

Formaldehyde and VOC Tracer Relationships by PTR-MS

Project H104B

**Tom Jobson
Washington State University**

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Motivation

- TERC 2007-2008 Strategic Research Plan has identified production of new radicals from formaldehyde (HCHO) as a fundamental research issue (section 4.3)
- SRP notes in the conclusion that there is a pressing need to incorporate “ ... enhanced sources of new radicals into air quality models...”

Impact of HCHO on HO_x radical budget:



radical production rate key to modeling ozone production rates

➤ Key Questions:

What is the variability of HCHO mixing ratios (night and day)?

Moody Tower 2006: ~ 1 – 30 ppbV

What are the sources of HCHO?

Are there industrial emissions of HCHO that can be controlled?

HCHO Sources

Formaldehyde Sources

(1) **Primary** – direct emissions

Industrial Emissions (i.e. flaring)

Vehicle Exhaust (gasoline, diesel)

(2) **Secondary** - produced in the oxidation of many organics

ethene, propene : Industrial Emissions

isoprene (daytime) : Natural VOC emissions

alkenes, alkanes, aromatics : Vehicle / Industrial Emissions

- Source attribution must be variable due to variability in both source types.
- **Identify and measure tracers to attribute HCHO to various sources:**
 - Primary and secondary**
 - Natural and anthropogenic**
 - Vehicle emissions and HSC emissions**

Project Objective

Measure HCHO and a suite of VOCs and CO to determine relative importance of *primary* and *secondary* sources of HCHO.

- Use correlations between HCHO and other species to reveal HCHO origins.
- Apply statistical methods such as positive matrix factorization to quantify what drives HCHO variability (meteorology, chemical tracers).

Karl et al., JGR, 2003 : TexAQS 2000 at La Porte

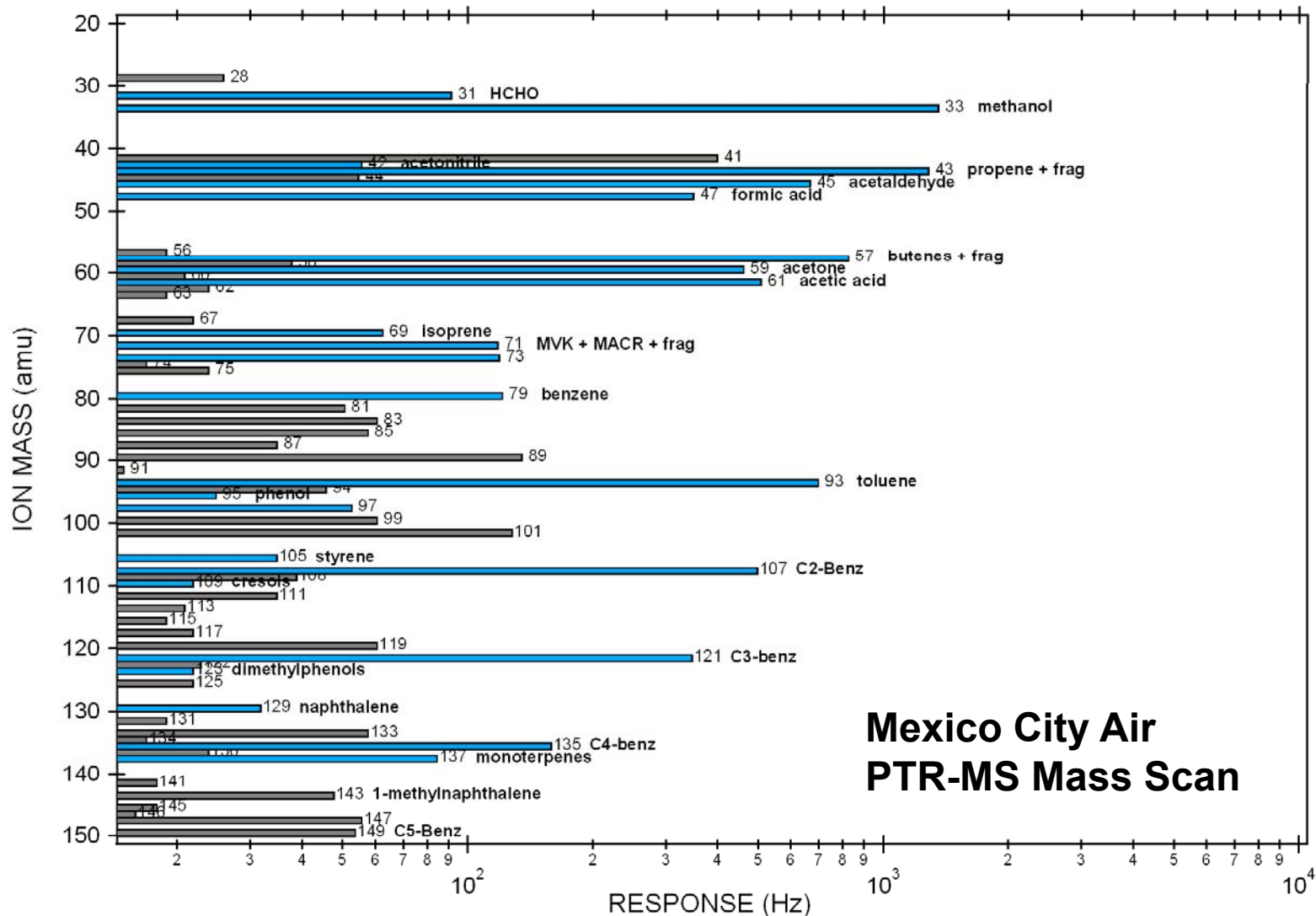
Friedfeld et al., (2002) related HCHO in Houston (Deer Park site) to CO (primary) and O₃ (secondary) concentrations in a source attribution study : 66% = secondary

Rappengluck et al. Moody Tower 2006 → Observed strong correlation between CO and HCHO for *urban* air masses, different correlation for day time *ship channel* air masses. SO₂ and HCHO observed to co-vary suggesting industrial sources.

- Field measurements at Moody Tower for 1 month as part of **SHARP**

Measurement Approach

Use PTR-MS instrument: $\text{H}_3\text{O}^+ + \text{R} \rightarrow \text{RH}^+ + \text{H}_2\text{O}$ (in-situ measurement)



Measure species in blue (~ 25 masses)

Measure HCHO correlation with other organics.

Mexico City Air
PTR-MS Mass Scan

Proposed Tracer Mass List

Mass	Species	Sources
Oxygenated species		
31	formaldehyde	photoproduct & direct emissions
33	methanol	solvents
45	acetaldehyde	photoproduct
47	formic acid	O ₃ + alkene reaction product
59	acetone + propanal	solvents + photoproducts
61	acetic acid	photoproduct from CH ₃ C(O)OO + HO ₂
71	MVK + MACR	isoprene photoproducts
77	PAN: CH ₃ C(O)OONO ₂	photoproduct from CH ₃ C(O)OO + NO ₂
Aromatic compounds		
79	benzene	vehicle emissions / industrial
93	toluene	vehicle emissions / industrial
105	styrene	industrial
107	C₂ benzenes (C₈H₁₀)	vehicle emissions
121	C₃ benzenes (C₉H₁₂)	vehicle emissions
135	C₄ benzenes (C₁₀H₁₄)	vehicle emissions
129	naphthalene	vehicle emissions
95	phenol	vehicle emissions
109	cresols	toluene photoproducts
Natural VOC emissions		
69	isoprene	tree emissions
137	monoterpenes	tree emissions
Industrial tracers		
49	methyl mercaptan	pulp and paper industry
54	acrylonitrile	air toxic
43	propene*	refineries
57	butenes*	refineries
Biomass burning tracers		
42	acetonitrile	plant material combustion

PTR-MS can measure a range of primary and secondary VOC tracers.

High time resolution →
GOOD STATISTICS

Need good measurements of secondary tracers (oxygenated species).

✓ Permeation tubes for HCHO, acetic acid, formic acid (received in Sept)

Synthesize PAN for perm source (on going)

bold = calibrated using compressed gas standard (naphthalene, phenol, cresol use relative response factors)

HCHO Measurement

Problem: Water vapor dependent response that reduces sensitivity



When humidity increases back reaction increases reducing HCHO⁺ count rates (Ionmata, ACP, 2008)

Rate constant for back reaction increases with ion energy (= ion velocity in the drift tube reaction chamber of the PTR-MS)

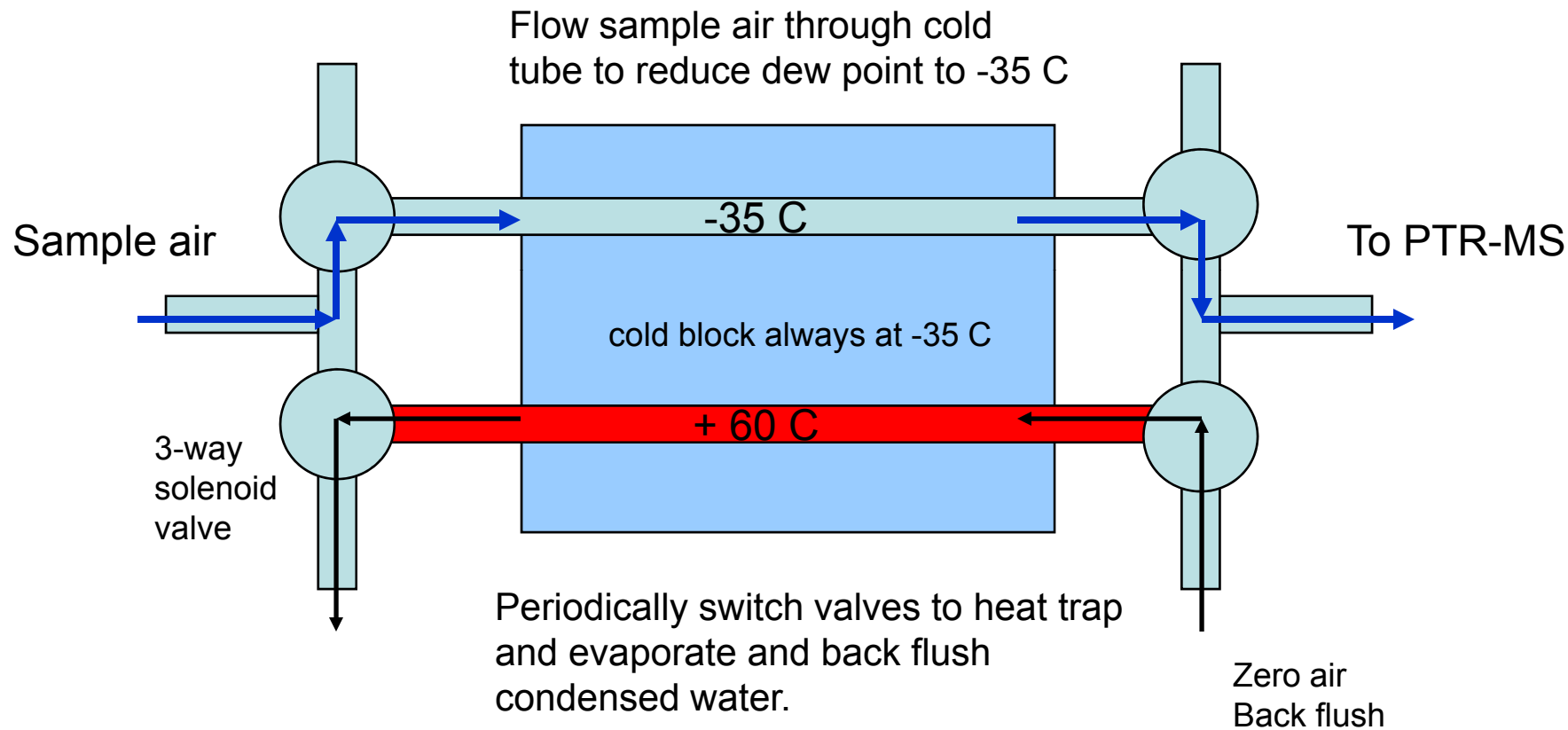
Solution:

- 1) Operate PTR-MS as normal and correct for water vapor (PTR-MS measures H₂O mixing ratio in sample air)
- 2) Reduce H₂O concentration in the PTR-MS reaction chamber by removing water vapor from sample air

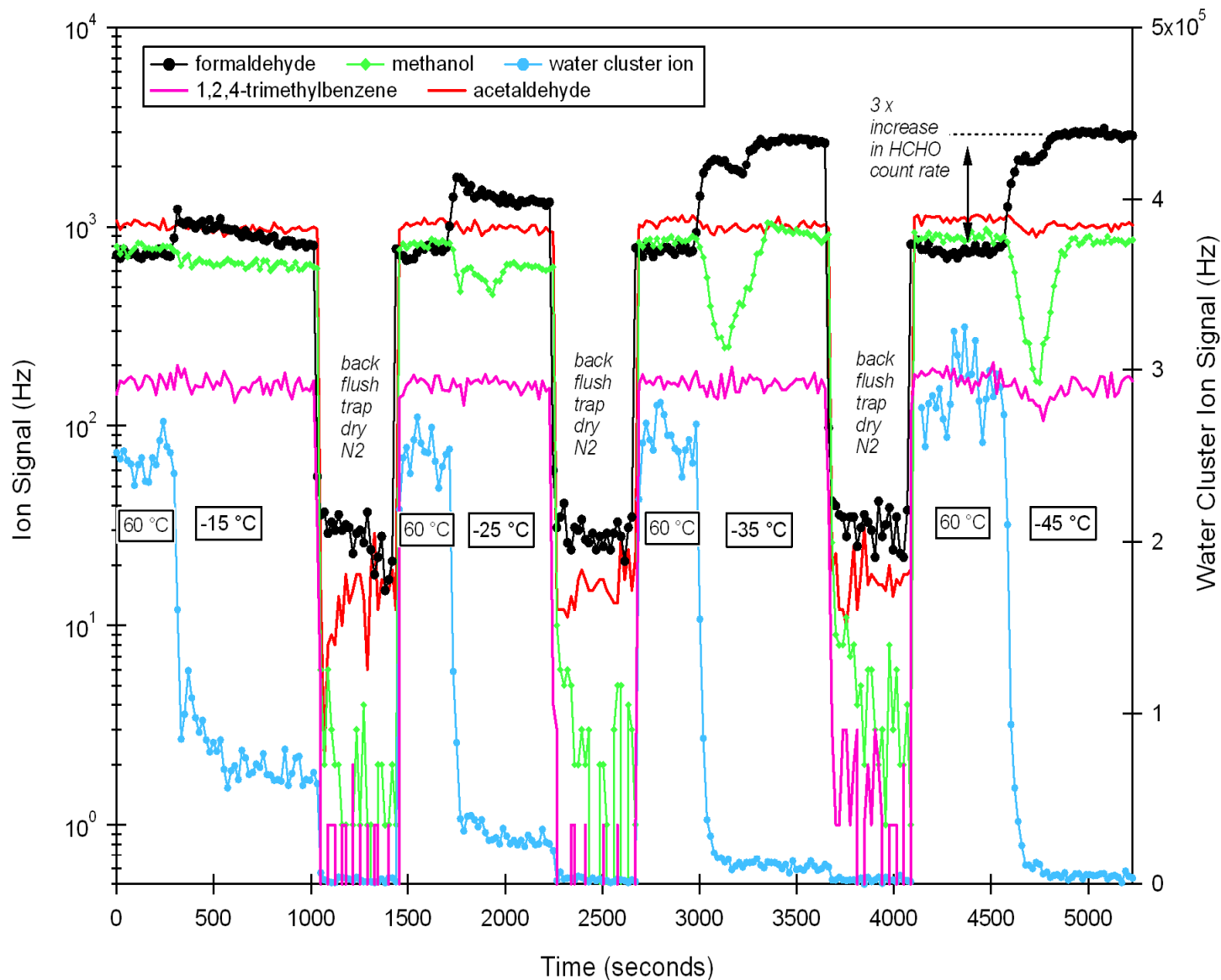
Advantages:

- i) increase sensitivity & remove variable calibration factor
- ii) can operate PTR-MS drift tube at lower electric fields to further increase sensitivity

Cold Trap to Remove Water Vapor



Impact of Drying Sample Air



50% RH sample air (22 C)

120 Td drift condition

Sample flow rate through trap = 100 sccm

Results

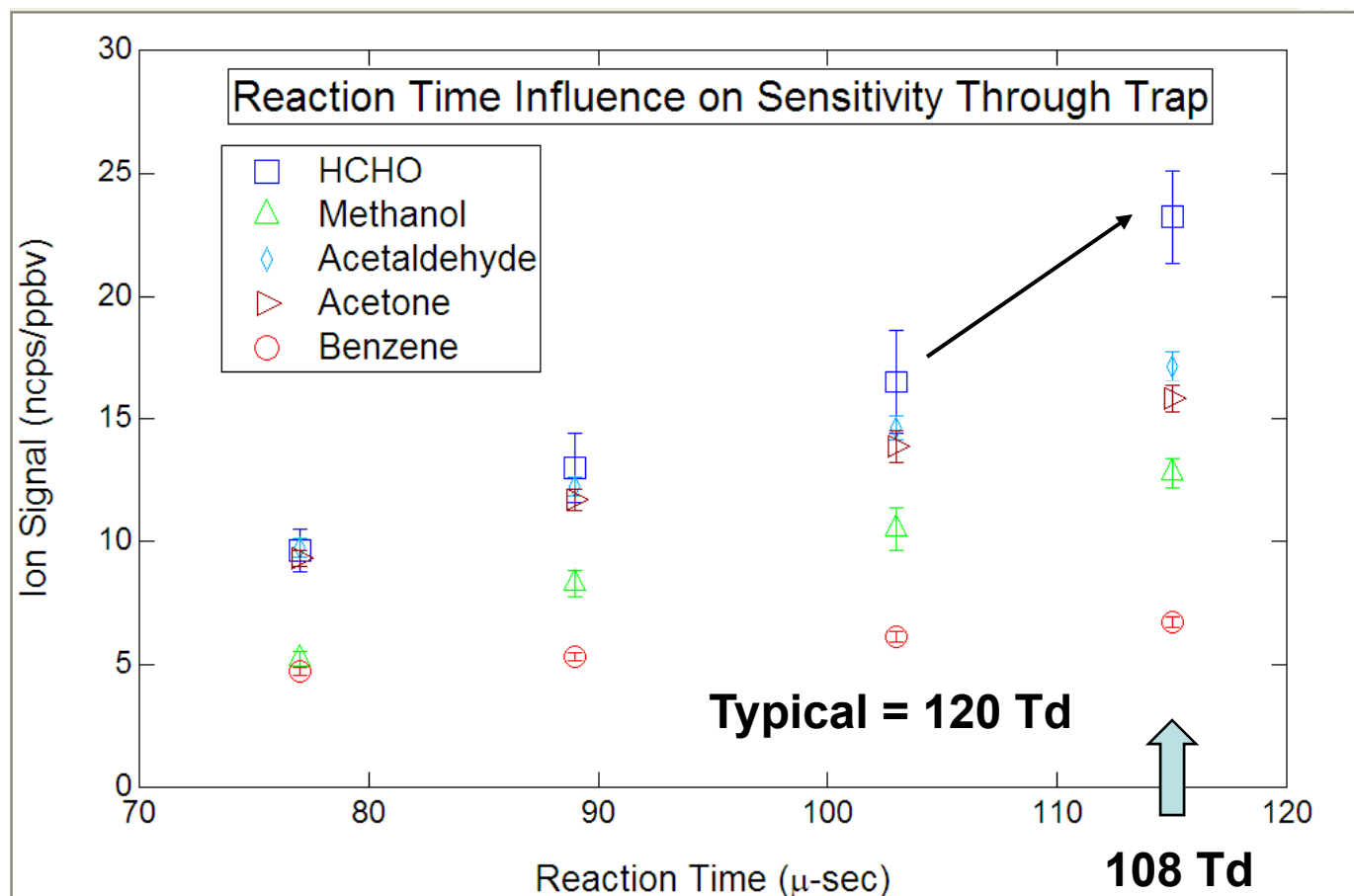
Removes water

The colder the better!

Increase HCHO sensitivity by 3 X

Traps needs to "condition", increase sample flow to reduce conditioning time.

Benefits of Lower Electric Field



Can increase sensitivity to HCHO by another factor of 2-3 by operating at lower electric field strength (80-90 Td possible)

This is possible if sample air is dry.

We are in the process of optimizing the sampling system and PTR-MS operating conditions to maximize our sensitivity to HCHO, acetic acid, and formic acid. HCHO DL ~ 200 pptv at typical Td.

Moody Tower Data Needs

Measurements I would like to use from **SHARP** to compliment this project

- √ 1) Surface meteorology (wind direction, speed)
- √ 2) Ozone, NO_x, SO₂
- √ 3) Hantzsch based HCHO measurement to compare too
Recent HCHO intercomparison between PTR-MS, DOAS, Hantzsch, and DNPH methods in the SAPHIR chamber indicate “fair agreement”
Whisthlaer et al., ACP, 8, 2189 (2008).
- ? 4) Fast olefin measurements to identify alkene plumes
Alkene photooxidation important source of HCHO
GC based measurements at Moody can speciate alkenes but time resolution is low.
PTR-MS is blind to ethene.

*Since HRVOCs are the story of Houston photochemistry it seems prudent to have a **Rapid Alkene Detector** for SHARP. Compliments existing GC based hydrocarbon measurements at Moody Tower.*