

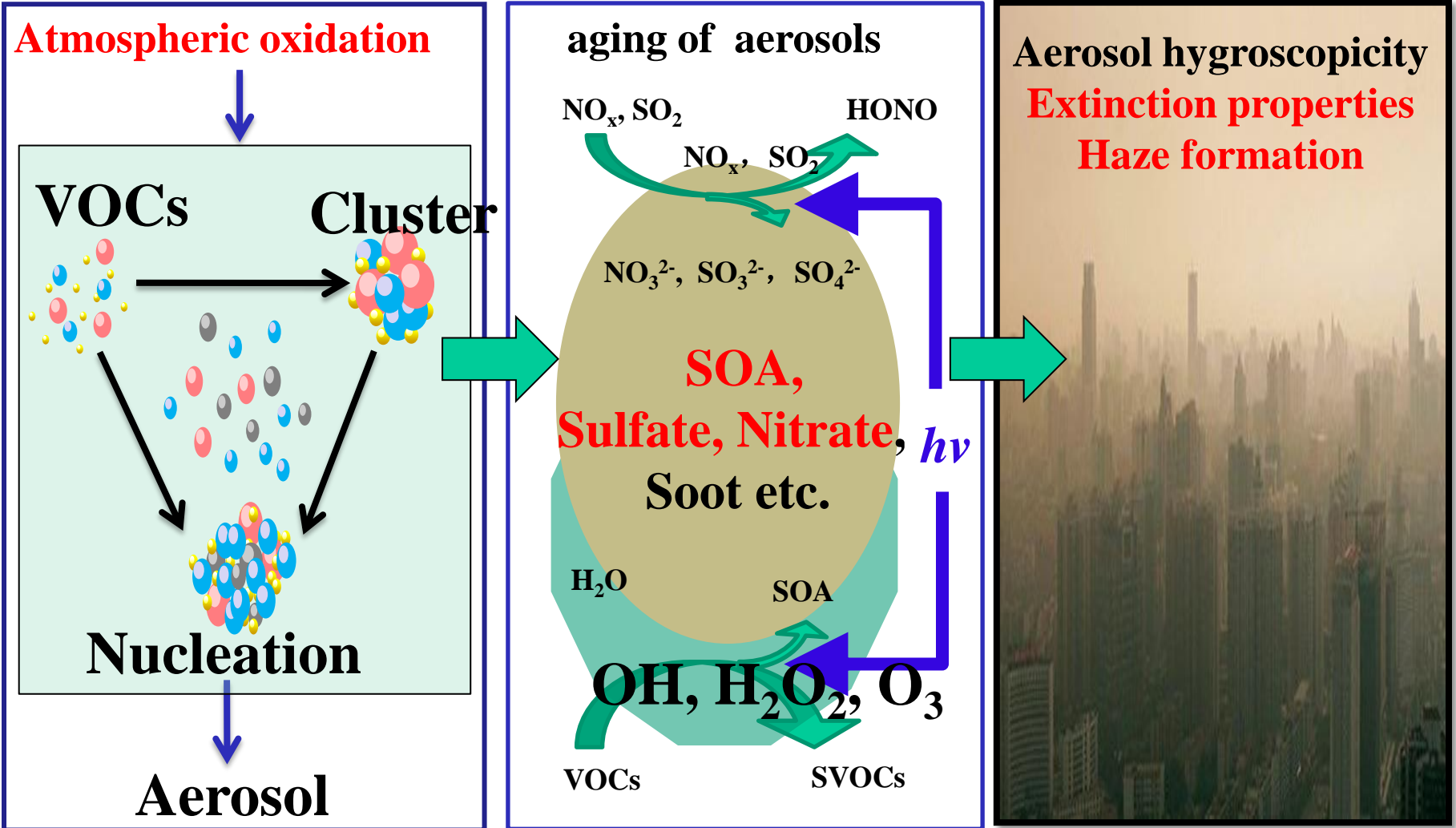
**2016 BC workshop**

**Heterogeneous Process  
Studies on the Formation of  
Secondary Aerosol**

**Maofa Ge**

**Institute of Chemistry  
Chinese Academy of Sciences  
June-27-2016**

# Aerosol Heterogeneous Chemistry



# ICCAS Platform

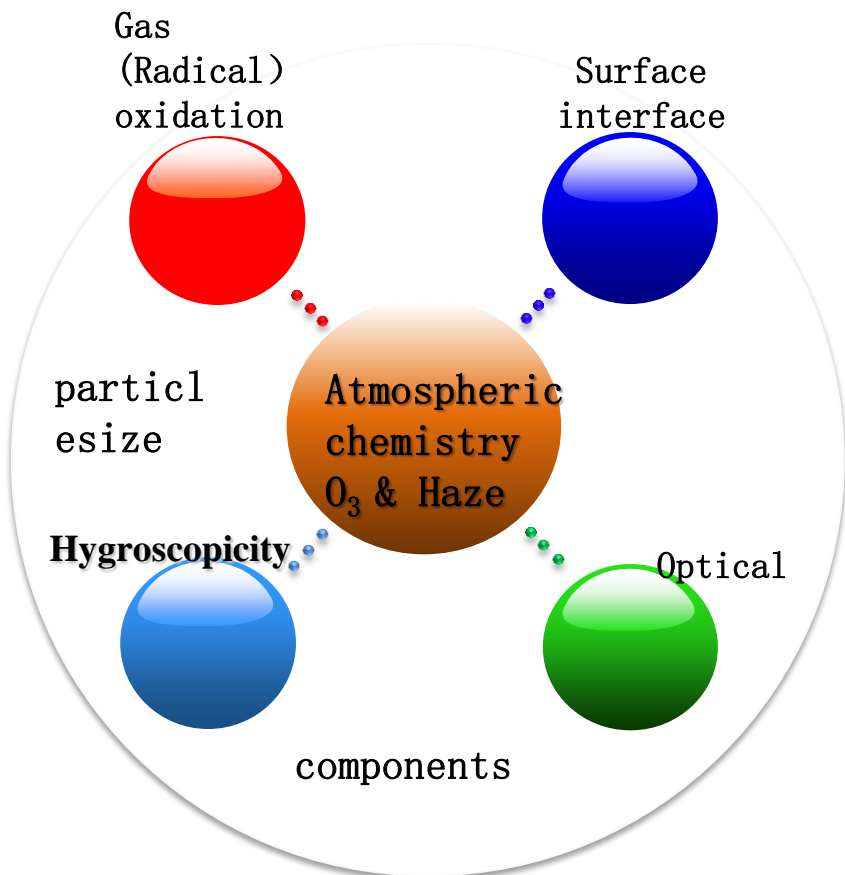
## Physical & Atmospheric chemistry

Radical chemistry  
PES-MS

Gas phase chemistry  
& Photo-oxidation  
Smog chamber

Gas-solid  
DRIFT-IR, Matrix  
IR & Raman

Gas-liquid  
VUV laser-MS  
PTR-MS



- online & long time simulations
- gas-aerosol measurements
- aerosol size, components, optics

Aerosol  
size  
DMA-CPC

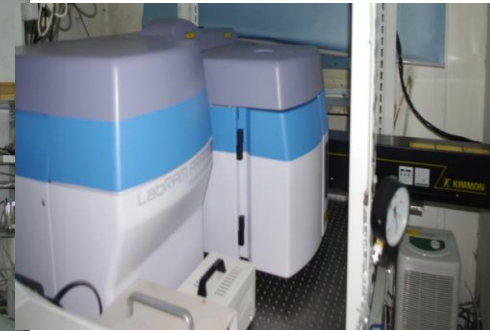
Aerosol  
Chemical component  
CI-MS

Aerosol  
Optical Property  
CRDS

Aerosol  
Hygroscopicity  
H-TDMA

# ICCAS Platform

**aerosol : size/components/optics**



**EI-MS**

**Flow Tube; Knudsen cell**

**DRIFT-IR**

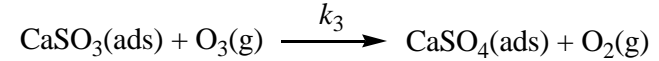
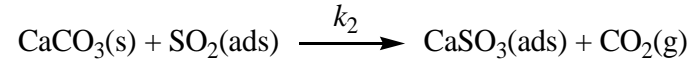
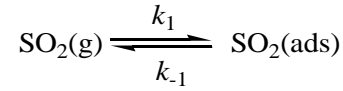
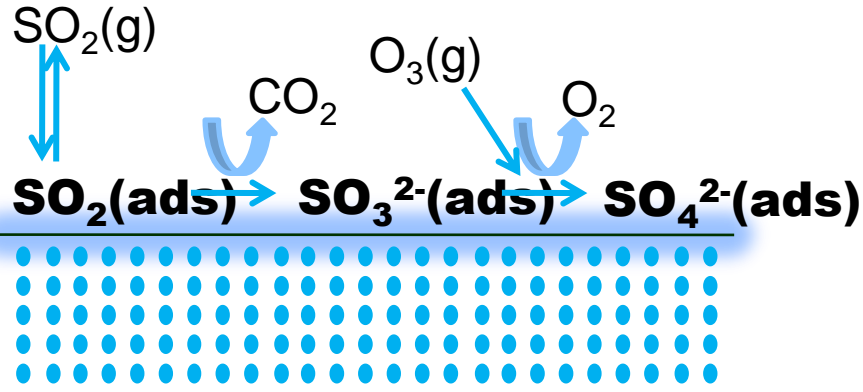
**Raman**



**Gas-solid/liquid reaction, kinetics**  
**cavity ring down spectrometry: aerosol extinction**

**H-TDMA**

# Gas-solid kinetics: Mechanism



$$r = \frac{d\{\text{SO}_4^{2-}\}}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [\text{SO}_2] = k[\text{SO}_2]$$

$$k = \frac{k_1 k_2}{k_{-1} + k_2}$$

Limiting cases :  $k = \frac{k_1 k_2}{k_{-1} + k_2}$

(1) 当  $k_{-1} \ll k_2$  时,  $k = k_1$ ; **250-230K**

$$E_a = RT^2 \frac{d \ln k}{d(1/T)} = RT^2 \frac{d \ln k_1}{d(1/T)} = E_{a1}$$

The apparent activation energy :  $14.63 \pm 0.20$  kJ/mol

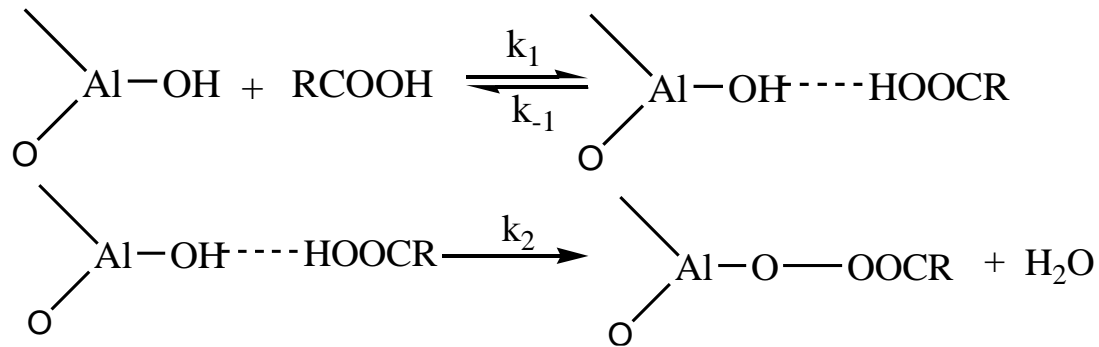
(2) 当  $k_2 \ll k_{-1}$  时,  $\frac{k_1 k_2}{k_{-1}} = K k_2$  ; **298-250K**

$$E_a = RT^2 \frac{d \ln k}{d(1/T)} = RT^2 \frac{d \ln (K k_2)}{d(1/T)} = RT^2 \frac{d \ln (K)}{d(1/T)} + RT^2 \frac{d \ln (k_2)}{d(1/T)} = \Delta H_{ads} + E_{a2}$$

**The balance between the two limiting cases can be used to interpret the turning point on the rate of sulfate formation.**

# Gas-solid kinetics: Mechanism

## Organic acid on mineral dust



Heterogeneous process: Important

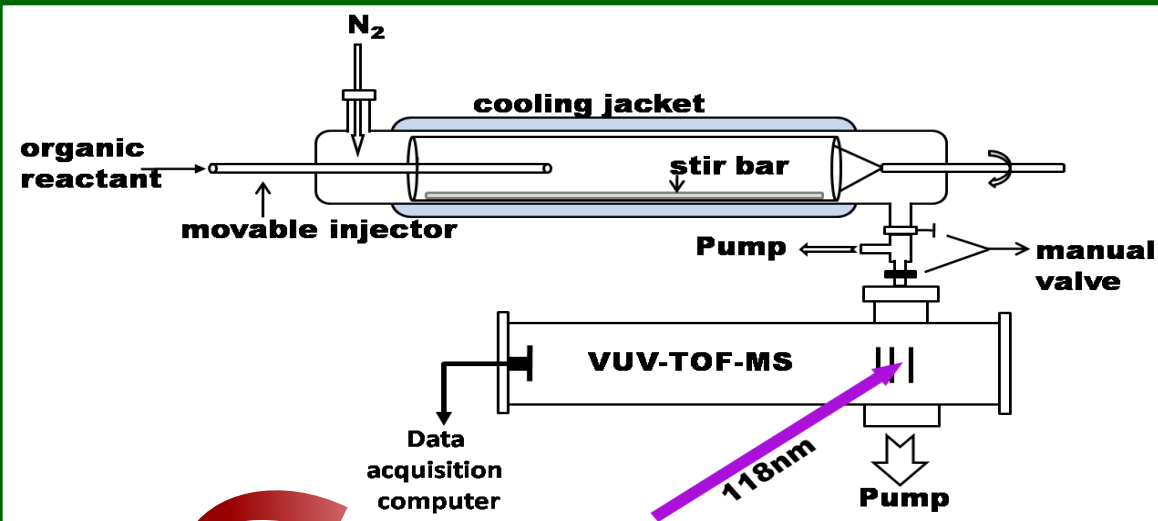
### Atmospheric lifetime

	dust	OH
HCOOH	8-13h	86 days
CH <sub>3</sub> COOH	4-5h	46days

$$\tau = \frac{4}{\gamma \langle v \rangle SA} \quad SA = 150 \mu\text{m}^2 \text{cm}^{-3}$$

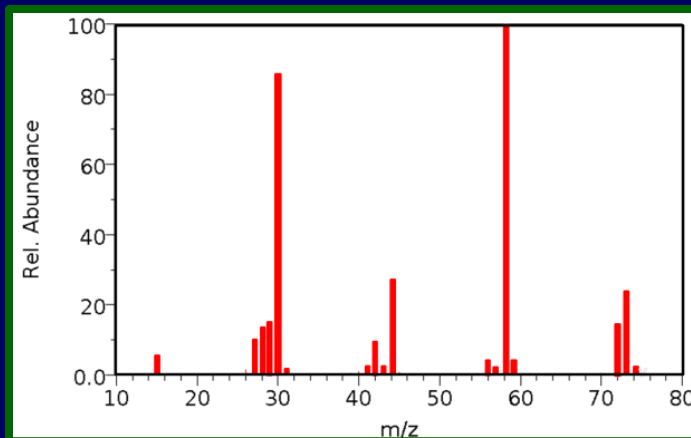
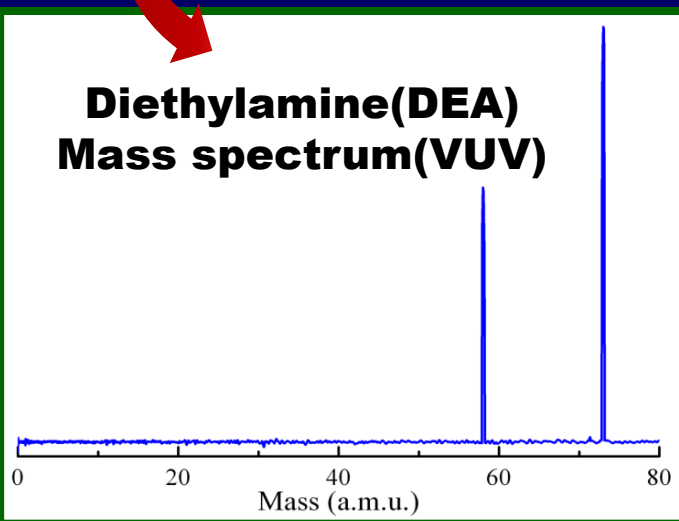


# Gas-liquid Kinetics



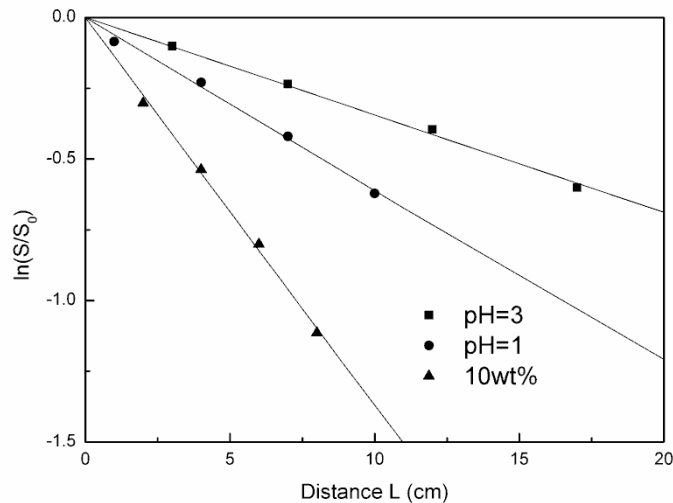
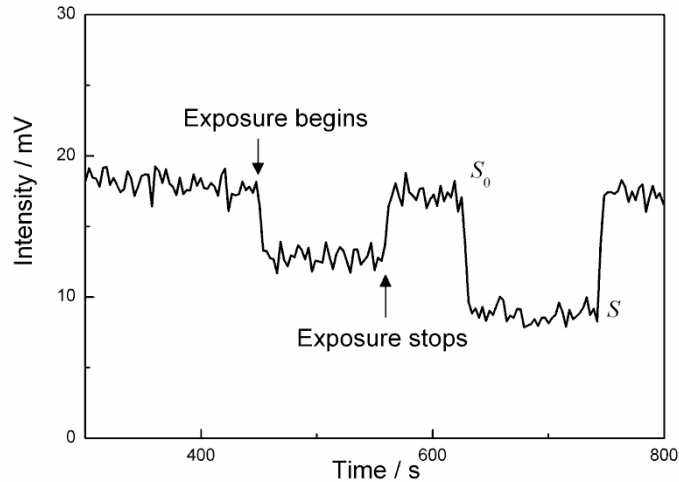
**Schematic diagram of experimental setup  
Rotating Wetted-Wall Flow Tube PIMS**

**Diethylamine(DEA)  
Mass spectrum(VUV)**



**NIST:DEA MS (EI)**

# Gas-liquid Kinetics



**First-order rate  $k_{obs}$ :**

$$\ln(S / S_0) = -k_{obs} L / v_{ave}$$

**Diffusion-limited rate  $k_{diff}$ :**

$$k_{diff} = 3.66 D_i / r^2$$

**Surface rate constant  $k$ :**

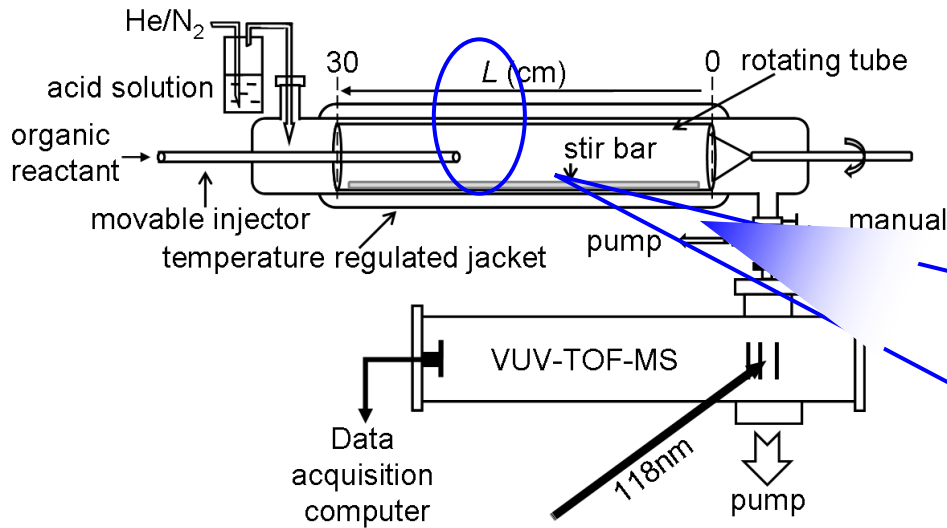
$$1 / k = 1 / k_{obs} - 1 / k_{diff}$$

**Reactive uptake coefficient:**

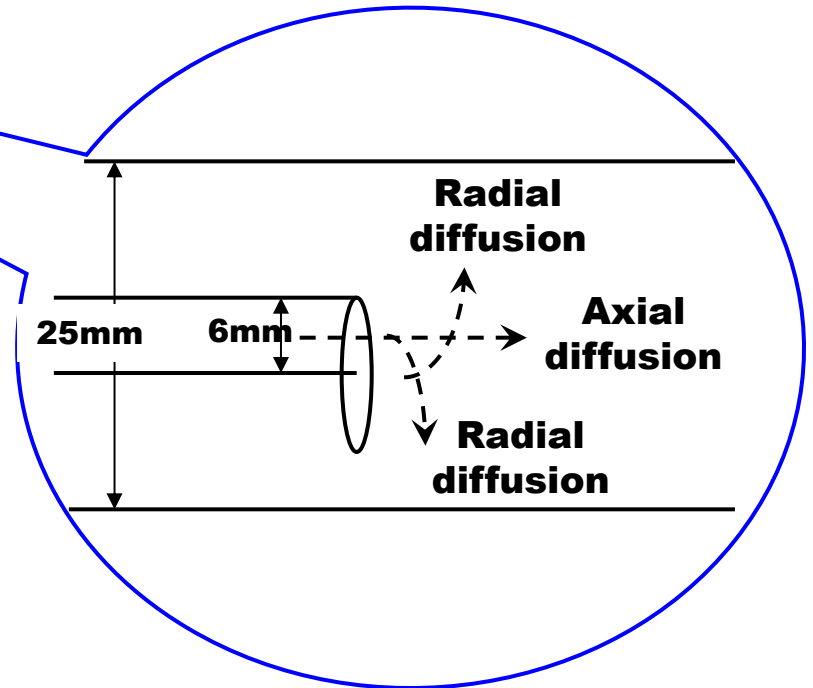
$$\gamma = \frac{4kV}{wA}$$



# Gas-liquid Kinetics



**Restrain diffusion  
Is possible!**



## ➤ Axial diffusion

If The system Peclet Number **sufficiently large** the axial **diffusion** velocity will be much less than the **flow** velocity

$$Pe = 2rv/D_i; \quad Pe \geq 10 \text{ is necessary,}$$

$$k_{diff} = K_d \cdot D_i / r^2 \quad (K_d = 3.66)$$

## ➤ Radial diffusion

The precondition:  $k_{obs} < k_{diff} / 2$

$$0.5 < k_{obs} / k < 1$$

**Carefully design !**

# Epoxide

- The uptake of two epoxides under different pressures :

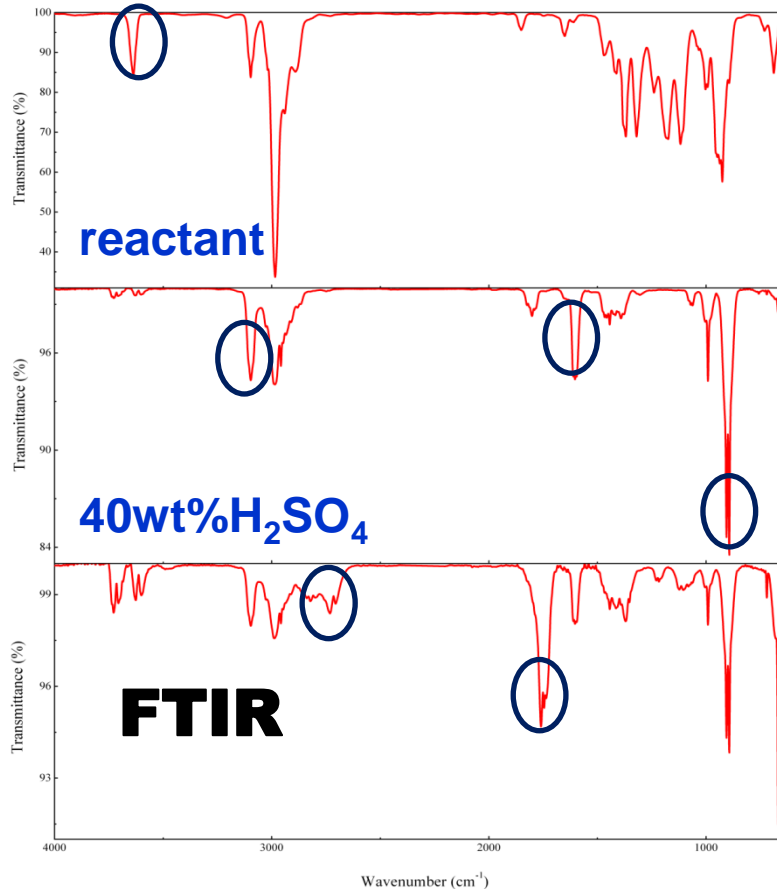
	H <sub>2</sub> SO <sub>4</sub>	P(Torr)	$\gamma \pm 1\sigma (\times 10^{-5})$
isoprene epoxide	pH=3	180.0	$1.89 \pm 0.14$
		46.0	$1.87 \pm 0.09$
butadiene diepoxide	pH=7	131.0	$8.78 \pm 0.21$
		65.5	$8.49 \pm 0.15$

- Using rotating cylinder with inner radius of 8 mm for isoprene epoxide

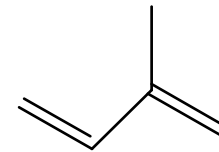
		$r = 12.5 \text{ mm}$		$r = 8.0 \text{ mm}$		
H <sub>2</sub> SO <sub>4</sub>	P (Torr)	$k_{diff}$	$\gamma \pm 1\sigma (\times 10^{-4})$	P (Torr)	$k_{diff}$	$\gamma \pm 1\sigma (\times 10^{-4})$
pH=3	180.0	0.976	$0.189 \pm 0.014$	46.0	18.354	$0.189 \pm 0.006$
1 wt %	48.2	3.510	$2.78 \pm 0.083$	26.2	26.734	$2.81 \pm 0.057$
10 wt %	27.1	10.336	$7.99 \pm 0.116$	25.2	28.901	$8.14 \pm 0.180$

# Role of $\text{H}_2\text{O}_2$ : $\text{MBO} + \text{H}_2\text{SO}_4$

**MBO: 2-methyl-3-buten-2-ol**

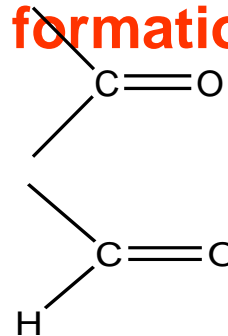


- ◆  $\text{H}_2\text{SO}_4$   
OH disappear  
C=C increase



GC:  
5.778s (5.77s)

- ◆  $\text{H}_2\text{SO}_4$ -1wt% $\text{H}_2\text{O}_2$   
OH disappear, **HC=O**  
**formation**

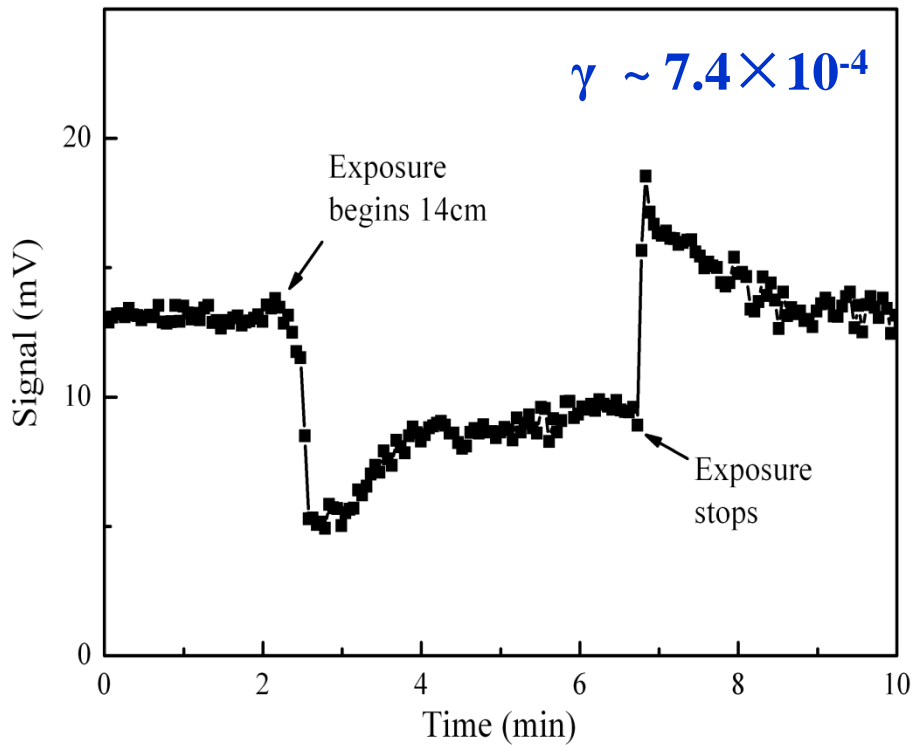


GC:  
5.264s (5.273s)

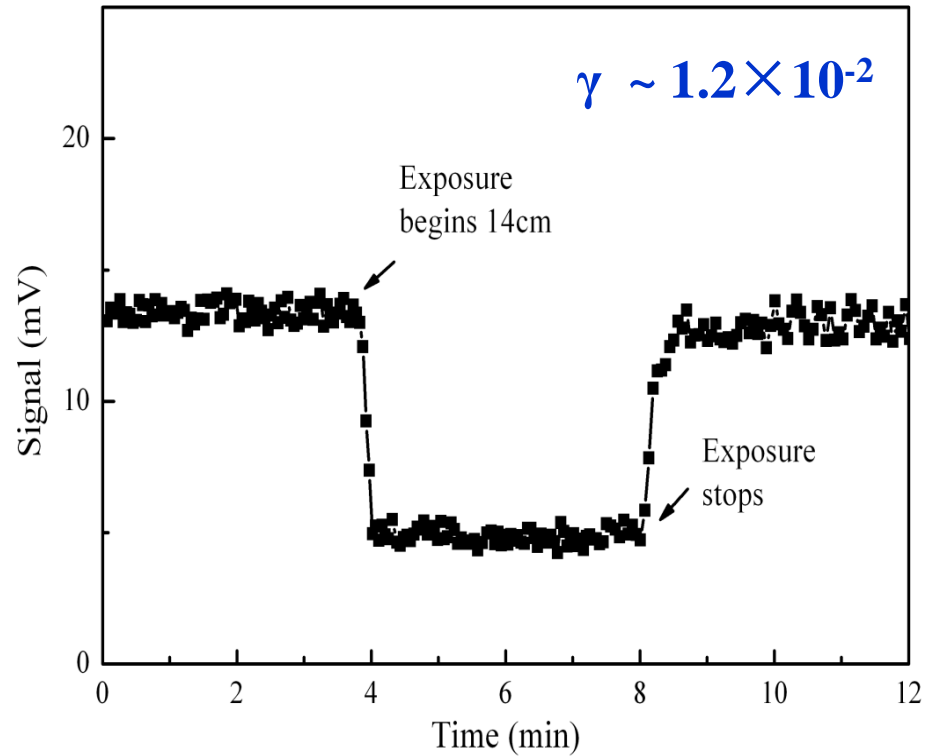
IR/GC/MS; with  $\text{H}_2\text{O}_2$ :

formation aldehyde and ketone; and polymerization;  
SVOC and **SOA formation**

# Role of $\text{H}_2\text{O}_2$ : $\text{MBO} + \text{H}_2\text{SO}_4$



$\text{H}_2\text{SO}_4$  solution

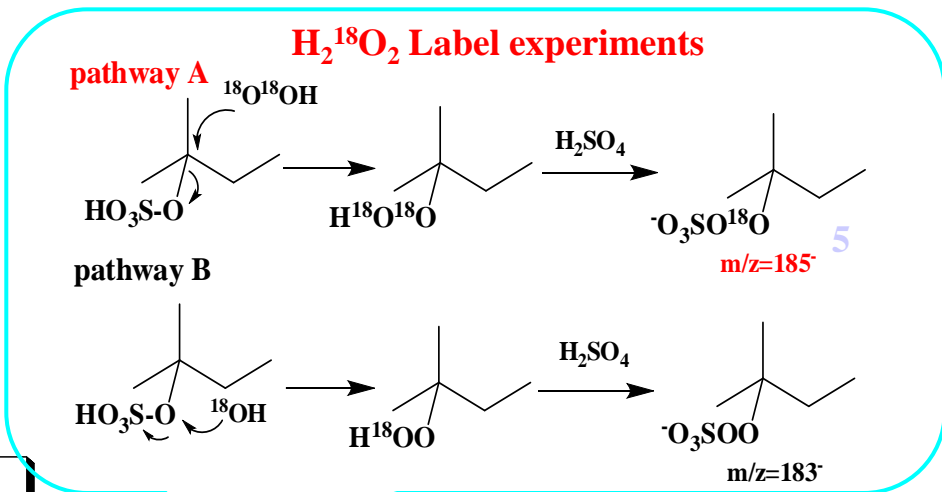
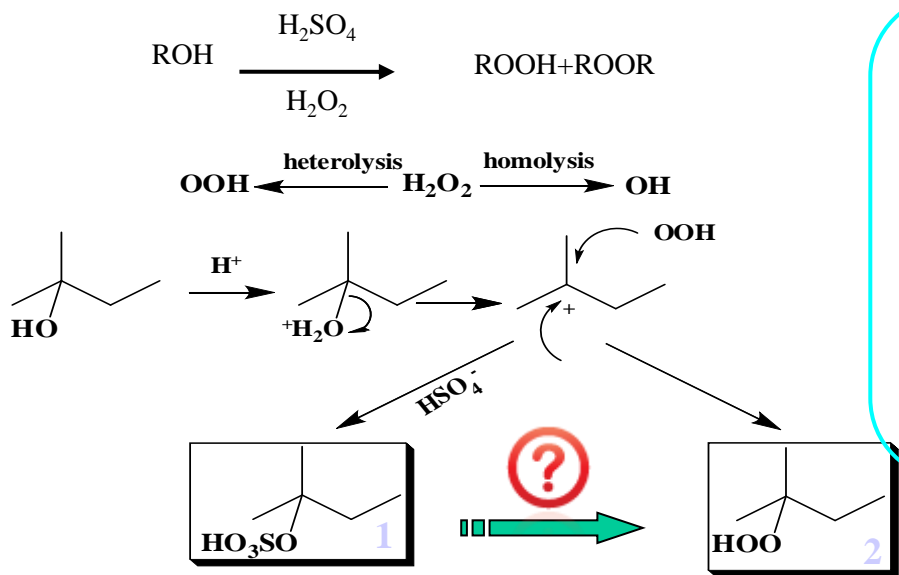


$\text{H}_2\text{SO}_4 - (1/4\text{wt}\%)\text{H}_2\text{O}_2$

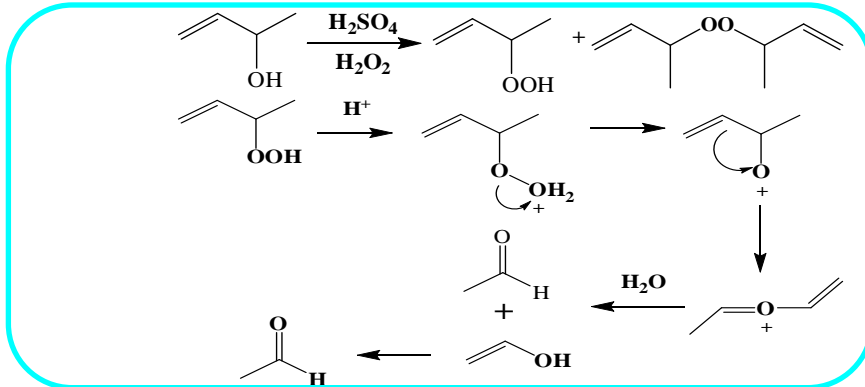
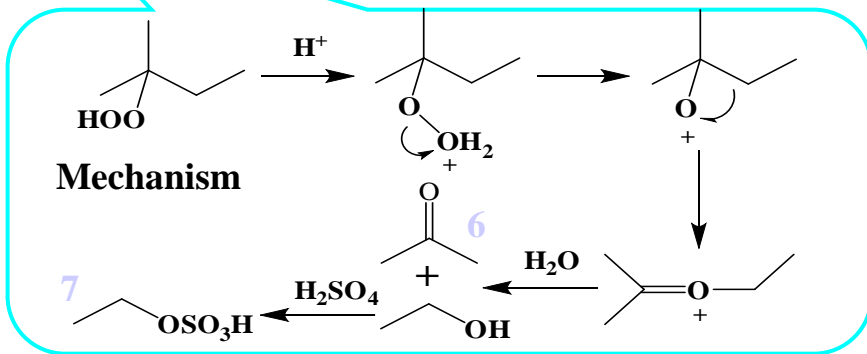
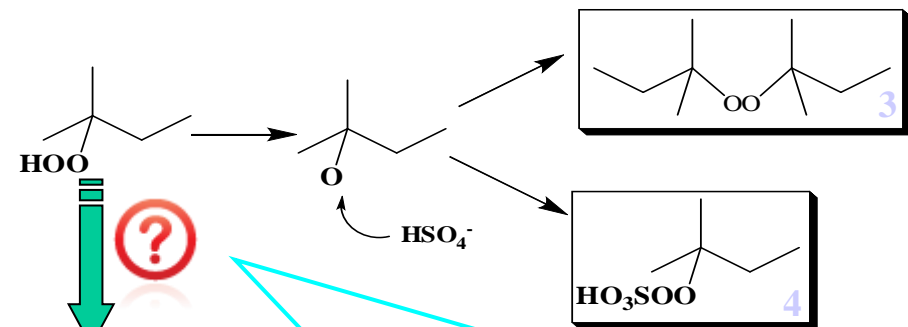


Uptake: increase 16 times!

# Main route and product



product	1, 4, 5, 7	2	3	6
	ESI-MS	VUV-TOF-MS GC-MS	GC-MS	VUV-TOF-MS IR

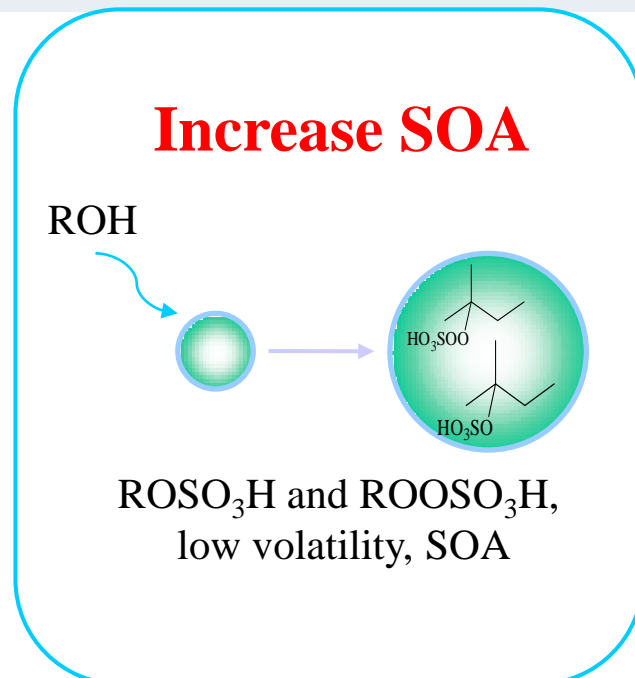
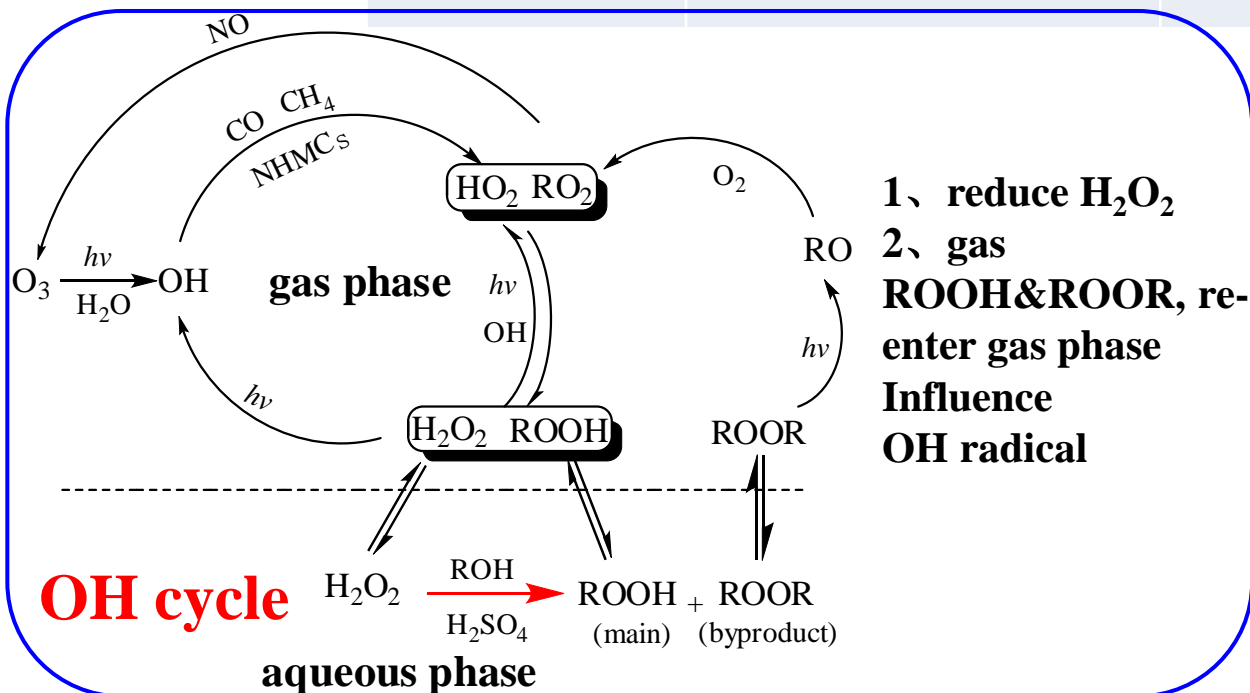




# New insight

**ROH**  
Atmospheric  
Chemistry

ROOH	source	sink
Past	main $HO_2 + RO_2 \longrightarrow ROOH$ $O_3 + \text{alkene} \longrightarrow ROOH$ less By burning	Gas phase $ROOH \xrightarrow{h\nu} RO + OH$ $ROOH \longrightarrow \text{干、湿沉降}$ $ROOH \xrightarrow{OH} RO_2 + H_2O$ Liquid phase Oxidation $SO_2$ Reaction with M
present	$ROH \xrightarrow[H_2O_2]{H_2SO_4} ROOH$	$ROOH \xrightarrow[H_2O_2]{H_2SO_4} ROOSO_3H$ $ROOH \xrightarrow{\text{重排}} \text{Acetone}$





# Smog chamber simulation

## Real atmospheric conditions



### Chamber

70L , 3000 L, 2X(5m<sup>3</sup>)  
FEP Teflon film

- \* Reaction rate
- \* Mechanism



# Atmospheric lifetime(EVE/PVE)

$$\tau = 1 / (k_x [X]), \quad x = \text{OH}, \text{NO}_3, \text{O}_3, \text{Cl}$$

	concn/mol cm <sup>-3</sup>		T
OH	$9.7 \times 10^6$		h
NO <sub>3</sub>	$7.4 \times 10^6$		7h
O <sub>3</sub>	$7.4 \times 10^6$		h
Cl	$5.0 \times 10^6$		6h
	concn/mol cm <sup>-3</sup>		
OH	$9.7 \times 10^6$		4h
NO <sub>3</sub>	$7.4 \times 10^6$		3h
O <sub>3</sub>	$7.4 \times 10^{11}$		h
Cl	$5.0 \times 10^3$	$4.3 \times 10^{-10}$	129.2h

Kinetics Database

NIST  
National Institute of Standards and Technology

Kinetics Database Resources

Author(s): Du, L.; Xu, Y.F.; Ge, M.F.; Jia, L.; Yao, L.; Wang, W.G.  
Title: Rate constant of the gas phase reaction of dimethyl sulfide (CH<sub>3</sub>SCH<sub>3</sub>) with ozone

Journal: Chem. Phys. Lett.  
Volume: 436  
Page(s): 36 - 40  
Year: 2007

Reference type: Journal Squib: 2007DU/XU36-4

Simple Reaction Search

Kinetics Database

Search Reaction Database

Reaction: (CH<sub>3</sub>)<sub>2</sub>S + O<sub>3</sub>

Reaction order: 2  
Temperature: 301 K  
Pressure: 1.01E5 Pa

Rate expression: 1.04x  
Category: Experiment

Data type: Absolute value  
Pressure dependence: ?

Experimental procedure: ?  
Excitation technique: TI

Time resolution: By end  
Analytical technique: V

Comments: Reaction rate large excess of DMS to determine important for the loss of DM

View full bibliographic record

Set Unit Preferences

Feedback

Rate Our Products and Services

Help

Other Databases

NIST Standard Reference Data Program

Simple Reaction Search

Search Reaction Database

Search Bibliographic Database

Set Unit Preferences

Feedback

Rate Our Products and Services

Author(s): Du, L.; Xu, Y.F.; Ge, M.F.; Jia, L.; Wang, G.C.; Wang, D.X.

Title: Determination of rate constants for ozone reactions with acetylene under atmospheric conditions

Journal: Acta Chim. Sin.  
Volume: 64

Page(s): 2133 - 2137  
Year: 2006

Reference type: Journal article  
Squib: 2006DU/XU2133-2137

Reaction: C<sub>2</sub>H<sub>2</sub> + O<sub>3</sub> → Products

Reaction order: 2  
Temperature: 288 K  
Pressure: 1.01E5 Pa

Rate expression:  $4.13 \times 10^{-21} [\text{cm}^3 \text{ molecule}^{-1} \text{ s}]$

Category: Experiment

Data type: Absolute value measured directly

Experimental procedure: Static or low flow - Data taken vs time

Excitation technique: Discharge

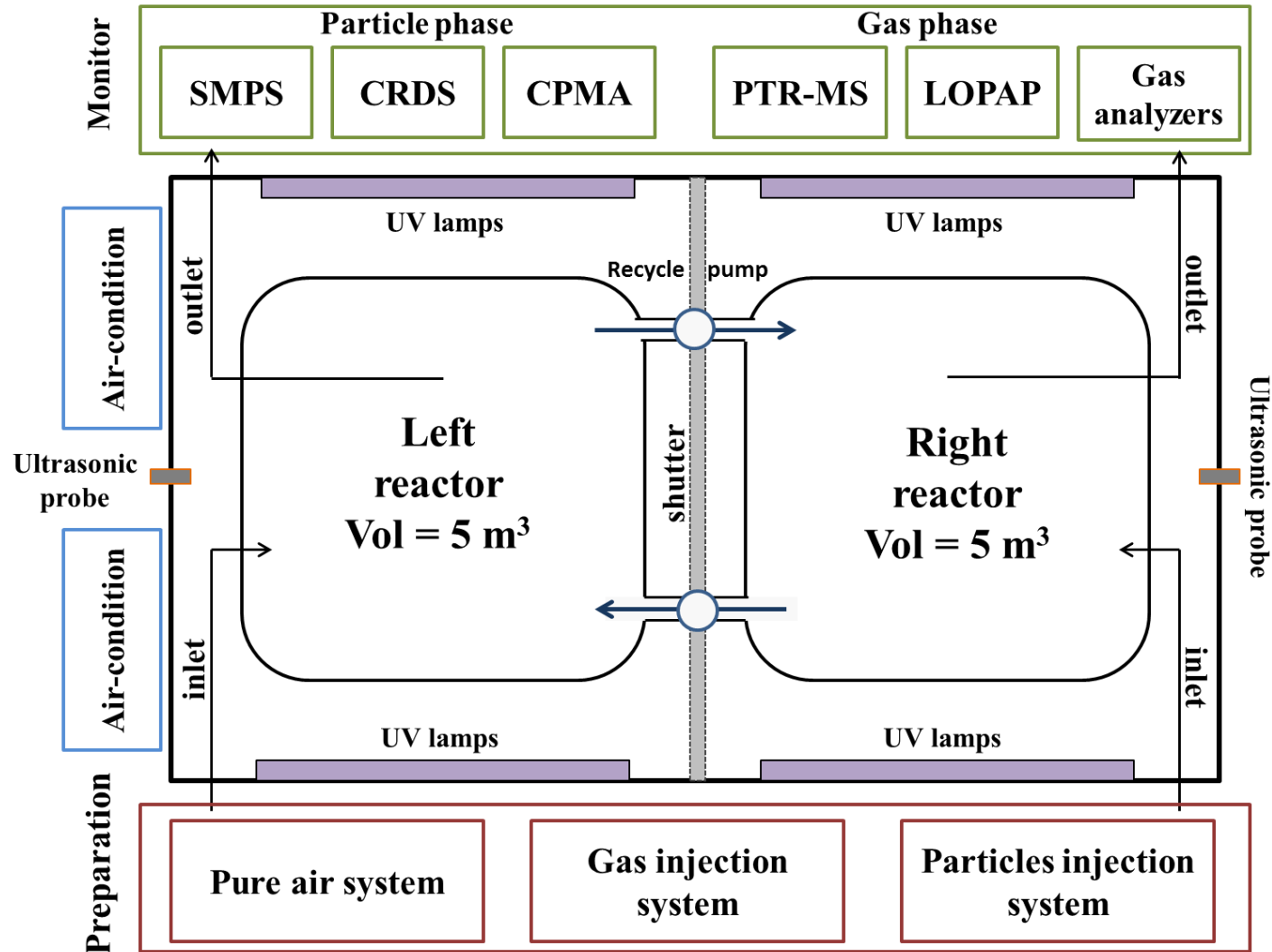
Time resolution: In real time

Analytical technique: Gas chromatography

View full bibliographic record.

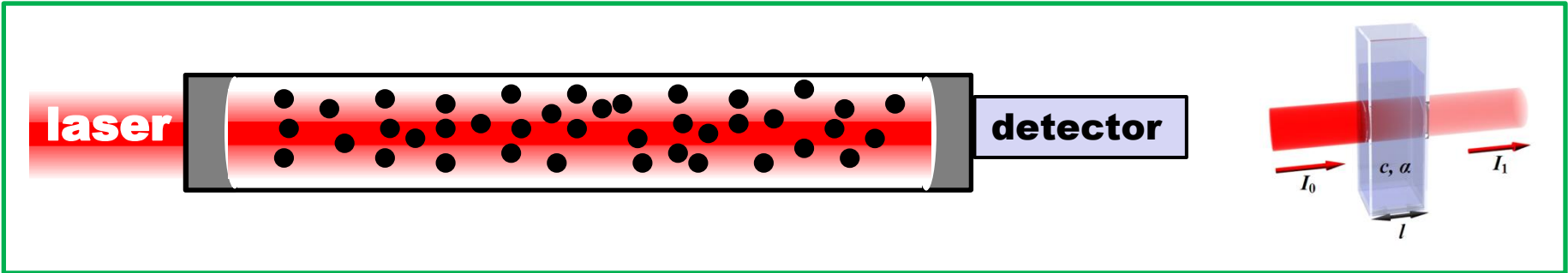
NIST  
National Institute of Standards and Technology

# ICCAS-TRC (twin-reactor chamber)



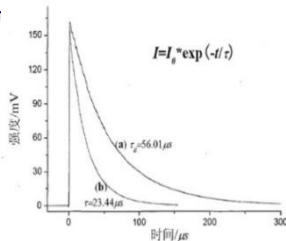
Smog chamber with various instruments for gas and particle measurements

# Cavity ring down spectroscopy



CRDS consists of **two highly reflective concave mirrors** with a reflectivity of 99.995%

**The extinction coefficient is computed** by comparing the **decay time ( $\tau$ )** of a pulse laser trapped in the resonator both with and without aerosol



$$\alpha_{\text{ext}} = \frac{L}{cd} \left( \frac{1}{\tau_0} - \frac{1}{\tau} \right)$$

$$\alpha_{\text{ext}} = N\sigma_{\text{ext}} = \frac{1}{4} \pi D^2 N Q_{\text{ext}}$$

## Advantages

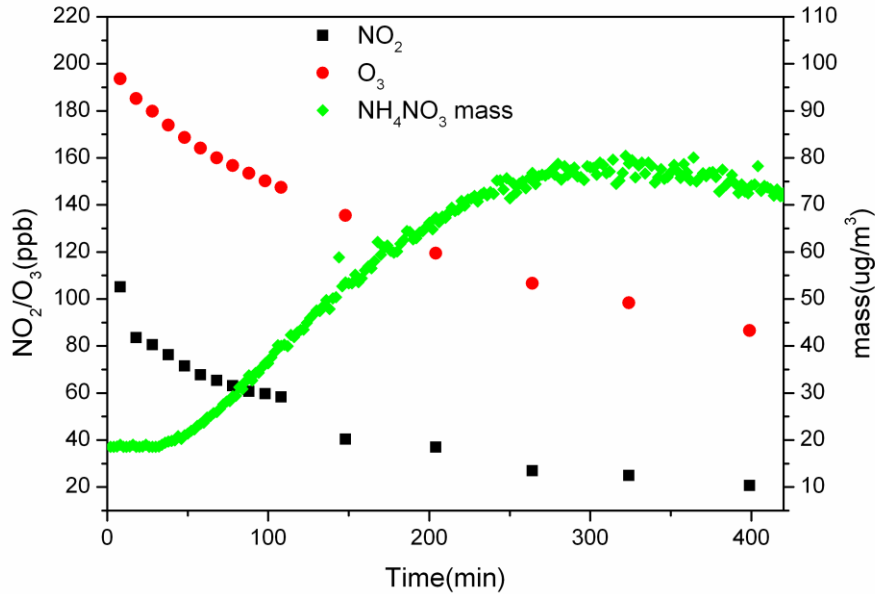
**@immune to shot-to-shot : variations of the laser intensity**

**@measuring the absolute extinction of aerosol sample ; without instrument calibration**

**@high sensitivity**

**@long effective path length**

# Ammonium nitrate formation

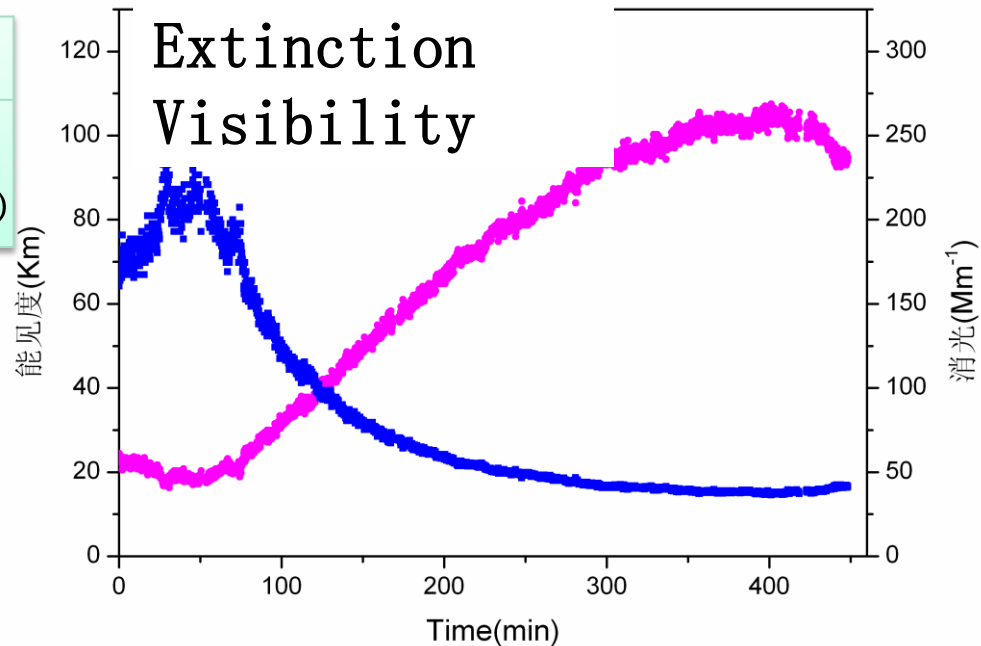


Smog chamber:  
 RH < 30%, rich  $\text{NH}_3$   
 $\text{NO}_2$ ,  $\text{O}_3$  and seed aerosol  
 $\text{NH}_4\text{NO}_3$  increase  
 continue 7 hour

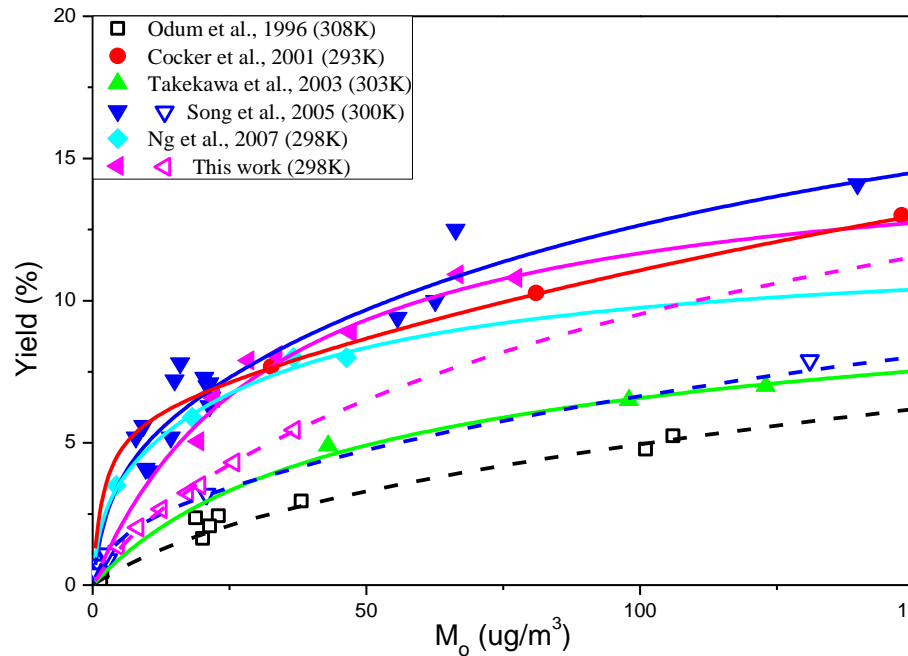


	$\text{NO}_3^-$	$\text{NH}_4^+$
velocity ( $\mu\text{g} \cdot \text{m}^{-3} \cdot \text{h}^{-1}$ )	7.75 (6 obs.)	2.25 (4.5 obs.)

**ICCAS-TRC :**  
**SIA formation experiment**



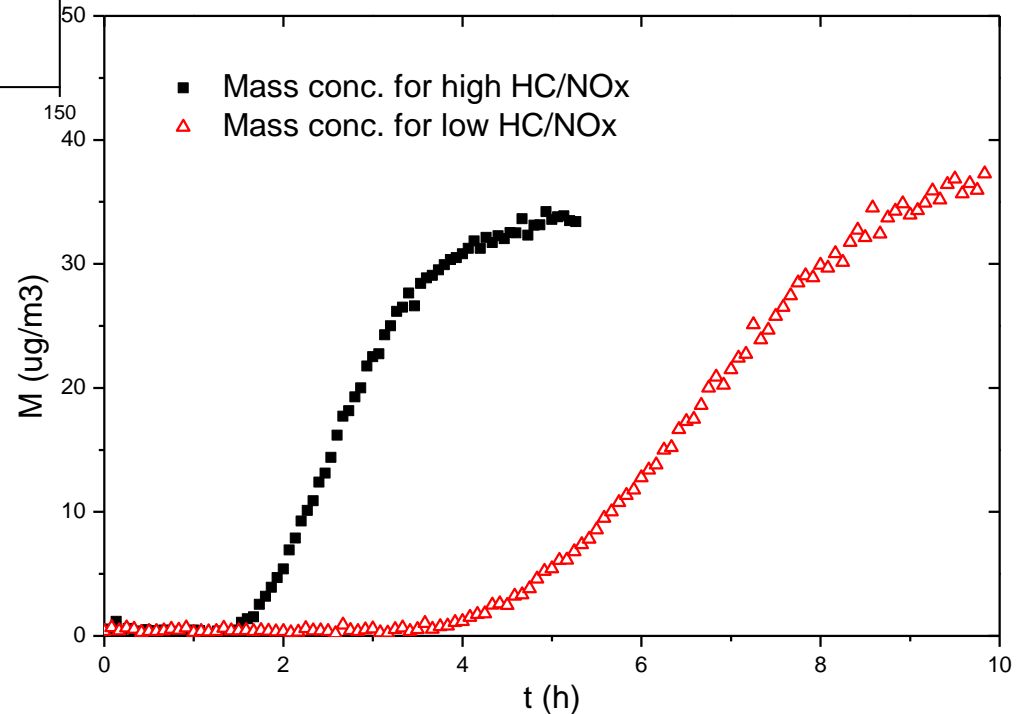
# ICCAS-TRC : SOA formation



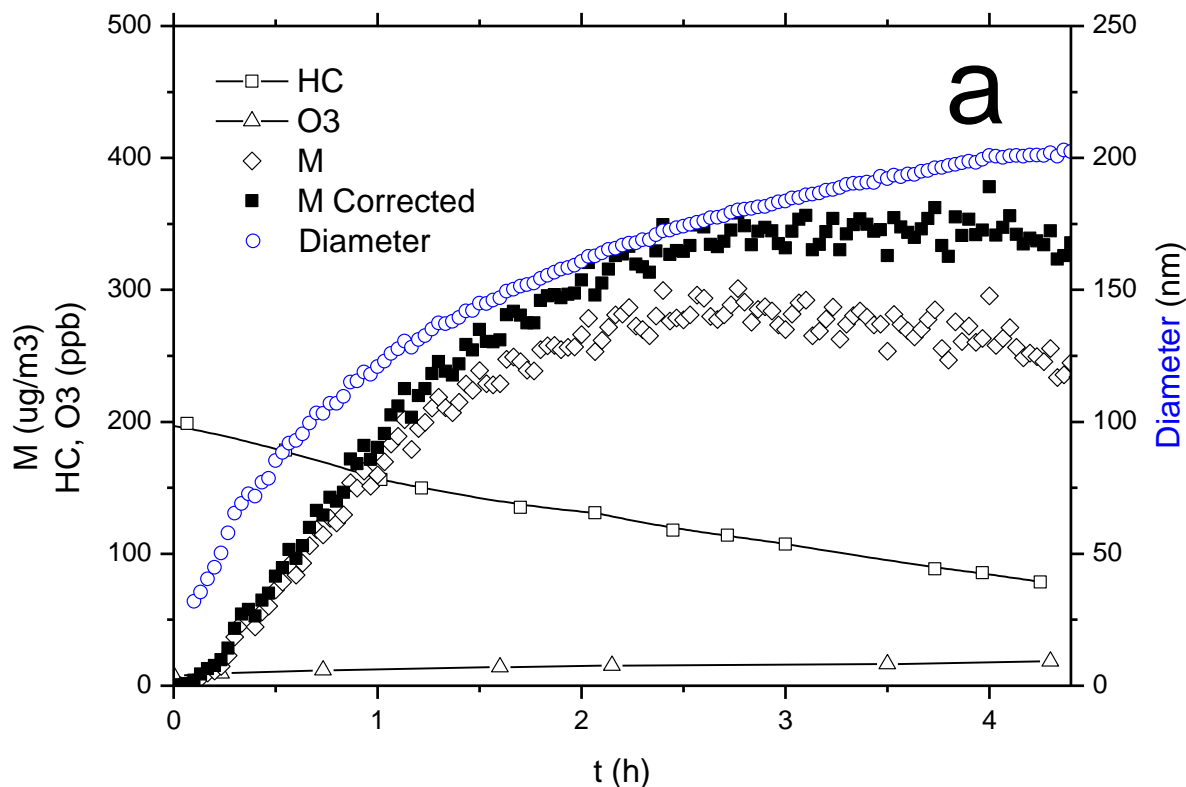
**simulation:**

**Temp, RH, light source, VOCs  
Low & High HC/NO<sub>x</sub>**

**Advantage:**  
**Measure 2 chamber at the  
same time;**  
**Change : only single factor,**



# Photooxidation of aromatic hydrocarbons



Finding:  
NO<sub>x</sub> influence  
SOA formation

Low NO<sub>x</sub>: PM formation just after light on  
High NO<sub>x</sub>: PM formation need 2 h

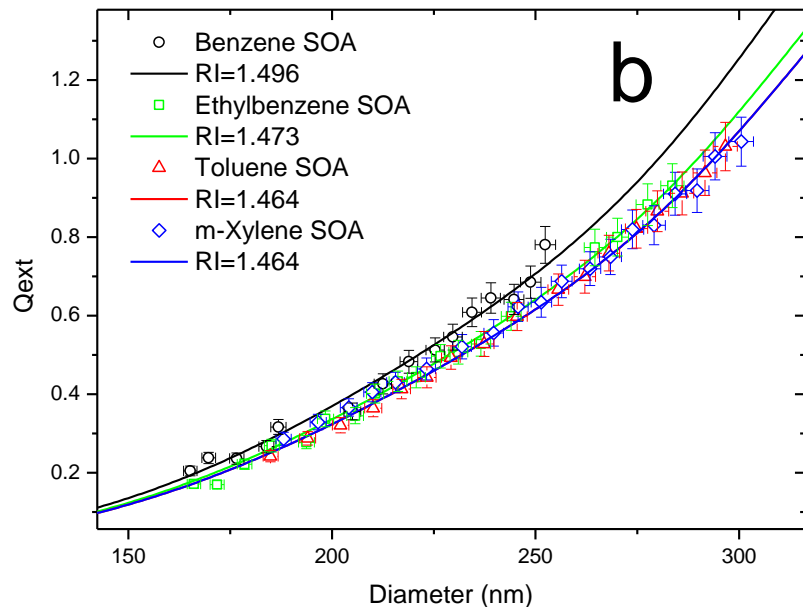
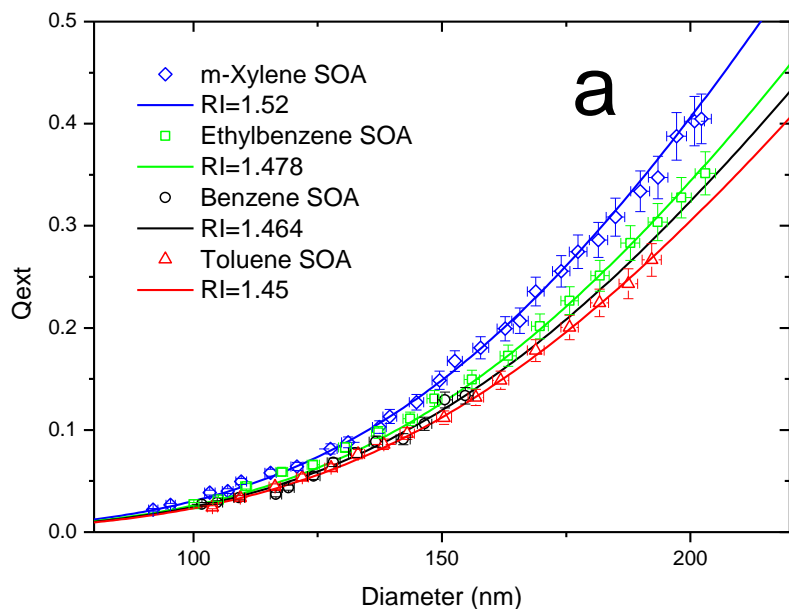
**Fig a; low-NO<sub>x</sub> experiment : 200 ppb m-xylene, 5 ppm H<sub>2</sub>O<sub>2</sub>**

**Low-NO<sub>x</sub> experiments:** H<sub>2</sub>O<sub>2</sub> was used as the OH precursor. The background NO<sub>x</sub> level in the chamber : <1 ppb, the initial concentration of H<sub>2</sub>O<sub>2</sub> : 1–5 ppm.

**High-NO<sub>x</sub> :** NO<sub>2</sub> was introduced from a 50 ppm standard gas cylinder.



# Photo-oxidation of aromatic hydrocarbons

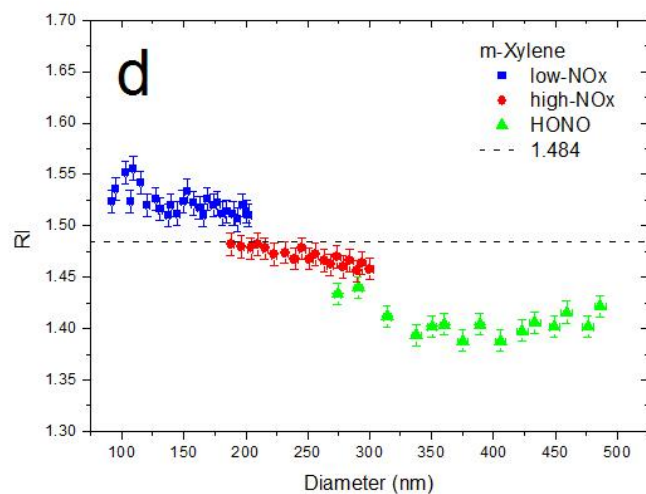
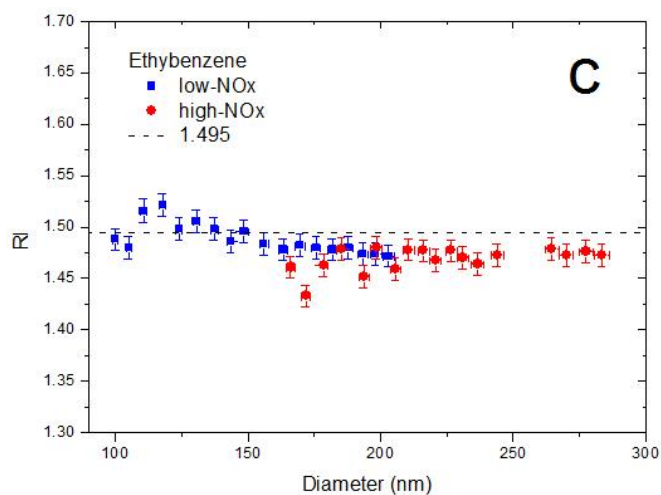
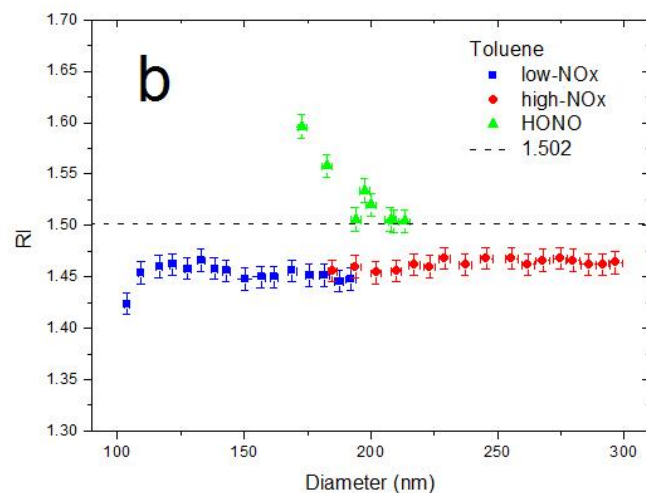
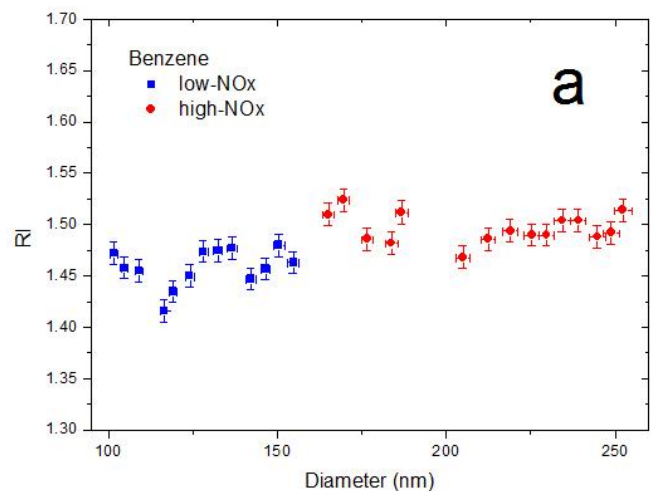


**Dependence of the extinction efficiencies of the SOA particles on the surface mean diameter at a wavelength of 532 nm and the retrieved RIs**

**(a) low- $\text{NO}_x$**

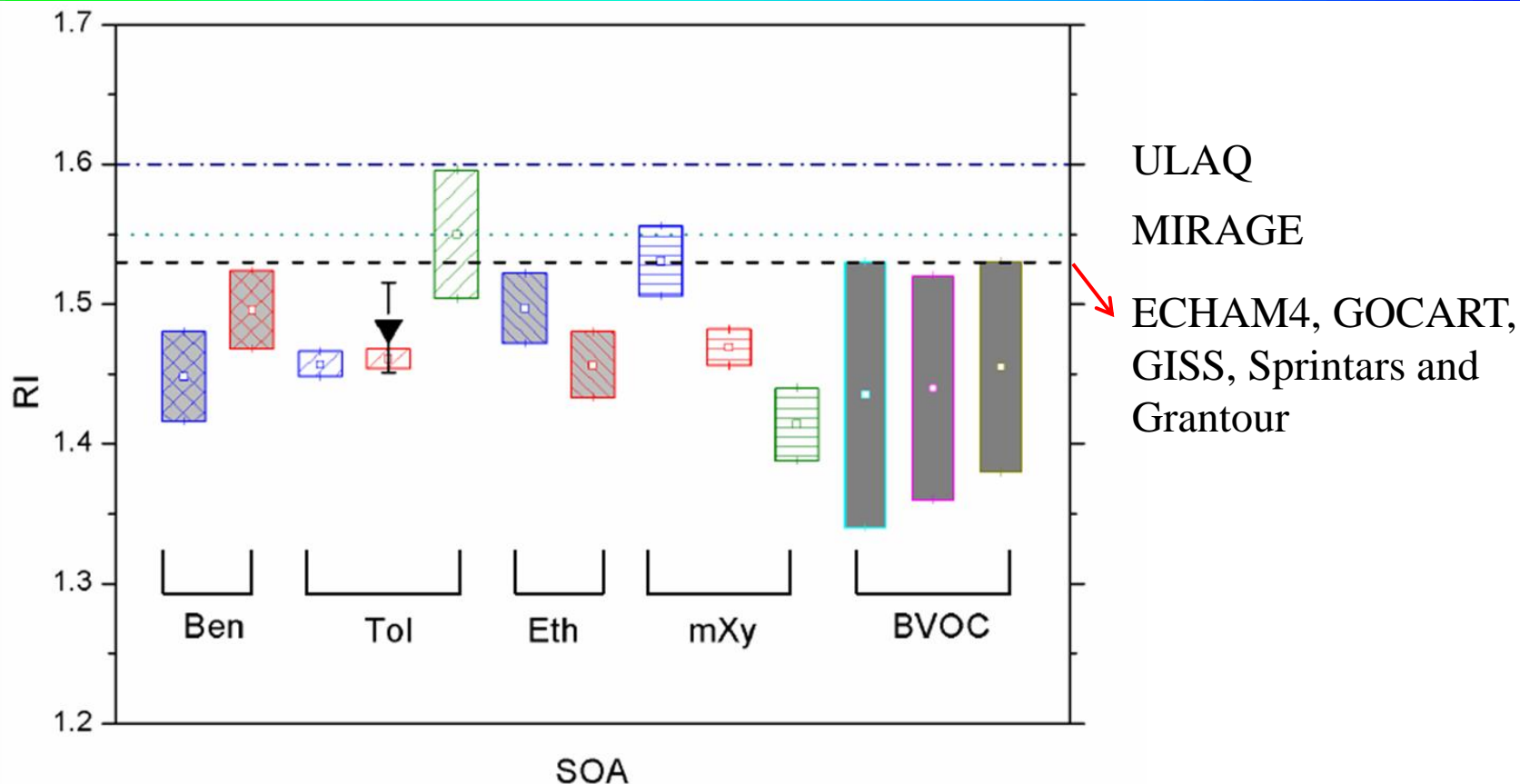
**(b) high- $\text{NO}_x$  experiments**

# Photo-oxidation of aromatic hydrocarbons



The RIs of the SOAs are altered differently as the NO<sub>x</sub> concentration increases as follows: the RIs of the SOAs derived from **benzene and toluene increase**, whereas those of the SOAs derived from **ethylbenzene and m-xylene decrease**.

# Photo-oxidation of aromatic hydrocarbons



**RI**

SOA

ULAQ  
MIRAGE  
ECHAM4, GOCART,  
GISS, Sprintars and  
Grantour

Ben Tol Eth mXy BVOC

RI of the different SOA particles: comparison between experimental data & model values. **The commonly used model values for the RIs of organic aerosols are generally higher than the experimental data for the SOAs formed from VOCs, which may cause the overestimation of direct radiative forcing of organic particles to a certain extent.**

# Photo-oxidation of aromatic hydrocarbons

**1, The RIs of the BTEX SOAs are closely related to the initial NO<sub>x</sub> concentration, with different aromatics displaying different trends.**

**For the benzene and toluene SOAs, the RI value increases as the NO<sub>x</sub> level rises, whereas for the ethylbenzene and m-xylene SOAs, the RI value decreases correspondingly. This result is caused by the different molecular structures and the RO<sub>2</sub> + NO pathway that occurs under the high-NO<sub>x</sub> condition.**

**2, The dependence of the RI value on the initial hydrocarbon and oxidant concentrations was also investigated, revealing that the initial concentrations of these reagents have little influence on the optical properties of the SOA.**

**3, For gas-phase oxidation with no seed particles, the BTEX SOAs have no obvious absorption at 532 nm. However, the SOA particles formed under other conditions may absorb light in the visible range, further studies should be performed.**

# **Future Activities**

---

**1 Smog chamber experiments  
SOA formation and extinction properties**

**2 Develop new techniques  
CIMS etc**

**3 BC  
Aerosol heterogeneous photochemistry**

# **Acknowledgements**

**Dr W. Wang, Dr. L. Du, Dr. S. Tong, Dr. L. Wang,  
Dr. L. Wu, Dr. Z. Liu, Dr. Q Liu, Dr. K Li,**

**Fund: National Natural Science Foundation(NSFC)  
Chinese Academy of Sciences(CAS),**

**<http://gemaofa.iccas.ac.cn>**