FACULTY OF GRADUATE STUDIES

Graduate Programme in Chemistry

ORAL EXAMINATION PROSPECTUS

Patryk Wojtal

A Candidate for the Degree of
Doctor of Philosophy

Title of Thesis:
Nocturnal Measurements of HONO, NO_2, and NO_3 by Differential Optical Absorption Spectroscopy in Polluted Marine and Urban Atmospheres

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Public Lecture
1:00 PM
Thursday, December 12, 2013
Room 317 Petrie SEB

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Oral Examination
2:00 PM
Thursday, December 12, 2013
Room 006A Steacie Building

ABSTRACT

Nitrogen oxides are ubiquitous throughout the lower atmosphere and significantly affect the chemistry of the atmosphere, air quality, and climate. A dataset obtained using differential optical absorption spectroscopy (DOAS) was analyzed in order to quantify the NO_3, HONO and NO_2 concentrations at Saturna Island, and concentrations of N_2O_5 were calculated. Nocturnal measurements of NO_3, NO_2 and HONO were performed using active-DOAS at York University.

A method for calculating the lifetimes of NO_3 without assuming a steady-state approximation was determined and non steady-state lifetimes of NO_3 were calculated for both studies. The direct (via NO_3) and indirect (via N_2O_5) rate loss constants of NO_3 from the combined nocturnal reservoir (NO_3+N_2O_5) were determined as a function of time of night. Measurements of HONO over the polluted open ocean were performed for the first time. Rapidly established steady-states of HONO were observed, persisting throughout the night until sunrise. During the steady-state period ($d[HONO]/dt \approx 0$), HONO was independent of the air mass source and NO_2, leading to a 0° order HONO formation with respect to NO_2, contrary to expectations. Potential reservoirs of HONO were explored and a conceptual model for HONO formation over aqueous surfaces was hypothesized. Subsequently, nocturnal measurements of HONO in the urban area were made at York University for a total of 242 nights. This urban dataset showed two types of HONO behavior. Firstly, a "steady-state" behavior was clearly observed for a subset of the data-set, similar to that observed in the aqueous environment at Saturna. Secondly, HONO concentrations were observed to highly correlate with NO_2 for another subset of the data-set ($d([HONO]/[NO_2])/dt \approx 0$), showing evidence of 1° order behavior as expected for the accepted heterogeneous NO_2 hydrolysis mechanism of HONO formation ($2NO_2 + H_2O \rightarrow HONO + HNO_3$). Steady-states of HONO were observed during atmospherically unstable nights, while HONO was strongly correlated with NO_2 during stable nights. It was discovered that the main parameters distinguishing these two types of behavior was atmospheric stability and NO_2 concentration.