The Role of Heterogeneous Chemistry of Volatile Organic Compounds in The Photochemical Oxidant Cycle: A Modeling and Laboratory Study

Investigators:

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Co-PI: Vicki Grassian, Center for Global & Regional Environmental Research, and Department of Chemistry

Post-Docs & Students: Dr. Grant Underwood; Dr. Peng Li; Mr. Mahesh Phadnis; Mr. Chul Song; and Mr. Shan He.

Outputs:

Presentations:

1. Carmichael, G., "Modelling Aerosol Effects on Tropospheric Air Quality", Workshop on Measuring Chemistry Interactions: Molecular to Global Scales, PNNL, Richland Washington, Sept. 25-26, 1998

2. Carmichael, G., "Regional Tropospheric Heterogeneous Chemistry: Impacts of Particles from Foss Blown Soils", Keynote address, 6th International Conference on Atmospheric Sciences and Applica 1998.

3. Song, C., Mahesh J. Phadnis, and Gregory R. Carmichael, "Numerical Investigation of the intera carbonaceous and mineral aerosol particles", 17th Annual AAAR Conference, Cincinnati, Ohio, USA, 1998.

4. Song C. and Gregory R. Carmichael, "The aging processes of sea-salt and dust particles durin International Symposium on Global Atmospheric Chemistry, University of Washington, Seattle, USA,

5. Grassian, V., "Heterogeneous Reactions on Mineral Oxides: A Combined Laboratory and Modelir Geophysical Society Meeting, San Francisco, Dec. 6-10, 1998.

Journal Articles:

Several manuscripts are currently being written on the spectroscopic and Knudsen cell studies.

1. Ping Li, Vicki Grassian and Gregory Carmichael "Heterogeneous Chemistry of Carbonyl Compounds on to Geophysical Research Letters.

2. Ping Li, Elizabeth Covington, Vicki Grassian and Gregory Carmichael "Transmission FT-IR and Diff Study of the Surface Chemistry of Formaldehyde, Acetaldehyde, Acetone and Propionaldehyde on Ox Journal of Physical Chemistry.

3. Ping Li, Song, Vicki Grassian and Gregory Carmichael "A Combined Laboratory and Modeling Stu Chemistry of Carbonyl Compounds in the Troposphere" to be submitted to The journal of Geophysi

4. Mohamed El-Maazawi, Anne Finken and Vicki Grassian "Photooxidation of Acetone on TiO_2" to be su
Chemistry.

Several manuscripts, including one thesis, have been submitted and are being written on a combir
understanding the chemistry of nitrogen oxides on the photochemical oxidant cycle.

5. Goodman, A. L.; Miller, T. M. and Grassian, V.H. “Heterogeneous Reactions of Nitrogen Dioxide (
Sci. and Technology A , 16, 2585-2590, 1998.

6. Miller, T. M. and Grassian, V. H. “Heterogeneous Chemistry of NO_2 on Mineral Oxide Surfaces: Spectroscopic Evidence for Oxide-Coordinated and Water-Solvated Surface Nitrate” Geophysical Research Letters , 20, 3835-3838, 1998.

7. Goodman, A.L.; Underwood, G. M. and Grassian, V. H. "A Spectroscopic Investigation of the
H_2O(a)gHONO(g) + HNO_3(a) on Hydrated Silica Particles: Characterization of Gas-Phase and A(
publication in Geophysical Research Letters.

8. Miller, T. M. Underwood, G. M. and Grassian, V.H. "Transmission FT-IR and Knudsen Cell Study (
Gaseous Nitrogen Dioxide on Mineral Oxide Particles" submitted for publication as an article i
Environmental Section.

9. G. M. Underwood, T. M. Miller, E. T. Balster, C. H. Song, M. Phadnis, G. C. Carmichael1,
Reactions of NO_2 on Mineral Oxides: A Combined Laboratory and Modeling Study" to be submitted to

10. Miller, T. M., Ph.D. Dissertation, University of Iowa "Heterogeneous Reactions of Nitrogen Ox

11. Song, C., and G. Carmichael, "The Aging Process Of Naturally-Emitted Aerosol (Sea-Salt And M
Transport", Atmospheric Environment, in press, 1999

12. Song, C., and G. Carmichael, "Alkalinity-Based HNO_3 Deposition Onto The Aerosol Particles
Research, submitted Nov., 1999

13. Phadnis, M., G. Carmichael, I. Uno and C. Song, " Reduced Ozone Levels in Volcanic Plumes in
Research Letterssubmitted, Jan. 1999.

Modeling Analysis:

The importance of these heterogeneous reactions involving mineral oxide and min
studied using a combined aerosol/gas-phase chemistry model in which multicompo
heterogeneous chemistry on the aerosol surface are explicitly included in the mode
Zhang, 1994; Zhang and Carmichael, 1999). In this model, aerosol interactions with
arise through the adsorption of trace species and the gas-to-particle conversions
the aerosol growth and surface heterogeneous reaction processes. The interactions l
are modeled using a combined thermodynamics and kinetics approach:

$$\frac{dC_i}{dt} = \int_{r_2}^{r_1} 4\pi r^2 F(r) \frac{dn}{dr} dr \quad (1)$$

$$F(r) = \frac{D_j (C_j - C_j^e)/r}{1 + f(K_n, \alpha) K_n} \quad (2)$$

$$f(K_n, \alpha) = \frac{1.333 + 0.71 K_n^{-1}}{1 + K_n^{-1}} + \frac{4(1-\alpha)}{\alpha} \quad (3)$$

where k_j is the overall mass-transfer coefficient, C_i the adsorbed species
concentration of the absorbing species and C_j^e is the equilibrium gas-phase concer
equilibrium with the the surface adsobed species (this term can be related to surfa
the gas phase diffusion coefficient, K_n is the dimensionless Knudsen number, F(r)
surface of the aerosol particle with radius r in molecules cm^{-1} s^{-1}, dn/dr is the
particles, and α is the accommodation coefficient (or sticking coefficient).

Experimental Considerations

•

- **Spectroscopic measurements to**
  - Provide mechanistic information on the molecular level
  - Need to have techniques that can detect gas-phase **<u>and</u>** surface- bound species

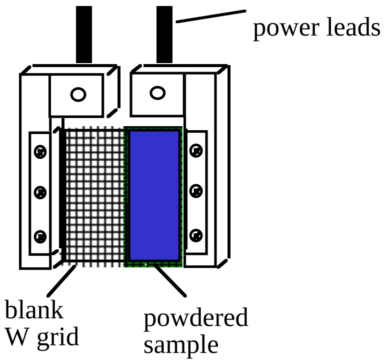
- **Kinetic measurements to provide quantitative information**
  - Determine uptake coefficients and reaction probabilities

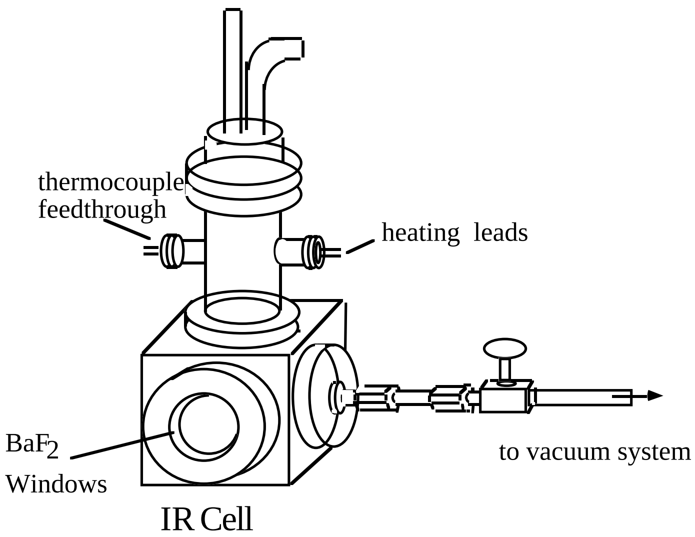
- **Provide data as input for global atmospheric models**
  - Reaction probabilities, reaction mechanism, surface coverages (saturation)

Experimental Methods

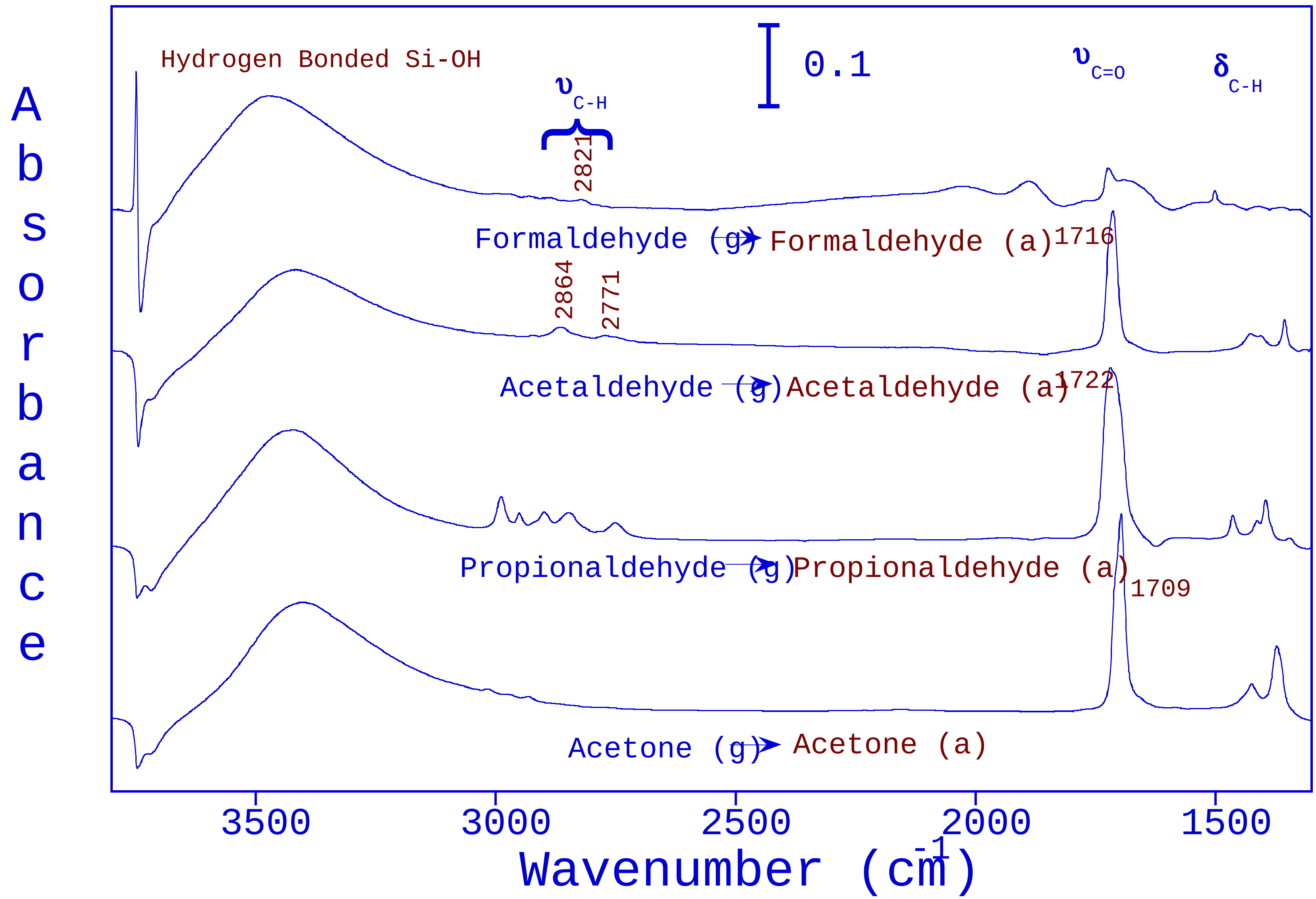
Transmission FT-IR Spectroscopy

(to characterize gas-phase and surface-bound species)

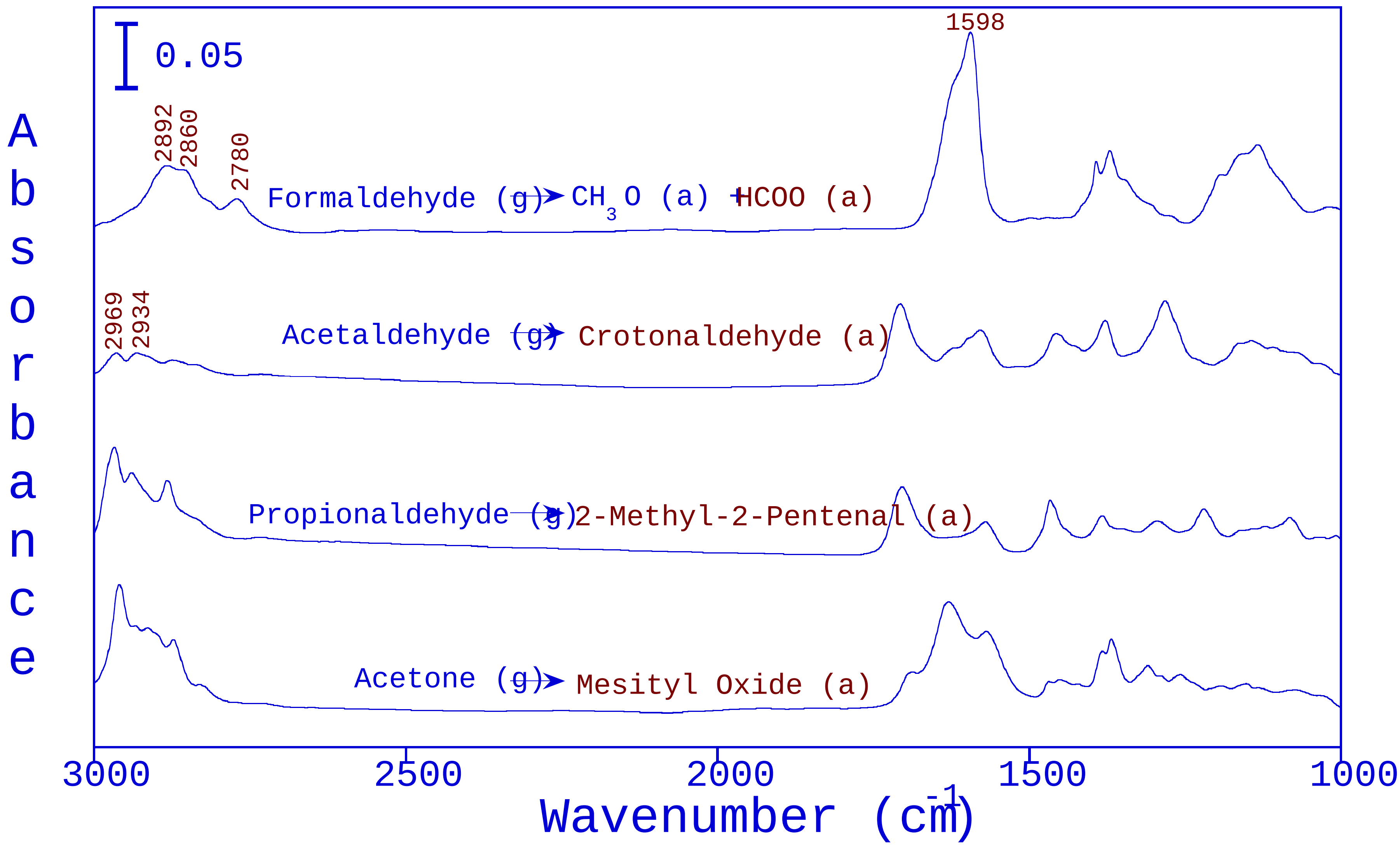




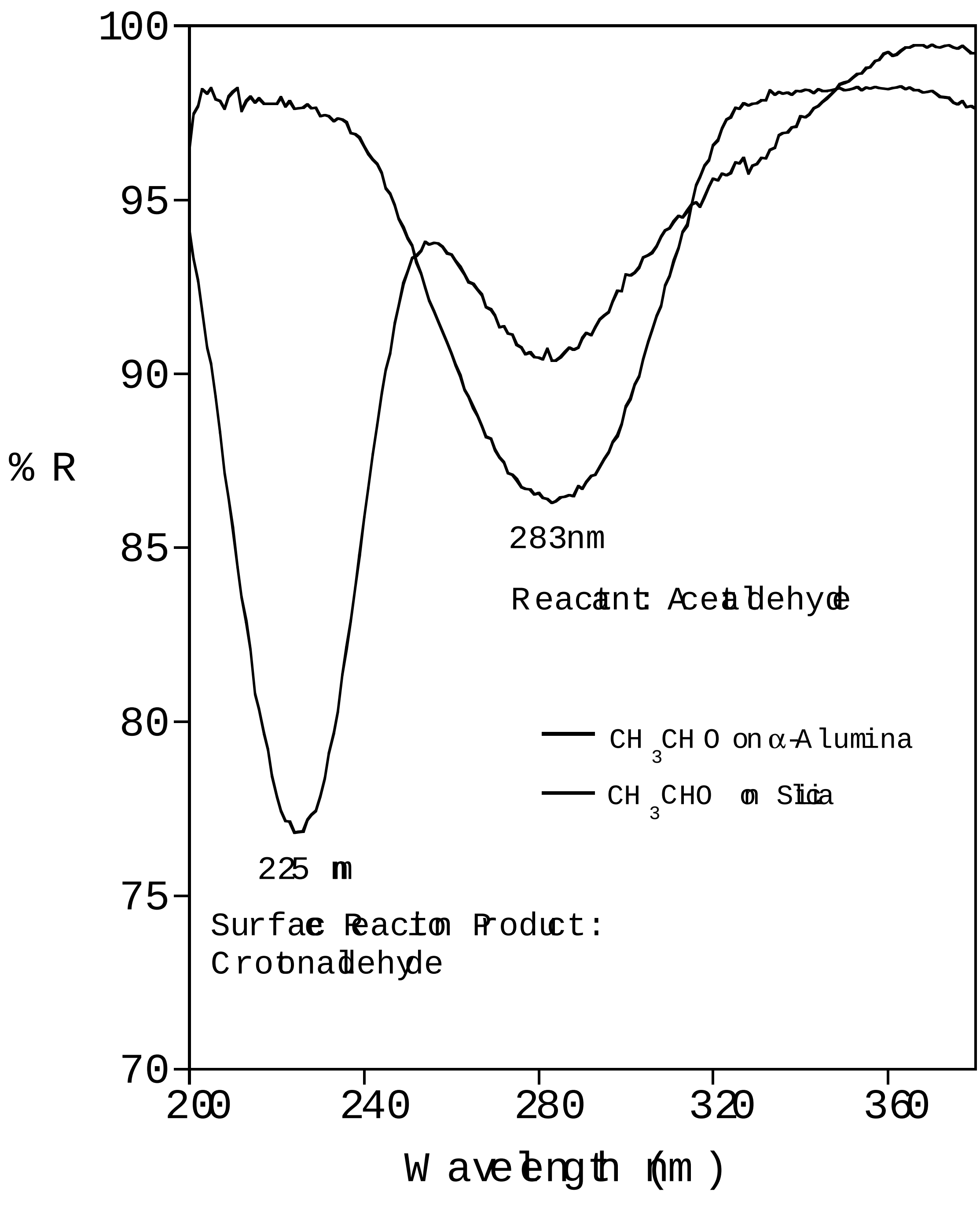
Transmission FT-IR Spectra of Carbonyl Comp
Adsorbed on Silica



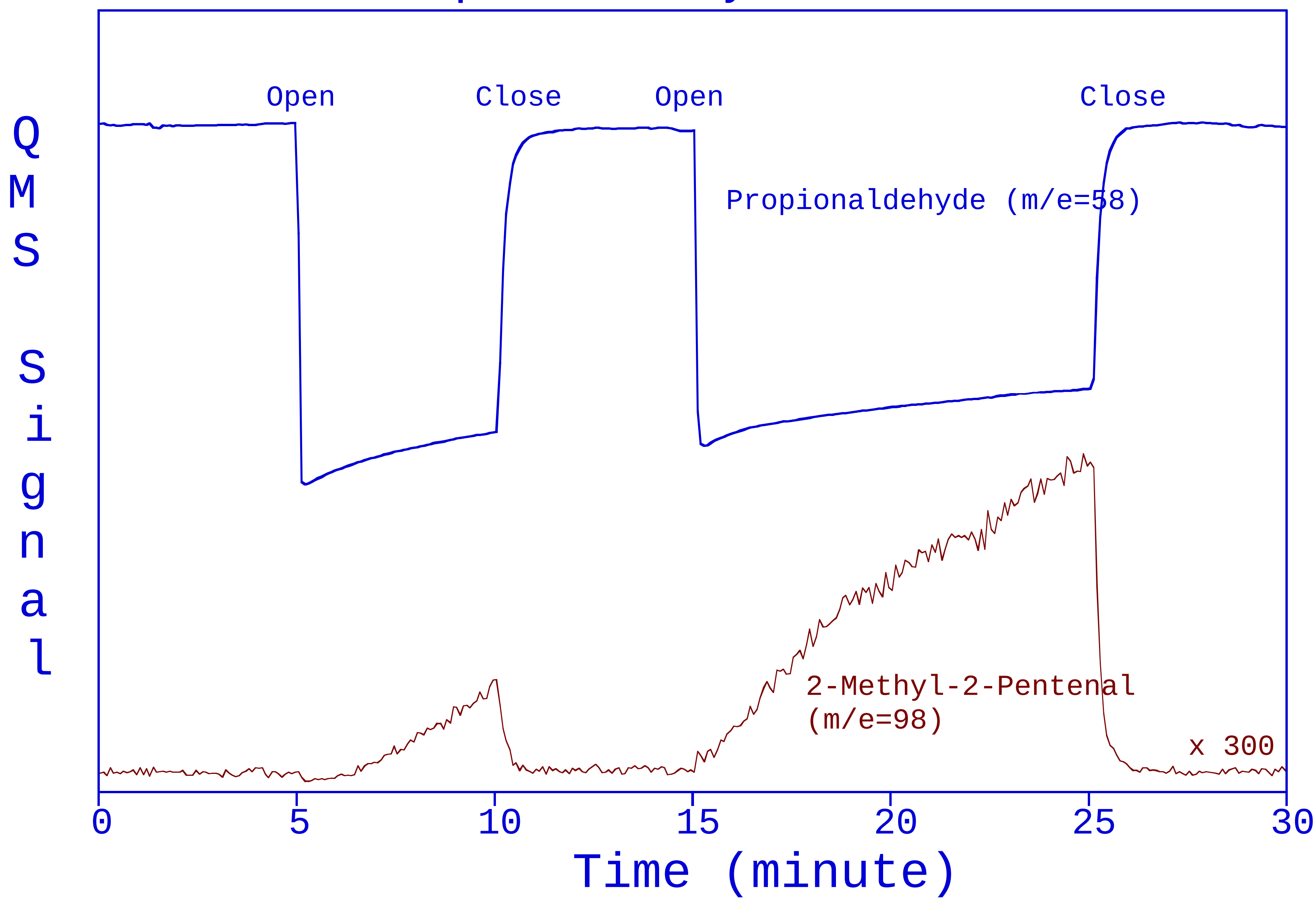
Transmission FT-IR Spectra of Carbonyl Com
Adsorbed on α-Alumina



Diffuse Reflectance UV-Vis Spectra of Acetaldehyde Adsorption on Silica and α-Alumina



Knudsen Cell Data: Heterogeneous Reaction
Propionaldehyde on α-Alumina



Tabulated Values of the Initial Uptake Coe
Acetaldehyde, Acetone and Propionaldehyde

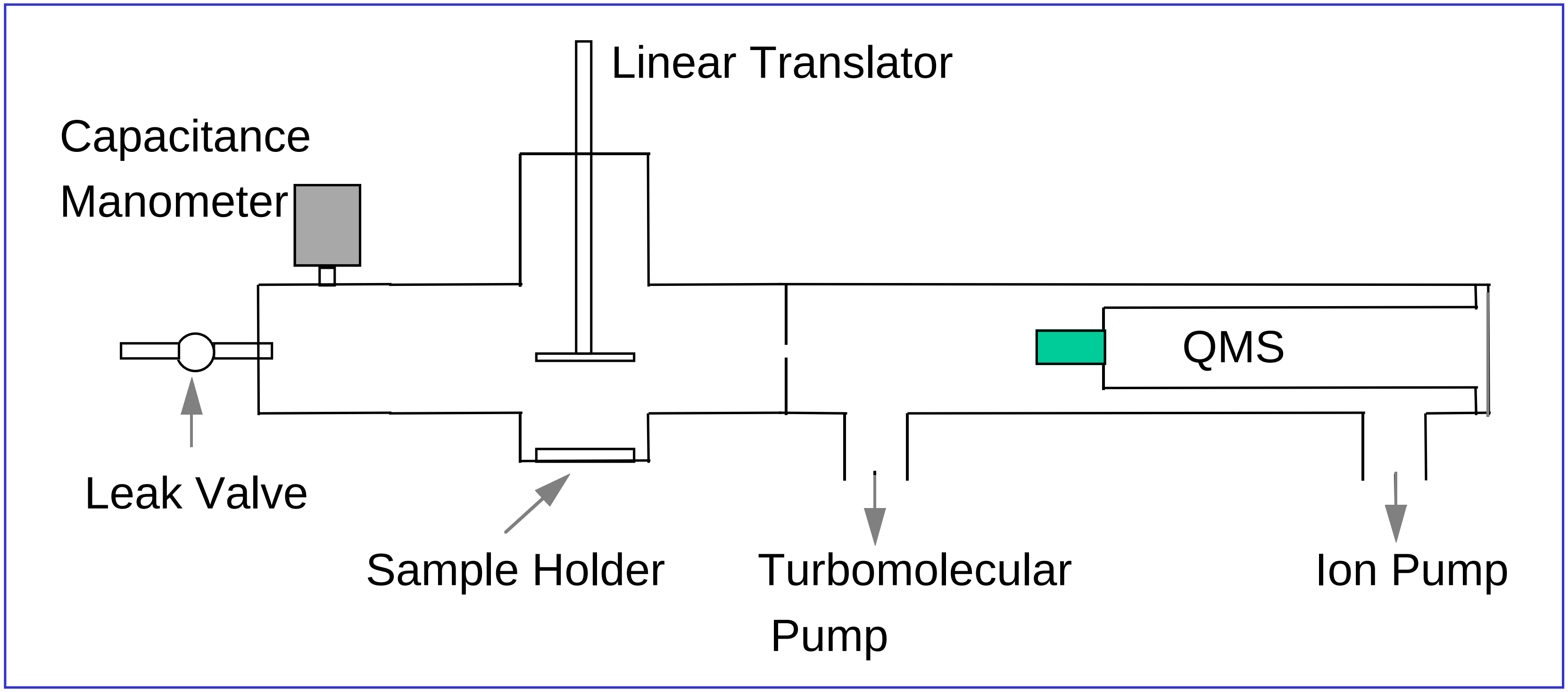
	CH_3CHO	CH_3COCH_3	CH_3CH_2CHO
SiO_2	0.0029	0.0093	0.0042
Fe_2O_3	0.0021	0.0067	n. m.
CaO	0.0116	0.0074	n. m.
MgO	0.0074	0.0082	n. m.
α-Al_2O_3	0.0062	0.0065	0.0195
γ-Al_2O_3	0.0131	n. m.	n. m.
TiO_2	0.0206	0.0230	0.0242
C-Black	0.0150	0.0232	0.0285

n. m. = not measured

Experimental Methods

Knudsen Cell Reactor

(used to determine uptake coefficients)



$$\gamma = \left(\frac{A_H}{A_S}\right) \times \left(\frac{I_0 - I_r}{I_r}\right)$$

Where

A_H is the area of the aperture hole to the QMS

A_s is the geometric area of the reactive surface

I_o is the calibrated mass spectrometer signal without the metal oxide particles exposed

I_r is the calibrated mass spectrometer signal with cover raised and the metal oxide particles exposed

Tabulated Values of the Initial Uptake Coe
Nitrogen Dioxide and Nitric Acid

	*NO_2	HNO_3
Fe_2O_3	3×10^{-3}	2×10^{-2}
China Loes	1×10^{-3}	1×10^{-1}
TiO_2	8×10^{-4}	2×10^{-1}
α-Al_2O_3	4×10^{-4}	4×10^{-2}
MgO	4×10^{-4}	5×10^{-1}
CaO	2×10^{-4}	7×10^{-2}
SiO_2	$<1 \times 10^{-5}$	4×10^{-3}

*Step 1:

$NO_2(g) \rightarrow NO_2(a)$

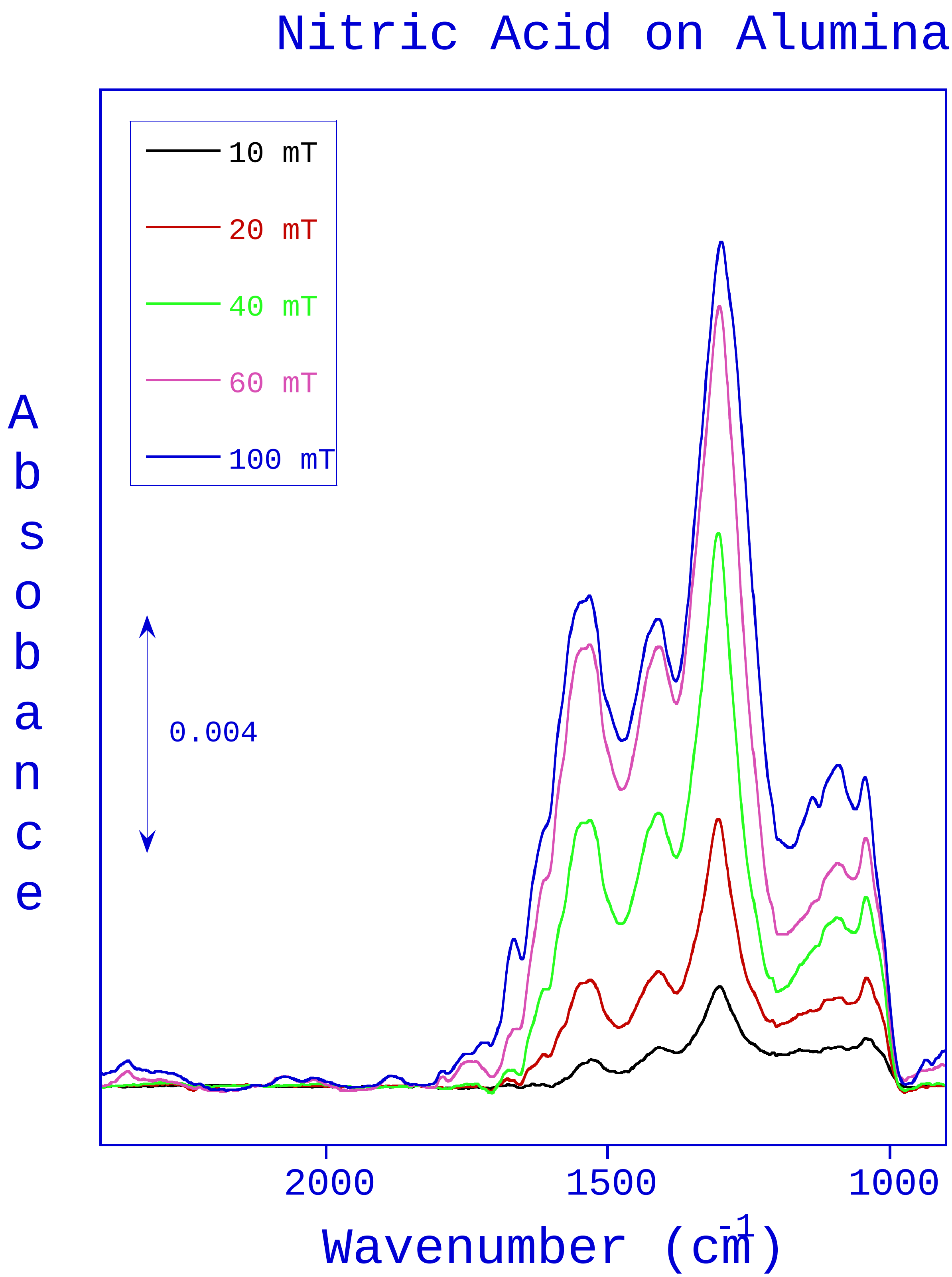
Step 2 (at ~30% coverage):

$NO_2(g) + NO_2(a) \rightarrow NO_3(a) + NO(g)$

Reaction Saturates at ~5 $\times 10^{14}$ cm^{-2}

**$HNO_3(g) \rightarrow HNO_3(a)$

Uptake Coefficients for HNO_3 are
1-3 orders of magnitude lar
for NO_2



Nitric Acid on Alumina
10 mT
20 mT
40 mT
60 mT
100 mT
0.004
Absobance
2000
1500
1000
Wavenumber (cm-1)

Motivation/Objectives: The need to analyze ozone and aerosols together, and the lack of fundamental information on potentially important chemical processes, provide the motivation for this proposed work. The importance of heterogeneous reactions in tropospheric ozone and aerosol formation, and their impact on O_3-precursor relationships will be studied through a multidisciplinary approach which combines modeling and laboratory components. The research is directed towards efforts to significantly enhance our understanding of one of the most uncertain areas of atmospheric chemistry, i.e., heterogeneous processes. The combined laboratory and modeling studies will improve our basic understanding of the chemistry on aerosol surfaces, will demonstrate and elucidate the interactions and interrelationships between ozone and aerosol processes, will assess whether these processes can alter the O_3-precursor relationships upon which present emission reduction strategies are based, and will provide needed scientific information regarding linkages between tropospheric ozone and secondary aerosol abatement. The new laboratory data and the modeling efforts to predict the aerosol composition of both the inorganic and organic fractions, will also be of direct value to aerosol radiative forcing and climate change studies.

The specific objectives of this study are to:

- Evaluate the extent to which heterogeneous chemistry affects the photochemical oxidant cycle, particularly, tropospheric ozone formation;
- Conduct laboratory studies on heterogeneous reactions involving VOCs on aerosol surfaces; and
- Explore the sensitivity of ozone and aerosol composition to changes in precursor emissions on regional scales.

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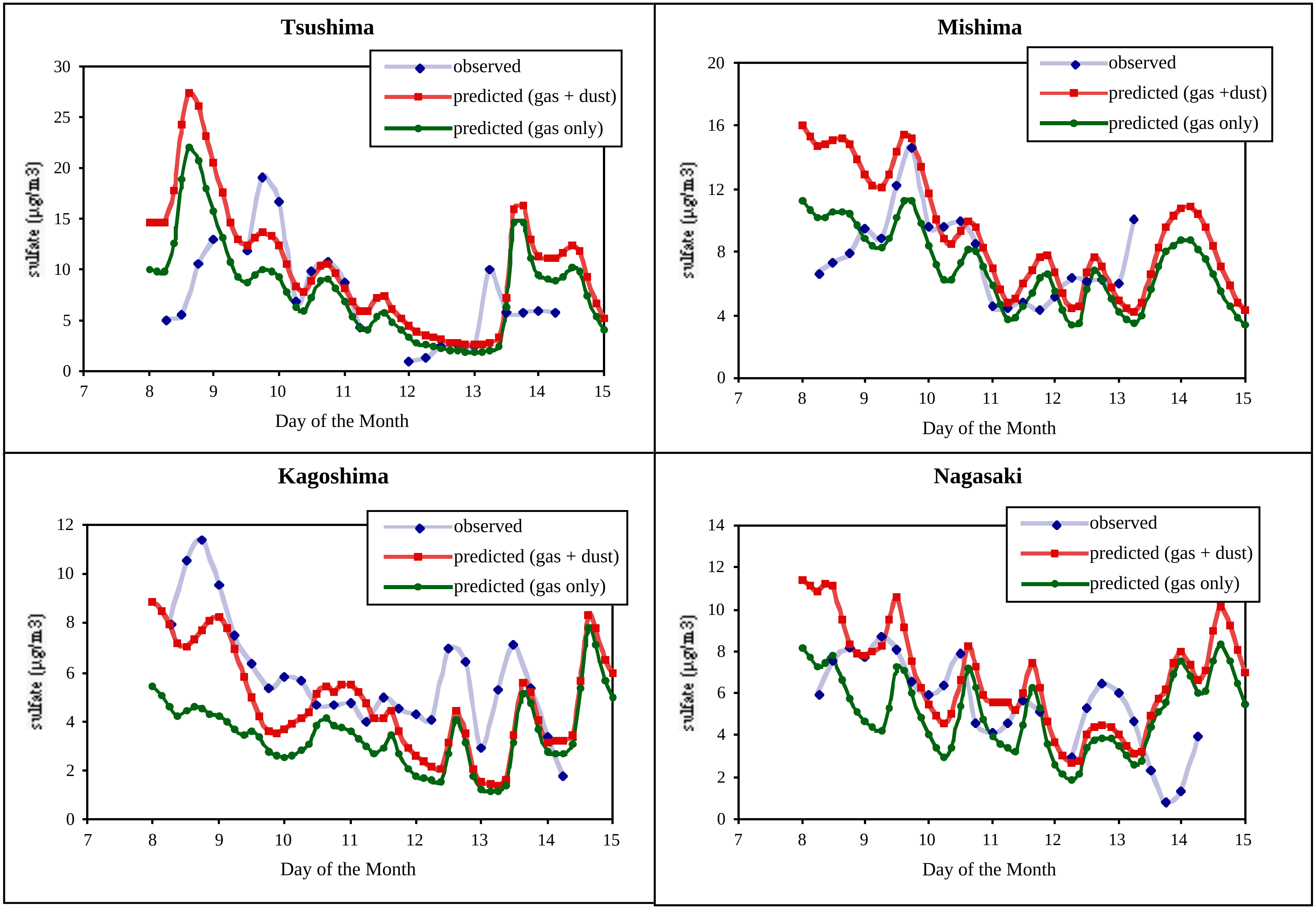
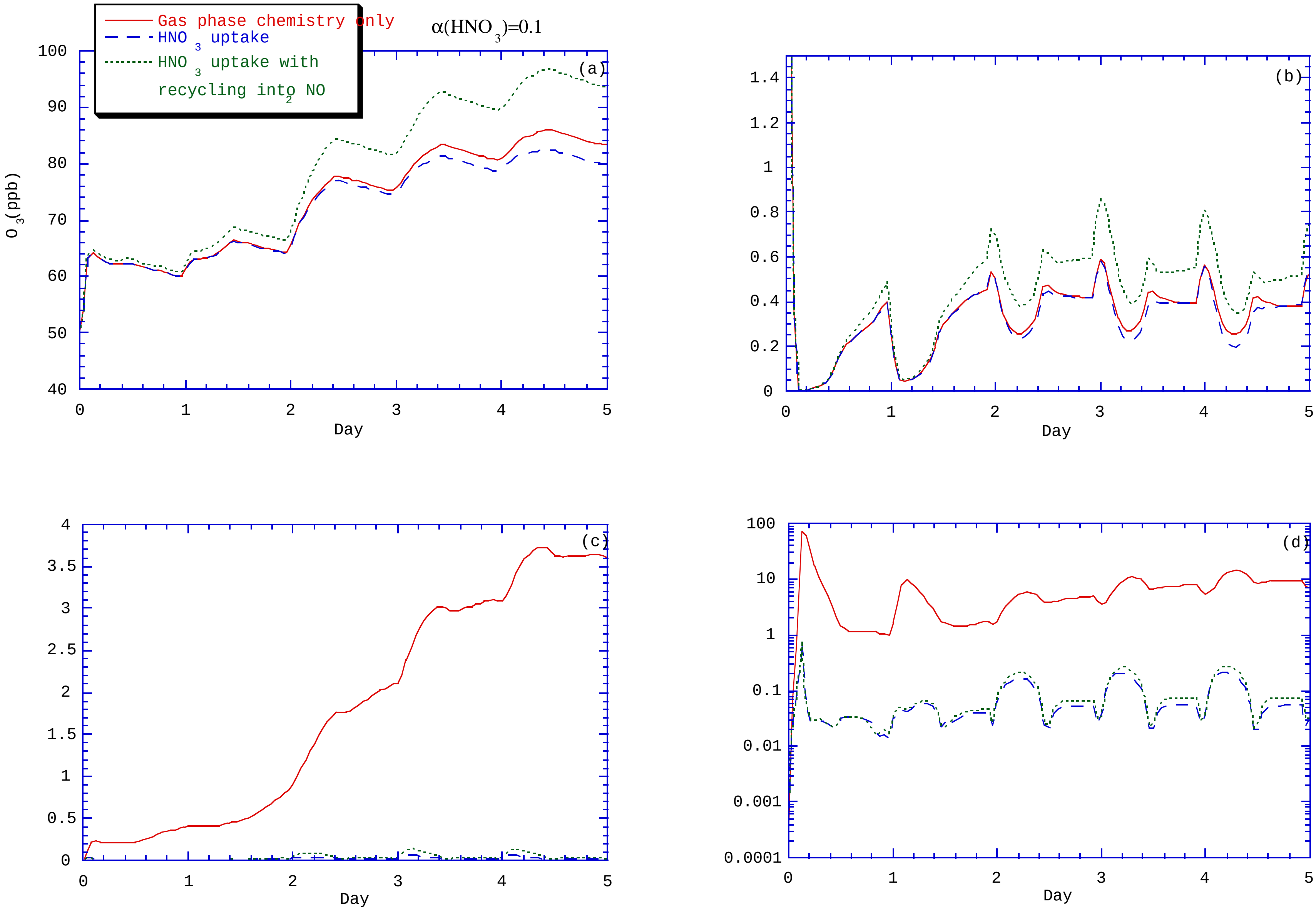
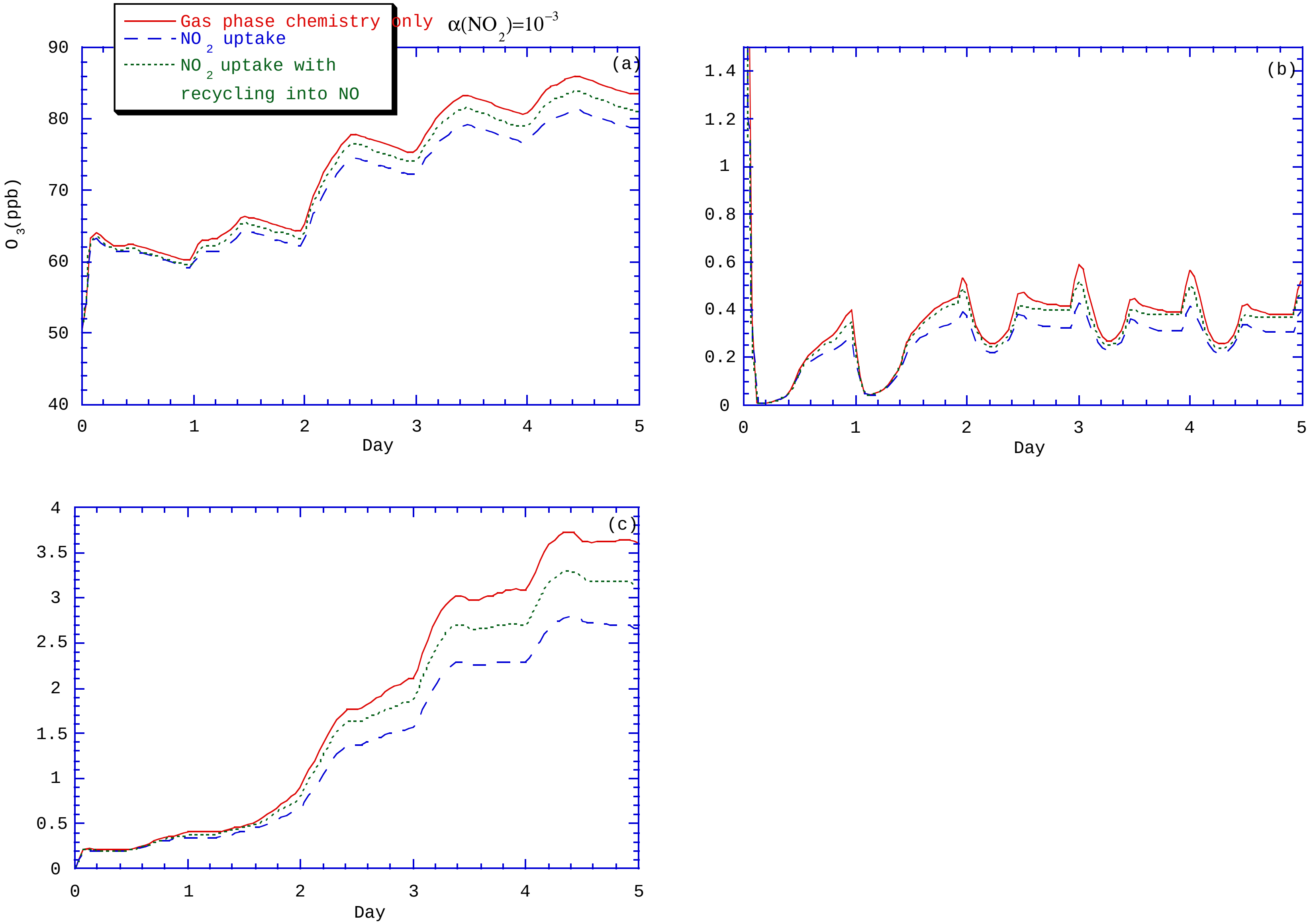


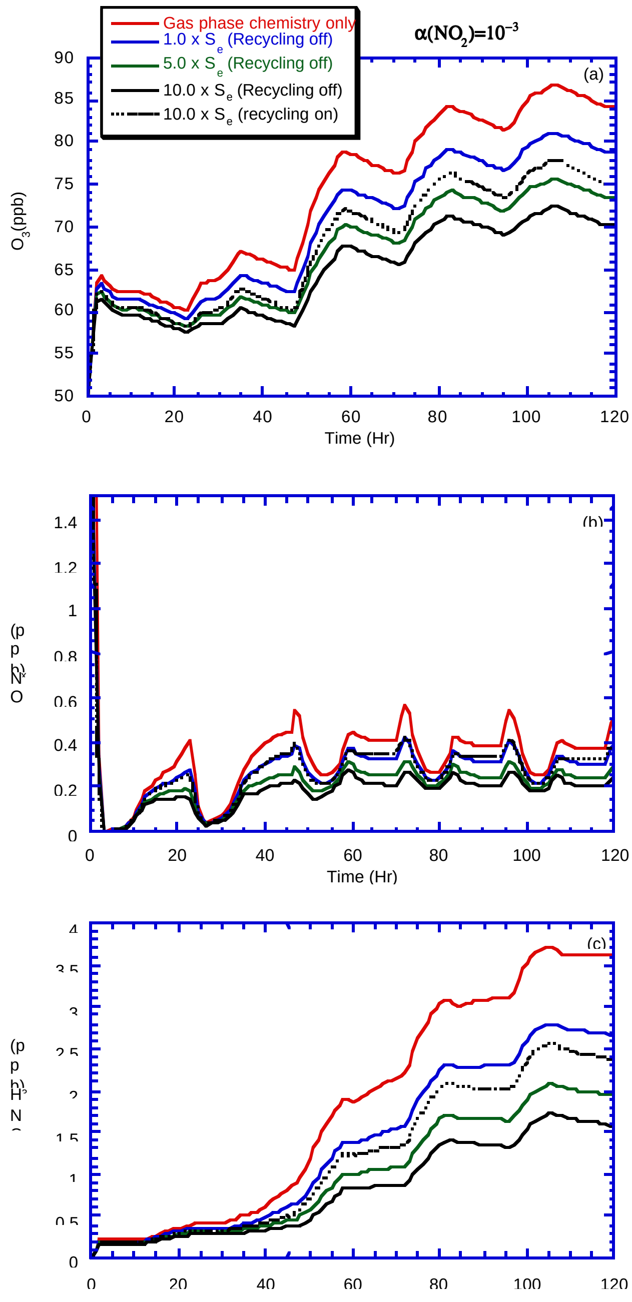
Tsushima
observed
predicted (gas + dust)
predicted (gas only)
sulfate (µg/m3)
0
5
10
15
20
25
30
7
8
9
10
11
12
13
14
15
Day of the Month
Mishima
observed
predicted (gas +dust)
predicted (gas only)
sulfate (µg/m3)
0
4
8
12
16
20
7
8
9
10
11
12
13
14
15
Day of the Month
Kagoshima
observed
predicted (gas + dust)
predicted (gas only)
sulfate (µg/m3)
0
2
4
6
8
10
12
7
8
9
10
11
12
13
14
15
Day of the Month
Nagasaki
observed
predicted (gas + dust)
predicted (gas only)
sulfate (µg/m3)
0
2
4
6
8
10
12
14
7
8
9
10
11
12
13
14
15
Day of the Month



Gas phase chemistry only
HNO 3 uptake
HNO 3 uptake with recycling into NO 2
α(HNO 3)=0.1
O 3 (ppb)
(a)
(b)
(c)
(d)
Day



Gas phase chemistry only
NO 2 uptake
NO 2 uptake with recycling into NO
α(NO2)=10−3
(a)
(b)
(c)
O3(ppb)
Day
90
80
70
60
50
40
1.4
1.2
1
0.8
0.6
0.4
0.2
0
4
3.5
3
2.5
2
1.5
1
0.5
0
0
1
2
3
4
5



Gas phase chemistry only
1.0 x S e (Recycling off)
5.0 x S e (Recycling off)
10.0 x S e (Recycling off)
10.0 x S e (recycling on)
α(NO2)=10−3
(a)
O3(ppb)
Time (Hr)
(c)
Time (Hr)