
- Detachment by collisions of ions with the metastable molecule $O_2(a^1\Delta_g)$ is generally suggested to be a significant loss process for the negative oxygen ions (Katsch et al., 2000; Franklin, 2000; Ivanov et al., 1999)
- What is the role of recombination ?

Ion-ion recombination

- For mutual neutralization of O^+ by O^-

$$O^- + O^+ \longrightarrow O + O$$

we propose

$$4.0 \times 10^{-14}\,(300/T_i)^{0.43} \qquad m^3/s.$$

- These replace $2.7 \times 10^{-13}(300/T_i)^{1/2}$ m^3/s and $2.0 \times 10^{-13}(300/T_i)^{1/2}$ m^3/s (Eliasson and Kogelshatz, 1986; Kossyi et al., 1992) that are commonly used
- This is based on recent cross section measurements by Hayton and Peart (1993) (Gudmundsson and Lieberman, 2004)

Ion-ion recombination

- For mutual neutralization of O_2^+ by O^-

$$O^- + O_2^+ \longrightarrow O + O_2$$

$$O^- + O_2^+ \longrightarrow 3O$$

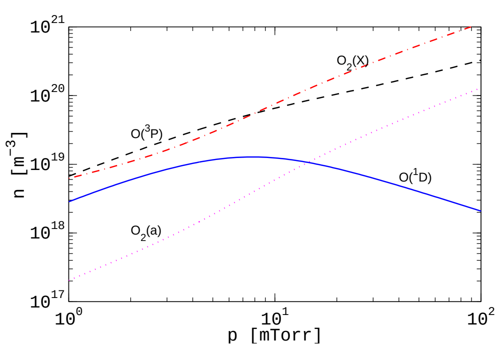
we propose

$$2.6 \times 10^{-14}\,(300/T_i)^{0.43} \qquad m^3/s.$$

for each reaction

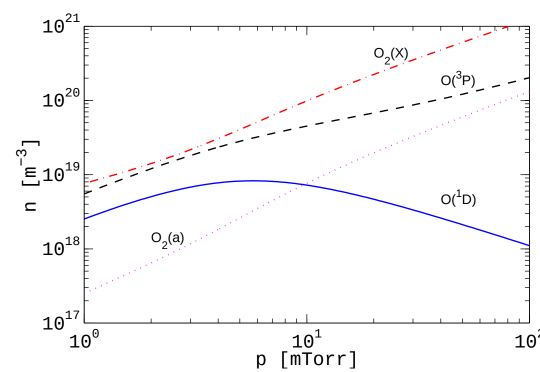
- These replace values of 2.0×10^{-13} m^3/s, 1.0×10^{-13} m^3/s and 0.96×10^{-13} m^3/s (Kossyi et al., 1992; Eliasson and Kogelshatz, 1986) commonly used
- This is based on recent cross section measurements by Padgett and Peart (1998) (Gudmundsson and Lieberman, 2004)

Neutrals



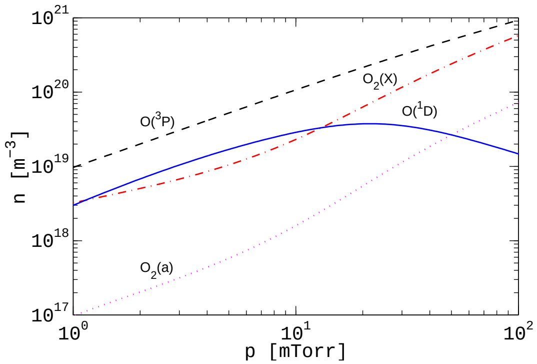
- The neutral densities at $P_{abs} = 500$ W
- Atomic oxygen is of great importance below 10 mTorr
- Molecular oxygen dominates above 10 mTorr
- The densities of $O(^1D)$ and $O_2(a^1\Delta_g)$ are significant

Neutrals



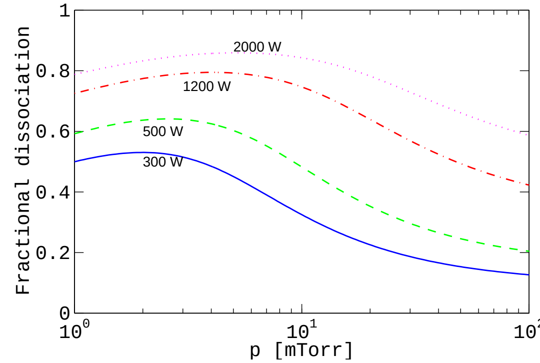
- The neutral densities at $P_{abs} = 300$ W
- Molecular oxygen dominates the entire pressure range $1 - 100$ mTorr

Neutrals



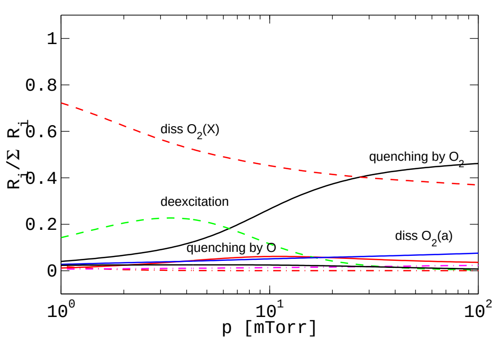
- The neutral densities at $P_{\text{abs}} = 2000$ W
- Atomic oxygen dominates the entire pressure range 1 – 100 mTorr

Dissociation



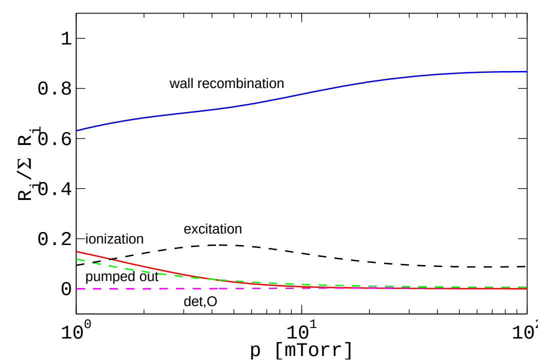
- The fractional dissociation
  - increases with increased applied power
  - decreases with increased neutral gas pressure

Creation of $O(^3P)$



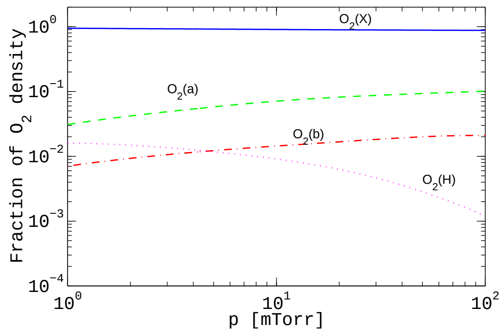
- Dissociation from $O_2(X)$ is the main source of $O(^3P)$
- Deexcitation from $O(^1D)$ is important below 20 mTorr
- The role of quenching of $O(^1D)$ by $O_2(X)$ increases with increasing pressure

Loss of $O(^3P)$



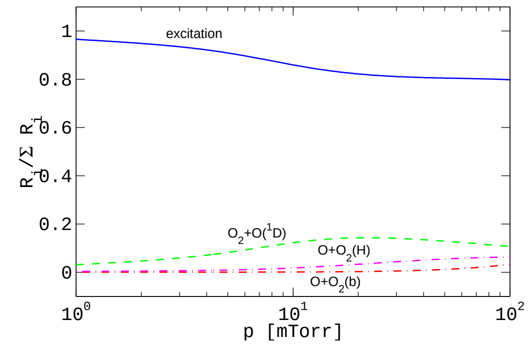
- The oxygen atom $O(^3P)$ is mainly lost through recombination at the wall
- We assume a wall recombination coefficient of $\gamma_{\text{rec,O}} = 0.5$

Metastable O_2



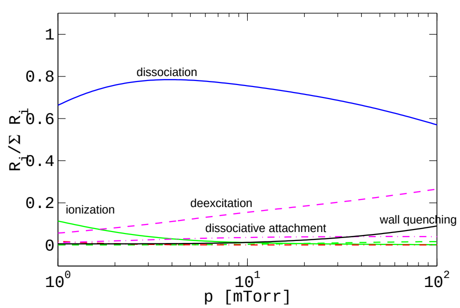
- The density of the metastable singlet delta state $O_2(a^1\Delta_g)$ is roughly 2 – 11 % of the total O_2 density in the pressure range of interest
- The density of the $O_2(b^1\Sigma_g^+)$ and the Herzberg states is roughly 1 – 2 % of the total O_2 density

Creation of $O_2(a^1\Delta_g)$



- The metastable $O_2(a^1\Delta_g)$ is mainly created by electron impact excitation

Loss of $O_2(a^1\Delta_g)$

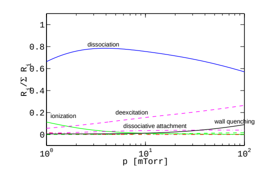


- The metastable $O_2(a^1\Delta_g)$ is mainly lost through by electron impact dissociation

$$e + O_2(a^1\Delta_g) \longrightarrow O(^3P) + O(^3P) + e$$

$$e + O_2(a^1\Delta_g) \longrightarrow O(^3P) + O(^1D) + e$$

Loss of $O_2(a^1\Delta_g)$



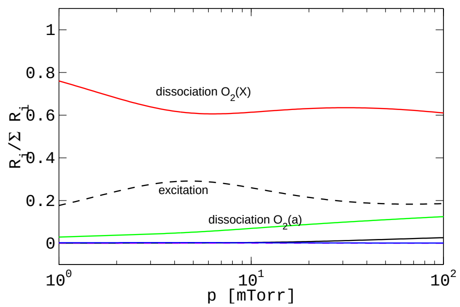
- Deexcitation

$$e + O_2(a^1\Delta_g) \longrightarrow O_2(X^3\Sigma_g^-) + e$$

plays increasing role with increasing pressure

- The contribution of ionization is roughly 10 % at 1 mTorr and falls with increased pressure
- The contribution of quenching at the wall is negligible up to 10 mTorr pressure and increases to roughly 10 % at 100 mTorr

Creation of $O(^1D)$



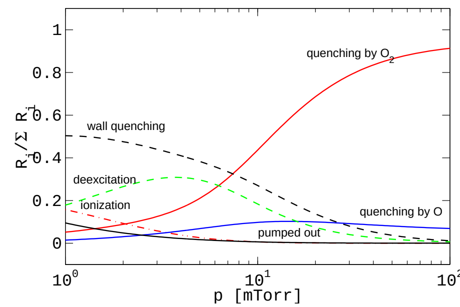
- The metastable $O(^1D)$ is mainly from dissociation

$$e + O_2(X^3\Sigma_g^-) \longrightarrow O(^3P) + O(^1D) + e$$

- The second most important source is direct excitation

$$e + O(^3P) \longrightarrow O(^1D) + e$$

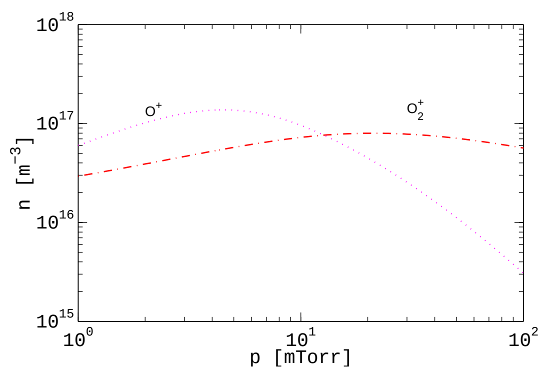
Loss of $O(^1D)$



- The $O(^1D)$ is mainly lost by recombination at the wall at low pressures
- At higher pressure quenching by molecular oxygen is the main loss

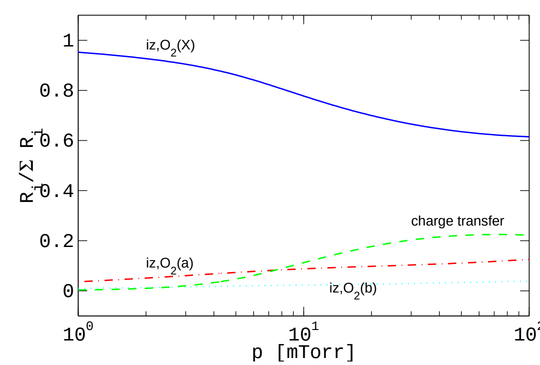
$$O(^1D) + O_2 \longrightarrow \text{products}$$

Positive ions



- The O^+ ion is the dominant positive ion below 10 mTorr
- The O_2^+ ion is the dominant positive ion above 20 mTorr

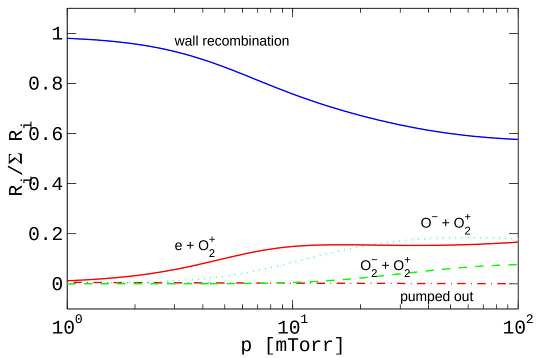
Creation of O_2^+



- The O_2^+ ion is mainly created by electron impact ionization of the oxygen molecule in the ground state

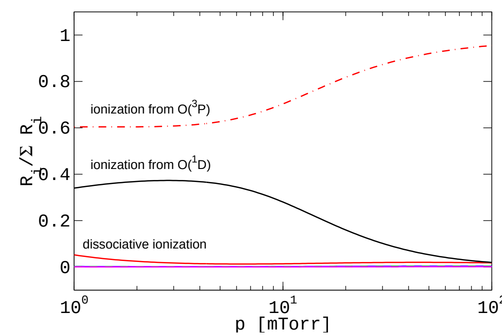
$$e + O_2(X^3\Sigma_g^-) \longrightarrow O_2^+ + 2e$$

Loss of O_2^+



- The O_2^+ ion is mainly lost to the chamber walls
- Recombination is important, in particular at higher pressure

Creation of O^+

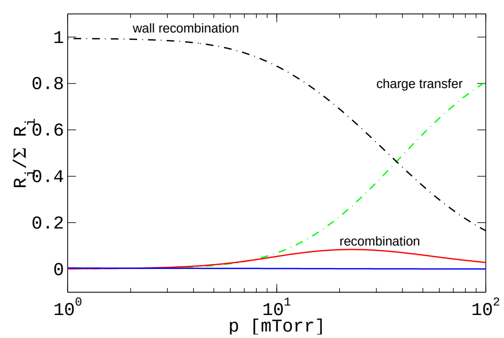


- The O^+ ion is mainly created by electron impact ionization from the oxygen atom

$$e + O_2(^3P) \longrightarrow O^+ + 2e$$

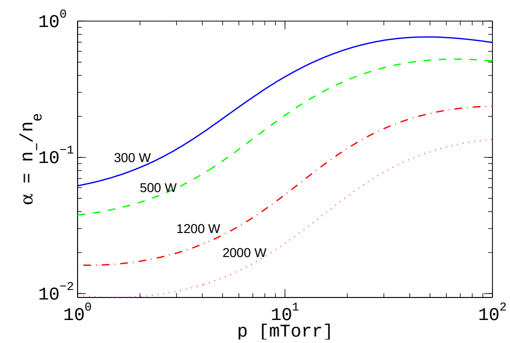
$$e + O_2(^1D) \longrightarrow O^+ + 2e$$

Loss of O^+



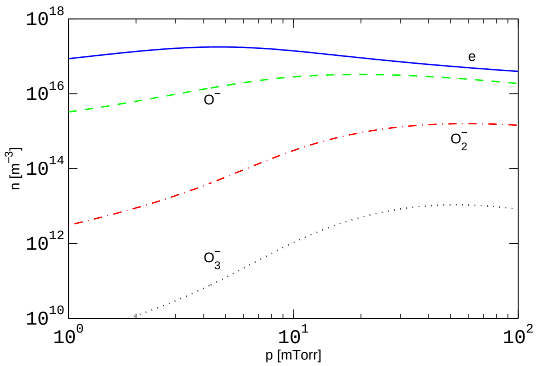
- The O^+ ion is mainly lost to the chamber walls
- Charge transfer is important at higher pressure

Negative ions



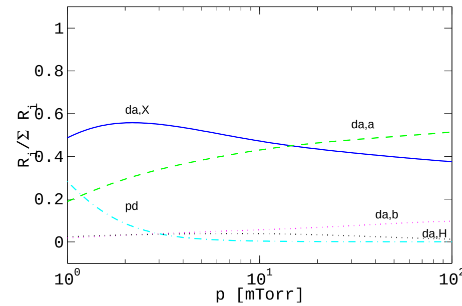
- Oxygen discharges are weakly electronegative
- The electronegativity increases with decreasing applied power and increasing pressure

Negative ions



- The dominant negative ion is O^-
- The density of O_2^- and O_3^- is significantly smaller

Creation of O^-

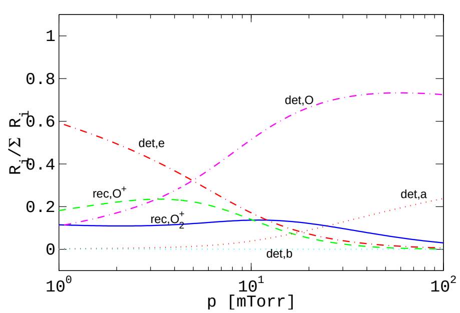


- Creation of O^- is mainly through dissociative electron attachment to the oxygen molecule

$$e + O_2(X) \longrightarrow O^- + O$$

$$e + O_2(a) \longrightarrow O^- + O$$

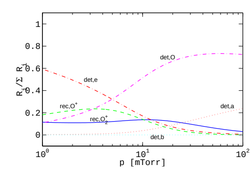
Loss of O^-



- At low pressure (< 3 mTorr) electron impact detachment dominates

$$e + O^- \longrightarrow O(^3P) + 2e$$

Loss of O^-



- At higher pressure (> 20 mTorr) associative detachment by oxygen atom dominates

$$O(^3P) + O^- \longrightarrow O_2 + e$$

- At low pressures (< 10 mTorr) ion-ion recombination accounts for roughly 30 – 40 % of the total O^- loss
- Detachment by $O_2(a)$ is negligible below 10 mTorr, its role increases with increasing pressure and its contribution is roughly 22 % at 100 mTorr

Summary

- A global (volume averaged) model of an oxygen discharge has been demonstrated
- New rate coefficients for ion-ion recombination are proposed
- The reaction rates for creation and loss of the main species of the oxygen discharge have been reviewed
- Creation of O^- is mainly through dissociative electron attachment to the oxygen molecule in ground state and the singlet delta state
- Electron impact detachment dominates destruction of O^- at low pressure
- Associative detachment dominates destruction of O^- at high pressure

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