

# Exploring NO<sub>y</sub> chemistry in levitated aqueous aerosol droplets

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## Introduction

Chemistry of reactive nitrogen oxides, NO<sub>y</sub>, is crucial for our understanding of composition and properties of the Earth's atmosphere. The proof-of-principle experiments demonstrated that we are able to study the atmospheric fate of nitrogen oxides that has significant impact on global climate and hydrological cycle, thus affecting the likelihood of local floods and acid rain.

## Atmospheric aerosol

Atmospheric aerosol is a variable, yet critical component of the climate system and has substantial impact on climate change.<sup>[1-3]</sup> Aerosols affect climate directly, by scattering and absorbing solar radiation, and indirectly, by acting as cloud condensation nuclei, CCN. Clouds may reduce the incident radiation on the surface, increase or decrease temperatures, and suppress rainfall. The chemical composition of aerosol alters the hydrological cycle, which affects quality and availability of fresh water. The need for an improved understanding of the factors affecting the hydrological cycle is well-illustrated by the rapidly increasing frequency of extreme flood events in the UK. The effect of aerosol on radiative forcing and cloud formation has been repeatedly identified<sup>[4,5]</sup> as the largest uncertainty in assessing the impact of particulate matter on climate change. National and international institutions declared climate change to be the greatest environmental challenge facing the world today. Atmospheric aerosol not only impacts climate, but also directly affects human health: it may suppress defence mechanisms, respiratory and cardiovascular functions and cause allergic and infectious diseases. Aerosol is important for the biosphere through spreading reproductive materials and micro-organisms.

## NO<sub>y</sub>-initiated aerosol ageing

Once in the atmosphere, aerosol particles change size and composition through chemical reactions, condensation of vapour species, evaporation, coagulation with other particles, or by activation in regions of water supersaturation (relative humidity, RH, above 100%) to become fog and cloud droplets.<sup>[6]</sup> Chemical ageing of organic atmospheric aerosol proceeds mainly via its interaction with initiators of atmospheric oxidation such as hydroxyl radicals, OH, ozone, O<sub>3</sub>, and nitrogen oxides, in particular nitrate radicals, NO<sub>3</sub>, but also NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>. Reactions of NO<sub>3</sub> are only important at night, since the radical is

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readily photolysed during daytime. The main importance of N<sub>2</sub>O<sub>5</sub> lies in its heterogeneous chemistry, but several recent studies have investigated its gas-phase behaviour (e.g. Brown *et al.*<sup>[7]</sup> for atmospheric measurements and Pfrang *et al.*<sup>[8]</sup> for laboratory studies). The chemistry of nitrogen oxides is particularly relevant because of its potential impact on photochemical ozone production, in turn responsible for smog formation and influencing the formation of secondary organic aerosol.<sup>[9]</sup> NO<sub>2</sub> is somewhat less reactive than either O<sub>3</sub> or NO<sub>3</sub>, but is nevertheless very important in the NO<sub>x</sub> cycle. The importance of photo-enhanced uptake of NO<sub>2</sub> on both solid organic compounds and mineral dust particles has been highlighted.<sup>[10]</sup>

## Humic-like substances, HULIS

The term HUMic-Like Substances, HULIS, describes probably one of the most intriguing classes of atmospherically relevant species and attracted substantial interest at the Faraday Discussions 137. Several papers were presented investigating the atmospheric importance of HULIS<sup>[11]</sup> and the discussion at the meeting demonstrated that research on HULIS is very timely. HULIS describes organic species found in cloud, fog, rain and aerosol that resemble organic material in river/sea water and soils. HULIS is suggested to be formed within the aerosol and may be present in as much as 20–50% of aerosol particles.<sup>[12]</sup> HULIS is very difficult to chemically characterise owing to its complexity, size and non-uniformity. However, consensus is starting to form on a HULIS model structure consisting of an aromatic core bearing substituted aliphatic chains with –COOH, –CH<sub>2</sub>OH, –COCH<sub>3</sub> groups. Cappiello *et al.*<sup>[13]</sup> performed a molecular characterisation of HULIS-type water-soluble organic compounds in fogwater. Their analysis of a range of different air masses showed common base structures. These structures are the basis on which we chose the compounds to represent HULIS in our experimental studies. Sources of HULIS include a small terrestrial, marine, biomass burning and secondary aerosol formation (condensation, reaction and oligomerisation). The presence or oxidative degradation of HULIS in cloud, fog and aerosol has been found to lead to droplet activation and enhanced cloud formation.<sup>[14]</sup> The reactions of HULIS proxies with initiators of atmospheric oxidation such as NO<sub>2</sub>, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>



Fig. 1. Successful application of a newly developed flow cell with inert sliding injector for study of interaction of levitated particles with the initiators of atmospheric oxidation  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ . Additional ports allow horizontal visualisation (e.g. using a borescope).

thus need to be studied to determine if they (1) lower the critical supersaturation required for cloud formation and (2) lead to the formation of oligomers. The rate for these reactions must be quantified to determine if they are atmospherically important.

### Experimental

Aerosols were generated by ultrasonically nebulising a solution of HULIS-type molecules (such as benzoate and fumarate)<sup>[15]</sup> in water (containing sodium chloride or ammonium sulphate). Optically levitated HULIS droplets typically contained a concentration of  $\sim 0.1$ - $1\text{M}$ . The aerosol droplets were mixed with a humidified stream of nitrogen ( $\text{RH} \sim 95\%$ ) and blown into a newly developed aluminium flow cell on the stage of an optical microscope (Fig. 1). The cell allowed flexible injection through seven different ports, most of them suitable for attachment of an inert PTFE sliding injector. This sliding injector was used for introduction of the nitrogen oxides (in a flow of dry oxygen) after passing through a 500 ml reaction bulb. Four ports also allowed horizontal visualisation using a fibre-optic borescope. A droplet ( $3$ - $15\ \mu\text{m}$  diameter) was trapped in the focus of an argon-ion laser ( $\lambda = 514.5\ \text{nm}$ ,  $\sim 7\ \text{mW}$  at the point of focus). The remaining particles were flushed from the cell. The scattered laser radiation was collected and analyzed on a spectrometer via a notch filter. Spectra were recorded continuously over 5-10 second timescales. The trapped particle was illuminated with an optically filtered microscope light onto a CCD via the microscope optics to provide an optical image of the particle. A still image was recorded every 10-30 seconds in order to size the droplet.

A typical experiment would monitor size and Raman signal of the droplet for a few minutes. Subsequently, the dry oxygen flow would be subjected to a Hg pen-ray lamp to produce  $\text{O}_3$  (ppm range) which then entered the 500 ml reaction bulb. An additional flow of a  $\text{NO}_2$  mixture (1000 ppm in air) into this reaction bulb would initiate the  $\text{NO}_y$  generation chemistry. The reaction was monitored until there was no discernable HULIS remaining in the Raman spectra. Experiments were also undertaken without oxidants present. Raman spectra were used to detect possible products.

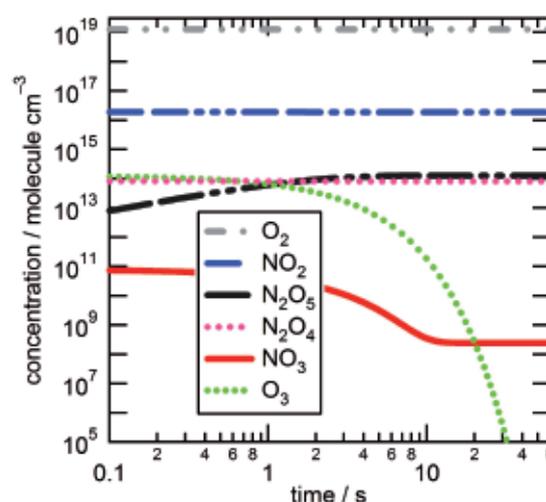


Fig. 2. Gas-phase concentration profiles (kinetic model considering nitrogen oxide reactions). Concentrations of key species have been confirmed spectroscopically.

### In-situ $\text{NO}_y$ generation

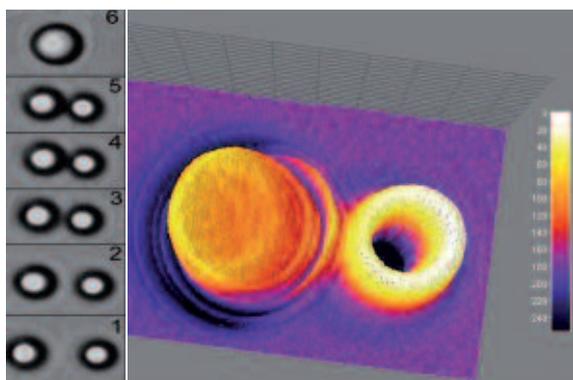
A reliable in-situ  $\text{NO}_y$  generation method is vital for the present experimental studies. To this end, we developed a suitable flow reaction system and confirmed adequate concentrations in the flow cell in UV-Vis and FTIR spectroscopic studies within the Lasers for Science Facility which were also matched by a kinetic model (Fig. 2). We chose flow rates and volume of reaction bulb, so that the  $\text{N}_2\text{O}_5$ -precursor  $\text{O}_3$  is quantitatively consumed before the oxidants enter the flow cell. We could also vary the  $\text{NO}_3/\text{N}_2\text{O}_5$  ratio to distinguish between reactions of these two species.

### Results

Changes in chemical composition (Raman) and droplet size (optical microscopy) could be followed for uptake of  $\text{NO}_2$ ,  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  on droplets containing  $\text{NaCl}$  or  $(\text{NH}_4)_2\text{SO}_4$  as well as the HULIS proxy sodium fumarate. Detailed analysis to extract kinetic parameters and assign product peaks is currently being undertaken. Uptake of nitrogen oxides into the droplet led to the appearance of a nitrate peak (at  $\sim 1050\ \text{cm}^{-1}$ ), accompanied by disappearance of the  $\text{SO}_4^{2-}$  peak: the change in pH caused by  $\text{N}_2\text{O}_5$  uptake is likely to lead to conversion of  $\text{SO}_4^{2-}$  to  $\text{HSO}_4^-$ . Exposure of the HULIS droplet to the nitrogen oxides led to oxidative consumption of fumarate and we also obtained evidence for formation of Raman-active products.

### Conclusions

We performed very successful proof-of-principle studies opening up a wide range of experimental systems for investigation. We demonstrated that the study of reactions of nitrogen oxides with optically levitated micron-size aqueous droplets containing HULIS-proxies is feasible. Our in-situ method for nitrogen oxide generation in a mobile gas-handling system has for the first time been coupled to a laser Raman tweezers system. We are currently extracting kinetic parameters and identifying functional groups of reaction products for peer-reviewed publication.



**Fig. 3. (a) Preliminary tests using two optical traps to bring two charged  $\sim 6 \mu\text{m}$  droplets to coalescence (arbitrary time steps: 1–6). (b) False-colour image of the interaction of two charged droplets.**

### Outlook: preliminary tests on probing charge effects on airborne aerosol

Charges impact on the behaviour of atmospheric aerosol: both coalescence efficiencies<sup>[16]</sup> and the thermodynamic stability of droplets<sup>[17]</sup> will be affected. This impact of charges on cloud behaviour is not well understood. We performed preliminary tests charging droplets levitated in two optical traps (Fig. 3(a)). A qualitative charging effect could be demonstrated (Fig. 3(b)), but quantification would benefit from longer-term access to levitation and charge measuring facilities.

### Acknowledgements

We are very grateful to the CLF, Rutherford Appleton Laboratory, UK for grant 81025 and for support for the STFC Strategic Initiative Grant HS30635. This work was in part supported by NERC CASE award NER/S/U/2006/14253.

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