

**THE ROLE OF HETEROGENEOUS CHEMISTRY OF
VOLATILE ORGANIC COMPOUNDS IN THE
PHOTOCHEMICAL OXIDANT CYCLE:
A MODELING AND LABORATORY STUDY**

INVESTIGATORS

PI: Gregory R. Carmichael, Center for Global & Regional Environmental Research, and the Department of Chemical & Biochemical Engineering

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

Co-I: Florian Potra, Center for Global & Regional Environmental Research, Departments of Mathematics and Computer Science

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 O₃-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 O₃-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.

APPROACH

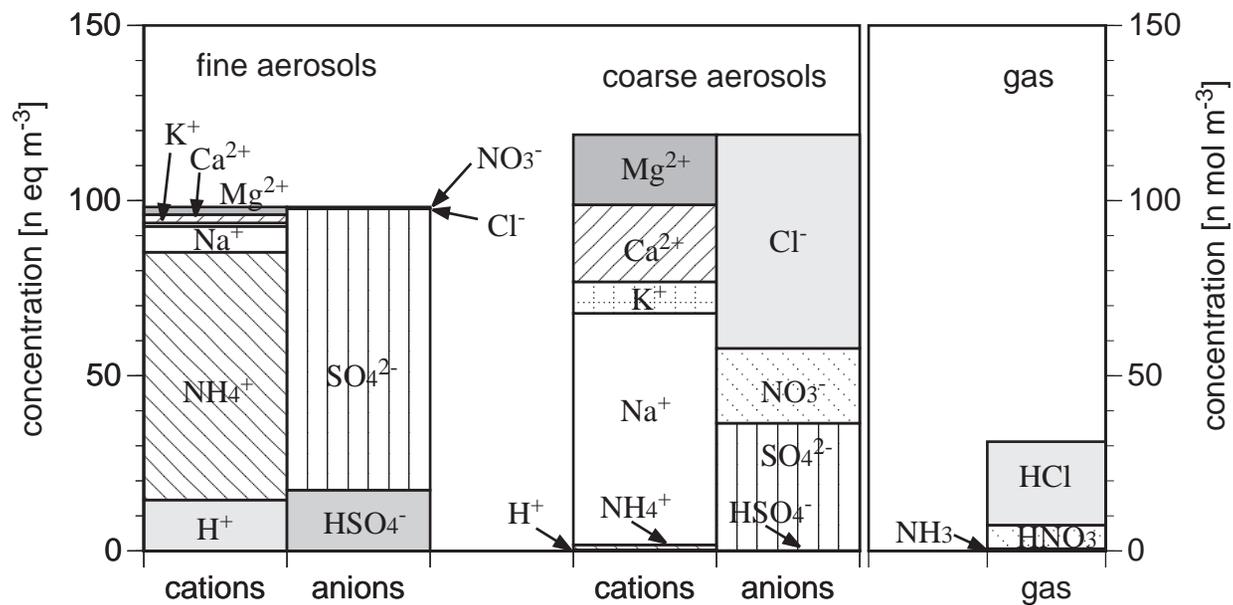
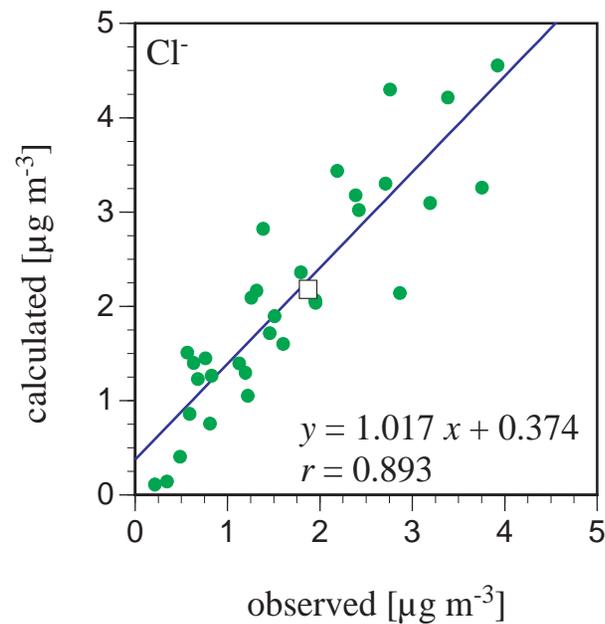
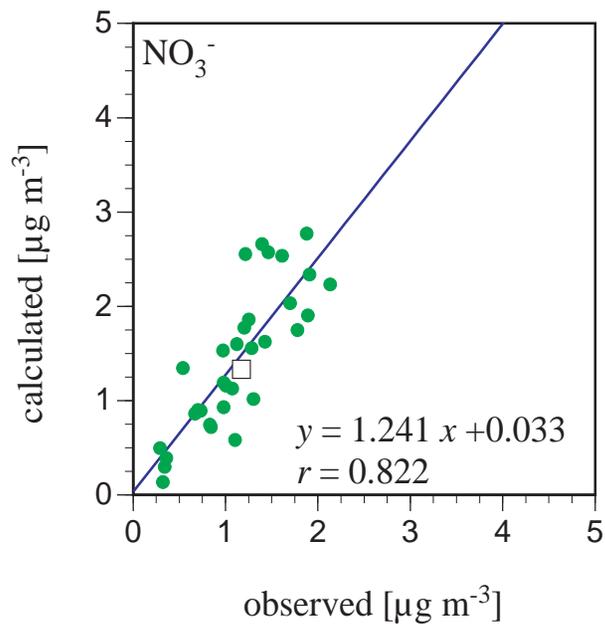
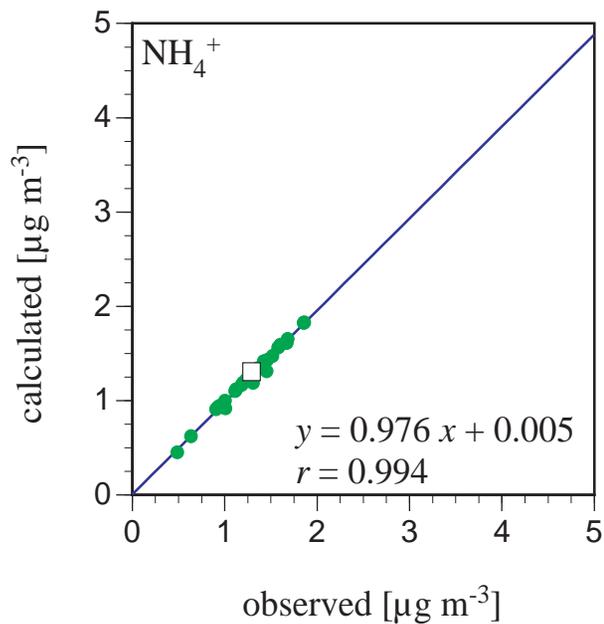
MODELING

LABORATORY

FIELD
STUDY

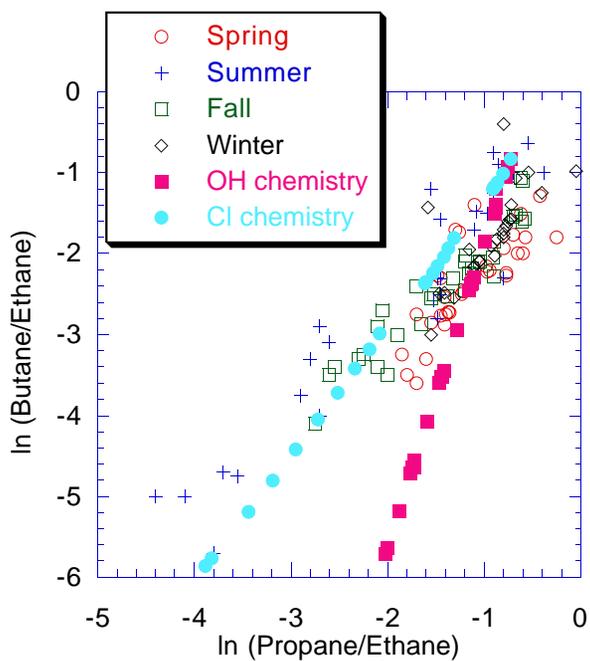
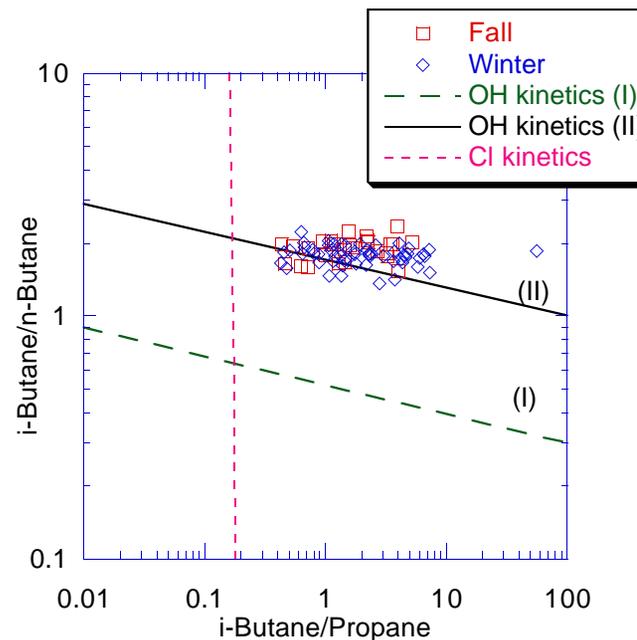
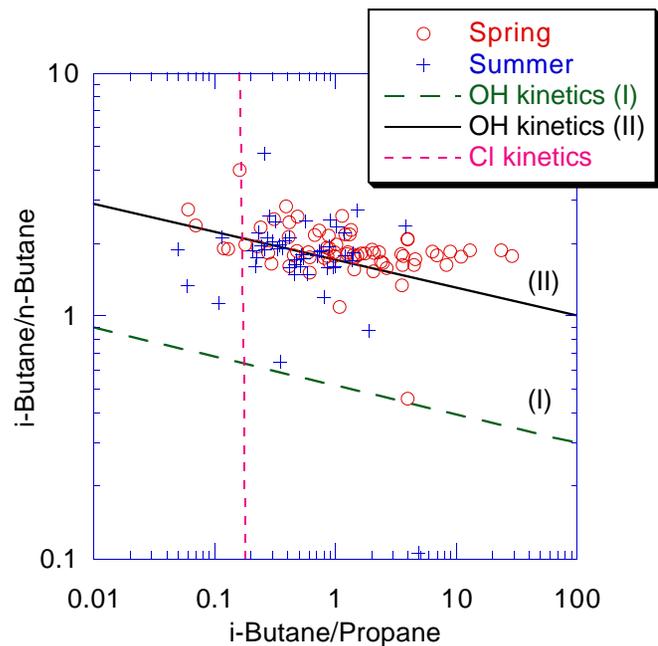
3D STEM-III transport/chemistry/deposition model
Dynamics of Aerosol Processes
Combined Kinetics/Thermodynamics Approach
New Approach for Secondary Organic Aerosol Partitioning
Sensitivity Analysis and Improved Numerical Methods

Spectroscopic and Kinetic Measurements of Heterogeneous Processes Involving Mineral Dust and Carbonaceous Particles
Determine Heterogeneous Reaction Probabilities of VOCs, O₃ and O₃-precursors for input into Atmospheric Models
Study the Effect of Solar Radiation on Reaction and Adsorption of VOCs

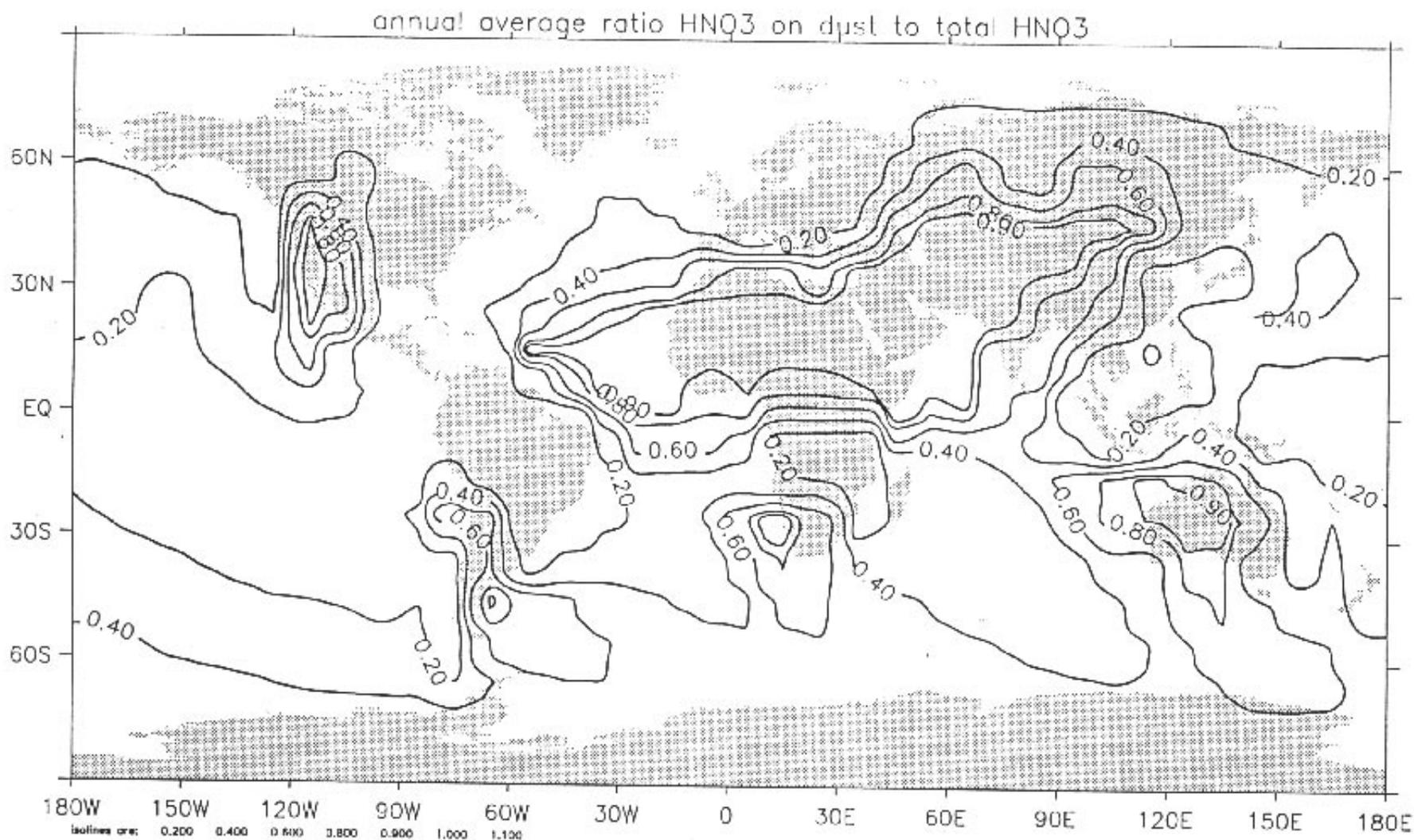


Observed and model calculated (two-bin model) NH_4^+ , NO_3^- and Cl^- at Cheju Island, South Korea. (top panel)

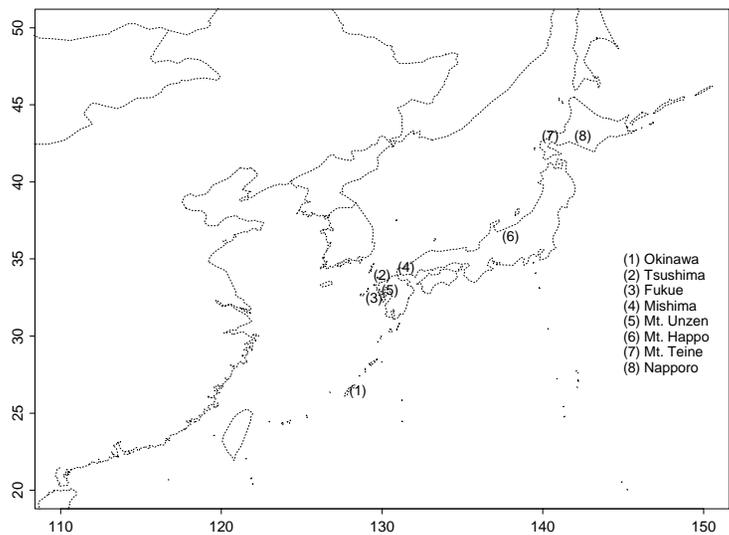
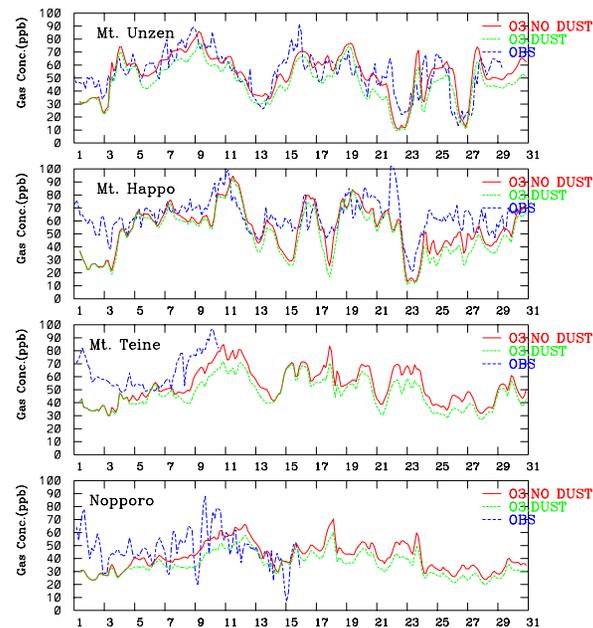
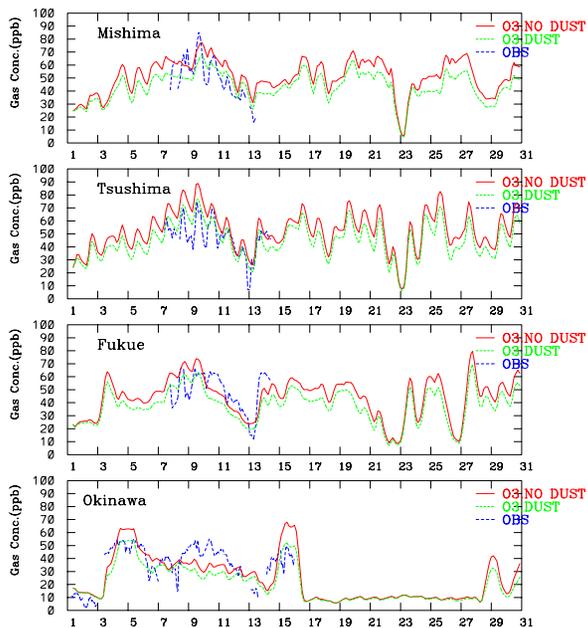
Model calculated aerosol and gas phase composition for the mean conditions at Cheju Island, South Korea. (left panel)



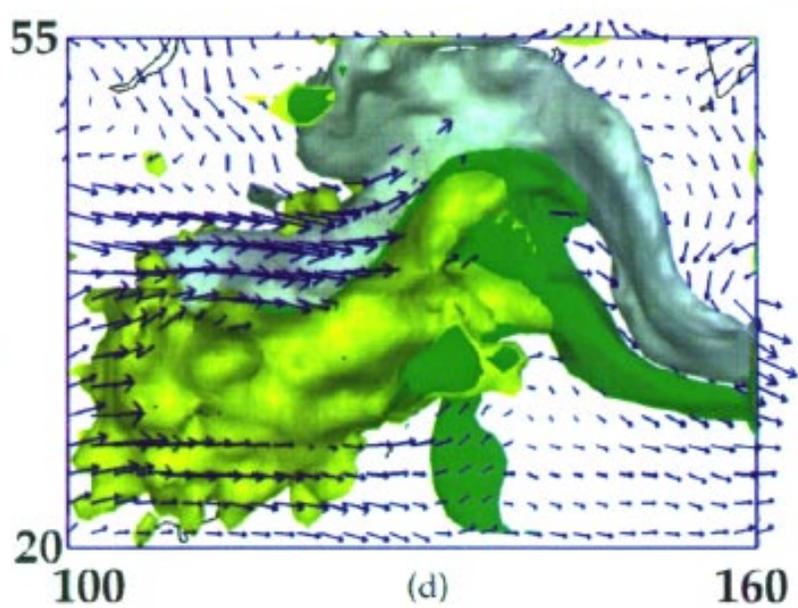
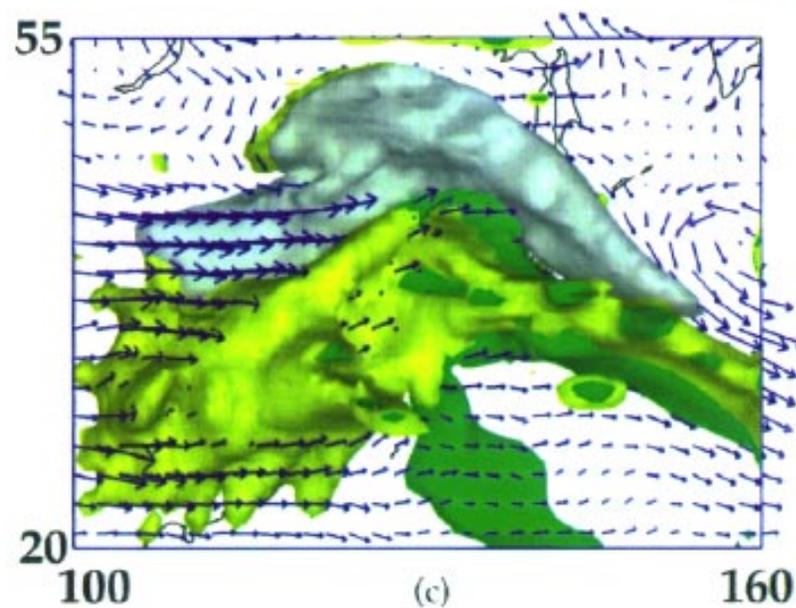
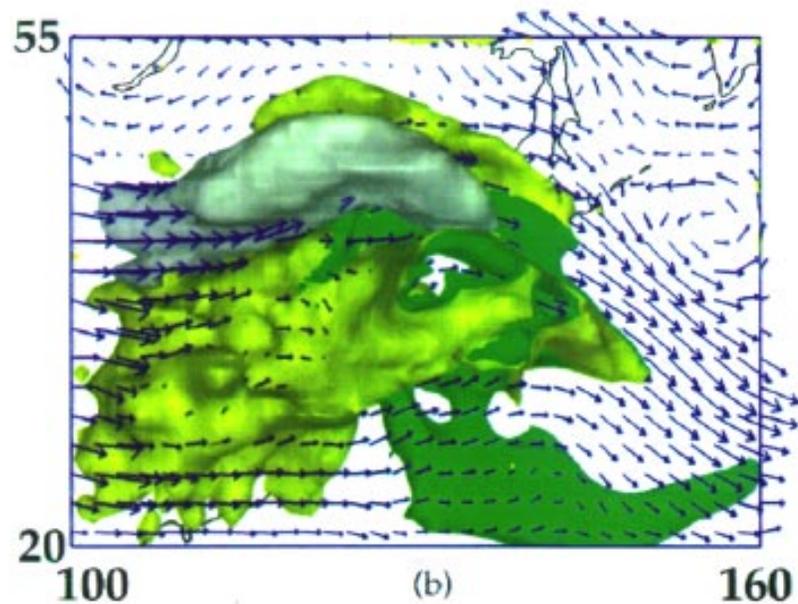
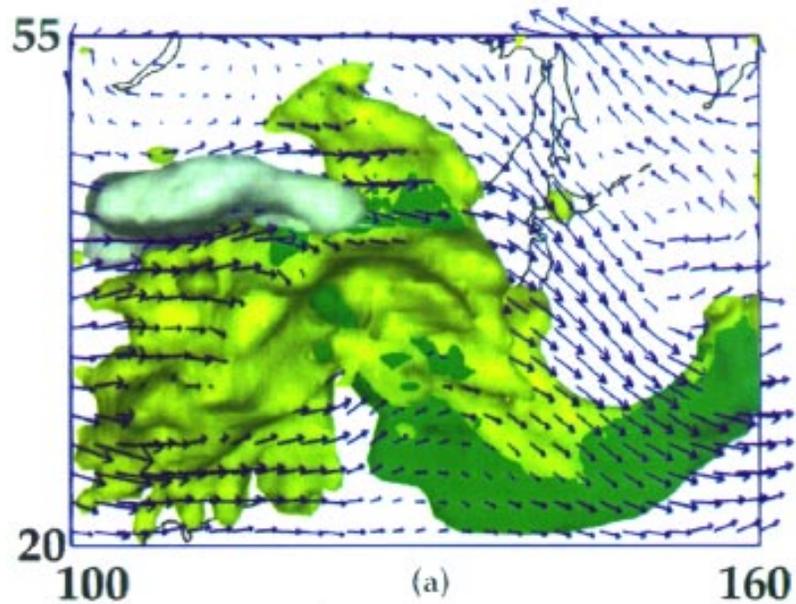
Role of Cl radicals in the marine boundary layer in east Asia. Simulations using the coupled gas-aerosol chemistry model. Model used to analyze 2 years of NMHC data sampled twice at Cheju Island, South Korea.



Calculated annual fraction of particulate nitrate on mineral aerosol to total nitrate. (Dentener et al., JGR, 101: 22869-22889).

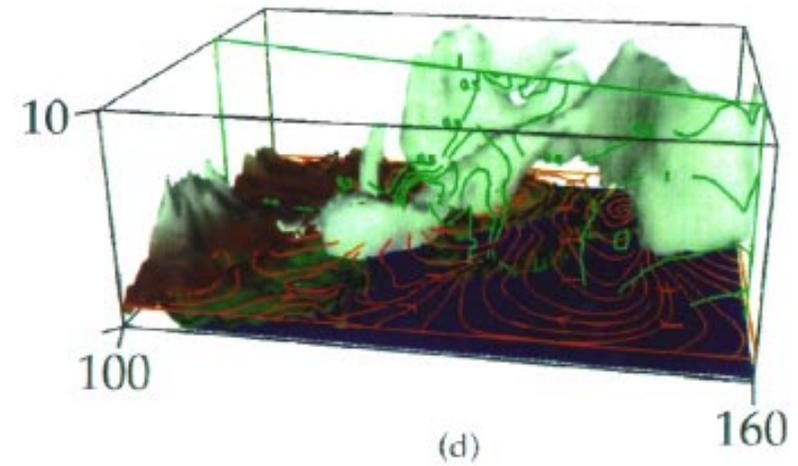
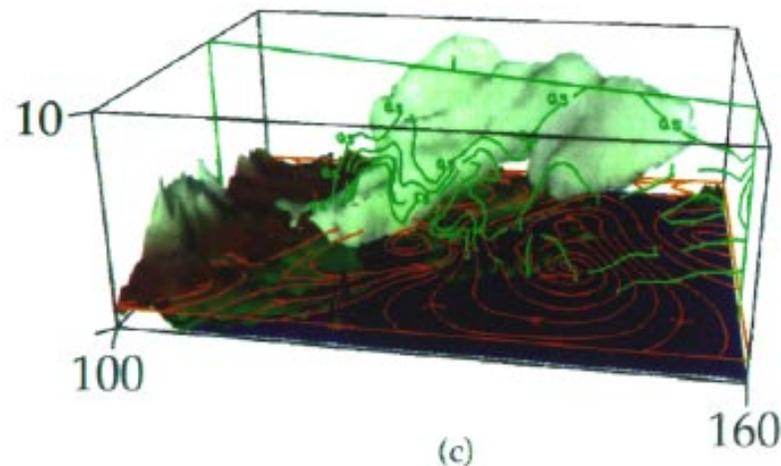
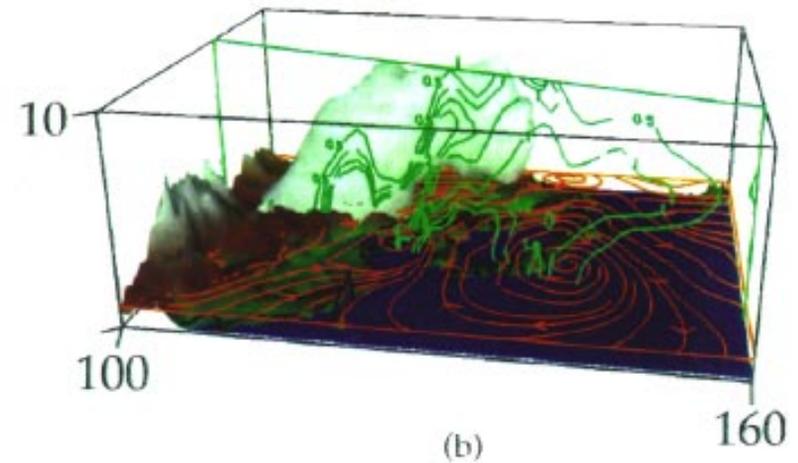
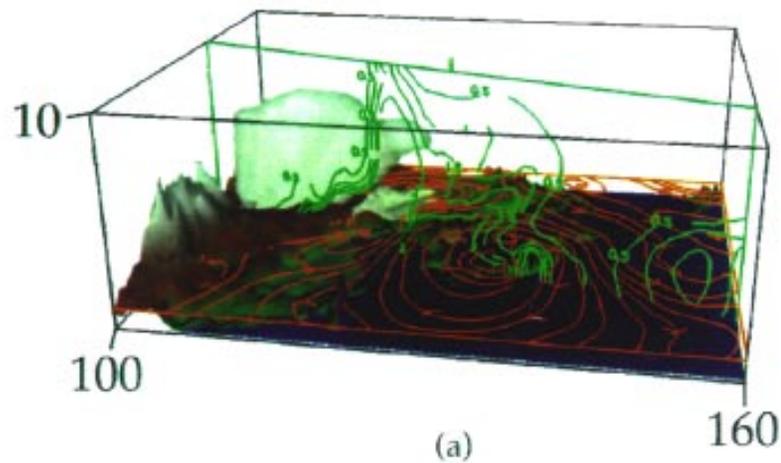


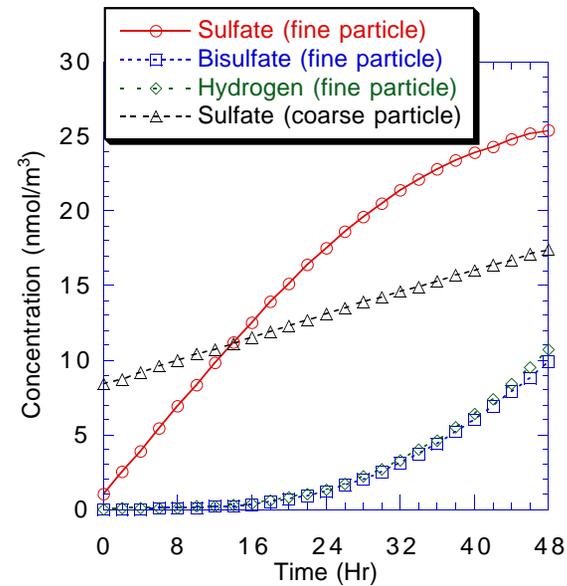
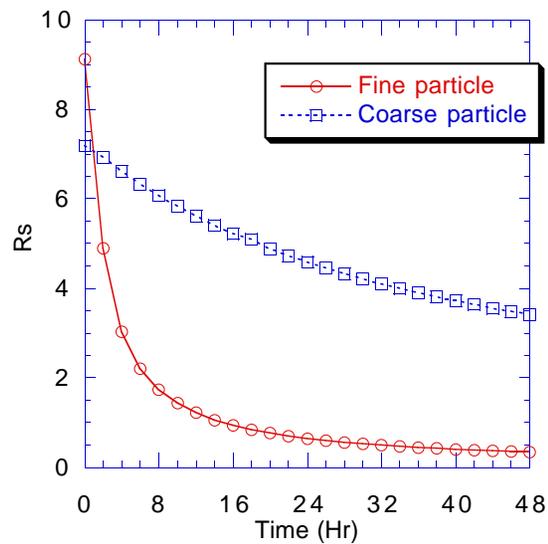
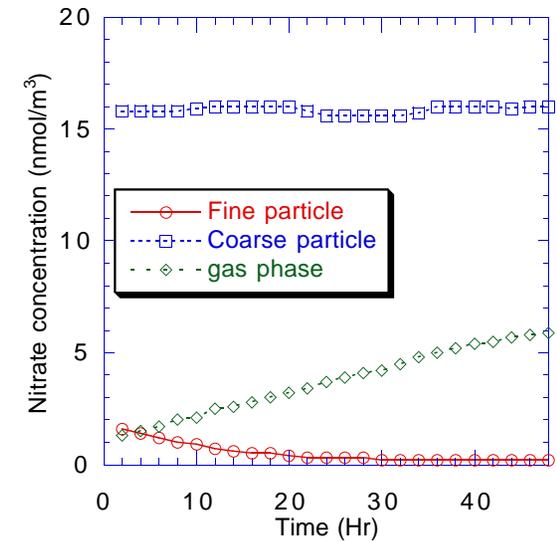
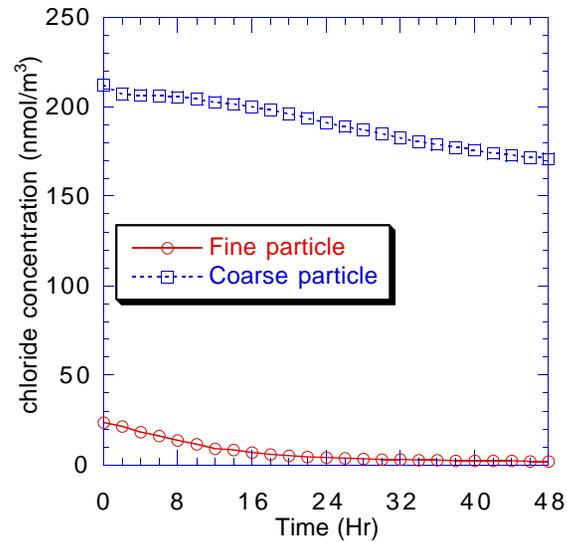
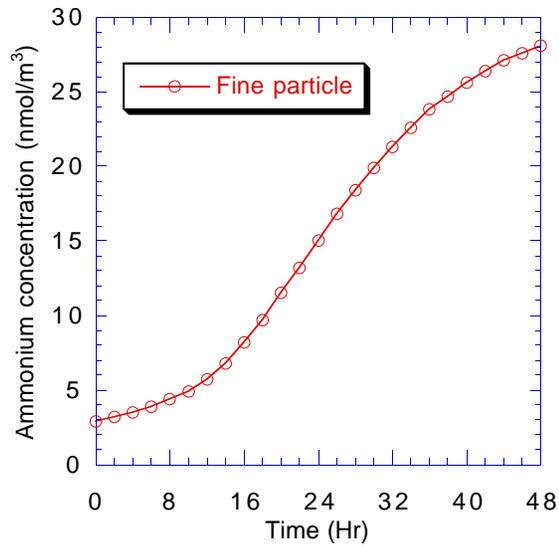
Comparison between model predicted and observed ozone concentrations at eight locations in Japan for May 1987. Shown are values for tropospheric chemistry with and without the presence of mineral dust.



The calculated distributions of dust and SO_x at 15:00 LT March 6, 03:00 LT March 7, 15:00 LT March 7, and 03:00 LT March 8. The isosurfaces of dust (gray, 40 $\mu\text{g}/\text{m}^3$), SO₂ (yellow, 0.65 ppb) and sulfate (green, 1.25 $\mu\text{g}/\text{m}^3$) are presented along with the horizontal velocity vectors at 4 km. [Xiao *et al.*, JGR, 102, 28,589-28,612]

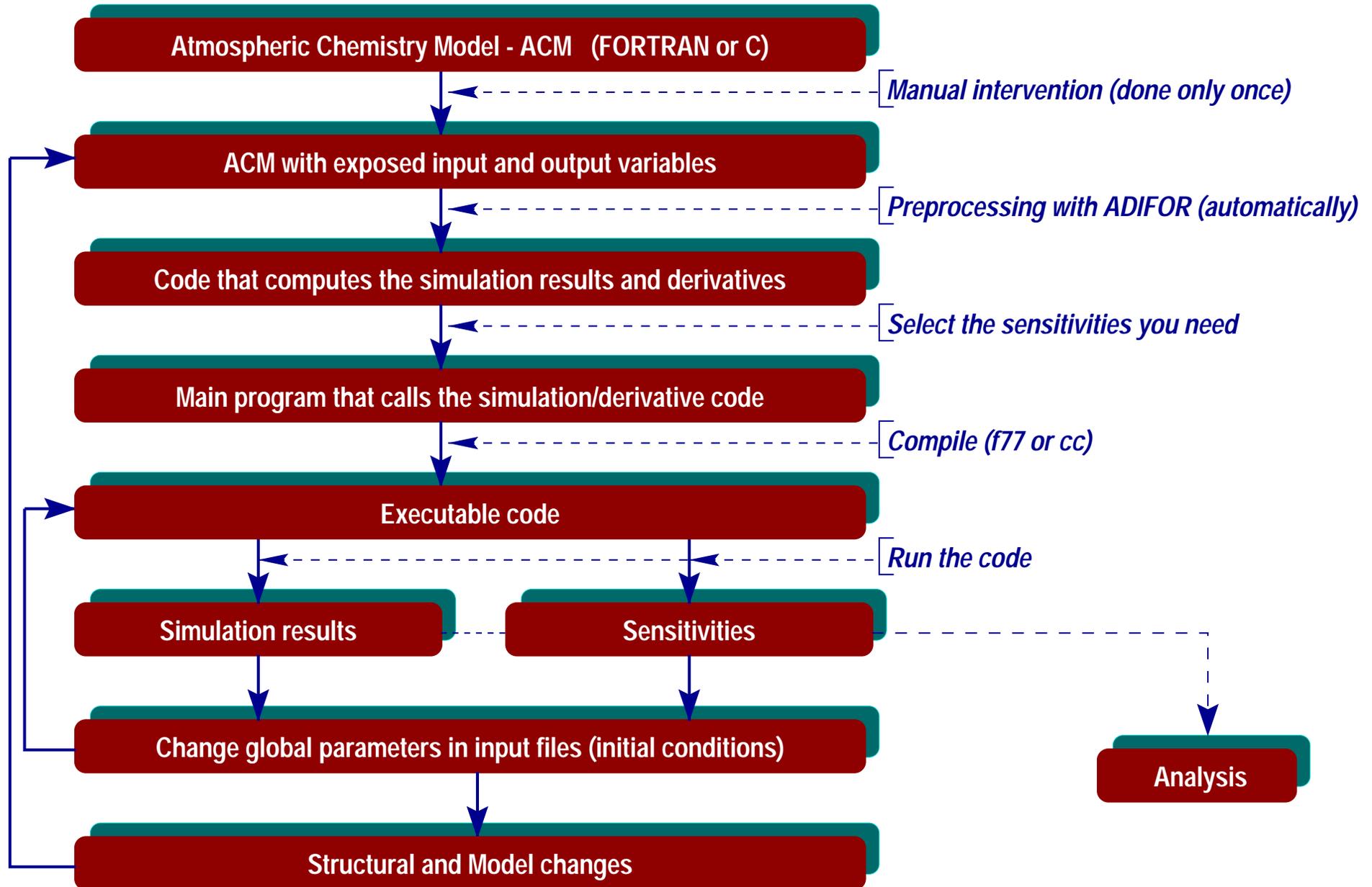
The calculated distributions of dust and SO_x at 15:00 LT March 6, 03:00 LT March 7, 15:00 LT March 7, and 03:00 LT March 8. The isosurface of dust ($40 \mu\text{g}/\text{m}^3$) are shown along with the sulfate distribution (in green) along the plane of the flight path during PEM West B. Also shown are the streamlines at 1 km (orange). [Xiao *et al.*, JGR, 102, 28,589-28,612]





Rs, a measure of the acidity of the aerosol, is defined as the ratio of the total alkaline cation conc. to the SO₄ conc. in the aerosol.

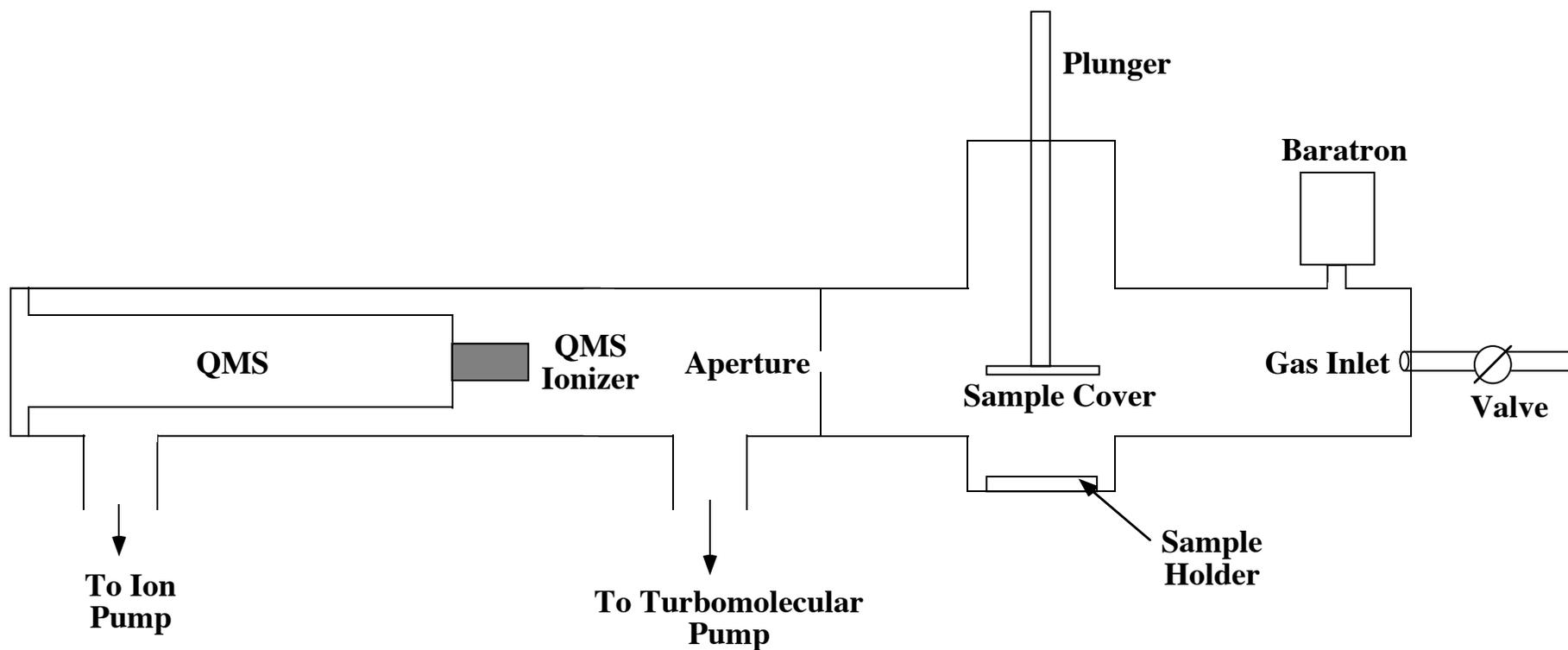
Sensitivity analysis with ADIFOR



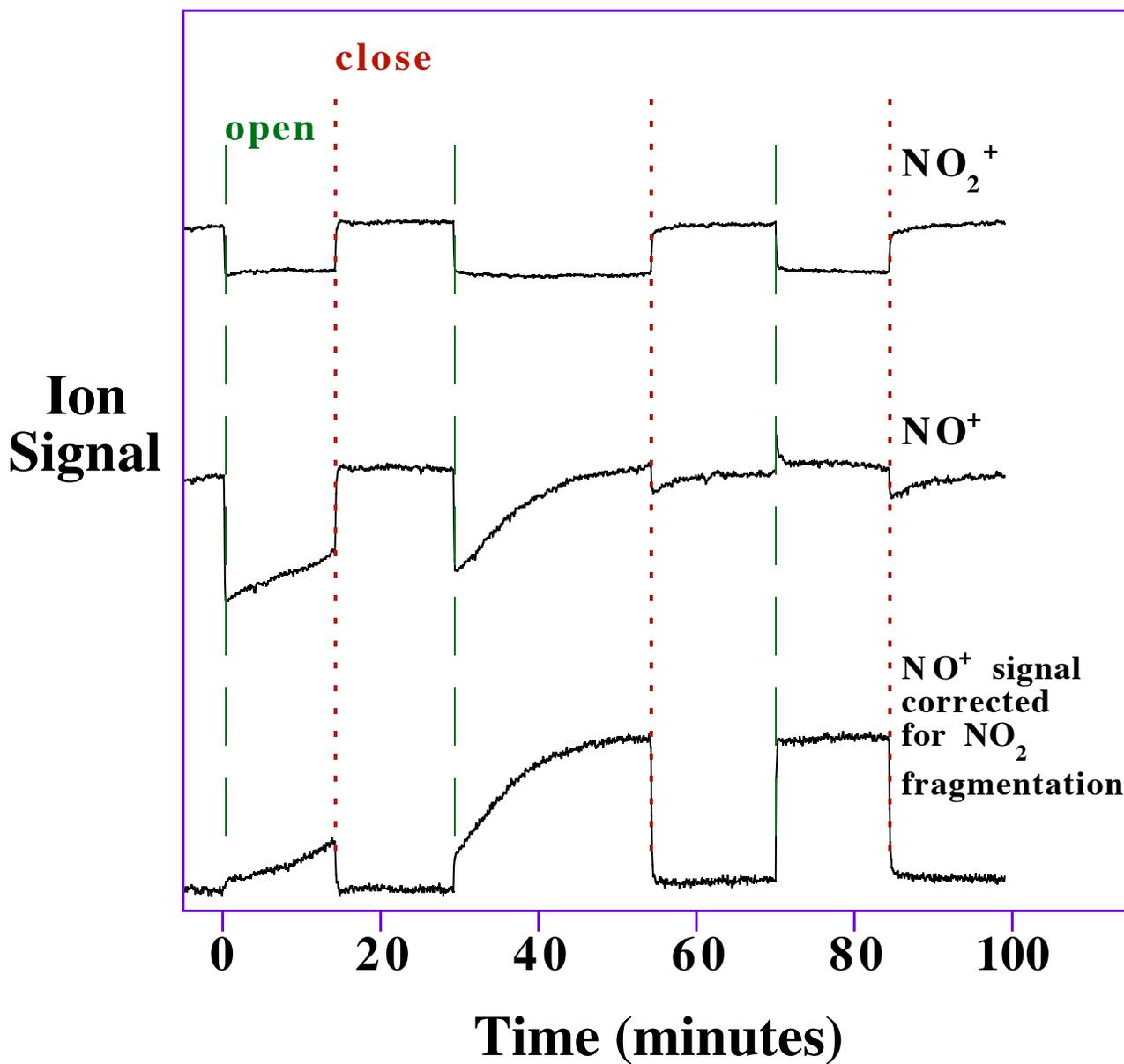
Experimental Considerations

- **Spectroscopic measurements to provide both qualitative (what reactions are possible) and quantitative information**
 - Provide mechanistic information on the molecular level
 - Need to have techniques that can detect gas-phase and surface-bound species
- **Kinetic measurements to provide quantitative information**
 - Determine reaction probabilities, γ
- **Provide data as input for global atmospheric models**

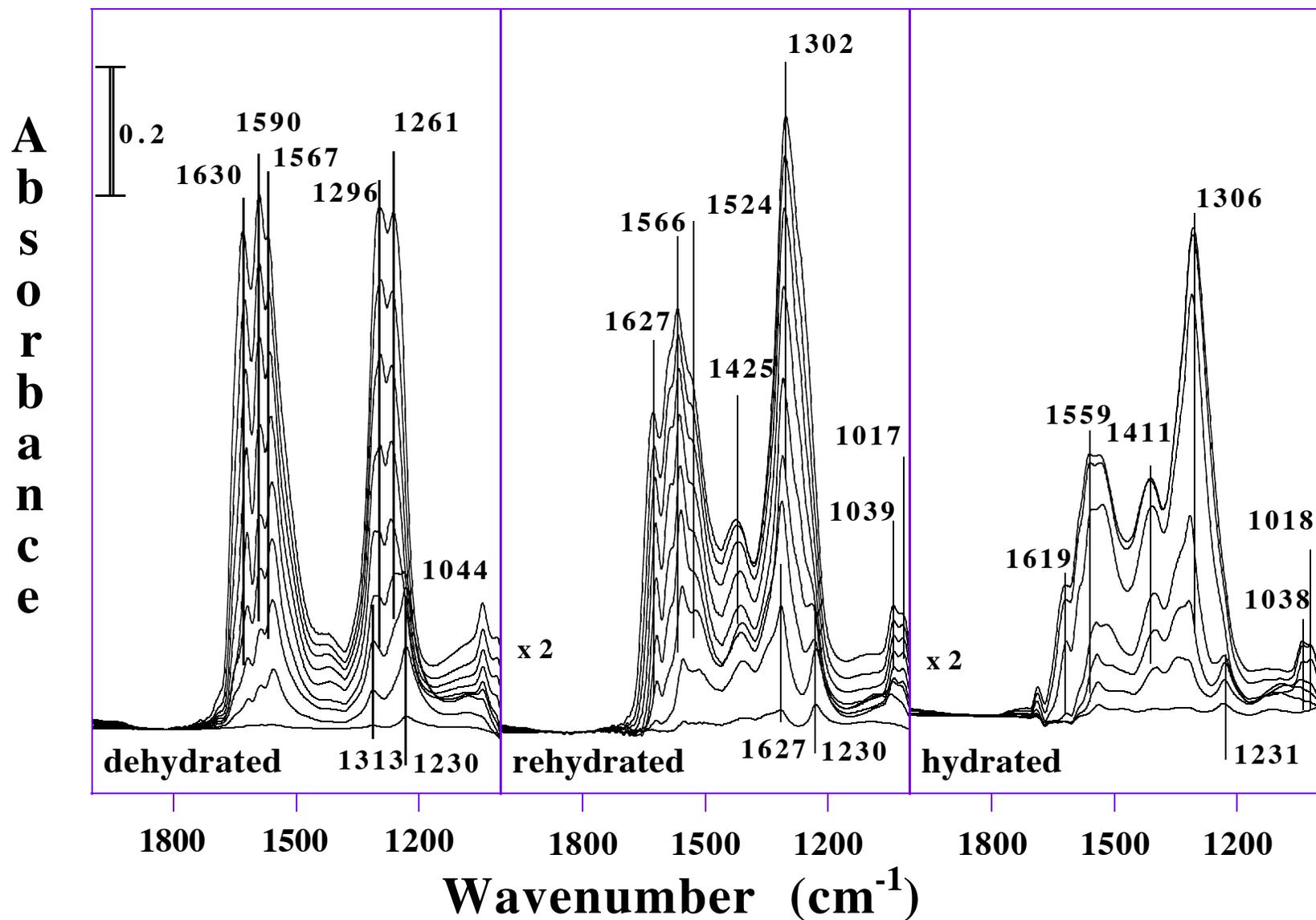
Knudsen Cell Reactor for Reaction Probability Measurements



Measured Mass Spectrometer Signals of NO^+ and NO_2^+ During NO_2 Reaction with Hydrated Aluminum Oxide Particles



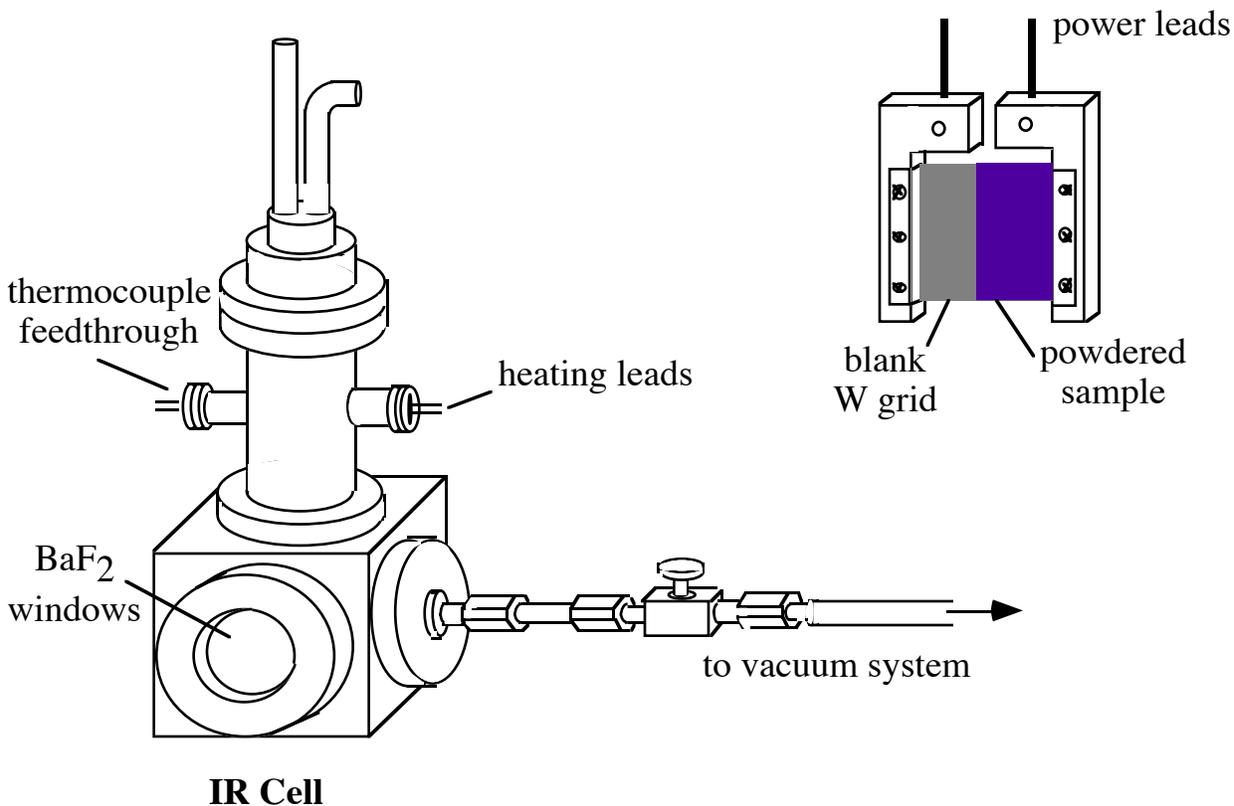
NO₂ Adsorbed on Dehydrated, Rehydrated and Hydrated Aluminum Oxide



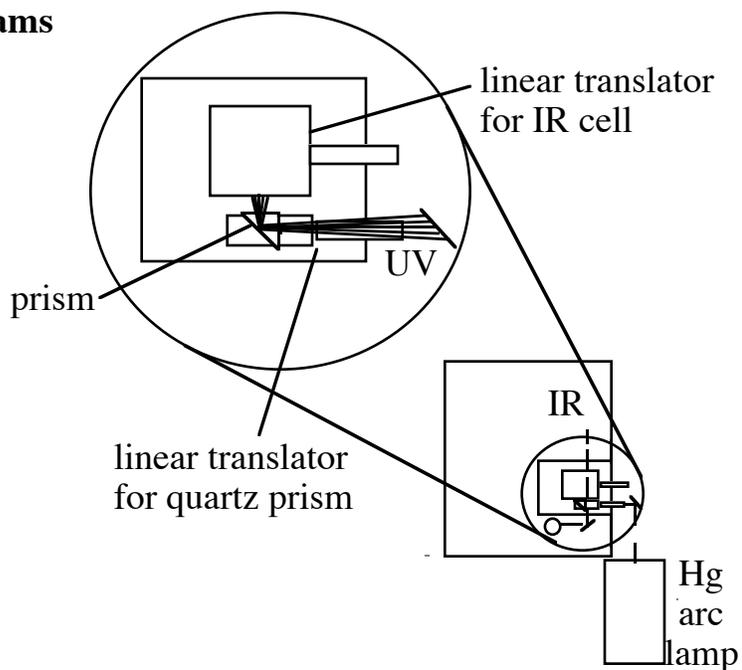
Experimental Methods

Transmission FT-IR Spectroscopy

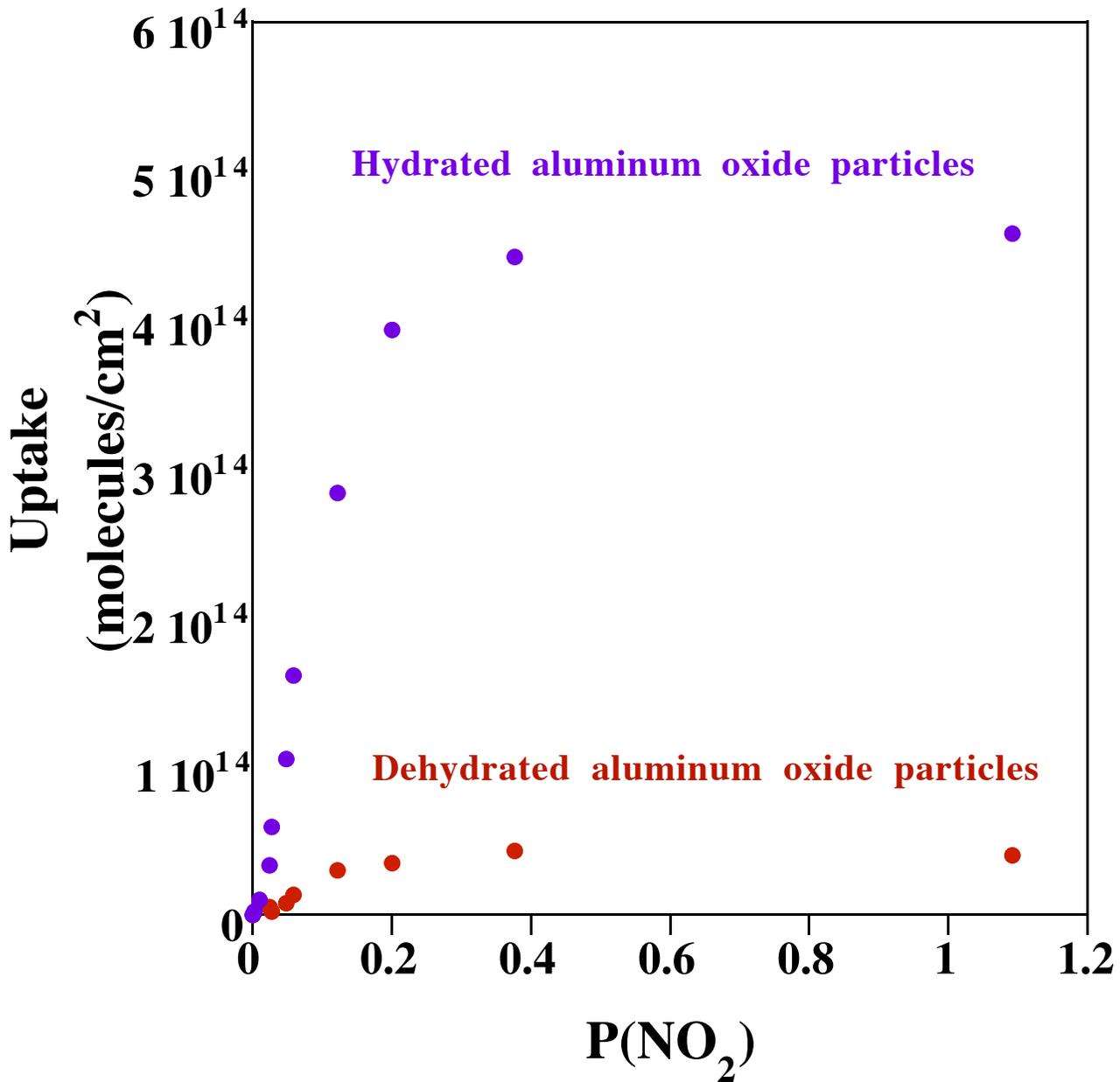
(to characterize gas-phase and surface-bound species)



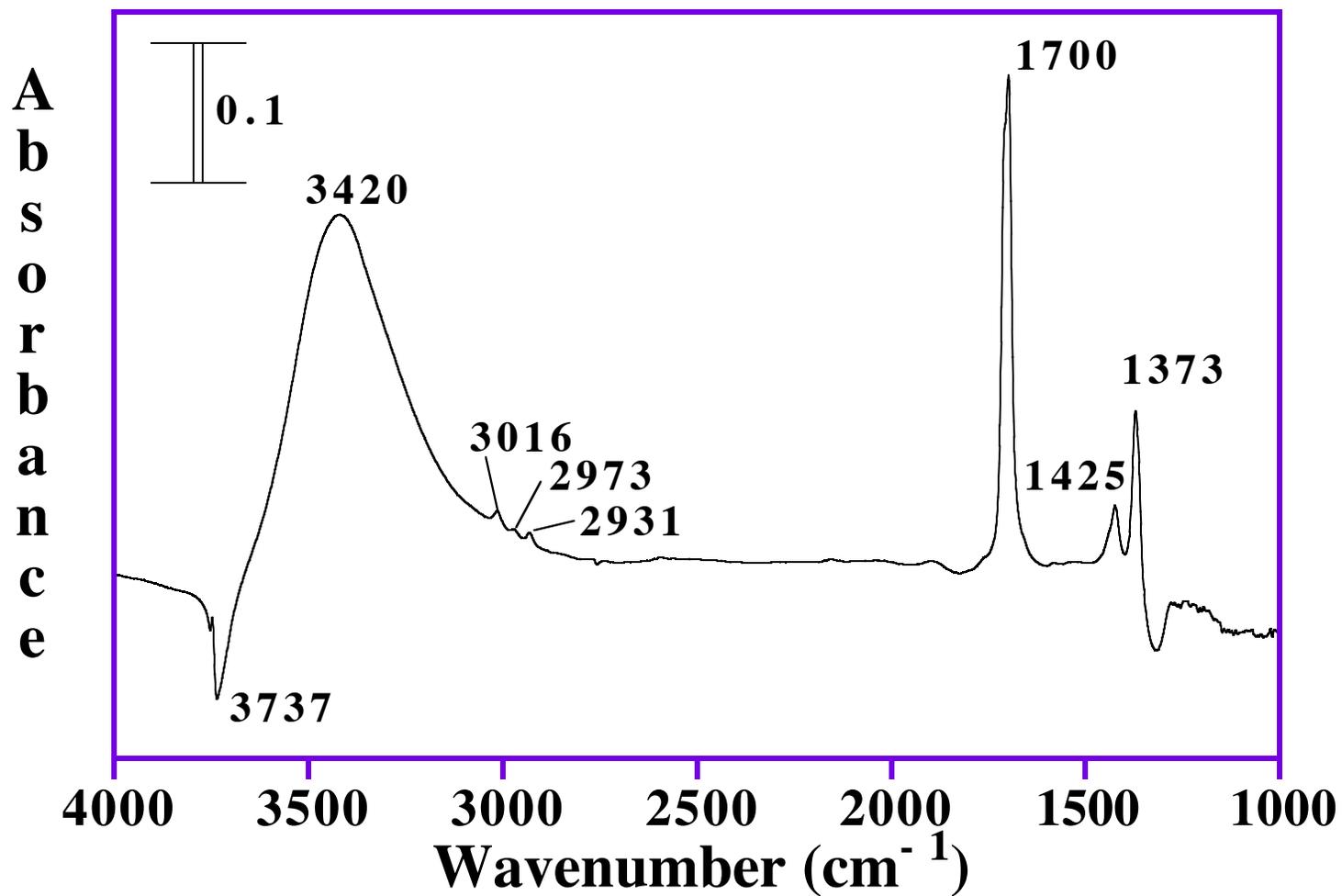
Optical Path for IR and UV Beams



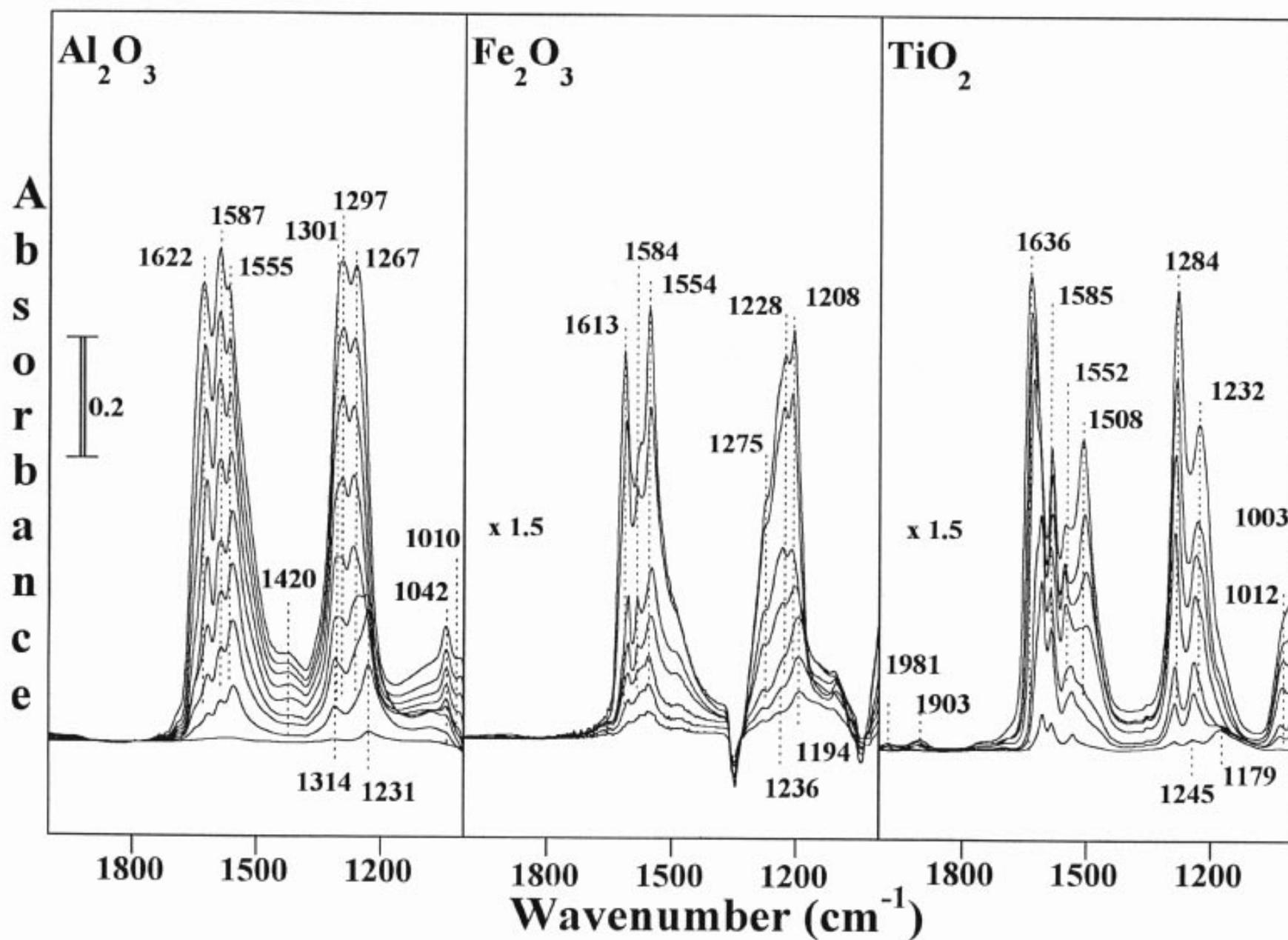
Uptake of NO_2 on Dehydrated and Rehydrated Aluminum Oxide Particles



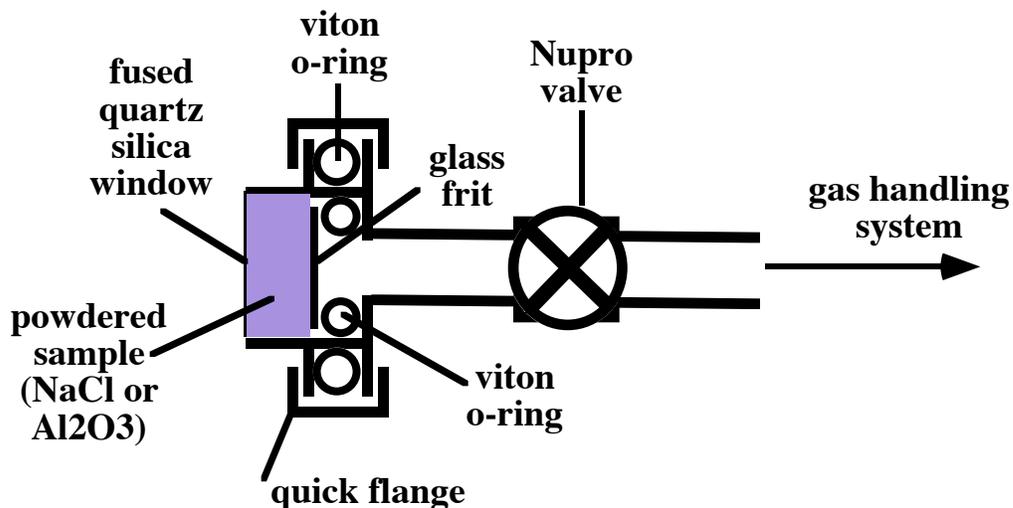
Acetone Adsorbed on Dry Silica Particles



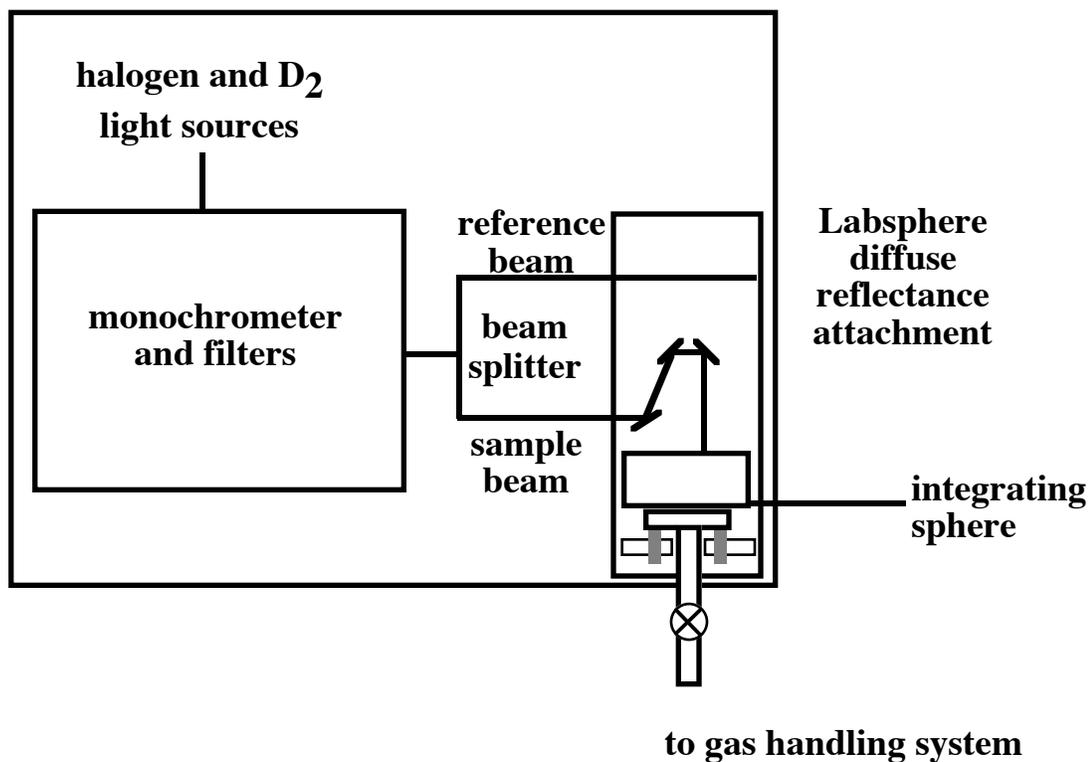
NO_2 Adsorbed on Dehydrated Aluminum, Iron, and Titanium Oxides



UV/Vis Diffuse Reflectance Spectroscopy



Lambda 20 - Perkin Elmer Spectrometer



Reaction probability of NO₂ on hydrated metal oxide particles

$$\gamma = \frac{A_h}{A_s} \frac{N_o - N_r}{N_r}$$

A_h is the area of the aperture hole to the QMS
A_s is the geometric area of the reactive surface
N_o is the mass spectrometer signal without the reactive surface exposed
N_r is the mass spectrometer signal with the reactive surface exposed

| | $\gamma_o \times 10^{-4}$ |
|---------------------------------------------|-------------------------------------------------------|
| Al₂O₃ | 4_{±1} (σ - 10 runs) |
| Fe₂O₃ | - |
| TiO₂ | 2_{±1} (σ - 6 runs) |
| near 3×10^{-4} at room temperature | |

Comparison to measurements made on other particles

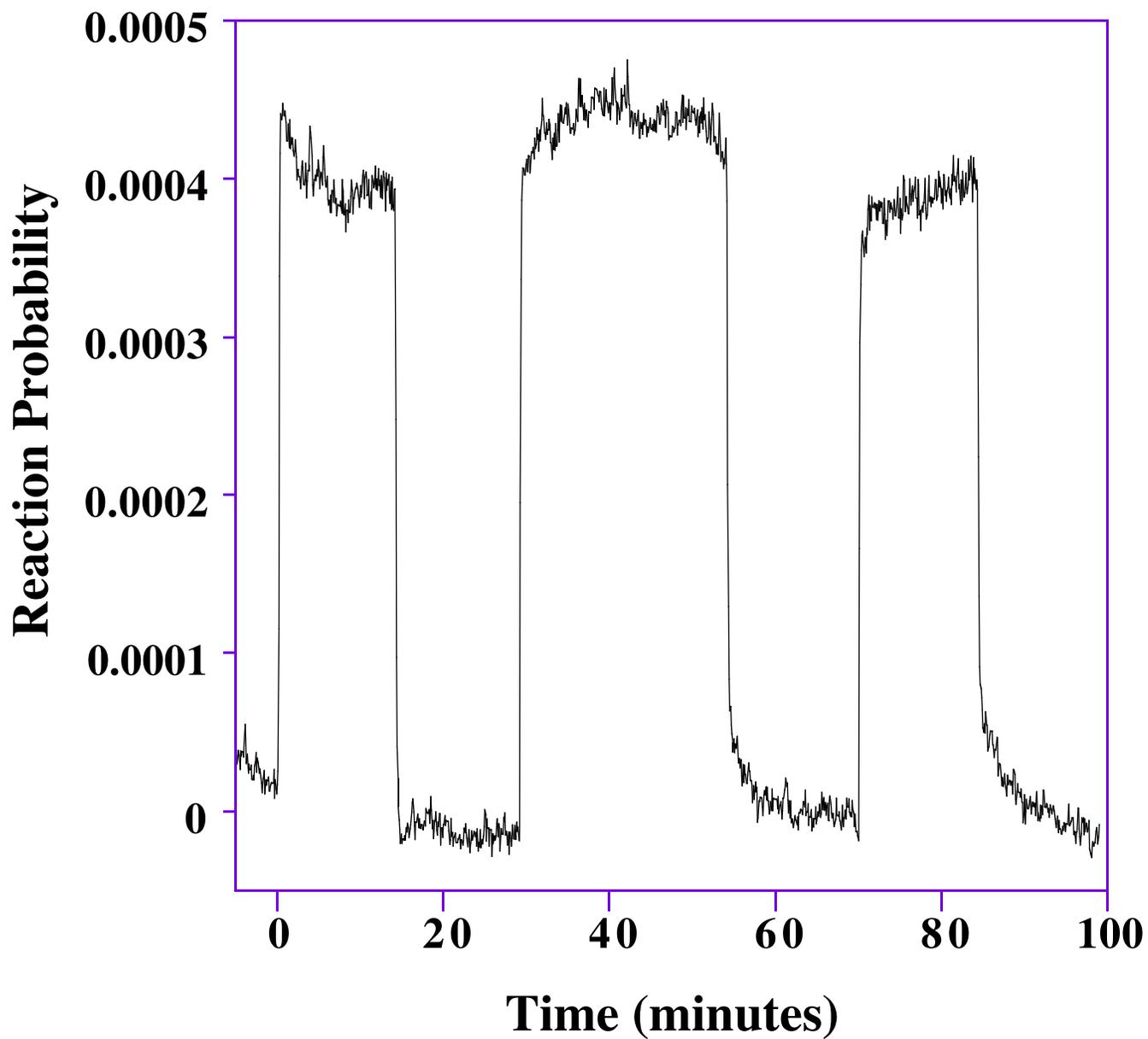
$$\gamma_o(\text{carbon black}) > \gamma_o(\text{metal oxide}) > \gamma_o(\text{NaCl})$$

carbon black: 0.11; Rogaski, Golden, Williams GRL, 24, 381-384 (1997)

carbon black: 0.06; Tabor, Gutzwiller, Rossi JPC, 98, 6172-6186 (1994)

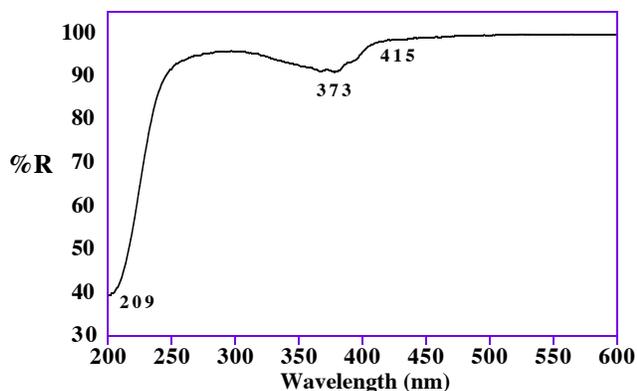
NaCl: $< 10^{-5}$; Beichert, Finlayson-Pitts JPC, 100, 15218-15228 (1996)

Measured Reaction Probability of Reaction of NO_2 with Hydrated Aluminum Oxide Particles

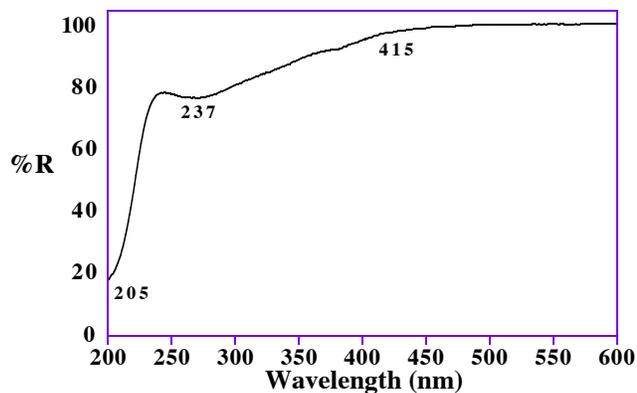
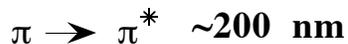


UV/Vis Diffuse Reflectance Spectroscopy of Nitrite and Nitrate on Al_2O_3 from NO_2 Adsorption

At low coverage, the UV/Vis reflectance spectrum is consistent with adsorbed nitrite



At high coverage, the UV/Vis reflectance spectrum is consistent with adsorbed nitrate



Directions: The importance of heterogeneous reactions in tropospheric ozone formation and its impact on O₃- aerosol precursor relationships will be studied using both box and three-dimensional models. Heterogeneous chemistry effects will be evaluated initially with a time-dependent multi-phase chemistry box model. A combined aerosol/gas-phase chemistry model has been developed for this purpose, in which the detailed multicomponent aerosol dynamics and heterogeneous chemistry on the aerosol surface are explicitly included. The important heterogeneous processes will be identified through sensitivity studies. Regional simulations for both the eastern and western United States using the heterogeneous chemistry based on laboratory and box model studies will also be performed in order to evaluate these processes under different aerosol, emissions and ambient conditions. Simulations with and without aerosol reactions, and for various levels of NO_x and VOC emissions will be conducted to evaluate how the heterogeneous reactions perturb the ozone and secondary aerosol precursor relationships. The modeling activity will both provide a means to rapidly evaluate the significance of the new laboratory findings *and* will help guide the laboratory studies. Laboratory studies will be directed to those areas which have high sensitivity and high uncertainty. The experimental methods to be used in the laboratory studies include Fourier-transform infrared spectroscopy and Knudsen cell measurements. A molecular level understanding of the mechanism of adsorption and reaction of atmospheric gases on aerosol surfaces will be obtained from the infrared data and more quantitative reaction probability data will be obtained from the Knudsen cell measurements.