

Density and temperature measurements in inductively-coupled plasmas in Cl₂/O₂, pure gases and mixtures, using a new high sensitivity ultra broad-band absorption spectroscopy setup

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Abstract: A new high sensitivity ultra broad-band absorption spectroscopy setup is used to analyse inductively-coupled plasmas in pure Cl₂, pure O₂ and mixtures. The high signal-to-noise ratio and baseline stability ($2 \cdot 10^{-5}$) allows the measurement of rotational and vibrational temperatures in pure O₂ plasmas, of Cl₂ density, vibrational temperature and negative ion density in pure Cl₂ and of oxychloride densities and temperatures in mixtures.

Keywords: ICP, Cl₂/O₂, absorption spectroscopy

1. Introduction

The experimental study of Inductively-Coupled Plasmas (ICP) in pure Cl₂, pure O₂ and in mixtures is of great interest for model validation. Moreover, plasmas of Cl₂/O₂ are widely used (often with HBr) in the fabrication of CMOS transistor gates. Numerous simulations of these plasmas have been developed, but only a few experimental results exist to validate them.

In this paper we provide results obtained using a new high sensitivity broad-band absorption spectroscopy setup. It uses an intense, stable and broad-band (200 - 800 nm) light source (Energetiq LDSL-EQ99), achromatic optics and an aberration-free spectrograph (Acton SCT-320).

In a plasma of pure O₂, highly vibrationally excited molecules were observed via the Schumann-Runge absorption bands [2], allowing the O₂ vibrational and rotational temperatures to be determined. In pure Cl₂, the vibrational temperature is determined and negative ions are detected. In Cl₂/O₂, oxychloride reaction product densities and temperatures are measured.

Measurements were made over a range of experimental parameters: total gas pressure [5-80] mTorr, injected radio-frequency (RF) power [100-500] W and gas composition (in the Cl₂/O₂ case).

2. Experimental setup

The reactor used for all the experiments has been presented elsewhere by Booth *et al.* [1]. Briefly, it is a cylindrical chamber (55 cm diameter, 10 cm high) with a 4-turn planar coil that produces the plasma through a dielectric window. The power is injected by a RF generator that can be pulsed. The pressure is regulated between 5 and 80 mTorr by a valve above the turbo-molecular pump. Mass flow controllers are used to regulate the gas flow or specify a particular ratio in Cl₂/O₂ plasmas.

The absorption spectroscopy setup is presented in Fig. 1. The spherical beam of the light source (Energetiq LDLS-EQ99) is collimated with a parabolic mirror and

directed through the reactor by a flat mirror. This light source is very broad-band (200-800) nm, intense and highly stable (after two hours heating). The light beam crosses the reactor at mid-height and is focused onto the entrance slit of an aberration-free spectrograph (Acton SCT-320). Three gratings (2400-1200-300) 1/mm provide spectral ranges of (30-60-240) nm respectively in a single measurement. The light is then analysed by a 1024 element photodiode array. All these items are mounted on a single chassis in order to reduce the noise due to vibration.

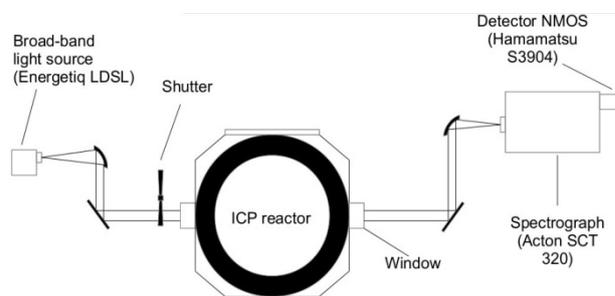


Fig. 1. Absorption spectroscopy setup.

Absorbance spectra are recorded using a LabView program which controls a shutter and the plasma extinction/ignition.

The absorbance, $A(\lambda)$, is determined using a four-stage procedure:

- 1 : $L_1(\lambda) = \text{Plasma on/Light on}$
- 2 : $L_2(\lambda) = \text{Plasma on/Light off}$
- 3 : $L_3(\lambda) = \text{Plasma off/Light on}$
- 4 : $L_4(\lambda) = \text{Plasma off/Light off}$
- $A(\lambda) = -\ln \left(\frac{L_1(\lambda) - L_2(\lambda)}{L_3(\lambda) - L_4(\lambda)} \right)$

Signal averaging over a few minutes allows the (wavelength independent) shot noise to be reduced below

10^{-5} , allowing absorbancies as low as 10^{-4} to be easily seen. For longer integration times residual fluctuations in the lamp spectrum become the limiting factor; typically the baseline is flat to within $2 \cdot 10^{-5}$ across the spectral range 210-450 nm, but with a fluctuating (but wavelength independent) offset of the order of $\pm 2 \cdot 10^{-4}$. This vertical offset does not impact the spectra shape. This setup has significantly improved sensitivity compared previous studies using Xe arc lamps[2].; more recently UV light-emitting diodes (UV-LED) have shown improved noise levels [3], but only have spectral ranges of a few 10^3 's of nm.

3. Results and discussion

Fig. 2 shows an example spectrum obtained in pure O_2 at 10 mTorr 500 W. Numerous bands corresponding to vibrational transitions within the Schumann-Runge bands [4] can be seen (some transitions have been indicated on the figure showing the presence of molecules in vibrational levels up to $v'' = 19$) over a wide spectral range [250-400] nm (other bands are present further but more difficult to distinguish). These transitions would not be visible in room-temperature O_2 . In order to determine the vibrational distribution we simulated the absorption of various vibrational bands using the PGOPHER freeware [5], with spectroscopic constants from the literature [4]. Fig. 3 shows the vibrational state populations ($v = 9$ to 15) at 80 mTorr 500 W. A change in slope is clearly visible around $v = 12$; this could be explained by spatially-varying vibrational temperatures. A full investigation as a function of experimental conditions is ongoing.

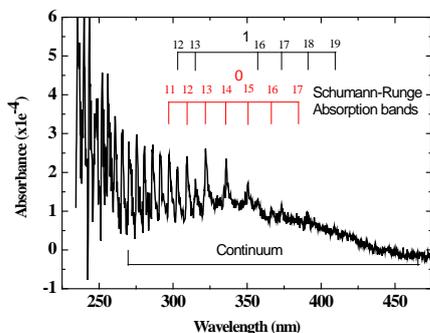


Fig. 2. O_2 spectrum at 10 mTorr 500 W. Some Schumann-Runge absorptions transitions are indicated in the figure.

Using the 2400 g/mm grating to analyse the (0-11) band around 300 nm at higher resolution shows the rotational structure, as shown in Fig. 4 (80 mTorr 500 W). By fitting these results with simulated spectra (PGOPHER) the O_2 rotational temperature (which can be considered to be in equilibrium with the gas translational temperature at this pressure) was determined as a function of gas pressure and RF power, as shown in Fig. 5.

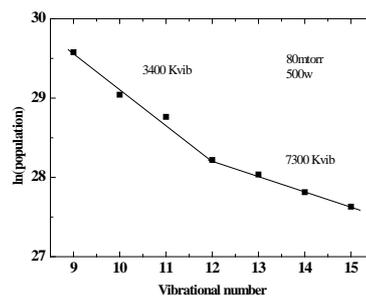


Fig. 3. Densities of various vibrational levels as a function of the vibrational number. Example at 80 mTorr 500 W.

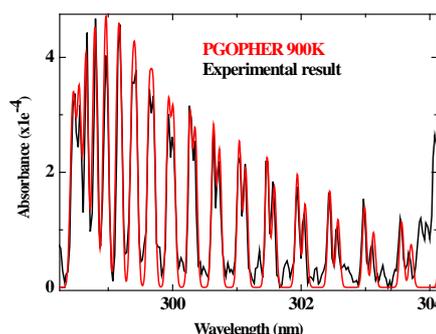


Fig. 4. Rotationally resolved spectrum of the Schumann-Runge (0-11) band at 300 nm, 80 mTorr 500 W. The simulation with PGOPHER is shown in red.

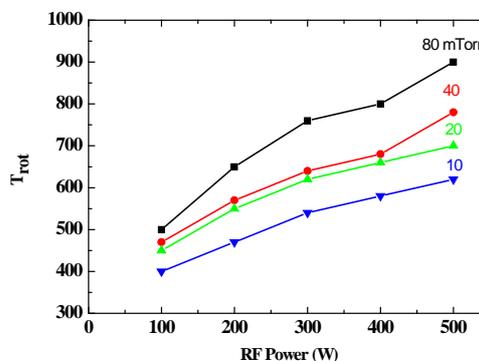


Fig. 5. Rotational temperatures as a function of power and pressure in an ICP of pure O_2 . The results are obtained by simulation with PGOPHER.

The gas temperature is significantly above ambient, and increases both with power and pressure, reaching up to 900 K. Various mechanisms can be invoked to explain these high vibrational and rotational temperatures, including electron impact excitation of O_2 molecules and the energy released by recombination of O_2 at the reactor walls, combine with (V-T) energy transfer processes.

Fig. 6 shows absorption spectra measured in pure Cl_2 plasmas at 10 mTorr for power varying from 100 to 500 W. The Cl_2 absorption continuum centred around 330 nm is clearly visible. The absorbance decreases as a

function of RF power, due both to Cl_2 dissociation and to gas heating and dilation (at constant pressure). The line-integrated Cl_2 density first drops quickly with power, but then does not decrease much below 50% as power is increased. It is possible there is near-complete dissociation of Cl_2 at the reactor centre, with residual absorbance due to cold, undissociated Cl_2 close to the reactor walls.

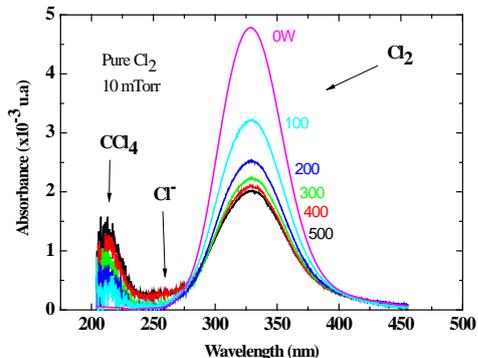


Fig. 6. Absorption continuum spectra of the Cl_2 molecule at 10 mTorr for injected powers comprised between 100 and 500 W. Cl^- ions as well as CCl_4 can be seen.

At the long wavelength side (> 450 nm) the absorbance tends towards zero under all conditions. However below 275 nm an offset appears which increases with RF power. This continuum absorption can be attributed to Cl^- photo-detachment [6], corresponding to a negative ion density of the order $5 \times 10^{11} \text{ cm}^{-3}$.

Between 200 and 250 nm, another broad absorption band can be seen. This appears to correspond to CCl_4 molecules, formed by reaction of chlorine with carbon in the O-ring seals.

As for the pure O_2 case, we wanted to measure the vibrational temperature of the Cl_2 molecule. Fig. 7 shows the absorption cross sections from the four lowest vibrational levels of the Cl_2 molecule. The experimental spectra are dominated by the $v = 0$ level, indicating the vibrational temperature is quite low. Fig. 8 shows the same data as Fig. 7 but normalized, showing a slight increase of the width of the absorption band with RF power, indicating the presence of vibrationally excited molecules. The vibrational distribution was deduced by fitting experimental spectra using the cross-sections of Fig. 7. The population densities for the different vibrational levels were then determined and plotted as a function of the vibrational number. Fig. 9 shows a result for 10 mTorr and 500 W. A bi-Maxwellian distribution is observed, with a cold (435 K) distribution with a high temperature (1000 K) tail.

Fig. 10 show the absorption spectrum in a plasma of 50% Cl_2 / 50% O_2 at 10 mTorr 500 W. In addition to the Cl_2 absorption continuum and the Schumann-Runge bands of O_2 , we can see the appearance of other vibrational structures. These correspond to oxychloride

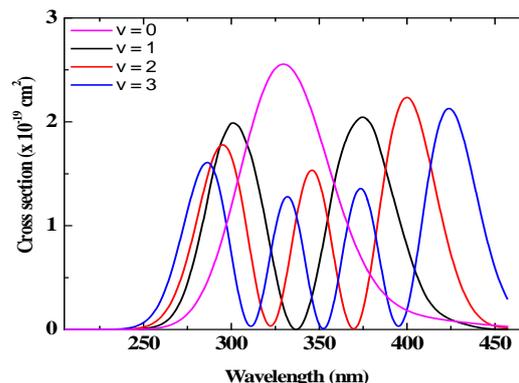


Fig. 7. Absorption cross sections from the four first vibrational levels of the Cl_2 molecule.

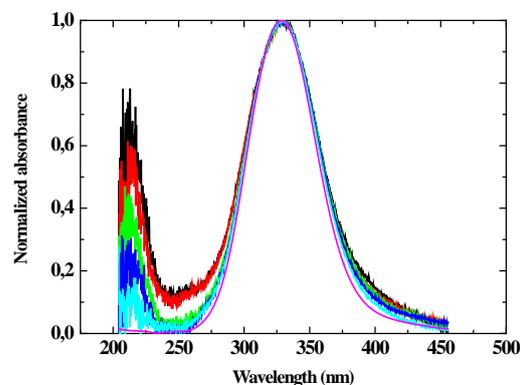


Fig. 8. Same data as Fig. 7 but normalized to unity.

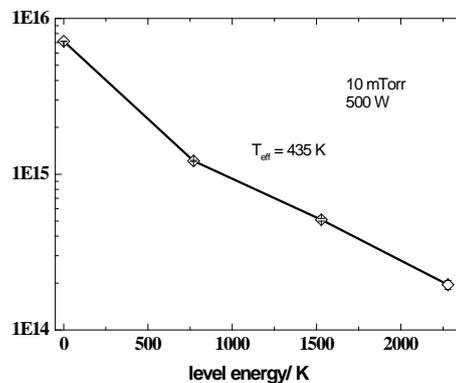


Fig. 9. Population of Cl_2 vibrational levels as a function of energy on log scale.

reaction products, especially ClO and OClO . Fig. 11 shows a first estimation of the variation of the densities of these species as a function of the gas composition was made using cross sections found in the literature [7]. We can see that both oxychlorides are formed when Cl_2 or O_2 is added. ClO reaches a maximum at 50% Cl_2 and 50% O_2 . OClO increases monotonically with O_2 content but has much lower density than ClO .

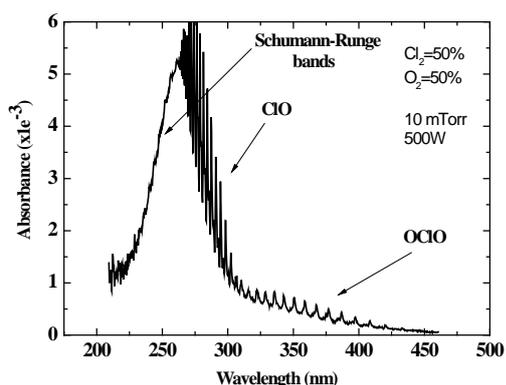


Fig. 10. Experimental spectrum in Cl_2/O_2 mixture, 50% Cl_2 and O_2 at 10 mTorr 500 W. Oxychlorides vibrational structures are visible.

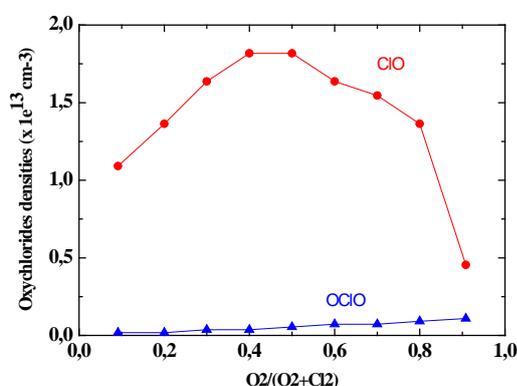


Fig. 11. ClO and OClO densities as a function of gas composition at 10 mTorr and 500 W.

Further analysis of these spectra using PGOPHER to analyse the densities, rotational and vibrational temperatures is in progress.

4. Conclusion

Gas rotational and vibrational temperatures have been measured in ICP's of pure O_2 ; vibrational temperatures were measured in ICP's of pure Cl_2 as well as the negative ion density; in Cl_2/O_2 mixture the densities of oxychlorides were measured for the first time (to our knowledge) by absorption spectroscopy. These results provide a comprehensive data set for model validation. Finally we have demonstrated the potential of our new absorption spectroscopy setup: its high sensitivity and signal to noise ratio as well as excellent baseline stability open many new possibilities for plasma chemical analysis.

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