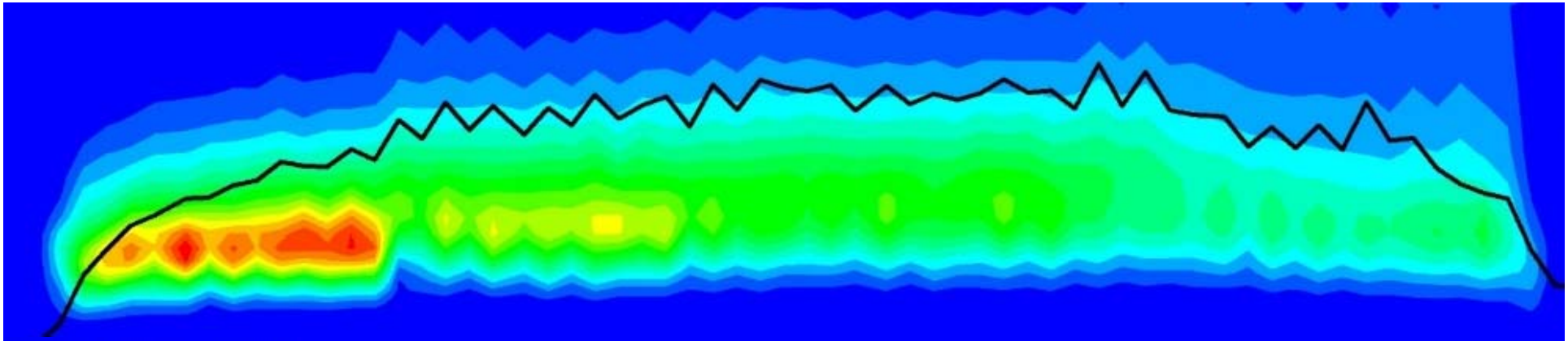


Effect of relative humidity on the mechanism of new particle formation from monoterpene oxidation

James N. Smith, Sabrina Chee (UC Irvine)

Xiaoxiao Li, Jiming Hao, Jingkun Jiang (Tsinghua Univ.)

Jonathan Abbatt (Univ. Toronto)

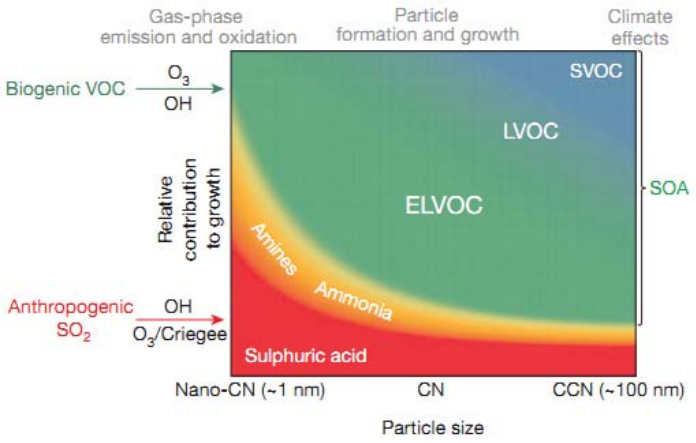
Atmospheric Chemistry Mechanisms Conference 2018
December 7, 2018
Davis, CA

AEROSOL LAB School of Environment Tsinghua University THE ABBATT GROUP UNIVERSITY OF TORONTO

Motivation: Why is continental New Particle Formation (NPF) reduced during periods of high Relative Humidity (RH)?

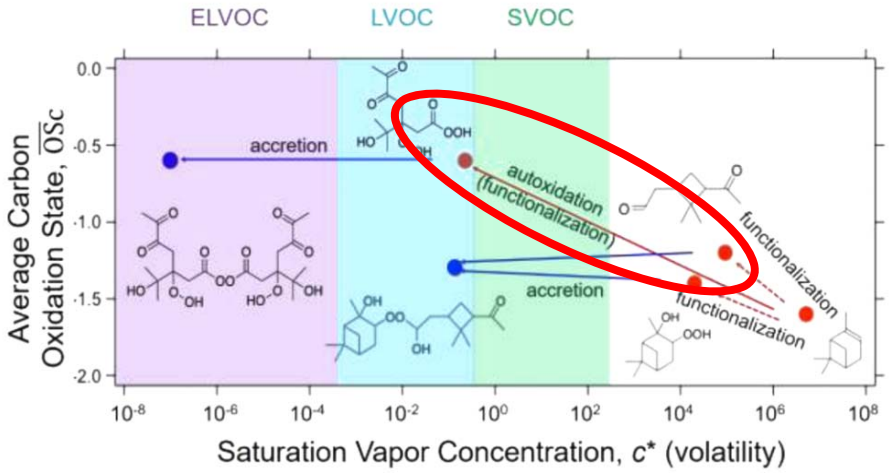
- Indirect: High RH is accompanied by increased in condensation sink and decrease in solar radiation, both of which decrease NPF
- **Direct: $H_2O_{(g)}$ may directly influence the formation of NPF precursors or clusters**

Extremely low volatility organic compounds (ELVOC) are important compounds for NPF



Ehn, et al. 2014, Nature

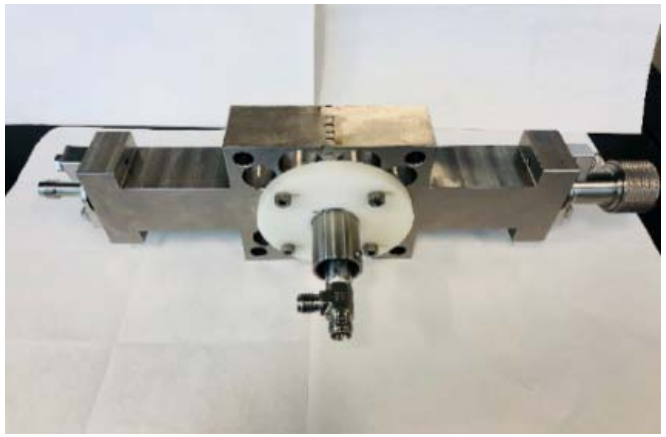
Formation of the observed Highly Oxidized Molecules (HOM) via RO_2 autoxidation

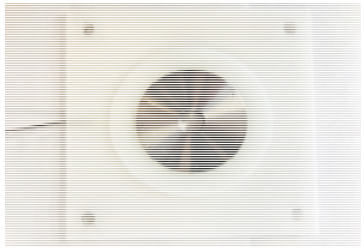


Barsanti, 2017, JPCL

Is the formation of NPF-related HOM suppressed by $H_2O_{(g)}$?

New Instrument for measuring gas phase HOM: Transverse Ionization Chemical Ionization Mass Spectrometer (TI-CIMS)



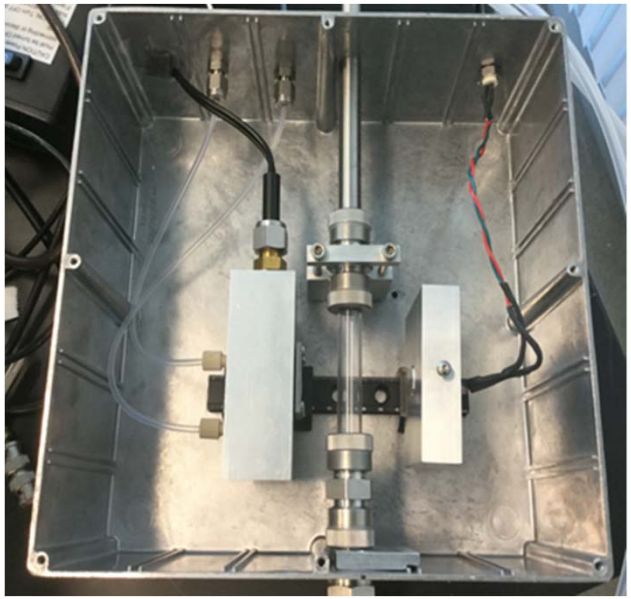


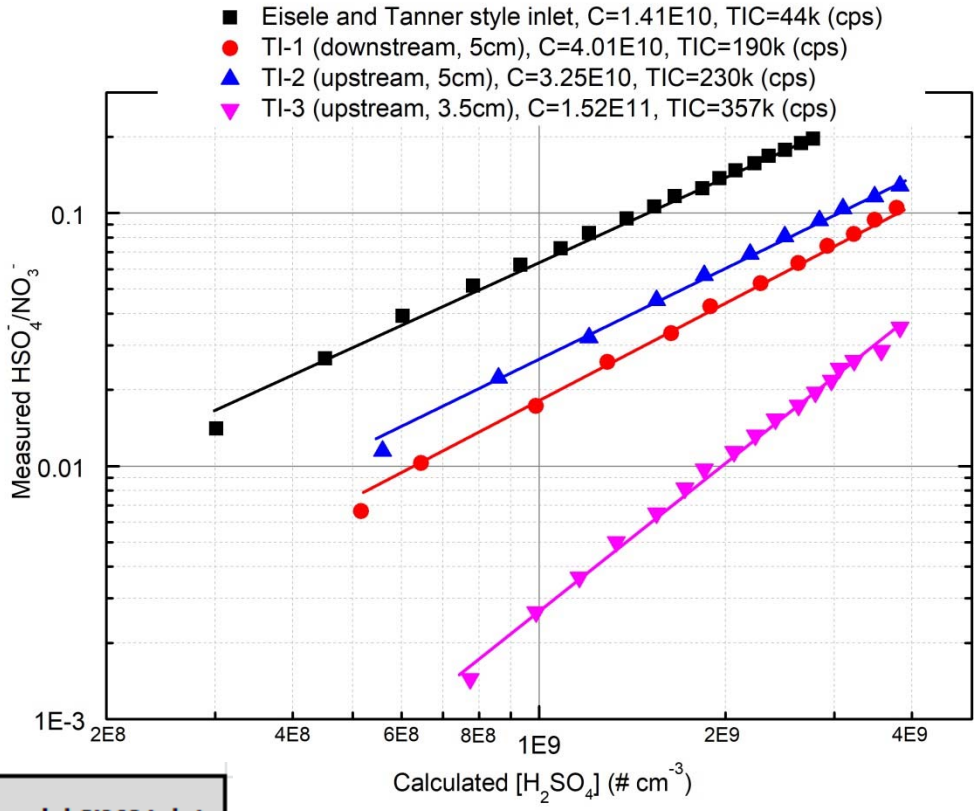
- No sheath air required … simpler for experiments
- Based on the **Cluster CIMS inlet** designed by Zhao and Eisele, adapted for TOFWERK ToF mass specs
- Position of the ion source relative to inlet orifice is adjustable to change reaction time
- Curtain gas passed over inlet orifice reduces water clustering
- For this study, NO_3^- analyte and mass analysis by a LTOF-MS.

Zhao, Eisele et al., JGR, 2010
Hanson, et al., EST, 2011
Li et al., ACPD, 2018

TI inlet sensitivity to H_2SO_4 is higher than the Aerodyne CIMS inlet based on the design by Eisele and Tanner

H_2SO_4 calibrator (Kürten et al., 2012)

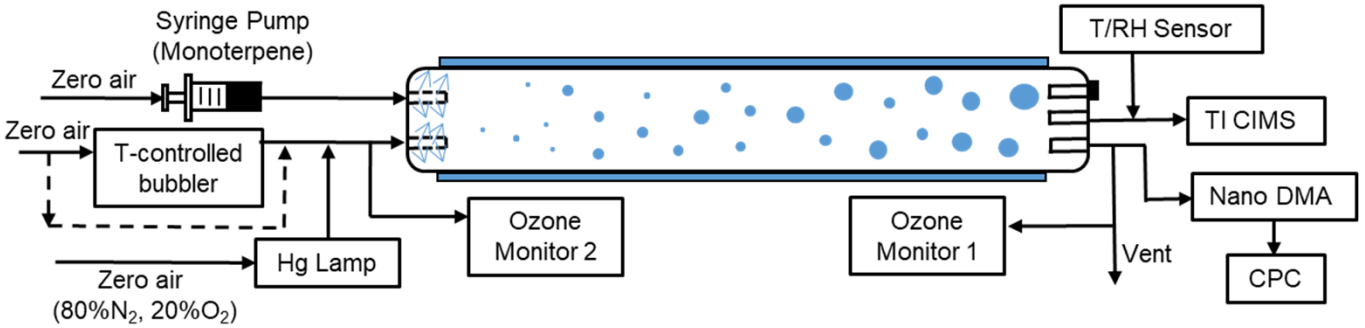




Performance	TI Inlet	Commercial CIMS Inlet (Eisele and Tanner, 1993)
Sensitity & Linearity	Good	Good
Calibration Factor: $C = [H_2SO_4]/([HSO_4^-]/[NO_3^-])$	3.25E+10	1.40E+10
Max. reaction time	80 ms	200 ms
Total Ion Counts	230K cps	44K cps
Lower Detection Limit (3σ for 1 min zero air meas.)	9.3E+4 cm^{-3}	1.26E+5 cm^{-3}

Li et al., ACPD, 2018

Instrument Setup and Experimental Conditions

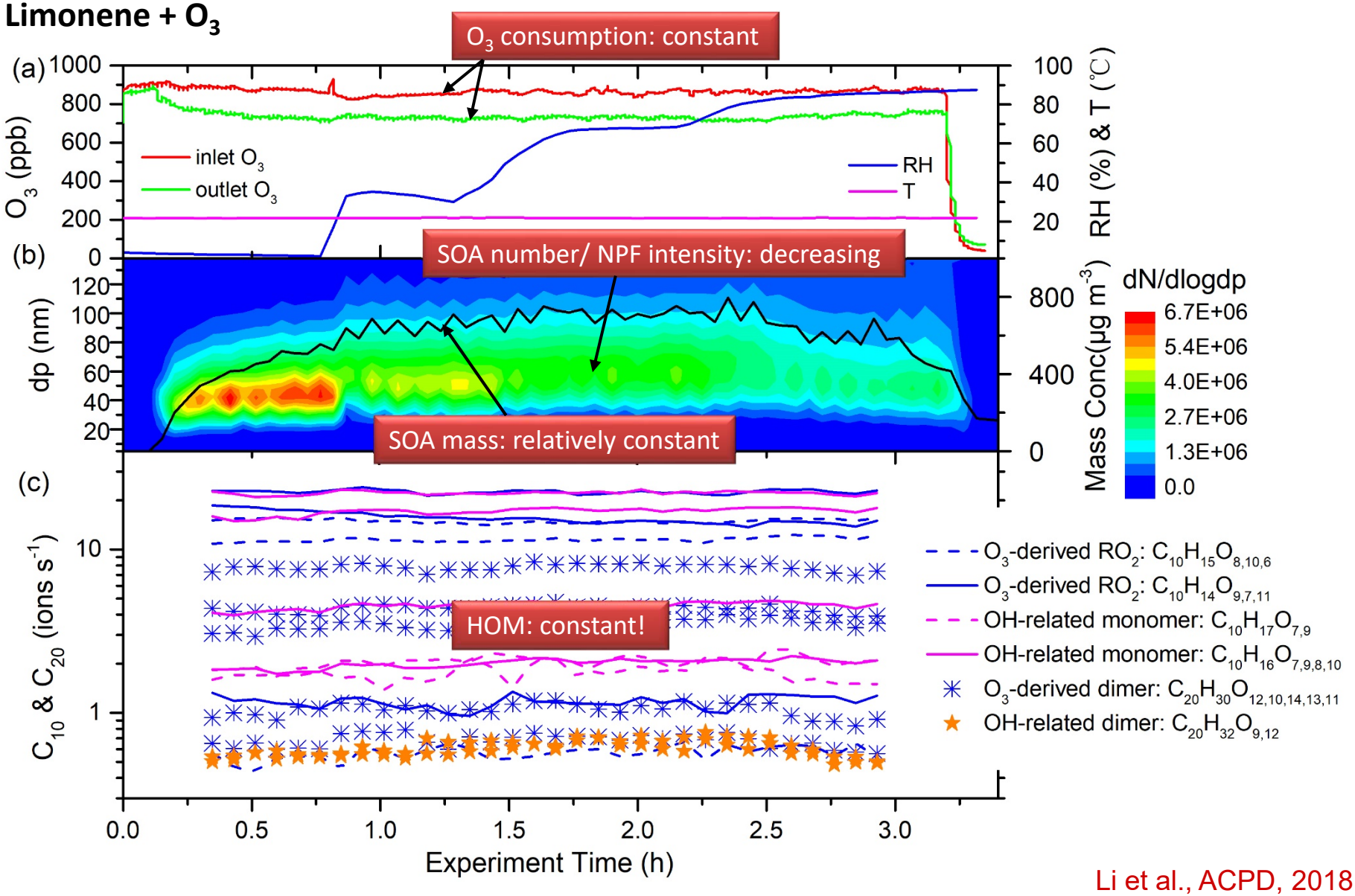


Precursor	[precursor] (ppbv)	[O_3](ppbv)	[C_6H_{12}] (ppmv)
limonene	1085	900±10	0
	1085	900±10	217
	54	350±5	0
α-pinene	1111	900±10	0
	1111	900±10	222
	54	350±5	0
△^{3}-carene	1111	900±10	0
	1111	900±10	222
	54	350±5	0

- RH: 1 - 90%
- High and low monoterpene concentration to study impact of new particle formation.
- O_3 with / without C_6H_{12} OH scavenger
- Low NOx

Li et al., ACPD, 2018

SOA number concentration decrease with increasing RH, however, detected HOM do not change!

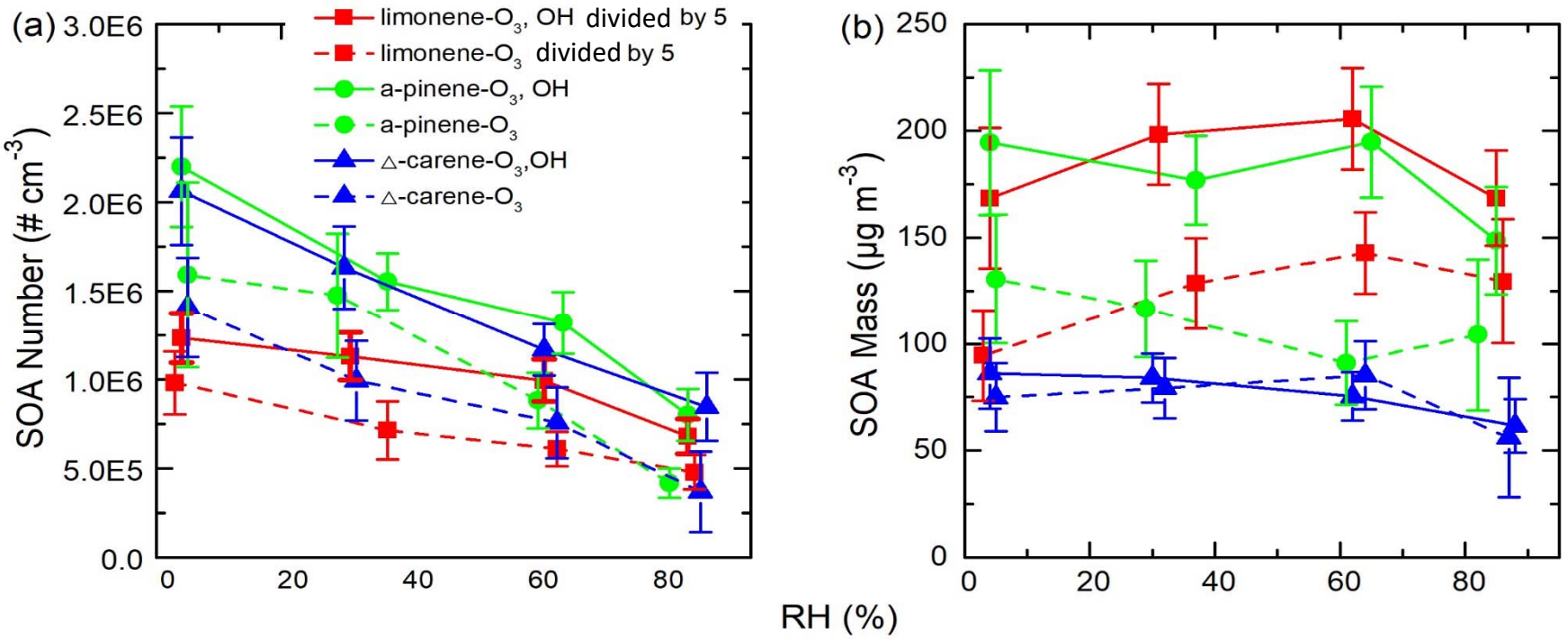


Li et al., ACPD, 2018

Decrease of number concentration at high RH is more consistent than change in mass concentration

SOA Number Concentration: decreasing by 2~3 factors

SOA Mass Concentration: changing within 2 factors

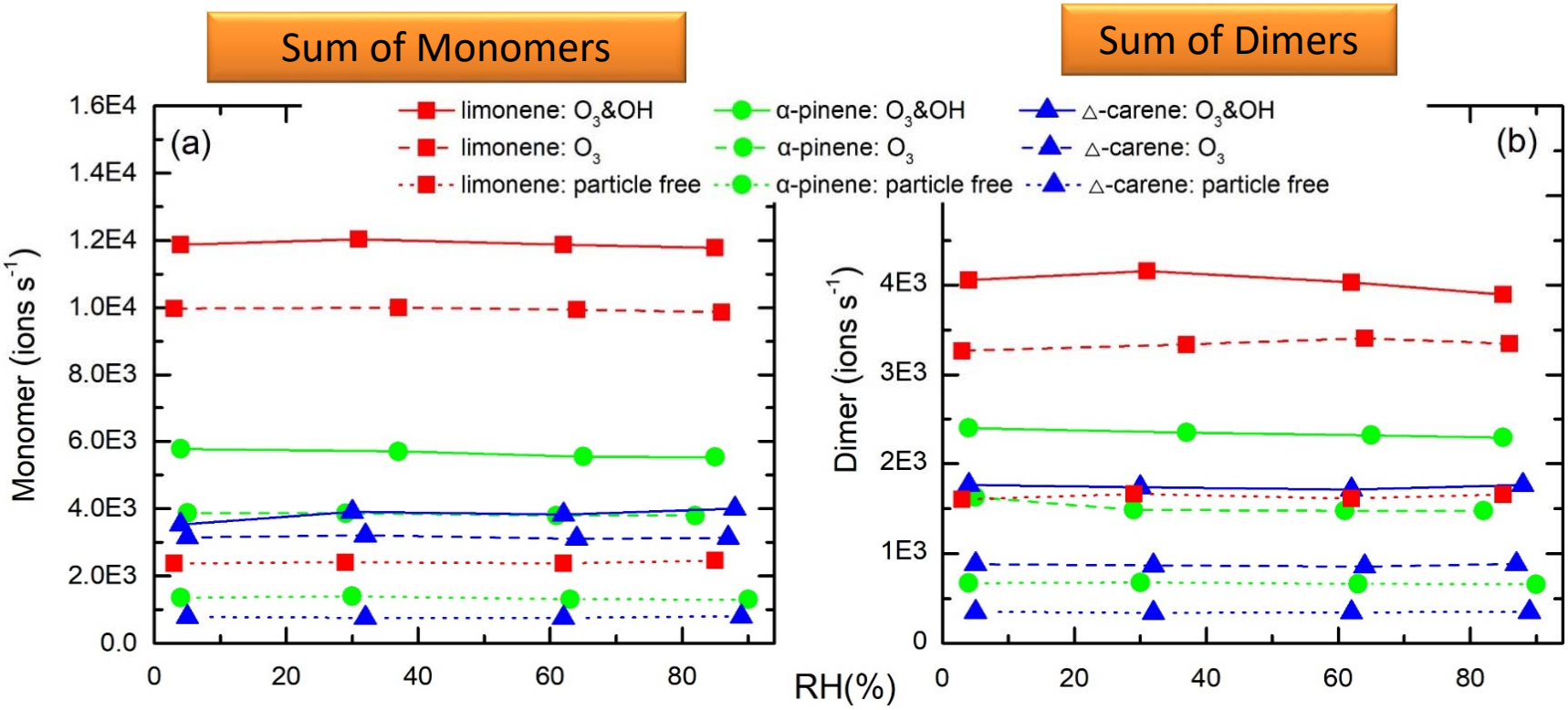


- ✓ Consistent with the result from Bonn et al., (2002);
- ✓ Water's influence on NPF (ELVOCs) is much larger than it's influence on SOA mass (LVOCs/SVOCs) generation.

Li et al., ACPD, 2018

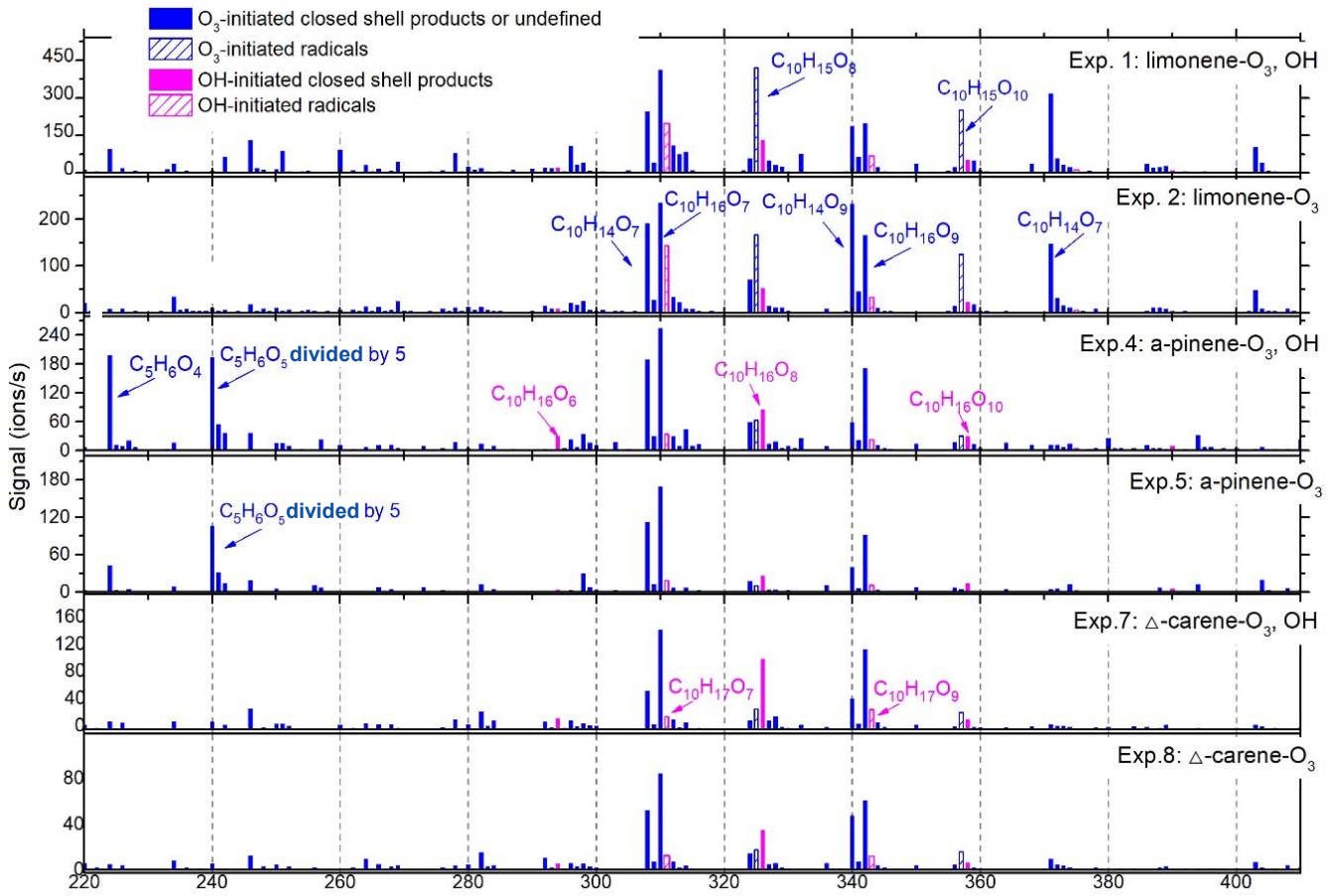
RH have no significant influence on the detected HOM

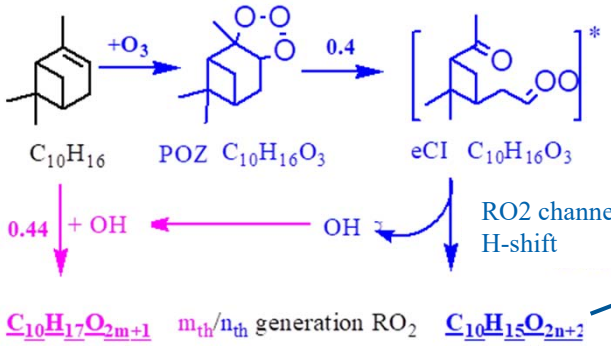
>400 peaks identified in each spectrum … none of which changed with RH!

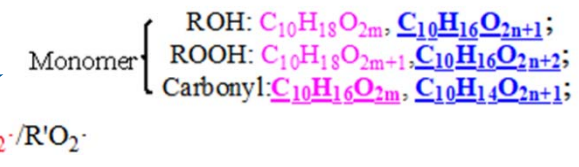


Li et al., ACPD, 2018

Discussion: Why don't HOM **monomers** change with RH?

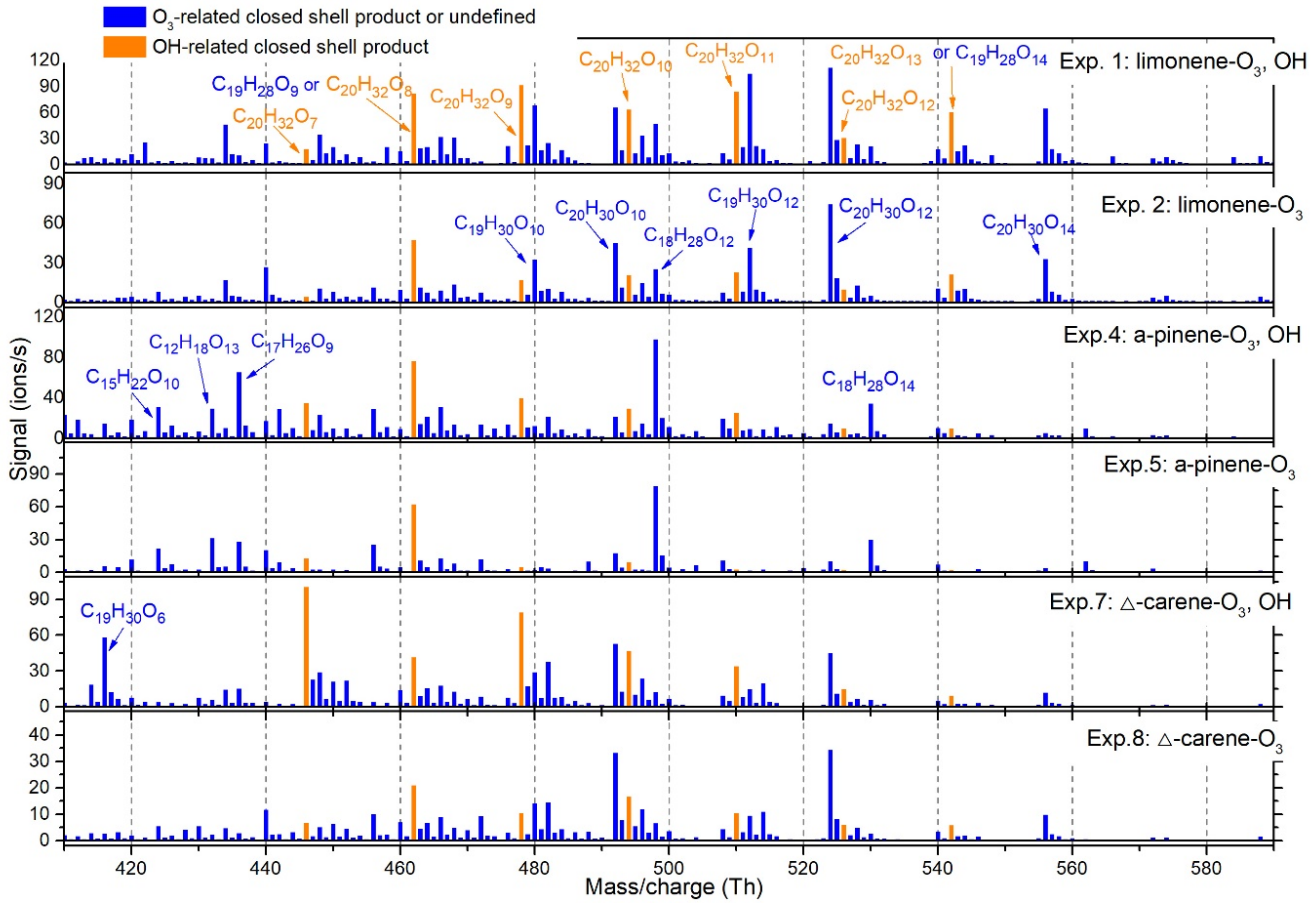


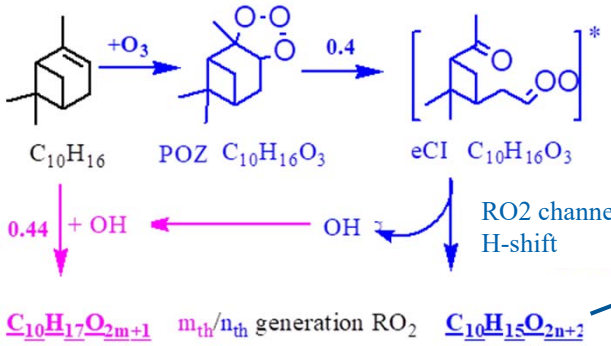




RO_2+$R'O_2$ chemistry dominates over RO_2+HO_2 in our system.

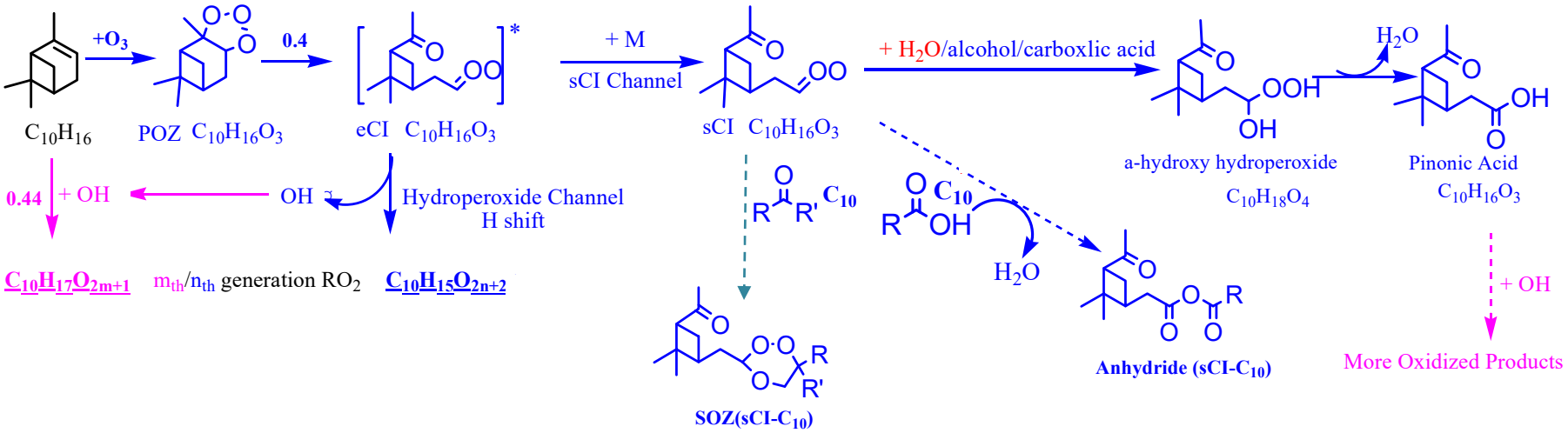
Discussion: Why don't HOM **dimers** change with RH?





It's reasonable that dimers are not influenced by $H_2O_{(g)}$

Discussion: sCI accretion products may explain the decreasing SOA number concentration and observed constant HOM formation



Conditions	RO_2 forms HOM	sCI further oxidized by OH	sCI forms SOZ (sCI-C_{10})	sCI forms anhydride (sCI-C_{10})
Formed in the gas phase	✓	✓	?	?
Contributes to nucleation/early growth	✓	✓	✓	✓
Suppressed by water vapor	⊘	⊘	✓	✓
NOT detected by nitrate-CIMS	⊘	⊘	✓	✓

Another possibility: Water vapor plays a role in hindering cluster growth and/or causing cluster fragmentation and evaporation

Conclusions

High RH suppresses NPF from monoterpene oxidation, but not by decreasing RO_2 autoxidation products.

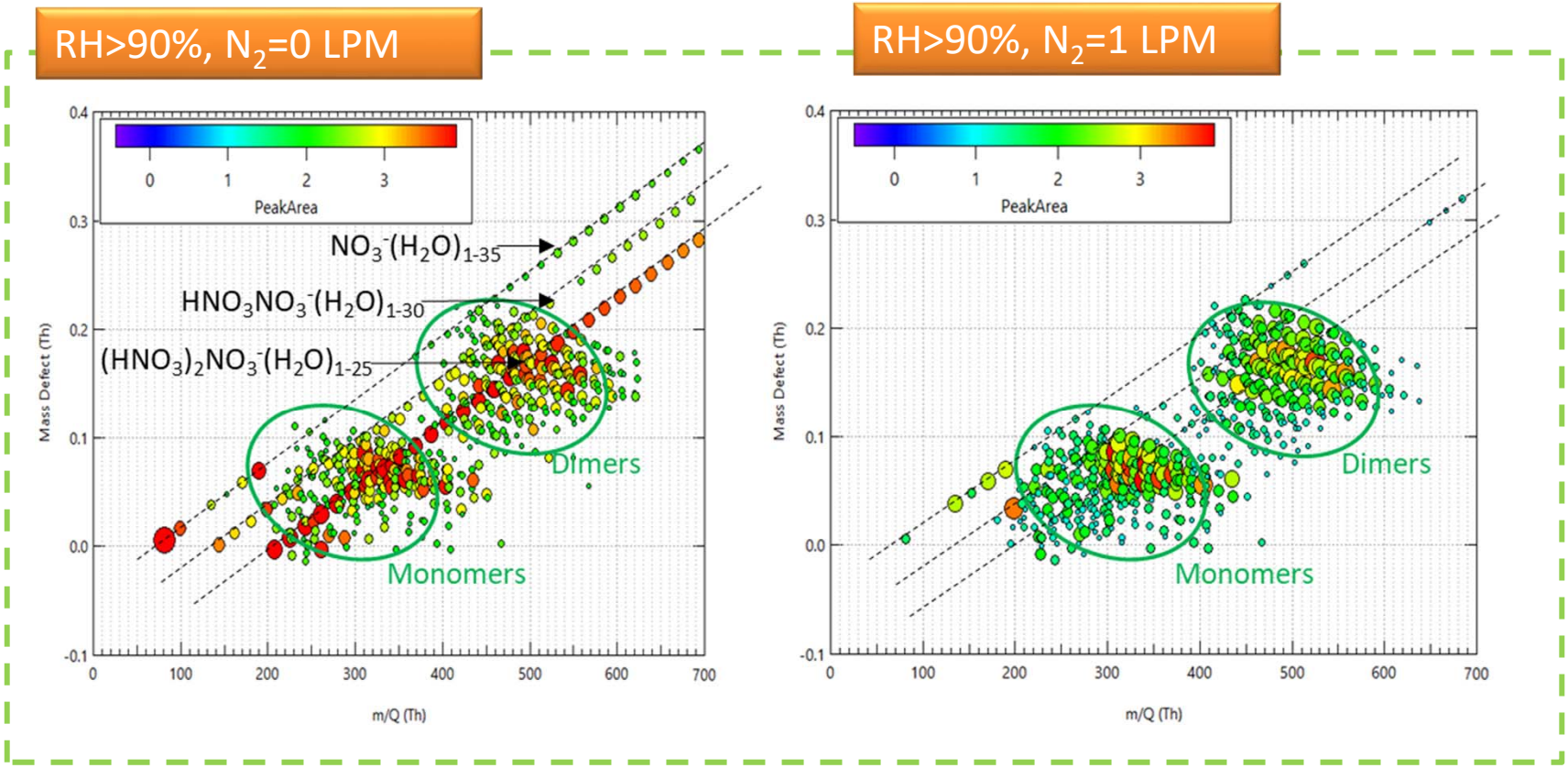
Cannot rule out the contribution of sCI accretion products, which are not visible using NO_3-CIMS.

Also possible that HOM clusters may react with water vapor in such as way as to suppress further growth

Acknowledgements

DOE NSF AGS

Supplementary N_2 curtain gas significantly removes H_2O influence on detection, making the quantification of HOMs at different RH comparable.

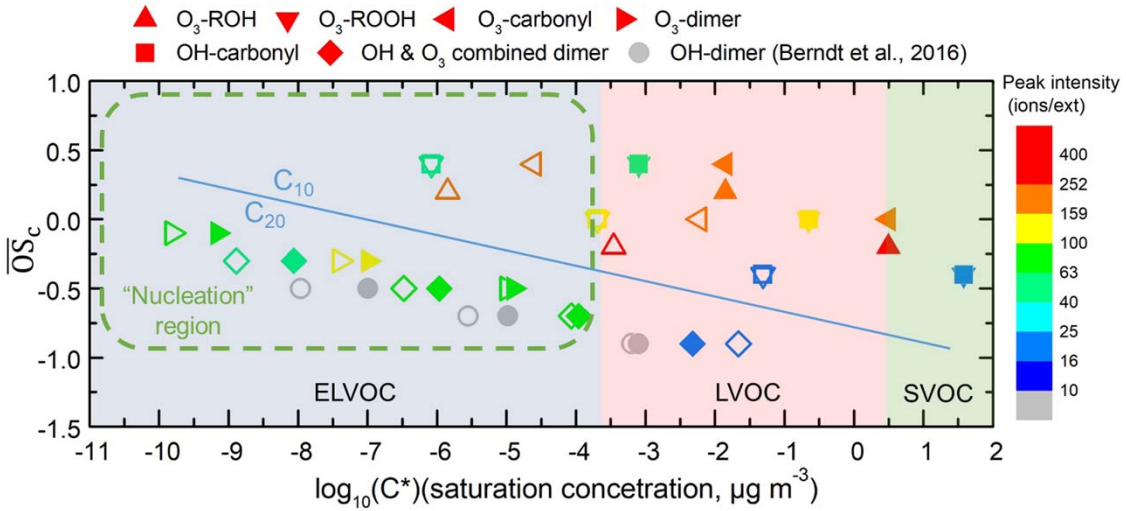


✓ The existence of water clusters in high RH largely complicates peak identification and accurate quantification.

Supplementary

Prediction of vapor saturation mass concentration (C*) of the OH and O_3 generated C_{10} and C_{20}

Predicted Volatility of the major C_{10} and C_{20} closed shell products



- SIMPOL.1 (open points)

  A group contribution method |(Pankow and Asher, 2008)
- Molecular Corridor method (filled points)

  Molecular formula based method (Li et al., 2016)

- ✓ The difference of C* predicted from the two methods was within one order of magnitude for C_{20} HOMs, and 3~4 orders of magnitude for C_{10} HOMs.
- ✓ Despite these differences, nearly all of the C_{20} HOMs can be classified as ELVOCs, while C_{10} products are mostly LVOCs.
- ✓ Typically, the volatilities of O_3-derived C_{20} HOMs were less than OH-related HOMs.