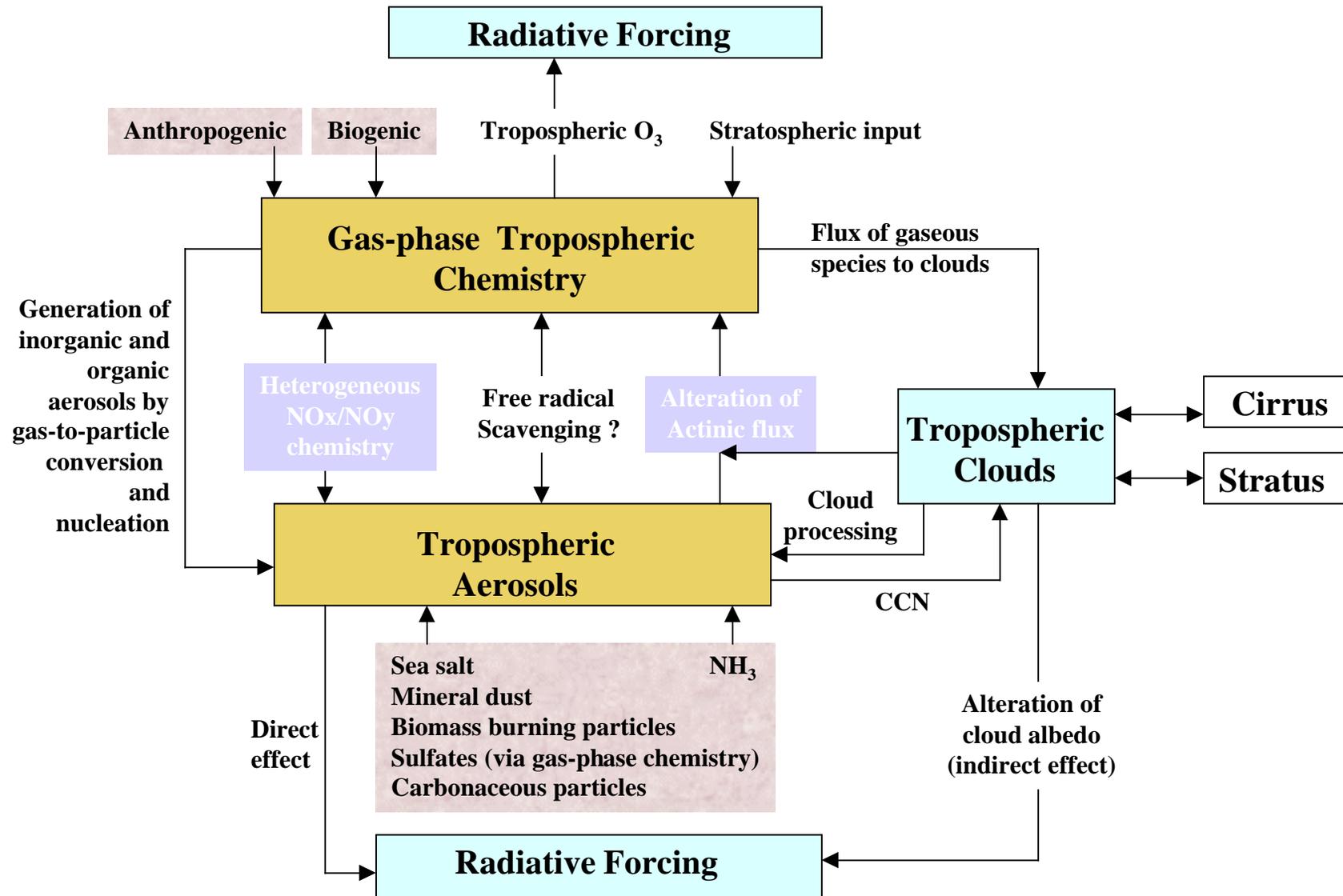


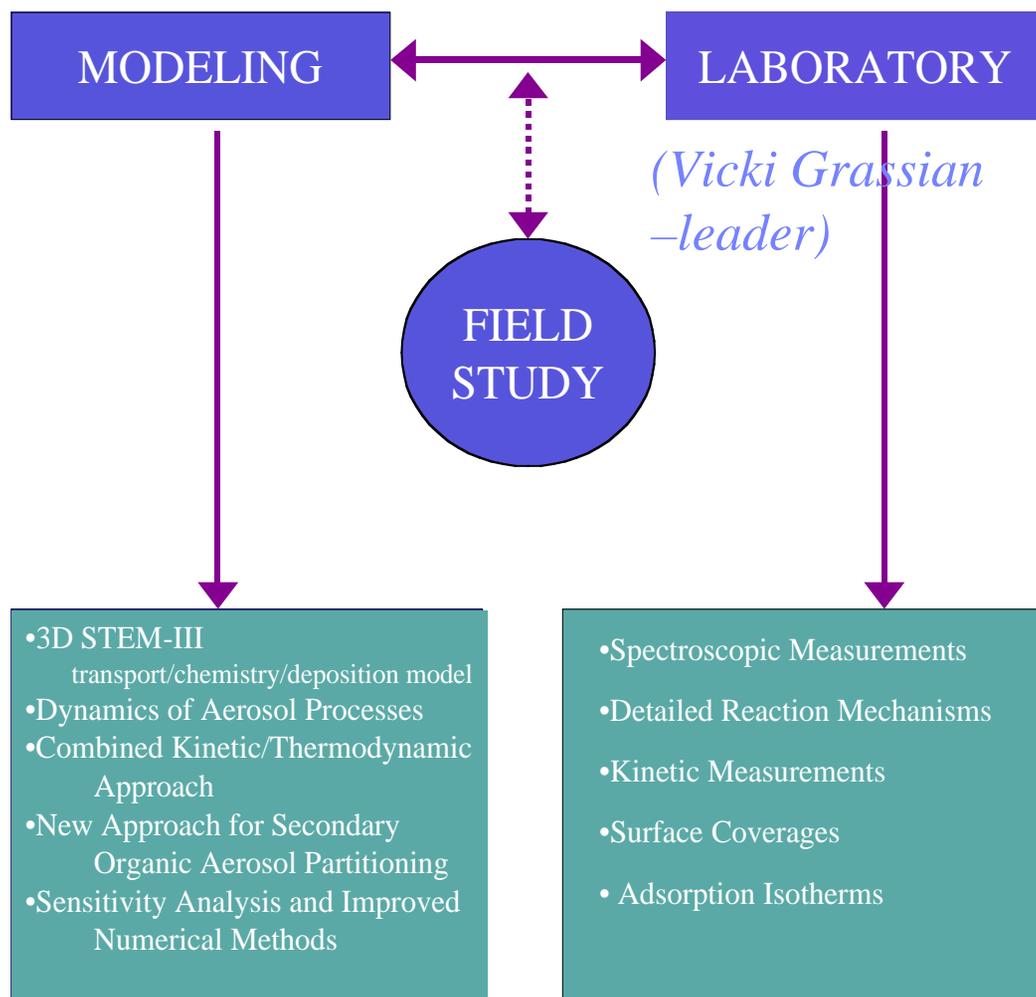
Important science questions regarding heterogeneous atmospheric chemistry remain:

- **What are the reaction products (in the gas and or aerosol phases)?**
- **How do these chemical processes impact aerosol composition and properties (e.g., impact water uptake, alter radiative properties, etc.)?**
- **How do they influence gas phase chemical processes (e.g., partitioning of nitric acid, altering $\text{NO}_2/\text{HO}_x/\text{O}_3$ distributions)?**
- **Under what situations are such reactions expected to be important (at night, in urban environments, upper troposphere, etc.)?**
- **What processes restrict or enhance the effectiveness of these reactions (e.g., aerosol aging which may include things like surface saturation effects and surface regeneration effects, etc.)?**
- **What is the role of H_2O , solar light ($h\nu$), temperature and reactant mixtures (carbonyls, NO_x and O_3 together in the same air mass), etc. in increasing/decreasing the importance of heterogeneous reactions on aerosol surfaces?**

A Key Science Issue: Chemistry/Aerosol/Regional Climate Coupling



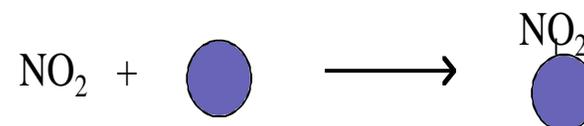
THE APPROACH



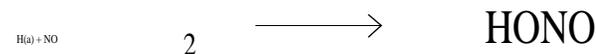
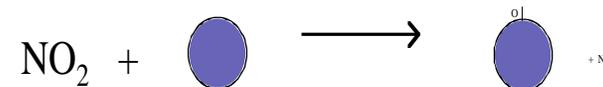
Chemical Role of Aerosol Particles in the Atmosphere

Can change the chemical balance of the atmosphere in two ways

Sink



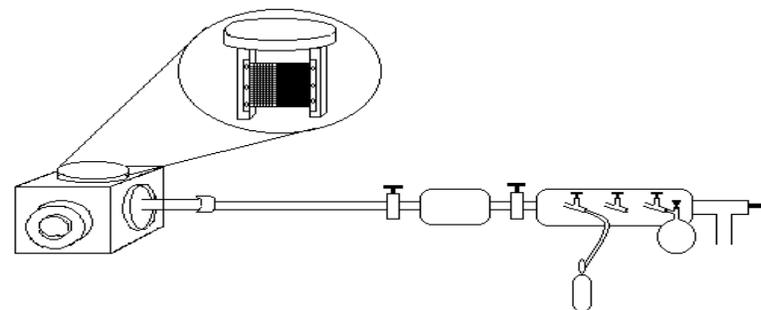
Reactive Surface



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

Transmission FT-IR Spectroscopy
 Diffuse Reflectance UV-vis Spectroscopy
 Mass Spectrometry



- **Kinetic measurements** to provide quantitative information
 - Determine uptake coefficients (sticking coefficients, reaction probabilities) γ

Knudsen cell apparatus

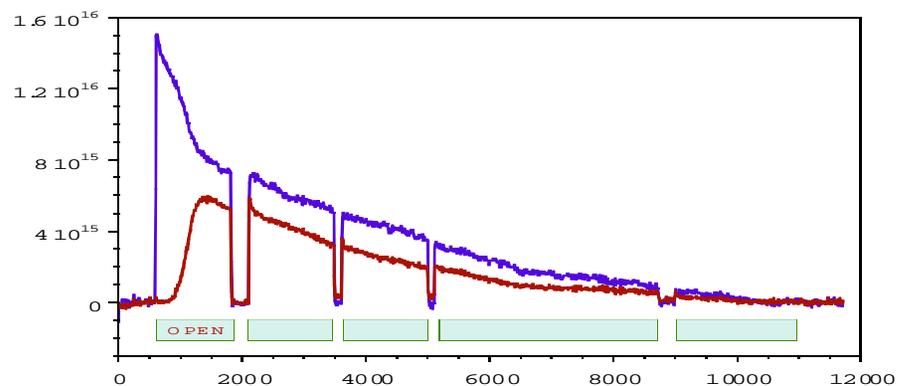


- **Provide data as input for global atmospheric models** - removal rate of gas-phase species j

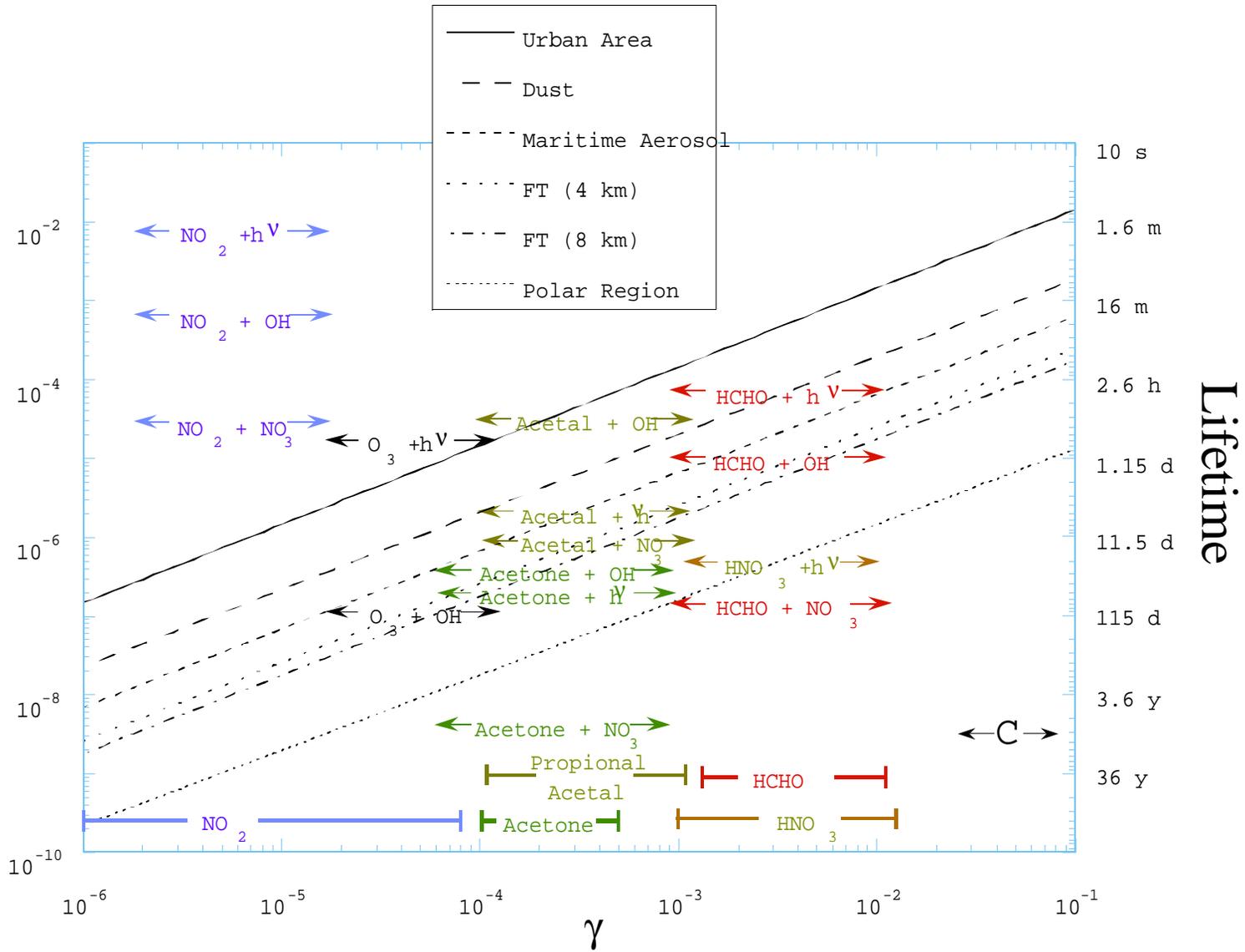
$$k_j = \int_{r_1}^{r_2} k_{d,j}(r) n(r) dr$$

$$k_{d,j} = \frac{4\pi r^2 D_j \gamma}{1 + K_n (\lambda + 4(1-\gamma)/3\gamma)}$$

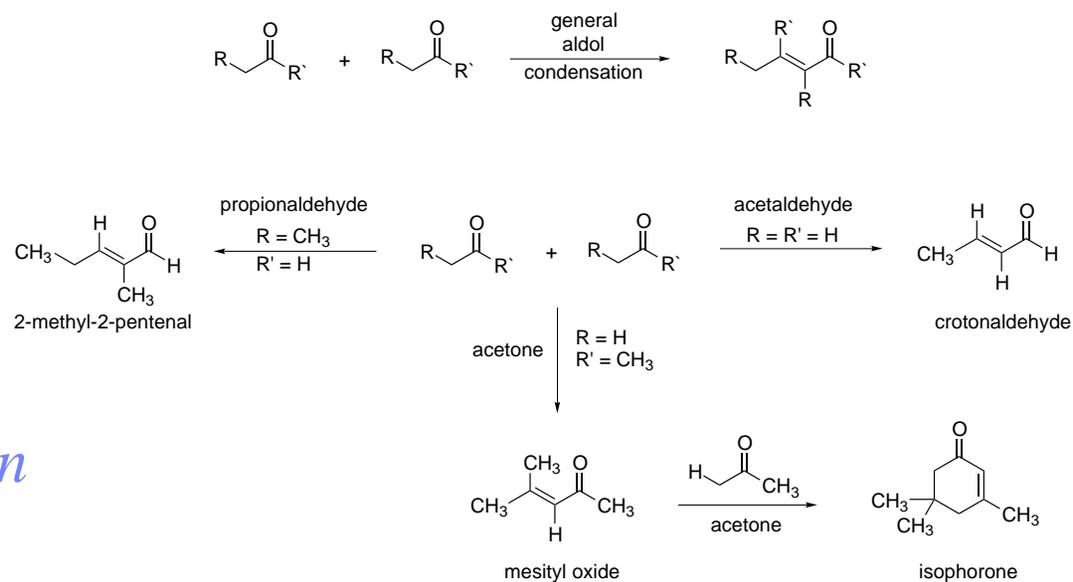
$n(r)dr$ = number density of particles between r and $r+dr$



Mass Transfer Coefficient



Scheme for Aldol Condensation Reaction on Oxide Particles (Al₂O₃, Fe₂O₃, TiO₂, CaO, and MgO)



Li et al., JGR, in press, 2001

**Saturated
Carbonyl**



**Higher Molecular Weight
Unsaturated Carbonyl**

Impacts on RO₂? On Organic aerosol mass?, others?

Summary of Combined Laboratory and Modeling Study

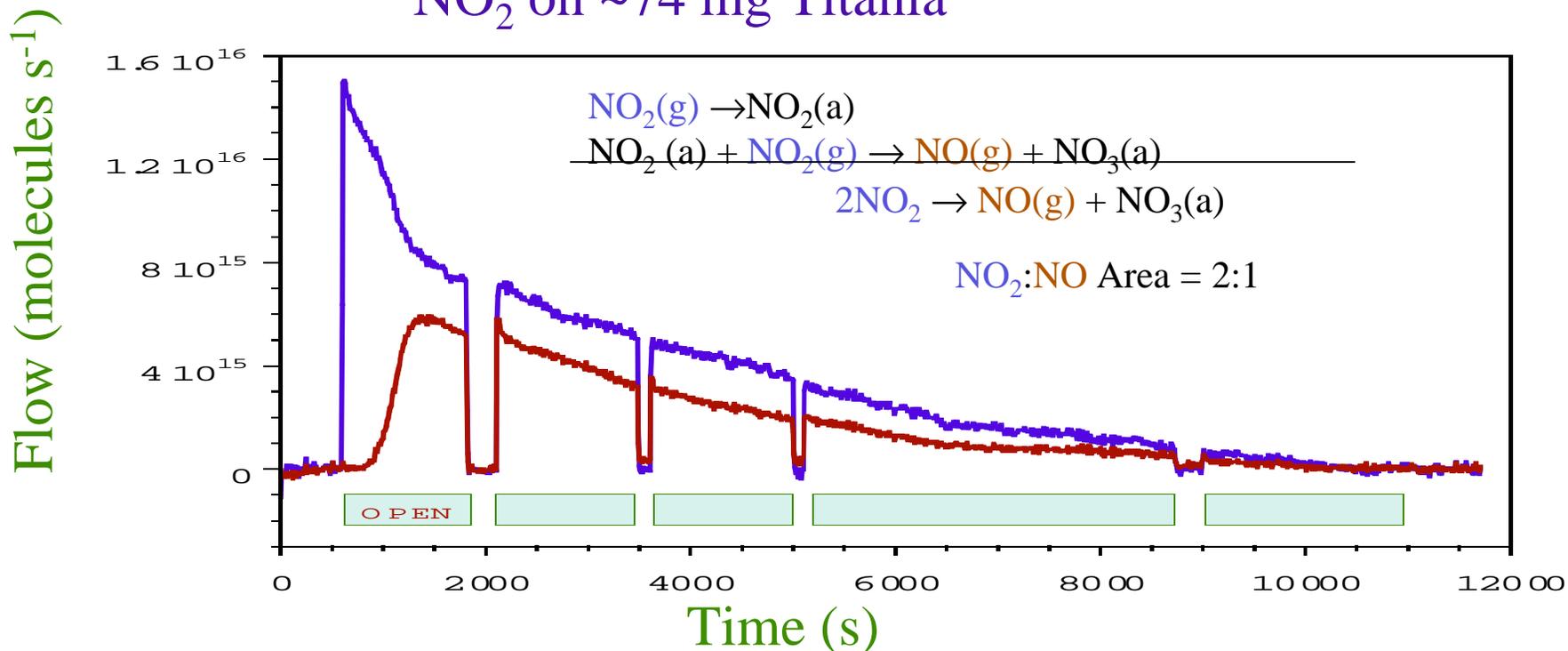
- Spectroscopic probes of gas-phase and adsorbed species along with kinetic measurements provide the necessary information to evaluate reactions of potential importance in the troposphere
 - **reaction mechanisms, surface coverage, saturation**
 - **uptake coefficients**
- Diffusion of gases into powdered samples can have a very significant effect on the measured uptake coefficient for powdered samples
 - **multiple collisions amplify the observed uptake coefficient**
- Atmospheric implications of uptake measurements determined from box-model analysis
 - **heterogeneous pathways are competitive with other carbonyl loss mechanisms (e.g. reaction with OH radical)**

Summary of Combined Laboratory and Modeling Study

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Knudsen Cell Data

NO₂ on ~74 mg Titania



NO₂ molecules reacted = 3.2x10¹⁹ so 1.6x10¹⁹ NO₃ adsorbed

Total BET area = 37,000 cm²

Surface coverage = 4.3x10¹⁴ NO₃/cm²

(Note: using 11.88 cm² → 1.3x10¹⁸ NO₃/cm²)

Diffusion is Facile

Role of Adsorbed H₂O in Surface Reactions of Potential Atmospheric Importance

I. Heterogeneous Reaction of NO₂ on SiO₂



- HONO is produced
HONO is a source of OH radical,
The OH radical drives the daytime chemistry of the troposphere
- H₂O is a reactant
- HNO₃ is a surface-bound product
 - adsorbed product never fully characterized until this work

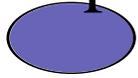
II. Heterogeneous Reaction of HNO₃ on Oxide and CaCO₃ Particles



- H₂O is a product (and medium for dissociation)
- Is the reaction limited to the particle surface?

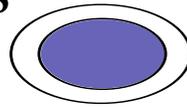
Role of Adsorbed Water in Heterogeneous Atmospheric Chemistry

tropospheric particles



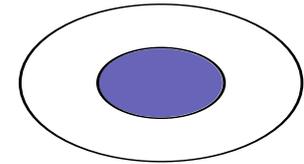
dry particle

surface sites
defect sites



particle with surface
adsorbed water

surface sites, blocked sites
coadsorption



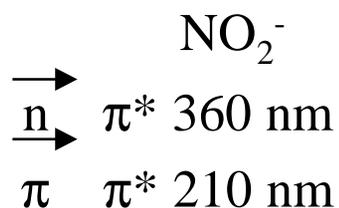
particle
immersed in a liquid
water droplet

solubility, K_{sp}
ionic species

Chemistry of atmospheric gases with the *same* particle may be *different* for each of these conditions

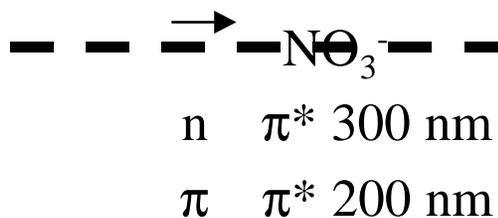
UV/Vis Diffuse Reflectance Spectroscopy of Nitrite and Nitrate on Al₂O₃ from NO₂ Adsorption

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



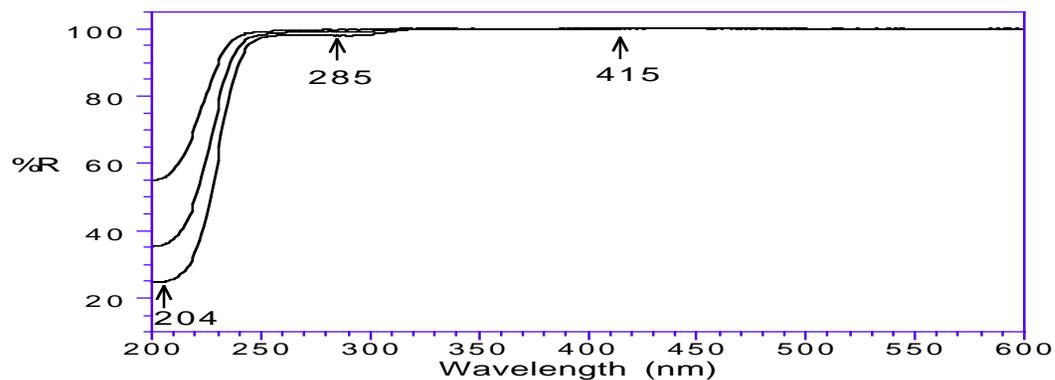
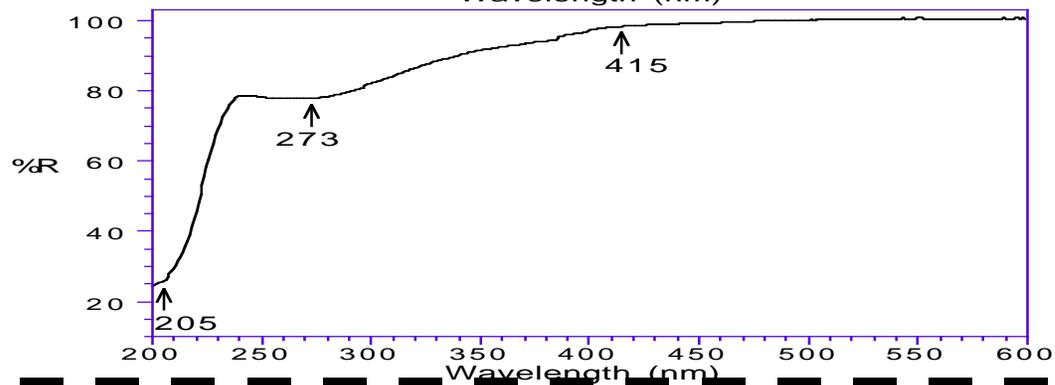
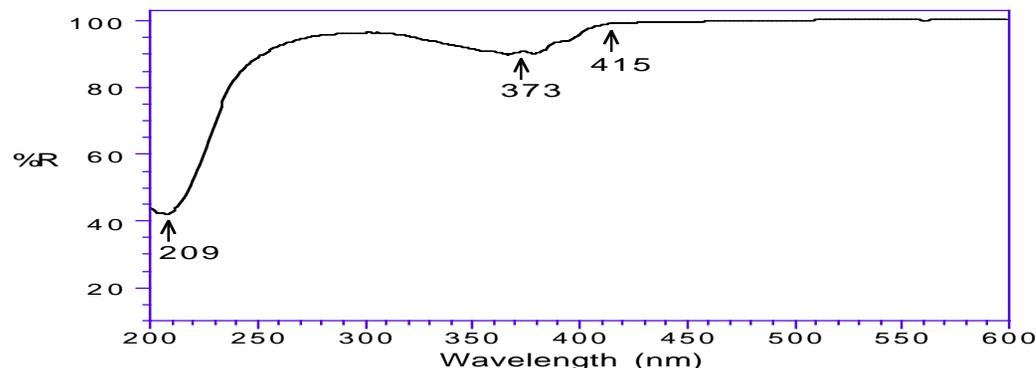
- At high coverage, the UV/Vis reflectance spectrum is consistent with adsorbed

nitrate

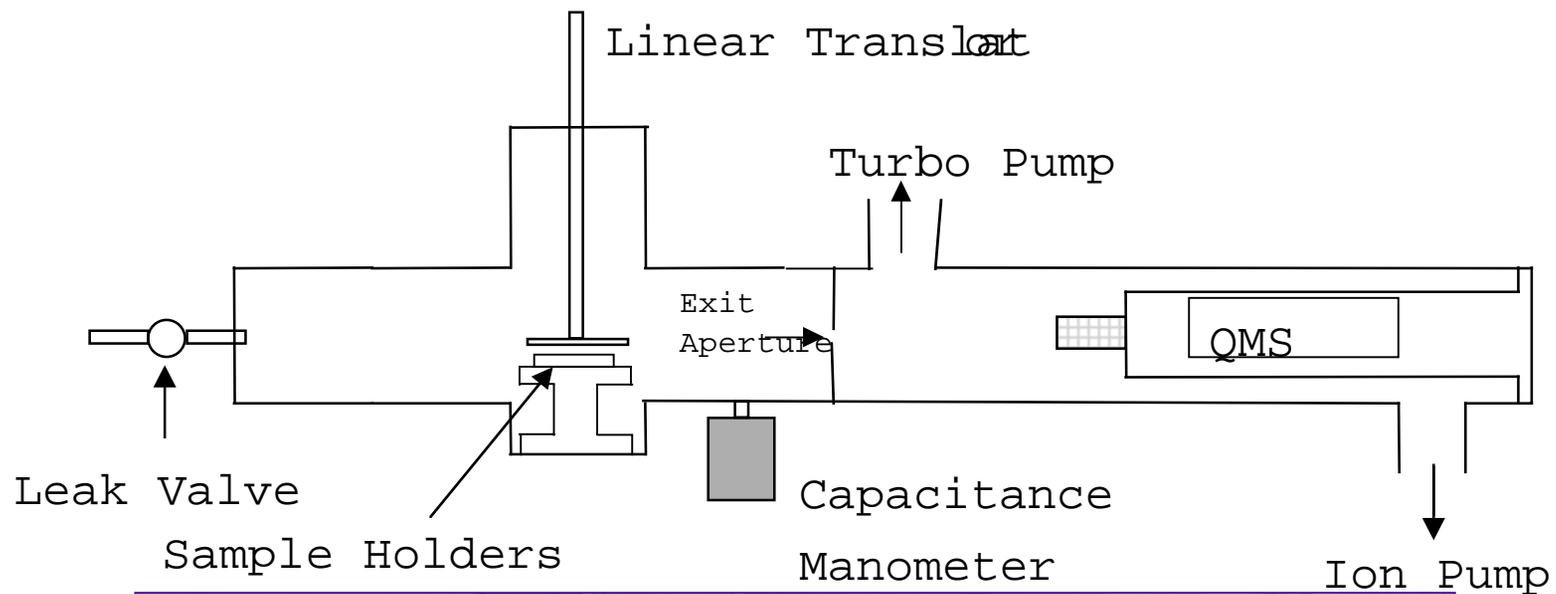


- For the NaCl + NO₂ reaction, UV/Vis reflectance spectra are consistent with adsorbed

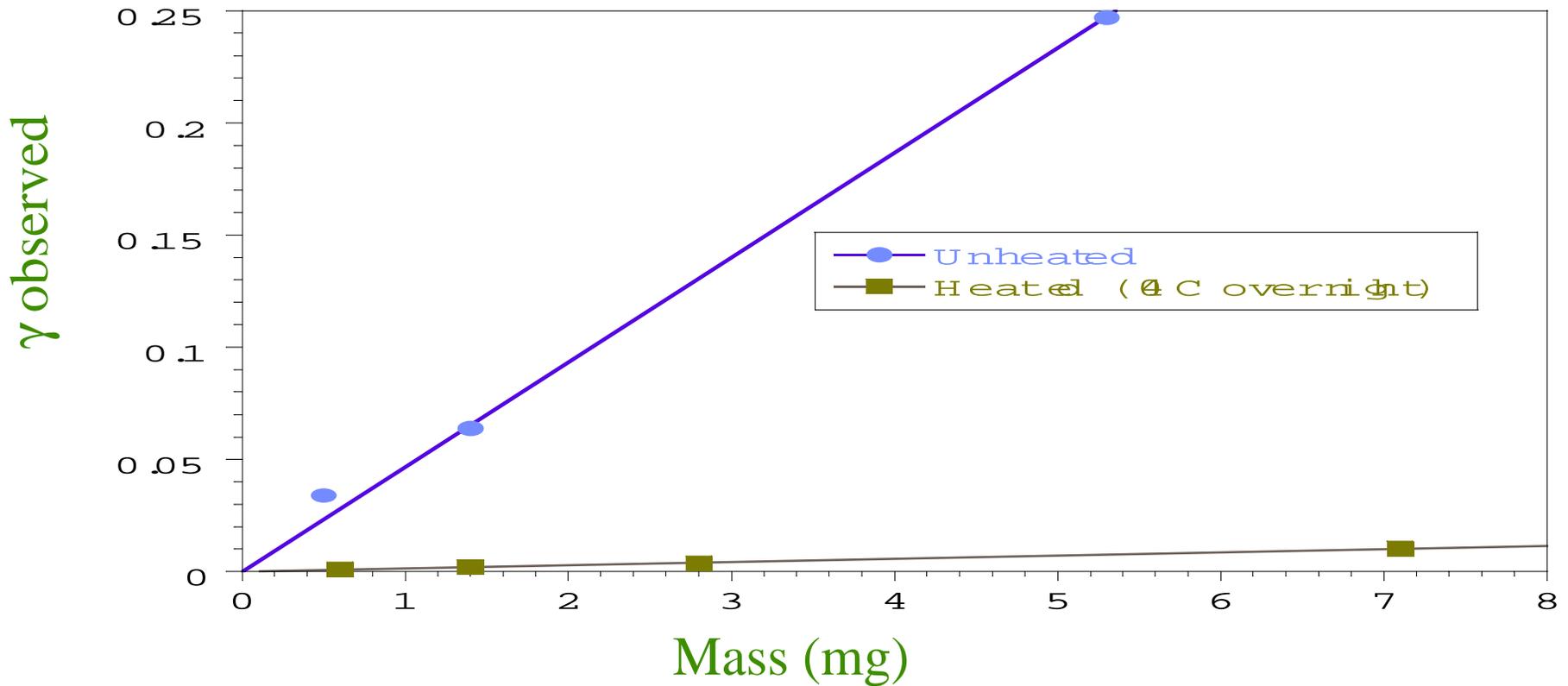
nitrate at all coverages



Knudsen Cell Reactor

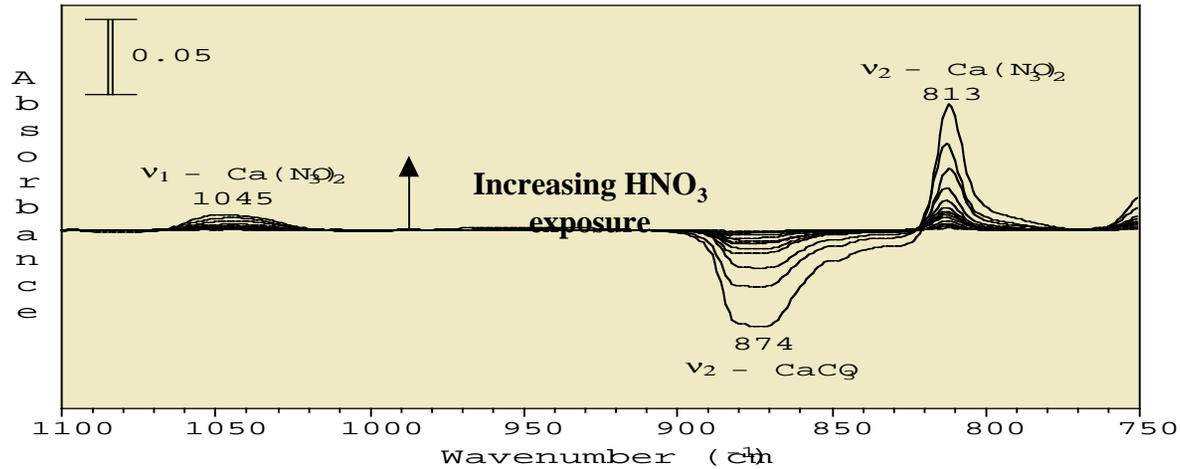


Water Dependence-HNO₃ Uptake on CaO



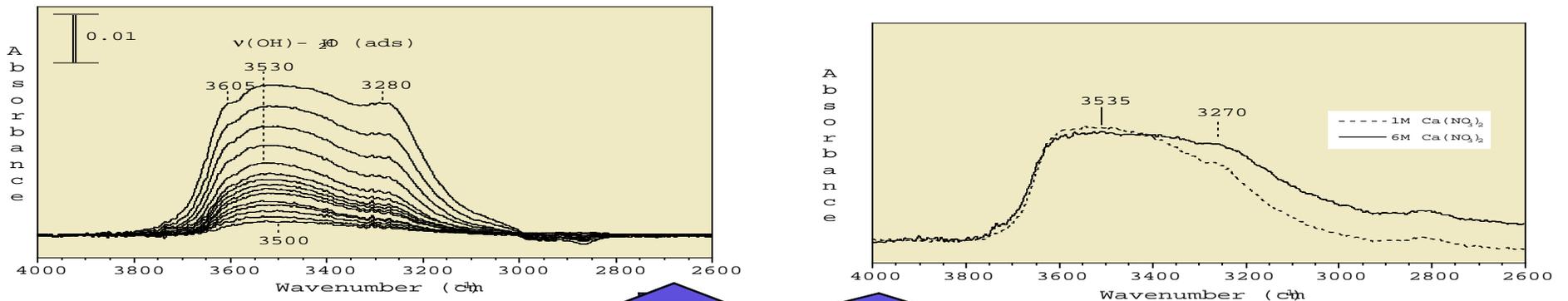
Reaction of HNO_3 on CaCO_3 at 20% RH

1. No Surface Saturation



and

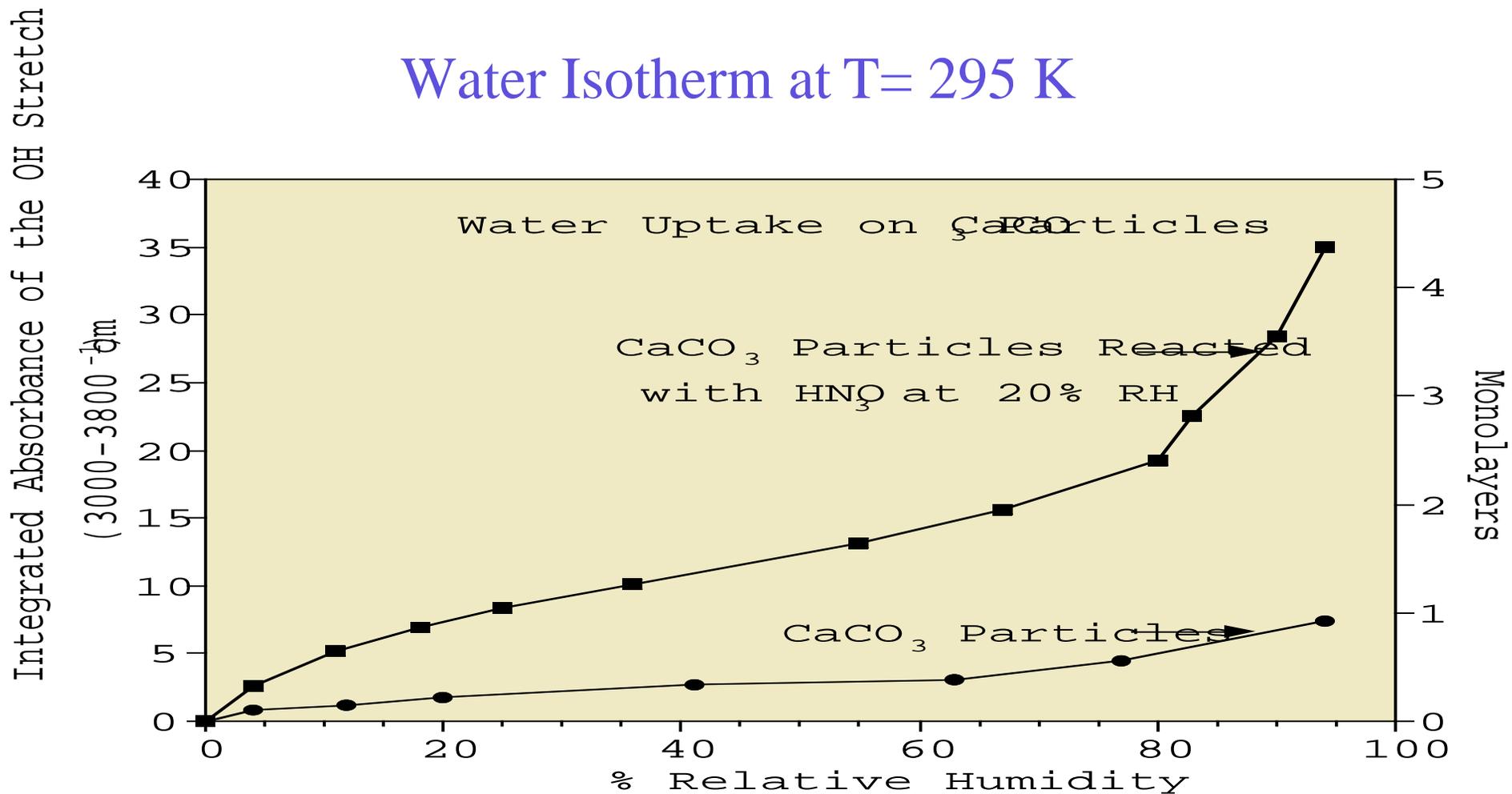
2. There is enhanced Water Adsorption as Nitric Acid Reacts with CaCO_3



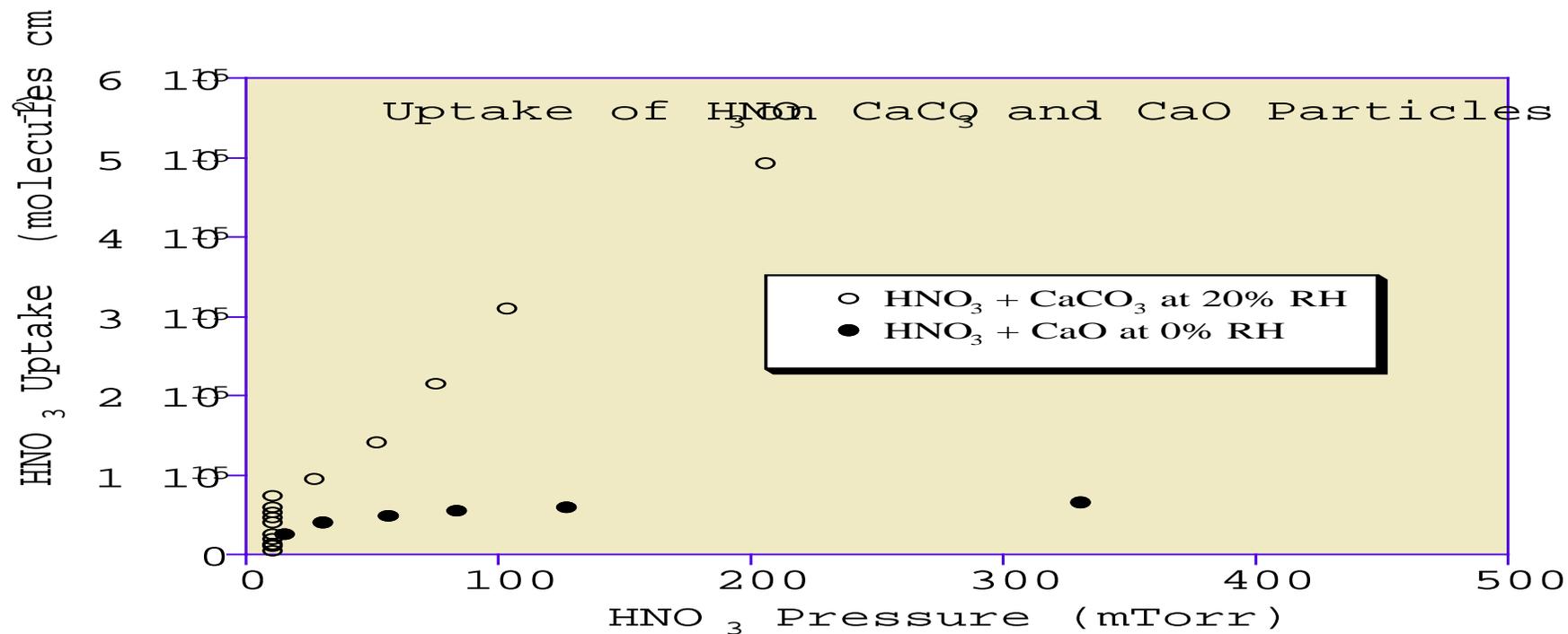
“Adsorbed Solution”
and Liquid Solution Spectra

“i i”

Water Isotherm at T= 295 K



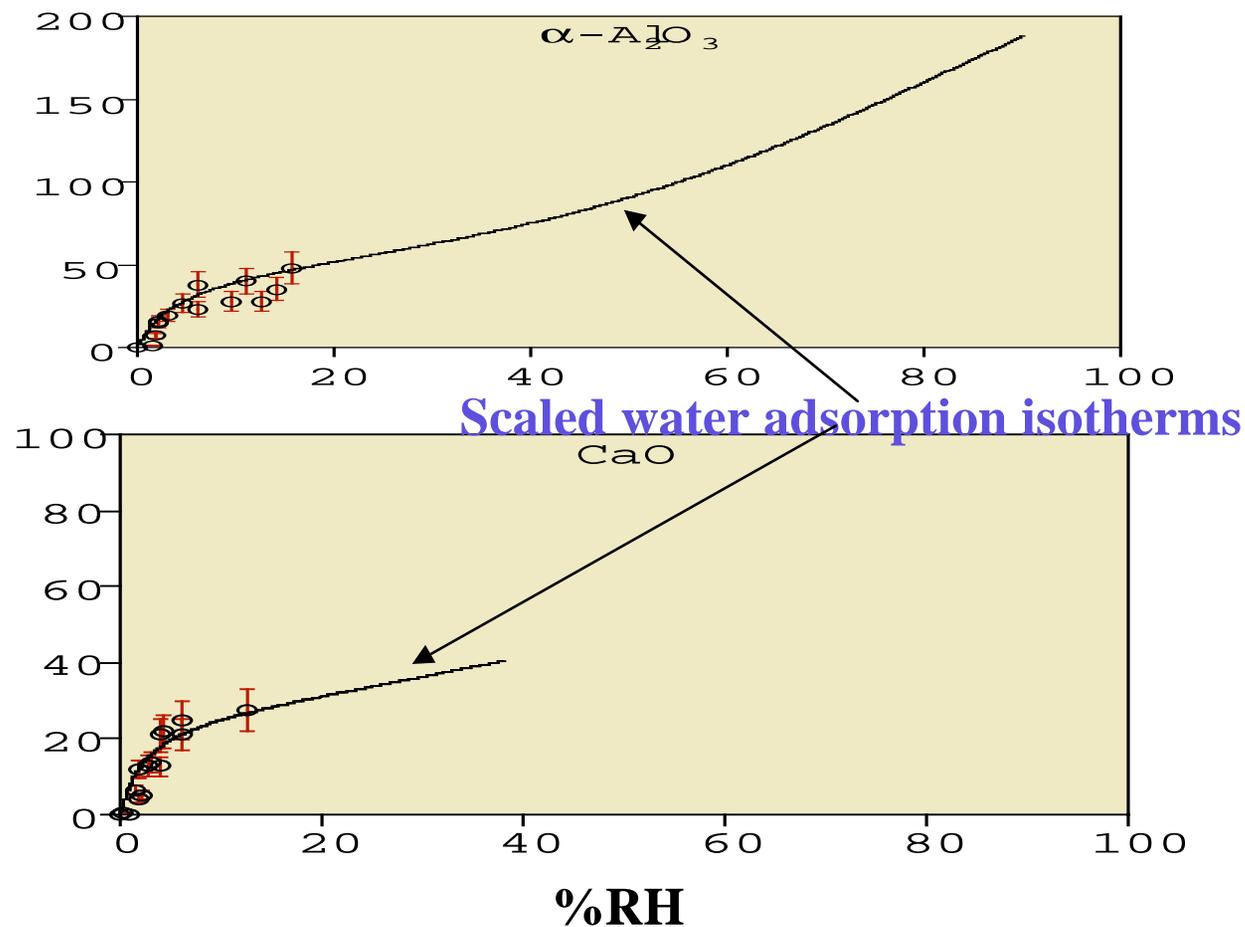
HNO₃ Uptake on CaCO₃ in the Presence of Water - Greater than a monolayer



Reaction not limited to surface atoms

Enhanced Nitric Acid Uptake Kinetics in the Presence of Adsorbed Water Measured by FT-IR Spectroscopy

$$\frac{\gamma_{\text{H}_2\text{O}}}{\gamma_{\text{dry}}}$$

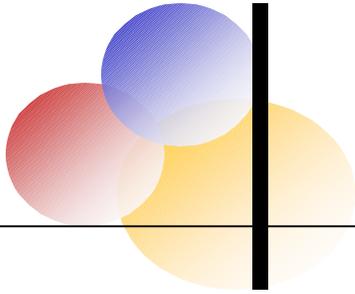


$$\gamma = \frac{\text{Rate of Adsorption}}{\text{Collision Rate}}$$

$$= \frac{\text{Rate of Formation of Nitrate}}{\text{Collision Rate}}$$

Summary of Results

- Spectroscopic probes of gas-phase and adsorbed species along with kinetic measurements provide the necessary information to evaluate reactions of potential importance in the troposphere
 - **stoichiometry**
 - **reaction mechanisms surface coverage, saturation**
 - **uptake coefficients**
 - **increased water uptake**
(potential CCN nuclei)
- Diffusion of gases into powdered samples can have a very significant effect on the measured uptake coefficient for powdered samples
 - **multiple collisions amplify the observed uptake coefficient**
- Atmospheric implications of uptake measurements determined from box-model analysis
 - **heterogeneous reactions may be a sink for nitric acid and SO₂**
 - **heterogeneous reactions are too slow for NO₂ to have an effect**
- Water plays an important role in heterogeneous reactions of HNO₃ on



Follow /

I. Discrepancy

Samples are from different sources

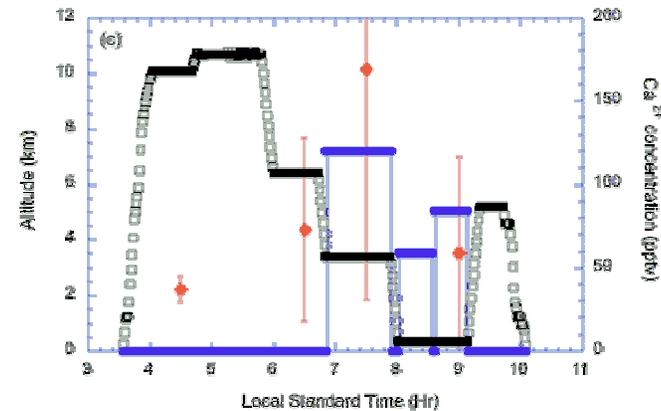
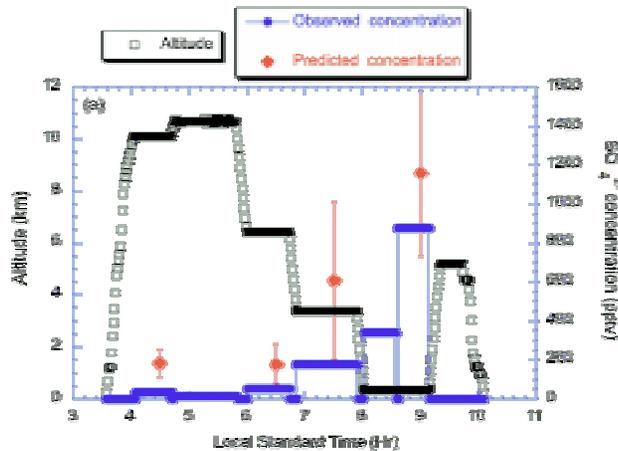
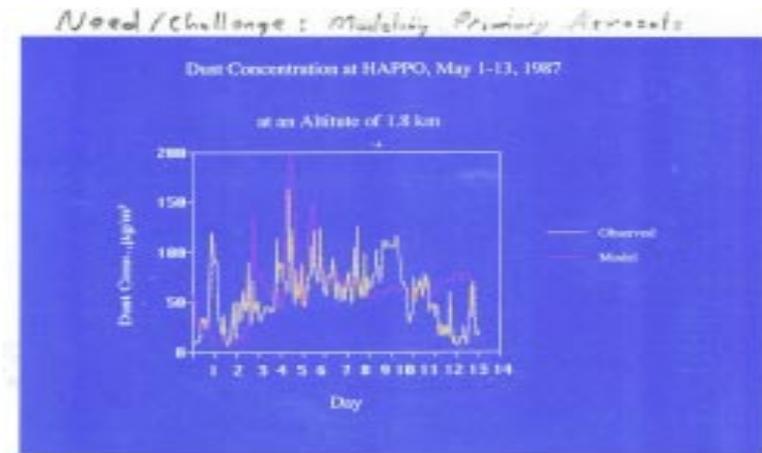
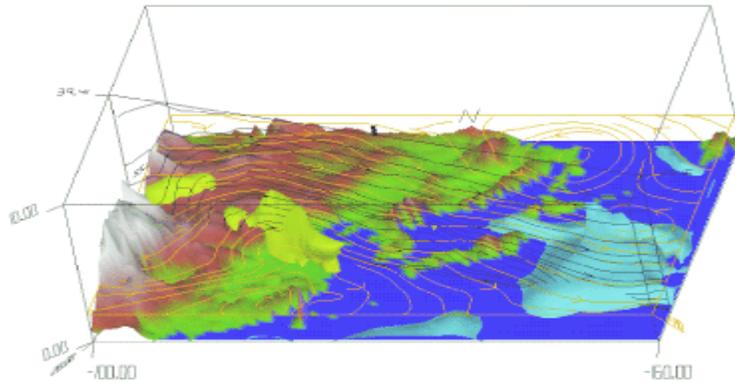
Reporting initial γ and/or average γ .

Discrepancy
in the values of
 γ

Accessible surface area for reaction not accurately accounted for.

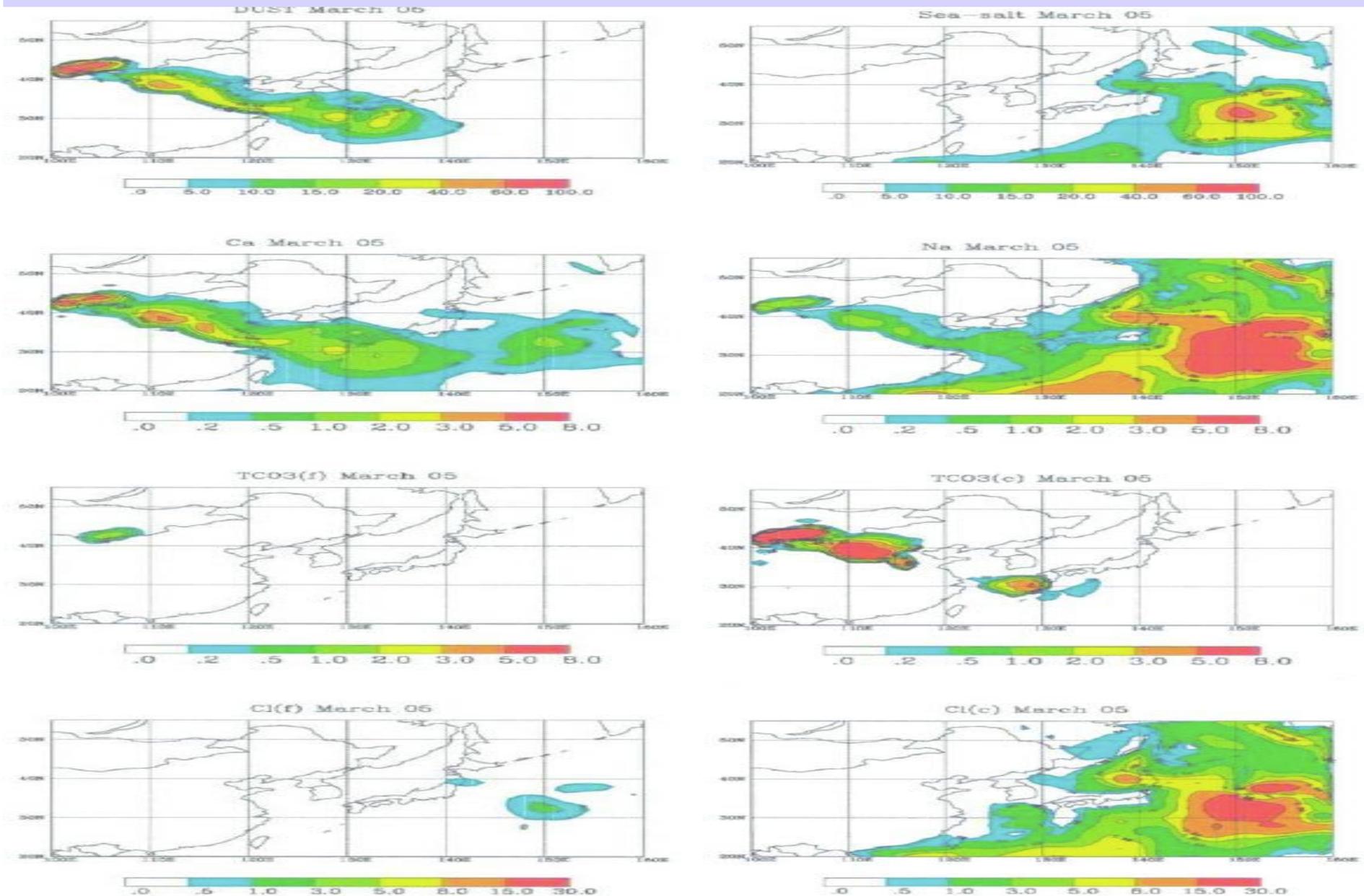
Different experimental conditions: Temp., RH, P_{NO_2}

Model is Able to Capture Many Important Observed Features

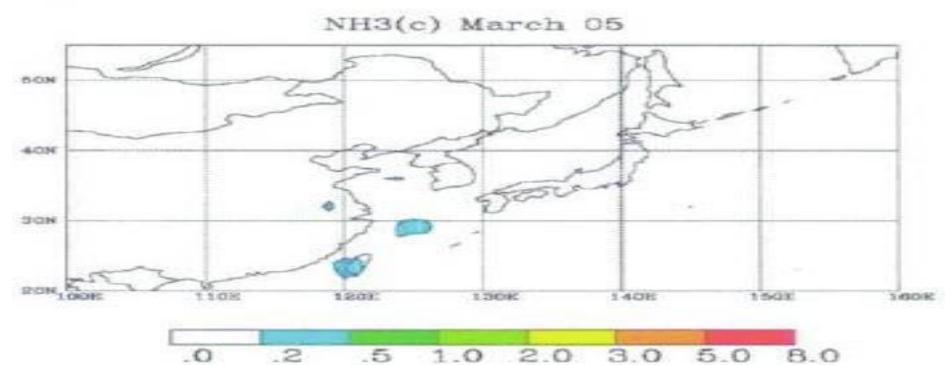
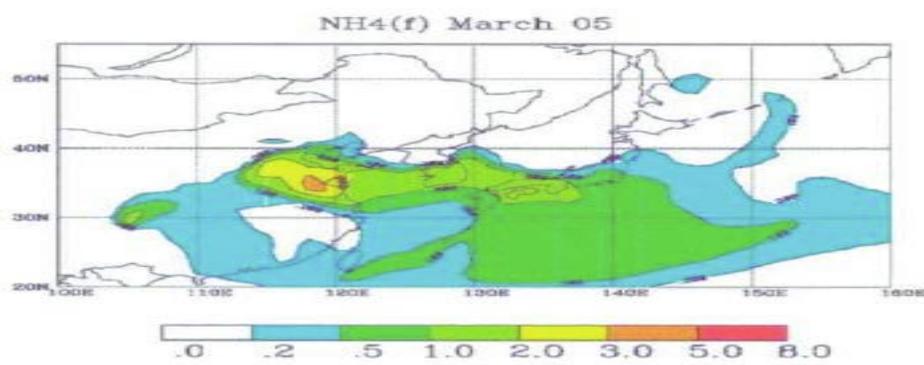
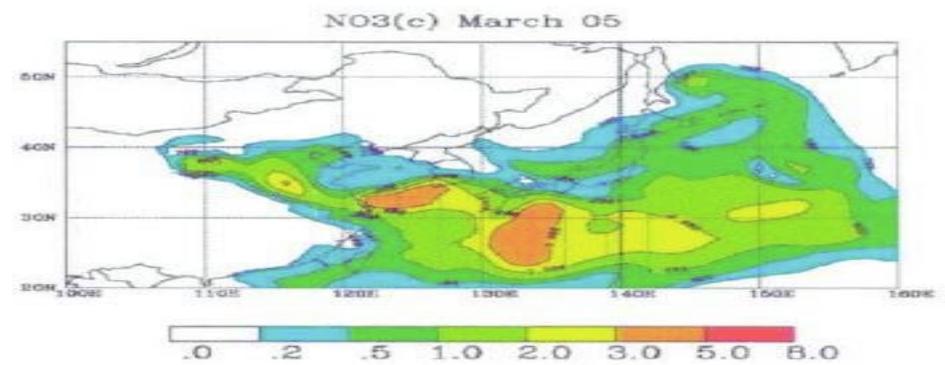
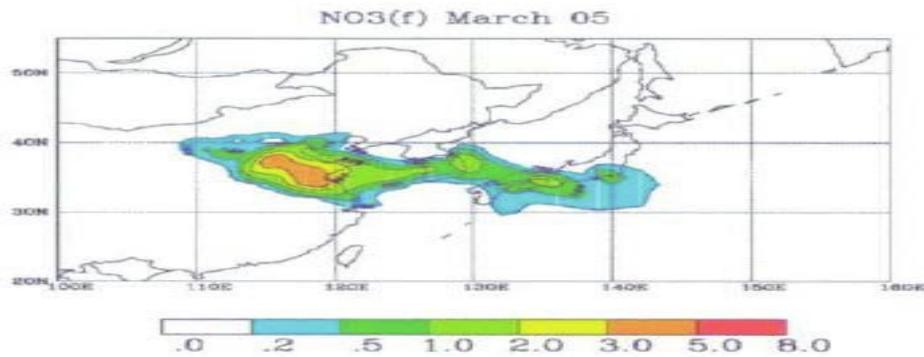
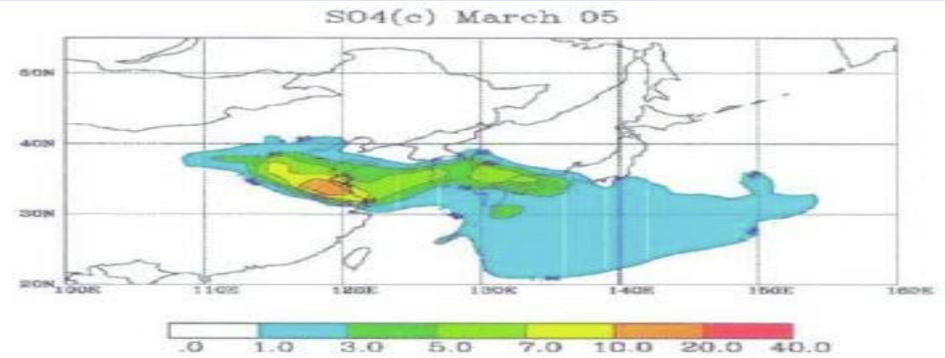
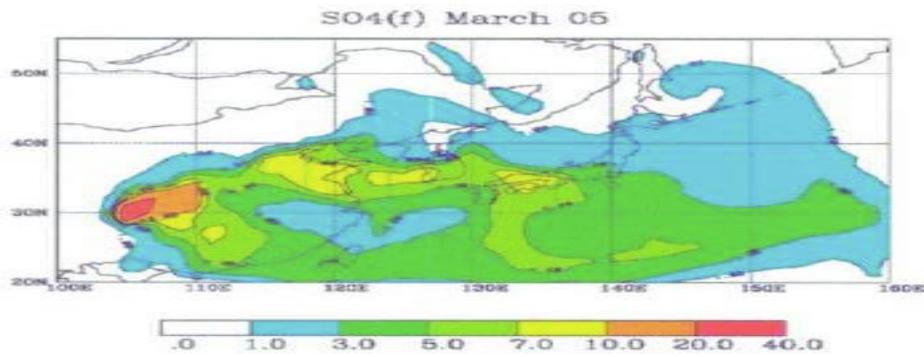


Phadnis et al., J. Atmos. Chem., 36:285 (2000); Song et al., JGR, in press (2001)

Calculated Fine and Coarse Mode Aerosol Distributions in the Boundary Layer; PEM-WEST B

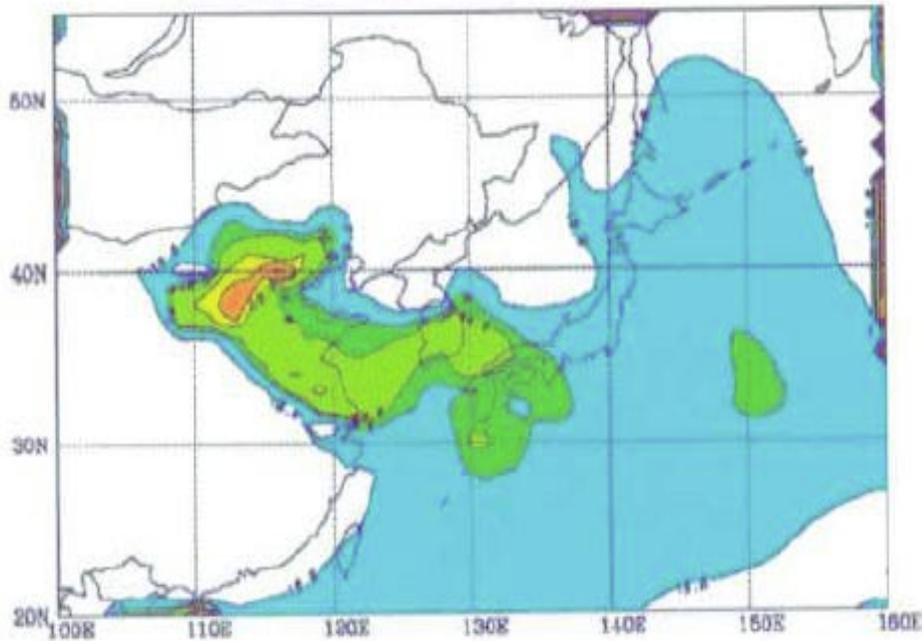


Calculated Fine and Coarse Mode Aerosol Distributions in the Boundary Layer; PEM-WEST B

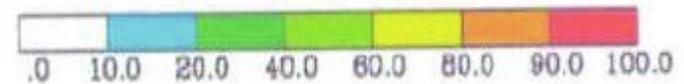
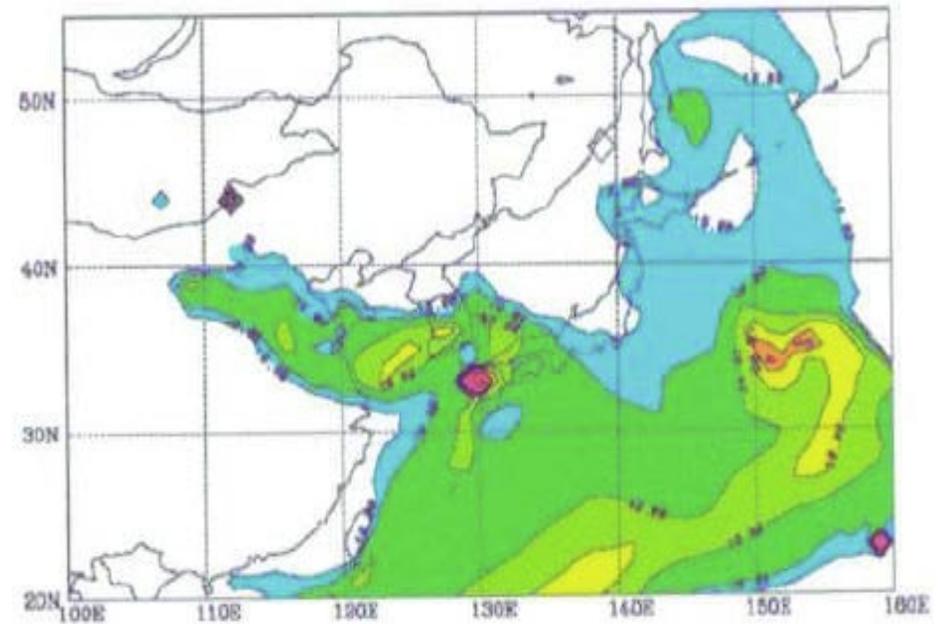


**INTERACTIONS OF SO₂ WITH MINERAL AEROSOL CHANGE
SULFATE SIZE DISTRIBUTION AS WELL AS THE CHEMICAL
LIFETIMES OF SULFUR. THESE INTERACTIONS HAVE
IMPLICATIONS FOR *RADIATIVE FORCING***

S04(c)/(S04(f)+S04(c)) March 05

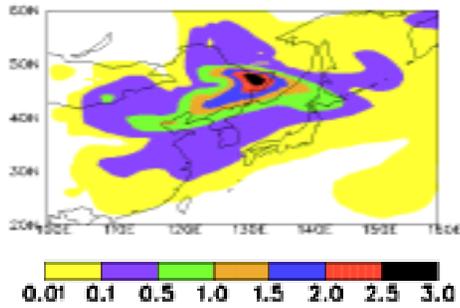
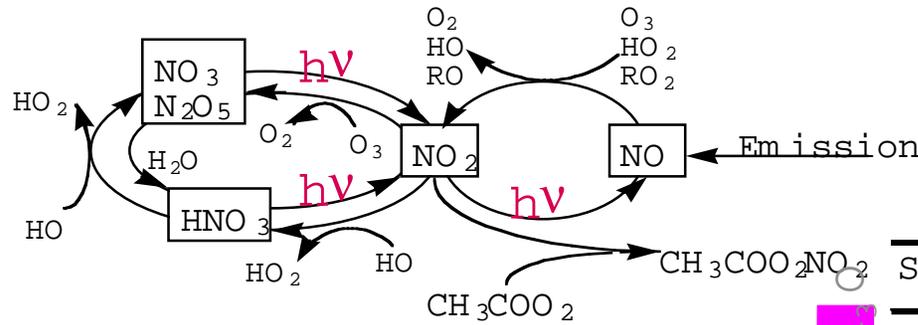


S02 percent change March 05

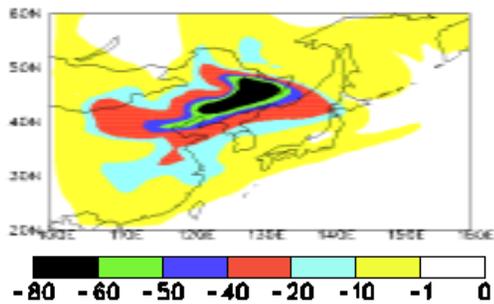


Song et al., JGR in press

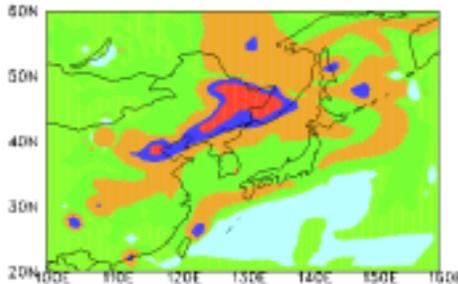
Impact of Aerosols on the Photochemical Oxidant Cycle Through Photolysis Rates



Mineral Optical Depth



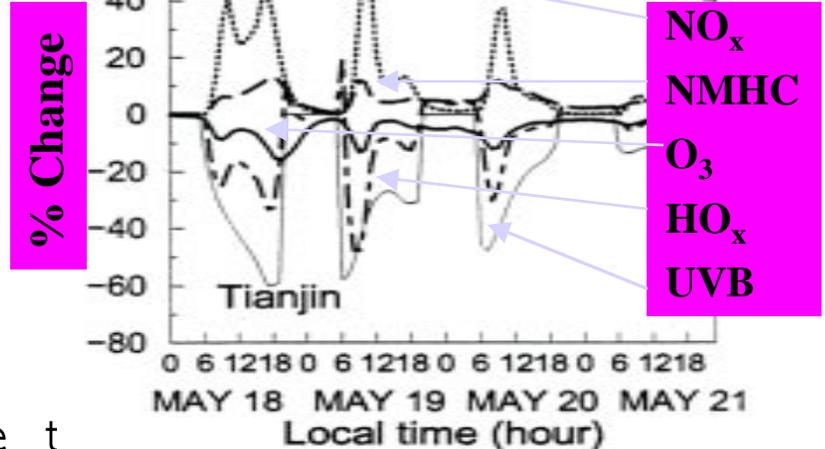
% Change NO_2 Photolysis



Ozone variations (%) due to

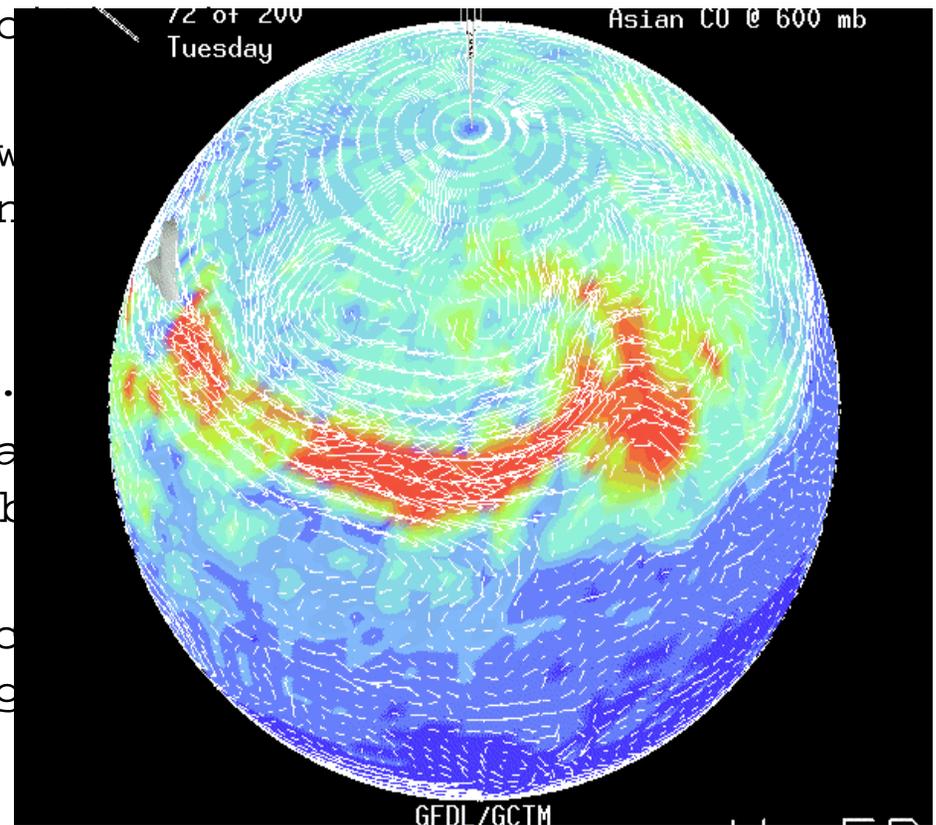
Dust Impact on

Season	Aerosol impact on	$\Delta\text{Sulfate}$ 0%	ΔSoot %	$\Delta\text{Mineral}$ %	ΔTSP %
Winter	+	18.9	48 ³ .6	13.2	58.7
	-	-8.6	-25.8	-5.8	-33.0
Spring	+	1.3			
	-	13.1	24.4	9.7	36.8
Summer	+	1.5			
	-	13.7	25.4	8.3	37.6
Fall	+	15.5	27.3	9.2	40.3
	-	-6.1	-13.5	-3.8	-20.6



The Changing Air Quality of the Northern Hemispheric Pacific Basin

- ¥ Pressures are from the Pacific Countries and beyond.
- ¥ Changing patterns and growth of energy use and resulting emissions are the primary factors with East and West following different paths.
- ¥ Impacts are local, regional (East and West), basin, and global.
- ¥ Complexities in transport and chemistry over the Pacific challenge present modeling and measurement efforts.



Contribution of Fossil Fuel Burrr Tropospheric Ozone

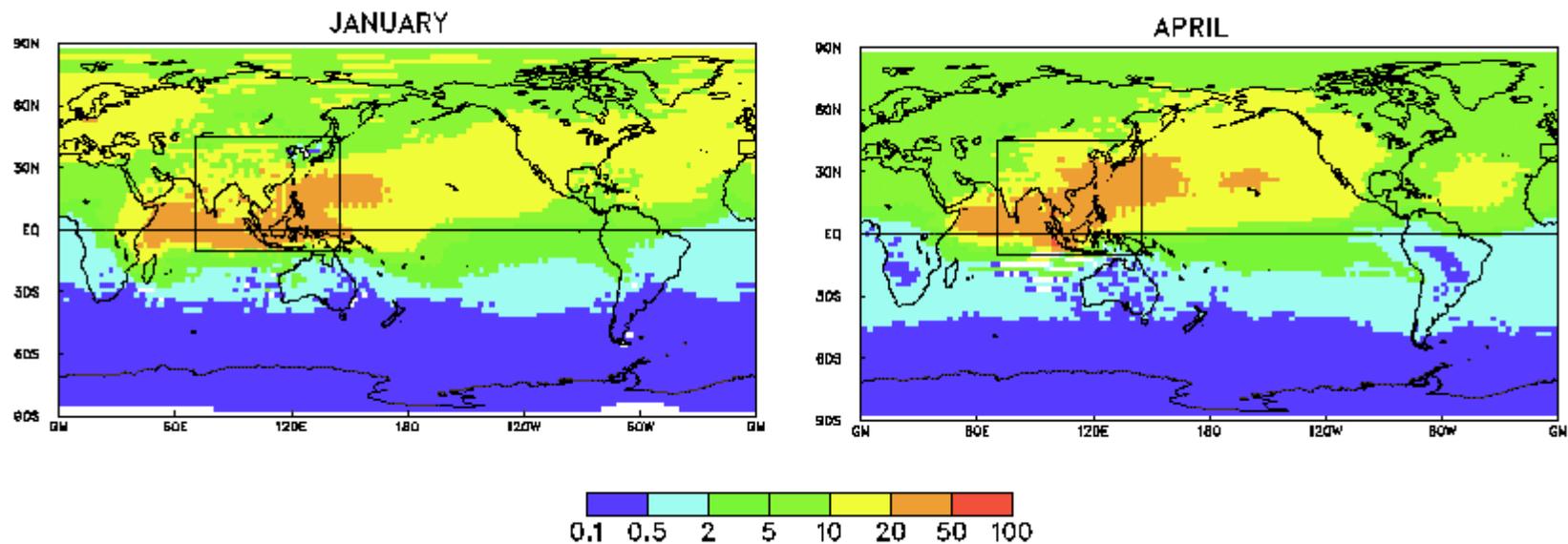
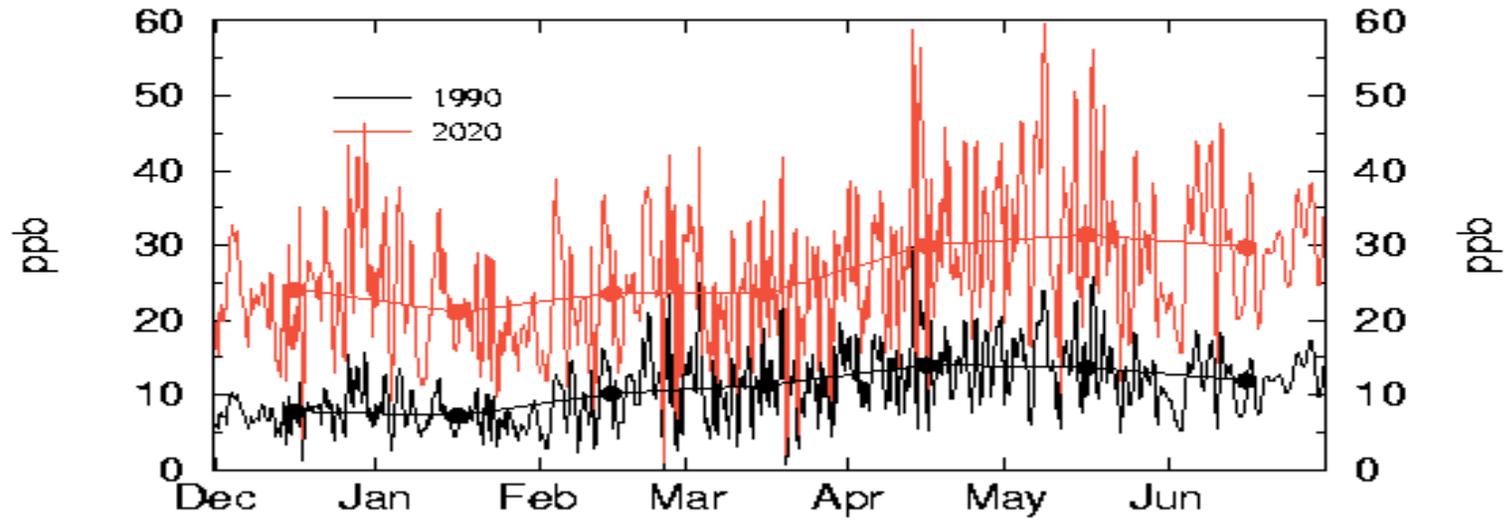


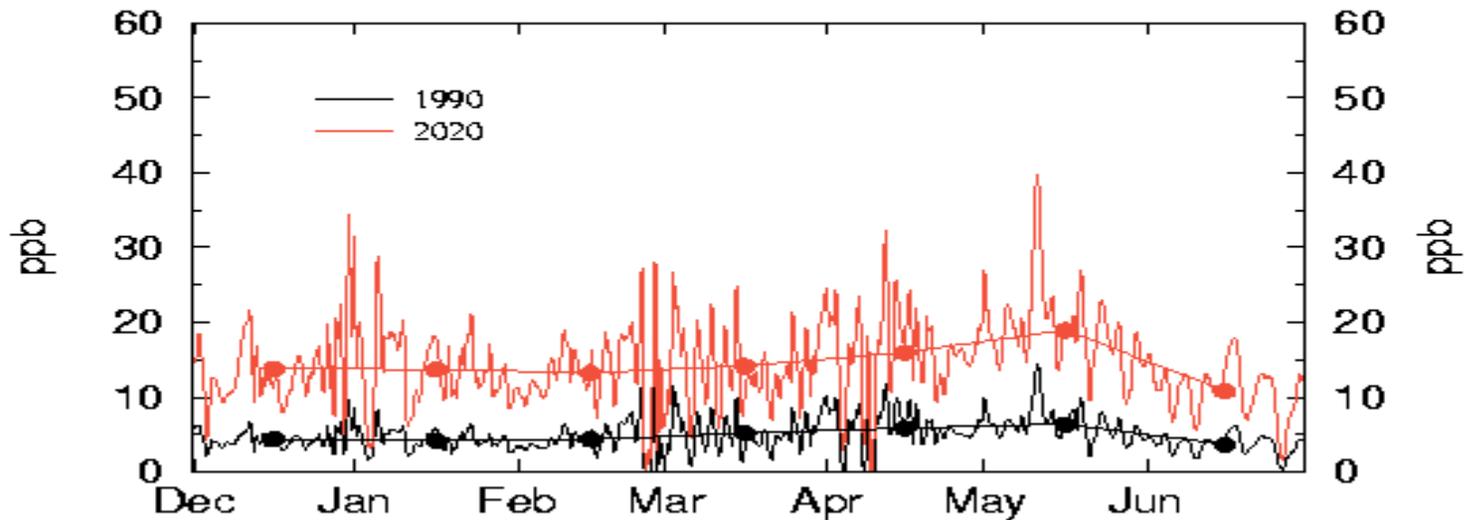
Figure 3.14. Percentage of total ozone accounted for by Asian fossil fuel NOx emission at 940 mb (sigma surface) for January, April

Yienger et al, JGR 200

Asian Contribution to Total Ambient Ozone over Central California 500mb (6hour averages)



940mb (6hour averages)

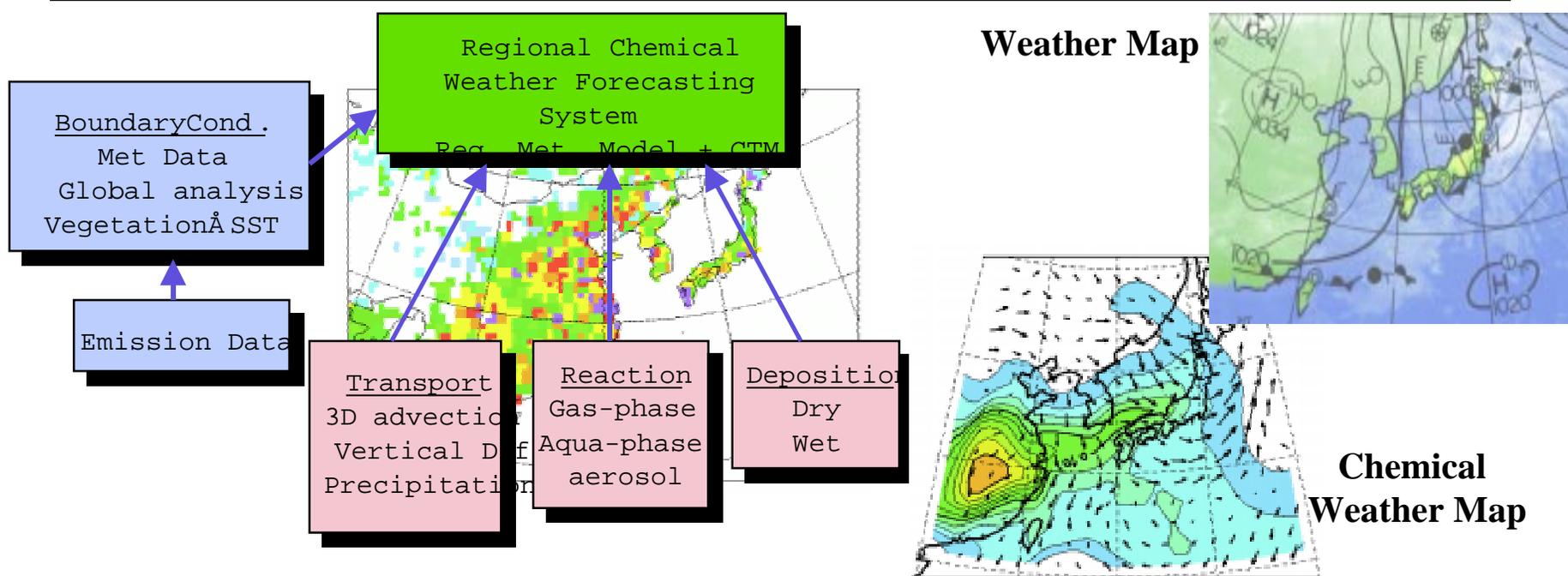


Development and Application of Chemical Weather Forecasting System over East Asia

Itsushi Uno (RIAM/Kyushu-U), Gregory R. Carmichael (UI/CGRER)

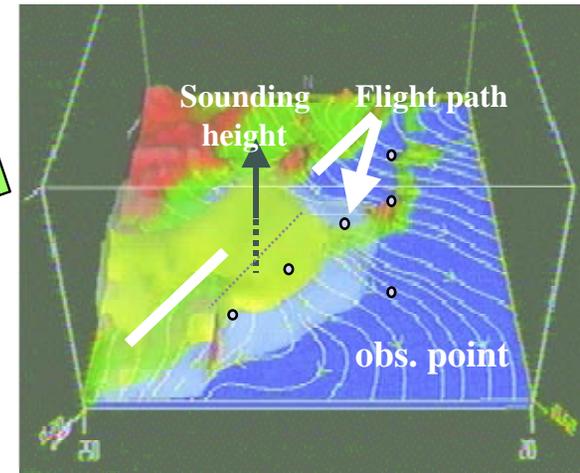
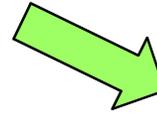
We are developing and applying an operational chemical weather forecasting system based on 3-D on-line regional scale chemical transport model fully coupled with RAMS (Regional Atmospheric Modeling System, Pielke *et al.*, 1992). This system consists of several important components; i) operational global forecast data set access to NCEP and JMA, ii) RAMS weather forecast for 72-96 hours based on the NCEP & JMA data as a lateral boundary condition, iii) On-line chemical transport calculation of important chemical tracers (SO_2/SO_4 , mineral dust, black carbon and sea-salt, etc.) and iv) post-processing of “chemical weather forecast” results with 2/3-D graphics into the WWW-page.

One of the main purposes of this system is to understand the regional transboundary air pollution and to schedule/design the operational field monitoring campaign during the ACE(Aerosol Characterization Experiment)-Asia and Trace-P intensive observations.



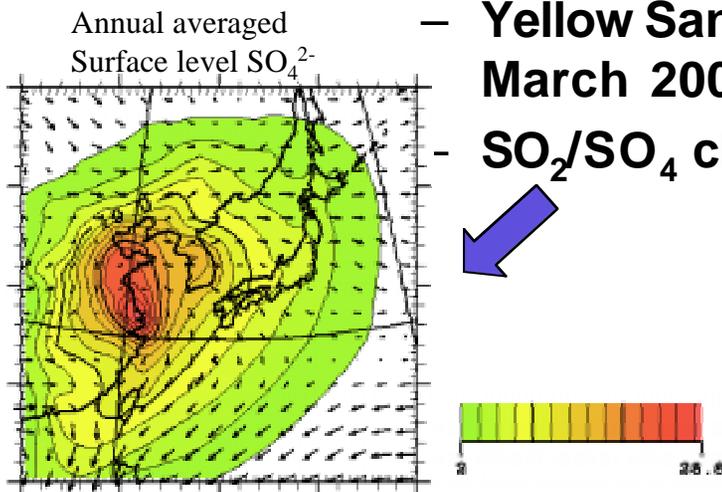
Application & Model Validation

- ACE-Asia & TRACE-P Field Campaign Planning
- Field Observation Design
- Traffic (Aviation)
- Visibility
- Environmental Assessment

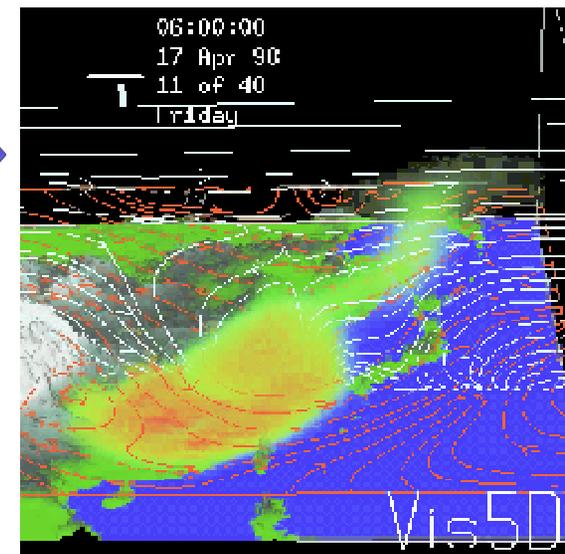


- Model Validation for Episodic Application

- Yellow Sand (Kosa) April 1998 & March 2000
- SO_2/SO_4 climate simulation

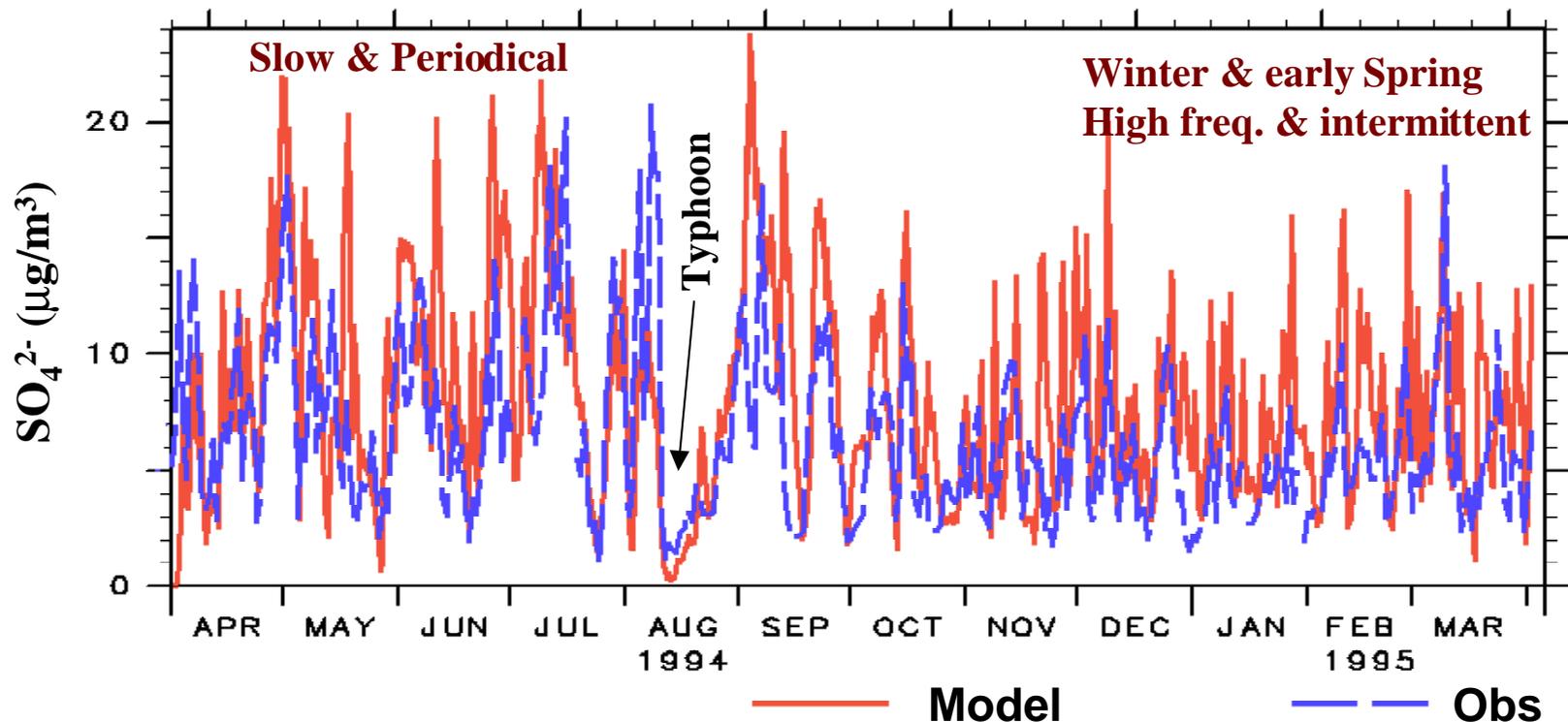


Simulated Kosa Onset April 98



Observation at Osaka and Model Results

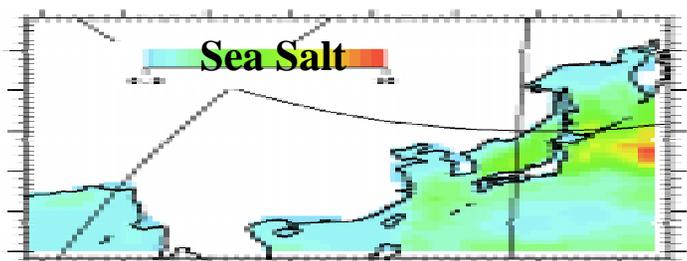
Observed sulfate concentration at Osaka compared with model results show a good agreement, and the intermittency during the winter season and the periodicity typical of spring/fall rainy seasons, when the alternance of high/low pressure systems characterize the meteorology of the region, is nicely reproduced by the numerical model (RAMS on-line transport model).



Modeled twelve hours averaged concentration (straight line) and daily averaged observation (dot line)

Tracer Species (2)

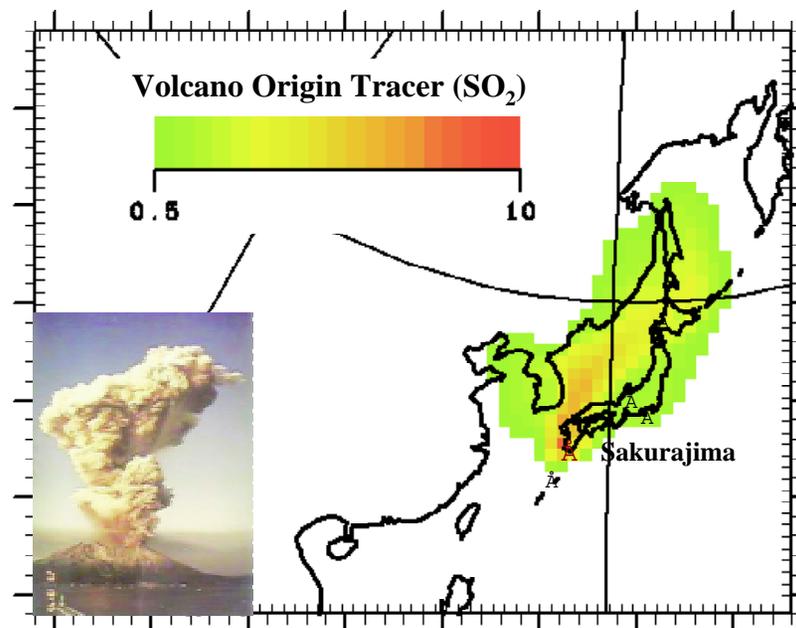
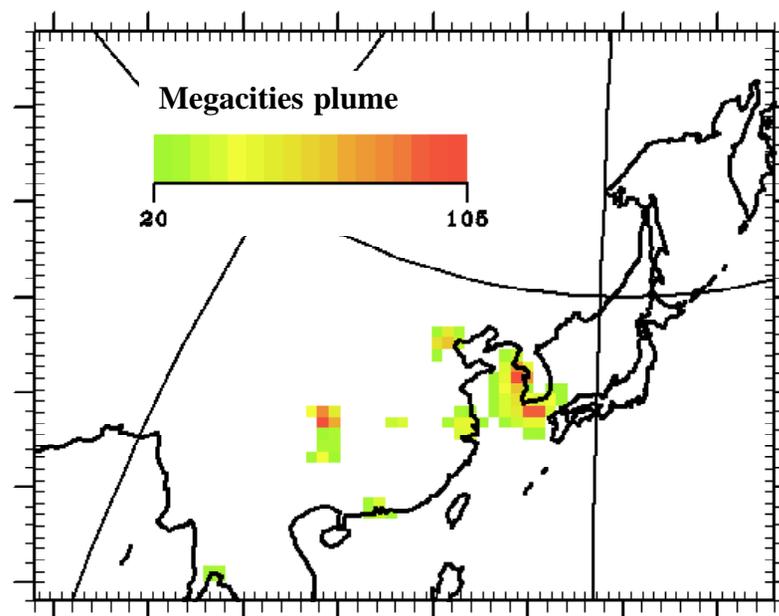
Several useful atmospheric tracers to
Understand the origin of air mass



12 bin Sea Salt from Gong et al.
Production rate depends on wind speed

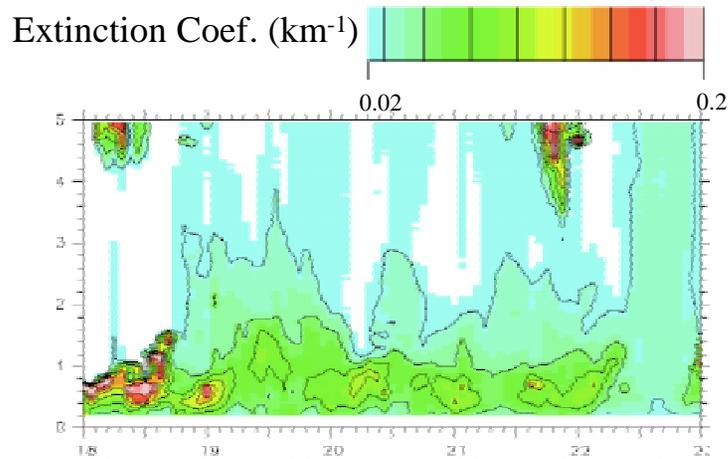
Tracers/Markers:

SO ₂ /Sulfate	DMS
BC	OC
Volcanic	Megacities
CO fossil	CO-Biomass
Ethane	Ethene
Sea Salt	Radon
Lightning NO _x	Dust 12 size bins

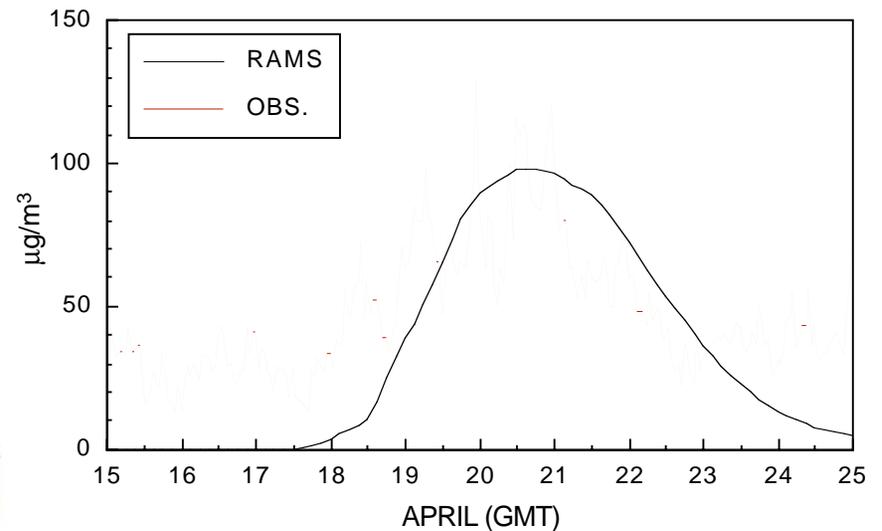


Tokyo & Tsukuba (observation and model results)

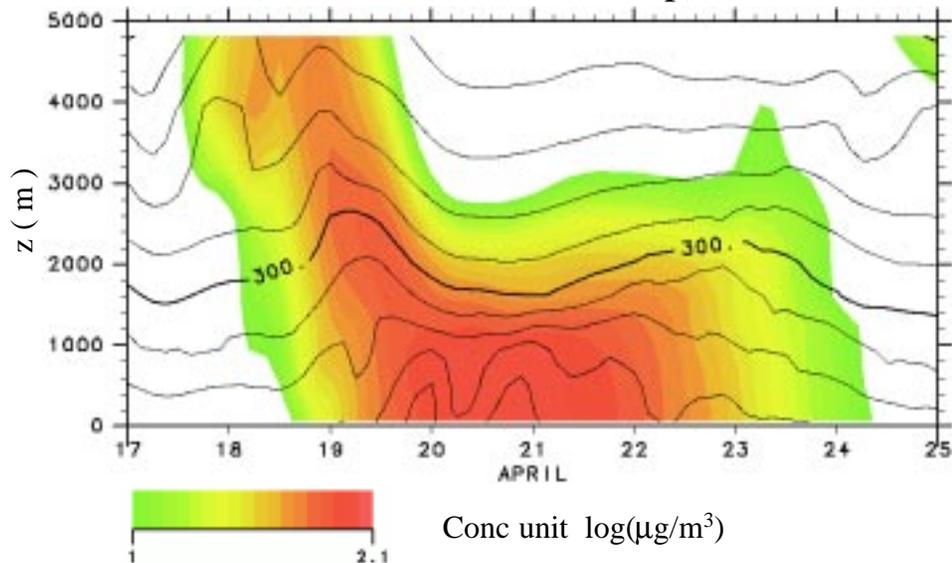
National Inst. Env. Studies Compact Mie Lidar



SPM (Observation and Model) at Tokyo



Model (Dust and Potential Temp)



Elevated dust layer comes first and then dense dust layer appears in PBL (below 2km) associated with the movement of low-pressure system

The Future: A Close Integration of Measurements and Models

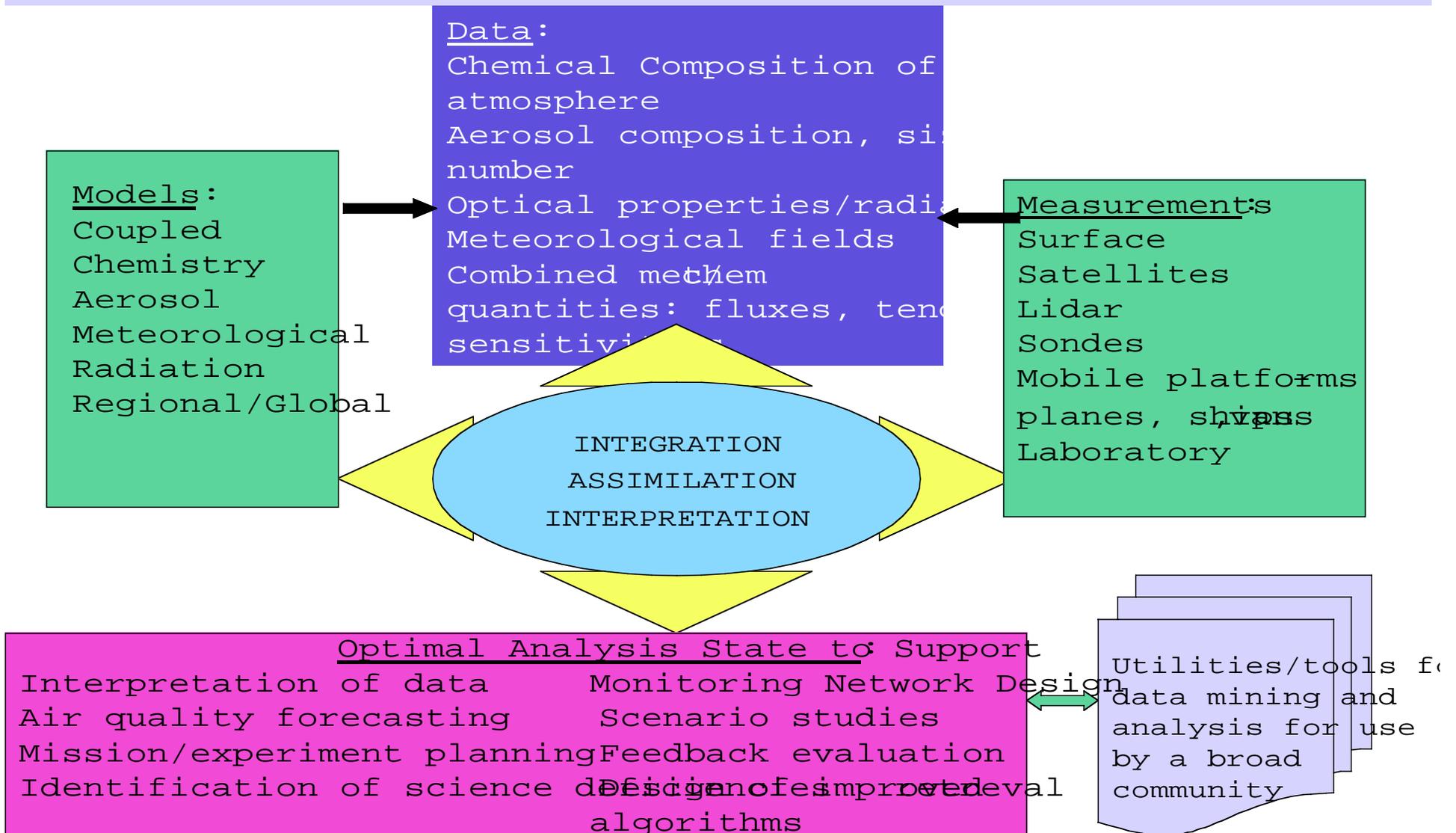


Table 3. Estimated Organic Mass Fraction (percent) of the Aerosol Due to the Irreversible Uptake of Acetone Onto the Mineral Aerosol Size Distributions Summarized in Table 2^a

k, s ⁻¹	Organic Mass Fraction, %						
	1 Hour	5 Hour	10 Hour	1 Day	5 Days	10 Days	20 Days
10 ⁻⁴	16	50	66	82	96	97	98
10 ⁻⁵	2	10	16	31	69	82	90
10 ⁻⁶	0.2	1	1.9	<u>4.5</u>	<u>19</u>	<u>31.8</u>	48.3
10 ⁻⁷	0.02	0.1	0.2	0.5	2.3	4.5	8.5

^aThe pseudo-first-order reaction coefficients span the range of values calculated by using the measured acetone uptake rates as shown in Figure 14. These illustrative examples are for 1 ppb acetone; an aerosol volume density of $2.8 \cdot 10^{-12}$ cm³ aerosol/cm³ air; and an aerosol mineral density of 1.5 g/cm³.

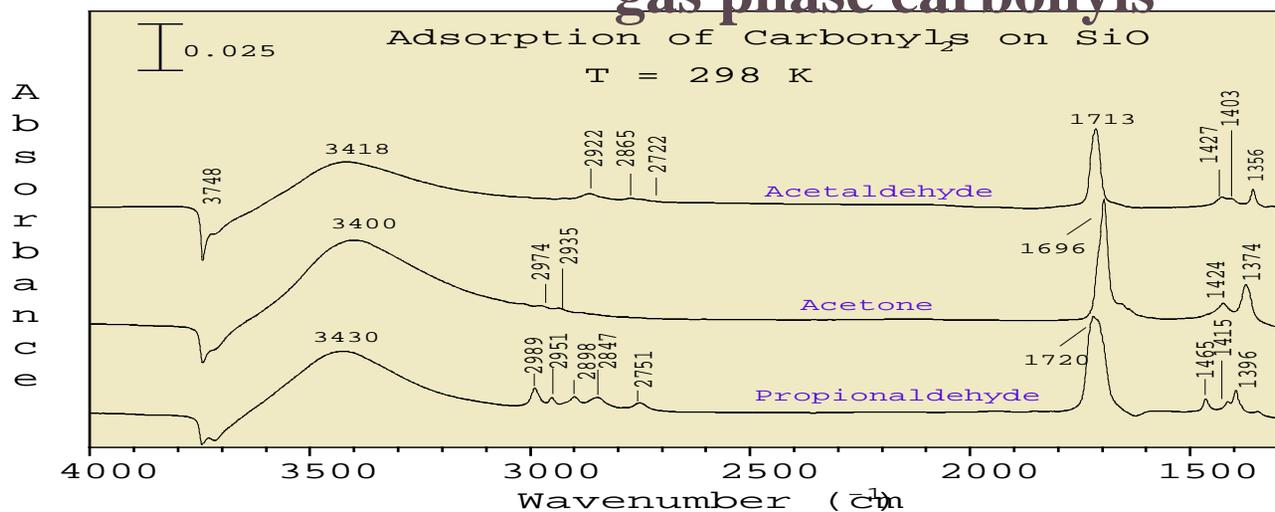
^bExposure time.

JGR in press.

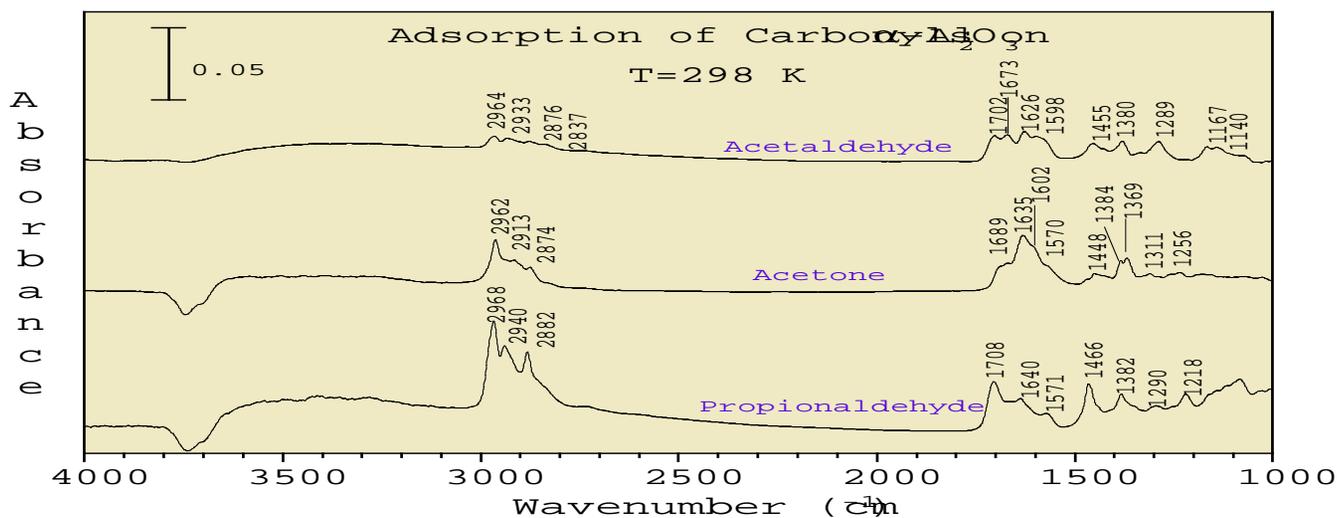
able 6 The effect of increasing uptake coefficient (γ) on atmospheric mixing ratios. The units are %, calculated relative to the no surface reaction case.

	ΔO_3^{\max}	ΔNO_x^{\max}	ΔHNO_3^{\max}
$\gamma_{NO_2} = 10^{-5}$	-0.13	-0.19	-0.83
$\gamma_{NO_2} = 10^{-4}$	-0.39	-0.39	-1.86
$\gamma_{NO_2} = 10^{-3}$	-3.37	-7.50	-15.3
$\gamma_{NO_2} = 10^{-2}$	-12.8	-18.1	-45.6

Transmission FT-IR spectroscopy of SiO_2 and $\alpha\text{-Al}_2\text{O}_3$ in the presence of gas phase carbonyls



reversible
adsorption
on SiO_2



irreversible
adsorption
and product
formation
on $\alpha\text{-Al}_2\text{O}_3$

Summary of Laboratory Results

Acetone

Sample	BET (m ² /g)	Mass (g)	Total BET (m ²)	Correction Factor (n)	γ_{obs}	$\gamma_{t, BET}$
α -Fe ₂ O ₃	2.3	0.0300	0.069	58	7.3×10^{-3}	1.3×10^{-4}
γ -Fe ₂ O ₃	50	0.0040	0.200	167	1.9×10^{-2}	1.1×10^{-4}
α -Al ₂ O ₃	14	0.0072	0.101	84	1.7×10^{-3}	2.0×10^{-5}
γ -Al ₂ O ₃	101	0.0110	1.111	930	8.0×10^{-3}	8.6×10^{-6}
TiO ₂	50	0.0012	0.060	50	1.8×10^{-2}	3.6×10^{-4}
SiO ₂	200	0.0012	0.960	803	5.0×10^{-3}	6.2×10^{-6}
CaO	3.9	0.0045	0.018	15	1.8×10^{-3}	1.2×10^{-4}
MgO	14.9	0.0054	0.081	67	4.0×10^{-3}	6.0×10^{-5}
Carbon black	460	0.0010	0.460	385	2.4×10^{-2}	6.2×10^{-5}
China Loess	11	0.0154	0.169	142	1.3×10^{-2}	9.2×10^{-5}
Saharan Sand	3.1	1.5118	4.687	3922	1.2×10^{-1}	3.1×10^{-5}

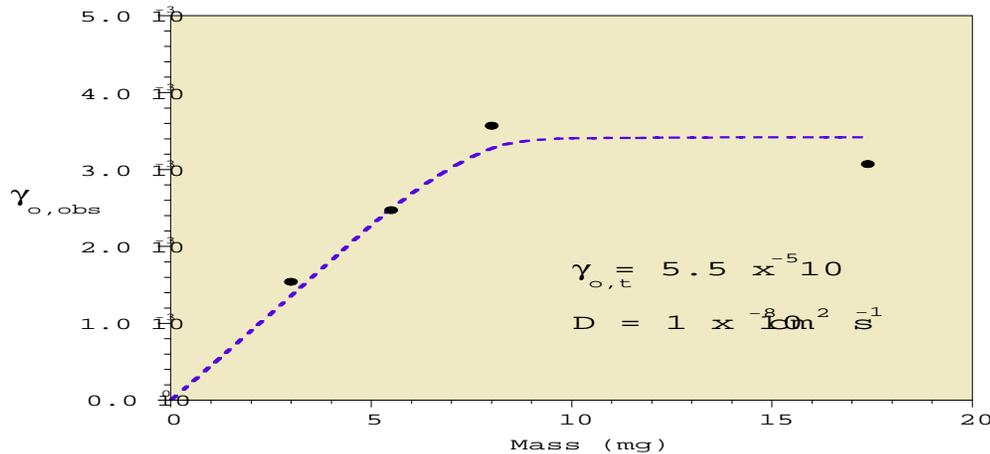
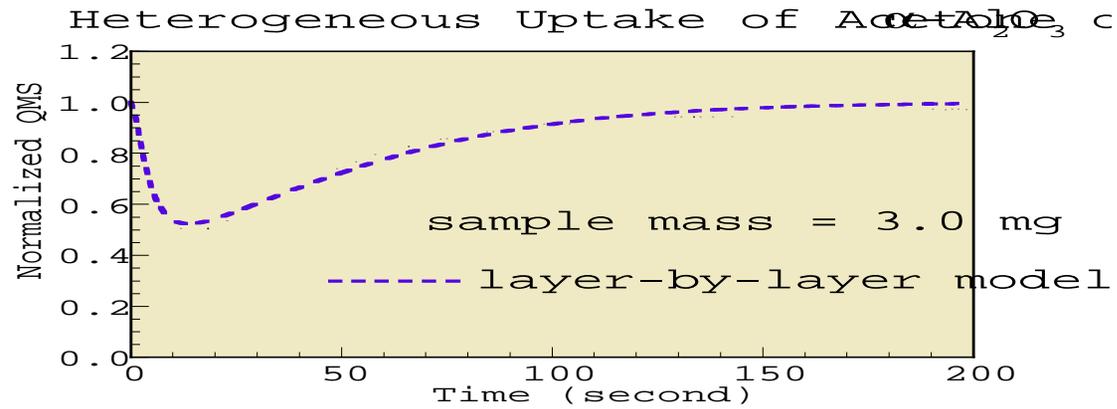
Acetaldehyde

Oxide	BET (m ² /g)	Mass (g)	Total BET (m ²)	Correction Factor (n)	γ_{obs}	$\gamma_{t, BET}$
α -Fe ₂ O ₃	2.3	0.0107	0.025	21	6.0×10^{-5}	2.9×10^{-6}
α -Al ₂ O ₃	14	0.0123	0.172	144	4.6×10^{-3}	3.2×10^{-5}
γ -Al ₂ O ₃	101	0.0190	1.919	1606	1.04×10^{-2}	6.5×10^{-6}
TiO ₂	50	0.0019	0.095	79	7.4×10^{-3}	9.4×10^{-5}
SiO ₂ -200	200	0.0053	1.060	887	6.2×10^{-3}	7.0×10^{-6}
CaO	3.9	0.0047	0.018	15	4.5×10^{-3}	3.0×10^{-4}
MgO	14.9	0.0081	0.121	101	8.5×10^{-3}	8.4×10^{-5}
Carbon black	460	0.0008	0.368	308	2.4×10^{-2}	7.8×10^{-5}
China Loess	11	0.0031	0.034	29	1.5×10^{-4}	5.2×10^{-6}
Saharan Sand	3.1	1.1849	3.673	3074	1.5×10^{-2}	4.9×10^{-6}

For acetone and acetaldehyde

$$4 \times 10^{-6} < \gamma < 5 \times 10^{-4}$$

Layer-by-Layer Model

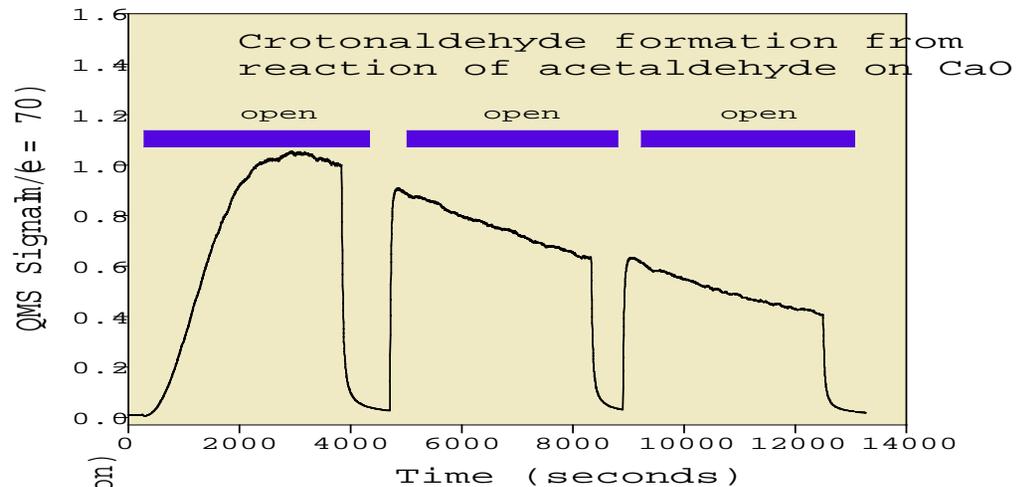


$\gamma_{\text{layer-by-layer}} = 5.5 \times 10^{-5}$

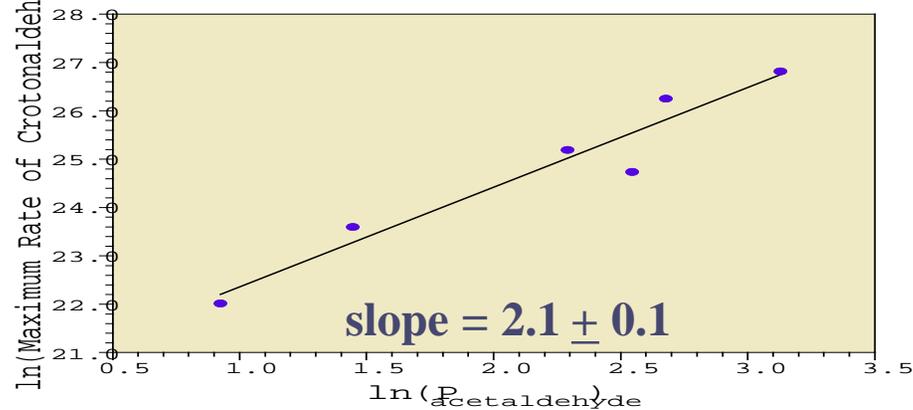
$\gamma_{\text{LMD}} = 3.8 \times 10^{-5}$

Initial uptake coefficients determined from LMD are lower than layer-by-layer model by a factor of 1.5.

Kinetics of the Formation of the Aldol Condensation Product

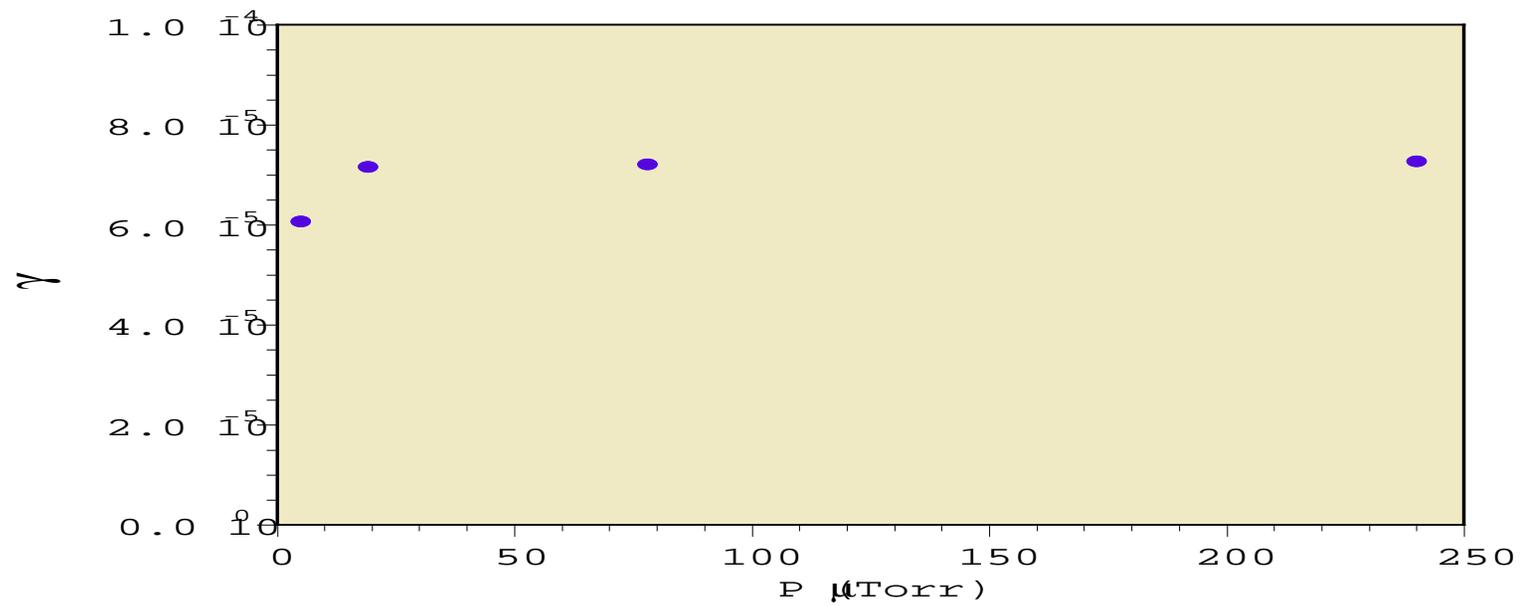


gas-phase
crotonaldehyde
formation
<1% of acetaldehyde
reacted



∴ formation of
crotonaldehyde
is second order
in acetaldehyde
pressure

Uptake of Acetaldehyde is First Order



Summary of Combined Laboratory and Modeling Study

- Spectroscopic probes of gas-phase and adsorbed species along with kinetic measurements provide the necessary information to evaluate reactions of potential importance in the troposphere
 - **reaction mechanisms, surface coverage, saturation**
 - **uptake coefficients**
- Diffusion of gases into powdered samples can have a very significant effect on the measured uptake coefficient for powdered samples
 - **multiple collisions amplify the observed uptake coefficient**
- Atmospheric implications of uptake measurements determined from box-model analysis
 - **heterogeneous pathways are competitive with other carbonyl loss mechanisms (e.g. reaction with OH radical)**

Future Directions

In the Laboratory Studies:

- continue to improve our efforts in measuring heterogeneous reaction kinetics on particle surfaces;
- investigate heterogeneous reactions of atmospheric gases, especially nitrogen oxides and VOCs, on mineral oxides, mineral dust and soot in greater detail as a function of relative humidity and temperature;
- determine the effects of aerosol aging on the heterogeneous reactivity;
- determine the effects of solar light ($h\nu$) and increased complexity of reactant mixtures (VOCs, NO_x and other trace atmospheric cases such as O_3 together);
- use microscopic techniques such as atomic force microscopy, transmission and scanning electron microscopy coupled with energy dispersive x-ray analysis to study changes in particle morphology;
- use transmission and scanning electron microscopy coupled with energy dispersive x-ray analysis for single particle analysis of authentic mineral dust samples.

Future Directions

In Modeling Studies:

- **continue to investigate the uptake of VOCs on aerosol surfaces;**
- **further evaluate the relative importance of various surfaces and reaction pathways;**
- **perform three-dimensional modeling analysis to provide a more realistic representation of heterogeneous interactions under a broad-range of chemical regimes (which vary both in space and time) and to test hypothesis in and aid the analysis of ACP field studies.**

STEM-II Modeling

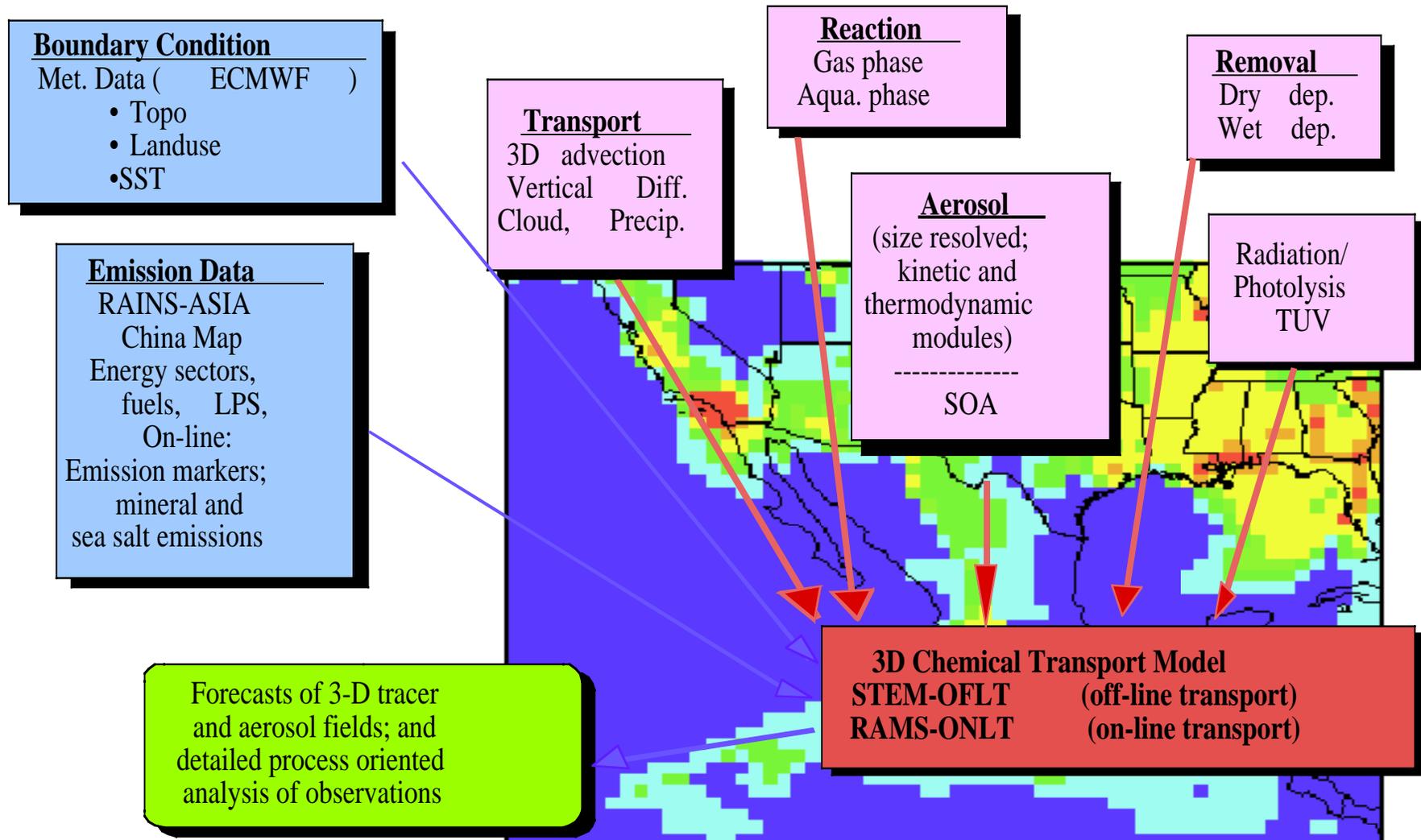
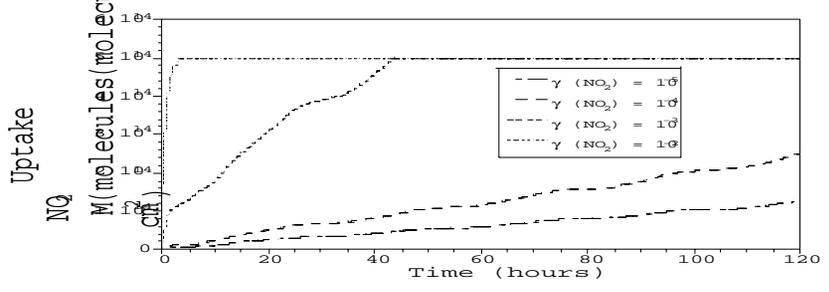
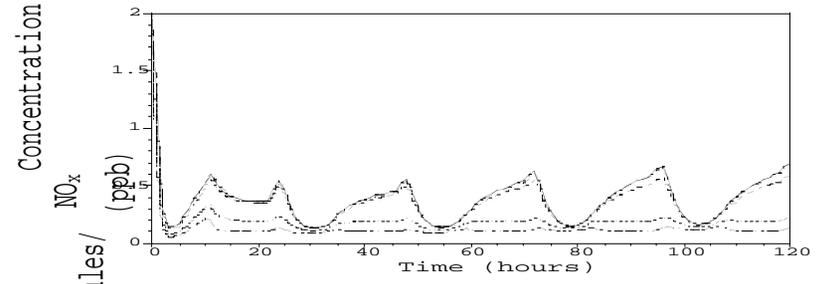
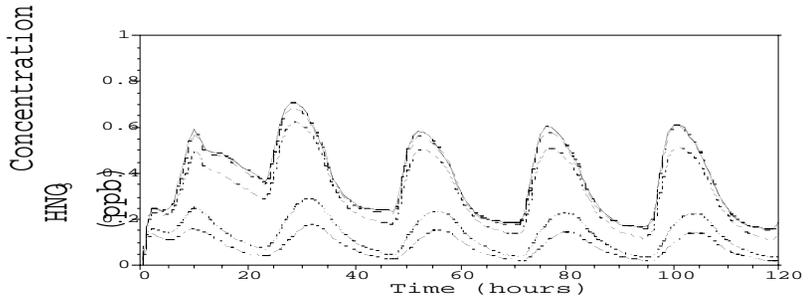
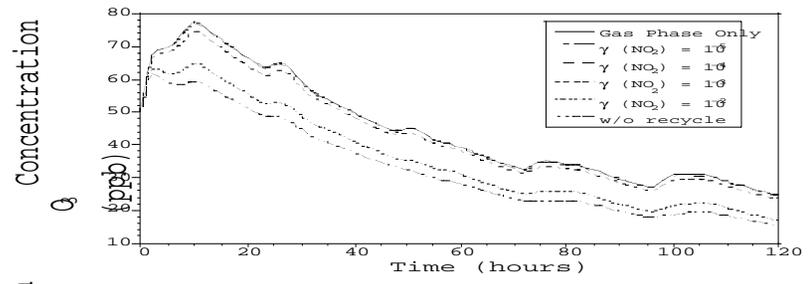


Table 3.

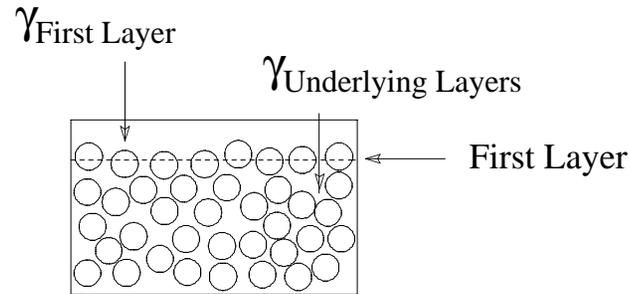
Effect of reaction probability on atmospheric mixing ratios when saturation are included.

	ΔO_3^{\max}	ΔNO_x^{\max}	ΔHNO_3^{\max}
$\gamma_{NO_2} = 10^5$	-0.13	-0.19	-0.83
$\gamma_{NO_2} = 10^4$	-0.39	-0.39	-1.86
$\gamma_{NO_2} = 10^3$	-3.37	-7.50	-15.3
$\gamma_{NO_2} = 10^2$	-12.8	-18.1	-45.6



Knudsen Cell Analysis for Porous Samples

- Uptake depends on surface area of first and underlying layers



Linear Mass Regime (LMR)

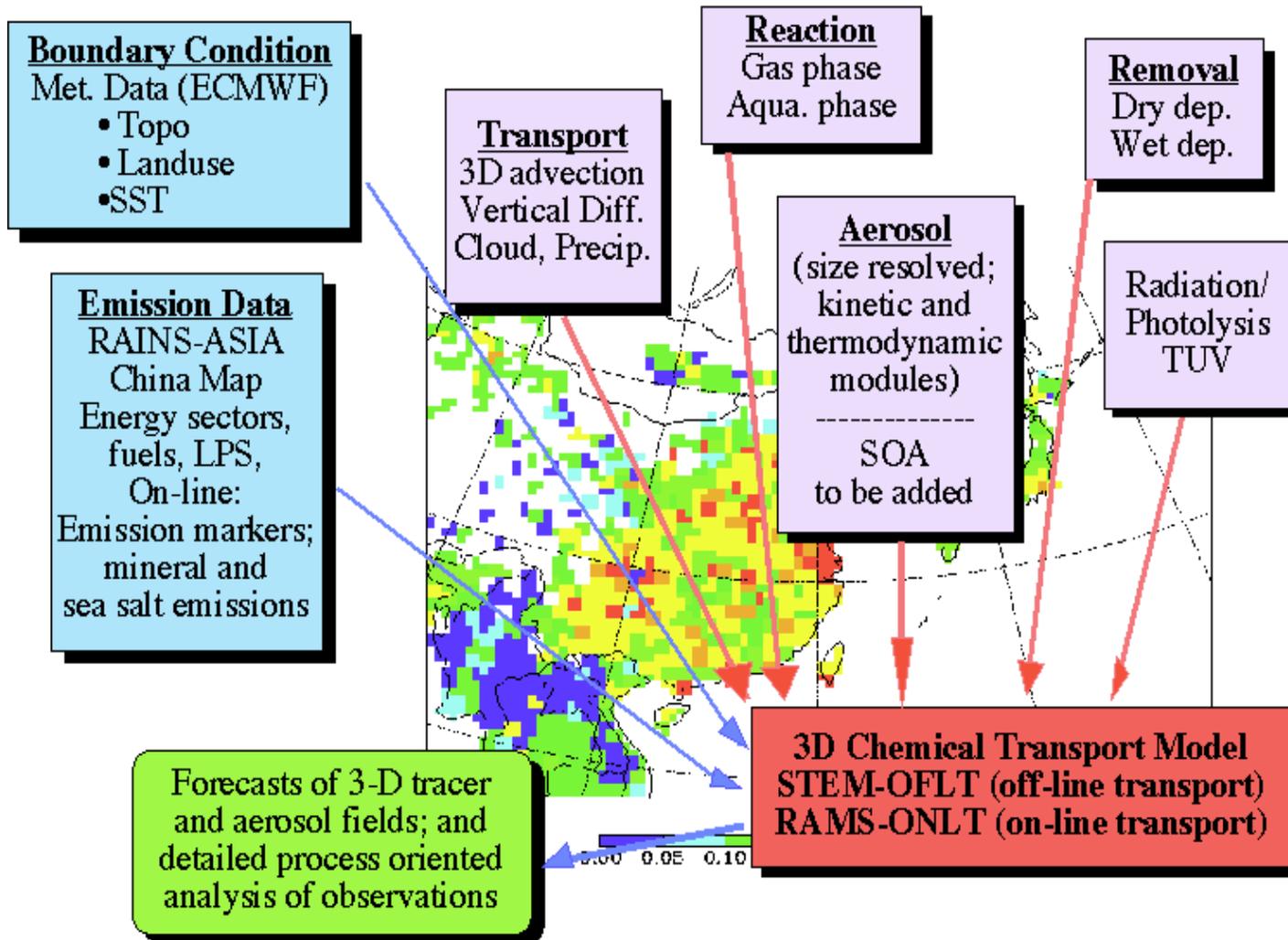
- Simulate Data
- Surface saturation
 - Diffusion

- Consider roughness factor to account for increased number of collisions

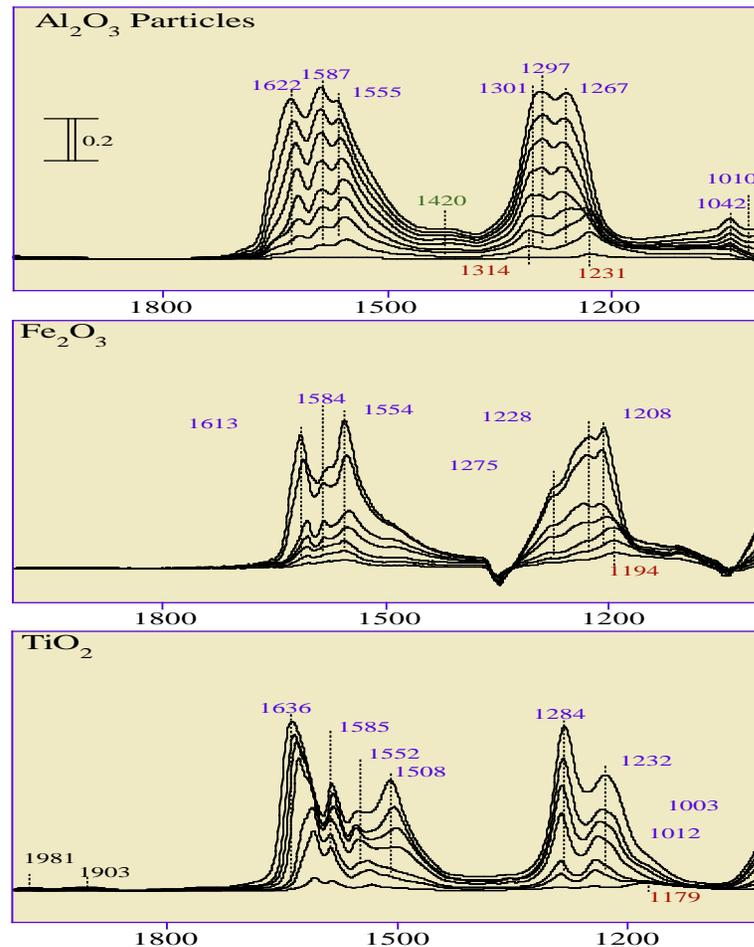
$$\frac{\text{measured surface area}}{\text{spherical surface area}} = A_{\text{BET}}/4\pi r^2$$

Three-Dimensional Combined Transport/Chemistry Analysis (STEM-III)

On/Off Line Transport Model



FT-IR spectra of dry Al_2O_3 , Fe_2O_3 and TiO_2 as a function of NO_2 exposure ($P = 0.005$ to 1.0 Torr)



NO_3^-

NO_2^-

NO

adsorbed species identified as coordinated

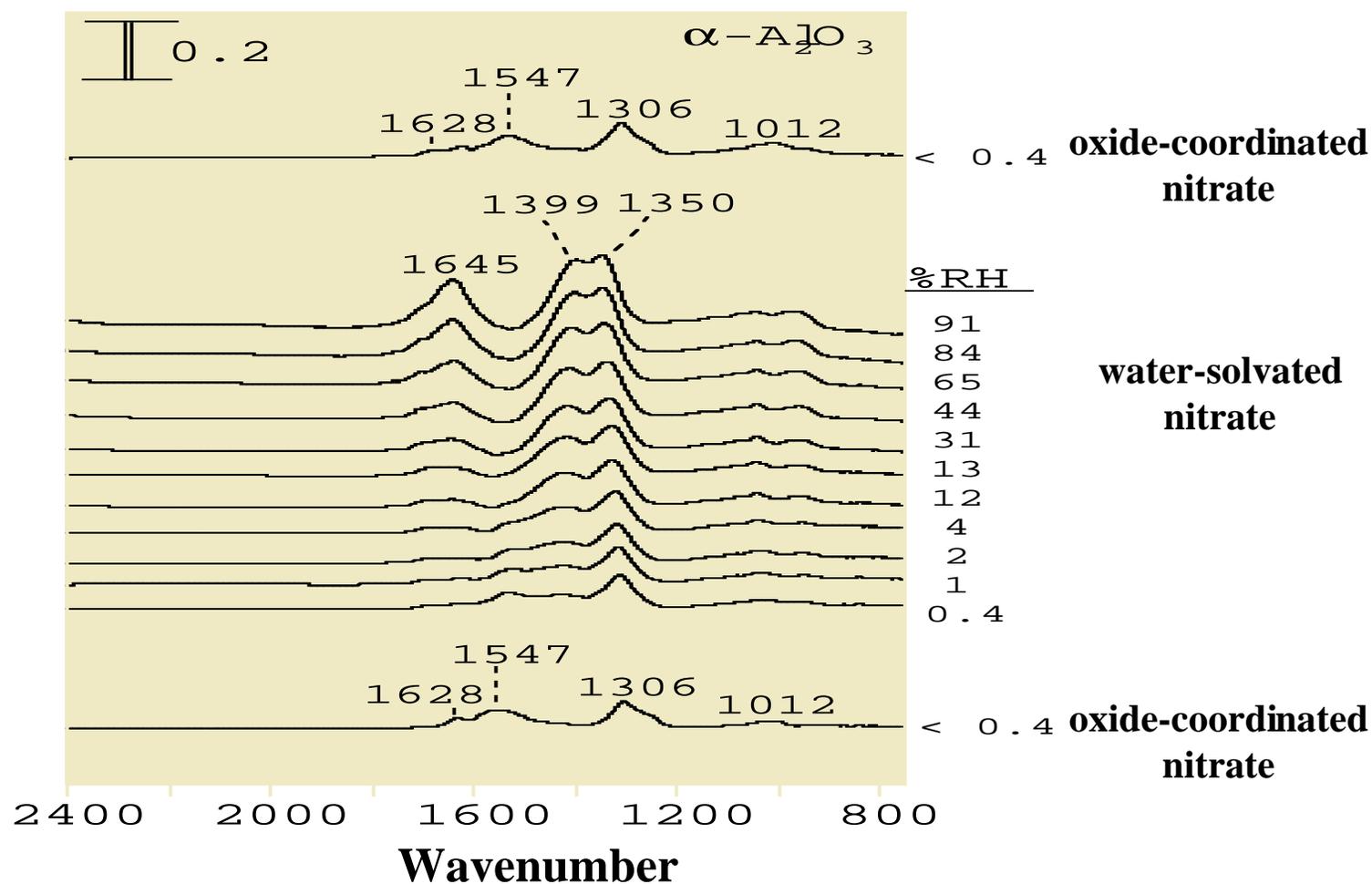
nitrate, **nitrite** and nitrosyl

Al_2O_3 : γ -alumina, $100 \text{ m}^2/\text{g}$ (Degussa)

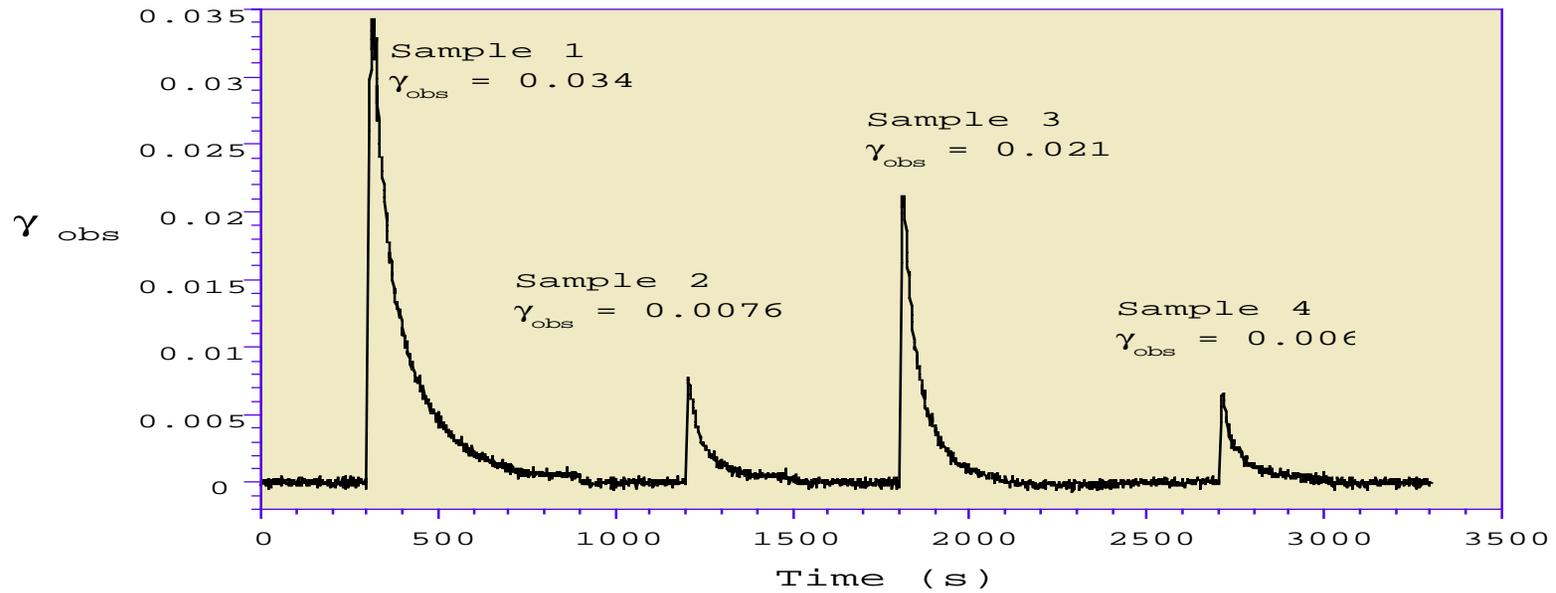
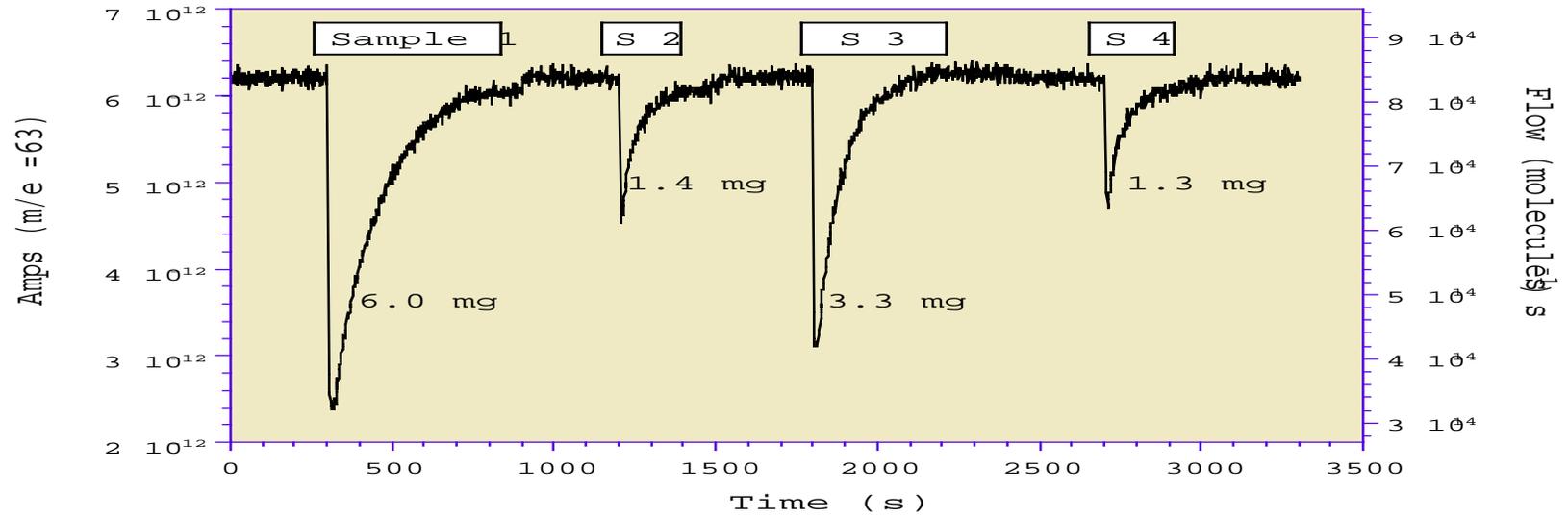
TiO_2 : P25, rutile(20%) and anatase(80%), $50 \text{ m}^2/\text{g}$ (Degussa)

Fe_2O_3 : hematite, $50 \text{ m}^2/\text{g}$ (Alfa Aesar), Fe_2O_3

Water adsorption on $\alpha\text{-Al}_2\text{O}_3$ following reaction of HNO_3

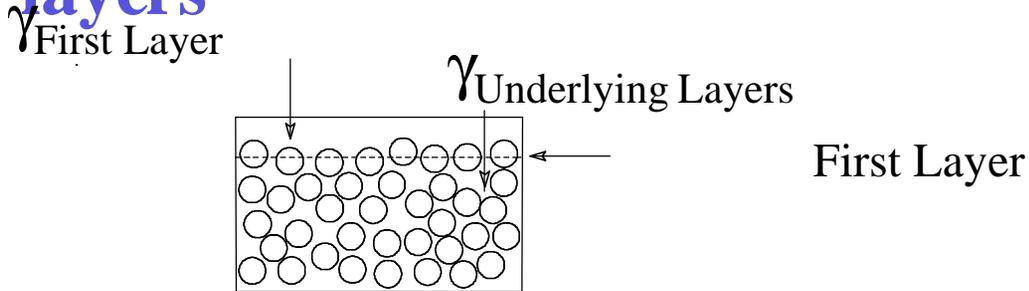


Nitric Acid Uptake on $\alpha\text{-Al}_2\text{O}_3$



Knudsen Cell Analysis for Porous Samples

- Uptake depends on surface area of first and underlying layers



Linear Mass Regime (LMR)

Simulate Data

- Surface saturation
- Diffusion

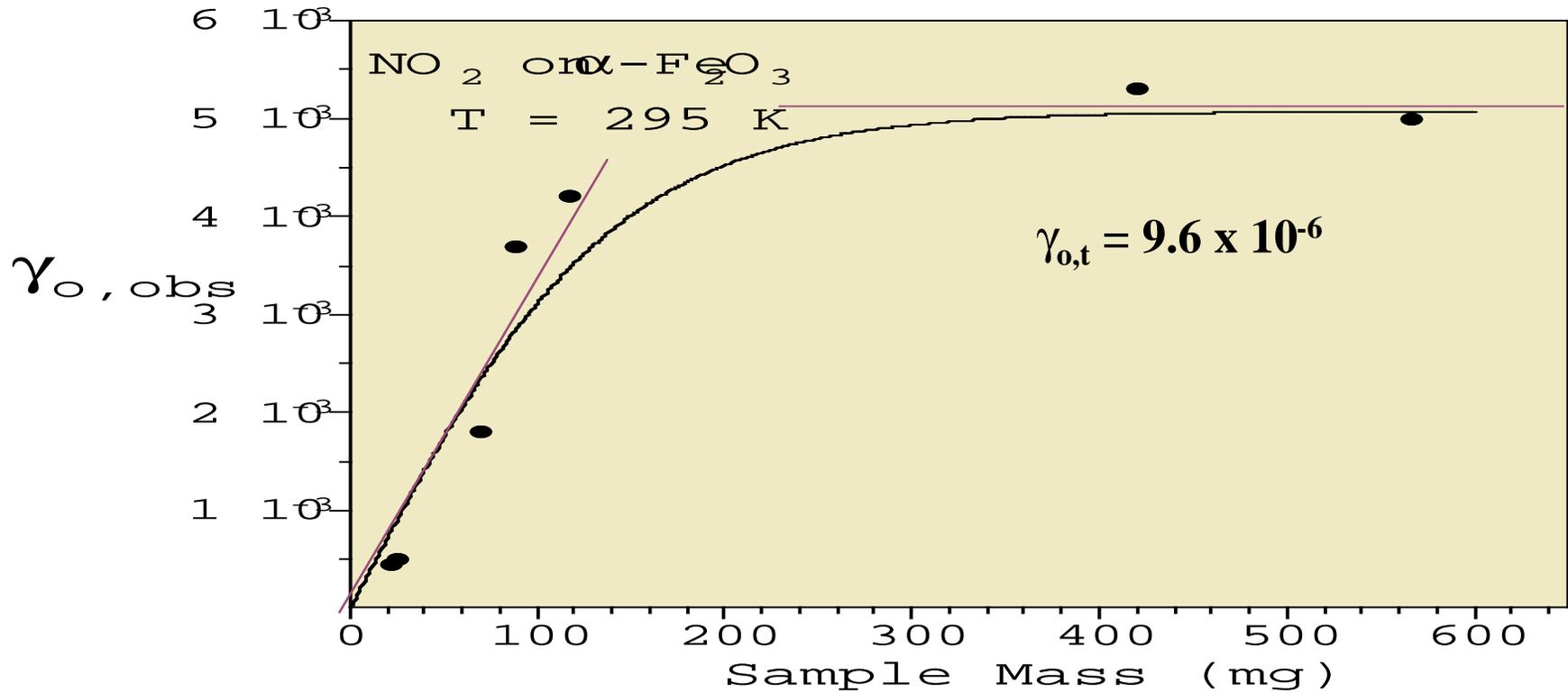
- Consider roughness factor to account for increased number of collisions

$\frac{\text{measured surface area}}{\text{spherical surface area}}$

$$= A_{\text{BET}}/4\pi r^2$$

Initial Uptake Versus Mass

Plateau Region Observed at Higher Masses

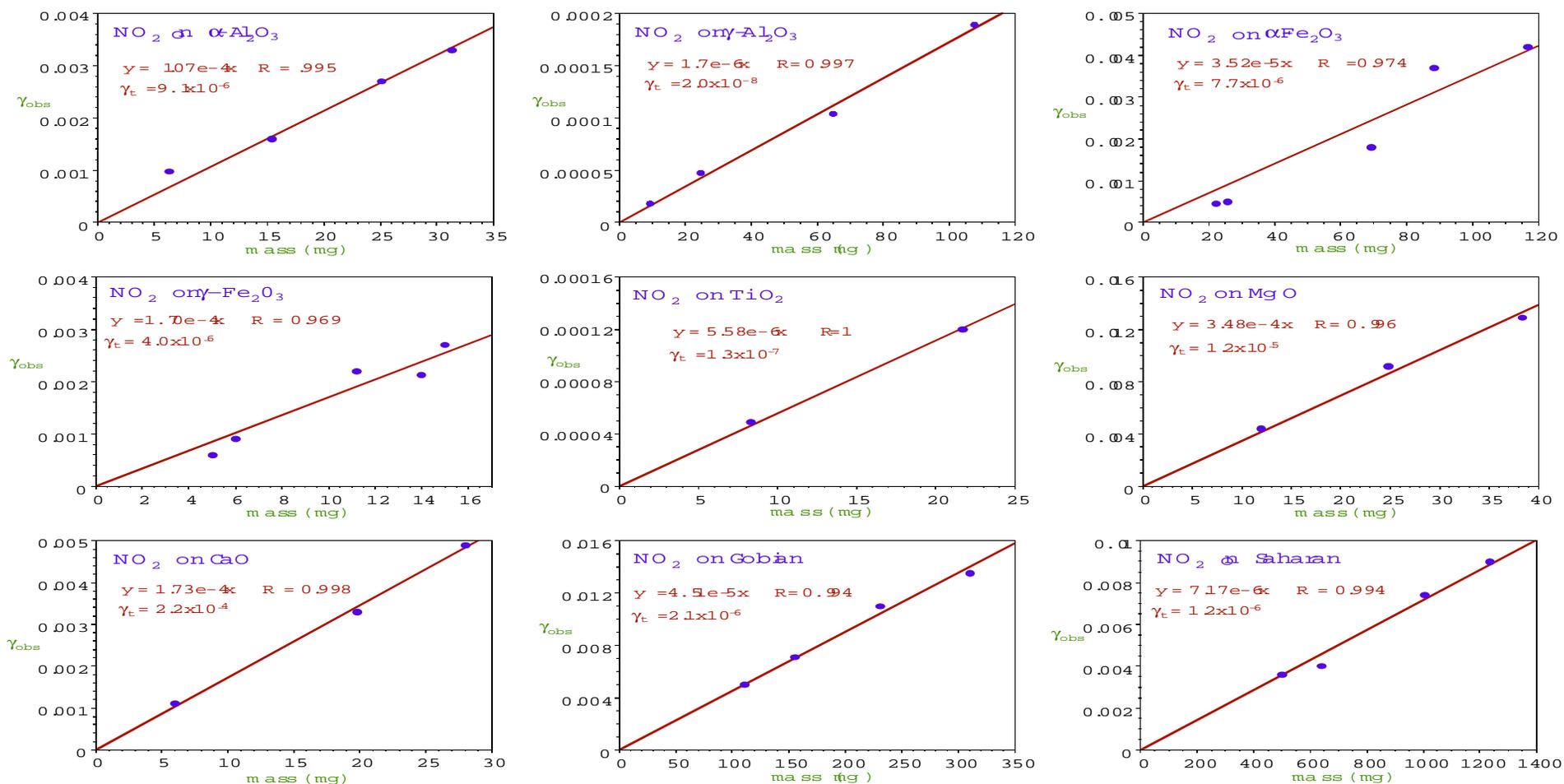


Black line through data is fit of the data to a model that accounts for diffusion into the sample. Note two regions-

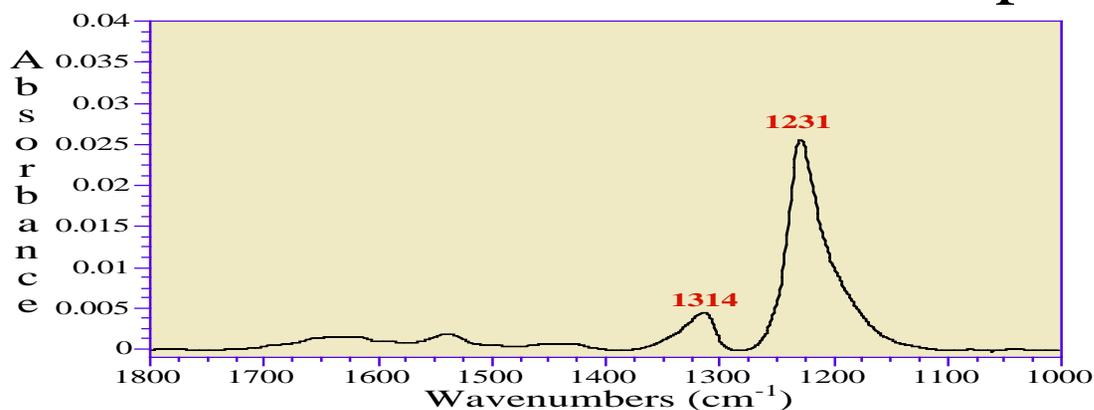
linear mass-dependent regime
plateau regime

Knudsen Cell Data-NO₂

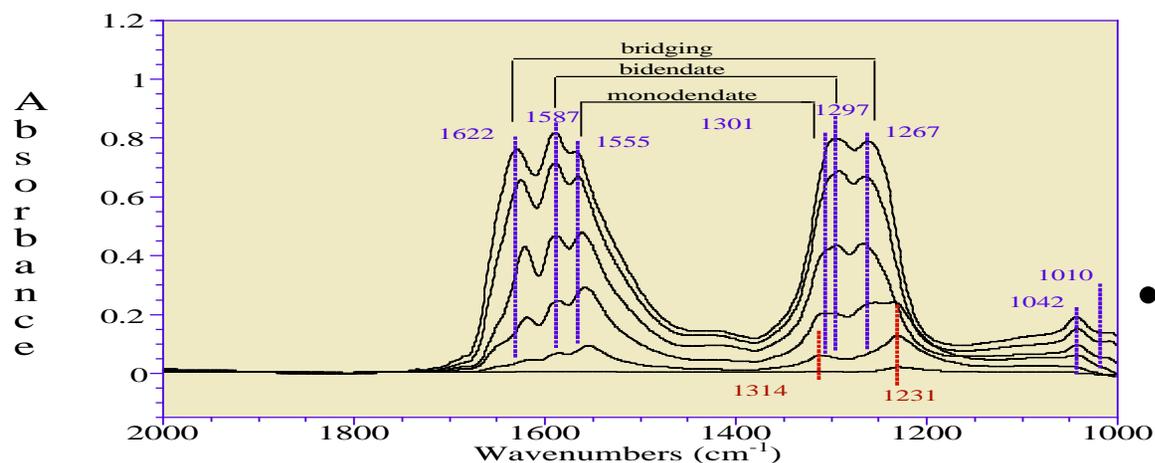
Linear Mass Regime



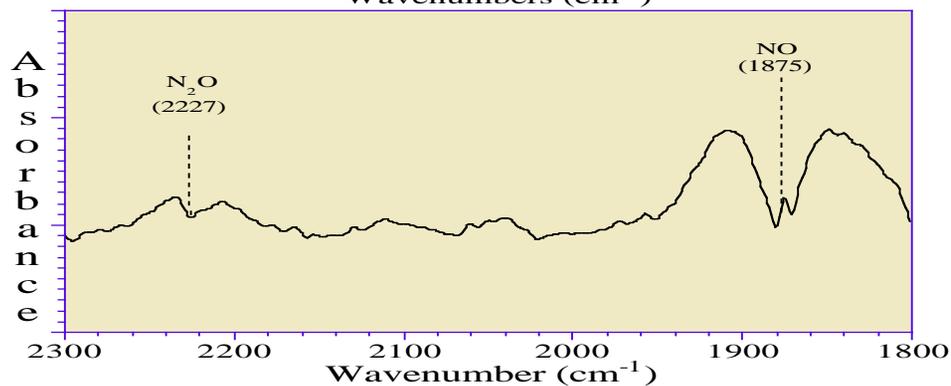
Nitrite and Nitrate on Al_2O_3 Particles from NO_2 Adsorption



- IR spectrum at low coverage consist of **nitrite** absorptions.



- IR spectra at high coverage consist of **nitrate** absorptions.



- Gas-phase products also form (NO >> NO_2)

Role of Adsorbed H₂O in Surface Reactions of Potential Atmospheric Importance

I. Heterogeneous Reaction of NO₂ on SiO₂



- HONO is produced
 - HONO is a source of OH radical,
 - The OH radical drives the daytime chemistry of the troposphere
- H₂O is a reactant
- HNO₃ is a surface-bound product

II. Heterogeneous Reaction of HNO₃ on Oxide and CaCO₃ Particles



- H₂O is a product (and medium for dissociation)
- Is the reaction limited to the particle surface?

**Initial Uptake Coefficients of NO₂ and HNO₃
Used in Atmospheric Models
- Surface Area and Roughness**

Sample	R	Adj. γ_{NO_2}	Adj. γ_{HNO_3}
SiO ₂	1	not measurable	6×10^{-6}
α -Al ₂ O ₃	9.4	9×10^{-5}	2×10^{-3}
α -Fe ₂ O ₃	1.3	1×10^{-5}	7×10^{-3}
TiO ₂	1	9×10^{-6}	1×10^{-4}
MgO	1.8	2×10^{-5}	1×10^{-3}
¹ CaO	1.7	4×10^{-6}	1×10^{-2}
¹ CaCO ₃	2.4	not measurable	2×10^{-4}
² Saharan Sand ?		R* 1×10^{-6}	R* 2×10^{-3}
China Loess	22	4×10^{-5}	1×10^{-3}

1. Strong water dependence for HNO₃ uptake
2. Large size distribution

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