Kinetics of active species in a DC discharge by synchrotron VUV absorption

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Abstract: The kinetics of reactive species in a DC positive column discharge in pure O_2 was studied using time-resolved Vacuum Ultraviolet (VUV) absorption spectroscopy in fully and partially modulated discharges. O_2 molecules in the ground (X) and metastable (a) states are measured directly. Measurements of the recovery of the O_2 X density in the afterglow shows several components with different lifetimes that can be attributed to gas cooling and O_2 b quenching (fast), O atom recombination at the walls (intermediate) and O_2 a quenching at the walls (slow). The composition of the plasma phase can be deduced from the amplitudes of these contributions. Partial modulation studies allow the kinetics of the plasma-on phase to be studied; in this case the kinetics is much faster due to the presence of electron-impact (excitation and de-excitation) processes.

Keywords: Oxygen DC Discharge Kinetics VUV absorption Surface reactions

1. General

Electrical discharges in oxygen gas are widespread in nature and occur in many plasma applications such as surface treatment and plasma medicine. They are also an ideal archetype for the understanding of molecular plasmas, showing the effects of dissociation/surface recombination, electron attachment, high densities of molecular and atomic metastable states, vibrational excitation and gas heating. Nevertheless, many uncertainties remain about the cross-section and reaction sets, as well as the surface processes, all essential for reliable modelling. We are making comprehensive measurements absolute densities and kinetics of the principal transient species in a well-characterised and reproducible system, a DC positive column in pure O_2. This provides a uniform plasma column with constant reduced field over a wide range of gas pressure and electron density (pressure 0.2-10 Torr, current 5-40 mA), ideal for model validation or improvement. A range of powerful diagnostic techniques are employed, including vacuum ultraviolet (120-200nm) absorption spectroscopy, cavity ringdown spectroscopy (CRDS), time resolved optical emission spectroscopy and high resolution two-photon laser-induced fluorescence (HR-TALIF)[1]. The present paper presents results of time-resolved absorption measurements performed using the monochromatic branch of the DESIRS VUV beamline at Synchrotron Soleil.

2. Experimental

The discharge is ignited in pure O_2 flowing in a borosilicate glass tube (id 20mm, length 56cm) between cylindrical electrodes located in side tubes. The discharge current stabilized by a non-inductive 68kΩ ballast resistor on the high-voltage cathode side. The current is modulated, either using a high-voltage switch (for 100% modulation) or by an FET switch in parallel with a 15kΩ resistor connecting the anode to ground. The surface temperature is controlled by thermostated fluid flowing in an outer envelope (5-50C). The tube ends are sealed by MgF_2 windows, allowing the VUV beam to pass along the tube axis. The VUV beam from the undulator is dispersed by a 10-metre spectrograph, using a 200lines/mm grating and an exit slit of 200 µm, giving an energy resolution of 10 meV. Part of the beam is sampled by a 45° MgF_2 beamsplitter, monitored by a scintillator and photomultiplier tube, to correct for beam intensity fluctuations. The transmitted beam is detected by a solar-blind photomultiplier. Optical emission perpendicularly to the axis of the tube was collected with a lens and analyzed with a 20cm monochromator and photomultiplier.

3. Results and discussion

An example of the recovery of the O_2 ground state density (measured at 7.1 eV) in the afterglow of a 100% modulate discharge is shown in Fig 1.

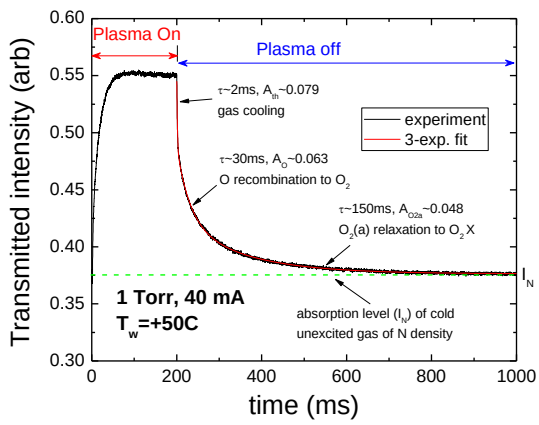

Fig. 1. VUV transmitted intensity in a 100% pulsed discharge at 1 Torr 40 mA

Three timescales can be distinguished clearly : 1) a fast process that we attribute to cooling and convection of the gas from the region near the walls to the central axis

(where the measurement is made), combined with quenching of O_2 b back to O_2 X, with a rate of $\approx 300s^{-1}$, 2) recombination of O atoms at the tube walls, with a rate of $\approx 30s^{-1}$, and 3) Quenching of O_2 a back to O_2 X at the tube walls, with a rate of $\approx 5s^{-1}$. We are able to unambiguously attribute these contributions due to independent, direct measurements of these species kinetics (either by VUV absorption or by optical emission). Therefore we can extrapolate back to the composition of the gas phase, without any other assumptions. The oxygen atom mole fraction deduced in this way is shown in Fig 2.

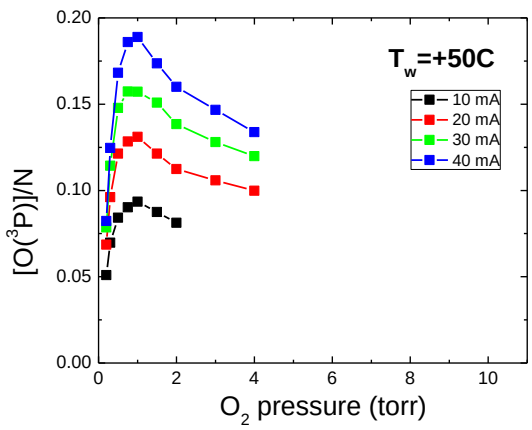

Fig. 2. Oxygen atom mole fraction as a function of gas pressure and discharge current, deduced from the O_2 X recovery in the afterglow.

We see that atoms represent up to 20% of the gas phase species, peaking at 1 Torr pressure and increasing with discharge current. Fig. 3 shows the oxygen atom loss frequency determined in two ways, in the steady state (partial modulation) by optical emission actinometry (844nm line), and in the afterglow from the O_2 X recovery.

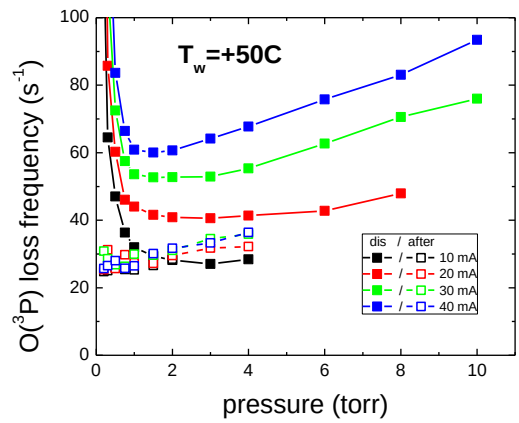

Fig. 3. Oxygen atom loss frequency determined in the afterglow (hollow symbols) by VUV absorption, and in a partially-modulated discharge (full symbols) by OES.

The results are striking different. First let us consider the results at pressures above 1 Torr. As we showed in a recent paper[2], oxygen atom recombination occurs via an Eley-Rideal mechanism with an activation energy of 0.15 eV. At higher discharge current and gas pressure the gas temperature increases significantly, resulting in atoms arriving at the surface with higher kinetic energy and recombining faster. The loss frequencies measured in the afterglow are in cold gas, so the surface recombination is slower and does not depend on the discharge current.

However, the rate in the afterglow at 4 Torr is about $10s^{-1}$ faster than in the discharge at 10 mA. This can be attributed to some reaction of O with O_2 to form O_3, a reaction that is much faster at low gas temperatures. At pressures below 1 Torr we recently reported that the surface recombination during the discharge is strongly increased by energetic ion bombardment[2]. Interestingly, this is not at all observed in the loss frequency determined in the afterglow. Therefore it appears that the surface recovers very quickly from the ion bombardment.

Figure 4 shows the mole fraction of O_2 $a^1\Delta_g$, which reaches up to 8% of the gas composition, and is maximal at low pressure. The O_2 $a^1\Delta_g$ loss frequency in the afterglow is shown in Fig. 5. It is quite slow, corresponding to surface quenching probabilities in the region of $\gamma=10^{-4}$. The changes in γ must be a consequence of the fluxes of reactive species to which it is exposed during the discharge. However, the O_2 $a^1\Delta_g$ loss frequency during the discharge (not shown) increases rapidly with discharge current, up to about $40s^{-1}$ at 40 mA. In this case election impact processes (mostly $e + O_2\ a^1\Delta_g \rightarrow e + O_2\ b^1\Sigma_g$, but also some super-elastic scattering : $e + O_2\ a^1\Delta_g \rightarrow e + O_2\ X\ ^3\Sigma_u$,) become dominant, and surface reactions only play a minor role.

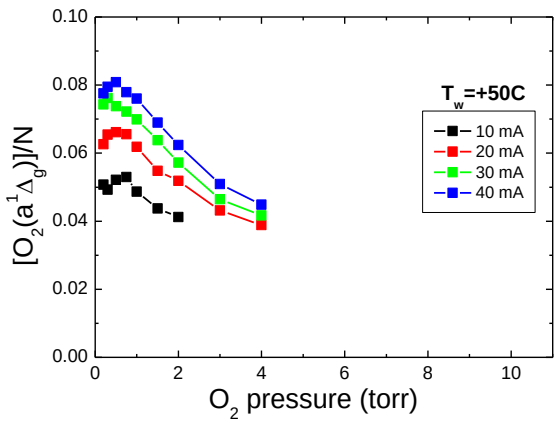

Fig. 4. O_2 a $^1\Delta_g$ mole fraction as a function of gas pressure and discharge current, deduced from the O_2 X recovery in the afterglow

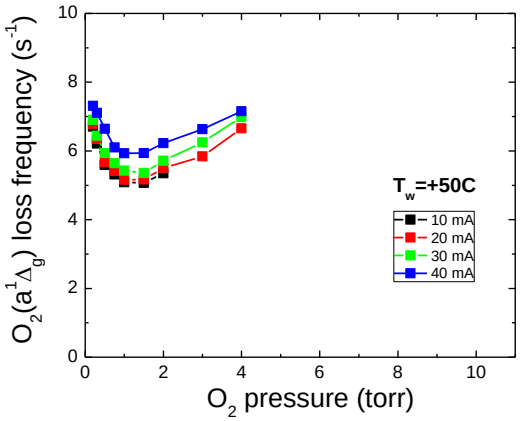

Fig. 5. O_2 a $^1\Delta_g$ loss frequency in the afterglow, as a function of gas pressure and discharge current.

4. Conclusions

We propose an unambiguous technique to determine the mole-fractions of the major components in an O_2 DC discharge, namely O_2 X and a $^1\Delta_g$ and oxygen ^3P atoms, as well as measurements of their loss frequencies both in the afterglow and in the steady-state discharge. Significant differences are seen between these two rates, which will be discussed in terms of the kinetic mechanisms, along with additional information provided by complementary diagnostic measurements.

5. Acknowledgements

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6. References

[1] J. P. Booth, D. Marinov, M. Foucher, O. Guaitella, D. Bresteau, L. Cabaret, and C. Drag, J Instrum **10**, C11003 (2015).

[2] J. P. Booth, O. Guaitella, A. Chatterjee, C. Drag, V. Guerra, D. Lopaev, S. Zyryanov, T. Rakhimova, D. Voloshin, and Y. A. Mankelevich, Plasma Sources Sci Technol **submitted** (2019).