TNA User Report

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Project title	Investigation of particle formation in the polluted marine atmosphere: simulation, characterization and reaction kinetics
Name of the accessed chamber	Irish Atmospheric Simulation Chamber (IASC)
Number of users in the project	1
Project objectives (max 100 words)	Significant levels of I_2 are common in the marine atmosphere, whose photolysis leads to the formation of marine aerosol. This type of daytime particle formation model in the pristine marine boundary layer has been extensively studied. However, the night time situation in the absence of photolytic reactions as well as the polluted marine atmosphere has received comparatively little attention in the literature. Therefore, we investigated marine particle formation in polluted atmospheres at night time, based on initial reactants I_2 and NO_3.
Description of work (max 100 words):	The kinetics of the I_2-N_2O_5 chemical system were investigated focusing on particle (aerosol) formation at the IASC facility in University College Cork (UCC) with direct measurement of I_2 and NO_3, particle size distribution , NOx, ozone and other iodine compounds such as $IONO_2$. We found that the reaction of laboratory generated I_2 with NO_3 leads to new particle formation. We also demonstrated that *Laminaria digitate* derived I_2 can produce particle by the reaction with NO_3 of ambient relevant concentration. Our results suggest that the reaction of I_2 with NO_3 may cause a significant particle formation at night time.

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[1] *PLEASE CHOOSE ONLY ONE DOMAIN* Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

[2] UNI= University and Other Higher Education Organisation;
RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);
SME= Small and Medium Enterprise;
PRV= Other Industrial and/or Profit Private Organisation;
OTH= Other type of organization.

[3] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

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Trans-National Access (TNA) Scientific Report

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Yosuke Sakamoto
Chamber name and location: Irish Atmospheric Simulation Chamber, University College Cork
Campaign name and period: 21/08/2018 – 28/09/2019
Text:

Introduction

Significant levels of molecular iodine, I_2, are common in the marine atmosphere, especially in regions with high occurrences of brown macroalgae, which are known to release I_2 under oxidative stress conditions. As a consequence of iodine photolysis and the generation of I atoms, the formation of marine aerosol has been widely investigated for pristine conditions (remote coastal areas) during daytime, where rapid reaction of I with O_3 leads to the formation of IO. The self reaction of IO forms OIO and I_2O_2 which can be removed from the gas phase by uptake onto pre-existing aerosol surfaces, or initiate new particle formation by forming higher oxides I_2O_y (y=2–5). This type of daytime particle formation in the pristine marine boundary layer involving gas phase iodine chemistry has been extensively studied and a modelling study demonstrated that the iodine derived particle formation could contribute to the regional ambient cloud condensation nucleus (CCN) burden, hence affecting radiative forcing. (McFiggans et al. 2010)

Scientific Objective

The daytime particle formation model in the pristine marine boundary layer involving gas phase iodine chemistry has been extensively studied. However, the night time situation in the absence of photolytic reactions as well as the polluted marine atmosphere has received comparatively little attention in the literature. The scientific objectives of this TNA programme is to investigate marine particle formation in polluted atmospheres at night time, based on initial reactants I_2 and NO_3 in the presence of NO_2 and/or H_2O (potentially also O_3 at low concentrations).

Advantage of using the IASC facility.

(i) The facility in Cork provides a unique ability to use brown macroalgae in the chamber to simulate realistic I_2 concentrations and to synthesize intermediate iodine oxide species under a range of conditions.

(ii) A novel range of high sensitivity absorption instrumentation will be coupled to the chamber, allowing a unique and rigorous experimental investigation of the I_2 oxidation kinetics by O_3 and NO_3.

(iii) Exploration of the applicability of online mass spectrometry of both gas and particle phases (ToF-CIMS, Aerodyne) has not been attempted before under the described conditions and would provide valuable insights into the species and mechanisms influencing aerosol generation and growth.

Experimental set up

The kinetics of the I_2-N_2O_5 chemical system was investigated focusing on particle (aerosol) formation at the IASC facility in UCC with the following instruments:

- Open path IBBCEAS (540 nm, I_2), direct measurement of molecular I_2.
- Open path IBBCEAS (662 nm, NO_3), direct measurement of NO_3.
- Scanning Mobility Particle Sizer (SMPS) - TSI (commercial)
- NO_2, NO (NOx) Chemiluminescence detector, Thermo (commercial)
- ToF-CIMS instrument, Aerodyne, with FIGAERO inlet.
- Peripheral sensors for humidity, temperature and pressure.

An instrument based on open-path incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) was established at UCC and utilized during this TNA campaign in the context of night-time reaction of the nitrate radical (NO_3) with halogen species that are present in the marine boundary layer. The setup was optimized for the detection of NO_3 around the maximum of the X-A absorption band at 662 ± 10 nm, but also for molecular iodine around 540 ± 10 nm, a region where the molecular iodine spectrum exhibits significant structure. The experimental design of the IBBCEAS instrument was similar to the one described in Gherman et al. (2008) and Varma et al. (2009). A sketch of the optical setup and details on experimental components are shown in **Figure 1.**

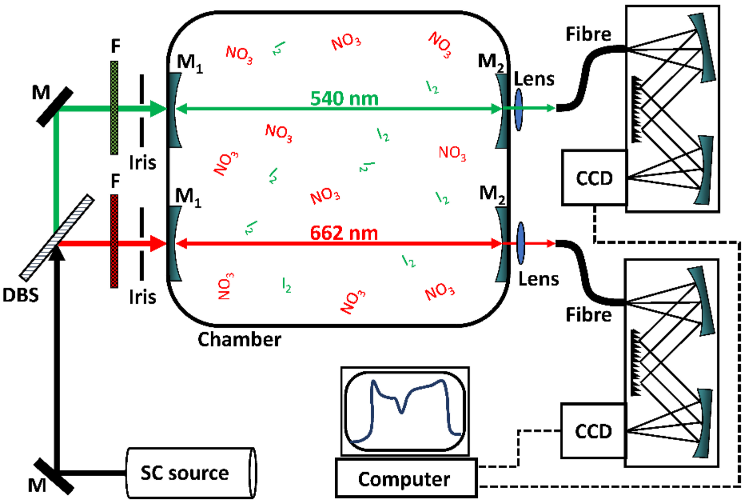

Figure 1. Schematic of the experimental setup IASC at UCC. DBS: dichroic beamsplitter; CCD: charged coupled device detector, F: Filter (bandwidth chosen according to the high reflectivity range of the mirrors; M, M_i: deflection and cavity mirrors.

The excitation light source was a super continuum (SC) laser (Fianium SC450). The emission from the SC source was split with a dichroic filter into two spectrally different components; one at wavelengths >600 nm (red channel) and one <600 nm (green channel). The light was spectrally filtered in either channel and guided with appropriate dielectric steering mirrors to two optically stable cavities with center wavelengths mentioned above. The dielectric cavity mirrors (r = –5 m, R ~ 0.999, diameter = 40 mm, Layertec GmbH) were placed inside mechanically stable holders on flanges that were rigidly attached on either side of the simulation chamber yielding a cavity length of 230 cm). The holders were purged with dry N_2 at a flow rate of ~50 sccm min^{-1}, the cylindrical purge volume had a diameter of 40 mm and was 10 cm long on either side of the cavities. The light transmitted through the cavities was imaged onto round-to-rectangular optical fiber bundles, which were connected to polychromator/CCD assemblies with entrance slit widths that were of the same size as the individual fibre strands in the bundle, i.e. 100 μm. The spectrometers were equipped with different gratings (600 lines mm^{-1}) calibrated with a neon pen-ray lamp. The resolution was found to be 0.24 nm in the red and 0.35 nm in the green channel. The CCDs were thermoelectrically cooled to -30 °C and the remaining dark noise was subtracted from all spectra before data reduction and fitting of data.

Data description

The following data are available in this project.

Preparatory activities:

- Spectrometer calibrations with reference light sources.
- Sensitivity tests of IBBCEAS with NO_2.

Chamber Experiments (**Table 1**):

- Reactants I_2 and N_2O_5 (=NO_2 + NO_3):
  - (i) Dark from dry to wet. (EXP. 1, 2, 3)
  - (ii) I_2 from sublimation vs. I_2 from *Laminaria Digitata* (**Figure 2**) in low humidity. (EXP.4)
- Reactants I_2 (from sublimation) and O_3:
  - Dark and illuminated conditions in low humidity. (EXP. 5,6)
- Reactants I_2 (from sublimation) and NO_2:
  - Dark condition in dry. (EXP.7)
- Reactants I_2 (from sublimation), O_3 and NO_2:
  - Dark conditions in dry. (EXP.8)

Figure 2. Left panel: *Laminaria Digitata* tested in this project. Right panel: setting of the algae in the chamber.

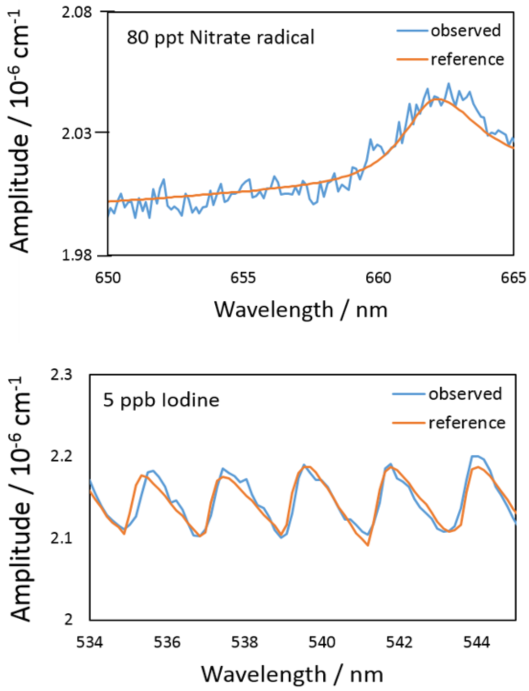

Figure 3. Upper panel: NO_3 spectrum of 80 pptv of NO_3 in humid air containing aerosol. Lower panel: I_2 spectrum of 5 ppbv in humid ambient air in the presence of NO_x, NO_3 and marine aerosol.

Results and Conclusion

The mirror reflectivity was calibrated by means of NO_2, which was filled into the chamber in steps of ca. 50 ppbv. Based on the mirror reflectivity of ~0.9994, spectra of NO_3 and I_2 were measured simultaneously. The absorption spectra were fitted with cross-sections from Yokelson et al. (1994) for NO_3 for and Saiz-Lopez et al. (2004) for I_2. Typical fit results are shown in **Figure 3.** The current setup at UCC has a detection limit of ~5 pptv for NO_3 in 5 s, and ~1 ppbv or I_2 in 1 s. The detection capability of the nitrate radical in connection with molecular iodine is of high relevance for marine aerosol formation experiments at night time.

Table 1 summarizes concentrations of reactants and observed maximum particle concentrations in the selected experiments. In the chamber experiments, we successfully confirmed the particle formation in the reaction of I_2 with NO_3 in the dark condition as shown in **Figure 4** where the reactants' concentrations were atmospherically

Table 1. Concentrations of reactants and maximum particle concentrations in the selected experiments.

EXP. #	Description*	$[I_2]_0$ / ppb	Maximum $[NO_3]$ / ppt	$[NO_2]_0$ / ppb	$[O_3]_0$ / ppb	RH / %	UV-Vis light	Maximum particle concentration / # cm^{-3}
1	NO_3, Dry	5	100	-	-	<1	-	30,000
2	NO_3, Wet	3	150	-	-	35	-	50,000
3	NO_3, Wet	3	150	-	-	55	-	40,000
4	NO_3, *Laminaria digitata*	40	60	-	-	4	-	50,000
5	$O_3 + hv$	3	-	-	100	16	on	80,000
6	O_3	7	-	-	40	3	-	2,000
7	NO_2	4	70	100	-	<1	-	-
8	$O_3 + NO_2$	5	-	10	40	<1	-	50,000

*I_2 was derived from sublimation of iodine crystal except for EXP. 4

relevant. (EXP.1) A short nucleation phase is followed by a longer growth phase.

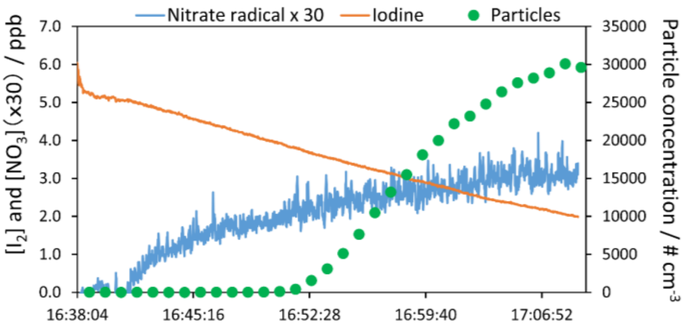

Figure 4. Particle formation in the reaction of I_2 from sublimation with NO_3 in the dry and dark conditon. (EXP.1)

Particle formation was observed under both dry and wet conditions (EXP. 1,2,3) where we found that the effect of water vapour on particle formation in terms of their number density is not significant. We also demonstrated that *Laminaria digitata*- derived I_2 can produce particle by the reaction with NO_3 of ambient relevant concentration. (EXP. 4). Particle formation under day-time conditions was explored with the aim of evaluating the relative impact of the night-time particle formation. (EXP. 5) It was found that particle formation under day time conditions was faster and the particle concentrations were approximately doubled in comparison to night-time conditions (with NO_3 only). However, the mixing ratio of O_3 was ca. 10^3 times larger than that of NO_3 during dark measurements and the experiment shows that night time particle formation is an important contributor to the overall appearance of particles in the polluted marine atmosphere. The particle formation with other reactants in the night time was also examined. The possible reactants, O_3 or NO_2, did not lead to particle bursts individually. (EXP. 6, 7) However, we found that once I_2 is mixed with both O_3 and NO_2, the reaction leads to particle formation. (EXP.8) In this case, NO_3 can form through $O_3 + NO_2 \rightarrow NO_3$ which then may contribute to the particle formation. Also, the reaction of I_2 with NO_3 produces Iodine atom, I, which can react with O_3 to produce I_2O_y. This secondary reaction may additionally enhance the particle formation. Further experiments are required to elucidate this contribution of secondary reactions.

Outcome and future work

The TNA project succesfully confirmed that the night time particle formation caused by iodine could be important even when we compare it with the day time formation. As a future work, we are going to analyze the results more deeply to determine reaction rate constants by kinetic analysis, identify particle formation mechanism by detailed gas and particle phase product analysis and hopefully evaluate their atmospheric impact.

The experiments and future activities will contribute to our understanding of particle formation in polluted marine atmospheres, i.e. in urban atmospheres of mega-cities in coastal regions. As marine aerosols strongly scatter radiation there is an impact on visibility in coastal mega-cities during dusk and dawn, and since particles also contribute to a cooling effect to the Earth's radiation budget, any new mechanisms on particle production are important to understand climate regulation. Improving our understanding of nitrogen oxide/iodine chemistry is a field that still holds surprises and is not comprehensively understood.

Figure 5. A photo of the PI with researchers at the IASC facility.

Acknowledgement

Support of this TNA project through Eurochamp-2020 is gratefully acknowledged. I would also like to sincerely thank the researchers from the IASC facility (**Figure 5**) for their substantial and professional help during this campaign.

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