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Laser Cavity Ringdown Spectroscopy of Oxygen Plasmas: Direct Measurement of the Densities of Oxygen Atoms, Ozone and Negative Ions and Gas Temperature

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Plasmas in oxygen, or oxygen-containing gas mixtures, are ubiquitous in naturally-occurring and man-made electrical discharges. Reliable modelling of these systems requires accurate cross-section and rate constant data, which ultimately depend on accurate measurements of the absolute density of the transient species present, of which O (^3P) atoms are one of the most important. Various methods have been proposed to measure oxygen atom densities, including optical emission actinometry and Two-photon Laser-induced fluorescence (TALIF), calibrated against Xe TALIF. However, both techniques depend on poorly-known cross-section data for their absolute calibration. Absorption spectroscopy has many advantages for absolute density measurements, since the Beer-Lambert law is inherently self-calibrating, and the only uncertainty comes from the accuracy of the transition strength (and knowledge of the absorber density profile along the beam path, if this is inhomogeneous). For oxygen atoms, the resonance transitions at 130nm have long been used, despite the difficulty of working with vacuum ultraviolet light. However, these allowed transitions are far too strong to be useful except for low atom densities or short absorption path lengths. An alternative is to measure the weak, forbidden forbidden $^3P_2 \rightarrow ^1D_2$ transition at 630nm. In this case, the single-pass absorption will be weak, of the order 10^{-5}, which cannot be measured directly. However, the use of cavity ring-down spectroscopy, using a cw single-mode diode laser and mirrors with reflectivity of the order 99.99%, allows such absorptions to be measured routinely.

We have made measurements in a DC positive column discharge in pure O_2. This system provides a long column (>50cm) of uniform plasma with known reduced electric field, ideal for model validation. The gas temperature is also easily determined, from the Doppler profile of the absorption peak. The oxygen atom mole-fraction reaches up to 30%, due to the low recombination probability of the borosilicate glass walls. Time-resolved CRDS was developed to measure the oxygen atom kinetics in pulse-modulated discharges, since the atom lifetime is slow compared to the cavity time (~20μs). These measurements also showed a time-varying continuum absorption below the O atom peak, which can be attributed to absorption by both O^- photodetachment and the Chappuis bands of ozone. The very different kinetics of these two species allows their two contributions to be separated, allowing the densities and kinetics of all three species to be determined.

Jean-Paul Booth is a CNRS research director at the Laboratoire de Physique de Plasmas at Ecole Polytechnique near Paris, where he has been since 2000. Before then he was a CNRS researcher at Université de Grenoble, following a PhD at the Physical Chemistry Laboratory of Oxford University. In 2006-08 he took time away from CNRS to work at Lam Research Corporation in California, where he was a technical director responsible for sensors and endpoint detection applied to plasma etch reactors. He specialises in the experimental study of the physics and chemistry occurring in (mostly) low pressure plasmas in reactive gases, and their interaction with surfaces. He has particularly focussed on radiofrequency plasmas for materials processing in the microelectronics industry, but is now working on more fundamental experimental studies of processes occurring in simple gases such as oxygen, and rigorous model validation. He has developed and applied many novel optical diagnostic techniques (one- and two-photon laser-induced fluorescence, broad-band absorption spectroscopy, cavity ring-down spectroscopy, synchrotron vacuum-ultraviolet absorption) to measure absolute reactive species densities and kinetics, as well as electrical probes, microwave resonance techniques for plasma physics parameters, and simpler sensors for in-situ control of industrial plasma processes. He also has an interest in the physics of capacitively-coupled radiofrequency plasmas: breakdown, electromagnetic effects in VHF plasmas, and tailored voltage waveform excitation for control of ion and electron fluxes and energy distributions.