Development of a Photo-fragmentation Laser Induced Fluorescence Instrument for the Measurement of Nitrous Acid

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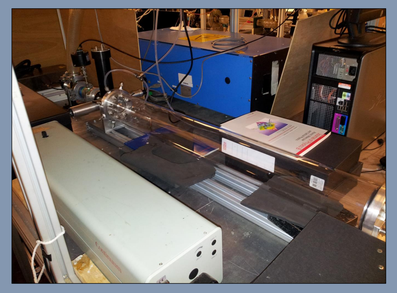


Figure 1. Image of the experimental set-up showing the flow tube connected to the detection cell.

1) Introduction

- OH is the major oxidant in the troposphere where it controls the lifetime of many species and contributes to the production of ozone.
- One such source is the photolysis of nitrous acid (HONO). HONO is primarily formed at night[1] (R(1)) and in the morning it is quickly photolysed contributing to a large portion of the morning OH.

$$2NO_2 + H_2O_{(ads)} \xrightarrow{surface} HONO_{(g)} + HNO_{3(ads)} \qquad R(1)$$

- During the day it's concentration is higher than models predict, figure 2, indicating that there is an unknown daytime source[2].
- The unknown source is believed to be a light induced heterogeneous reaction at surfaces.
- The aim of this project is to develop an instrument that will allow for the sensitive measurement of HONO with a good time resolution and minimal interferences. The instrument will then be used to identify if reactions on atmospheric aerosols could help fill the gap .

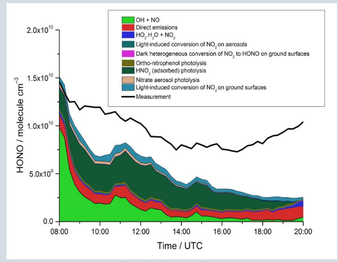


Figure 2. Diurnal variation modelled HONO, with different colours showing what proportion each source contributes of the total modelled HONO, compared to the measured HONO concentration, black line, during the Clearflo field campaign in London. The white space between the measured and total modelled HONO shows the missing source[2].

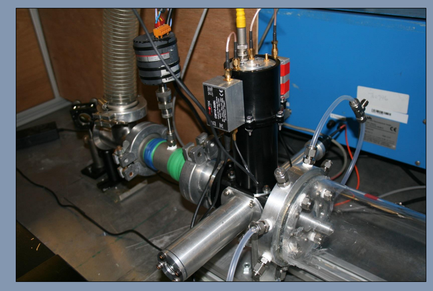


Figure 3. Image of the detection cell connected to the aerosol flow tube.

2) Instrumental Set-up For Sensitive detection of HONO

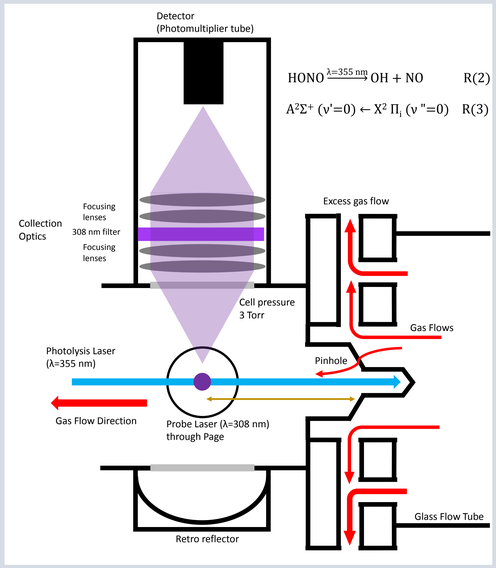


Figure 4. Cross section of the detection cell, showing how it is connected to the aerosol flow tube on the right and the optical arrangement for the collection of the OH fluorescence.

Photo-fragmentation Laser Induced Fluorescence (PF-LIF)

- Break up a non-fluorescing molecule into a species that is fluorescable.
- Detectable species excited using laser induced fluorescence and as it returns to its ground state it fluoresces and it is this fluorescence that is measured.

HONO Instrument

- HONO fragmented using 355 nm laser light, R(2), this overlaps well with one of the HONO absorption peaks, figure 7.
- OH fragment measured using the FAGE technique[3](OH excited using 308 nm light, OH then fluoresces at 308 nm, in order to separate laser light from fluorescence the measurement time is delayed after the laser. In order to extend the florescence lifetime the cell is kept at a low pressure, 3 Torr).
- Current design has the photolysis laser directed down the cell towards the inlet.
- The detection cell is connected to a flow tube to allow measurement of HONO production from aerosols.

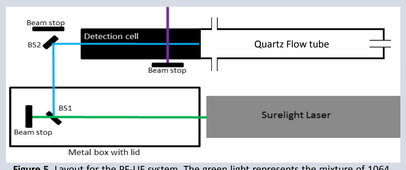


Figure 5. Layout for the PF-LIF system. The green light represents the mixture of 1064 nm, 534 nm and 355 laser light. The blue lines represent the 355 nm light and the purple line represents the 308 nm light. BS represents the beam splitter/coated dichroic mirror. Gas flows from the tight side of the flow tube with the detection cell sampling from the centre of the flow on the opposite end.

- Figure 6 shows an example scan, each point is an OH measurement, the photolysis laser fires at 10 Hz and the probe laser at 5000 Hz.
- Because OH is generated along the photolysis laser path we measure it as it passes the probe laser. A decay is seen because the OH generated near the inlet will diffuse to the outer edges of the cell so it will not be measured.

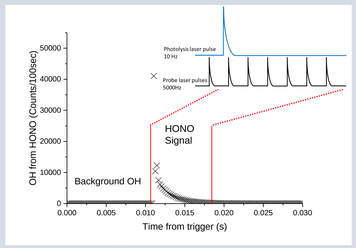


Figure 6. Example scan with photolysis laser trigger point at 0.01s and the generated OH is measured as it flows down the cell giving the observed curve, scan repeats every 0.1 s accumulating the data. Measurement from current source that generates 10^{14} molecules cm^{-3}

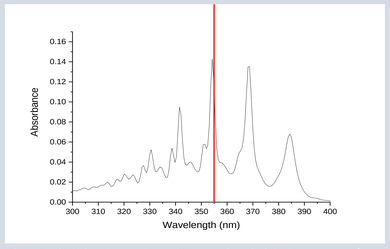


Figure 7. HONO absorption spectrum, 355 nm peak marked. Spectrum measure from our HONO source using UV/vis spectroscopy

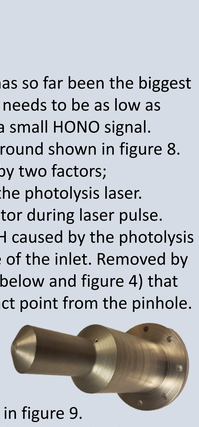
3) Results

a) Instrumental Optimisation

Background Signal

Reducing the background signal has so far been the biggest challenge. The background signal needs to be as low as possible in order to differentiate a small HONO signal. Initial experiments had the background shown in figure 8. This background signal is caused by two factors;

1. *Peak A* - Scattered light from the photolysis laser. Removed by turning off detector during laser pulse.
2. *Peak B* – Plasma generated OH caused by the photolysis laser hitting the metal surface of the inlet. Removed by designing an inlet (see image below and figure 4) that separates the photolysis impact point from the pinhole.



The current background is shown in figure 9.
The laser scatter peak has not yet been completely removed however it is currently at an acceptable level.

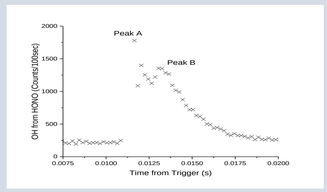


Figure 8. Initial background scan, nitrogen gas flow only, no modifications to cell design.

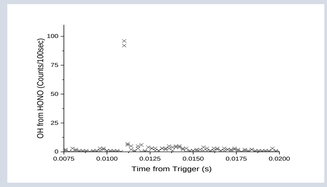


Figure 9. Current background scan, N2 gas flow, with all current modifications to the cell design.

Pressure Impact

Increasing cell pressure has 2 effects;

- An increase in the number of molecules in the cell = higher signal.
- A decrease in OH fluorescence lifetime = lower signal.

Figure 10 shows the balance of these where increased number density initially dominates but past 4 Torr signal is lost due to quenching of the fluorescence signal.

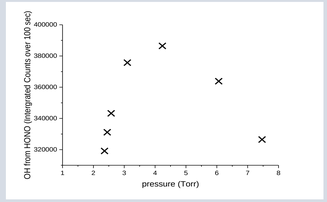


Figure 10. Effect on the total counts over a range of pressures.

b) Outdoor measurements of HONO

By sampling air from outside the lab we were able to see atmospheric levels of HONO. Figure 11 shows that there is an observable signal.

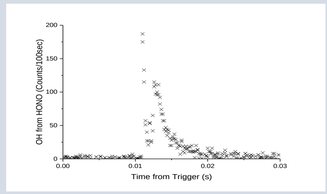


Figure 11. Outdoor measurement, 100 sec measurement.

c) Production of HONO from the aerosol flow tube walls

In the presence on NOx, we observe HONO production from the flow tube walls. As exposure time increases, the HONO signal is observed to increase; see fig. 12.

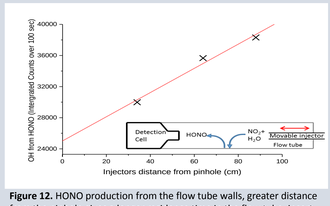


Figure 12. HONO production from the flow tube walls, greater distance from the pinhole gives a longer residence time in the flow tube, insert shows rough experimental set-up.

d) Calibration of the detection cell

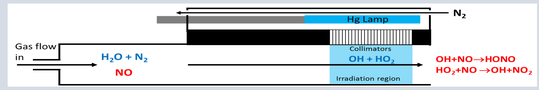


Figure13. Cross section of the calibration wand used to generate HONO for the calibration. A 40 SLM humidified nitrogen flow with a 5 SCCM NO flow enter from the left. The mercury lamp generates OH and HO_2 from the water which quickly react with the NO generating HONO. The end of the lamp is position about 2 cm from the pinhole.

Our aim is to develop a calibration method that will produce known amounts of HONO, without the need to calibrate the calibration source.

- A humidified gas flow is passed under a mercury lamp (185nm) generating known amounts of OH[4] (figure 13).
- Excess flow of NO added to the gas mix
- OH and NO react quickly to form HONO.
- HO_2 generated by the lamp also reacts to form more HONO.
- The amount of HONO produced is calculated using a reaction model in Kintecus[5].
- Results are plotted as a normalised signal against calculated HONO concentration.
- Figure 14 shows the calibration plot, calculated detection limit 50 ppt.

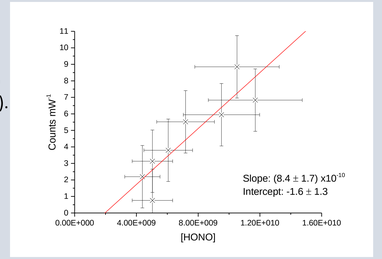


Figure 14. 3 overlaid calibration plot measuring HONO produced from the calibration wand. HONO concentration is varied by changing the lamp current which altered the amount of OH generated from water.

e) Aerosol Measurements

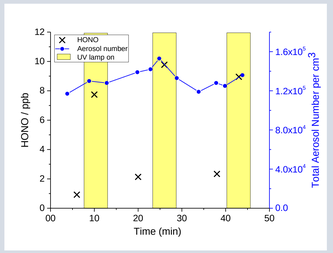


Figure 15. Results from a lamp on and off experiment with TiO2 aerosol. Average difference between lamp on and off - 7ppb, difference with no aerosols present - 1 ppb. Conditions used 65ppbNO_2 at 10% RH with a total residence time of 110s with 60s under a UVA lamp.

With the main aim of the project focusing on HONO production from aerosols we have begun the measurement of HONO produced when aerosols have been illuminated. An initial experiment using TiO_2 was done as this is a species known to generate HONO when exposed to UV light and NO_2.
Results from this experiment are shown in figure 15. Uptake coefficients were calculated, assuming all the NO_2 that is lost to the aerosol surface is converted to HONO, giving a value of 5 x 10^{-4} for dark conditions and 1.3 x 10^{-3} for illuminated conditions.
This value is similar to the 9.6 x 10^{-4} uptake coefficient under illuminated conditions for TiO_2 aerosols at 15% RH in Gustafsson et al.[6]

Work is ongoing studying the direct production of HONO from the ammonium nitrate aerosol.

4) Conclusions and Further Work

Results have shown that the instrument is able to detect HONO and as shown it should be able to see signal down to ppt levels. The instrument also is able to measure HONO generated on TiO_2 aerosols producing a uptake coefficient that is similar to a previous result by another group . Other work to be done includes;
Calibration: Try an alternative calibration method. This will be done by adding HCL to Sodium Nitrate which will form HONO as one of its products. The HONO concentration will be determined by FTIR. Reduction of detection limit by using a newer detector.
Aerosols Measurements: Further studies in the illuminated production of HONO from nitrate aerosols.
Background Production: Investigate ways to reduce production of HONO from the flow tube walls.

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