Developing a spectroscopic sensor for accurate, real time monitoring of NO_2

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Background

Nitrogen dioxide (NO_2) is a brown gas released when fuels are burned. NO_2 inflames the lining of the lungs making it dangerous to those with respiratory illnesses.

In 2021, the WHO revised air quality (AQ) guideline values from an annual mean limit of 40 to 10 µg/m³. A 24 h mean concentration of 25 µg/m³ was also introduced (Fig. 1). These stricter guidelines highlight the need for novel NO_2 monitoring techniques.

This project aims is to create a **low-cost**, **portable** sensor that is **selective** and **sensitive** to NO_2, making AQ monitoring more accessible for all.

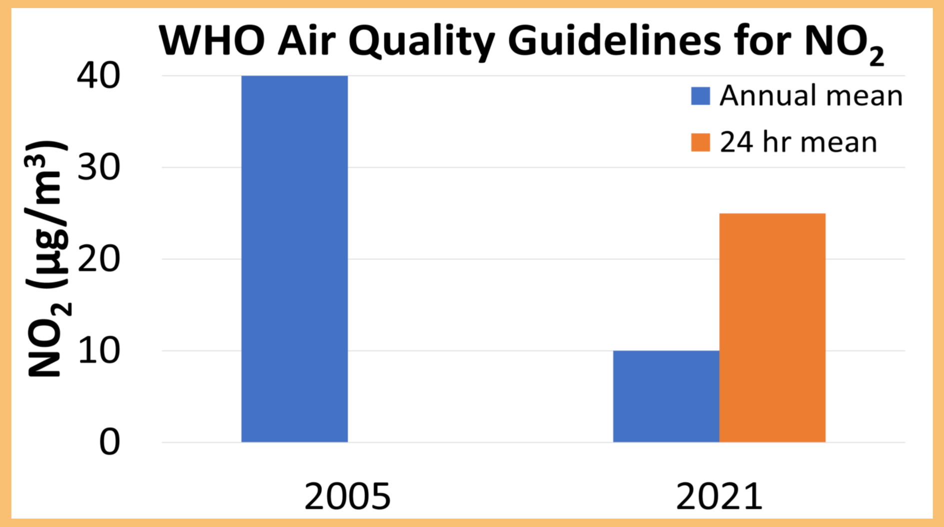

Figure 1. WHO air quality guidelines. Note the introduction of the new 24 h mean limit in 2021.

Early work

This system is based on 2-channel differential absorption spectroscopy (DAS). NO_2 has a highly structured absorption spectrum with neighbouring wavelengths of strong and weak absorption. By monitoring the fractional change in intensities of these wavelengths, changes in NO_2 concentrations can be monitored with good spectral selectivity to NO_2. A single narrow bandpass filter (nBPF) can be turned to select these wavelengths (Fig. 2).

This method was tested in a proof of principle calibration of the DAS system with a chemiluminescence reference monitor in an atmospheric simulation chamber (Fig. 3). The DAS response (averaged over 60 s) follows the same trends as the chemiluminescence (CL) detector, although the signal is relatively noisy with a **standard deviation (σ) of 35 ppb (65 µg/m³)** after 8000 s.

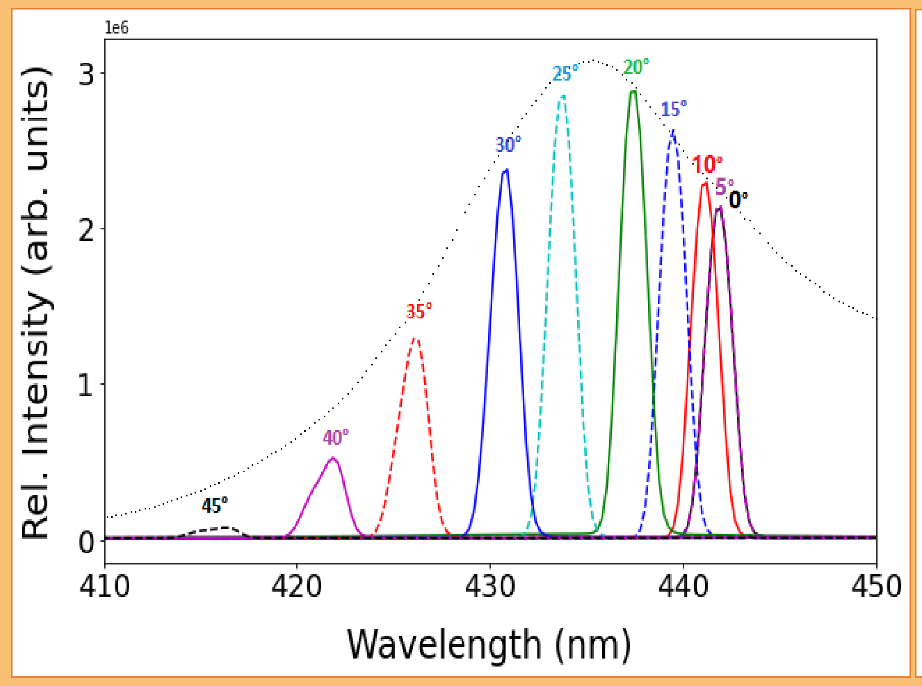

Figure 2. Angle dependence of narrow bandpass filter (nBPF) transmission when rotated in 5° increments. nBPF is used to select high and low absorbing operating wavelengths, λ_1 and λ_2. Bandwidth ~ 0.8 nm.

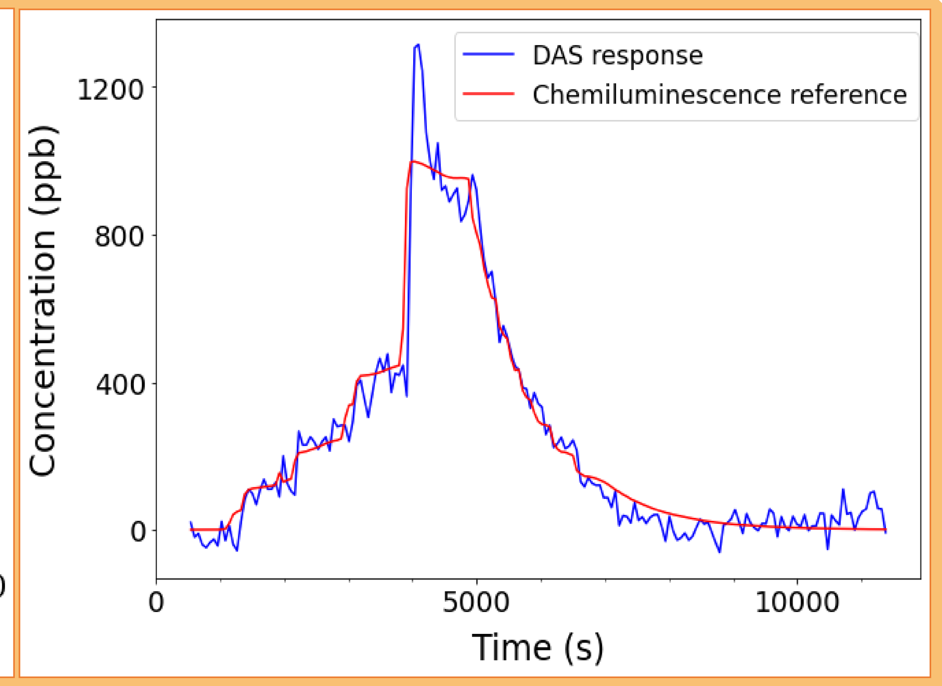

Figure 3. DAS response to changing NO_2 concentration recorded with CCD spectrometer and compared to CL reference NO_x analyser. Figure shows good correlation despite noise in DAS response.

Results

Experiment (A)

A model of a remote sensing system based on long-path DOAS methods was set up in-lab according to the schematic in Figure 4. A fibre also collected the light before filtering and sent to a CCD spectrograph as a reference response.

The concentration of NO_2 in the gas cell, calculated by the Beer-Lambert law, was incrementally increased before the cell was flushed (Fig. 5). There is hysteresis in the system (Fig. 6). The correlation between DAS and the reference is highly linear when looking at the addition and removal of NO_2 independently. The signals are well correlated throughout the experiment with $R^2 > 0.989$.

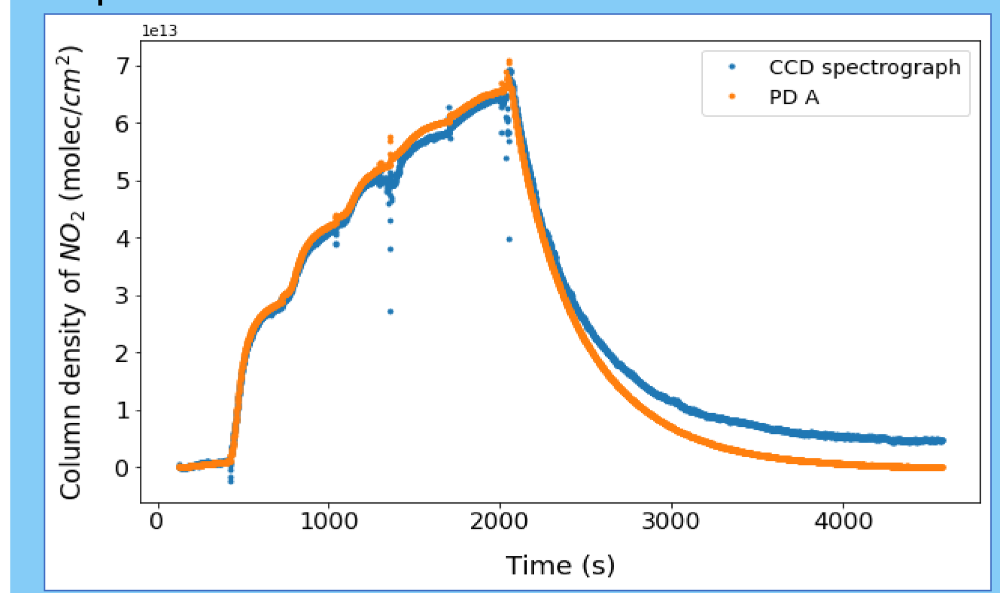

Figure 5. Column density of NO_2 over 1050 cm with standard deviation of 2 x 10¹¹ molecules/cm².

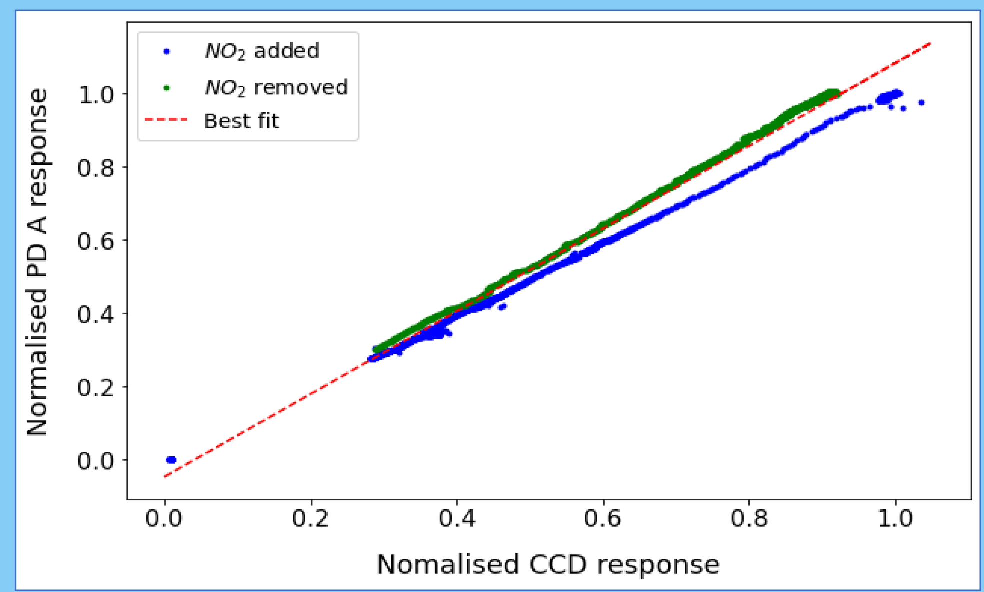

Figure 6. The correlation between PD A and CCD spectrograph is highly linear when looking at the addition and removal of NO_2 independently.

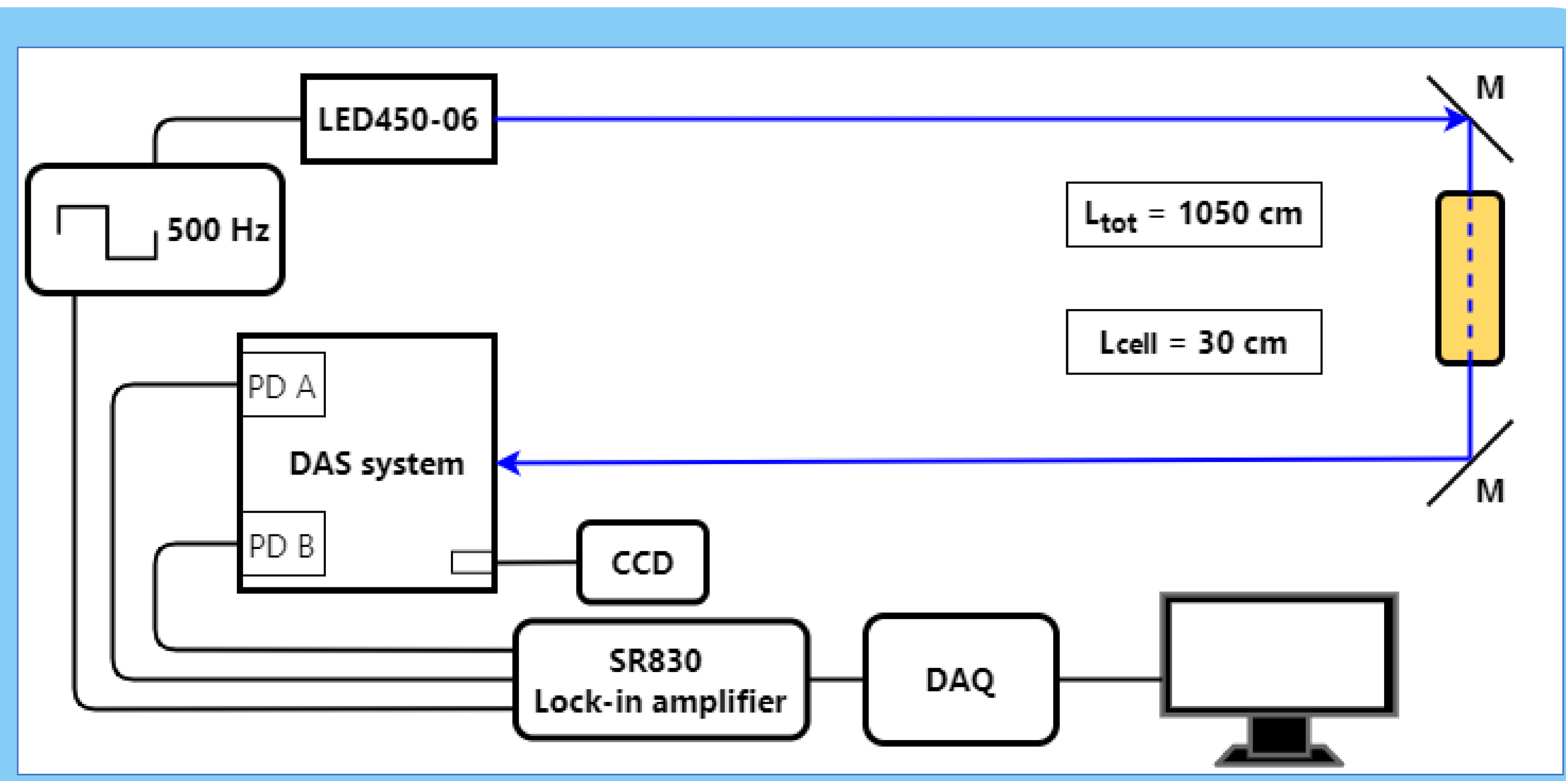

Figure 4. Schematic of experimental set-up A. Modulated LED signal is directed to a gas cell and reflected into the DAS system. Responses from photodiodes is amplified with SR830 lock-in amplifier PD: Photodiode (Thorlabs, DET10A).

Experiment (B)

A folded path of 800cm was created through a 200cm long atmospheric simulation chamber as shown in Figure 7. The concentration of NO_2 in the chamber was increased and monitored using a CL NO_x analyser (Teledyne T200). The absorbance measured by PD A was then plotted against NO_2 concentration showing $R^2 > 0.842$ (Fig. 8). A decrease in intensity of 1% in PD A corresponds to ~2ppm of NO_2.

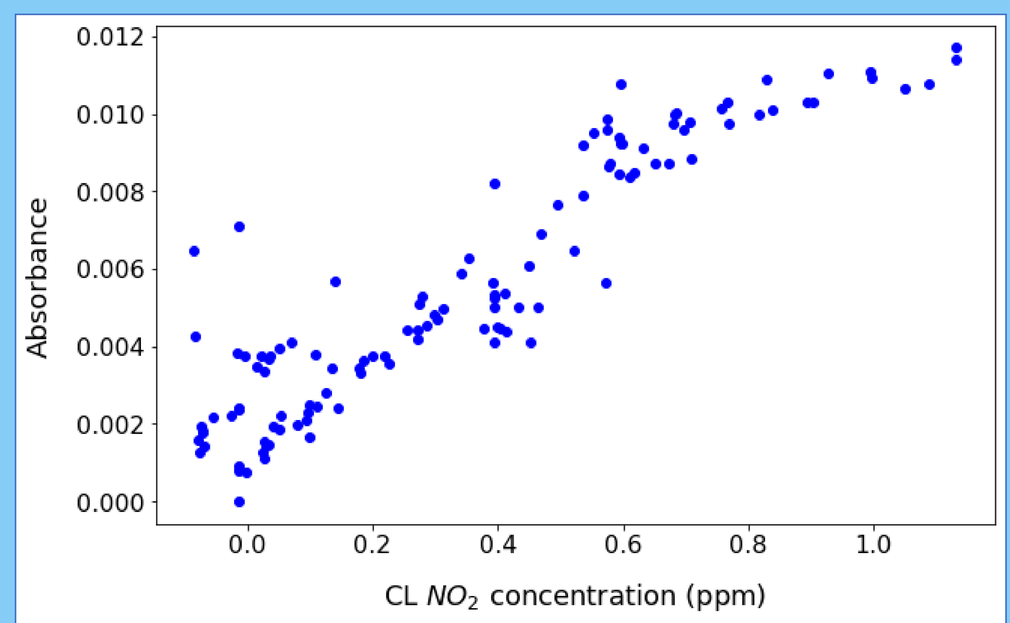

Figure 8. The correlation between PD A and CL NO_x analyser. Data is well correlated here with R^2>0.8.

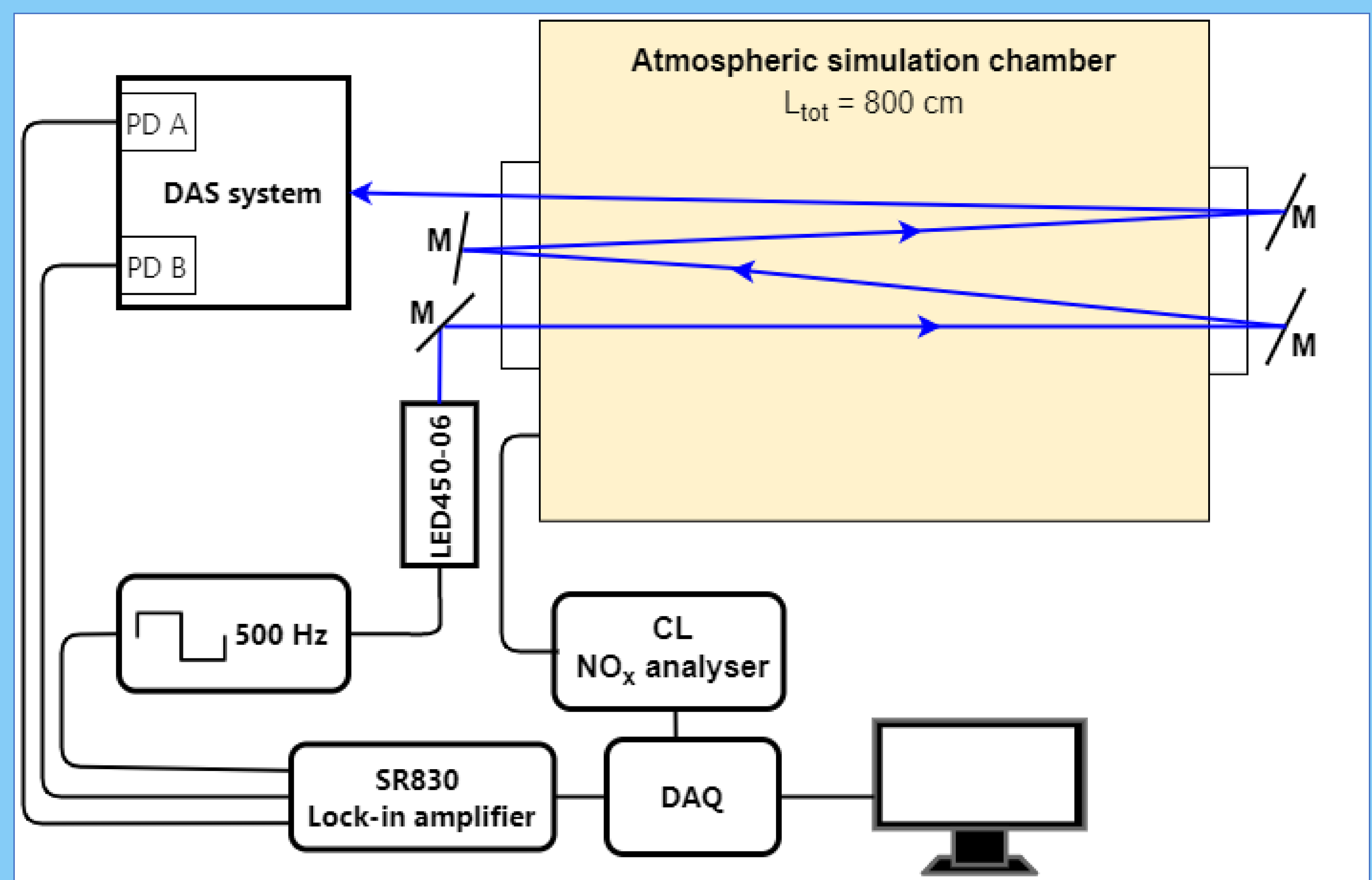

Figure 7. Schematic of experimental set-up B. The light path within the chamber (2m length) is folded to give pathlength = 8m. A CL NO_x analyser samples air from the chamber to give a reference NO_2 concentration. Data from the lock-in amplifier and the CL NO_x analyser is recorded to a DAQ and stored on a PC using DAQami software.

DAS system

Our novel differential absorption spectroscopy (DAS) system is shown in Figure 9. Light returning from the gas sample is split using a beam splitter. One beam is sent directly through the nBPF at two angles corresponding to λ_1=439.4nm and λ_2=437.3nm. Light is then collected by photodiode (PD) A and PD B and sent to a lock-in amplifier. Lenses are used to focus the light onto each photodiode.

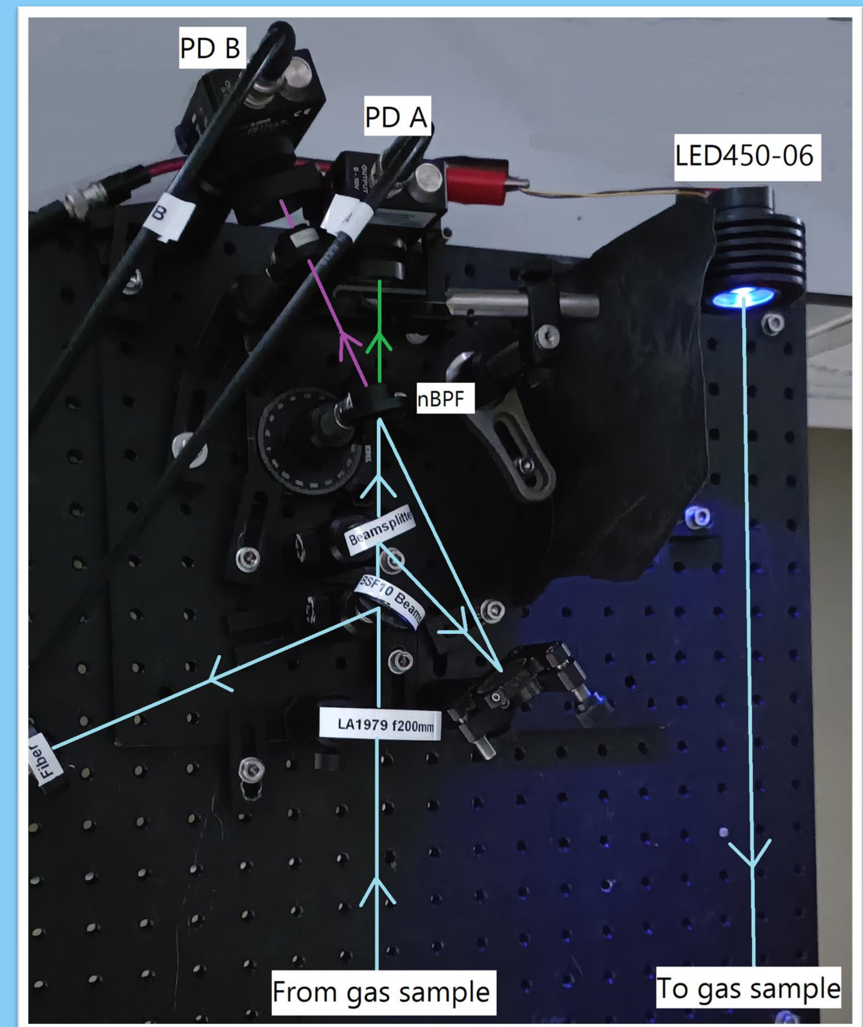

Figure 9. Differential absorption spectroscopy (DAS) scheme.

Future work

- Achieve longer folded path lengths within the atmospheric chamber to improve sensitivity to NO_2.
- Measure real NO_2 concentrations across a long path (e.g. across a road/car park).
- Use optical cavities to achieve long path lengths and to compact the system.
- Currently working with a benchtop signal generator and lock-in amplifier. These components may be replaced by custom circuitry to reduce the cost and size of the system.

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