



U.S. DEPARTMENT OF  
**ENERGY**

Office of  
Science

# Environmental Molecular Sciences Laboratory (EMSL) Scientific User Facilities for the BER Atmospheric System Research Program

Alex Guenther  
EMSL Atmospheric Aerosol Systems  
Science Theme Leader



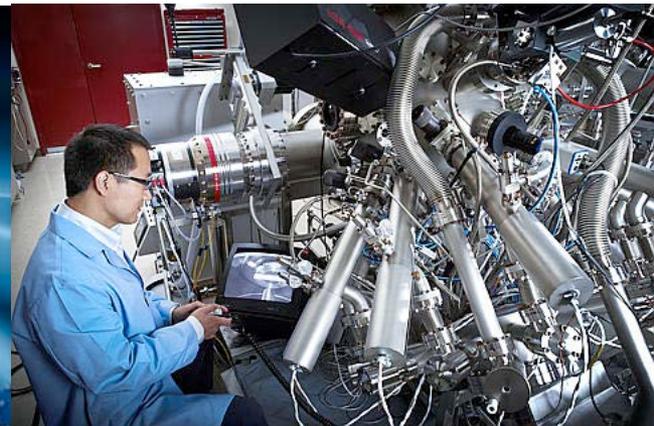
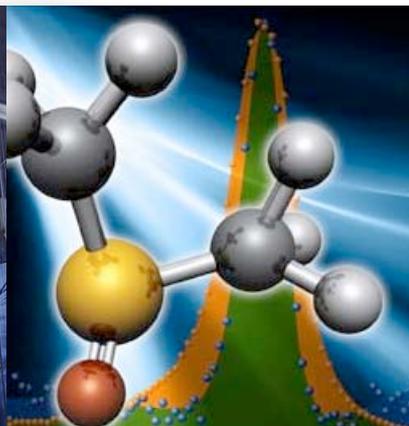
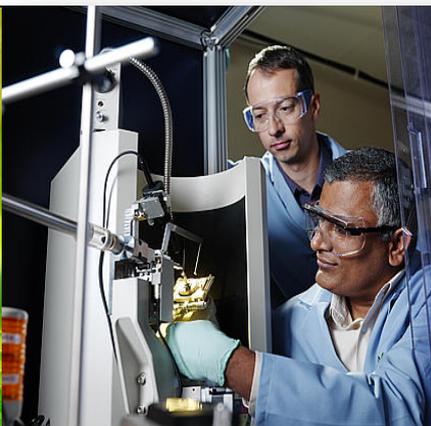
- What is EMSL?
- What capabilities does EMSL have?
- How can EMSL enhance your research?



# EMSL Signature Characteristics



- **Integration** - Our distinctive focus on integrating computational and experimental capabilities strengthens research at EMSL.
- **Unique Collaborative Environment** - EMSL brings together, under one roof, scientists of many disciplines and state-of-the-art instruments critical to their research.
- **Expertise** - EMSL scientists are experts in their fields and lead research in energy, environment, and climate.
- **State-of-the-Art Instrumentation** - EMSL offers an impressive suite of computational and experimental resources. We advance science by customizing and upgrading our instruments to meet researchers' needs.
- **Economical** - Taxpayer investment in EMSL makes research possible that would be otherwise unaffordable to many scientists.

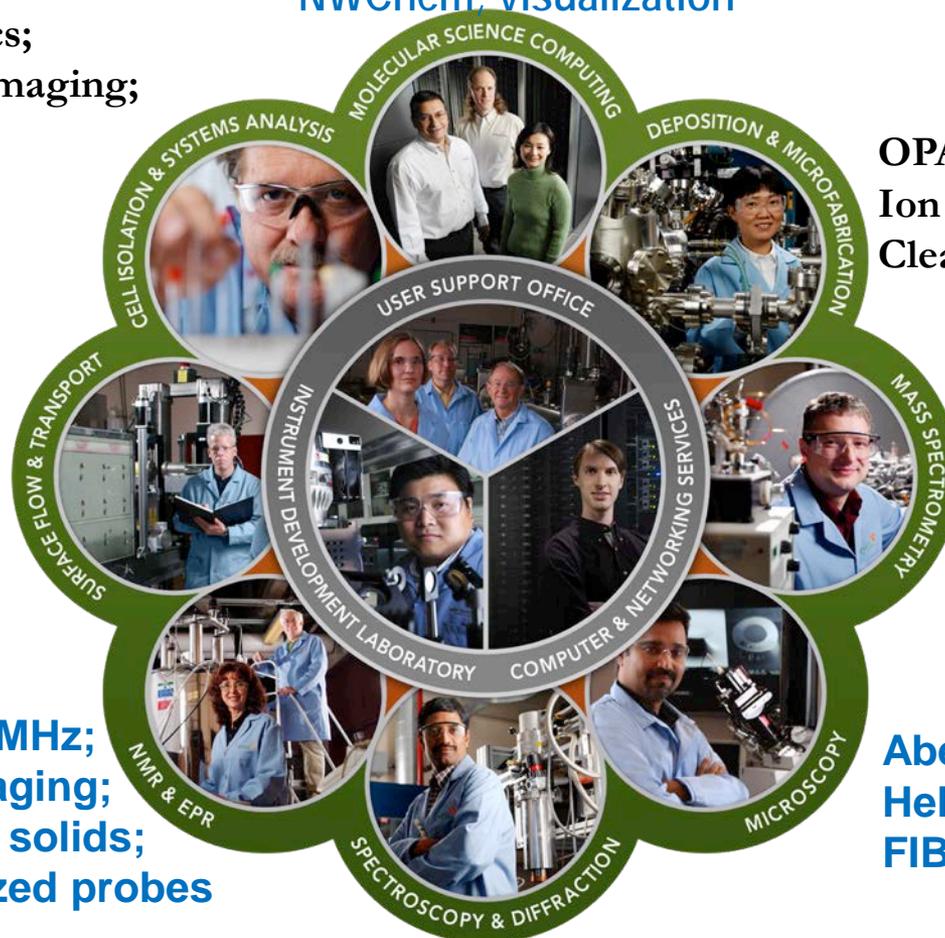


Cascade supercomputer  
NWChem; visualization

Transcriptomics;  
Multi photon imaging;  
Cell culture

Tomography;  
Microfluidics;  
Meter scale flow  
cells

300-900 MHz;  
NMR Imaging;  
Liquid & solids;  
Specialized probes



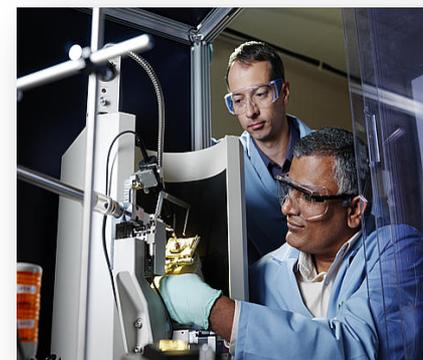
OPA-MBE;  
Ion Accelerator;  
Clean room

12, 15 & 21-T FTICR MS;  
LTQ Orbitraps; IMS-MS;  
DESI

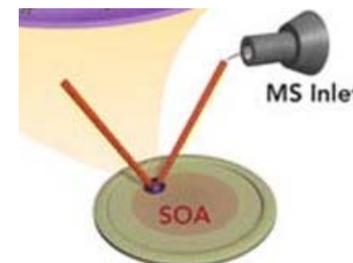
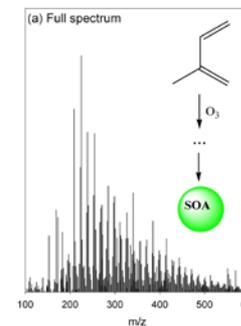
Aberration corrected TEM;  
Helium ion microscopy;  
FIB-SEM; cryo TEM, DTEM

XRD; Raman; FTIR;  
Mossbauer; SHG/SFG;  
XPS, SIMS; optical

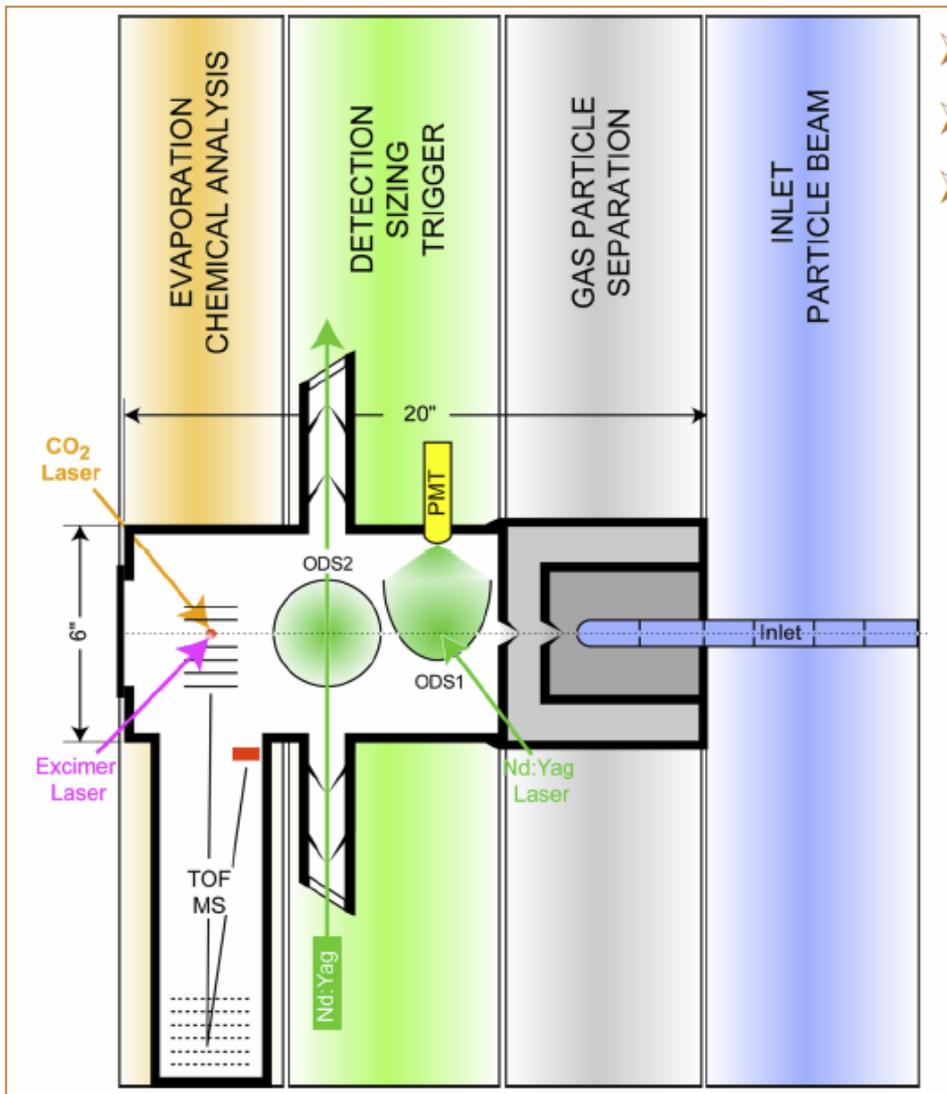
- EMSL capabilities that have been applied to aerosol studies
- EMSL capabilities that could be applied to aerosol studies
- Future EMSL capabilities for aerosol studies



- SPLAT II – Single Particle Laser Ablation Time-of-Flight mass spectrometer
- NanoDESI - Nanospray Desorption Electrospray Ionization Mass Spectrometry
- AMS – Aerosol mass spectrometry
- Electron Microscopy and x-ray analysis



# SPLAT : An Ultra-Sensitive, High Precision Instrument for Multidimensional Single Particle Characterization



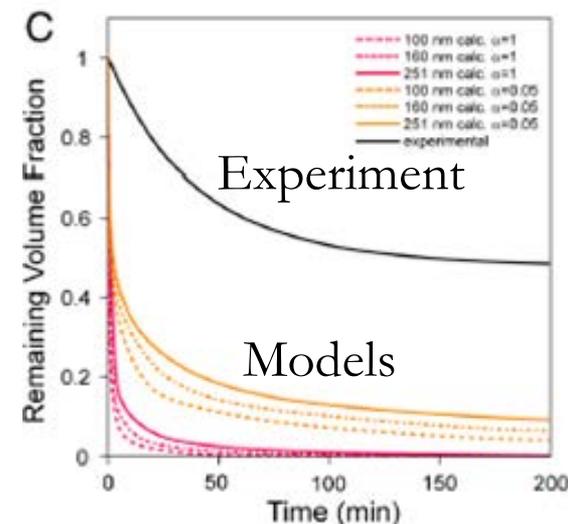
- Laboratory and field deployable
- Compact, portable, and aircraft-compatible
- Provides quantitative multidimensional information for individual particles
  - ✓ Number concentration
  - ✓ Size
  - ✓ Composition
  - ✓ Density
  - ✓ Shape (dynamic shape factor, asphericity, asymmetry)
  - ✓ Morphology
  - ✓ Hygroscopicity
  - ✓ Fractal dimension
  - ✓ CCN activity
  - ✓ IN activity

Zelenyuk, A., Yang, J., Imre, D. and Choi, E. (2009). *Aerosol Science and Technology*, 43:5,411-424.

Zelenyuk, A., and Imre (2009). *International Reviews in Physical Chemistry*, 28(2):309-358.

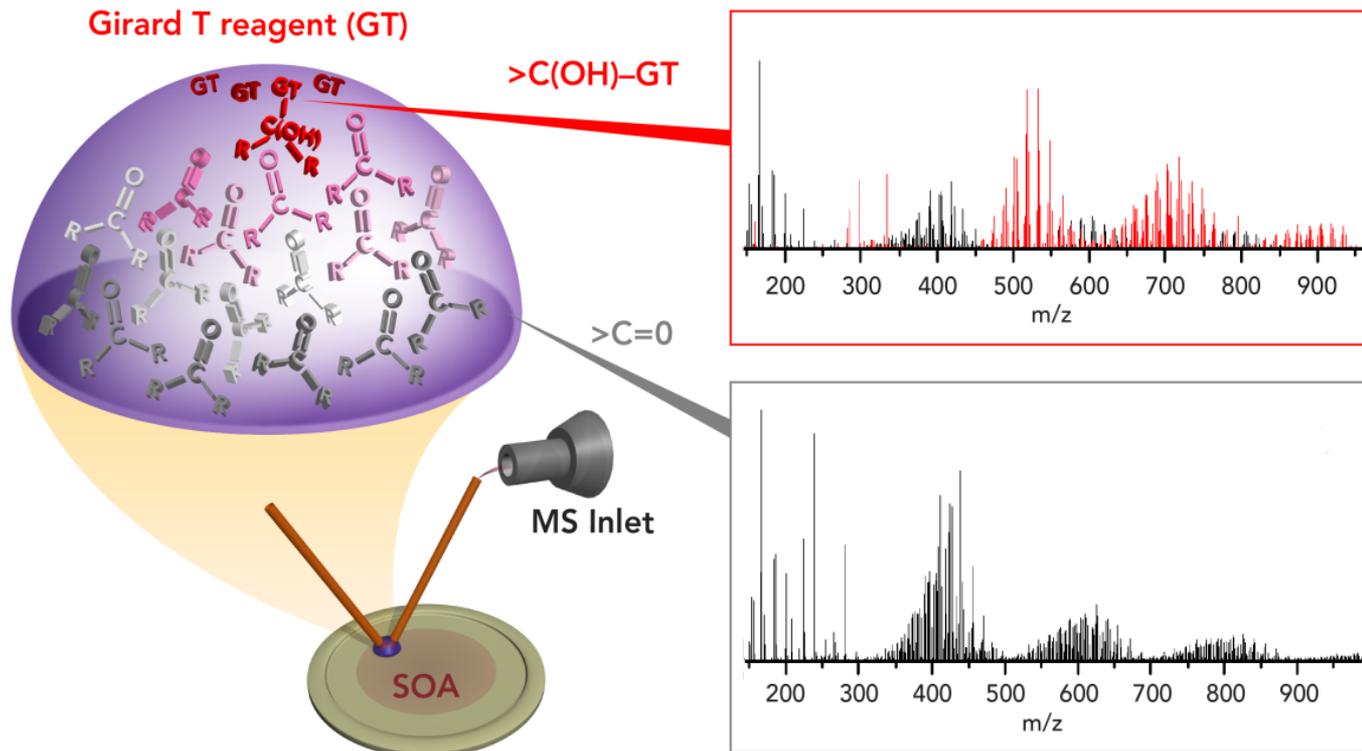
# Combined lab and field studies suggest why aerosol models fail

- Secondary organic aerosols (SOA) are much more prevalent than predicted
- Measurements including use of EMSL's single particle mass spectrometer (SPLAT II) show that the **composition** and **evaporation** rates of SOA particles differ significantly that assumed in environmental models
- In addition to unexpected composition, slower evaporation occurs because particles are solid (not liquid) and surface coatings slow evaporation.



*SPLAT II, shown here during a research flight aboard the Convair 580, allows real-time single particle analysis in the laboratory or in the field.*

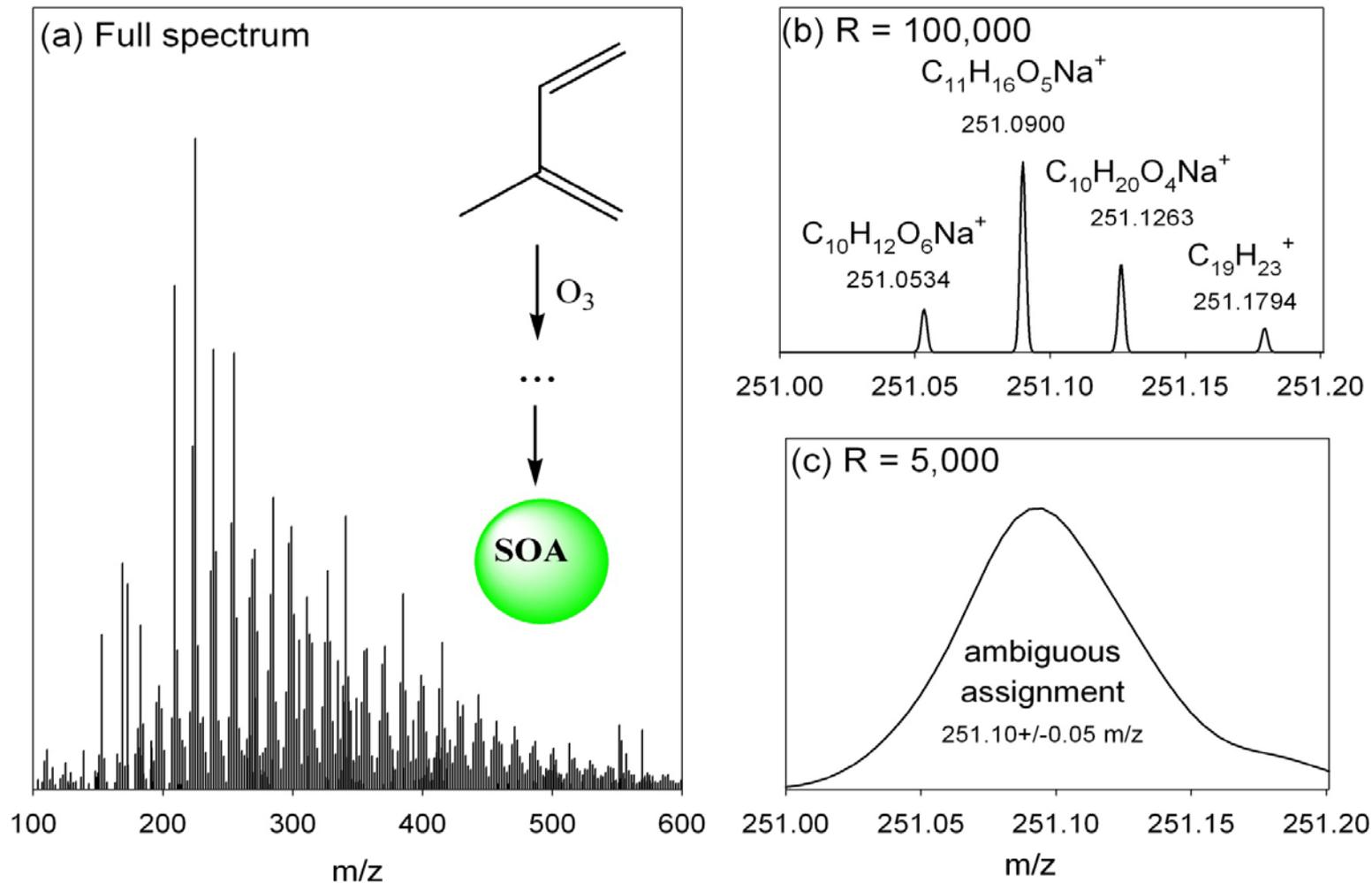
# Nanospray Desorption Electrospray Soft Ionization (nano-DESI) MS



**Reactivity and  
Aging of  
Aerosols**

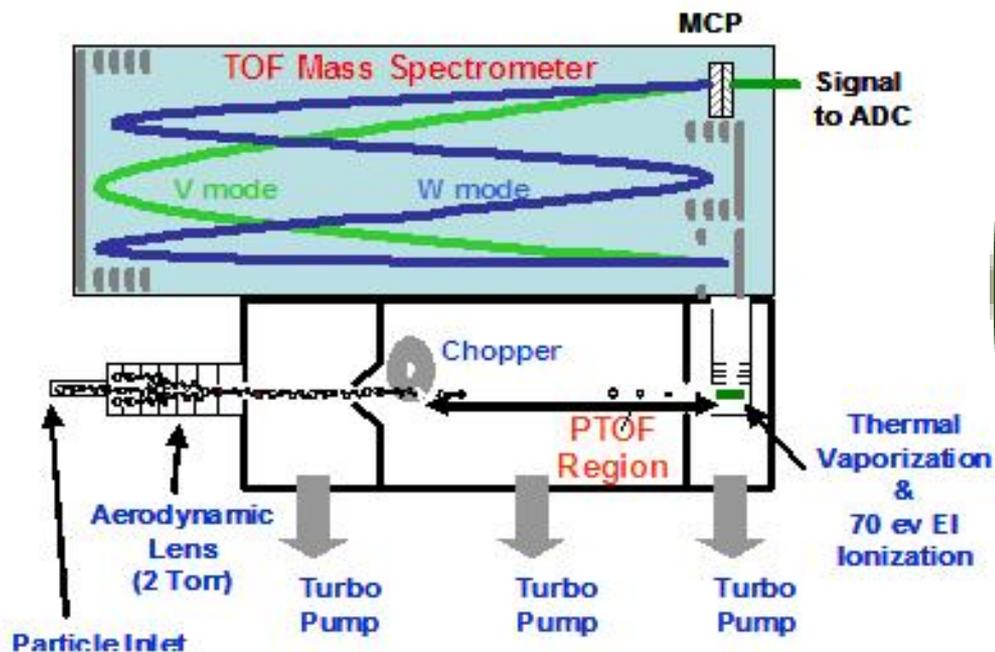
**Novel nano-DESI MS technique enables  
quantitative determination  
of hundreds of types of molecules  
in a complex mixture in situ**

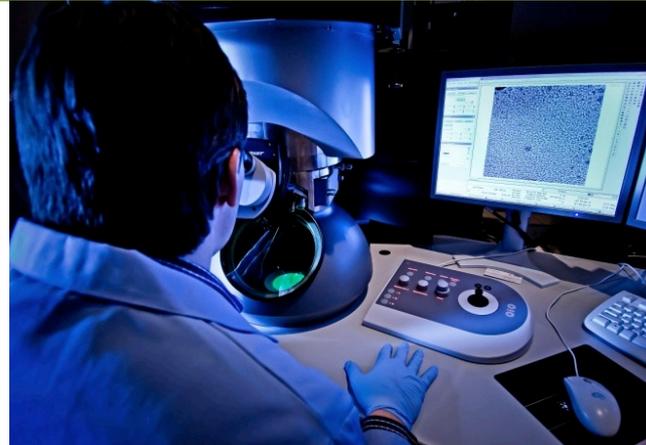
Nguyen et al. *High-resolution mass spectrometry analysis of secondary organic aerosol generated by ozonolysis of isoprene* *Atm. Environ.* 44 (2010) 1032-1042



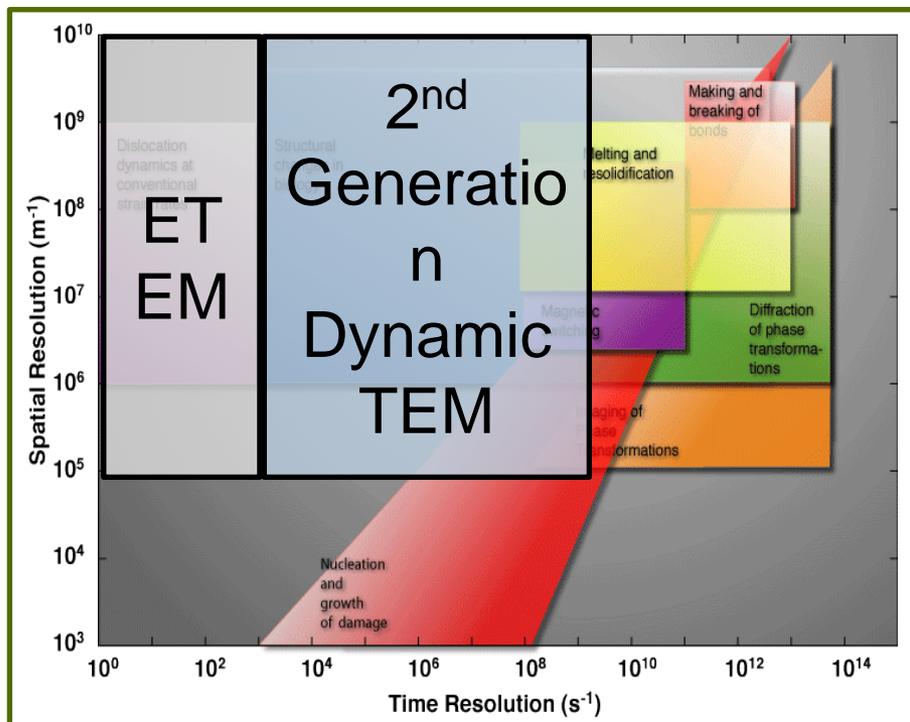
# Field deployment of Aerodyne HR Time-of-Flight Aerosol Mass Spectrometer

## Aerodyne HR-ToF-AMS





- More than 30 instruments available to users
- New 'Quiet Wing' houses 5 state-of-the-art microscopes
  - Scanning/Transmission EM with Electron Energy Loss Spectrometer
  - Aberration corrected Environmental TEM
  - Second generation Dynamic TEM
  - Helium Ion Microscope with Nanolithography capability
  - Ultra-High Vacuum, Low-Temperature, Scanning Probe
- Unique IR Scanning Near-field Optical Microscope



Environmental TEM capabilities probe reactions to ms timescale

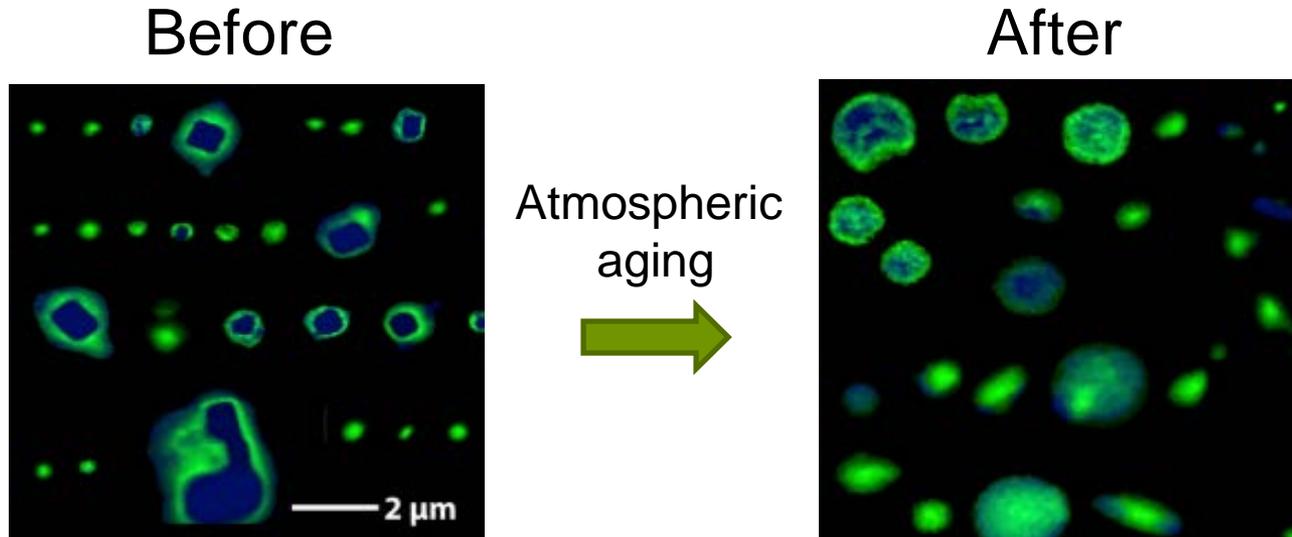


Dynamic TEM combines high resolution electron optics with pulsed lasers to observe processes on the  $\mu$ s to ns timescale

Time	Task
Q3 FY12	Move microscope to PNNL ( <b>complete</b> )
Q4 FY12	Verify TEM performance ( <b>complete</b> )
Q1 FY13	Build Lasers ( <b>complete</b> )
Q2 FY13	Gun design & build parts ( <b>complete</b> )
Q3 FY13	Modify gun ( <b>complete</b> )
Q4 FY13	Install gun, optimize lasers, obtain first pulses (underway)

# Following reactions of atmospheric particles in real time

Dynamic TEM In situ experiments could observe how weak organic acids mix with sea salt particles to modify climate related properties.

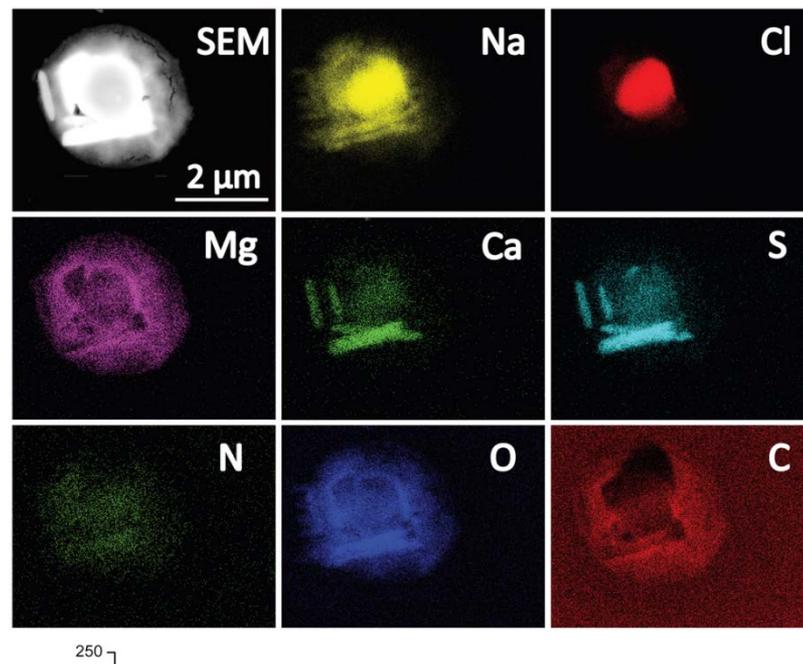


*Laskin et al, JGR, 2012, 117, D15302*

- Observe particle nucleation, growth, aggregation and transformation with damage – (currently see before and after)
- Determine the kinetics of growth and observing reaction mechanisms
- Observe how the optical properties of particles change as they age and transform

CARES campaign involved several EMSL capabilities:

- SPLAT II
- HR-ToF-AMS
- TRAC and Drum sample collection
- SEM/EDS



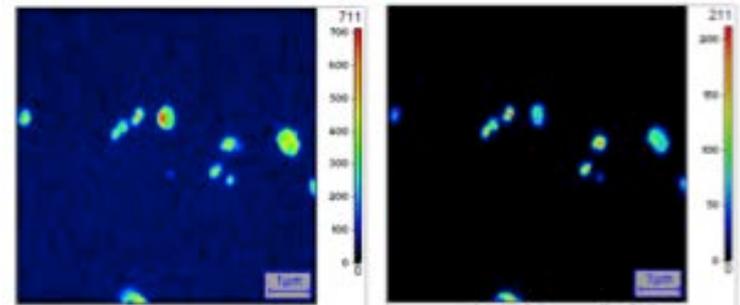
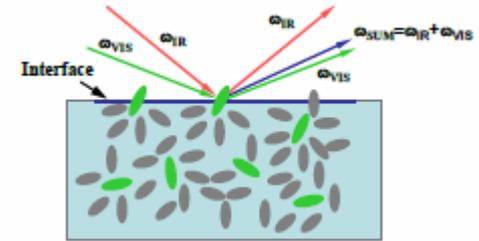
Zaveri et al. *Atmos. Chem. Phys.*, 12, 7647–7687, 2012

SEM image and EDX elemental maps indicating characteristic internal heterogeneity of aged sea-salt particles from the CARES field study.

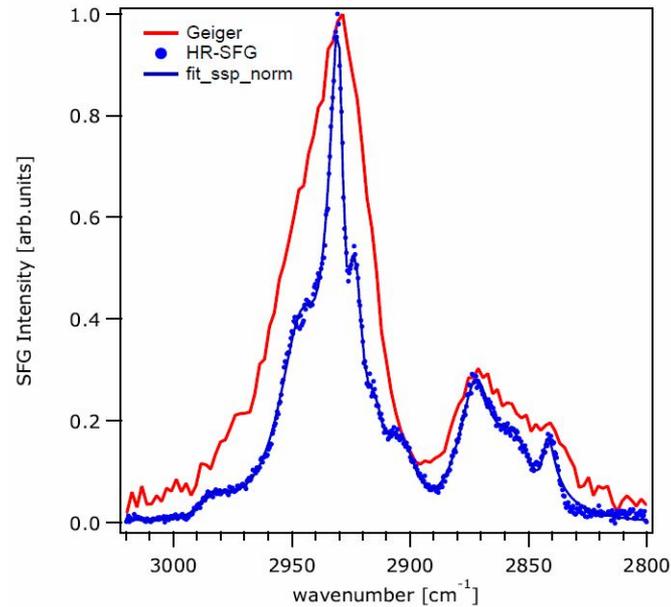
Tropospheric chemistry of internally mixed sea salt and organic particles: Surprising reactivity of NaCl with weak organic acids  
Alexander Laskin et al. *Journal of Geophysical Research* 2012

# Occasional or potential use for aerosol research

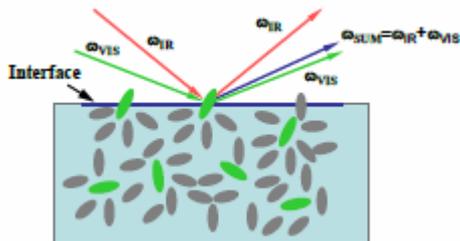
- Sum Frequency Generation
- Atom Probe Tomography
- TOF-SIMS, Nano-SIMS, High resolution SIMS
- Surface Science Capabilities
  - ◆ XPS
  - ◆ SPM/AFM
  - ◆ Model Systems
  - ◆ PIXE
- Molecular Science Computer Facility
- Metabolomics: biogenic organic aerosol precursors



# SFG-Sum frequency generation Infra-Red (IR) spectroscopy



SFG spectra of  $\alpha$ -pinene from a standard spectrometer (red), and EMSL's SFG spectrometer (blue),



SFG is a non-linear technique that provides IR spectral information (structure + dynamics) at interfaces only. It is therefore a technique that selectively probes surface structures

## ■ TOF-SIMS

- ◆ Outer surface sensitive
- ◆ 500 nm elements 1 $\mu$ m molecules
- ◆ Cs<sup>+</sup>, O<sup>+</sup>, C<sub>60</sub><sup>+</sup> and Bi<sup>+</sup> cluster beams
- ◆ Elemental and molecular mapping



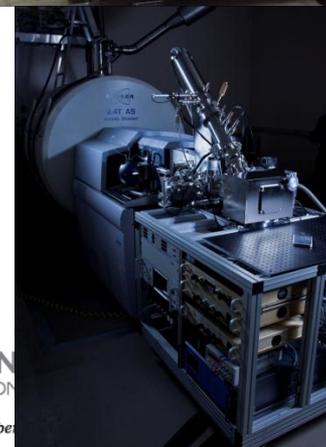
## ■ NanoSIMS

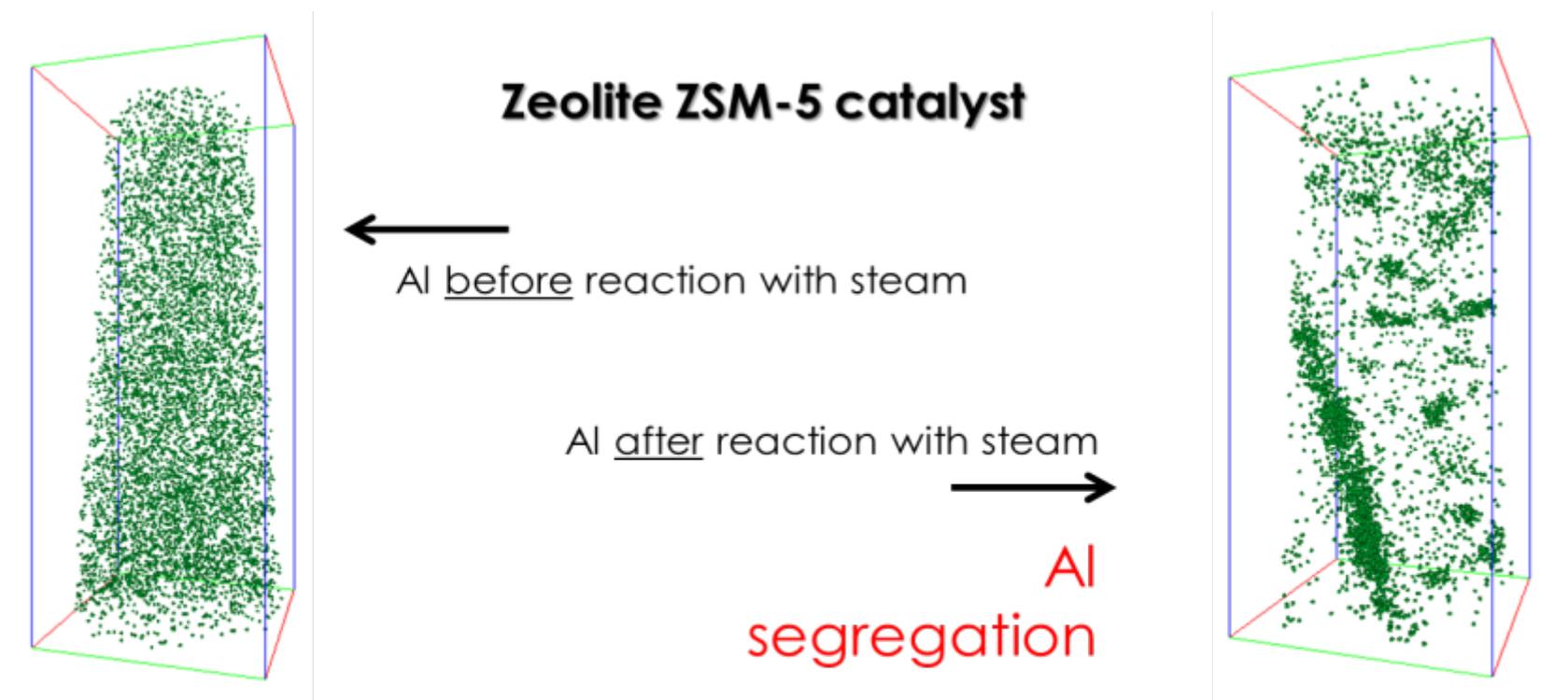
- ◆ "bulk" sensitive
- ◆ 50 nm Resolution
- ◆ O<sup>+</sup> and Ga<sup>+</sup> beams
- ◆ Elemental and isotopic mapping



## ■ High Mass Resolution SIMS

- ◆ High mass resolution
- ◆ C<sub>60</sub><sup>+</sup> source
- ◆ 10s  $\mu$ m





**3-D images with  $\sim 0.5\text{nm}$  spatial resolution & ppm selectivity**

- Solute & impurity diffusion & segregation
- Reaction fronts & interaction with grain boundaries
- Multimodal analysis with TEM methods (FIB sections)



Open source since Oct 2010

## NWChem is suite of methods for computational chemistry

- ◆ Gaussian-based DFT/TDDFT
- ◆ Plane wave based DFT
- ◆ High Accuracy Methods → MP, CC, EOMCC, MRCC
- ◆ Molecular Dynamics, Molecular Mechanics
- ◆ Integrated Methodologies → QM/MM
- ◆ Scripting → Python
- ◆ Workstations → Supercomputers

### Potential atmospheric-related computational studies:

- **brown carbon optical properties (refractive index)**
- **photochemistry of chromophores**
- **New particle formation and growth**
- **HOx recycling, BVOC oxidation**

[www.nwchem-sw.org](http://www.nwchem-sw.org)

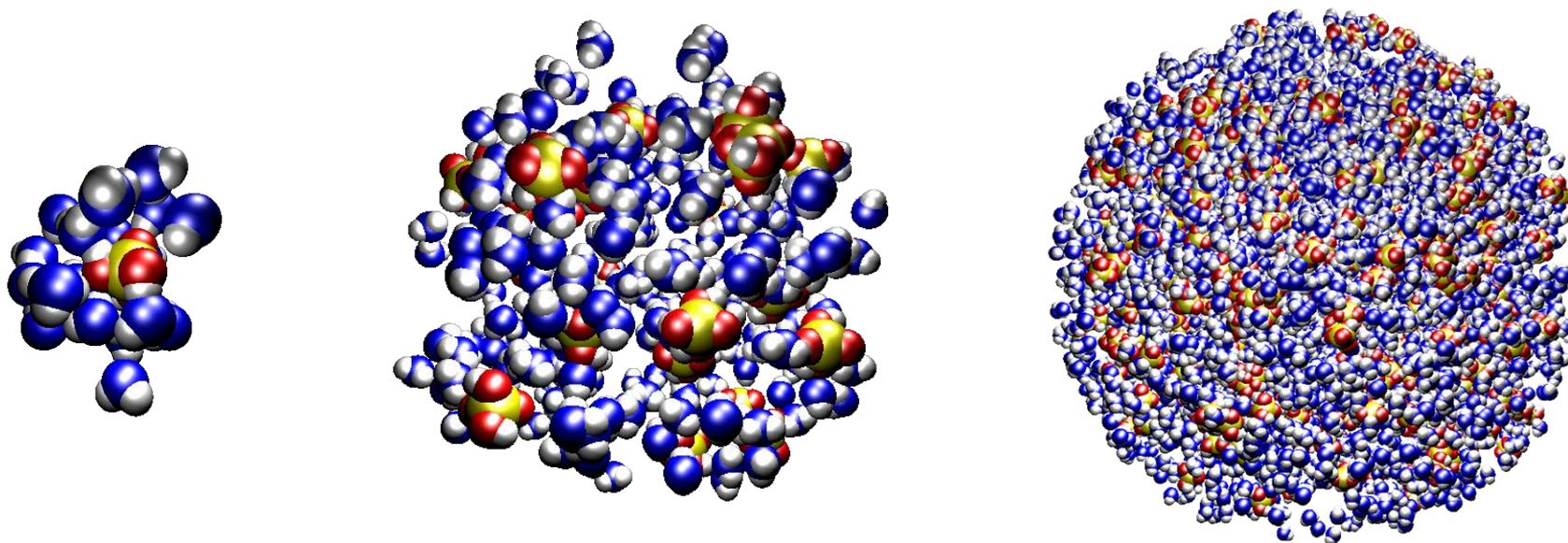
# Introducing Cascade (HPCS-4A)

- The HPCS-4A system has been named “Cascade”
- Powerful new system for NWChem & climate codes
  - ◆ 3.4 Petaflops theoretical peak performance
  - ◆ High processor count
  - ◆ Xeon Phi accelerators
  - ◆ Generous 8 GB RAM/core
- Installed in July, undergoing testing now
- Anticipate top-20 debut on November 2013 top 500 list



# Modeling nucleation processes from first principles

*Dynamic Nucleation Theory Monte Carlo capability can calculate monomer evaporation rates and deliver insight into nuclear processes*



Sulfuric acid – 20  
water cluster;  
critical size cluster  
for nucleation

250 Sulfuric acid –  
250 water cluster;  
nucleated particle  
with growth

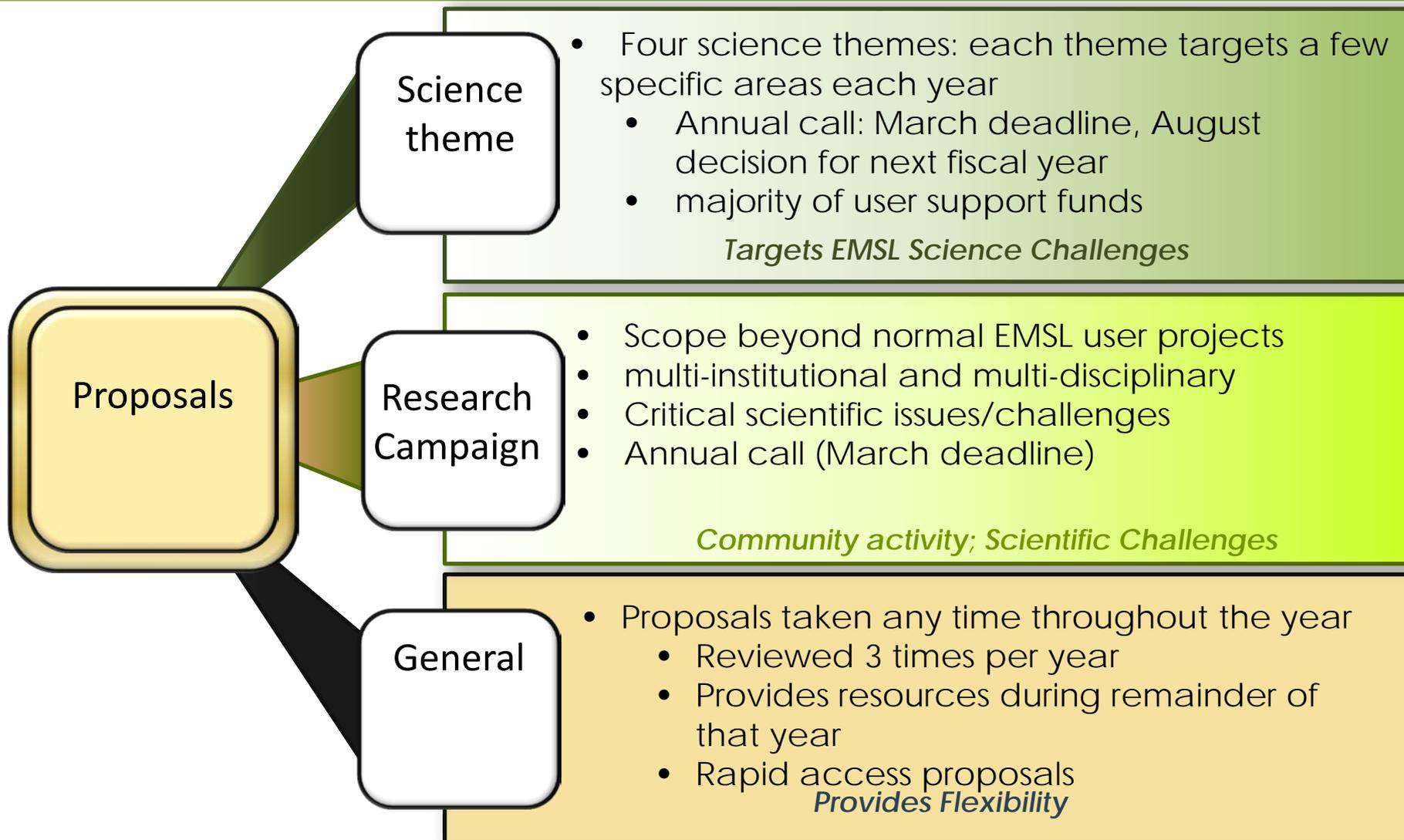
500 sulfuric acids – 4000  
water cluster; a nanodroplet  
of sulfuric acid

LD Crosby, SM. Kathmann, TL Windus, J.  
Comp. Chem. 30, 743 (2008)

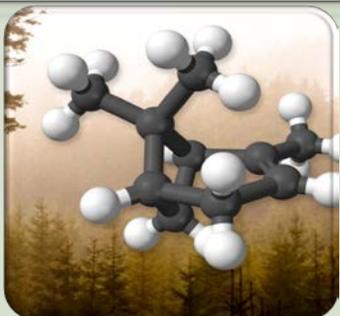
Constant push for **higher resolution**, **in situ real-time** and closer **linking of theory and experiment**

- Next generation NMR -Dynamic Nuclear Polarization – (up to 10X sensitivity, interface sensitive, environmental conditions, single particle analysis)
- Ultra-fast TEM: detailed in situ information at nanometer spatial resolution and pico-second time scale
- High throughput metabolomics
- Field Instruments

# Access to EMSL capabilities (instruments and expertise) is primarily through competitive proposals



Vision: Drive molecular-scale discovery and innovation to enable a predictive understanding for the benefit of BER and the nation



Alex Guenther

## ATMOSPHERIC AEROSOL SYSTEMS

*Biology, chemistry, & physics of aerosol sources, formation, aging, composition, optical properties to strengthen predictive understanding of climate*



Scott Baker

## BIOSYSTEM DYNAMICS & DESIGN

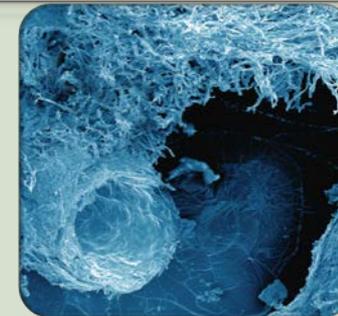
*Intra/intercellular complexes & dynamic processes in microbes, fungi, plant roots to advance systems biology for bioenergy and biorenewables*



Don Baer

## ENERGY MATERIALS & PROCESSES

*Dynamic transformation mechanisms & physical & chemical properties at critical interfaces in catalysts & energy materials*



Nancy Hess

## TERRESTRIAL SUBSURFACE ECOSYSTEMS

*Fluxes of nutrients, metabolites, & chemical signatures at biogeochemical interfaces in heterogeneous environs across multiple scales*

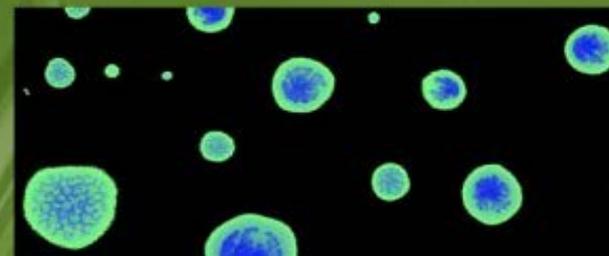
## Atmospheric Aerosol Chemistry, Climate Change, and Air Quality



## Science Theme Advisory Panel Workshop



January 30, 2013  
Report: July 2013



# EMSL annual user meeting (May 6&7 2014) is focused on atmospheric organics



## EMSL Integration 2014

*Dates set for annual user meeting: Atmospheric Organics*

EMSL's **annual user meeting** - EMSL Integration 2014 – has been scheduled for **May 6 and 7** in Richland, Washington.

This year, we're excited to focus on atmospheric organics. **Scot Martin**, Gordon McKay Professor of Environmental Chemistry at Harvard University, will be the keynote speaker. The meeting also will feature half-day workshops on the second day – more details to come over the next several weeks.

The meeting is open to all members of the scientific community, including past and current users and interested researchers.

There also will be a poster session with awards for top student posters.

*Registration will open in January.*



- EMSL scientists includes experts in applying EMSL capabilities to atmospheric aerosol systems research (e.g., SPLAT, nano-DESI, AMS, microscopy)
- There are other existing EMSL capabilities (and experts) that could be applied to aerosol research
- Potential for developing new EMSL capabilities and expertise for aerosol research
- EMSL annual user meeting on atmospheric organics in May 6&7 2014.
- Call for science theme proposals will open in December and have a March 3, 2014 deadline.



# Questions ?

Contact: [alex.guenther@pnnl.gov](mailto:alex.guenther@pnnl.gov)



ENVIRONMENTAL MOLECULAR SCIENCES LABORATORY