Atomic oxygen measurements with THz absorption spectroscopy, ps-TALIF, and CRDS: A comparison

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Despite an ever-growing number of applications of low-temperature plasma technology, the common processes that occur in the plasma active zone and post-discharge region are still poorly understood. In particular, the non-equilibrium plasma chemical kinetics, and especially the atomic and molecular origins of many chemical and transport processes confined near surfaces remain mysterious. A detailed understanding of the complex chemical reaction networks would enable customised compositions of reactive species to be tailored for a specific plasma application. This requires highly sensitive and selective measurements of transient atoms, molecules and free radicals, their spatial and temporal distributions, and their transport behaviour. Of importance is also the evaluation of the gas temperature via the rotational and vibrational temperatures of the species and their respective temperature profiles, as these determine not only the density distribution of the species but also play a key role in the chemical kinetics. To detect atomic and molecular species, absorption spectroscopy has become a popular method as it has several advantages over other optical diagnostic techniques. Moreover, molecular spectroscopy in the infrared region is highly favourable because of the plethora of molecular bands that can be accessed, enabling selective and very sensitive spectroscopic measurements of a large number of compounds. However, the direct selective detection of atoms is only possible in the far-infrared spectral region, in addition to the well-known vacuum-ultraviolet spectral region. For a long time, the electromagnetic radiation in the terahertz (THz) spectral region from microwaves to the far-infrared (100 GHz – 30 THz) was known as the so-called THz gap due to the lack of suitable radiation sources and detectors in this spectral range. During the last three decades, however, this has changed as the related technology has advanced and the emerging technology has started to leave the laboratory environment. This region contains many transitions of atoms and molecules that are of interest to the plasma community, such as O, Si, Al, F, N^+, OH, NH_3. In this contribution, the recent progress in spectroscopy in the THz spectral region to detect ground-state atomic oxygen will be discussed.

Terahertz absorption spectroscopy with quantum cascade lasers (QCLs) has recently been developed and implemented as a novel diagnostic technique for determining atomic oxygen densities in plasmas [1,2]. It is based on the detection of the $^3P_1 \leftarrow {}^3P_2$ fine structure transition of ground-state atomic oxygen at approximately 4.75 THz (i.e., approximately 63 µm or 158 cm^{-1}). THz absorption spectroscopy allows for direct measurements (i.e., no calibration is required) of absolute ground-state atomic oxygen densities, and its accuracy depends almost exclusively on the accuracy to which the line strength of the transition is known. Furthermore, the narrow laser linewidth of QCLs of just a few MHz makes it possible to determine the temperature from the detected absorption profiles as well. In addition, the experimental setup for THz absorption spectroscopy is relatively compact, especially compared to two-photon absorption laser induced fluorescence (TALIF) setups that typically involve bulky laser systems, and the requirements for the optical alignment are not as strict as for cavity ring-down spectroscopy (CRDS). These features make THz absorption spectroscopy an attractive diagnostic technique for atomic oxygen density measurements in plasmas.

To confirm the accuracy of THz absorption spectroscopy, we performed ps-TALIF [3] and CRDS measurements of atomic oxygen densities on the same capacitively coupled radio frequency (CCRF) oxygen discharge, for a variation of the applied power (20W to 100 W) and the gas pressure (0.7 mbar and 1.3 mbar). TALIF is currently the most established method for determining atomic oxygen densities and especially known for its high spatial and temporal resolution [4], while CRDS is an absorption technique that yields line-of-sight integrated densities in a similar manner as THz absorption spectroscopy [5]. The obtained atomic oxygen densities are in excellent agreement with each other, as can be seen in Fig. 1. This demonstrates that the three different diagnostic methods can be used interchangeably, provided that no spatial resolution is required. In addition, the results seem to confirm the new value for the two-photon absorption cross-section of xenon [6]; this has been a topic of discussion for years and remains one of the main systematic sources of error when performing TALIF experiments.

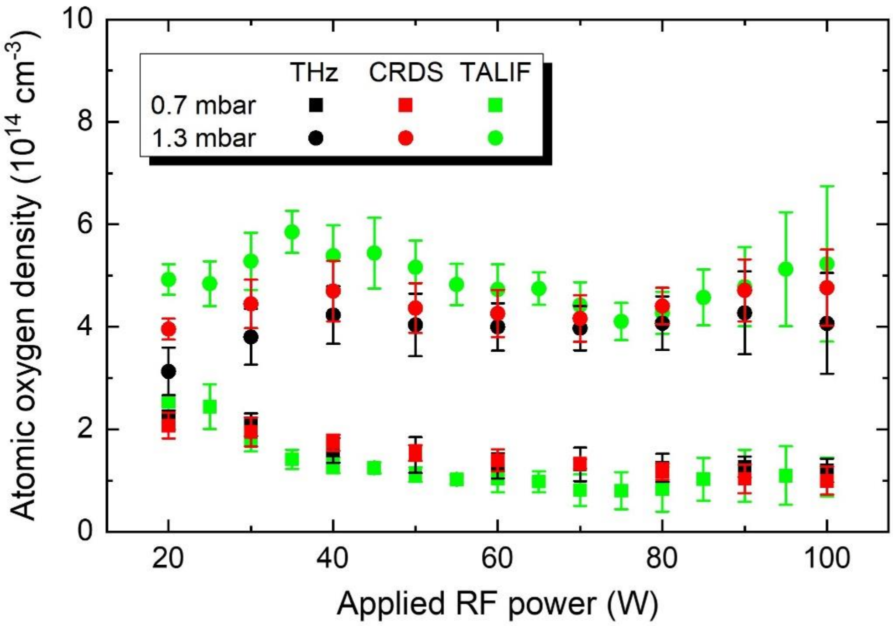

Fig. 1: Atomic oxygen densities measured with THz absorption spectroscopy, TALIF, and CRDS.

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