Quantitative Diagnostics of Inductively-Coupled Plasmas in $\text{O}_2$ : Densities and energy distributions

Jean-Paul Booth, Mickäel Foucher, Daniil Marinov, Andrew Gibson, Adriana Annušová and Vasco Guerra
Motivation

Why study low pressure RF inductive discharges in diatomic gases?
RF plasmas in $\text{Cl}_2 / \text{O}_2$ (& often HBr) at low pressure widely used for selective, anisotropic etching of Si, InP etc
Motivation: understand plasmas in molecular gases

Motivation:
understand plasmas in molecular gases

Most academic studies:
- Rare gas plasmas: Ar

Most applications:
- Mixtures of polyatomic gases:
  - CF$_4$
  - C$_4$F$_8$/O$_2$/Ar
  - SiH$_4$/H$_2$
  - Cl$_2$/HBr/O$_2$
Motivation:
understand plasmas in molecular gases

Rare gas plasmas: Ar

Diatomic gas plasmas:
O₂, Cl₂, H₂...

Mixtures of polyatomic gases:
• CF₄
• C₄F₈/O₂/Ar
• SiH₄/H₂
• Cl₂/HBr/O₂

Most plasma physics studies..

Shows most of the mechanisms occurring in polyatomics:
• Dissociation, surface recombination
• Electronegativity
• Vibrational + rotational excitation

- But simpler, can measure (nearly) everything!

Test (validate) and improve Models:
- “Global” 0D models with plasma chemistry
- 2D Fluid Plasma + chemistry model: HPEM

Most applications..
The Inductively Coupled Plasma Reactor at LPP:

**Chamber:**
- Anodized aluminium
- $\varnothing$ 55cm height 10cm

**Parameters:**
- Industrial Scale Reactor dimension for 300mm wafers
- Industrial gases ($O_2$, $Cl_2$, HBr)

**Operating Conditions:**
- Pressure: 5-100 mTorr
- Power: up to 500W
- All surfaces $Al_2O_3$
  (no substrate)
What we can measure?

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron density</td>
<td>Microwave resonant probe</td>
</tr>
<tr>
<td>Negative ions</td>
<td>+ laser photodetachment</td>
</tr>
<tr>
<td>O atom density</td>
<td>TALIF</td>
</tr>
<tr>
<td>Vibrational distribution</td>
<td>UV absorption spectroscopy</td>
</tr>
</tbody>
</table>

Gas temperature:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Measurement</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$ Trott</td>
<td>-</td>
<td>UV absorption spectroscopy</td>
</tr>
<tr>
<td>$Ar^m$ Doppler</td>
<td>-</td>
<td>IRLAS vs IRLIF</td>
</tr>
<tr>
<td>O atom Doppler</td>
<td>-</td>
<td>HR TALIF</td>
</tr>
</tbody>
</table>
Electron density: Hairpin probe

¼ wave resonator: ~ 3 GHz:
- measure plasma permittivity from frequency shift with plasma
- deduce electron density from permittivity

Avoids many of the problems of Langmuir probes:
- Probe contamination
- Return current path (insulating reactor walls!)
- RF compensation

Negative ions: detect electron pulse from laser photodetachment
Electron density

Broad maximum @ 40 mTorr

Approximately linear increase with RF power
Electron density

Broad maximum @ 40 mTorr

High Te, Vp: Energy dissipated accelerating ions across sheath

Energy dissipated in inelastic collisions

Negative ions?
Electron density: \( \text{O}_2 \) 200 W

Compare to HPEM

Predicts maximum at the correct pressure

High pressure trend poorly modelled

Electron density moves off-axis
Negative Ion density

Laser photodetachment / hairpin detection of photoelectrons

Courtesy of Nishant Sirse, Dublin City University
Electronegativity

$$\alpha = \frac{n_-}{n_e}$$

Negative ion density lower than electron density except at low pressure and power

Not responsible for electron depletion
Negative ion destruction: Associative Detachment

Atoms:

\[ \text{O}^- + \text{O} \rightarrow \text{O}_2 + \text{e} \]  (exothermic in \( \text{O}_2 \))

Metastable states: \( \text{O}_2 \, ^1\Delta_g \) (at \( \approx 1 \text{ eV} \))

\[ \text{O}^- + \text{O}_2 \, ^1\Delta_g \rightarrow \text{O}_3 + \text{e} \]
\[ \rightarrow \text{O}^- \, _2 + \text{O}_2 \]
\[ \rightarrow 2\text{O}_2 + \text{e} \]


As a result, \( \text{O}_2 \) plasmas have a much lower density of negative ions

Electro-negativity highest at low pressure and low power (\( \text{O} \) and \( \text{O}_2 \, ^1\Delta_g \) low)
Negative ion density: compare to HPEM Simulation

Pure $O_2$

Model strongly overestimates negative ion density!

Loss processes underestimated, or missing mechanisms?
Atom densities:
Two-Photon Absorption Laser-Induced Fluorescence (TALIF)

- High spatial and temporal resolution measurements
- Relative densities of ground-state O atoms
- Absolute densities: use calibration techniques

Pure O$_2$:
Atom density

O density increases:
- with pressure
- with RF power: but saturates

→ Dissociation fraction?
Pure O₂:
"Dissociation fraction"

Normalise to \( n_{0 \text{O}_2} \), the density of (cold) gas before plasma:

Maximal at 10 mTorr
\((n_e \text{ maximum at 40 mTorr})\)

Dissociation saturates @ 20-30%

Why not 100%?

Gas temperature?
O atom density: comparison to HPEM

Pure $\text{O}_2$ 200 W

Model strongly overestimates O atom density!

Error in dissociation cross-sections?
High-sensitivity ultra-broad-band Absorption spectroscopy

- Baseline noise $\approx 10^{-5}$, 250nm spectrum simultaneously
- Allows whole vibrational bands to be observed
Pure O$_2$ plasma
UV absorption

Cold O$_2$ doesn’t absorb above $\approx$200 nm...
Pure O$_2$ plasma
UV absorption

Levels up to v'' ≈ 18 half-way to dissociation!

Schumann-Runge bands from highly vibrationally excited O$_2$
Pure O$_2$ : UV absorption

Vibrational-state resolved absorption cross-sections
→ Extract vibrational distribution functions

(Courtesy of Christophe Laux / Specair)
Pure $O_2$ : UV absorption

Vibrational-state resolved absorption cross-sections
→ Extract vibrational distribution functions

(Courtesy of Christophe Laux / Specair)

(NB cannot measure below $v^\prime\prime=4$)
O₂ Vibrational distribution functions (function of RF power : 10 mTorr)

- Tail $T_v \approx 7000$ K
- Up to 3% of O₂ in $v = 4-18$
- Saturates at high power
O₂ Vibrational distribution functions
(function of pressure: 500W)

Tail $T_{\text{vib}}$ about 7000K
-independent of pressure or power!
Modelling the VDF: IST Lisbon

Lowest levels in equilibrium with $T_{gas}$

Higher levels much hotter

VDF determined by:
- electron impact excitation
- $V - T\, O_2 - O$

Population $[O_2(X,v)]\, (cm^{-3})$

10 mTorr $O_2\, 500W$

Temperature of first levels about 1000K

Tail temperature: -7000K

Experiment

Model
Effect of vibrational excitation on electron-induced processes

Excitation to \( >v=10 \) has a strong effect on both cross-sections:

- Lower threshold
- Higher cross-section

Dissociation and negative ion production significantly enhanced
Gas temperature:
Absorption spectra at higher resolution:

Look at one band in higher resolution:
Change grating 300l/mm to 2400l/mm:
Absorption spectra at higher resolution:

Observe rotational structure

At these pressures $T_{\text{trans}} \approx T_{\text{rot}} \ll T_{\text{vib}}$
Absorption spectra at higher resolution:

Fit to simulated spectra to determine $T_{\text{rot}}$: 

![Graph showing absorption spectra with experiment and simulation data at 600 K.](image)
O₂ rotational temperature

Fit to simulated spectra to determine $T_{\text{rot}}$:

$T_{\text{rot}}$ up to 900K!

Explains why O atom density does not exceed 30% of initial gas density
Gas temperature from $\text{Ar}^m$ IRLAS Doppler width

Add 10% Ar
Determine temperature from Doppler width of Ar metastable absorption at 772nm

Laser beam at reactor mid-plane:

NB measurement integrated over the reactor diameter, weighted by the $\text{Ar}^m$ density profile
Gas temperature from $\text{Ar}^m$ IRLAS Doppler width

Is thermal equilibrium $T_{\text{trans}} = T_{\text{rot}}$ established at the lowest pressures?
Compare the two techniques:

**Ar\textsuperscript{m} Doppler temperature:**

- \( T_{\text{gas}} \) from Ar\textsuperscript{m} IRLAS

**O\textsubscript{2} rotational temperature:**

- \( T_{\text{rot}} \)

Reasonable qualitative agreement
- but at low pressure, IRLAS is cooler than \( O_2 \ T_{\text{rot}} \)

Can we directly measure translational temperature of O atoms?
- with time and space resolution
- probe energy relaxation rates (surface and gas phase)?
Simulated gas temperature
(300W)

Reasonable trend but underestimated heating:

- underestimated energy release from dissociation?
- neglected heating mechanisms?
- overestimated thermal accommodation at walls?
High resolution TALIF for O atom temperature

D. Marinov, O. Guaitella, M. Foucher, JP. Booth
(LPP)

C. Drag, C. Blondel
(Lab Aime Cotton)
A lot of information is hidden in the line shape!
But it is not accessible because of the broad and often unknown laser line profile.
Doppler line width – a direct measure of the translational gas temperature

\[
\frac{\Delta \nu_{\text{FWHM}}}{\nu_0} = \sqrt{\frac{8kT \ln 2}{Mc^2}}
\]

At 300 K \( \Delta \nu_0 = 0.3 \text{ cm}^{-1} \)
Single mode pulsed laser (Aimé Cotton)

Let's have a beer

20 Hz
80 mJ/pulse
Single mode pulsed laser (Aimé Cotton)

- Doppler and sub-Doppler line profiles can be accurately measured.
**Laser performance**

Fundamental line width: determined by Fourier transform of pulse duration (22MHz) + locking jitter (25MHz)

<table>
<thead>
<tr>
<th></th>
<th>Wavelength (nm)</th>
<th>Laser energy (mJ)</th>
<th>Estimated line width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fundamental</td>
<td>902.32</td>
<td>10</td>
<td>47 MHz</td>
</tr>
<tr>
<td>Frequency doubled</td>
<td>451.16</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Frequency quadrupled</td>
<td>225.58</td>
<td>0.25</td>
<td>188 MHz (0.01cm⁻¹ @ 2 photon)</td>
</tr>
</tbody>
</table>

30x narrower than a dye laser!
O atoms in an O$_2$ DC discharge

1-4 Torr O$_2$ in a 2cm diameter tube
5-40 mA current
Gas temperature measurements in a low pressure dc glow discharge

Tg accuracy is ±10K

O₂ dc discharge 2 Torr – collisional broadening is negligible
Comparison to previous measurements

(T deduced from $O_2$ density : VUV absorption)

Good agreement within errors of previous measurements
Doppler-free TALIF spectroscopy

Laser line width
+ natural line width
+ collisional broadening
Doppler-free measurements of the fine structure components of O$^3P$

$O_2$ dc discharge 2 Torr
Measurements of the collisional broadening coefficients in the Doppler-free configuration

\[ \gamma_{O_2} = 0.38 \pm 0.08 \text{ cm}^{-1}/\text{atm} \]

The only literature value\(^1\) \(\gamma = 0.42 \text{ cm}^{-1}/\text{atm}\) in a \(O_2/CH_4\) flame at 2500 K

Pressure broadening in the $\mu$APPJ (normal TALIF configuration)

He/0.5\%O$_2$

$\gamma_{He} = 0.47$ cm$^{-1}$/atm at 300 K
Summary of HR TALIF

- **atm pressure:**
  - Pressure broadening

- **Low pressure Doppler:**
  - Translational gas temperature

- **low pressure sub-Doppler**
  - Pressure broadening
  - Fine structure
  - Atomic physics
Conclusions

**Comprehensive data set to test models of Oxygen plasmas**
- Atom densities and kinetics
- Molecule densities and energy distributions
- Electron (& negative ion) densities,
- Gas temperature

**Even for the simple case of pure diatomic gases,** state-of-the-art models are unable to correctly predict trends with gas pressure

- **Fundamental collision data is lacking or inaccurate**
- **Gas heating** is very significant and remains to be fully understood
- **Vibrational excitation** can be significant and may play a large role

**Future work:**
High resolution TALIF – in ICP reactor
- time and space resolution to understand relaxation kinetics

**FUNDING:**