1 Introduction

Night-time oxidation chemistry
- The hydroxyl radical, OH, dominates day-time oxidation of trace gases in the troposphere. Night-time oxidation is thought to be driven by the nitrate radical, NO$_3$ (Geyer et al., 2003)
- OH and HO$_2$ are produced at night via ozone- and NO$_2$-initiated alkene oxidation

The RONCO Project
- **RONCO**: Role of night-time chemistry in controlling the oxidising capacity of the atmosphere
- Aims: to advance our understanding of night-time chemistry and impact on the troposphere
- Measurements of gas- and aerosol-phase composition made onboard BAe-146 research aircraft
- Two measurement campaigns conducted from East Midlands Airport, UK, July 2010 and January 2011

Aims and questions
- Measure concentrations of OH and HO$_2$ at night
- What are the dominant HO$_2^-$ producing species at night?
- Is NO$_3$ a propagator/chain carrier of night-time OH and peroxy radical production?
- How do aerosol and NO$_3$ impact HO$_2$?

2 The Leeds FAGE Aircraft Instrument

- **FAGE**: Fluorescence Assay by Gas Expansion (Commane et al., 2010)
- Laser-induced fluorescence at low pressure (~1.8 Torr)
- Specialised inlet mounted in a window blank, ambient air sampled from outside the aircraft through 0.7 mm pinhole
- OH excited from ground state, $\lambda$TIF, to first electronically excited state, A$_2^\Sigma^+$, using light at $\lambda$ ~ 308 nm
- On-resonance fluorescence detected by temporal gated photon counting
- HO$_2$ detection by chemical conversion to OH using an excess of NO:
  - HO$_2$ + NO $\rightarrow$ OH + NO$_2$
  - Calibration with a known concentration of OH and HO$_2$:
    - H$_2$O + h$\nu$ ($\lambda$ = 165 nm) $\rightarrow$ OH + H
    - H + O$_2^*$ $\rightarrow$ HO$_2$

3 Measurements

- Highest night-time [HO$_2$]
  - ~ 13 ppt, measured during flight BS37 (see figure, left)
- OH was not detected at night above the instrument’s limit of detection during the summer and winter campaigns
- RO$_2$ radicals from alkenes are a potential source of interference in FAGE measurements of HO$_2$ (Commane et al., 2011)

4 Modelling

- DSMACC Box Model: Dynamically Simple Model of Atmospheric Chemical Complexity (Emmerson and Evans, 2009, Stone et al., 2010)
- Observably constrained box model run to steady state
- Chemistry scheme from Master Chemical Mechanism (MCM) (Jenkin et al., 2003, Saunders et al., 2002)
- What is controlling HO$_2$ at night?
- Can we explain observations of OH and HO$_2$ at night?
- What processes are controlling production and loss of HO$_2$?
- Mean modelled OH = 6 x 10$^4$ molecule cm$^{-3}$ (summer flights only), consistent with observations

5 Conclusions and Outlook

- As predicted by the rate of production and loss analysis, HO$_2$ correlates well with NO$_3$
- Night-time radical chemistry is much more complex than day-time
  - The model currently underpredicts HO$_2$
  - OH was not detected above the instrument’s limit of detection at night
- Laboratory studies are needed to assess potential interference from RO$_2$
  - The model will be used to elucidate the processes controlling HO$_2$ chemistry at night, and to explain the observed concentrations of OH and HO$_2$

References
- K. M. Emmerson and M. Evans, Atmos. Chem. Phys., 9, 1351-1360, 2009
- Stone, M. J., Evans et al., Atmos. Chem. Phys., 10, 9451-9462, 2010

Night-time aircraft measurements of OH and HO$_2$ using the FAGE technique
Hannah Bunyan*, Trevor Ingham, Daniel Stone, Stewart Vaughan, Mathew Evans and Dwayne Heard
(cmhmb@leeds.ac.uk), *School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK

**BAe-146 Research Aircraft, with HO$_2$ inlet circled in red**

**FAGE detection assembly installed on BAe-146 aircraft**

**Comparison between observed and modelled HO$_2$**: 1:1 Line (± 50%), Line of Best Fit: [HO$_2$ (obs) - (0.30 ± 0.00) [HO$_2$ (mod)] + (0.05 ± 0.01)] P = 0.22

**Processes controlling HO$_2$ (radical sources and sinks) in the model**
- Large number of reactions contributing to radical production and loss
- Production from alkenes + O$_3$, alkenes + NO, RCHO + NO
- Loss by OH + NO$_3$, decomposition of nitrated radicals, HO$_2$ + RO$_2$