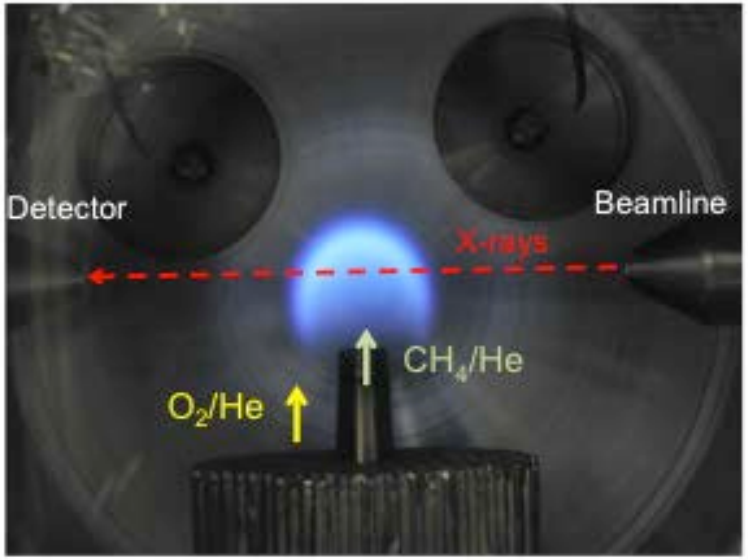
Characterization of Combustion Processes and Products Using Soft X-ray Spectroscopies

Hendrik Bluhm

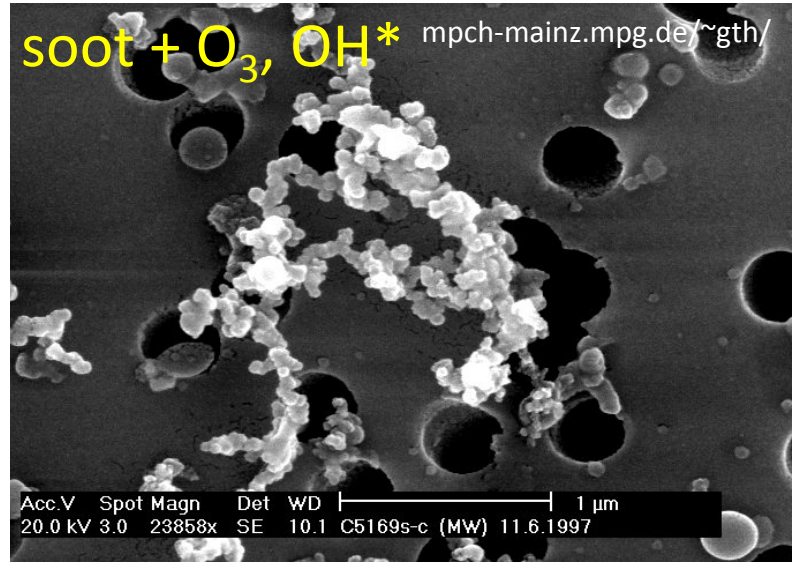
Chemical Sciences Division, Lawrence National Berkeley Laboratory

Near-edge X-ray Absorption Spectroscopy



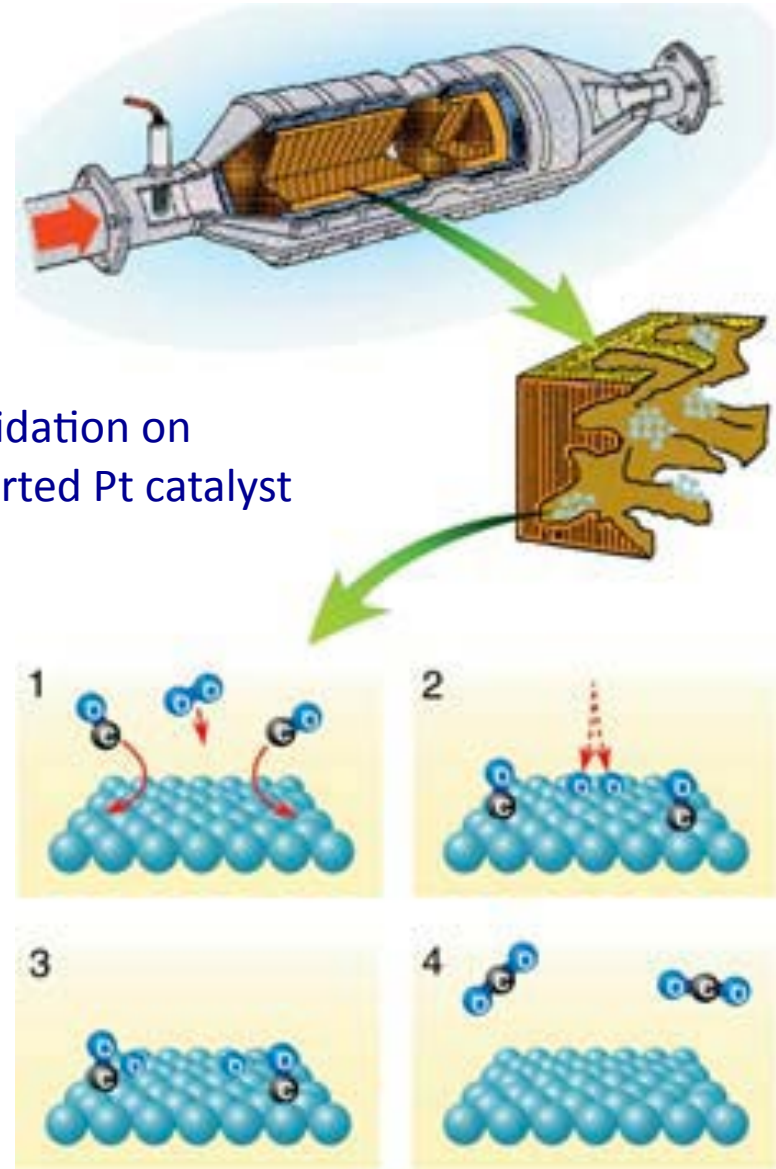
Gas phase composition and soot formation in flames (jointly with Sandia NL)

Ambient Pressure X-ray Photoelectron Spectroscopy



Heterogeneous chemistry of solid/vapor and liquid/vapor interfaces

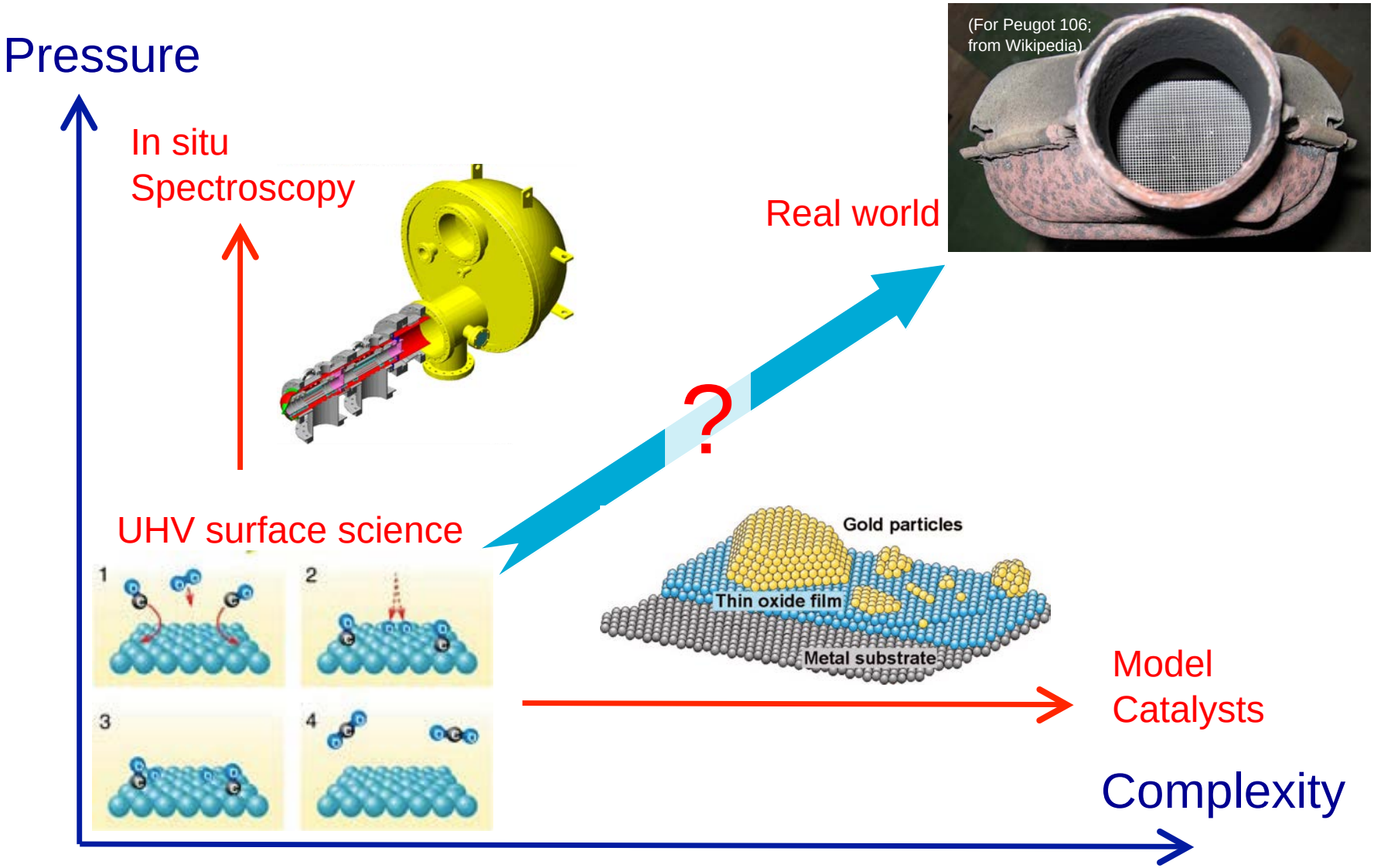
UHV Surface Science and Heterogeneous Catalysis



CO oxidation on supported Pt catalyst

Gerhard Ertl, Nobel Price (2007).

Bridging the Pressure and Materials Gap in Catalysis

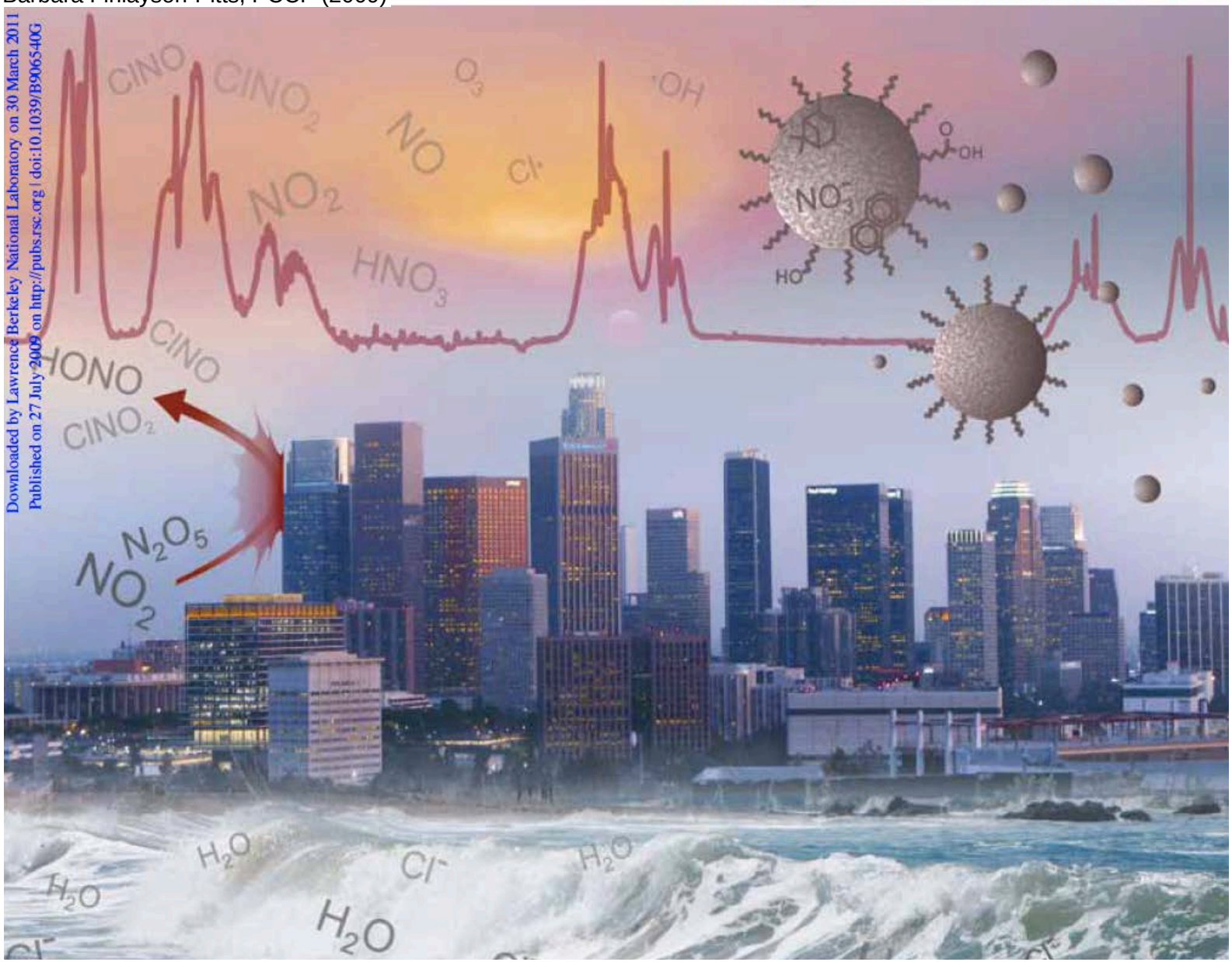


Interfacial Chemistry in the Environment and Atmosphere

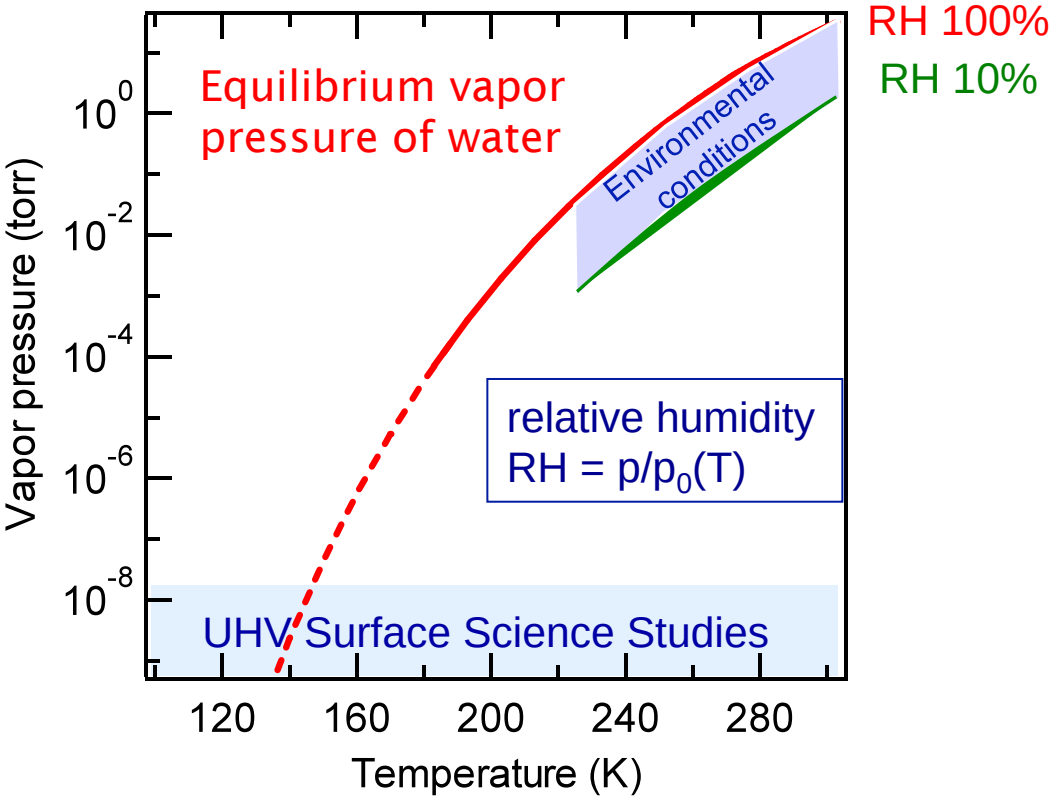
Barbara Finlayson-Pitts, PCCP (2009)

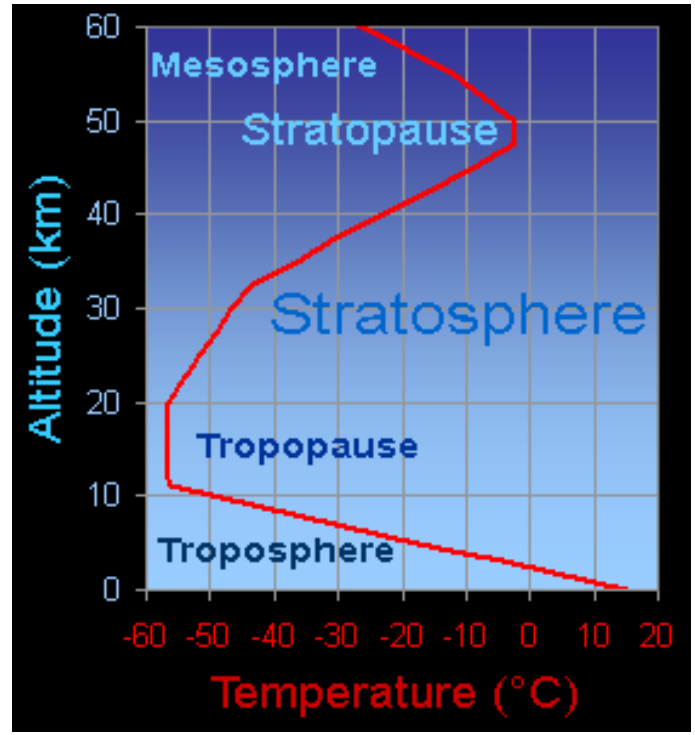
Volume 11 | Number 36 | 28 September 2009 | Pages 7741–8104

Downloaded by Lawrence Berkeley National Laboratory on 30 March 2011
Published on 27 July 2009 on http://pubs.rsc.org | doi:10.1039/B906540G



Partial Pressure of Water on Earth and in the Atmosphere





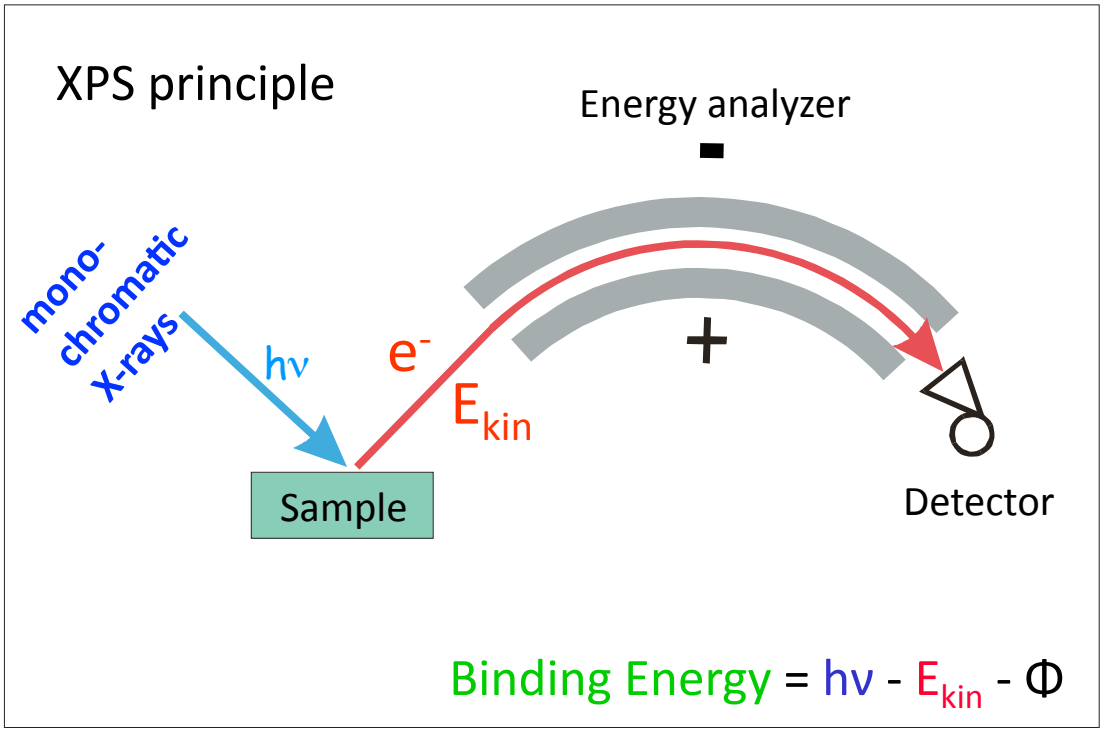
http://www.windows2universe.org/

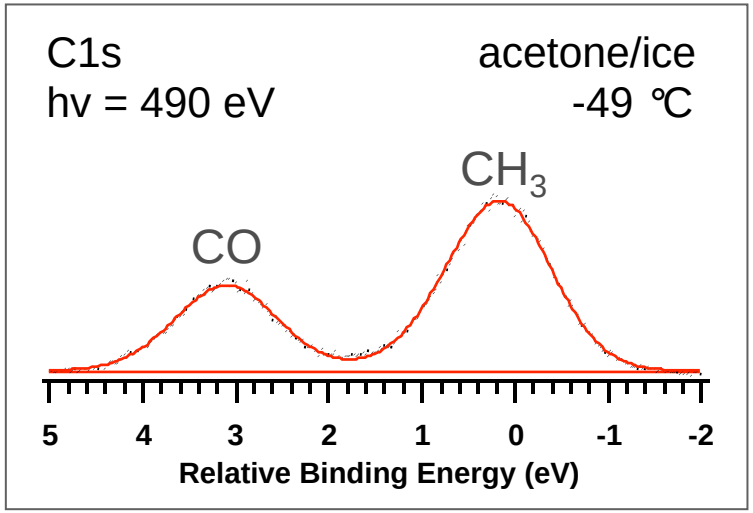
Only some surface sensitive techniques are applicable under elevated pressure conditions (non-linear optics, surface XRD, scanning probes)

X-ray Photoelectron Spectroscopy:

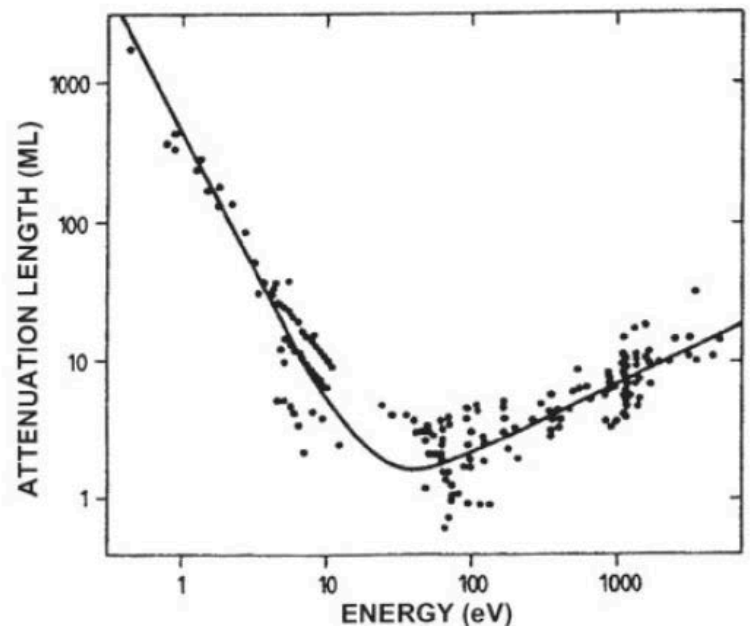
Surface sensitive, element specific, chemically sensitive, non-contact measurement of electrical potentials

X-ray Photoelectron Spectroscopy

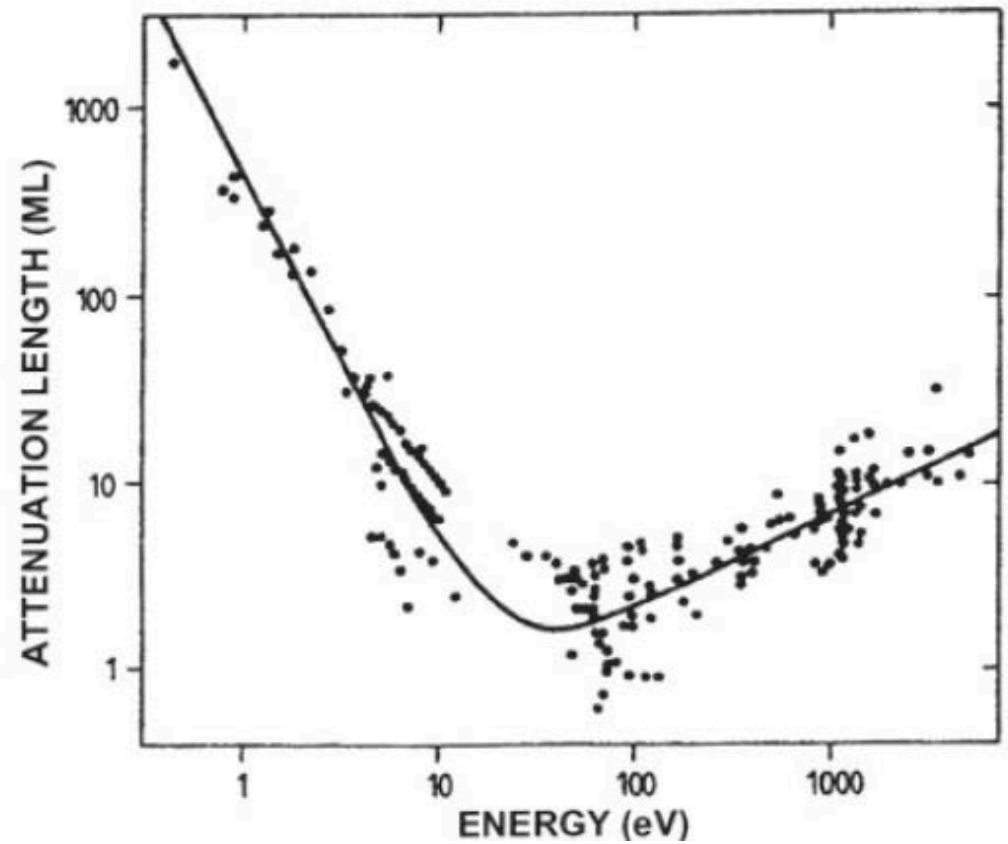


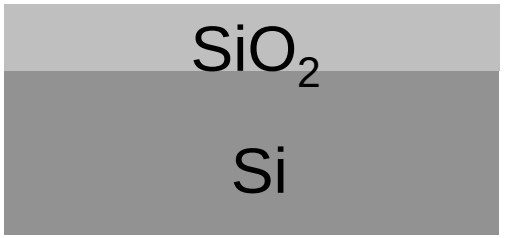


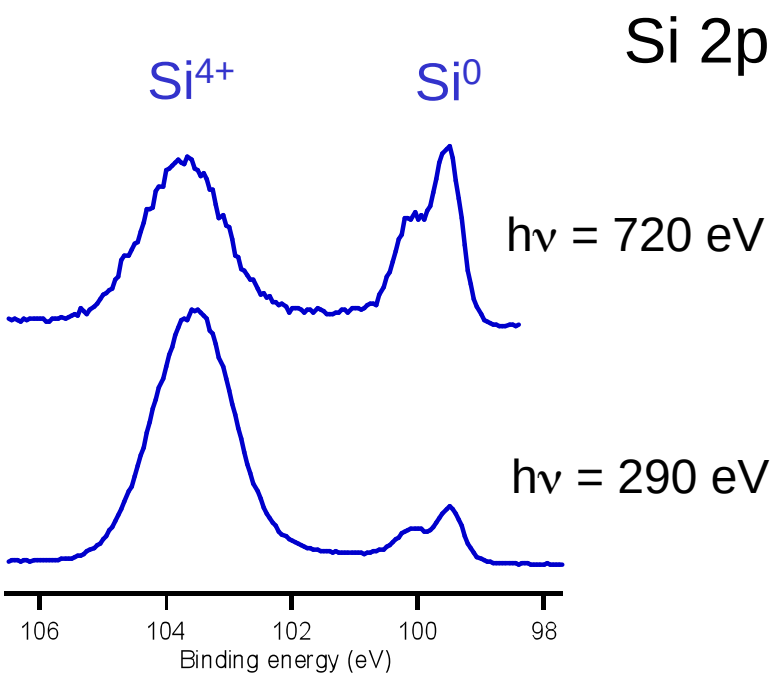
- element specific
- quantitative
- chemically specific
- surface sensitive



X-ray Photoelectron Spectroscopy: Depth Profiling





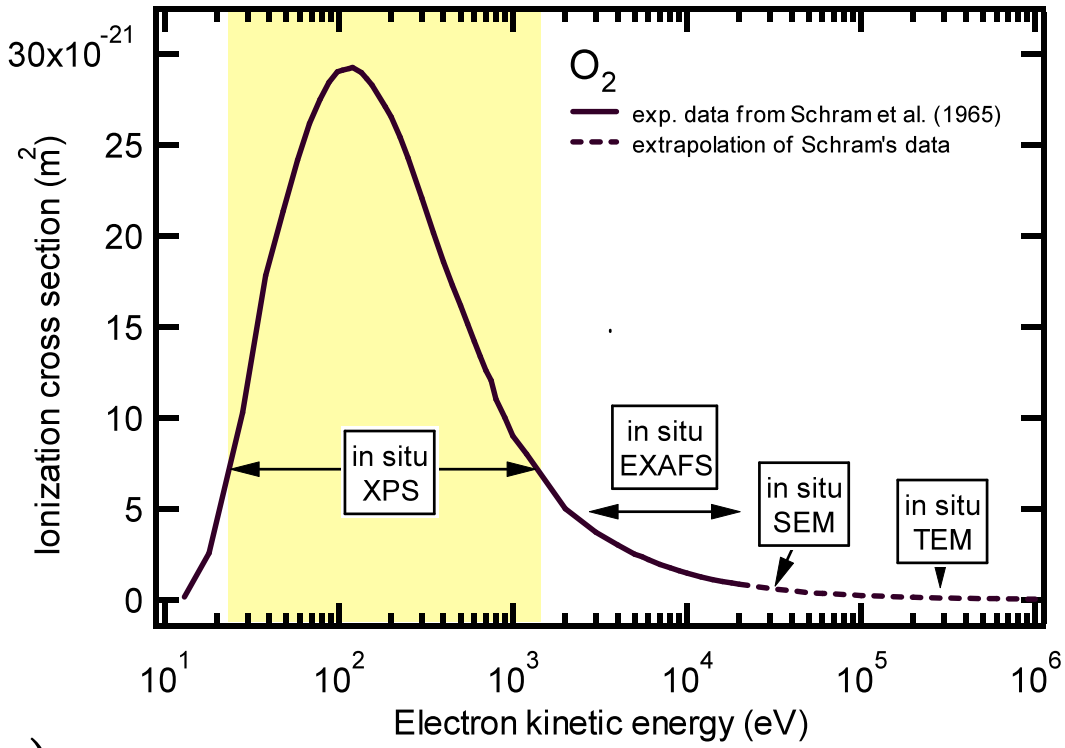


Ambient Pressure XPS: Obstacles

Fundamental limit:

elastic and inelastic scattering of electrons in the gas phase

inelastic scattering is mostly due to ionization of gas phase molecules



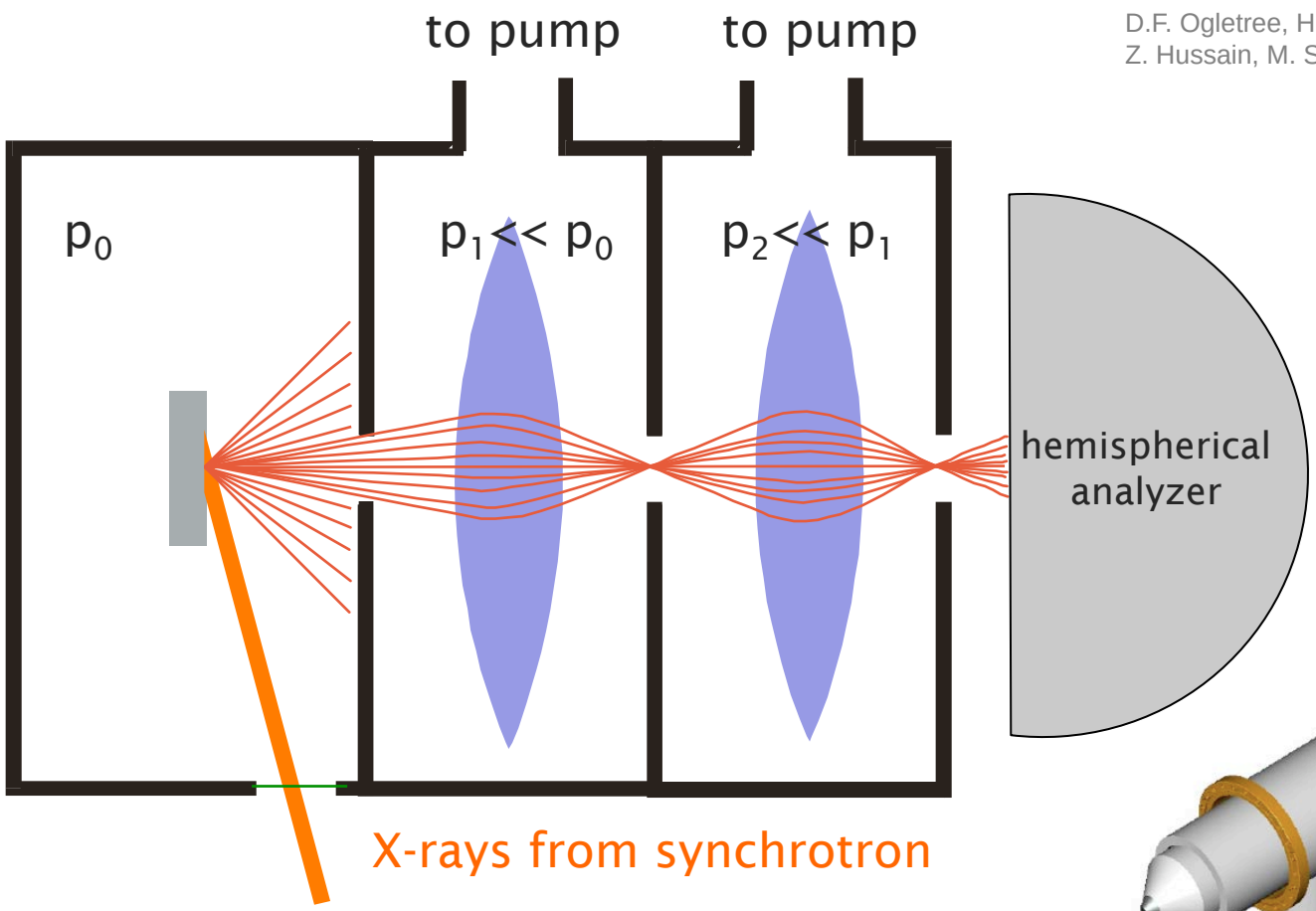
$$\frac{I_p}{I_{vac}}(E) \propto \exp\left(-z\sigma(E)p\right)$$

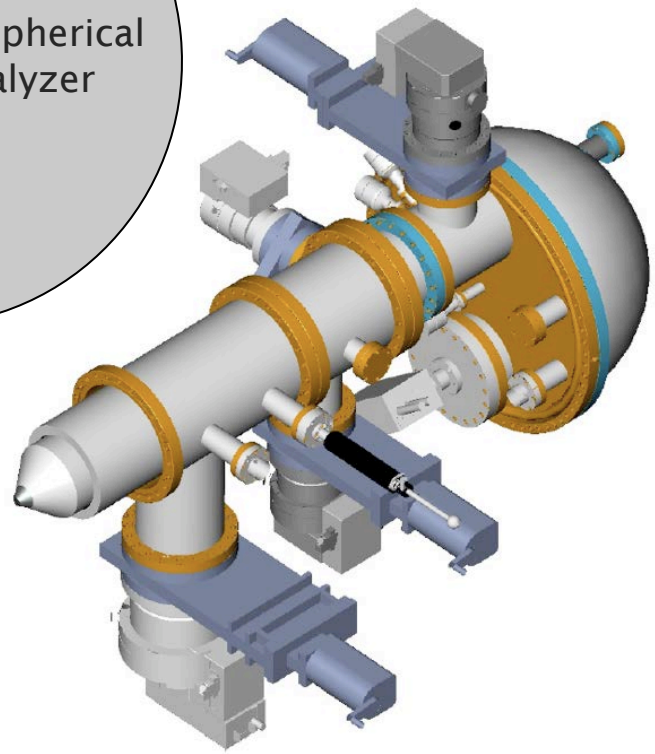
ionization cross section depends on molecule: $H_2 < He < O_2 < CH_3OH$

For calculations of total ionization cross sections see: Kim&Rudd, Phys. Rev. A 50, 3954 (1994).

Berkeley/Berlin Ambient Pressures XPS Design

D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley,
Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.





LBNL/FHI Berlin/Specs

Current pressure limit ~5 Torr
With 5 µm aperture and beam size ~100 Torr

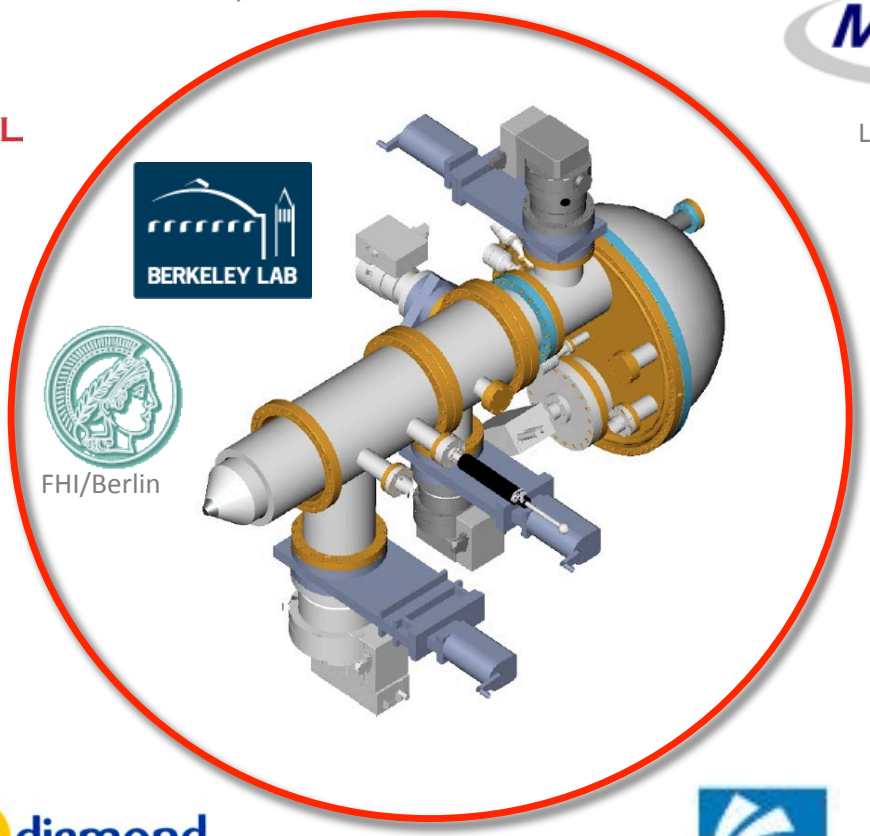
Ambient Pressure XPS Instruments at Synchrotrons

ALS ADVANCED LIGHT SOURCE
LBNL, Berkeley, CA

BESSY
Berlin/ Germany

MAX-lab
Lund/Sweden

SSRL
SSRL, Stanford, CA



BERKELEY LAB

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High Energy Accelerator Research Organization (KEK)
Institute of Materials Structure Science (IMSS)
Photon Factory
Tsukuba/Japan

ALBA
Synchrotron Light Facility
Barcelona/Spain*

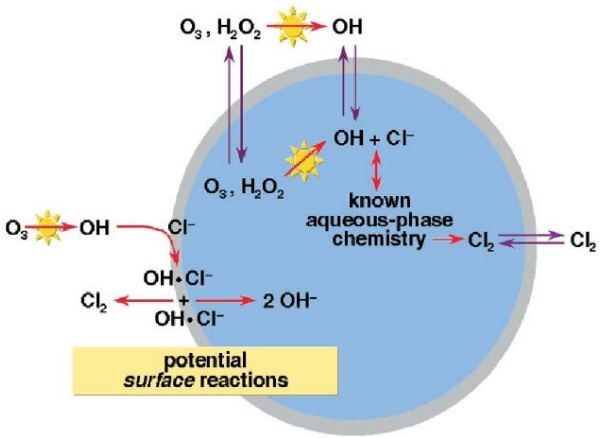
diamond
Oxfordshire/UK**

PAUL SCHERRER INSTITUT
PSI
Villigen/Switzerland**

LNLS
Campinas/Brazil*

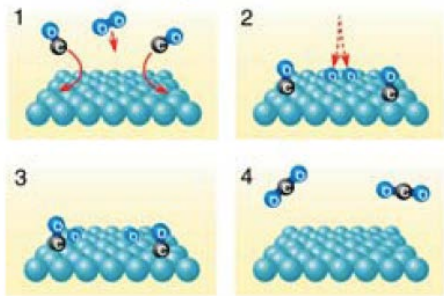
*in commissioning; **funded

Examples for the Application of Ambient Pressure XPS

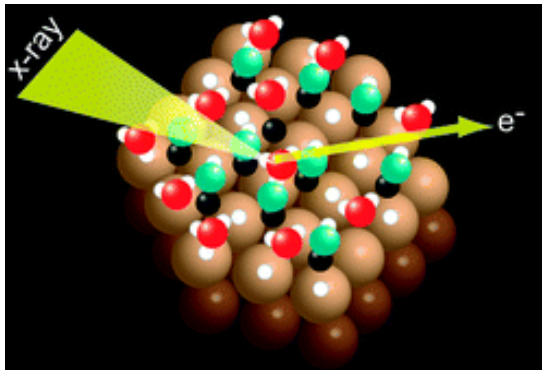


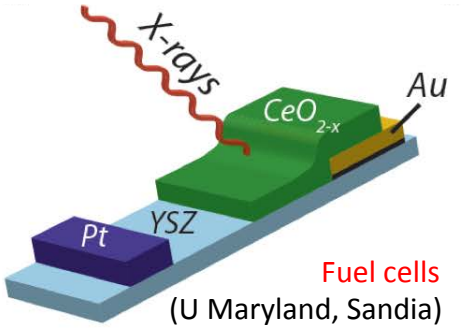
Chemistry of solution surfaces
(Hemminger, Ghosal, Krisch)

Heterogeneous catalysis (Somorjai, Salmeron, Besenbacher, de Groot, Lundgren, Nilsson, Starr)

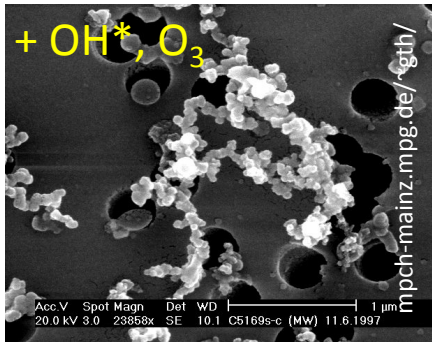


Reaction of water with oxides and metals
(Brown, Salmeron, Nilsson, Held, St. Gobain)

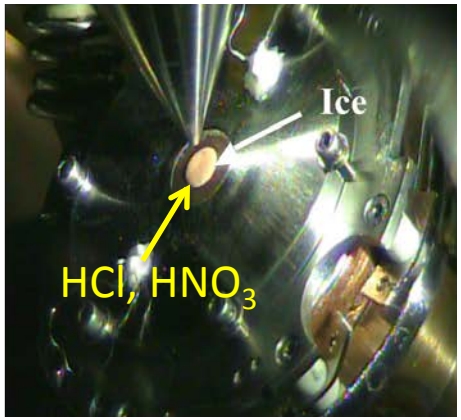




Fuel cells
(U Maryland, Sandia)



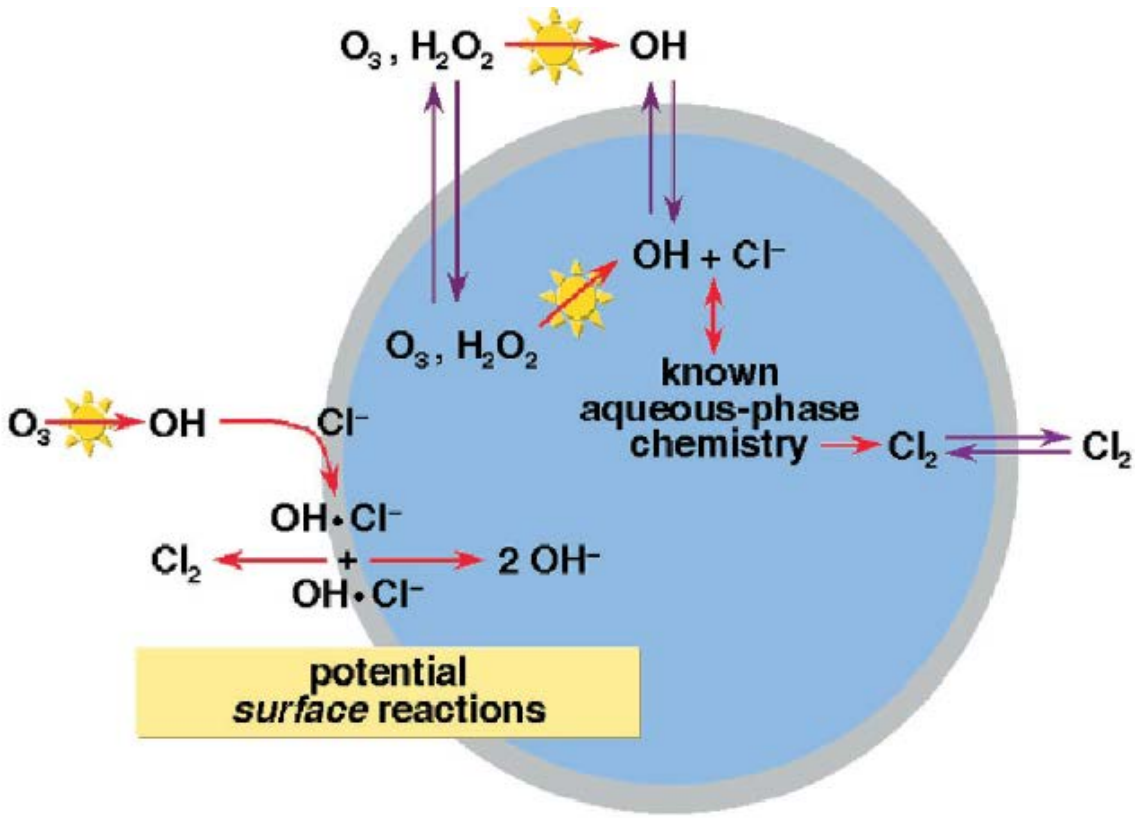
Heterogeneous chemistry of soot particles (Wilson)



Chemistry of ice surfaces
(Ammann, Newberg)

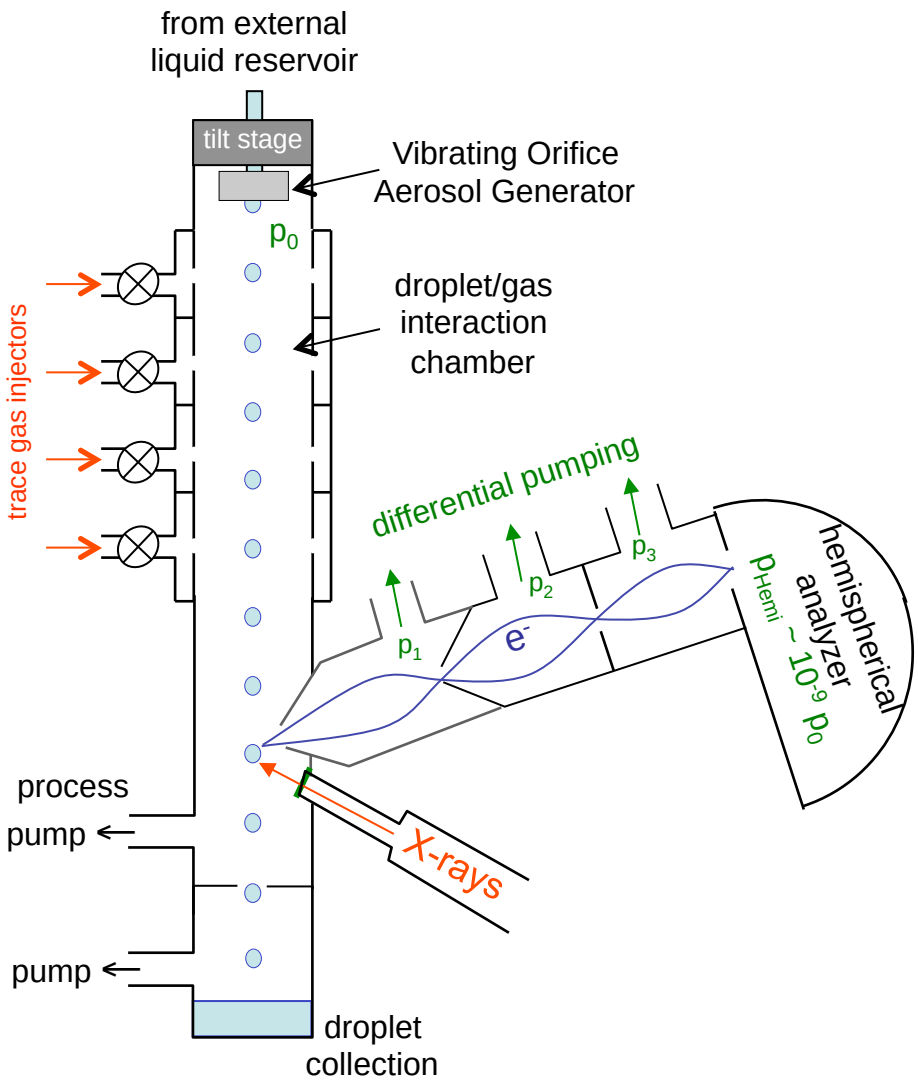
Surface of Aqueous Solution

Surface vs Bulk Chemical Composition



E.M. Knipping et al., Science 288, 301 (2000)

Kinetics of Heterogeneous Reactions at Liquid/Vapor Interfaces



Liquid droplet is in equilibrium with its vapor

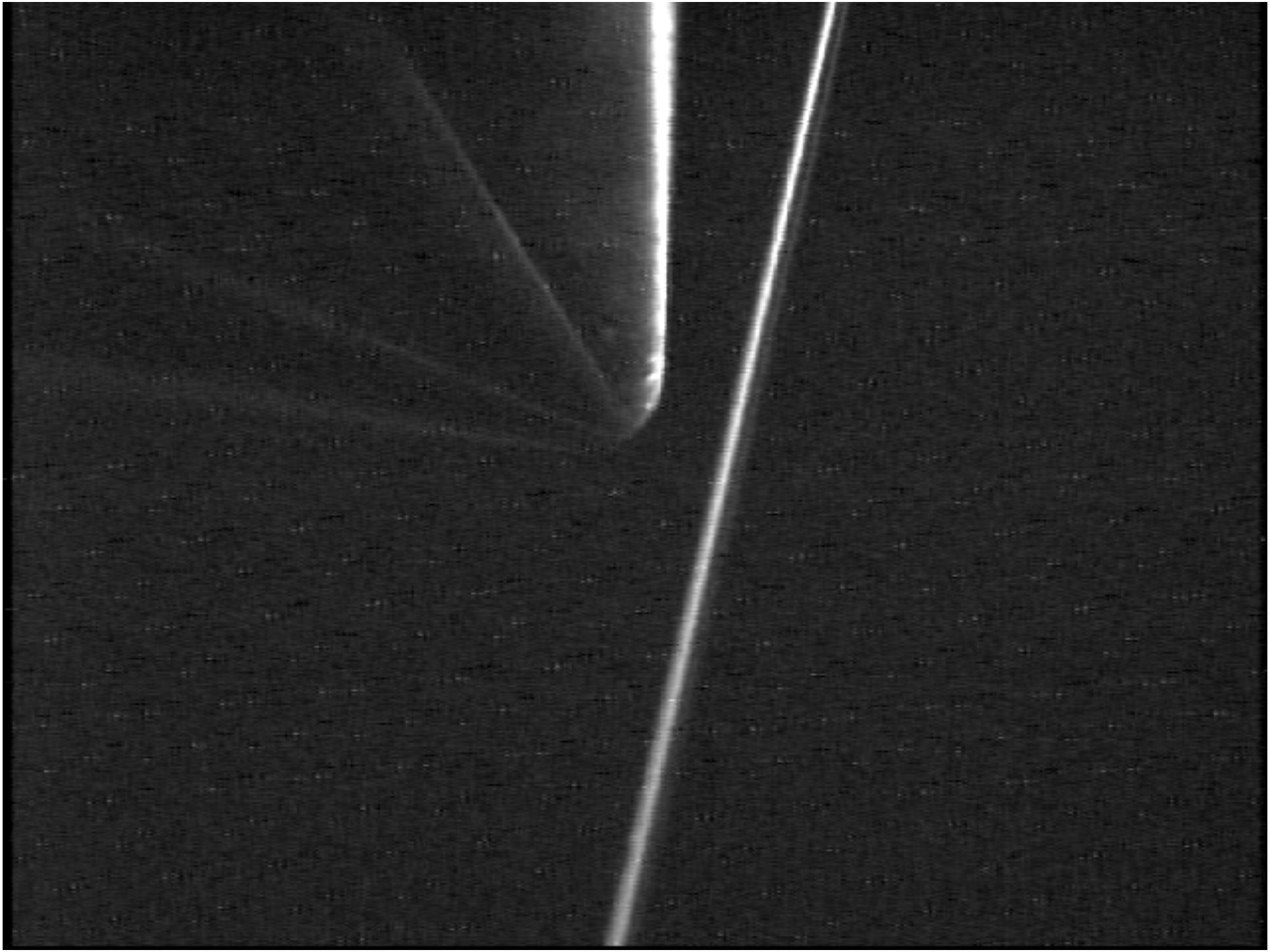
Short irradiation of droplets (~μs)
→ no beam damage

Continuously refreshed samples
→ contamination-free surface

Many types of liquids can be investigated
→ aqueous solutions, acids, fuels

Droplets are stable over long distances: Variable droplet gas interaction time
→ Kinetics of gas uptake by droplets

D.E. Starr, E.K. Wong, D.R. Worsnop, K.R. Wilson, H. Bluhm, Phys. Chem. Chem. Phys. (2008).



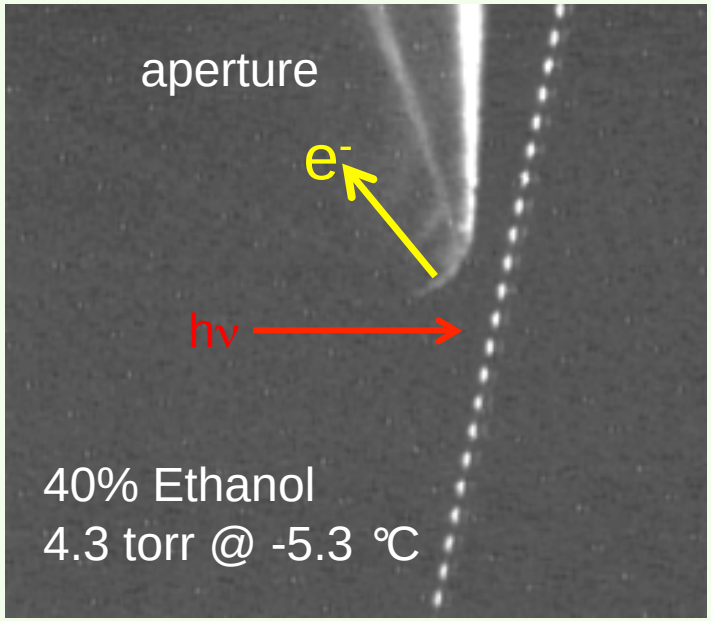
Droplet Train/APXPS: Proof-of-Principle Experiments

Typical operating conditions

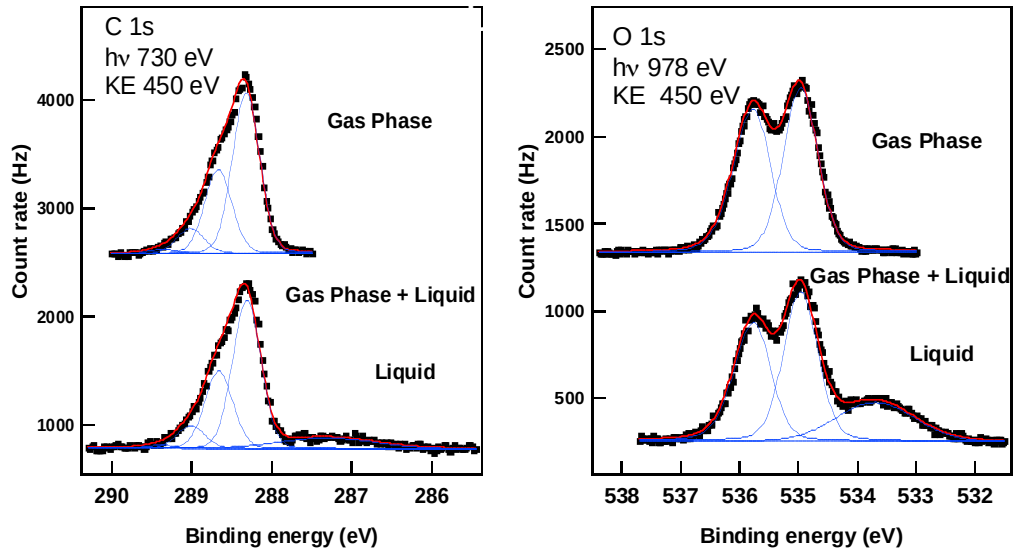
Flow rate: 2.2 ml/min
Piezoelectric driving frequency: 54 kHz
Orifice diameter: 50 μm
Droplet Velocity: 1870 cm/s

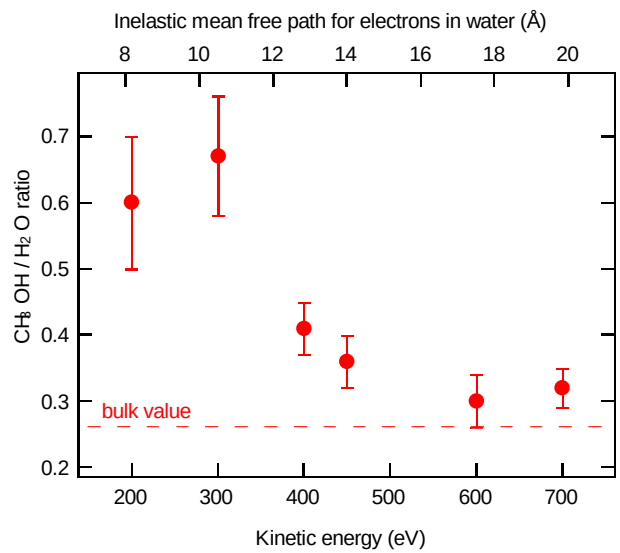
Time of travel from Orifice to Measurement Position (~ 3 cm): 1.6 ms

Surface Temperature Equilibration Time: ~ 0.5 ms



Enhancement of methanol at the surface of an aqueuoes (χ = 0.21) solution



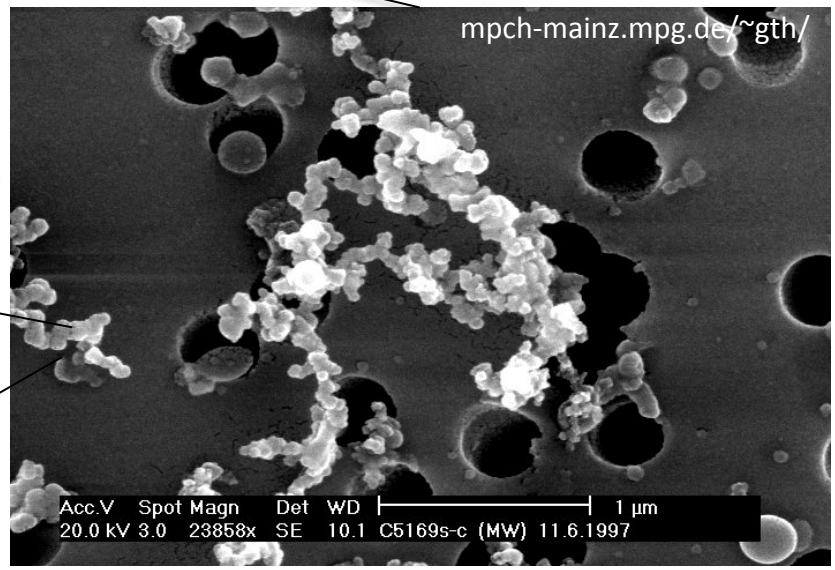


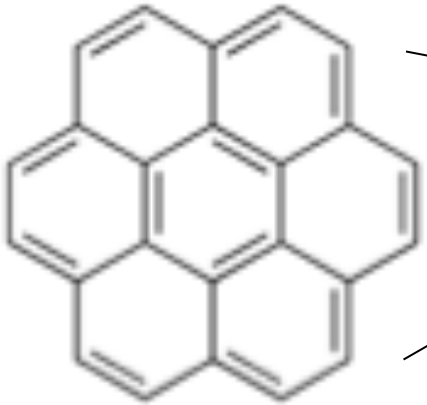
D.E. Starr, E.K. Wong, D.R. Worsnop, K.R. Wilson, H. Bluhm, Phys. Chem. Chem. Phys. (2008).

Oxidation of Soot

Reaction of Carbonaceous Aerosols with O_3 and OH

Diesel Soot



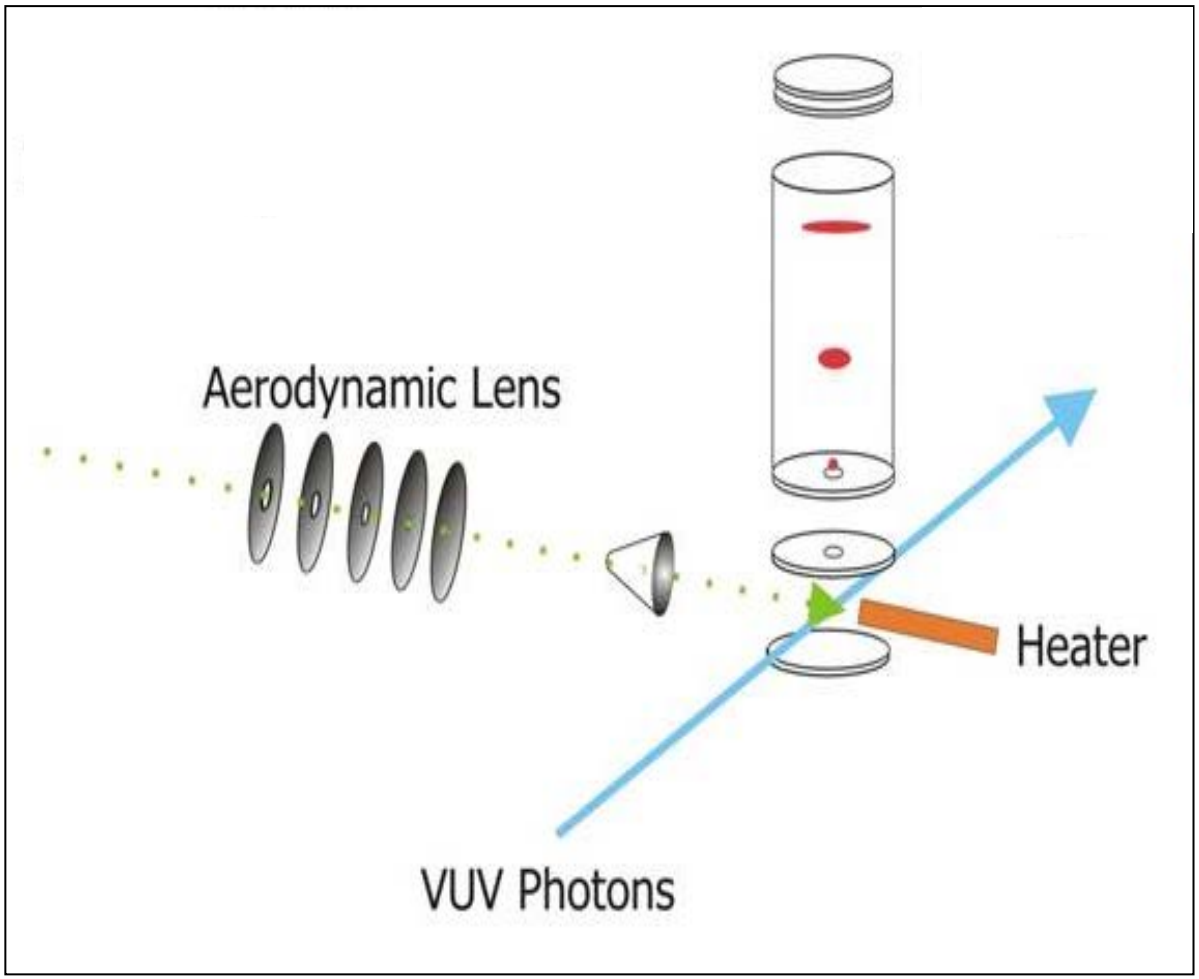


Coronene ($C_{24}H_{12}$) + O_3, OH --> ?

Bulk Measurement of Soot Oxidation: Aerosol Mass Spectroscopy

Vacuum Ultraviolet AMS

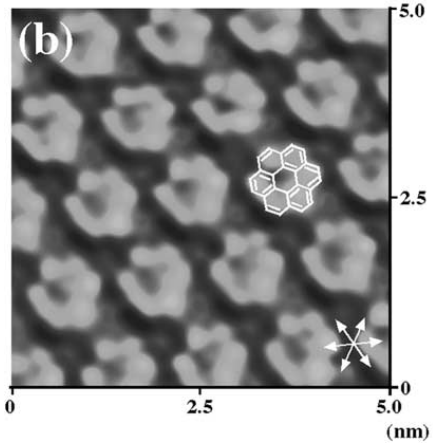
Chemical Dynamics Beamline
Advanced Light Source



Growth of Monolayer Coronene on Ag(111)

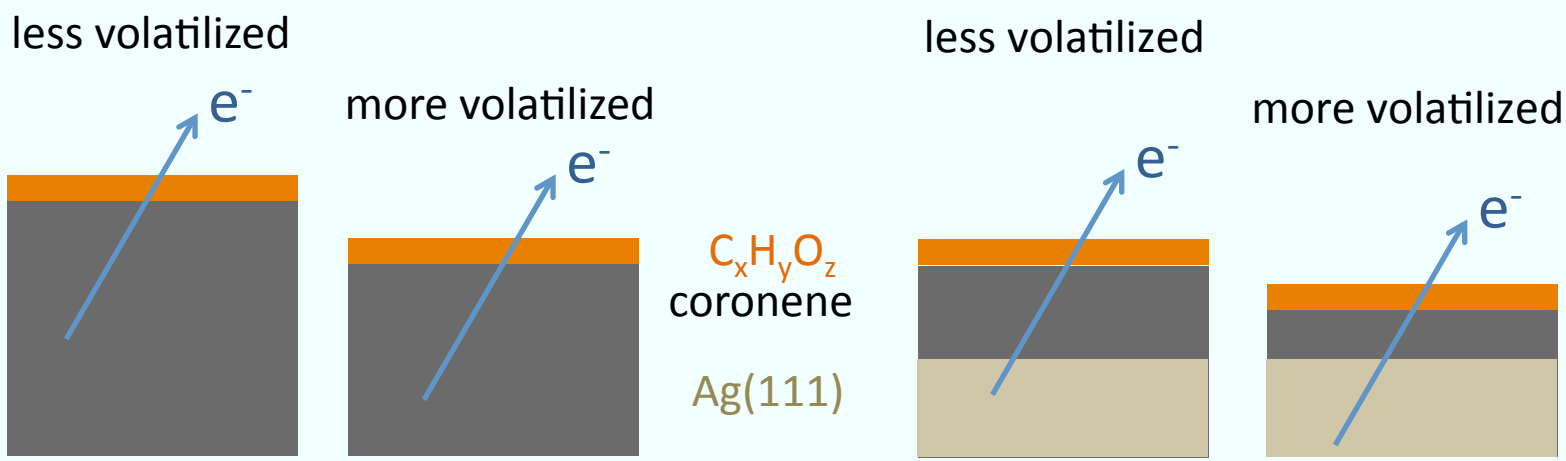
Coronene ($C_{24}H_{12}$)

Thermal evaporation
(~440 K) on Ag(111)



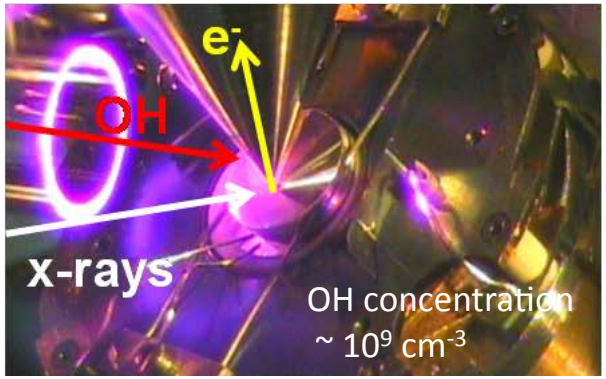
Yoshimoto et al., Electronanal. Chem. (2002).

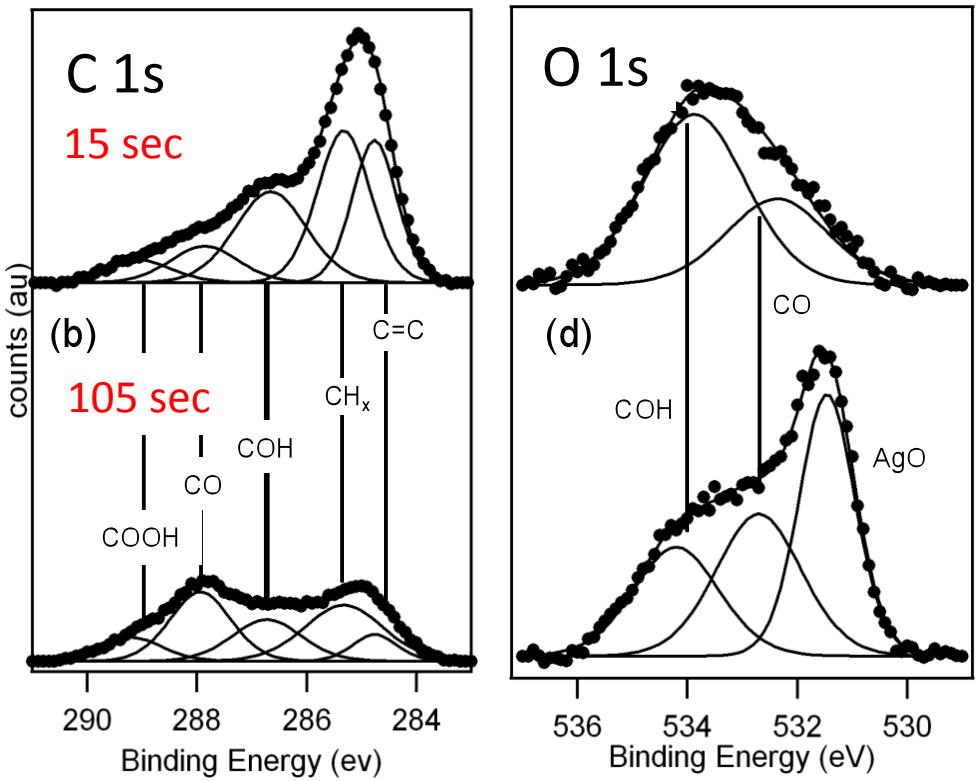
Volatilization can be determined using thin (d<λ) films

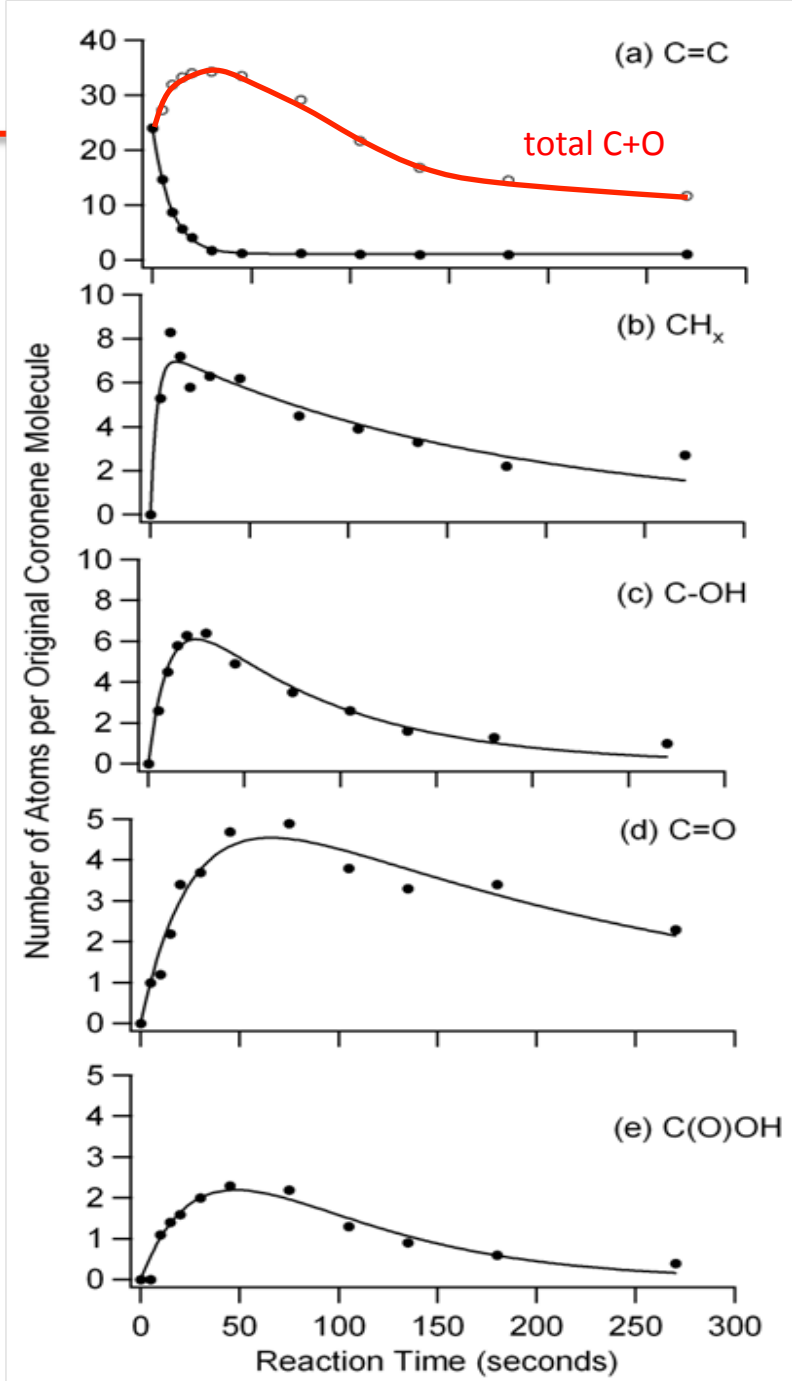


Bulk coronene sample vs. Thin film coronene sample

Reaction of Coronene with OH*

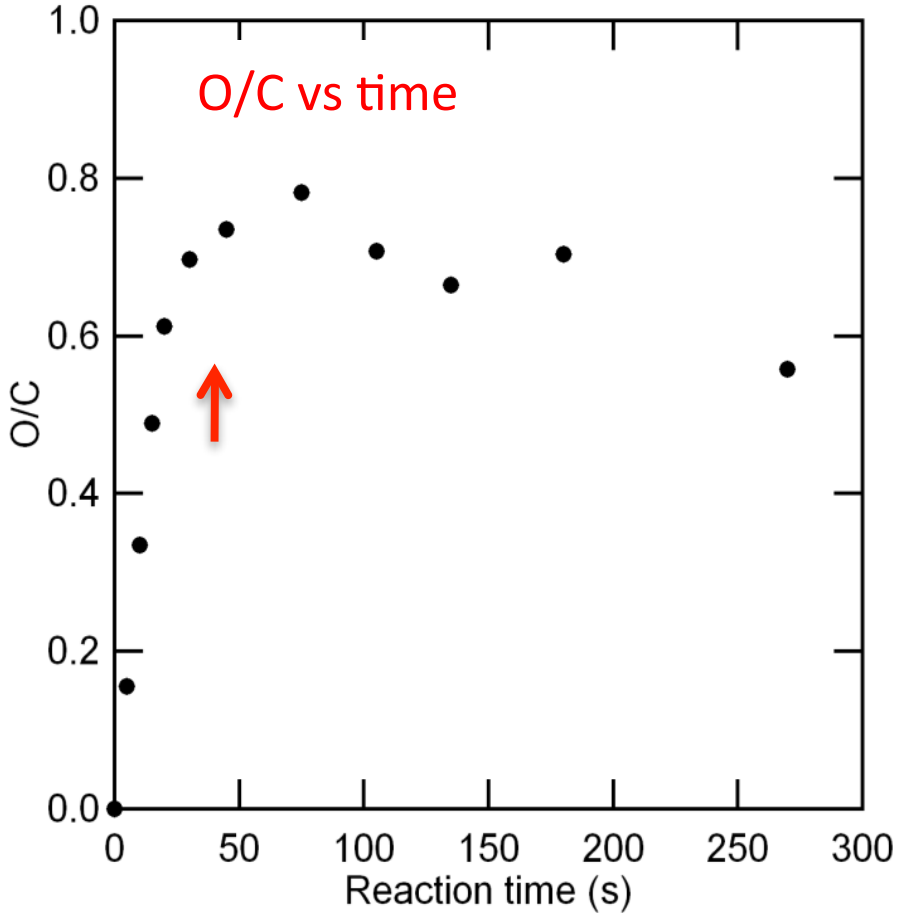


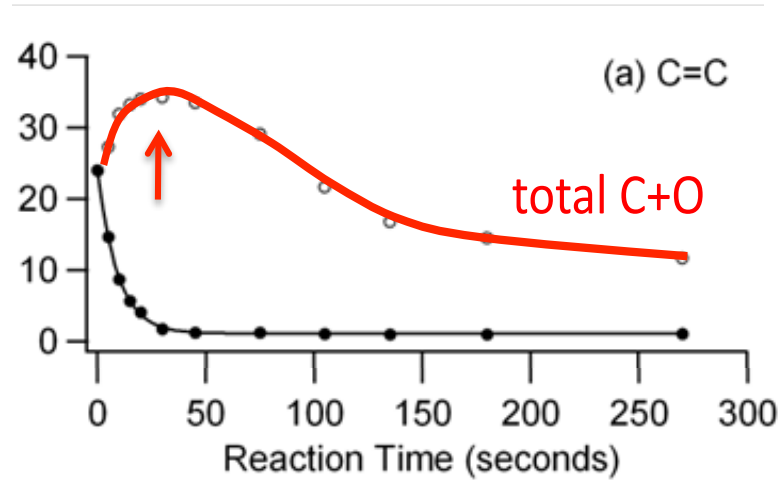




Mysak, Smith, Newberg, Ashby, Wilson, Bluhm, PCCP (2011).

Reaction of Coronene with OH radicals



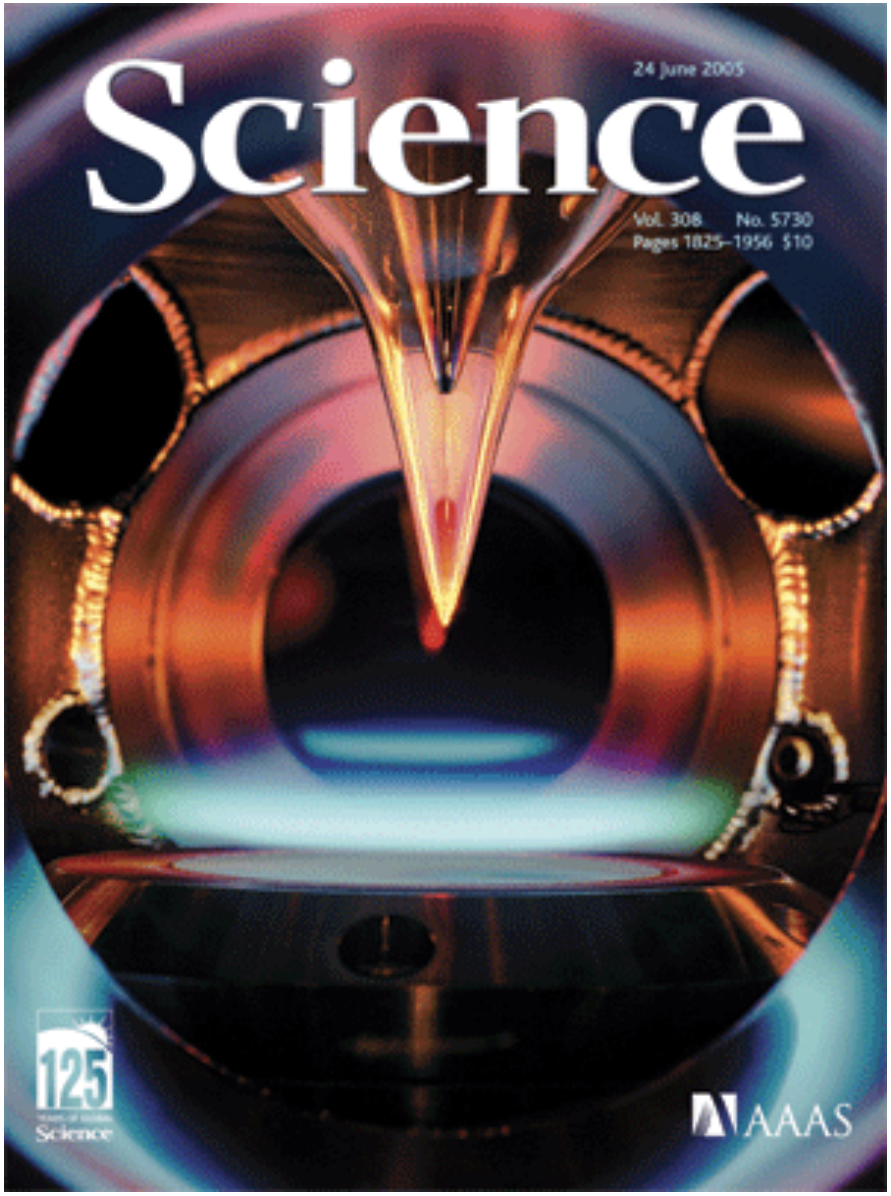


- Carbon loss starts immediately
- Initial growth through oxygen incorporation
- Mass loss starts at O/C ~ 0.6 to 0.7
- Competition between functionalization and volatilization

Mysak, Smith, Newberg, Ashby, Wilson, Bluhm, PCCP (2011).

Diagnostics of Flames Using Soft X-ray Absorption Spectroscopy

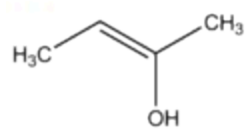
Application of Soft X-rays to The Investigation of Flames

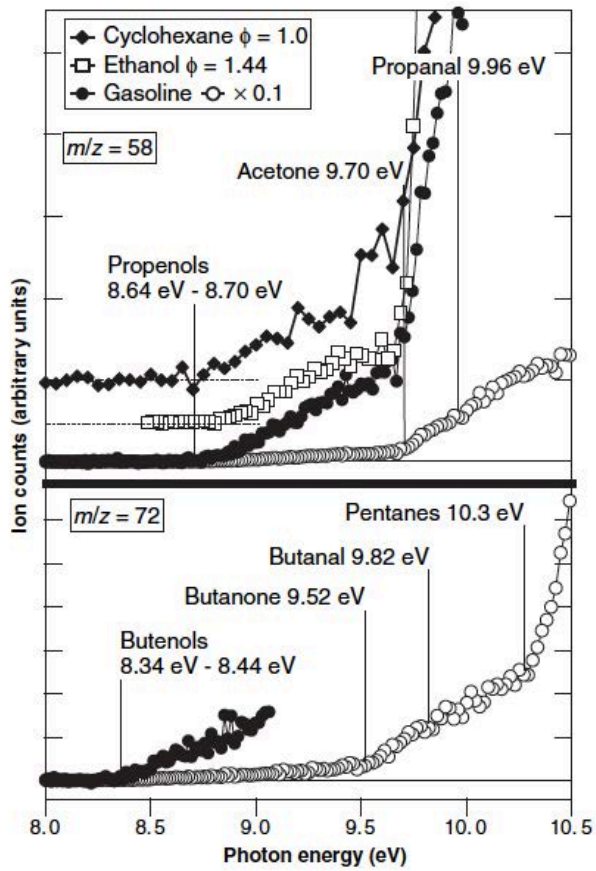


Enols Are Common Intermediates in Hydrocarbon Oxidation

Craig A. Taatjes,[1,2]* Nils Hansen,[1] Andrew McIlroy,[1] James A. Miller,[1] Juan P. Senosiain,[1] Stephen J. Klippenstein,[1] Fei Qi,[1,3] Liusi Sheng,[3] Yunwu Zhang,[3] Terrill A. Cool,[4] Juan Wang,[4] Phillip R. Westmoreland,[5] Matthew E. Law,[5] Tina Kasper,[6] Katharina Kohse-Höinghaus[6]

Fig. 2. Propenols and butenols in hydrocarbon flames. (**Top**) Photoionization efficiency spectra taken for $m/z = 58$, sampled from a cyclohexane flame 2.4 mm from the burner, from an ethanol flame 2.9 mm from the burner, and from a gasoline flame 4.0 mm from the burner. The ethanol and gasoline signals are vertically displaced for clarity. The ion signals were background-corrected and normalized by the measured photon flux (27). Ionization energies are indicated for several C_3H_6O species. The threshold near 8.7 eV is attributable to ionization of propenol isomers. (**Bottom**) Photoionization efficiency spectrum taken of $m/z = 72$, sampled from a gasoline flame 4.0 mm from the burner. Ionization energies are indicated for several mass-72 species. The threshold near 8.4 eV is attributable to photoionization of butenols.





Acknowledgements

Flame XAS

J. Frank
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Beamline 11.02

T. Tyliszczak
M.K. Gilles
A.L.D. Kilcoyne
D.K. Shuh

APPES development

D.F. Ogletree
E. Hebenstreit
C.S. Fadley
G. Lebedev
Z. Hussain
E.K. Wong
M. Salmeron

K. Ihmann
M. Haevecker
A. Knop-Gericke
E. Kleimenov
R. Schloegl

Droplet train development

D.E. Starr
E. Mysak
D.R. Worsnop
K.R. Wilson

PAH oxidation

E. Mysak
J.T. Newberg
J.D. Smith
K.R. Wilson

DOE
LBNL-LDRD
NSF