Measuring Atomic Oxygen Densities with a Terahertz QCL

ABSTRACT

Plasma applications heavily depend on atomic oxygen densities, but knowing those densities requires precise and accurate diagnostic techniques. Researchers from Germany have developed the first implementation of THz QCLs for high-resolution absorption spectroscopy on plasmas, detecting absolute densities of ground state atomic oxygen at the fine structure transition at 4.75 THz. Validated with three transitions of ammonia close to this atomic oxygen line, this technique and measurement accuracy is within 5% and the detection limit is 2×10^{13} cm^{-3}. This shows promising results for applications in plasma research that replace existing methods for measuring atomic oxygen densities with compactness without requiring calibration. Not only does this research expand the understanding of physio-chemical behavior of atomic oxygen, it also proves the diagnostic capabilities of THz absorption spectroscopy with QCLs.

OXYGEN AND PLASMAS

Plasmas, or the "fourth state of matter," are used in a wide variety of applications in industry and medical fields. Particularly, oxygen-containing plasmas can be used for etching, chemical vapor deposition, and plasma sterilization of medical instruments and devices.[1] Impurities and contaminants can be thoroughly removed with plasma when using high frequency voltages to ionize the gas. Atomic oxygen is a common gas used for these applications due to its highly reactive characteristics. Naturally occurring atomic oxygen does not exist for very long on Earth because of this high reactivity.

Oxygen plays a major role in the breakdown or erosion of polymers, whether in space applications with damages to spacecraft and organic materials or in surface modification of nanostructures in biomedical and industrial applications. In the biomedical field atomic oxygen can be used for texturing polymer surfaces that are eventually fused with bones, or, in contrast, it may be used to smooth surfaces to eliminate any chances to bond or adhere to the surface. One of the most common applications of atomic oxygen is plasma sterilization. Any type of implant greatly benefits from sterilization from plasmas. This type of sterilization can remove biologically active contaminants or organic debris. This reduces the risk of post-operation inflammation for the patient.[2] Therefore, it is critical to know the densities of oxygen atoms in oxygen-containing plasmas for future development of applications as well as to gain a fundamental understanding of the chemistry and reactivity of atomic oxygen.[1]

PROBLEMS AND GOALS

To measure atomic oxygen densities, very precise and accurate diagnostic techniques are required. The first method is two-photon absorption laser-induced fluorescence and is well-established. However, this technique can be complex, expensive and requires a calibration procedure to obtain absolute atomic oxygen densities. This involves a comparison of two-photon excitation cross sections for both oxygen and xenon.[1] These extra steps and complexity make this a suboptimal technique.

A second method is actinometry. Two emission lines are studied with optical emission spectroscopy at the approximate wavelengths of 777 nm and 844 nm of atomic oxygen. Although it is a simple method, it is based around a chemical actinometer that can perturb the plasma. Unfortunately, it also relies heavily on an accurate modeling of excitation and relaxation processes, a step that can introduce errors.[1] Other methods and techniques include chemical titration with NO molecules and catalytic probes.

Fortunately, there is a method that provides direct absolute ground state densities of atomic oxygen, and the accuracy to which it is measured is almost solely dependent on the accuracy to which the transition line strength is known.[1] This technique, used in many other diagnostic and detection applications, is absorption spectroscopy. For atomic oxygen, the absorption spectrum lies partially in the vacuum ultraviolet region of the electromagnetic spectrum, which does provide a challenge for these types of experiments. There are some weak transitions of atomic oxygen in the visible range, but these only become detectable when using cavity ring-down spectroscopy to enhance the signal strength. This adds more difficulty to the already challenging task. Stronger transitions between fine structure levels of

the ground state can be easier to detect. The strongest of which is located at approximately 63 µm, corresponding to a frequency of about 4.75 Terahertz (THz). With recent THz laser development in the last few decades, this transition can be used for absorption spectroscopy measurements. Specifically, quantum cascade lasers (QCLs) can provide promising and precise results in this THz range.

QCLs are commonly used in mid-infrared laser absorption spectroscopy and are an excellent choice for high-resolution spectroscopy. Due to their typical narrow linewidth (from a few MHz down to kHz range),[1] THz QCLs are suitable for detecting atomic oxygen in plasmas by using the fine structure transition at 4.75 THz. Thus, QCLs in THz absorption spectroscopy provide a diagnostic technique for measuring atomic oxygen densities.

METHOD

Researchers from the Leibniz Institute for Plasma Science and Technology and the Paul-Drude-Institut für Festkörperelektronik in Germany have developed the first implementation of THz QCLs for high-resolution absorption spectroscopy on plasmas, detecting absolute densities of ground state atomic oxygen at the fine structure transition at 4.75 THz. Measurement of the atomic oxygen densities were performed on a low-pressure capacitively coupled radio frequency (CCRF) oxygen discharge.[1]

The complete setup of the experiment, including the QCL, reference gas cell (RGC), mass flow controller (MFC), plasma reactor, and other electronics can be seen in **Figure 1**. The QCL utilized for the research exhibited single-mode operation with optical output powers ranging from 1 to 8 mW at operating temperatures below 70 K. This required containing the QCL in a cryocooler where temperature was regulated with < 5 mK stability. As for the supply current, the laser was tuned across a frequency range of approximately 3 GHz by linearly ramping the input current. By continuous ramping instead of discrete stepping of the current, faster measurements were achieved with much better spectral sampling rate. The current was supplied by Wavelength Electronics' QCL1000 OEM laser driver connected to a function generator to provide a sawtooth waveform with a frequency of 10 Hz with minimum and maximum current values of 480 and 600 mA, respectively.[1] A bolometer was used to detect laser radiation, based on measuring changes in temperature. Thus a chopper was used to modulate the signal to allow the bolometer to excite and relax. All results were averaged over 200 individual measurements to improve the signal-to-noise ratio.

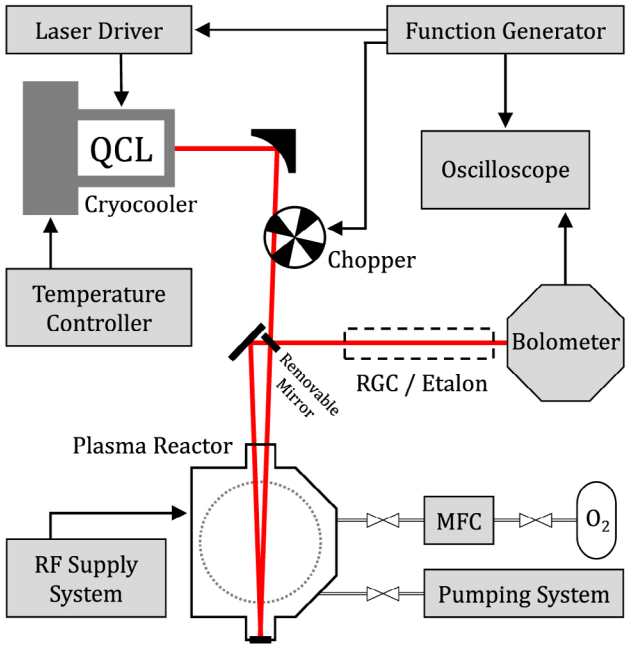

Figure 1. Schematic overview of the experimental setup for THz absorption spectroscopy. QCL: quantum cascade laser, RGC: reference gas cell, MFC: mass flow controller.[1]

For this setup, the plasma is an asymmetric CCRF discharge created in pure oxygen. The applied RF signal was varied between 20 and 100 W. A window in the plasma reactor allowed the laser beam to pass through the reactor, and a mirror in the back reflected the beam back toward the entrance window. The estimated effective absorption length was 84 ± 2 cm within the plasma reactor (assuming the oxygen atoms are distributed throughout the entire plasma reactor). Oxygen, from a gas cylinder with purity 99.998%, was pumped into the reactor, and the pressure was adjusted to 0.7 or 1.3 mbar.

An etalon or RGC could be placed in front of the bolometer with the removable mirror in place to shorten the optical path length and improve the signal intensity. An etalon can provide the relation between current and relative wavenumber. The RGC is used to obtain information on the instrumental function and to validate the measurement procedure. Ammonia was chosen as the reference gas as some of its absorption features are close to the fine structure transition of atomic oxygen as shown in **Figure 2**. Also shown are the laser tuning windows used in this experiment for the two selected laser temperatures. The window for the higher temperature was only used to detect the ammonia at the greater absorption feature, and the other at the lower temperature was used for most measurements, as lower temperatures corresponded to higher output powers.[1] Ammonia measurements validated the atomic oxygen spectra results.

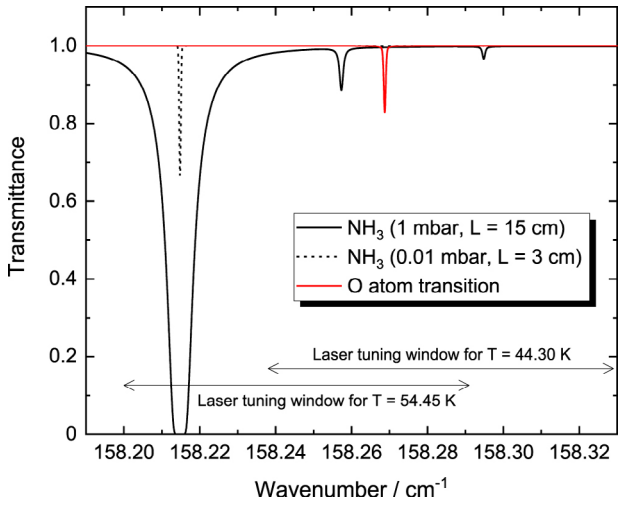

Figure 2. Simulated transmission spectra (T = 296 K) of ammonia and atomic oxygen from the HITRAN spectral database [3]. Laser tuning windows corresponding to laser currents between 480 and 600 mA are indicated for laser temperatures of 44.30 and 54.45 K.[1]

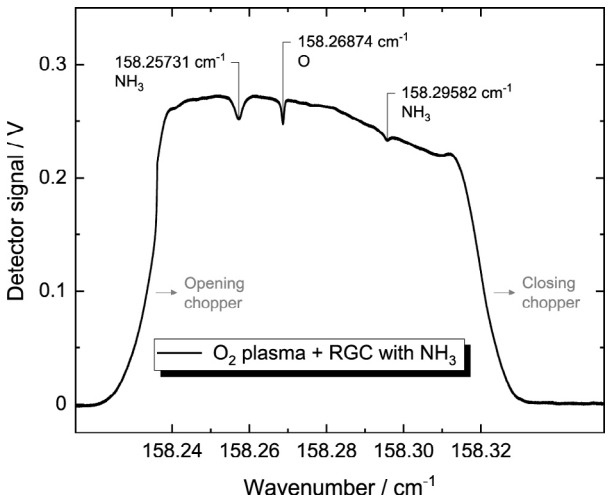

Figure 3. Raw spectrum from a simultaneous measurement of a RGC with NH_3 (p = 2 mbar, L = 15 cm) and an O_2 plasma (p = 1.3 mbar, P = 30 W), measured with a laser temperature of 44.30 K.[1]

RESULTS

The raw spectrum results for both measurements of ammonia (NH_3) and atomic oxygen can be seen in Figure 3. The absorption spectrum is generated from the laser radiation passing through the plasma reactor and the RGC filled with NH_3. The rising and falling slopes on either side of the absorption features are attributed to the opening and closing of the optical chopper. Two of the three ammonia transitions are shown in Figure 3 as well as the desired atomic oxygen fine structure transition. With the wavenumber axis shifted to match the known NH_3 transition at 158.257314 cm^{-1}, the fine structure transition of atomic oxygen matches well with the transition wavenumber of 158.268741 cm^{-1} in literature with uncertainty less than 0.0001 cm^{-1}.[1] Although the second ammonia transition has no further purpose in this study, it does show promising results for this setup in high-resolution spectroscopy in THz ranges.

The third NH_3 transition, at 158.214792 cm^{-1} lies outside of the laser tuning window in the previous figure, but it can be used for characterizing the broadening of spectral lineshapes due to its strong features. Most spectral profiles have symmetrical lineshapes, but both the ammonia and atomic oxygen spectral lines contained some amount of asymmetry. To fix this, the speed of the laser tuning was slowed down. The minimum and maximum current values were changed, reducing the wavenumber tuning range. This can be seen in Figure 4. The third (sR(7,3)) transition of ammonia was used to test the fix to the asymmetry of the spectral lines due to the line strength. Decreasing the laser tuning speed, reduced the asymmetry of the profiles.

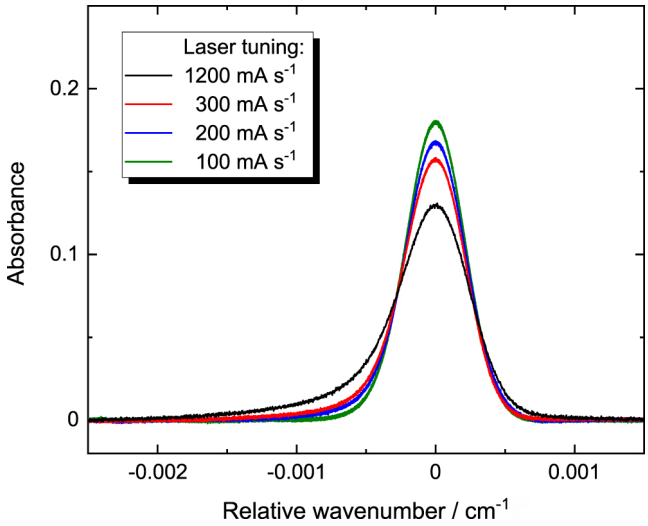

Figure 4. Comparison of the absorption spectra of a RGC with NH_3 ($p \approx 0.01$ mbar, L = 3 cm), showing the sR(7,3)-transition of $^{14}NH_3$ at 158.214792 cm^{-1}, for different laser tuning speeds and a laser temperature of 54.45 K.[1]

Figure 5 shows the spectral absorption profile of the atomic oxygen transition studied with the CCRF discharge in pure oxygen at a pressure of 1.3 mbar and an applied power of 30 W. A Gaussian fit was added to the profile, and the area under the fit can be used to find the value of the atomic oxygen density. After this, a Boltzmann distribution of the energy levels can be assumed, as the area under the fit will give the density for all three transitions of atomic oxygen. The temperature is also a determining factor when calculating the density. For the absorption profile shown in

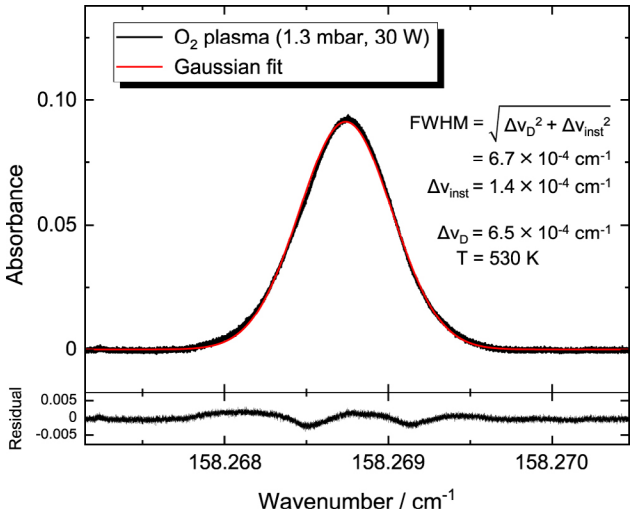

Figure 5. Spectral absorption profile of the fine structure transition of atomic oxygen at 158.268 741 cm^{-1}, measured in a CCRF O_2 discharge (p = 1.3 mbar, P = 30 W) using a laser tuning speed of 74 mA s^{-1} and a laser temperature of 44.30 K. A Gaussian function was fitted to the profile; the corresponding residual is given in the bottom part of the figure.[1]

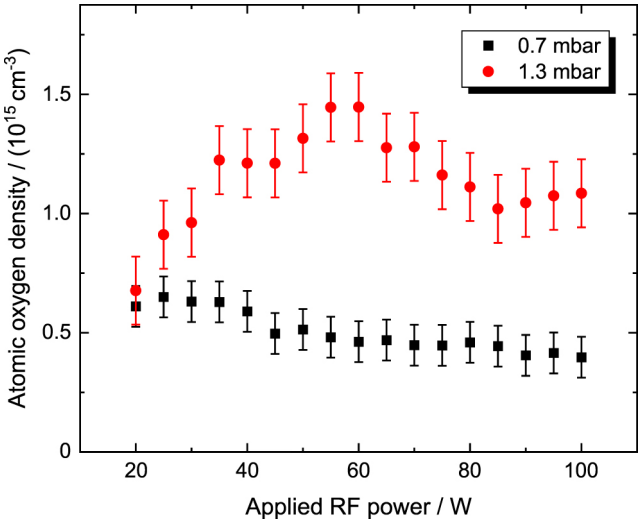

Figure 6. Comparison of atomic oxygen densities as a function of the applied RF power for different pressures. The vertical bars do not indicate the measurement error but the average spread of single data points.[1]

Figure 5, the total density of ground state atomic oxygen is calculated to be 9.6 x 10^{14} cm^{-3}. Although the total estimated possible error in this final calculation is 30%, the technique by itself has a precision of approximately 5%. Here the range is largely due to the uncertainty in temperature, absorption length, and averaging over unknown density and temperature distributions.[1] These are common sources of error in plasma studies, but this method has shown promising results.

Multiple measurements of atomic oxygen density were performed for different applied RF power and gas pressures. These results can be seen in Figure 6 with the vertical bars indicating average spread of single data points. These results clearly show a change in atomic oxygen density when varying the applied RF power or gas pressure. This indicates that the technique also is well suited to study external influences on the density of atomic oxygen.[1]

With this experiment, researchers have demonstrated the first tunable THz QCL for high-resolution absorption spectroscopy. The density of atomic oxygen was measured at the fine structure transition of 4.74477749 THz and was validated by reference gas measurements of well-defined ammonia transitions within an accuracy of 5%. With a current detection limit of 2 × 10^{13} cm^{-3}, this method has proved useful for measuring atomic oxygen densities in plasmas, creating an improved standard diagnostic technique.

WAVELENGTH'S ROLE

Measuring atomic oxygen density with high-resolution requires high precision and stable control of the quantum cascade laser when using terahertz frequencies. Wavelength Electronics' QCL driver, QCL1000 OEM, enabled precise current control with minimal electronic noise from the QCL. The driver also allows analog modulation of up to 2-3 MHz for wavelength modulation. This allowed the QCL to emit a sawtooth waveform as well as enabling laser tuning by changing the drive current. As laser linewidth is a major concern for QCLs, the QCL1000 OEM minimizes noise to as low as 0.7 µA up to 100kHz as well as keeping the average current noise density to as low as 2 nA / √Hz.

The stability of the QCL supply current is critical for consistent electrical bandwidth of the QCL. Wavelengths' QCL1000 OEM, can precisely deliver up to 1 A to the laser. Additional features, such as the brown-out, over- and reverse-voltage, soft-clamping current limit, and over-temperature circuits protect the user and the QCL from potential damage and electrical faults.

The QCL1000 OEM QCL driver enables sensitive terahertz absorption spectroscopy at a measurement accuracy within 5% with low noise and stable laser output. This makes the developed THz QCL system a reliable tool for real-field applications in standard diagnostic techniques for measuring atomic oxygen densities in plasmas.

REFERENCES

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USEFUL LINKS

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PRODUCTS USED
QCL1000 OEM

KEYWORDS
Terahertz, absorption spectroscopy, quantum cascade lasers, QCLs, atomic oxygen, plasmas, ammonia, high resolution, diagnostic

REVISION HISTORY

Document Number: CS-LD08

REVISION	DATE	NOTES
A	April 2023	Initial Release