

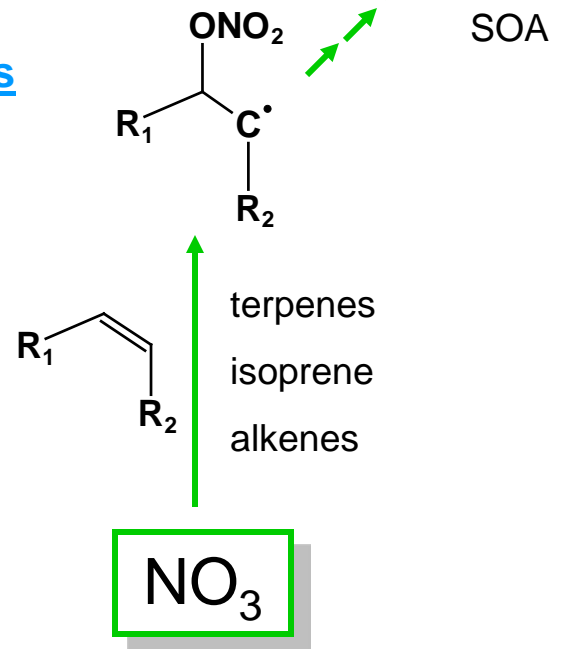
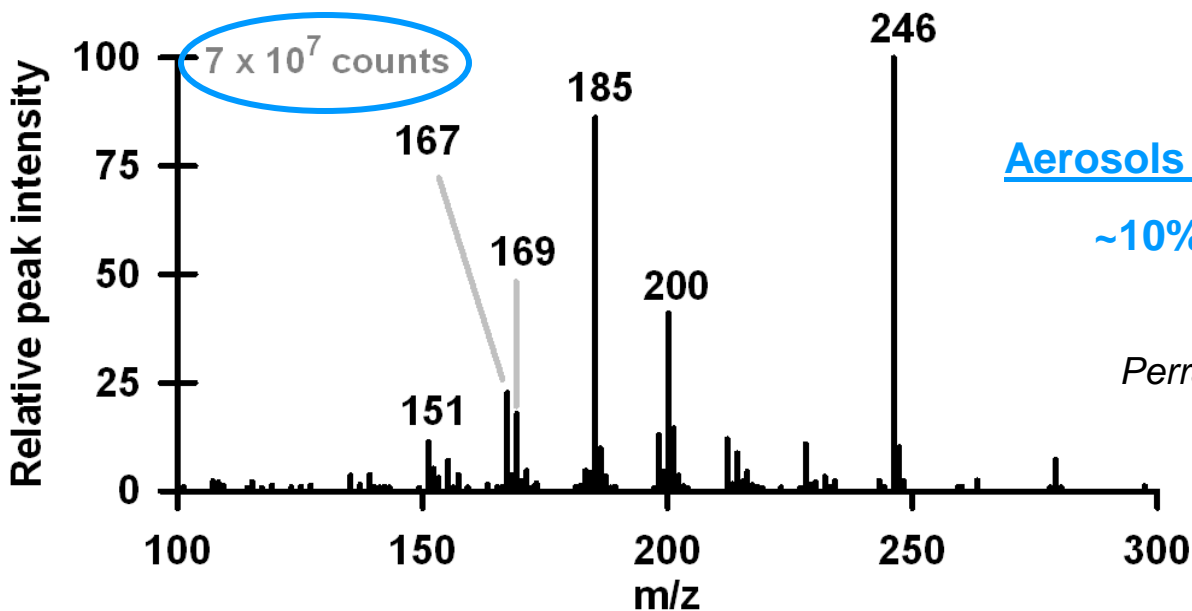
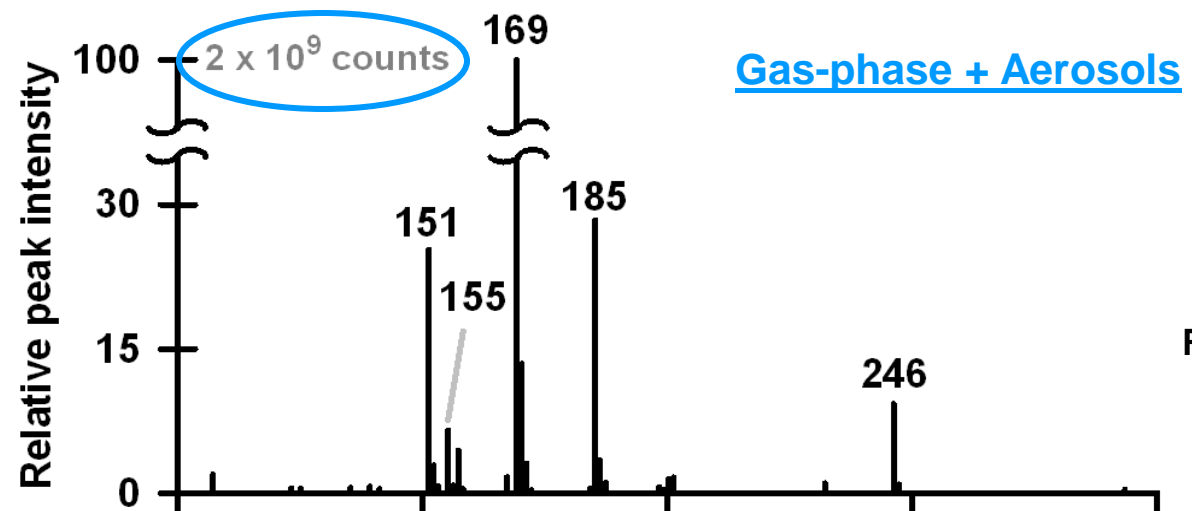
Synergism Between O_3 and NO_3 Radical Chemistry in the Formation and Composition of Secondary Organic Aerosols

Véronique Perraud, E. A. Bruns, M. J. Ezell, S. N. Johnson, Y. Yu,
M. L. Alexander, A. Zelenyuk, D. Imre and B. J. Finlayson-Pitts



Nitrate Radical Chemistry

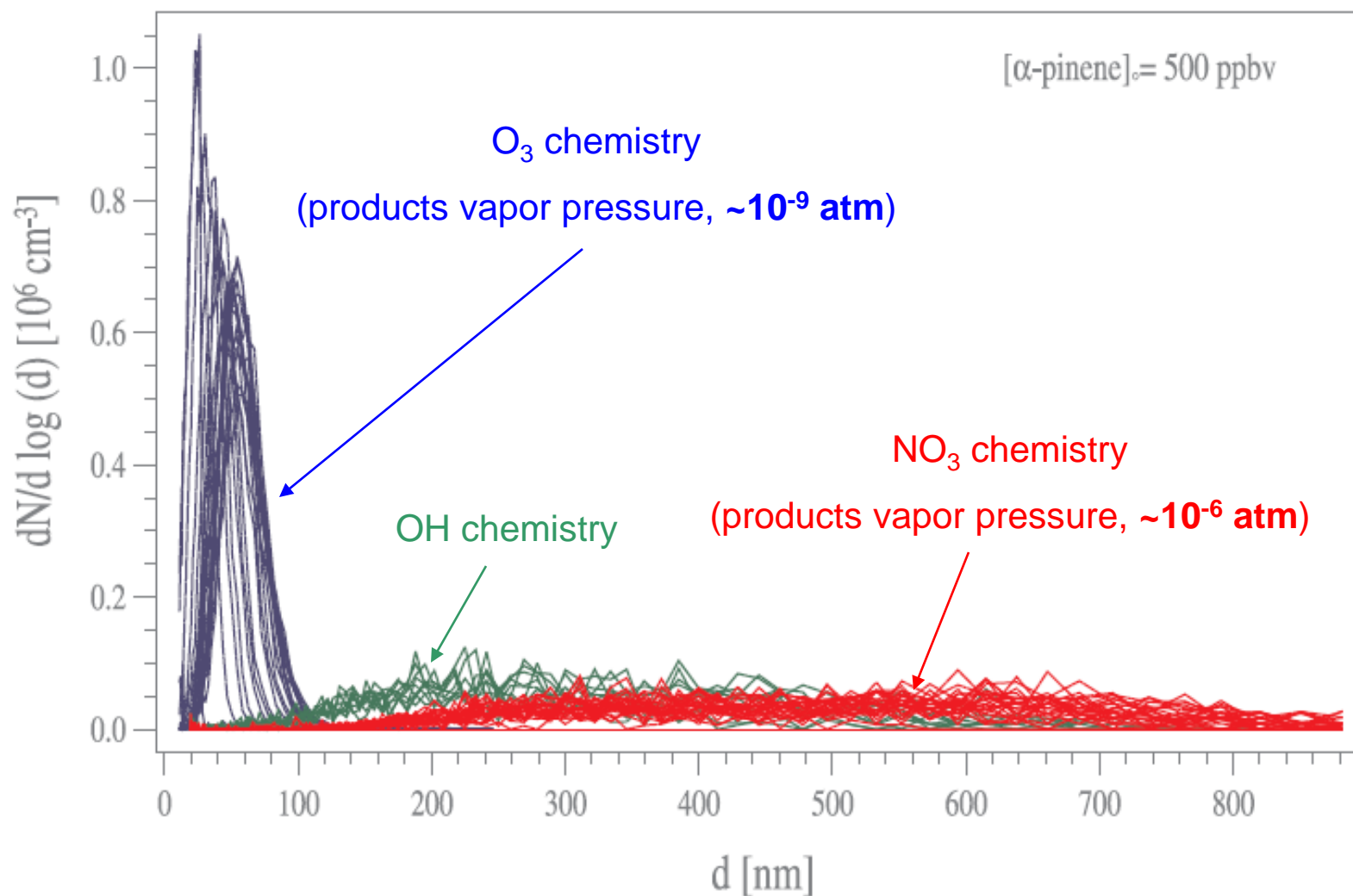
$N_2O_5 + \alpha\text{-pinene}$ / APCI-MS(+) analysis



Perraud et al., EST, 2010, 44, 5887-5893

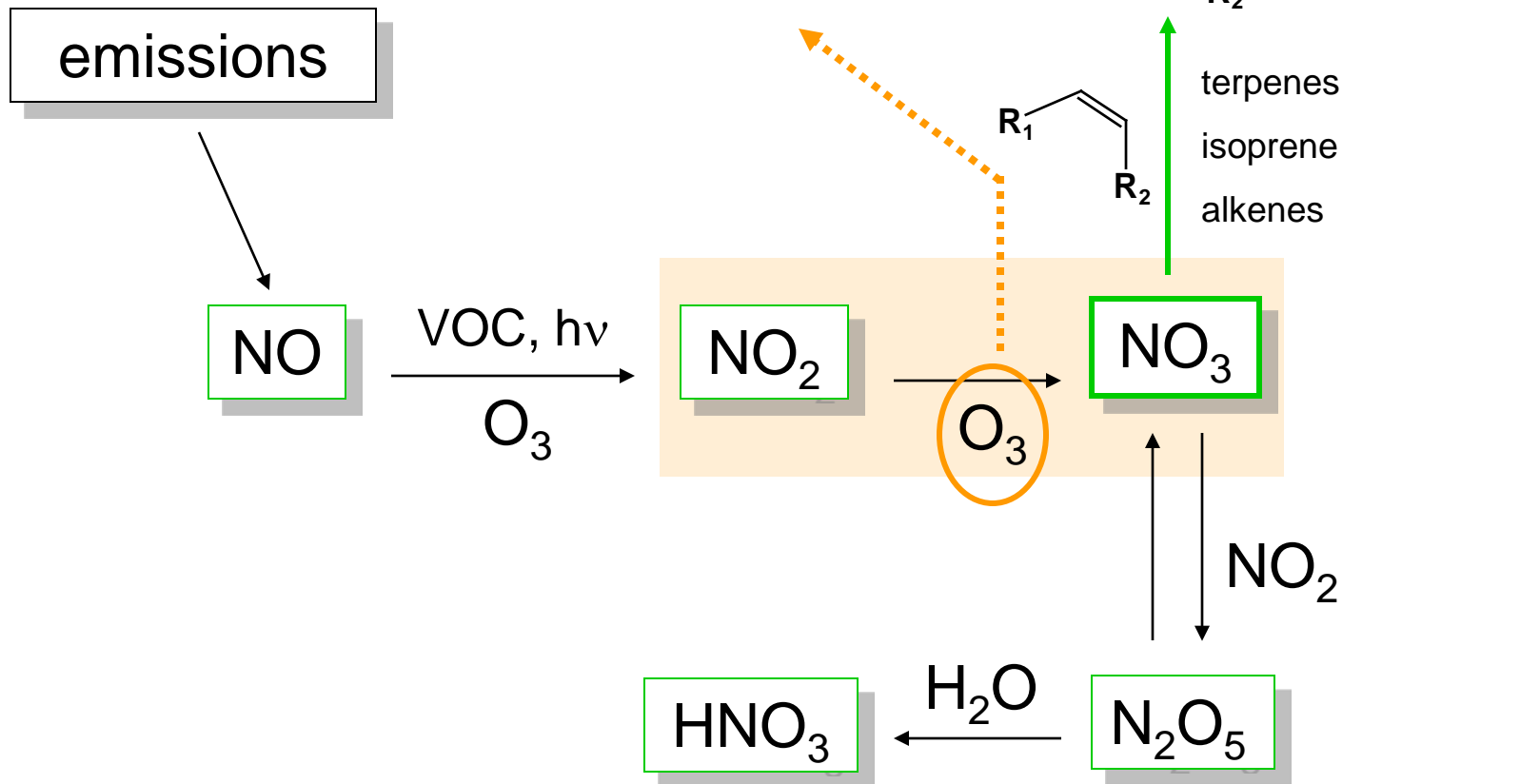
Nitrate Radical Chemistry

Bonn and Moortgat, *ACP*, **2002**, 2, 183-196



Nitrate Radical Chemistry

How does O_3 contribute to the chemistry ?



Large Volume Aerosol Flow Tube

- Initial conditions

- dry air (RH < 3%)
- room temperature (22°C)
- total flow : 20 L min⁻¹
- residence time: 1 hour

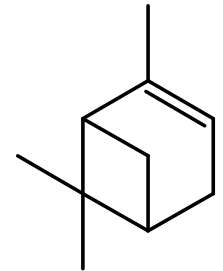
- Oxidant concentrations

$$[\text{O}_3]_0 = 1.4 \text{ ppm}$$

$$[\text{NO}_2]_0 = 6.3 \text{ ppm to } 0 \text{ ppm}$$

- Studied terpene

$$[\alpha\text{-pinene}]_0 = 1 \text{ ppm}$$



- Real-time measurements

- Scanning Mobility Particle Sizer (SMPS)
- Aerodynamic Particle Sizer (APS)
- HR-ToF-AMS and SPLAT-II MS

- Off-line analysis

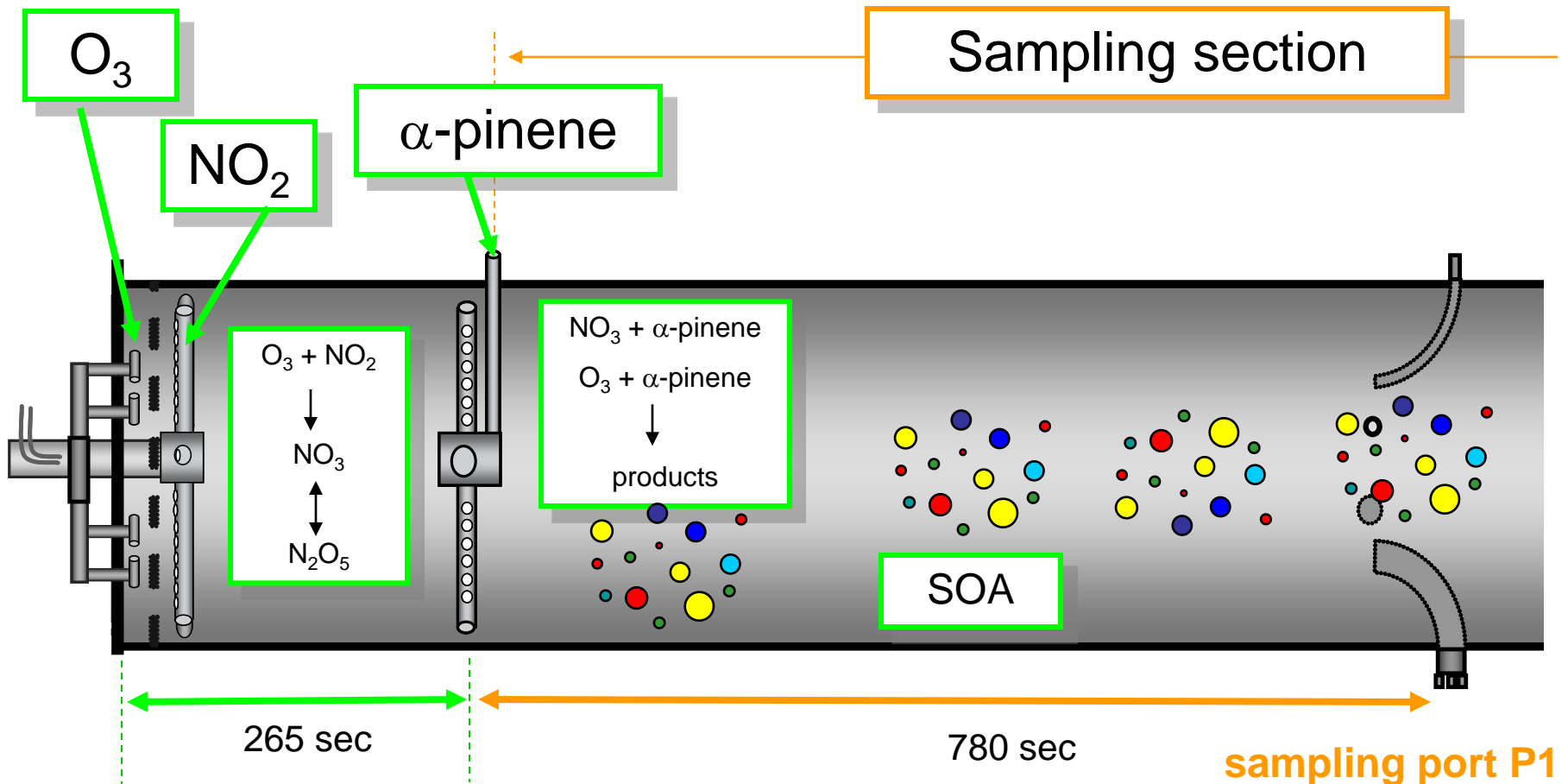
- ZnSe disc-impactor and analysis by FTIR
- Filters collection and LC-UV analysis

“Higher NO₂” = 2.4 ppm

“Lower NO₂” = 0.2ppm

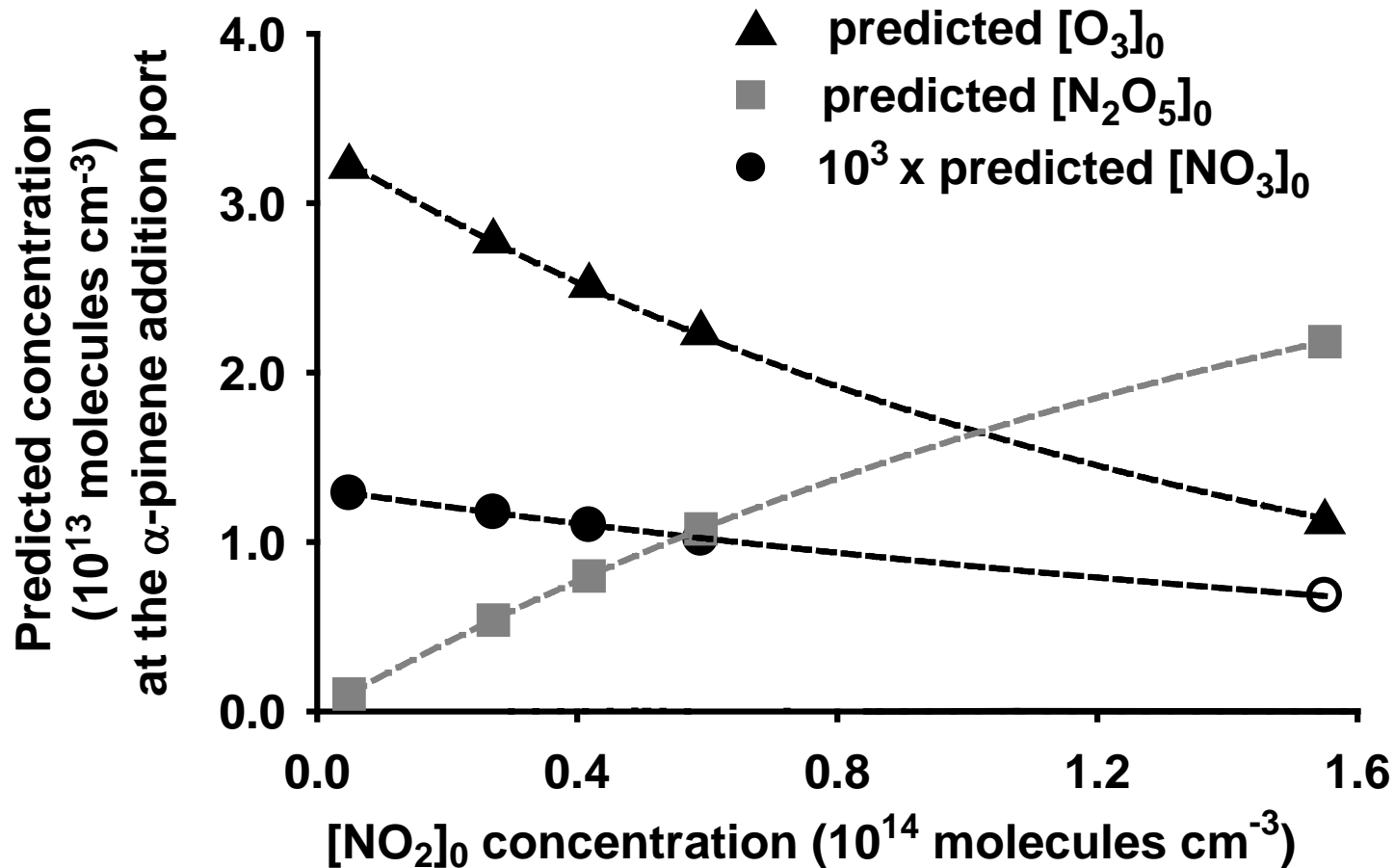
Prediction

- Box model using a simplified 96 step mechanism for $\text{NO}_2 + \text{O}_3 + \alpha\text{-pinene}$ system



Prediction

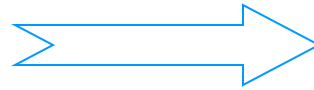
- Box model results from a simplified 96 step mechanism for $\text{NO}_2 + \text{O}_3$ system



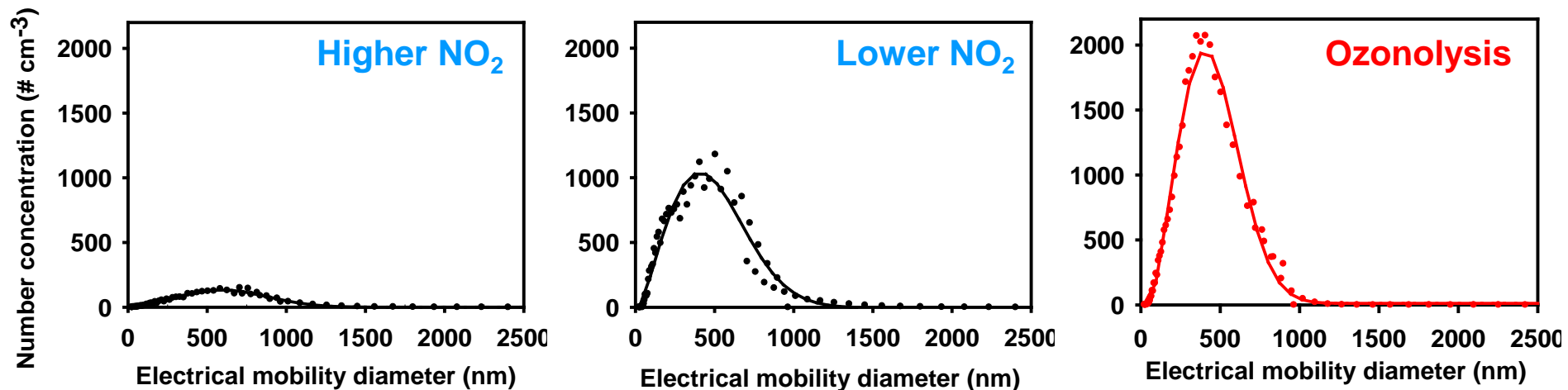
Particle concentration

SPLAT-II MS

- spherical particles
- density 1.19-1.21 g cm⁻³

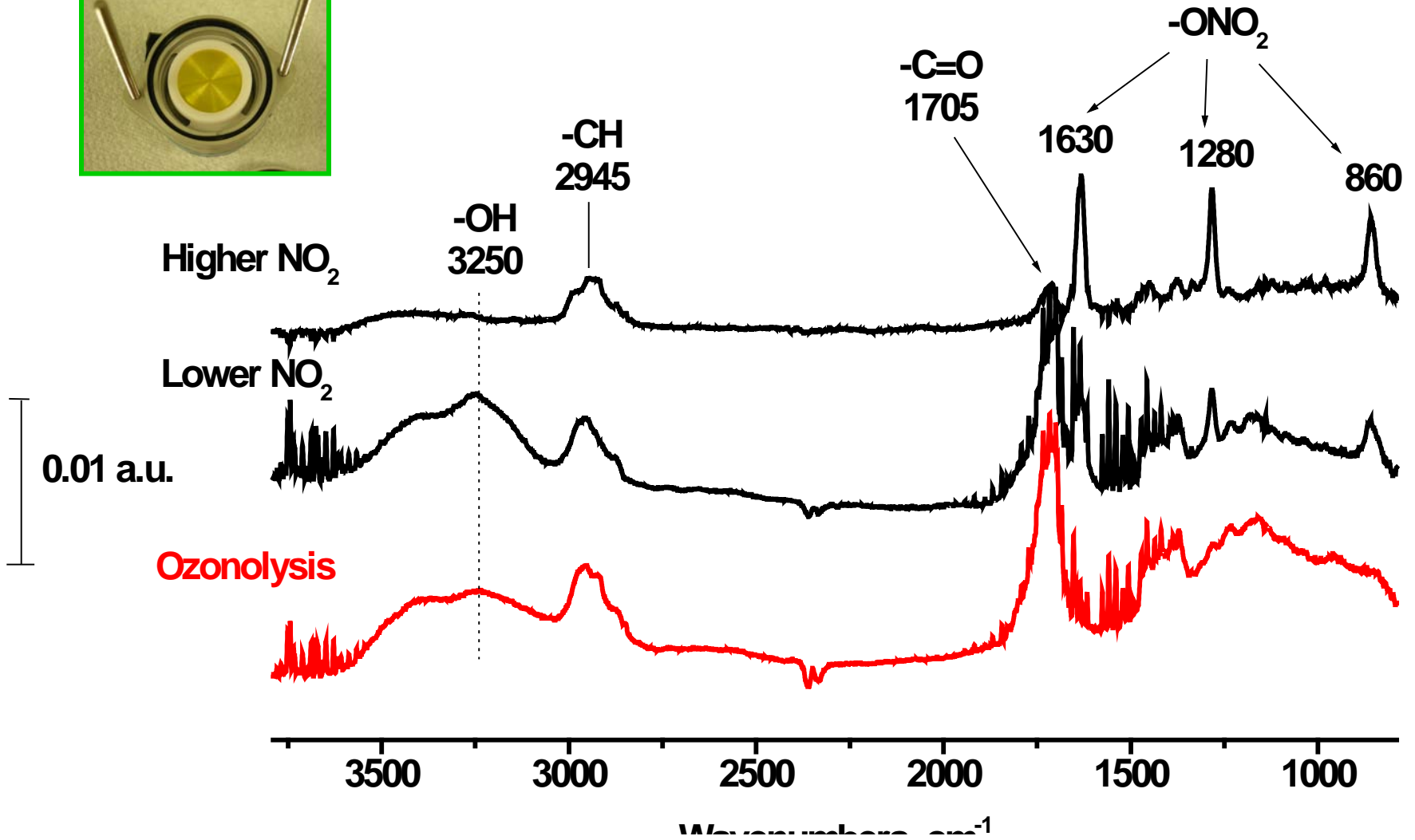
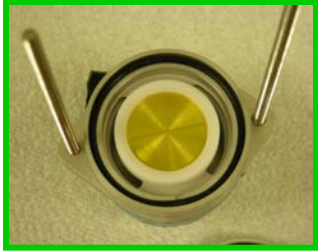


Combined SMPS-APS
size distribution

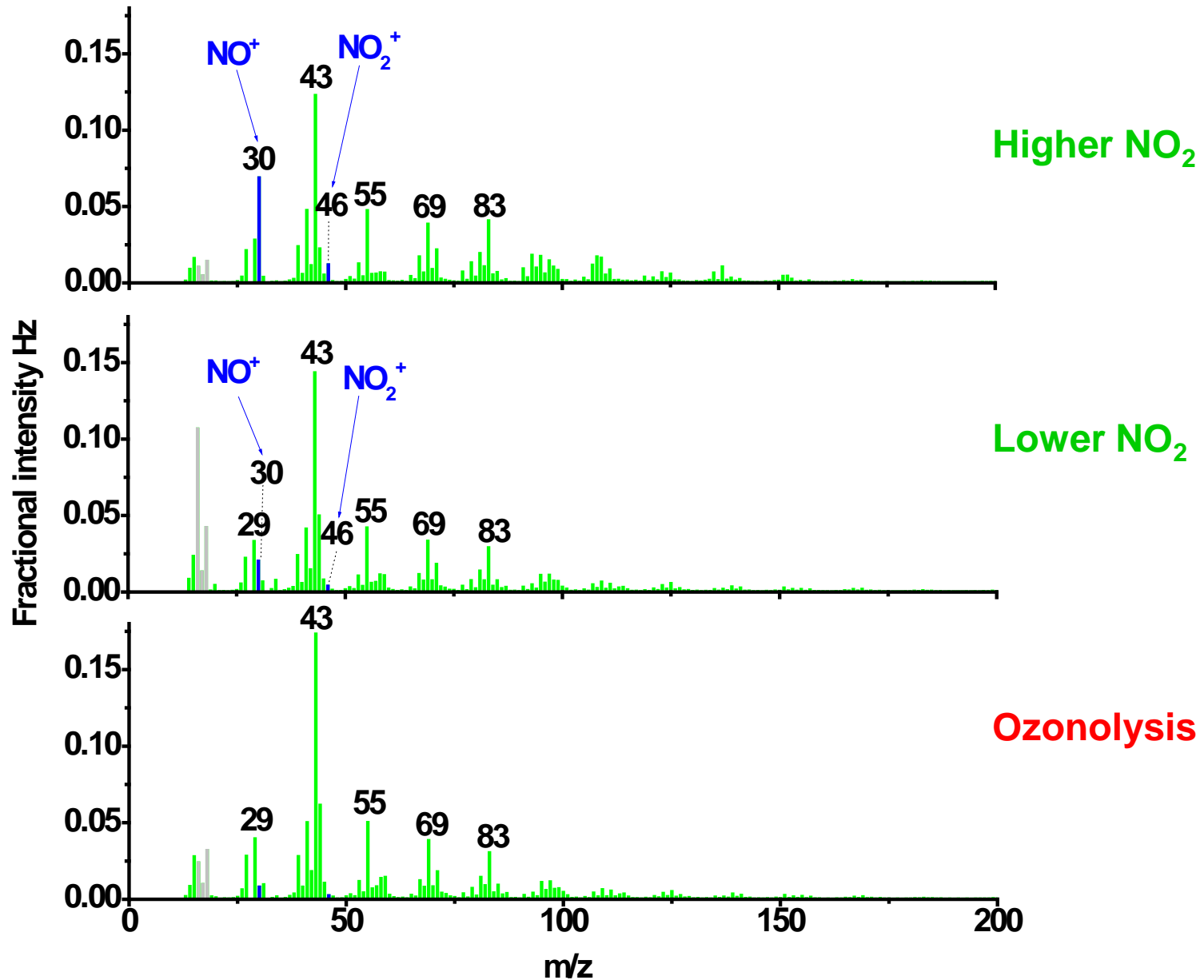


✓ O₃ chemistry contributes to the SOA formation

ZnSe disc impactor and FTIR analysis

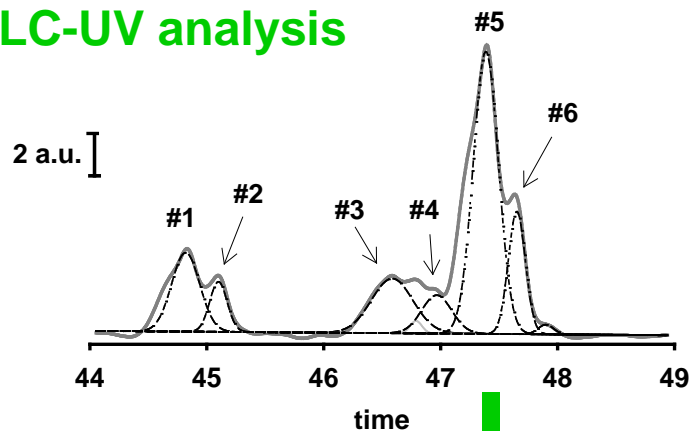


HR-ToF-AMS measurements



Mass fraction of organic nitrates in the SOA

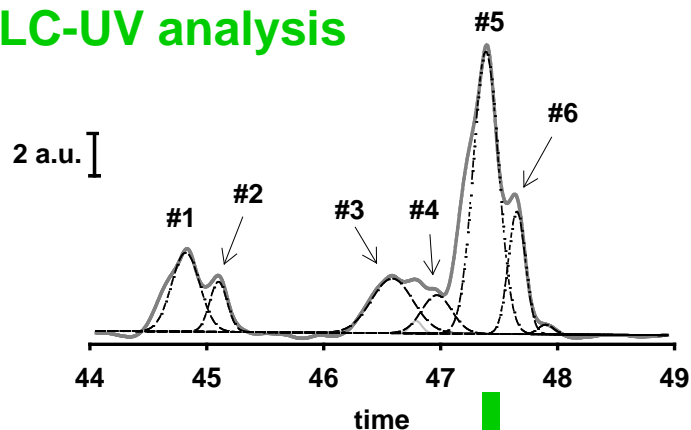
LC-UV analysis



$[\text{NO}_2]_0$ (ppm)	Mass RONO_2 in SOA ($\mu\text{g m}^{-3}$)
6.3	9
2.4	37
1.7	37
1.1	22
0.2	4
0	0

Mass fraction of organic nitrates in the SOA

LC-UV analysis



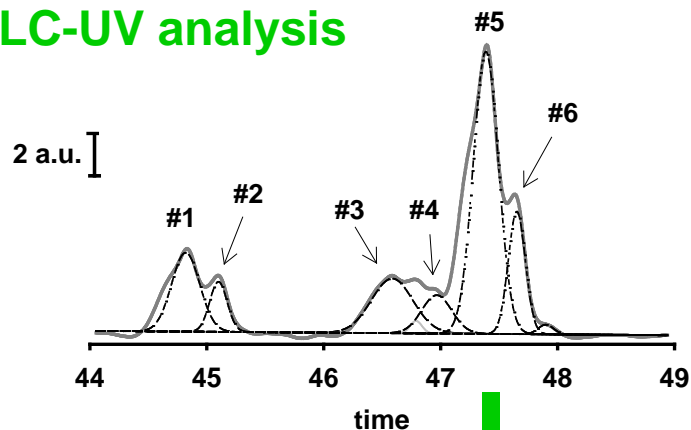
SMPS-APS data



$[\text{NO}_2]_0$ (ppm)	Mass RONO_2 in SOA ($\mu\text{g m}^{-3}$)	Total mass SOA ($\mu\text{g m}^{-3}$)
6.3	9	41
2.4	37	544
1.7	37	747
1.1	22	1097
0.2	4	2101
0	0	2762

Mass fraction of organic nitrates in the SOA

LC-UV analysis



SMPS-APS data



Mass fraction



$[\text{NO}_2]_0$ (ppm)	Mass RONO_2 in SOA ($\mu\text{g m}^{-3}$)	Total mass SOA ($\mu\text{g m}^{-3}$)
6.3	9	41
2.4	37	544
1.7	37	747
1.1	22	1097
0.2	4	2101
0	0	2762

f_{RONO_2} (%)

23%

7%

5%

2%

0.2%

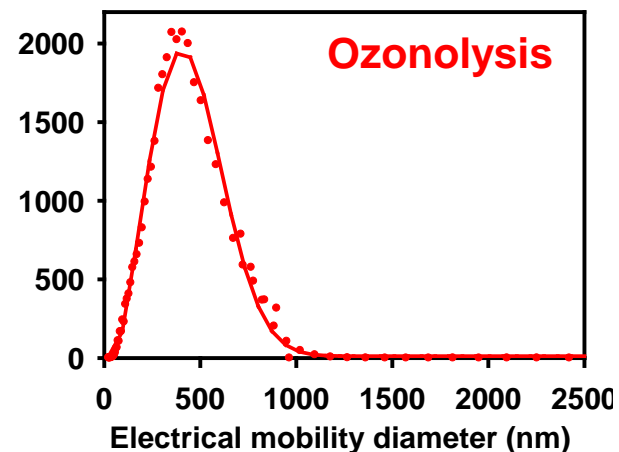
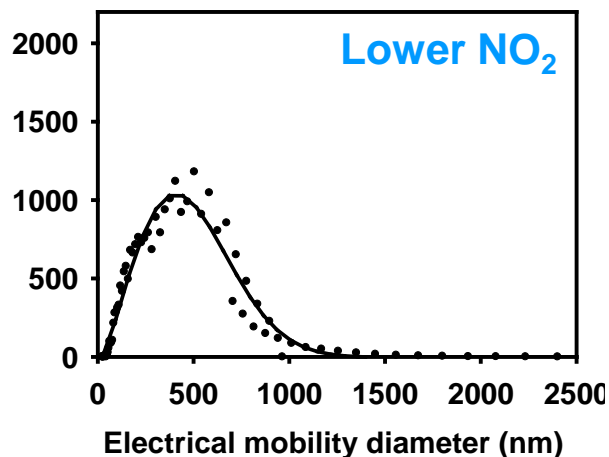
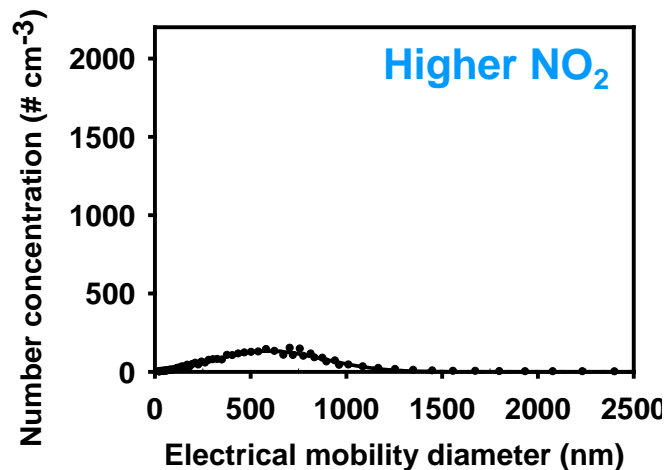
0%

Summary of O_3/NO_3 chemistry

$f_{RONO_2} = 7\%$ of SOA

$f_{RONO_2} = 0.2\%$ of SOA

$f_{RONO_2} = 0.0\%$ of SOA



✓ Using SOA yield and composition from single component systems can be misleading for atmospheric conditions where multiple oxidants are present

Partitioning of RONO₂ into SOA

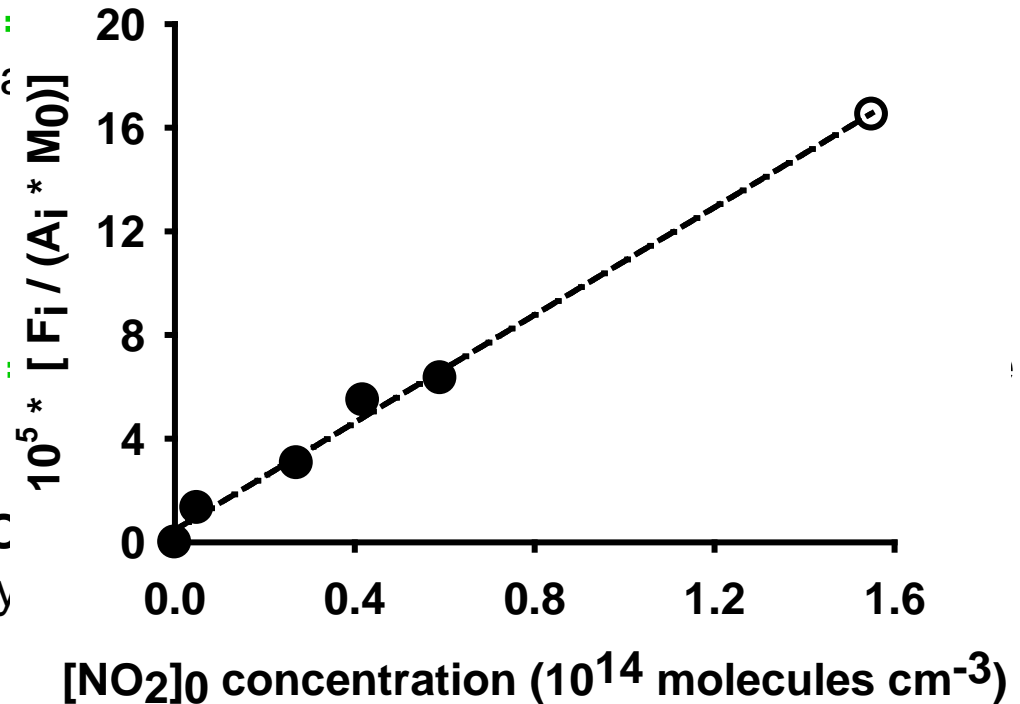
Partition coefficient

$$K_p = \frac{F_i / M_0}{A_i}$$

F_i = concentration of RONO₂ measured using LC-UV analy

M_0 :
mea

A_i :



- ✓ $F_i / (A_i * M_0)$ is not constant as expected.
- ✓ Results suggest that the equilibrium between RONO₂ in the gas phase and particles is not reached.

Conclusions

- SOA yields and composition from single component systems can be misleading for atmospheric conditions where multiple oxidants are present
- Partitioning of RONO_2 suggests that equilibrium between the gas phase and the particles is not reached for these products (see Zelenyuk et al.)

Acknowledgements



Finlayson-Pitts' research group

Collaborators from PNNL:
A. Zelenyuk and M. L. Alexander

P. Ziemann (UCR)



AirUCI

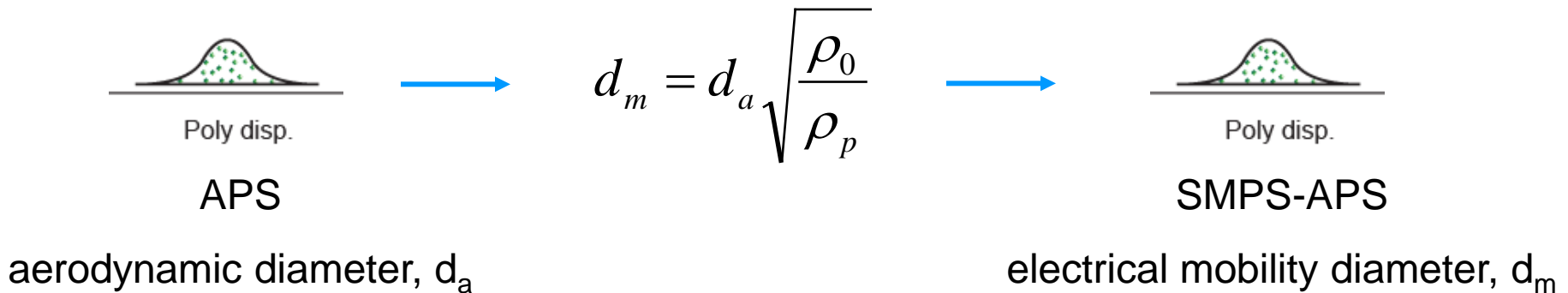
National Science Foundation

U.S. Department of Energy

Particle concentration

Combined SMPS-APS size distribution

spherical particles with density = 1.19-1.21 g cm⁻³ from SPLAT-II MS measurements



HR-ToF-AMS measurements

Previous Nitrate Speciation

(Bruns et al., 2010)

$\text{NO}^+/\text{NO}_2^+$ = 11 8 organic nitrate

$\text{NO}^+/\text{NO}_2^+$ = ~3 NO_2

$\text{NO}^+/\text{NO}_2^+$ = 2 NH_4NO_3

$\text{NO}^+/\text{NO}_2^+$ = 80 NaNO_3

Higher NO_2

$\text{NO}^+/\text{NO}_2^+$ = 4.9

Lower NO_2

$\text{NO}^+/\text{NO}_2^+$ = 5.8

Quantification AMS vs FTIR

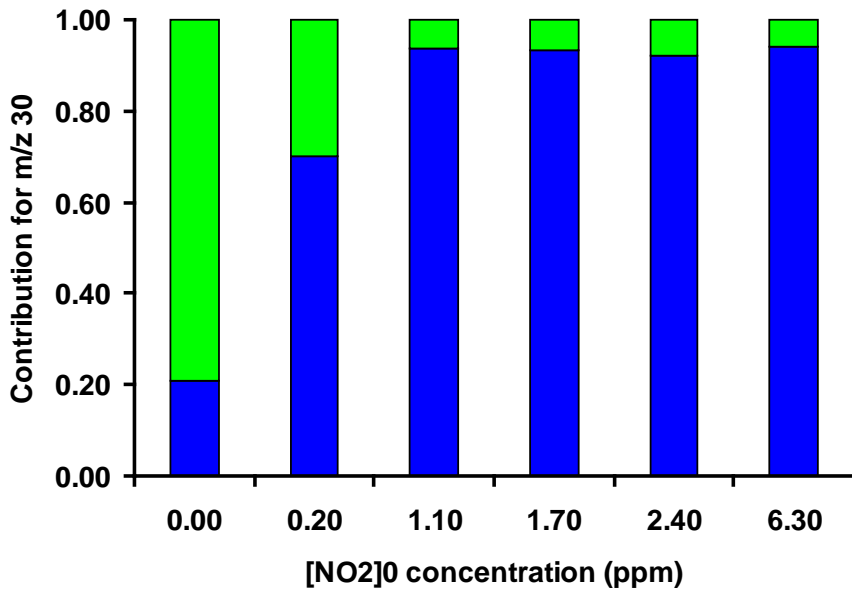
	HR-ToF-AMS N/H	FTIR n(-ONO ₂)/n(C-H)	FTIR / AMS
High NO ₂	0.030	0.077	2.6
Low NO ₂	0.015	0.040	2.5

- AMS systematically underestimates the N/H for organic nitrates consistent with the recent literature (*Farmer et al., 2010; Rollins et al., 2010; Bruns et al., 2010*) due to:

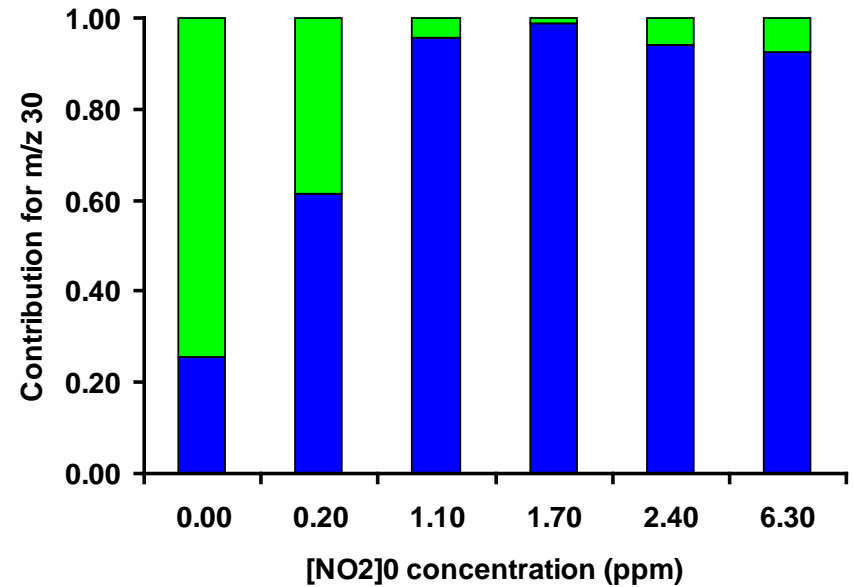


HR-ToF-AMS measurements

■ CH₂O⁺
■ NO⁺



■ CH₂O₂⁺
■ NO₂⁺



Partition of RONO₂ into SOA

$$K_{abs} = \frac{R * T}{MW_{om} * 10^6 * \zeta_i * \rho_{L,i}^0}$$

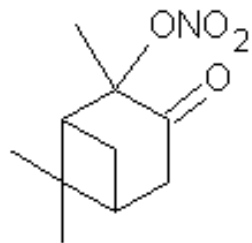
Organic nitrate, assuming $\zeta_i = 1$ and $MW_{om} = 200 \text{ g mol}^{-1}$)

range K_{abs} for individual compounds

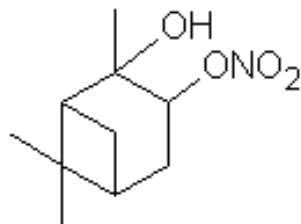
$$= 10^{-2} \text{ to } 10^{-5} \text{ m}^3 \mu\text{g}^{-1}$$

Teflon Chamber: APIMS analysis

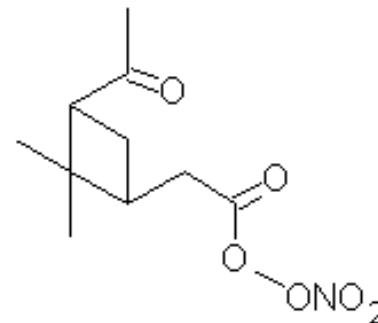
Identified organic nitrates



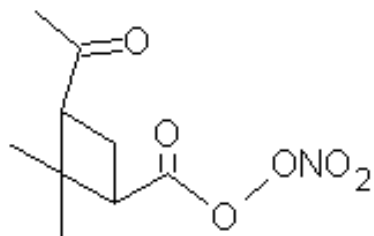
3-oxopinane-2-nitrate (MW 213)
 $\rho_{L,i}^0$ (295K) = 2.0×10^{-6} atm



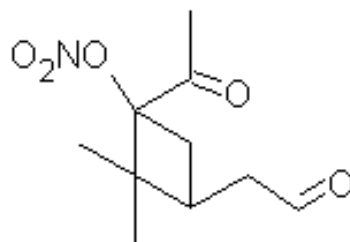
2-hydroxypinane-3-nitrate (MW 215)
 $\rho_{L,i}^0$ (295K) = 1.7×10^{-7} atm



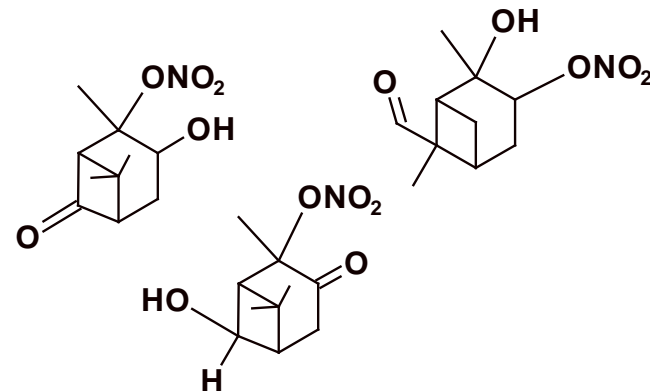
pinonaldehyde peroxyacetyl nitrate (MW 245)
 $\rho_{L,i}^0$ (295K) = 1.6×10^{-6} atm



norpinonaldehyde peroxyacetyl nitrate (MW 231)
 $\rho_{L,i}^0$ (295K) = 4.3×10^{-6} atm



(3-acetyl-2,2-dimethyl-3-nitrooxycyclobutyl)acetaldehyde (MW 229)
 $\rho_{L,i}^0$ (295K) = 9.7×10^{-8} atm



carbonyl hydroxynitrate (MW 229)
 $\rho_{L,i}^0$ (295K) = $(0.5-1.2) \times 10^{-8}$ atm