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Research needs in indoor surface chemistry

Hugo Destaillats

Lawrence Berkeley National Laboratory

Indoor Environment Group

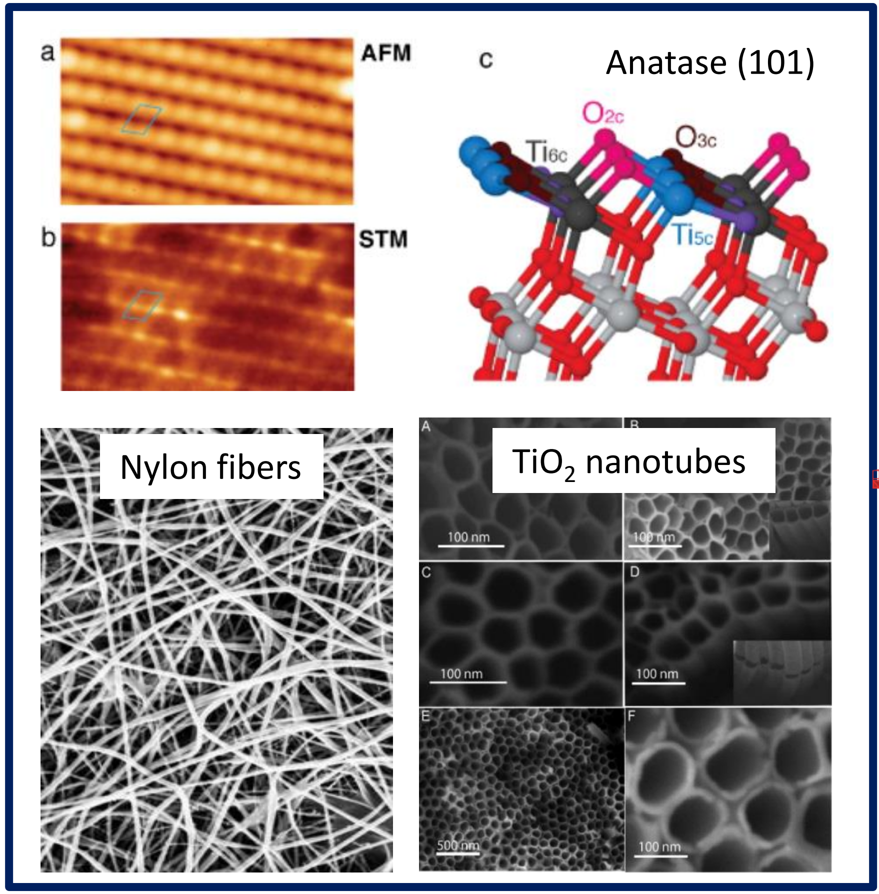
Emerging Science on Indoor Chemistry and Implications: An Information-Gathering Workshop

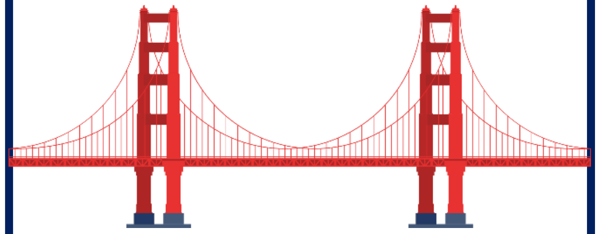
The National Academy of Sciences, Engineering, and Medicine

April 5, 2021

How do we study surfaces?

Molecular and structural approach





Partitioning and exposure

- 2D or 3D, small domains
- Known chemical composition
- Structure defined at the molecular level

- 3D, large reservoir
- Partially known chemical composition
- Not defined at the molecular level

Main questions

1. <u>Definitions</u>: What are indoor surfaces? What are good *model* indoor surfaces?

2. <u>Partitioning</u>: We need to better understand how surfaces act as pollutant sinks, reservoirs and secondary sources

3. <u>Surface chemistry</u>: What is unique, different and/or relevant about it?

4. <u>Occupant exposures</u>: What is the role of surfaces in mediating exposures to harmful chemicals? How can we assess the risks?

5. <u>Practical applications</u>: Can we remove pollution from surfaces?
   Can indoor surfaces be engineered to improve IAQ?

Recent review articles on indoor surface chemistry

INDOOR AIR
International Journal of Indoor Environment and Health

Received: 7 October 2019 | Revised: 18 March 2020 | Accepted: 19 March 2020

DOI: 10.1111/ina.12670

INVITED MAJOR REVIEWS

Indoor acids and bases

William W Nazaroff[1] | Charles J. Weschler[2,3]

Chem

Chem 6, 3203–3218, December 3, 2020

CellPress

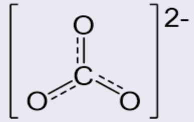
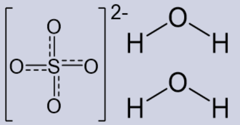
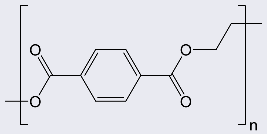
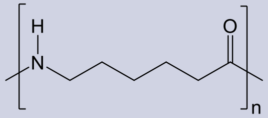
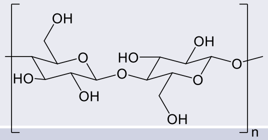
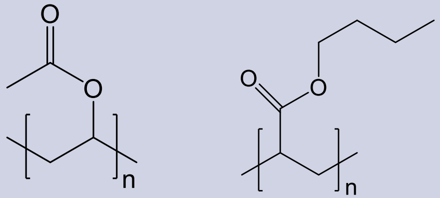
Review

Indoor Surface Chemistry: Developing a Molecular Picture of Reactions on Indoor Interfaces

Andrew P. Ault,[1,*] Vicki H. Grassian,[2,3,4,*] Nicola Carslaw,[5] Douglas B. Collins,[6,7] Hugo Destaillats,[8] D. James Donaldson,[6,9] Delphine K. Farmer,[10] Jose L. Jimenez,[11] V. Faye McNeill,[12] Glenn C. Morrison,[13] Rachel E. O'Brien,[14] Manabu Shiraiwa,[15] Marina E. Vance,[16] J.R. Wells,[17] and Wei Xiong[2,18]

Workshop: Molecular Insights into Chemical Reactions on Indoor Surfaces
Ann Arbor MI, May 8th 2018
(Sloan Foundation's Chemistry of Indoor Environments Program)

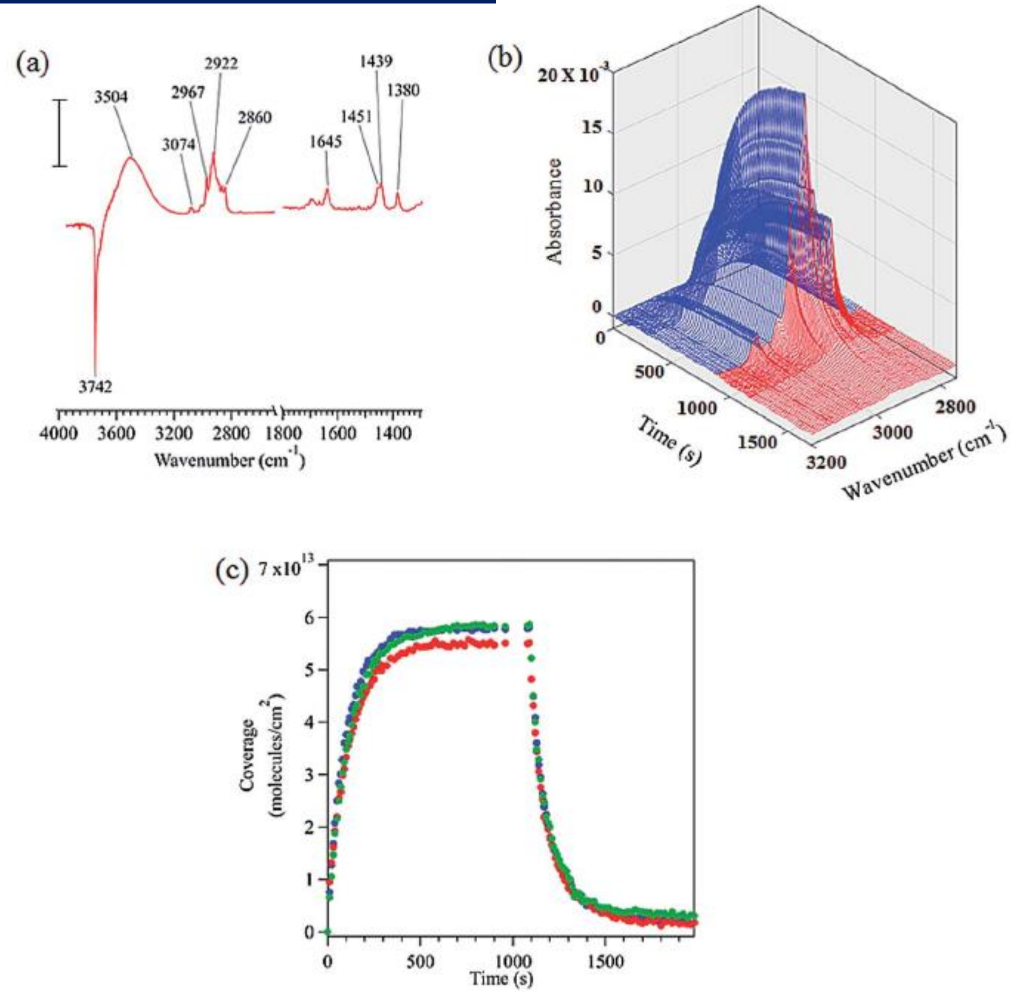
Model indoor materials for surface chemistry studies

Material	Category	Model System	Chemical Formulas	Chemical Structure
Glass	Inorganic	Silicon Dioxide	SiO_2	O O Si
Concrete	Inorganic	Quicklime (Cement) Limestone (Aggregate)	CaO $CaCO_3$	Ca^{2+} O^{2-}  Ca^{2+}
Drywall core	Inorganic	Gypsum	$CaSO_4 \cdot 2H_2O$	Ca^{2+} 
Fabric	Organic	Polyethylene terephthalate (PET, polyester)	$[C_{10}H_8O_4]_n$	
Carpet	Organic	Nylon (e.g. Nylon 6)	$[NH(CH_2)_5CO]_n$	
Wood/ cotton	Organic	Cellulose	$[C_6H_{10}O_5]_n$	
Latex-Painted Drywall	Mixed Inorganic/ Organic	Synthetic Rubber (e.g. Co-Polymer of Vinyl Acetate and Butyl Acrylate)	$[CH_3COOCH{=}CH_2]_n$ and $[CH_2CHCOO(CH_2)_3CH_3]_n$	

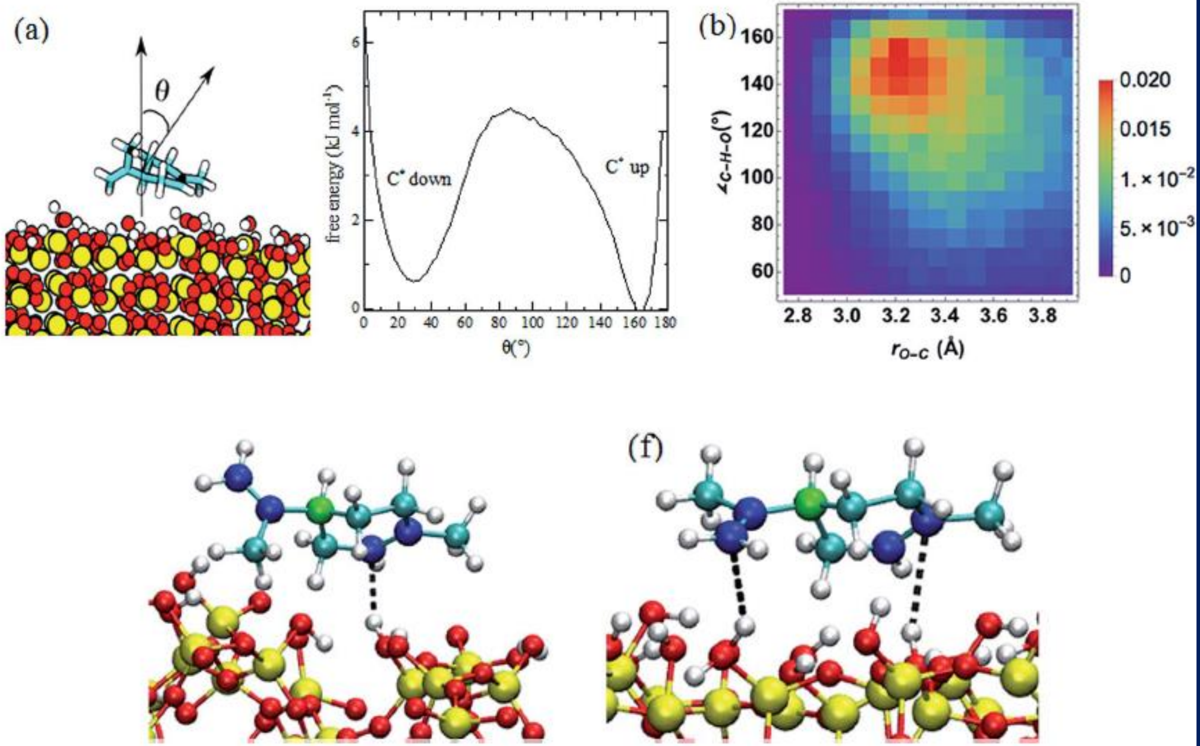
Ault et al., *Chem*, 2020

Adsorption of limonene on hydroxylated silica (RH = 0)

Infrared spectroscopy



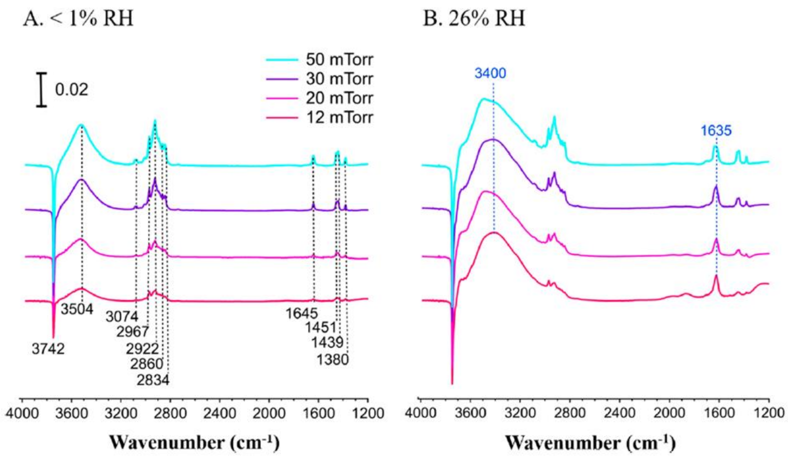
Atomistic molecular dynamics simulations

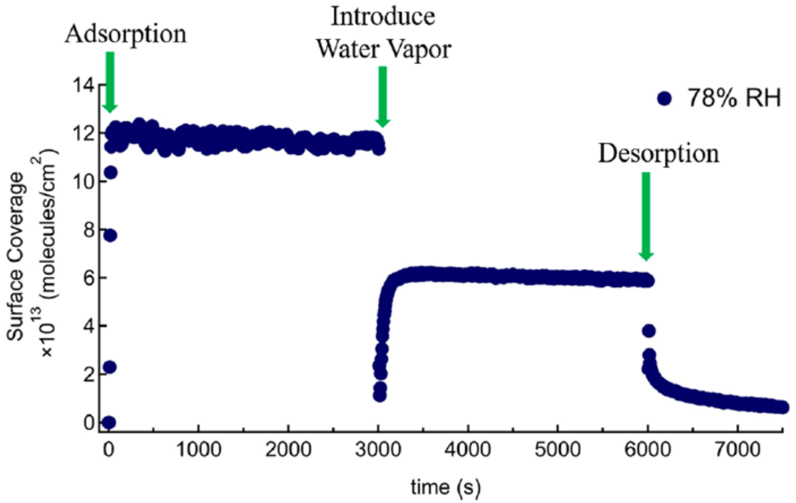


Fang et al., *Chem. Sci.*, 2019

Adsorption of limonene on hydroxylated silica (RH ≠ 0)

IR spectroscopy



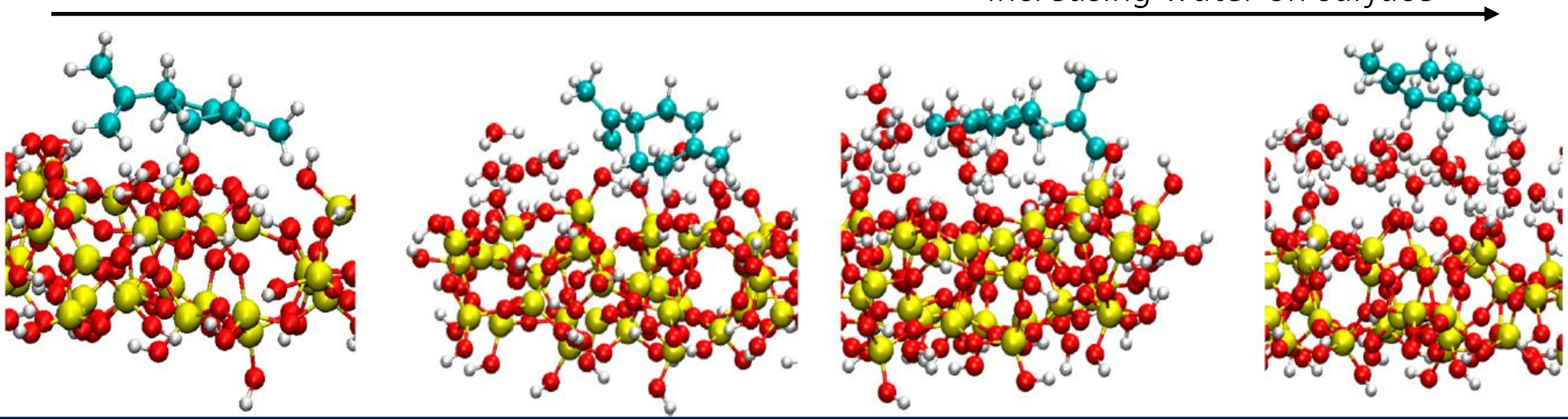


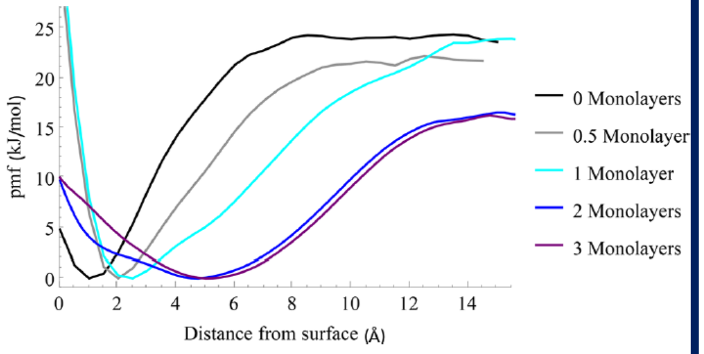
Tools to better understand the molecular basis of:

- Fugacity and partitioning
- Surface chemistry

MD simulations

Increasing water on surface

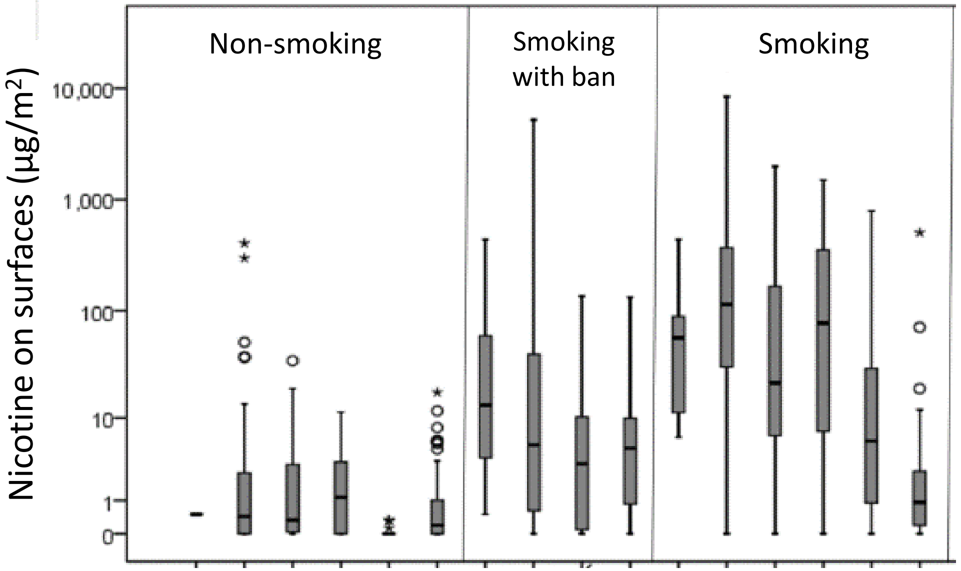




Frank et al., *J. Phys. Chem. A*, 2020

Indoor surfaces are coated with adventitious layers, dust, skin cells

Surface nicotine in homes, cars and hotels



[summary of multiple studies]

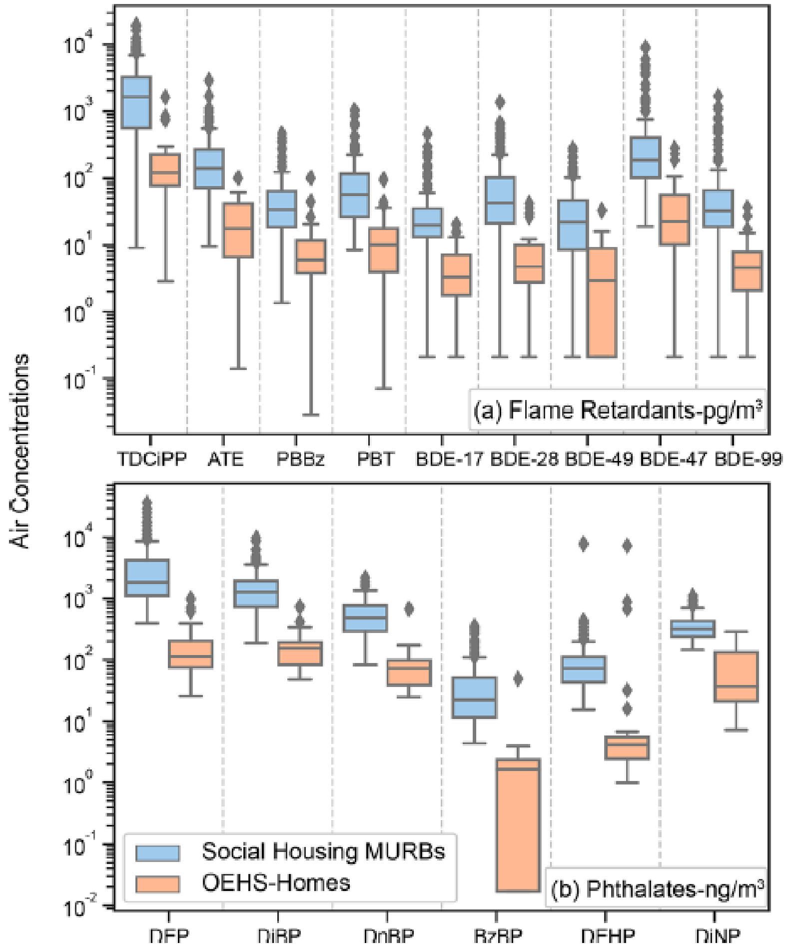
Quintana et al., *Nic. Tob. Res.*, 2013

Nicotine in house dust (µg/g)

	Nr. samples	% det.	median
Smokers	5	100	7.8
Non-smokers	20	95	0.51

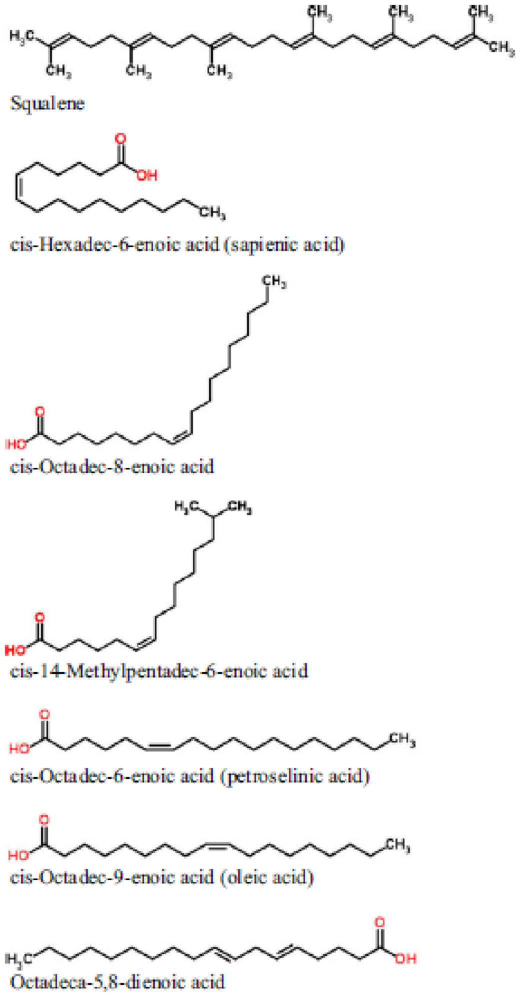
Whitehead et al., *Chem. Res. Toxicol.*, 2015

SVOC deposition on surfaces



Wan et al., *ES&T Lett.*, 2020

Desquamation



Weschler, *Indoor Air*, 2016

<u>Indoor ozone chemistry</u>: surfaces play a major role

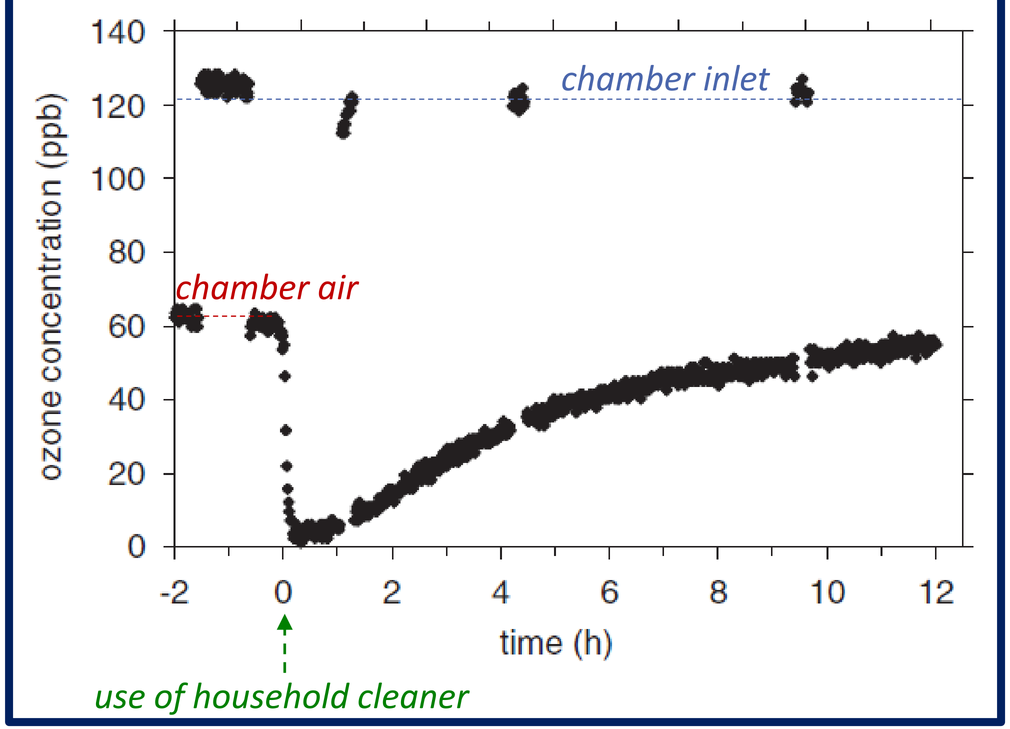
Surface removal rates are typically higher than air exchange

Table 3 Rate Constants (h^{-1}) for the Removal of Ozone by Surfaces in Different Indoor Environments

Indoor environment	Surface removal rate, $k_d(A/V)$, h^{-1}	Reference
Aluminum Room (11.9 m^3)	3.2	Mueller et al., 1973
Stainless Steel Room (14.9 m^3)	1.4	Ibid.
Bedroom (40.8 m^3)	7.2	Ibid.
Office (55.2 m^3)	4.0	Ibid.
Home (no forced air)	2.9	Sabersky et al., 1973
Home (forced air)	5.4	Ibid.
Department Store	4.3	Thompson et al., 1973
Office (24.1 m^3)	4.0	Allen et al., 1978
Office (20.7 m^3)	4.3	Ibid.
Office/Lab	4.3	Shair and Heitner, 1974
Office/Lab	3.2	Ibid.
Office/Lab	3.6	Ibid.
13 Buildings, 24 Ventilation Systems	3.6	Shair, 1981; assumes A/V = 2.8 m^{-1}
Museum	4.3	Nazaroff and Cass, 1986
Museum	4.3	Ibid.
Office/Lab	4.0	Weschler et al., 1989
Office/Lab	3.2	Ibid.
Office	2.5	Ibid.
Lab	2.5	Ibid.
Cleanroom	7.6	Ibid.
Telephone Office	0.8–1.0	Weschler et al., 1994; large office, small *A/V*
43 Homes	2.8±1.3	Lee et al., 1999

Weschler, *Indoor Air,* 2000

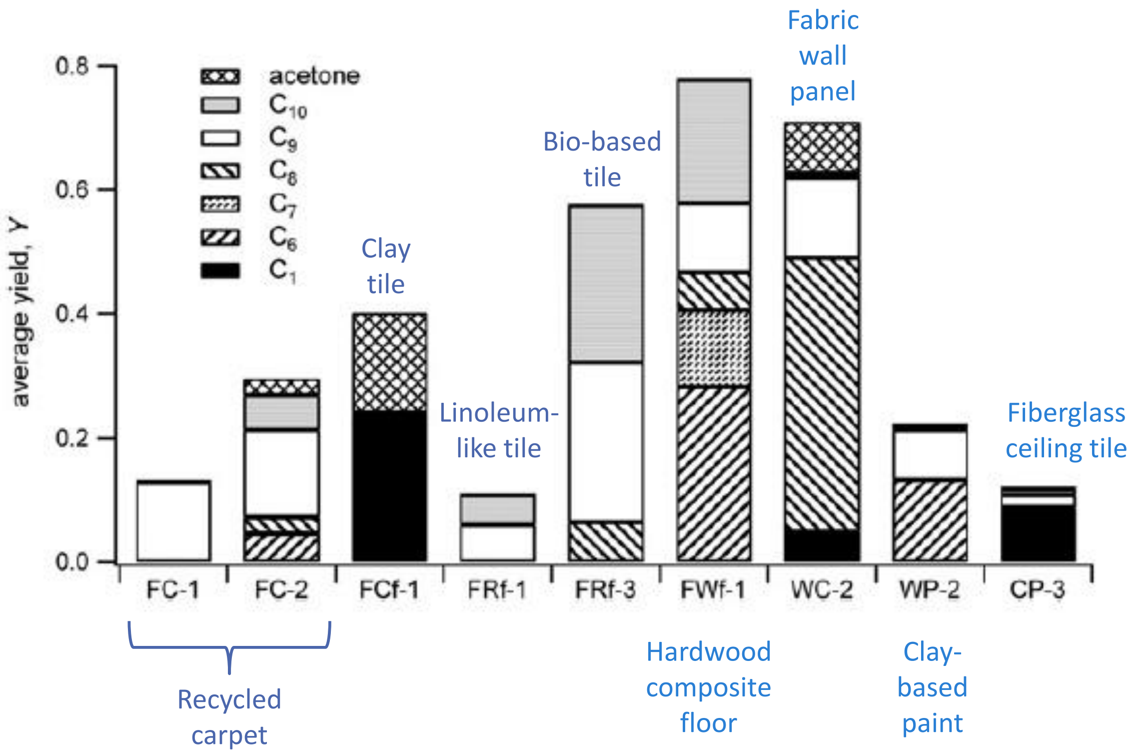
Surface deposition vs. gas phase reaction



Singer et al, *Atmos. Environ.,* 2006

Ozone deposition: reactivity and byproducts

O_3 reacts with materials, releasing secondary byproducts

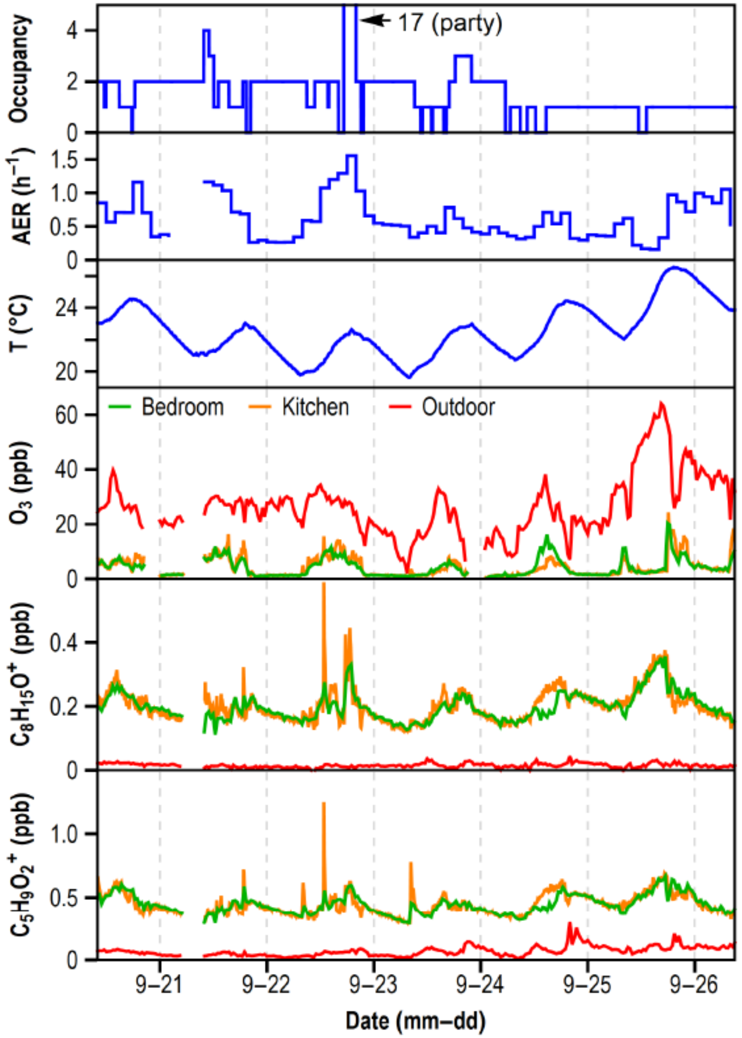


Lamble et al, *Atmos. Environ. 2011*

O_3 reacts with adsorbed and deposited compounds, releasing secondary byproducts

6-methyl-5-hepten-2-one (6-MHO)

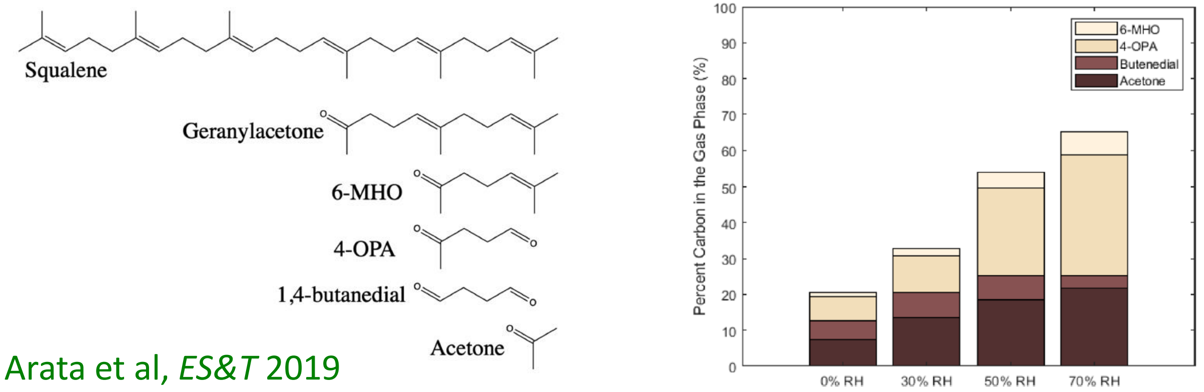
4-oxopentanal (4-OPA)



Liu et al, *PNAS 2021*

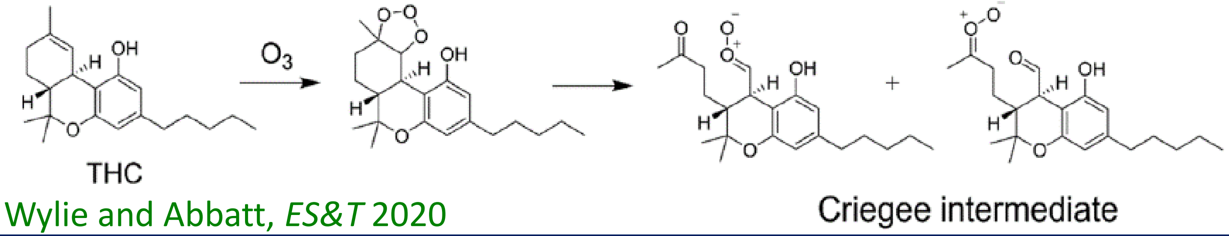
What are the mechanisms of ozone's reactive deposition?

Criegee reaction: Ozone + alkene



Arata et al, *ES&T* 2019

- Oxidation of linear and terminal alkenes leads to formation of VOCs, with increasing yields at higher RH

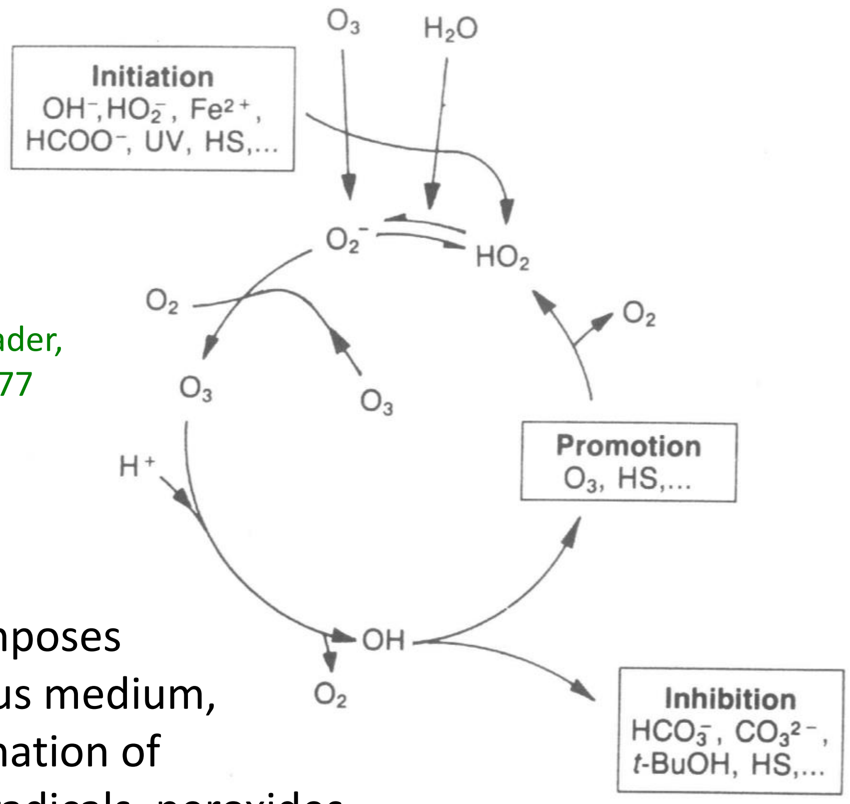


Wylie and Abbatt, *ES&T* 2020

- Oxidation of endocyclic double bond is less likely to produce small volatile fragments and secondary aerosols, due to the lower volatility and increased polarity of byproducts
- Greater potential for exposure via dermal uptake and ingestion

What mechanisms can describe the reaction of ozone with other species?

Hoigné and Bader, *Water Res.* 1977 (& others)



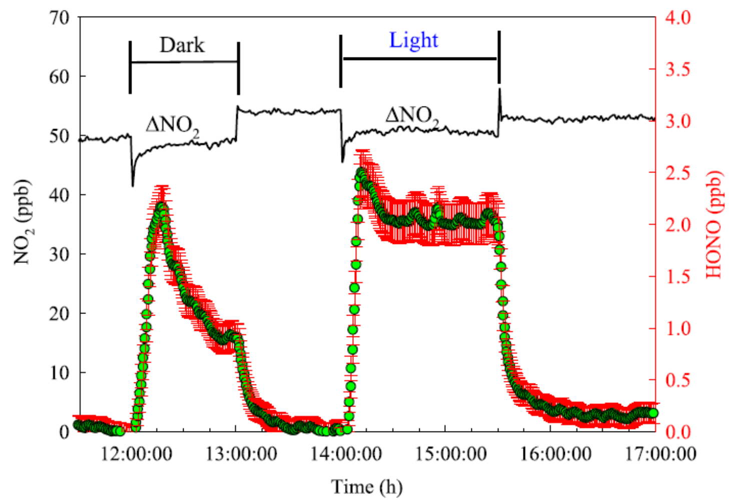
- O_3 decomposes in aqueous medium, with formation of reactive radicals, peroxides.
- Possible reaction with adsorbed species and substrate materials.

Chemistry of nitrogenated species on indoor surfaces

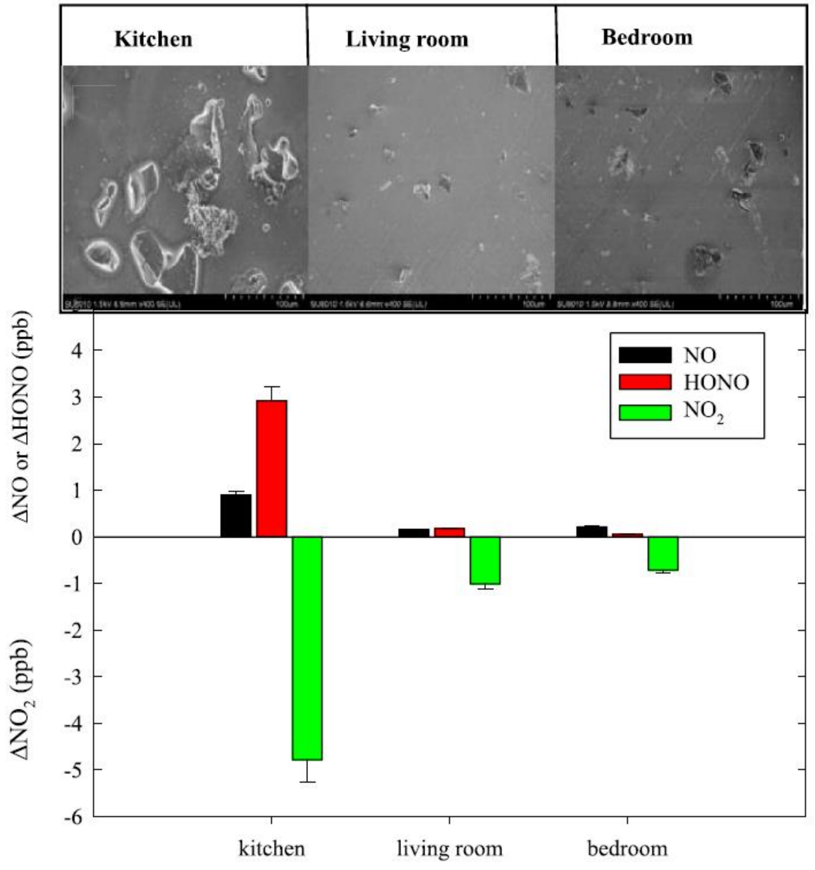
$$2\ NO_2 + H_2O \xrightarrow{\text{surface}} HONO + HNO_3$$

- Process catalyzed by grime collected on glass substrates placed in a home for 4 weeks
- Enhanced conversion with near UV irradiation (photosensitized by organics on surface films)

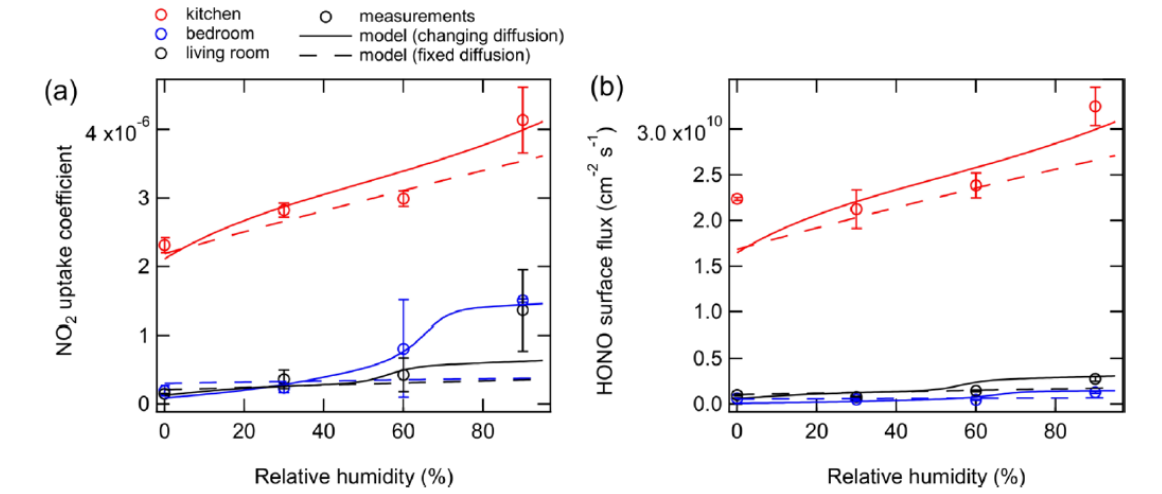
Flow tube reactor experiments



Kitchen soiling is most reactive



NO_2 uptake and HONO yield increased with RH

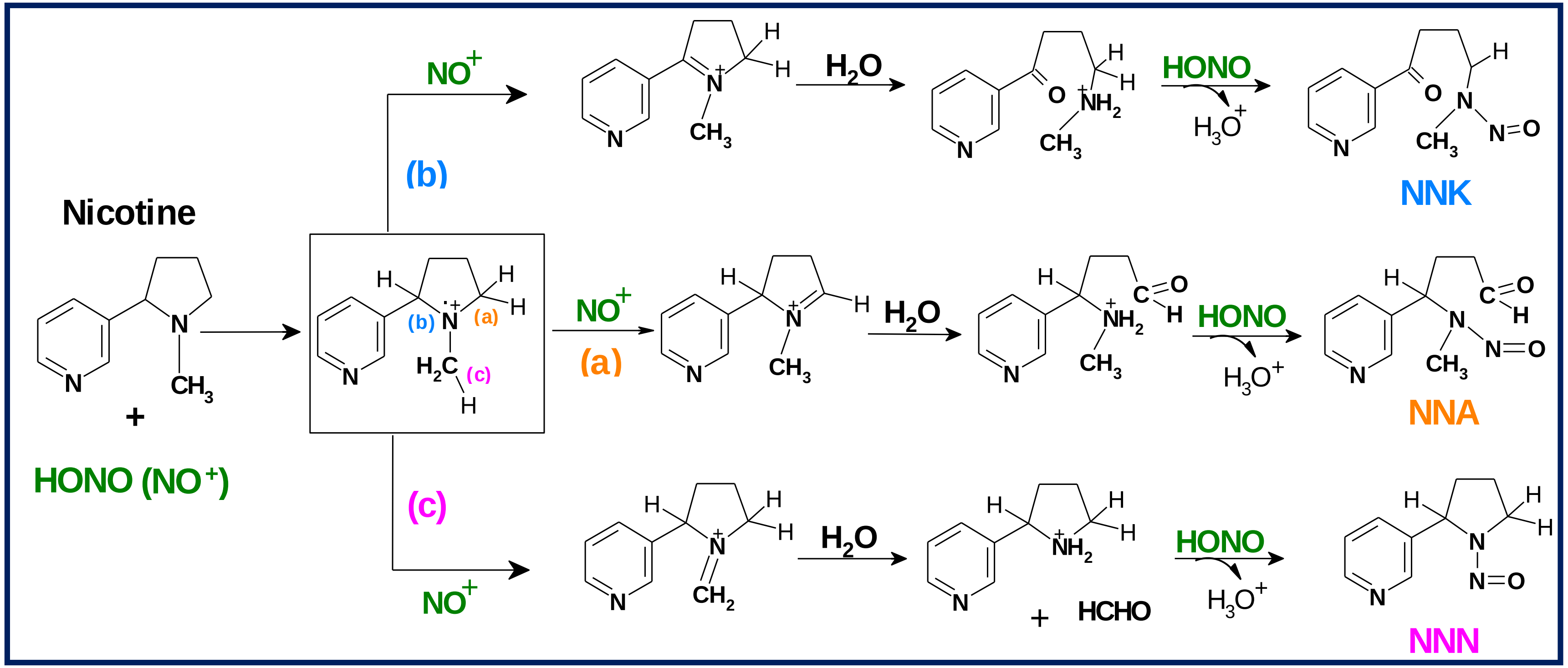


- HONO is precursor of OH radicals, and can react with other indoor species

Liu et al, *ES&T* 2020

Nitrosation of amines adsorbed to indoor surfaces

$$HONO + H^+ \rightleftharpoons NO^+ + H_2O$$



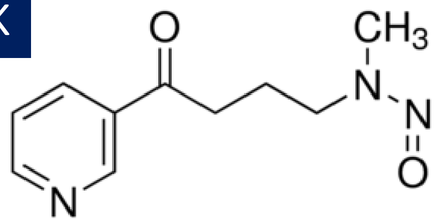
Sleiman et al, *PNAS* 2010

Amine nitrosation by HONO

- Postulated through formation of NO^+, a strong electrophile.
- In diluted aqueous solution, NO^+ (aq) forms at low pH
- Do we have such acidic conditions on the surface?
- What other mechanisms can catalyze NO^+ formation?

Exposure: harm metrics only available for some compounds and routes

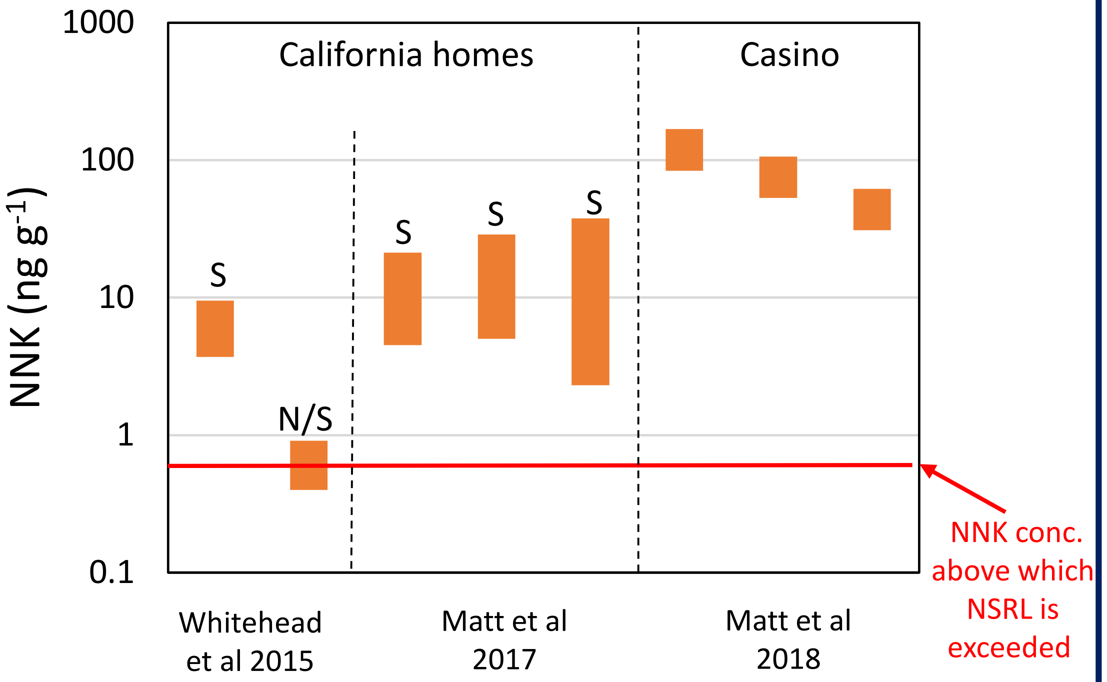
NNK



No Significant Risk Level (NSRL)

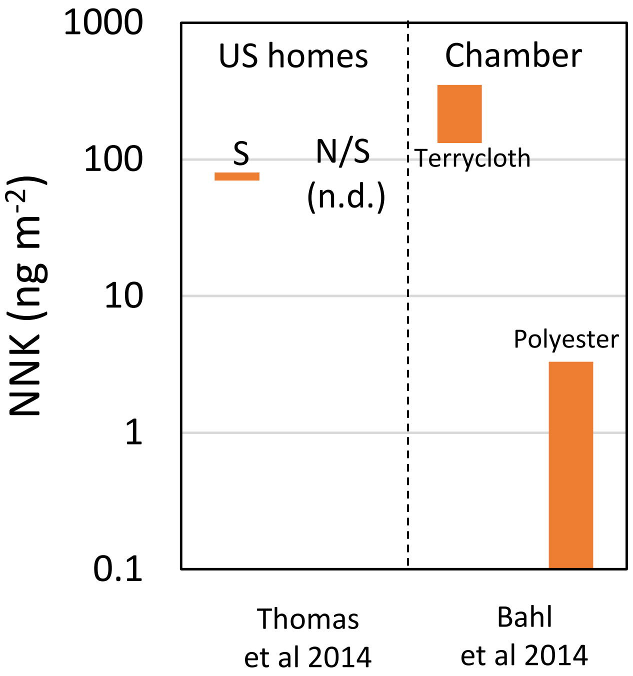
- Cal OEHHA's NSRL for NNK: **14 ng/day** (Prop. 65)
- NSRLs are defined as the daily level posing a 10^{-5} lifetime risk of cancer
- Cancer potency derived from rodents exposed via drinking water

INDOOR DUST



- Assuming an adult dust ingestion rate of 30 mg/day (US EPA), the NNK concentration above which NSRL is exceeded (24-h exposure) is ≈ **0.5 ng/mg**

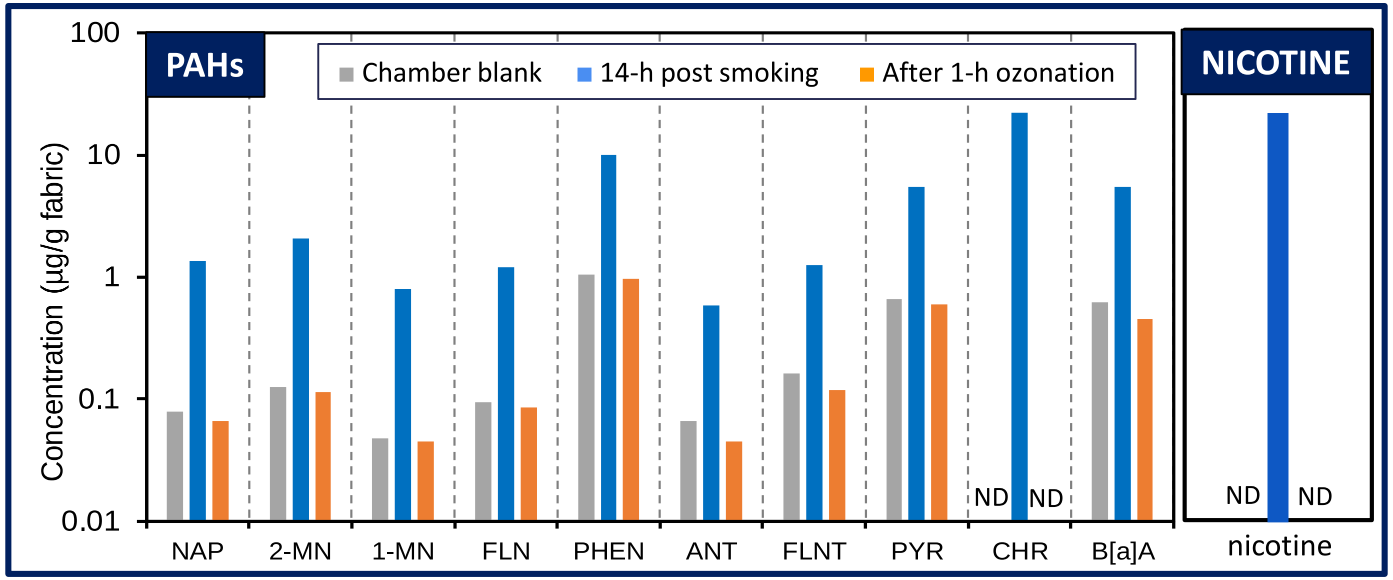
INDOOR SURFACES

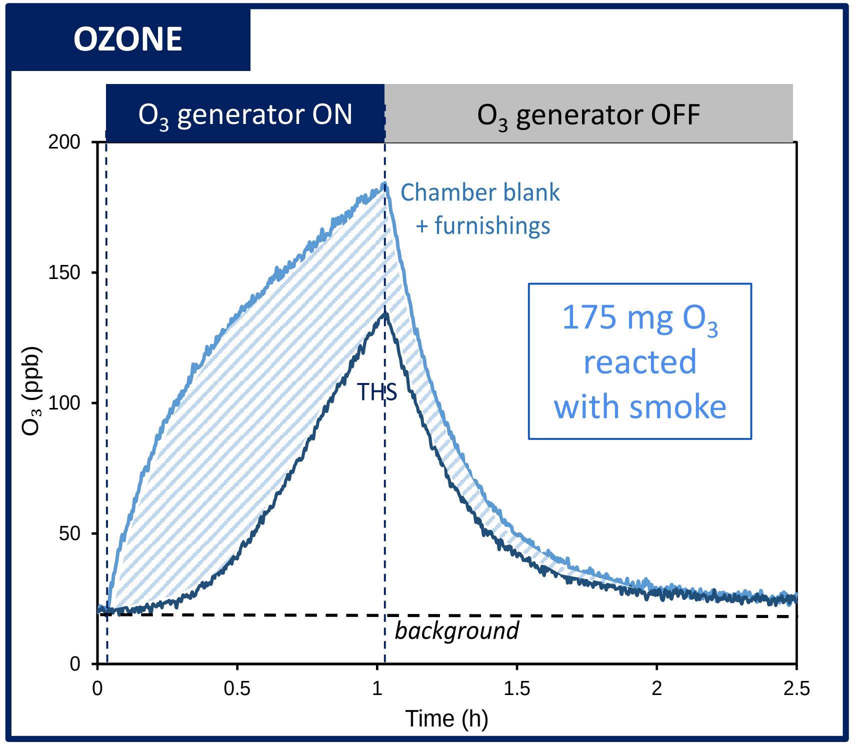


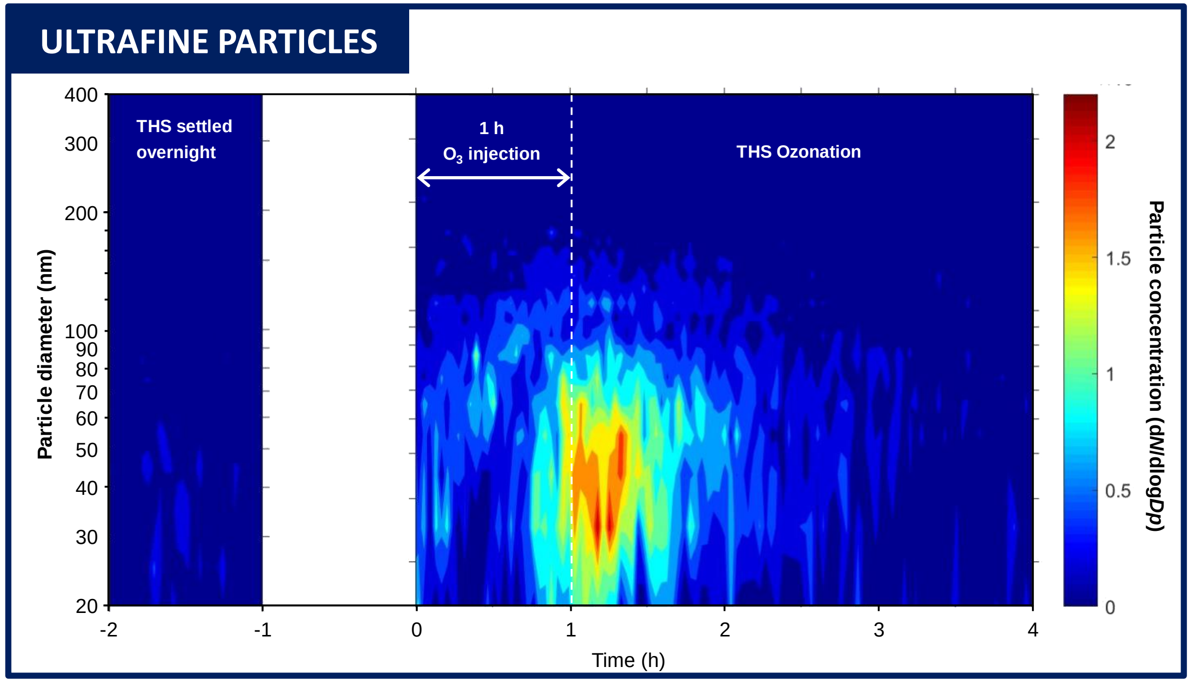
- No equivalent "yardstick" to assess exposure risk
- Walls ≠ fabrics ≠ other surfs.

Remediation: can we remove pollution from surfaces?

- Smoke from 6 cigarettes, settled for 14 hours
- Ozone generator (300 mg h^{-1}) operated for a 1-h period
- Samples: VOCs, PM, SVOCs on particles and adsorbed to indoor surfaces





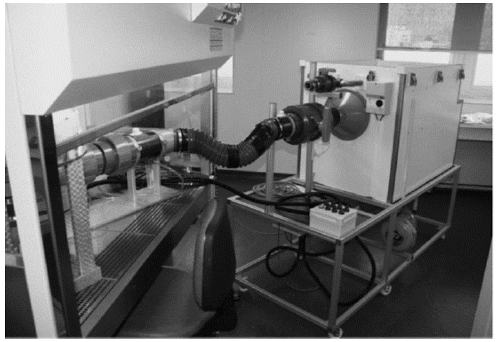


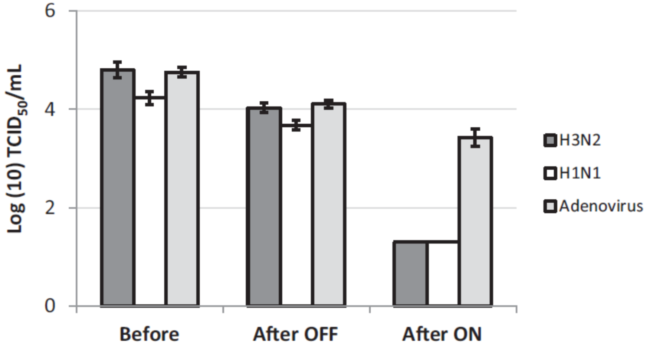
Tang et al, *Environ. Res.* 2021

Engineered surfaces can improve indoor environmental quality

- Indoor surfaces can be modified for air cleaning purposes
- Passive (e.g., walls) and active applications
- Reactive and/or adsorptive approaches

Can air cleaners remove pathogens?



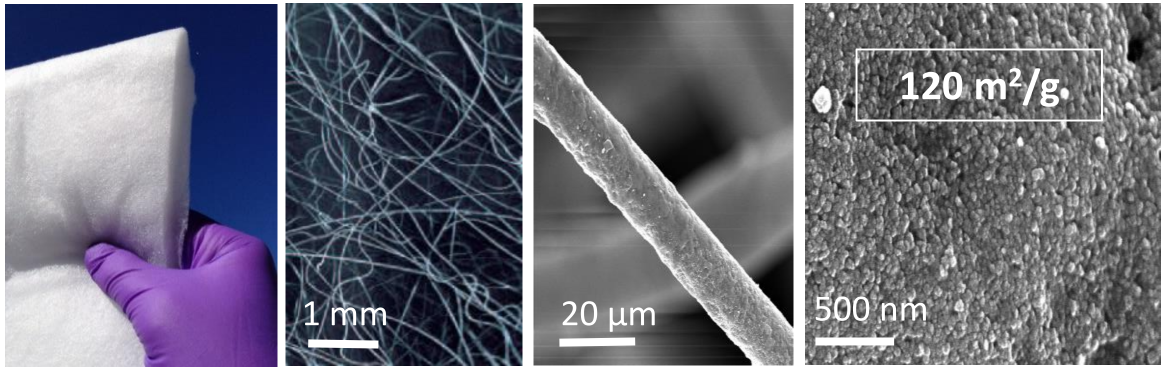


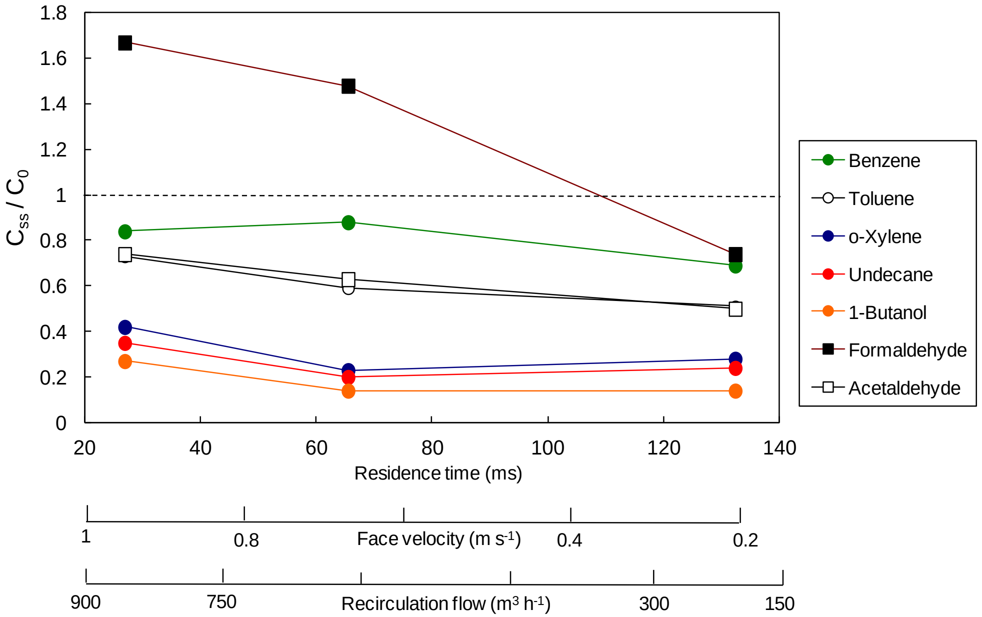
Virus titer before and after exposure to XP01 reactor.

- PCO developed for aircraft cabin air cleaning
- Removes VOCs and inactivates pathogens

Gorvel et al., *Clean Soil Air Water,* 2014

TiO_2-coated quartz fiber air cleaning filters





Destaillats et al., *Applied Catalysis B: Environmental,* 2012

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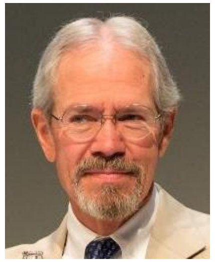
Tom Kirchstetter


Bill Nazaroff


Charlie Weschler

California Consortium on Thirdhand Smoke: *thirdhandsmoke.org*

Alfred P. Sloan Foundation

TOBACCO-RELATED DISEASE RESEARCH PROGRAM

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