

Laser absorption in the mid-IR for absolute density measurements of nitrogen containing molecules in low pressure-low temperature plasmas

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Most molecular absorption features lie within the mid-infrared region of the spectrum. As such, lasers that emit in the mid-IR can interrogate this fingerprint region to both identify present molecules and determine their concentration.

Utilizing this spectroscopic technique, we study nitrogen-containing plasmas at low-temperature, low-pressure conditions. Our investigation focuses on two systems: first, microwave-induced nitrogen-oxygen (N₂-O₂) plasma, where the objective is to measure nitric oxide (NO) density; and second, ECR-induced nitrogen-hydrogen (N₂-H₂) plasma, relevant due to its presence in ASML's lithography machines, with ammonia (NH₃) as the species of interest.

In the former case, we use a quantum cascade laser (QCL) centered near 1976 cm⁻¹ to scan across two R-branch transitions of NO in its ground electronic state [1], stimulated at the temperatures reached in the plasma. To do so, the QCL is fixed in temperature and modulated in current at 100 kHz frequency, allowing fast measurements and reaching a scan depth of 1.5 cm⁻¹. Measurements along both longitudinal and axial directions are carried out in the reactor, allowing for the retrieval of radially resolved information via Abel inversion and providing insight into fundamental plasma processes. Accurate determination of NO density is essential for validating model-predicted mechanisms [2] and for quantifying the local energy cost associated with NO production from N₂-O₂ mixtures.

For the N₂-H₂ plasma, we employ a broadband frequency comb spanning 3–11 μm, a spectral range in which ammonia exhibits strong absorption features. After interacting with the sample, the light is analyzed using a Fourier transform spectrometer in combination with a balanced detection scheme [3], allowing for high-resolution measurements with a high signal-to-noise ratio [4]. Specifically, our goal is to quantify ammonia at the plasma-surface interface and to obtain a spatially resolved concentration profile, which is essential for clarifying the underlying mechanisms and advancing our understanding of the system.

1. Gilvey J. et al., "Quantum-cascade-laser-absorption-spectroscopy diagnostic for temperature, pressure, and NO X² Π_{1/2} at 500 kHz in shock-heated air at elevated pressures," *Appl. Opt.* 62, A12-A24 (2023)
2. Altin, M. (2025). *Plasma modelling for sustainable nitrogen fixation: transport and excitation kinetics* [PhD thesis]. Maastricht University
3. Abbas, M. A., et al. "Fourier transform spectrometer based on high-repetition-rate mid-infrared supercontinuum sources for trace gas detection." *Optics Express* 29.14 (2021): 22315-22330.
4. Picqué, N., Hänsch, T.W. *Frequency comb spectroscopy. Nature Photon* 13, 146–157 (2019)