

Free molecular flow, thermal decomposition, and residence time in the AMS ion source

Daniel Murphy

NOAA ESRL Chemical Sciences Division

June 2015 AMS Clinic

- Heavier neutral molecules spend more time in the ion source.
- This means that the sensitivity should scale with \sqrt{M} .
- Thermal decomposition on vaporizer changes the neutral molecular weight.
- Heavy, thermally stable compounds are overestimated, whereas compounds that decompose to small pieces underestimated.
- Examples of ammonium nitrate and citric acid
- Changes the paradigm that (Total organic signal) = (Sum organic peaks).
- Likely some cancellation of errors for overall signal.
- Goal is physical understanding

Mean free path in the AMS ion source

- **Several estimates lead to mean free paths \gg dimensions of ion source**

1) Open area to front of vaporizer is $\leq 1 \text{ cm}^2$ or about 10 liter s^{-1} .

Pump is $200 \text{ to } 300 \text{ liter s}^{-1}$.

=> Source region at 20 to 30x chamber pressure

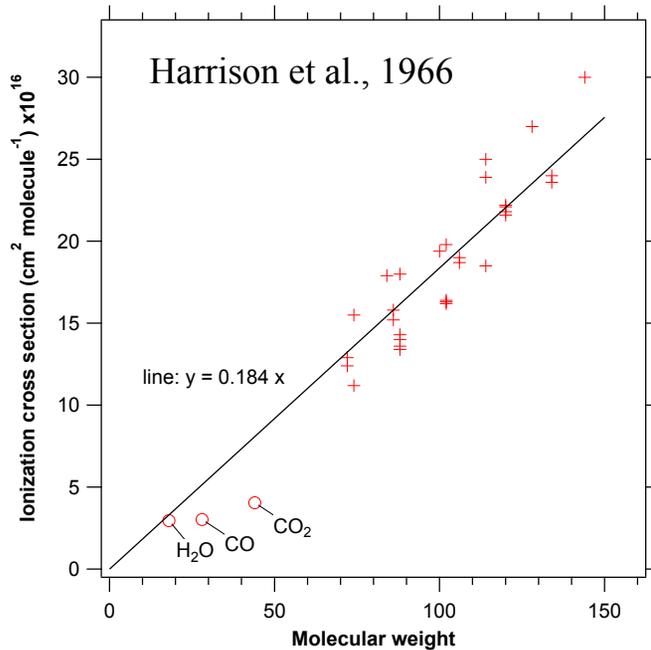
=> Mean free path in ion source perhaps $\sim 30 \text{ cm}$

2) Similar estimate if air beam signal is 100x peak signal from 500 nm particle

3) Source region must be in free molecular regime for the electron beam to work or for ions to be extracted properly.

- Large molecules have larger cross-section, but need several collisions with air to deflect them => similar or longer “path”

Existing AMS model



- Number of molecules per unit mass $\sim 1/M$
- Ionization cross section $\sim M$
- Ions per unit mass \sim constant
- That is, ions are proportional to mass
- Leads to convenient summation:

“Since **AMS ion intensities are proportional to the mass of the original molecules present** (Jimenez et al., 2003), M_C , M_O , and M_H are obtained as a sum of the appropriate ion intensities across the complete organic spectrum...”

Canagaratna et al., 2015. (emphasis added)

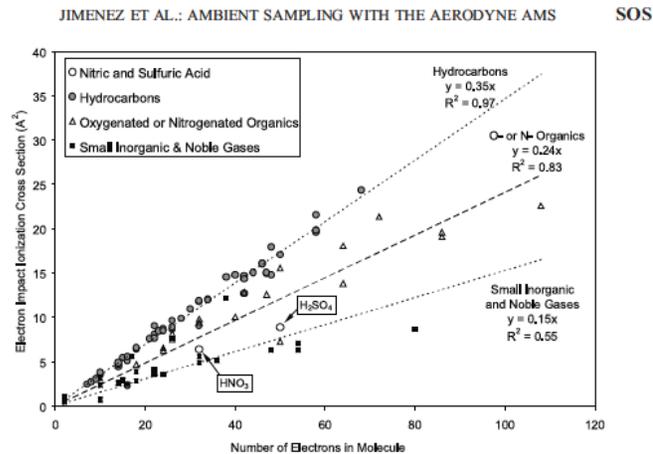
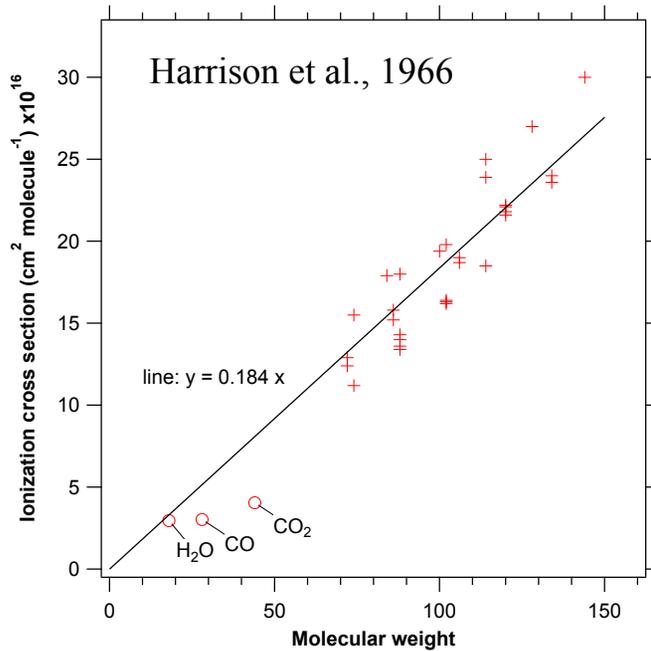


Figure 6. Electron impact ionization cross sections of small molecules versus number of electrons in the molecule.

Existing AMS model



- Number of molecules per unit mass $\sim 1/M$
- Ionization cross section $\sim M$
- Ions per unit mass \sim constant
- That is, ions are proportional to mass

- Implicit assumption:

The number of molecules in the ion source is proportional to the number of molecules that evaporate.

JIMENEZ ET AL.: AMBIENT SAMPLING WITH THE AERODYNE AMS SOS

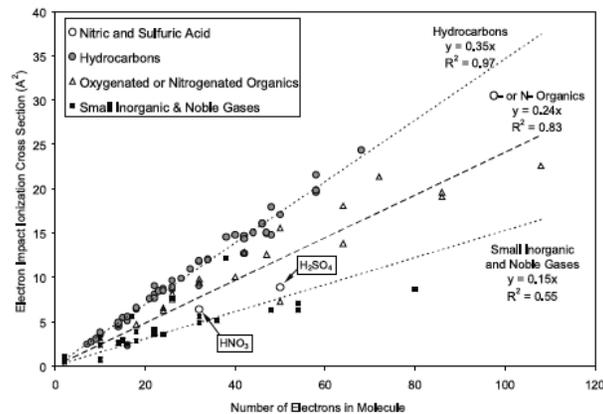


Figure 6. Electron impact ionization cross sections of small molecules versus number of electrons in the molecule.

Steady-state model



- Source of evaporating material with free molecular flow out the other end (Knudsen cell)
- What is number density n for an evaporation rate \dot{m} ?

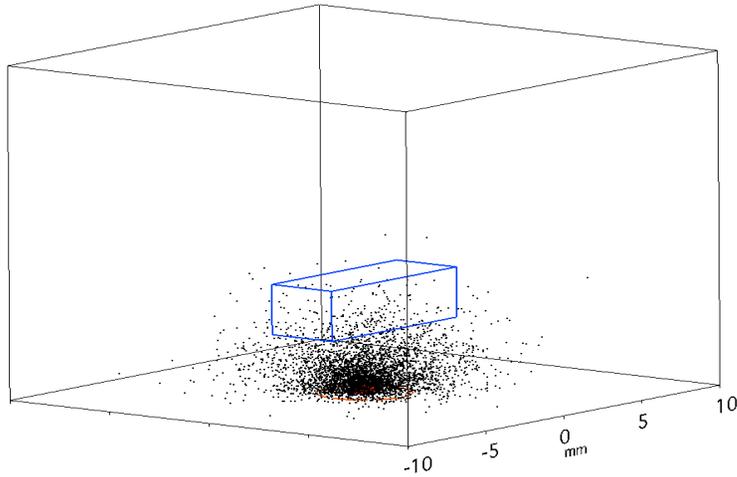
- Mass flux leaving cell = $Area * M * n * \bar{c} / 4$

$$\bar{c} = \sqrt{\frac{8kT}{\pi M}}$$

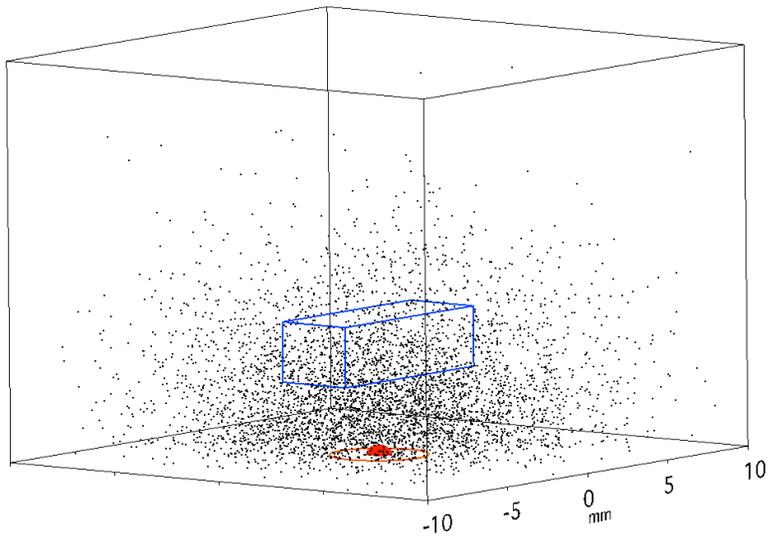
$$n = \frac{\dot{m}}{A} \sqrt{\frac{2\pi}{kTM}}$$

- Compare to closed cell $n = \dot{m} / MV$
- *With $\sigma \sim M$, sensitivity scales as \sqrt{M} instead of being independent of mass*

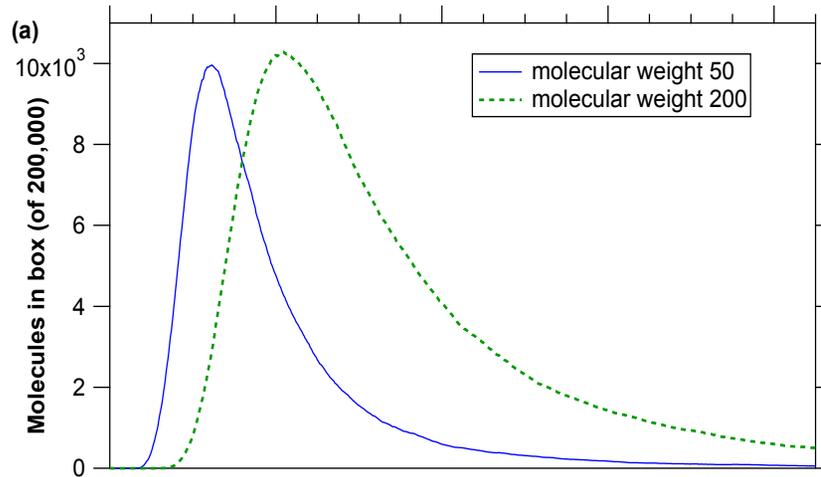
Pulsed evaporation model



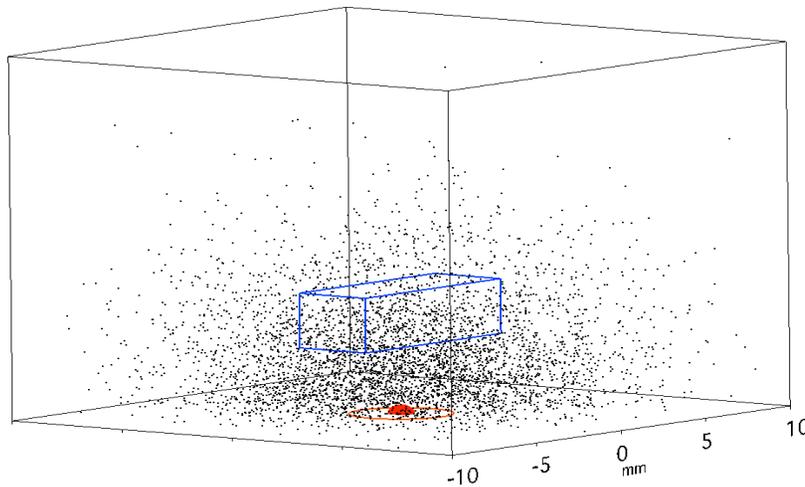
- Molecules with translational temperature of 500 C evaporate from the red dot for 5 μ s.
- Distributions at 10 and 20 μ s after start of evaporation.
- 5000 molecules shown; 200,000 modeled.



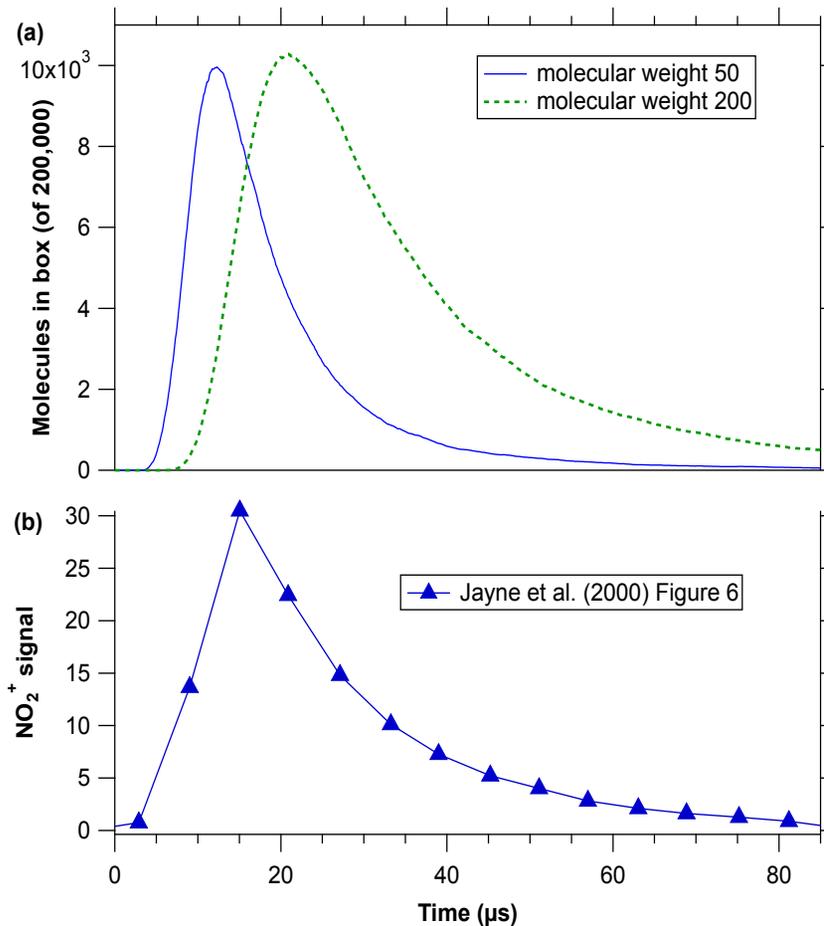
Pulsed model



- Heavier molecules are delayed and have a longer pulse.
- Mean number of molecules in blue box is proportional to \sqrt{M}

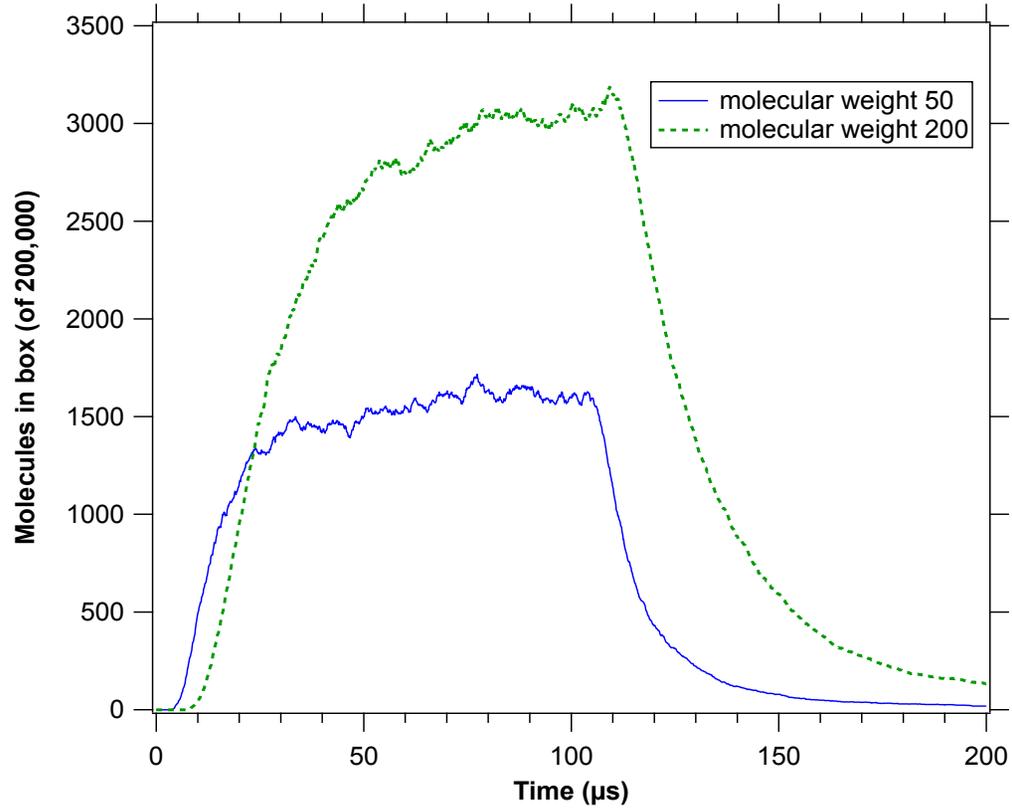


Pulsed model



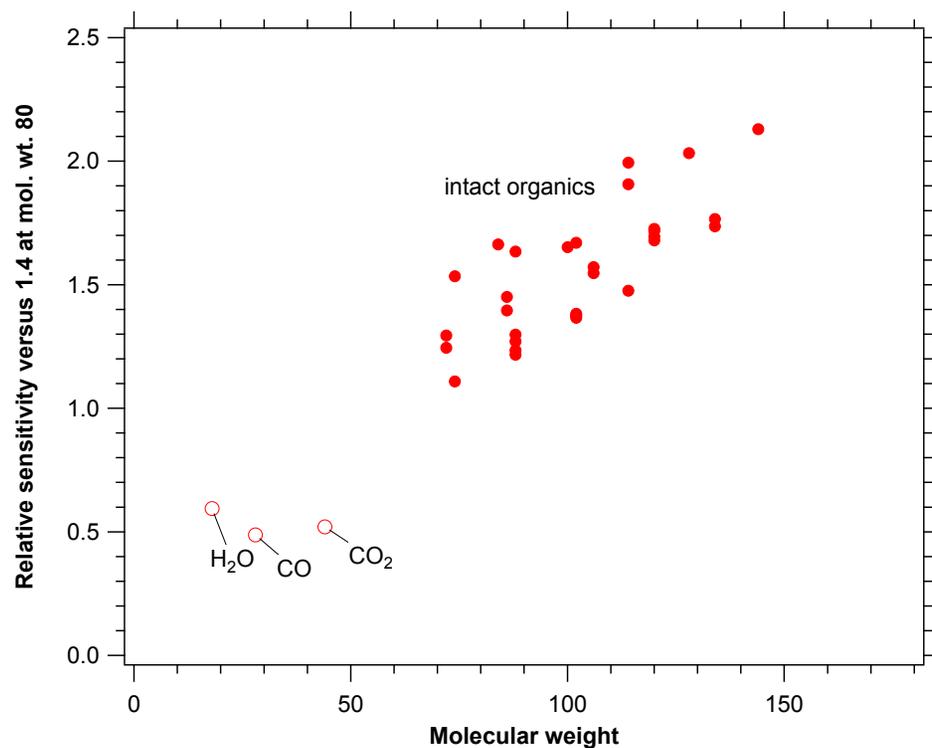
- Heavier molecules are delayed and have a longer pulse.
- Mean number of molecules in blue box is proportional to \sqrt{M}
- Reasonably reproduces shape from AMS. Exact shape depends on vaporizer and ion source dimensions.
- Significantly, the AMS shows a Maxwell-Boltzmann velocity distribution
=> free molecular flow model is appropriate.

Longer evaporation time



- Same model except 100 μs evaporation time
- Number of molecules still proportional to \sqrt{M}
- Flattish top a result of the assumed evaporation rate

Organic sensitivity with sqrt(M)



- Sensitivity to *intact* molecules increases with mass
- Don't know how far cross sections continue to be linear: limit is likely between 200 and 720.
 $\sqrt{240/80} \approx 1.7$
- Sensitivity to small fragments is 1/3 to 1/4 of species with mol. wt. 100 to 150.

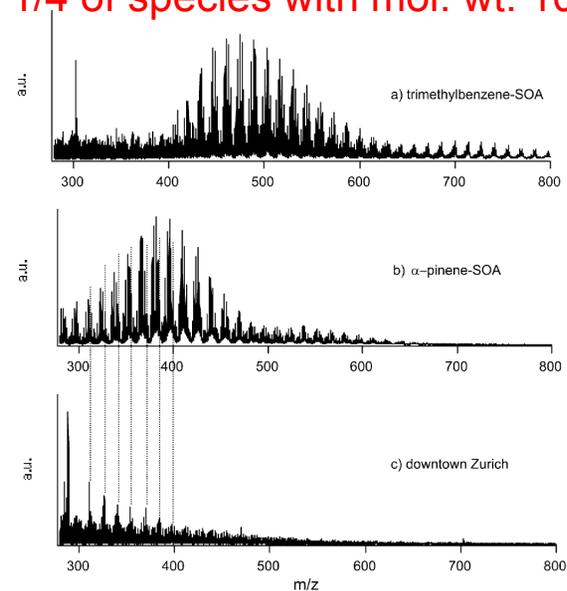
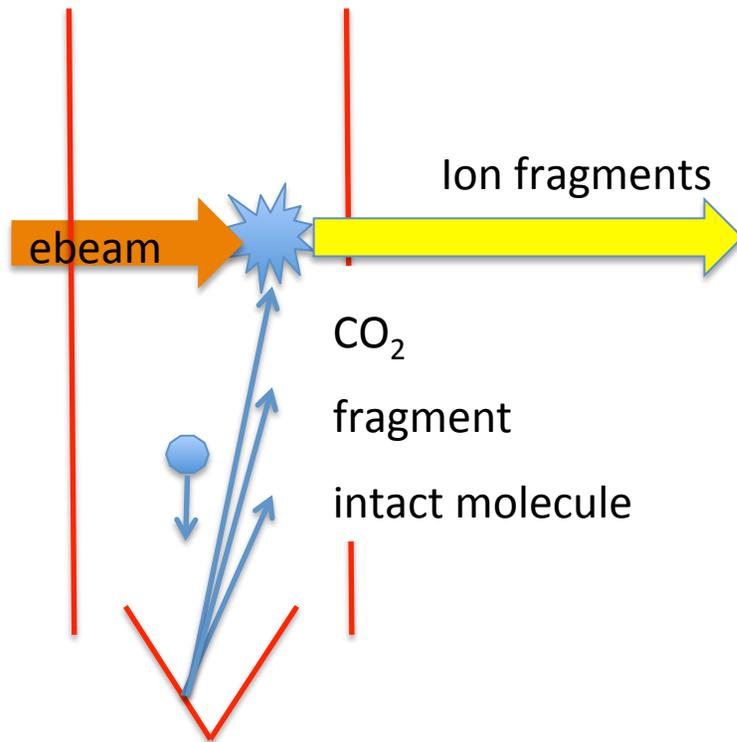


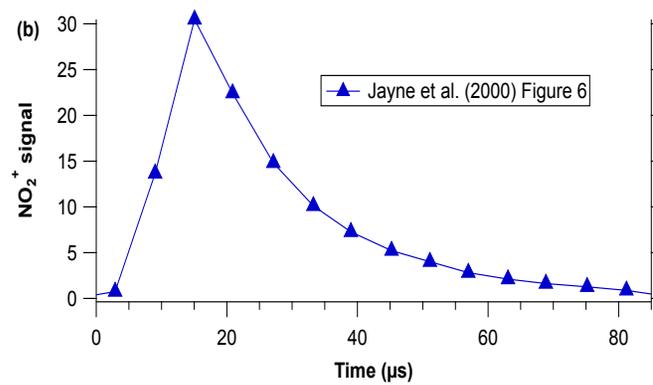
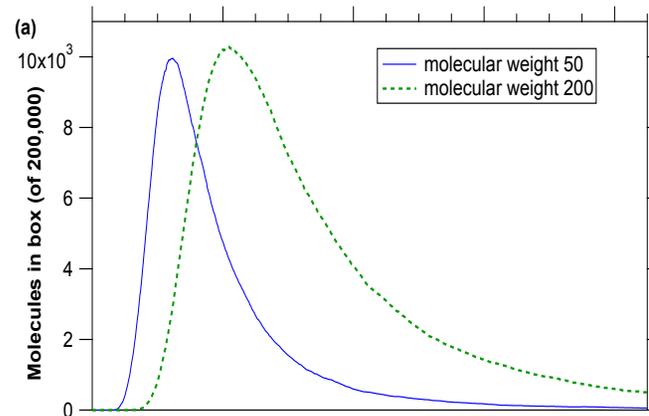
Fig. 4 Comparison of LDI-MS spectra for TMB-SOA, α -pinene-SOA, and ambient aerosol from downtown Zurich between m/z 280–800.

Thermal decomposition

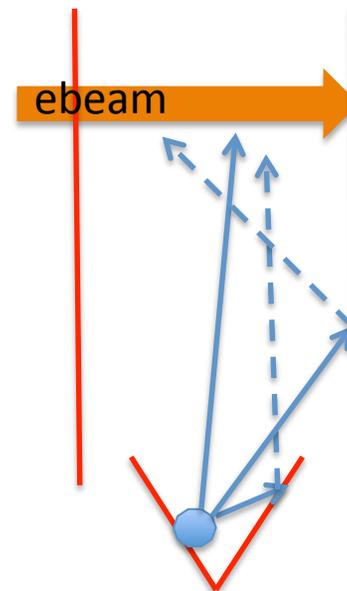


- Many molecules probably decompose on a 600 C surface
- CO₂ thought to be an important fragment
- **Massive fragmentation in the electron beam hides the evidence of thermal decomposition. Ions are only a lower bound on neutral mass.**
- Residence time makes decomposition much more important to quantitation than if thermal fragments have similar sensitivity to intact molecules.

What determines peak length profile?

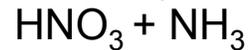


1. Speed of neutral molecules
2. Evaporation rate
3. Multiple paths
Thermal decomposition may be different for the various paths
4. Adsorption / reaction on surfaces



Ammonium nitrate

- Question: what gas-phase species are producing NO_2^+ and NH_n^+ during an ammonium nitrate calibration?



?

(N_2O , H_2O , NH_2OH , NO_2 , N_2 , NO , ...)

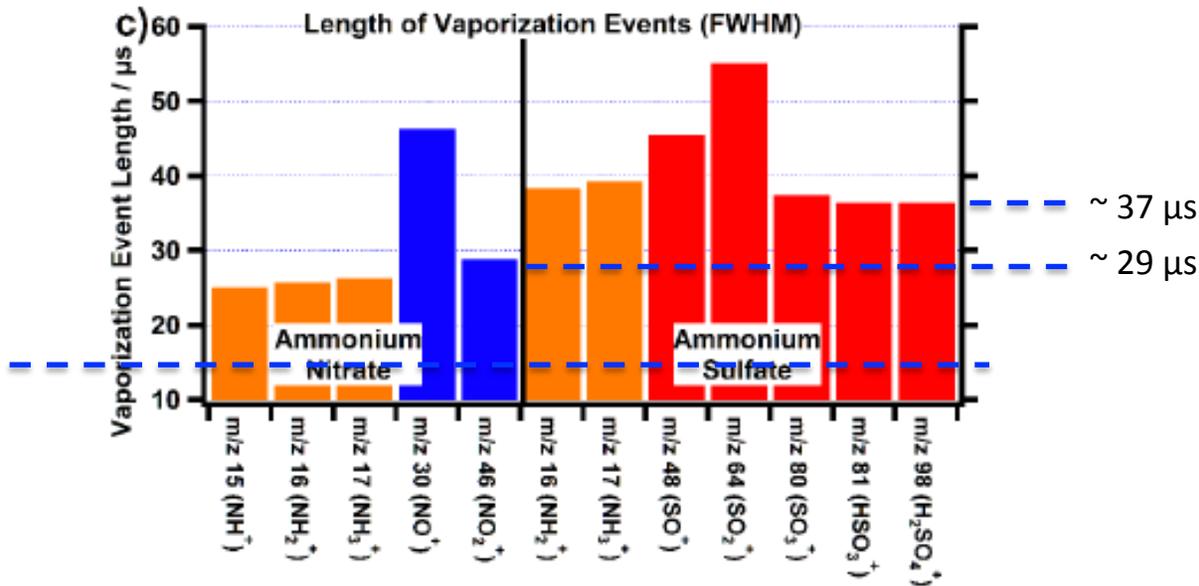
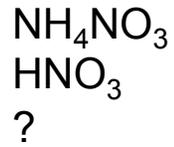
- Matters both for ionization cross-sections and residence time, especially for ammonia: gas phase NH_3 has 1.9x smaller residence time than NH_4NO_3 .

“particulate ammonium vaporises as ammonia (NH_3)”

Allan et al., 2004

Nitrate reference

- Open question: what gas-phase species is producing NO_2^+ during an ammonium nitrate calibration?



No unique solution because of possible multiple evaporation times, multiple paths, and temperatures

But... ammonium peaks aren't a lot shorter than 46 or 98.

$$29 \mu\text{s} * \sqrt{18/62} \approx 15 \mu\text{s}$$

$$37 \mu\text{s} * \sqrt{18/98} \approx 16 \mu\text{s}$$

Notes:

$$37/29 \approx \sqrt{132/80}$$

$$\approx \sqrt{98/62} \text{ as well}$$

Thermal decomposition: ammonium nitrate



$\sigma (\text{HNO}_3) \approx 7\text{e-}20 \text{ m}^2$
 $\sigma (\text{NH}_3) \approx 3\text{e-}20 \text{ m}^2$
VM factor ≈ 1.9



*$\sim 4.4\text{x}$ more $\text{NO}^+ + \text{NO}_2^+$
than NH_n^+ fragments*



RIE ammonium ≈ 0.8

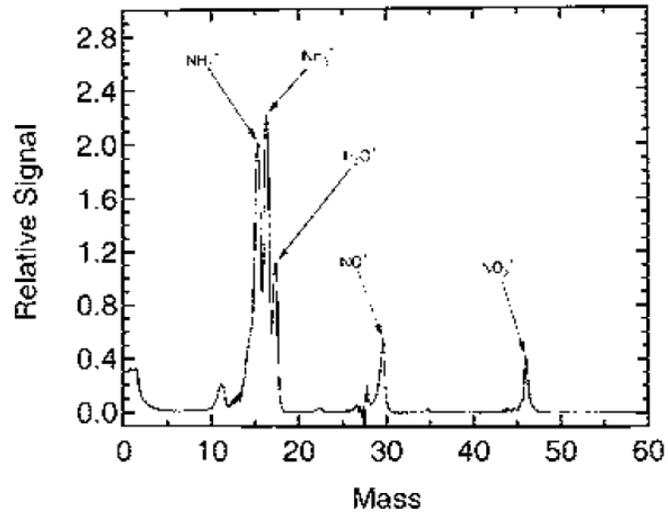
Thermal decomposition: ammonium nitrate



$\sigma(\text{HNO}_3) \approx 7\text{e-}20 \text{ m}^2$
 $\sigma(\text{NH}_3) \approx 3\text{e-}20 \text{ m}^2$
VM factor ≈ 1.9

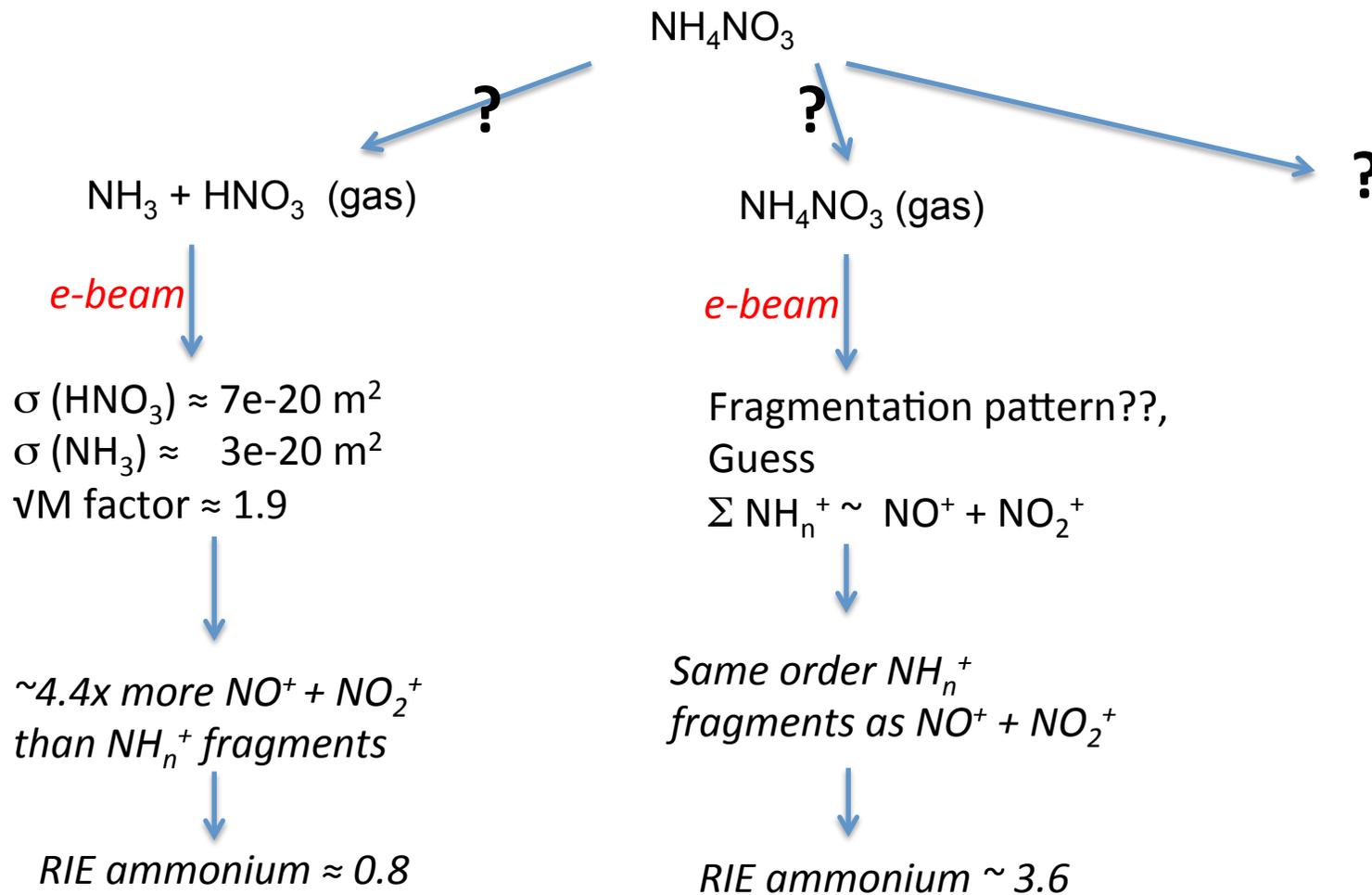
$\sim 4.4\text{x}$ more $\text{NO}^+ + \text{NO}_2^+$
than NH_n^+ fragments

RIE ammonium ≈ 0.8

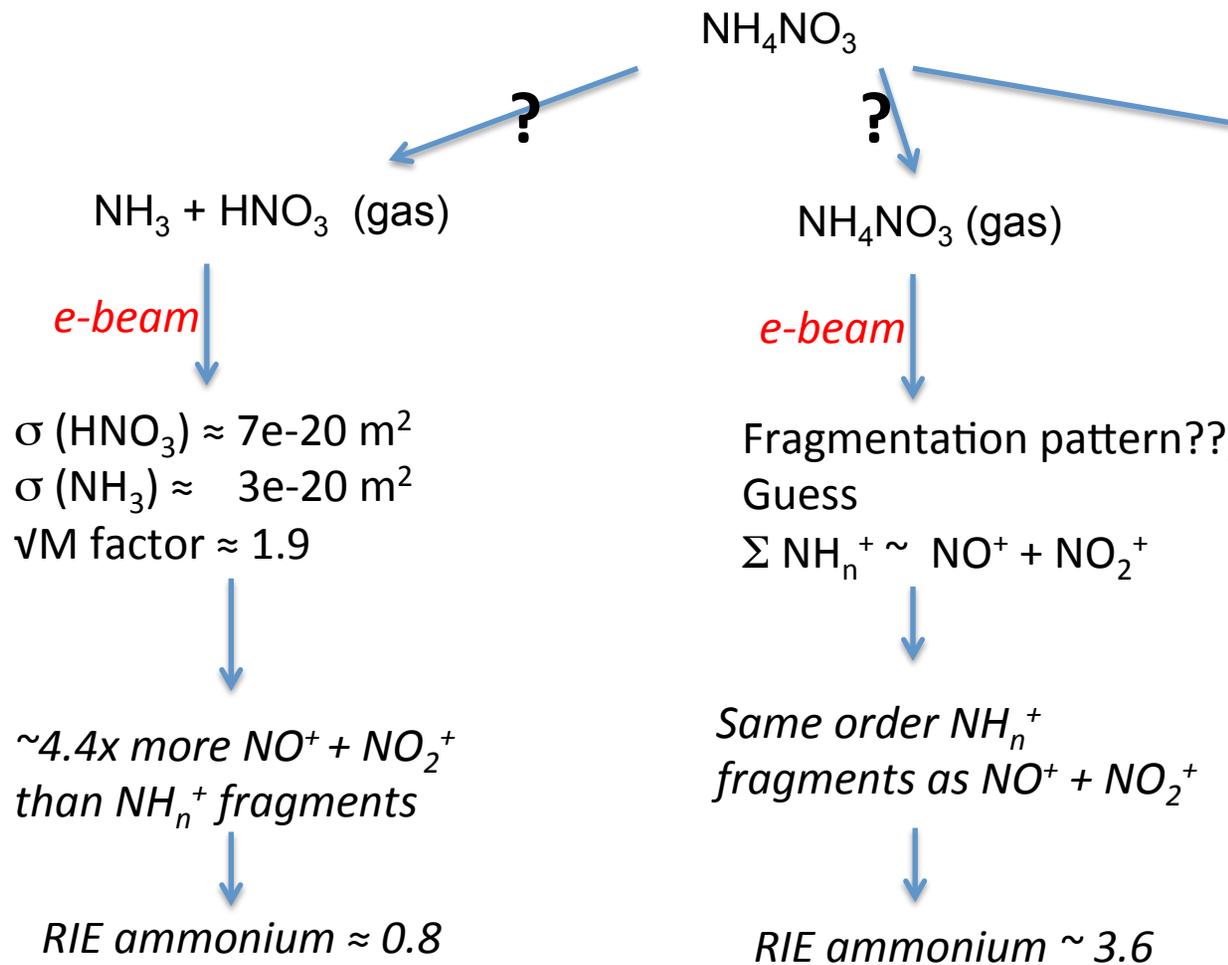


Jayne et al., 2000

Thermal decomposition: ammonium nitrate



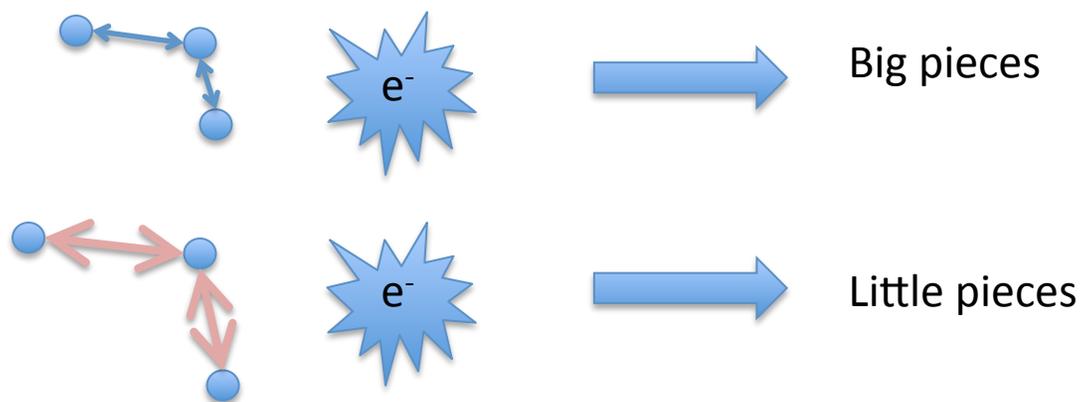
Thermal decomposition: ammonium nitrate



- Vaporization process can change sensitivity to ammonium by more than a factor of 4.
- Data are consistent with gas phase NH₄NO₃
- Not with NH₃ + HNO₃
- Does not prove gas phase NH₄NO₃
- NO⁺ peak length implies there is more than one mechanism

How much thermal decomposition of organics?

- **The short answer: it is very difficult to know.**
- More fragmentation in AMS than in library spectra has two explanations:
 - 1) Molecules thermally decompose on the vaporizer and smaller neutral fragments make smaller ion fragments.
 - 2) Thermally excited molecules fragment more when hit by electrons:



How much thermal decomposition?

- **The short answer: it is very difficult to know.**

- Not a lot of literature at appropriate heating rates:

AMS: Heat ~500 C in a few *microseconds*

Fastest bulk experiments: Heat ~500 C in a few *milliseconds*

Laser ablation: Heat >500 C in a few *nanoseconds*
possible exception: long pulse CO₂ laser ablation

- Not a lot of literature at appropriate size scales:

AMS: Submicron

Laser surface ablation: Usually mm spots => more chemistry in initial plume

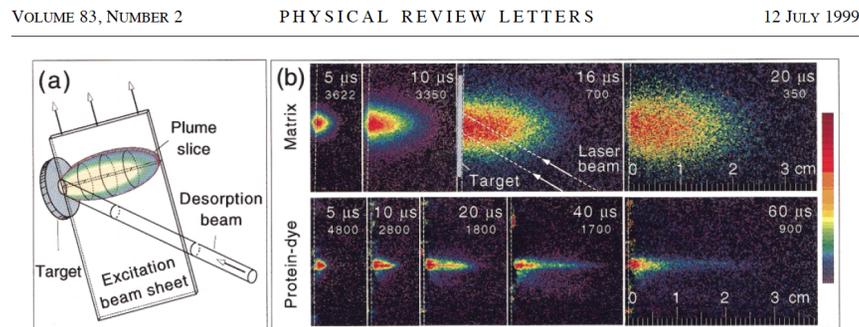


FIG. 1 (color). (a) Schematic of MALDI plume irradiation geometry. Desorption is generated by a KrF-laser beam ($3.1 \times 3.6 \text{ mm}^2$ elliptical beam spot). LIF excitation utilizes a sheet beam from a second laser fired at variable time delay after the

How much thermal decomposition?

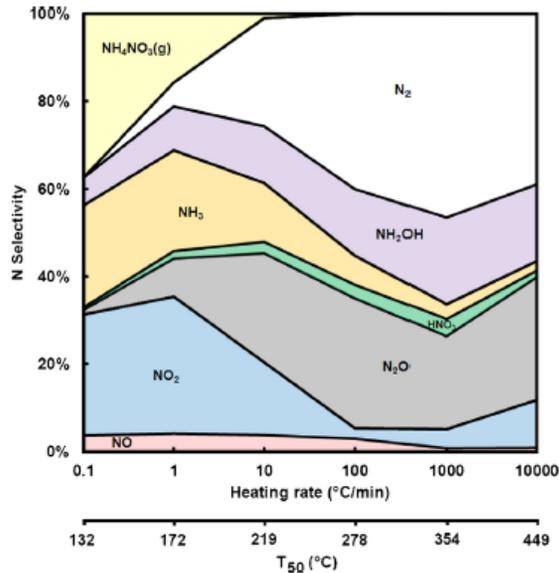


Fig. 8. Impact of heating rate on nitrogen selectivity among gas-phase products. The

- **An example of mismatched scales:**
- **2.5 mg -> 10¹¹ more mass**
- **Fastest heating rate 10⁶ slower**
- **Total gas pressure 10³ to 10⁷ higher >> bimolecular collision rate**

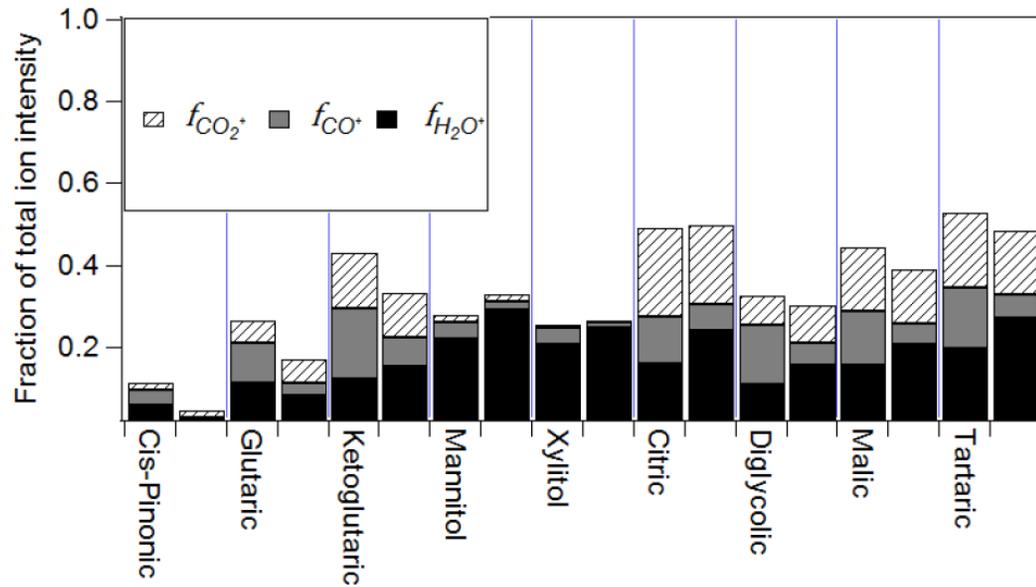
“Combined experimental and kinetic modeling approaches of ammonium nitrate thermal decomposition”

Skarlis et al., 2014

Information from VUV ionization

- Less fragmentation than e-beam, but still some, and it still depends on molecules' internal energy
- Possibly contradictory results: most other investigators have seen much less thermal decomposition than AMS studies
- Tungsten vaporizer hypothesis
- My informal take:
 - Parent molecules survive AND there is thermal decomposition.
 - Very difficult to compare the literature quantitatively
 - Different length and size scales
 - Other investigators have tended to emphasize the parent peaks
 - 118 nm VUV does not ionize gas-phase H₂O or CO₂.

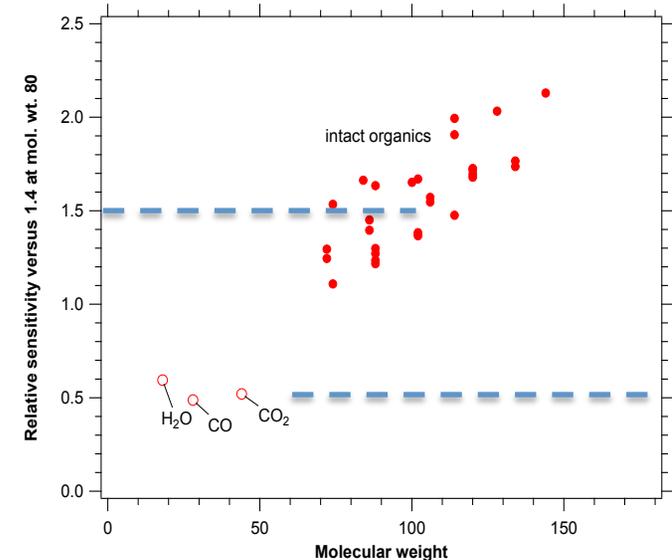
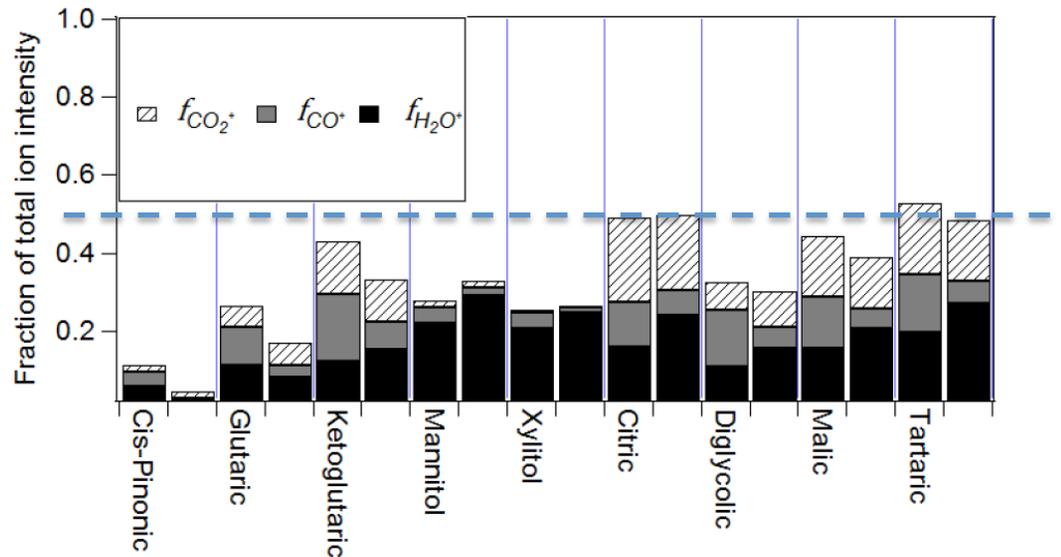
Thermal decomposition and sensitivity



Canagaratna et al., 2015, supplemental

- Work from the hypothesis that most CO_2 , CO , and H_2O are from thermal decomposition.
- What does this imply about overall sensitivity?

Thermal decomposition and sensitivity



- 50% of citric acid ion signal is from H_2O , CO , and CO_2
- For simplicity assume balance is from molecular wt. ~ 100 (e.g. $M-CO_2-H_2O$)
- Given sensitivity, 75% of mass in H_2O , CO , and CO_2 and 25% mass in molecular wt. 100.
- Overall sensitivity: (normalized to 1.4 at molecular wt. 80)
 $75\% \cdot 0.5 + 25\% \cdot 1.5 = 0.75$
- Compare: intact molecular weight 190 would have sensitivity $1.4 \cdot \sqrt{(190/80)} \approx 2.2$
 \Rightarrow thermal decomposition can change sensitivity by $2.2/0.75 \approx$ factor of 3.

Alfarra PhD thesis (Manchester, 2004)

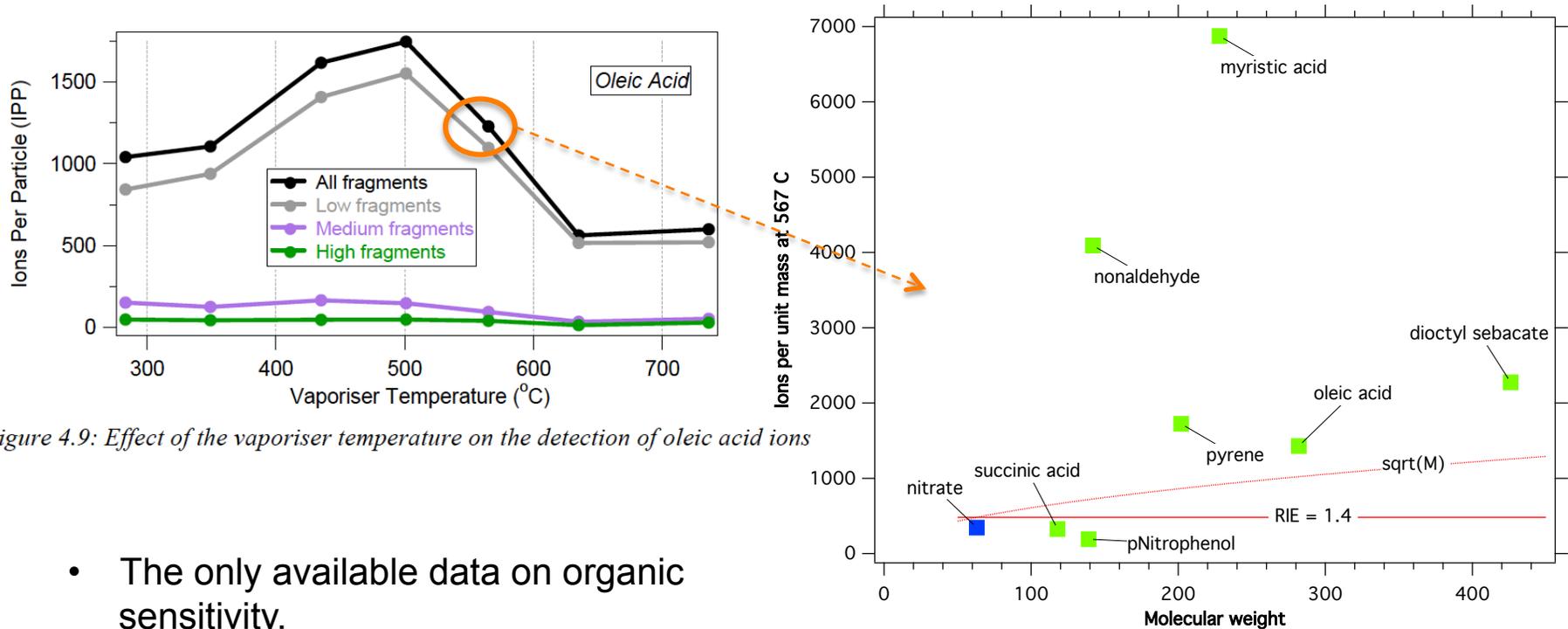


Figure 4.9: Effect of the vaporiser temperature on the detection of oleic acid ions

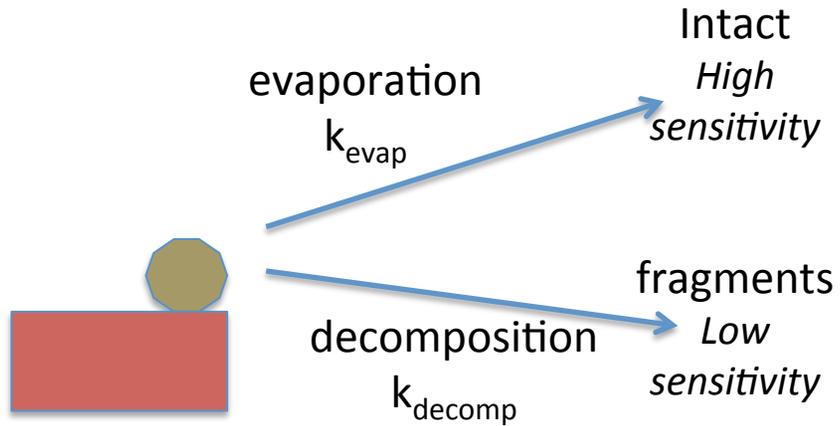
- The only available data on organic sensitivity.
- I credit these data with showing me that the sensitivity is not simple.
- How much of the 500 to 633 C change is bounce and how much is decomposition?

Inorganic compounds

- **Ammonia:**
 - IF both ammonium nitrate and sulfate thermally decompose, then the AMS is measuring gas phase ammonia.
 - => It should have the same (fairly low) sensitivity to ammonia from both.

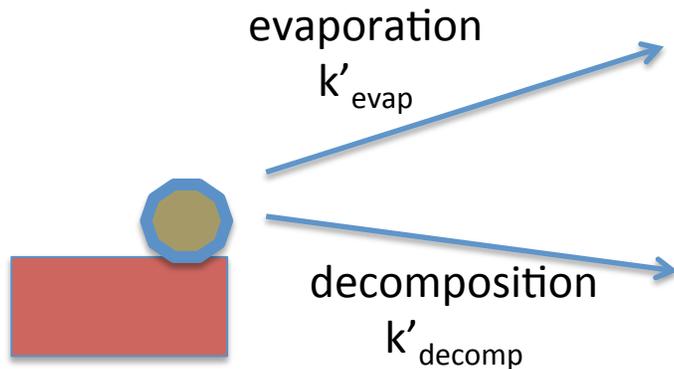
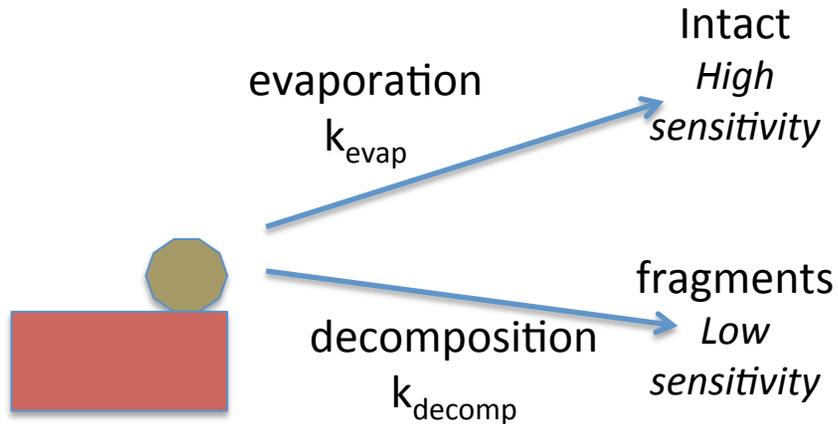
 - IF they both stay together, then there is not only a residence time difference but also a difference in fragmentation patterns.
 - => *Similar but not identical sensitivity to ammonium in nitrate, sulfate, or bisulfate.*
(similar sensitivity because nitrate and sulfate aren't that different)
- **Sulfate:** also expect similar but not identical sensitivity to sulfate in various forms
- **Chloride** may span a wide range from HCl to heavy neutrals like WCl_2 (Drewnick et al.)
- **Pb** will have a fairly large correction factor

Open question: Matrix effects?



- Overall sensitivity depends on the competition between evaporation and decomposition

Open question: Matrix effects?



- Overall sensitivity depends on the competition between evaporation and decomposition

- Could water content change the evaporation rate?
- Would that change the balance between evaporation and decomposition?

e.g. ammonium nitrate?

Miscellaneous technical points

- Temperature dependence as well as mass:
AMS is more sensitive to species that evaporate at lower T.
- The plausible range of absolute temperatures is small compared to the range of mass.
- There may not be time for classic distillation.
- \sqrt{M} residence time does not apply to the air beam because the beam does not have a Maxwell-Boltzmann velocity distribution
(note that some of the air signal is from the beam itself, some from air in the ion source that will have a M-B velocity distribution)
- Residence time and thermal decomposition apply to Q-AMS, C-TOF, HR-TOF: any design with same vaporizer. High-resolution information does not eliminate the residence time issue.
- Free molecular flow residence time does not apply to PTR-MS and other techniques with ion source at higher pressure.

$$n = \frac{\dot{m}}{A} \sqrt{\frac{2\pi}{kTM}}$$

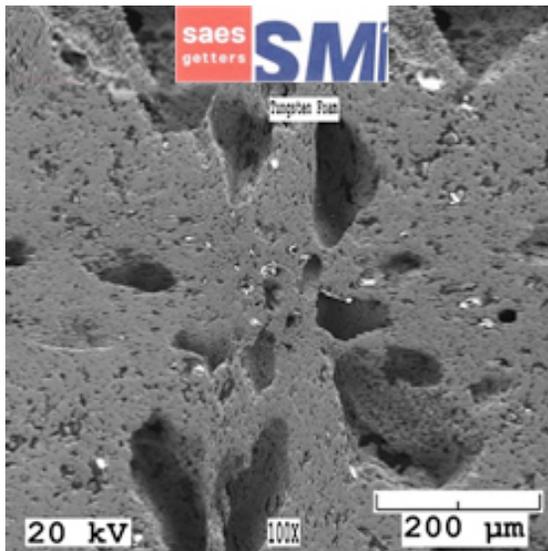
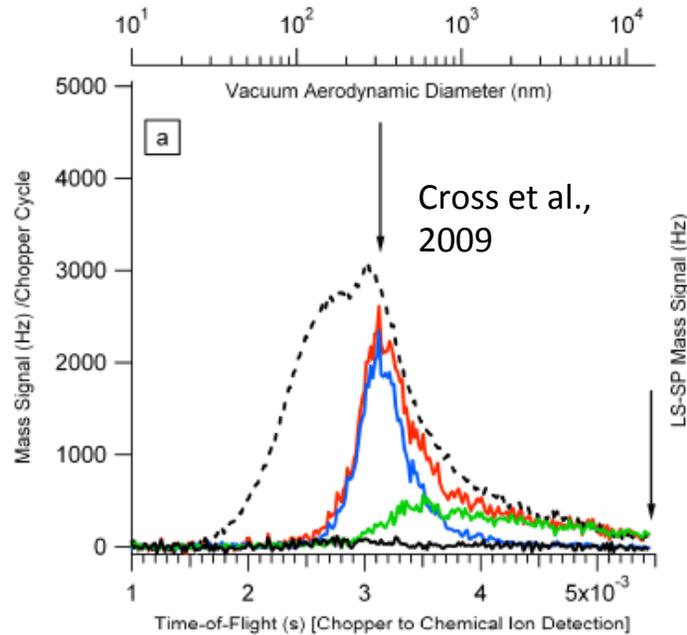
Overall organic sensitivity

- Both overestimates and underestimates of sensitivity are likely.
- Very likely some cancellation.
- Consistent factors of 2 or more would spoil some internal consistency.
 - scattering closure
 - hygroscopic growth
 - ...
- Overall, this changes the paradigm from
(Total organic signal) = (Sum organic peaks) to
Total organic signal must consider composition

Implications for some specific signals

- It seems very probable that POA and SOA have different sensitivities, but I don't even know the direction for sure.
(e.g. does motor oil thermally decompose more or less than SOA?)
- I'm concerned that some laboratory kinetic studies may be more affected than ambient data.
Was a given increase in organic signal because there was more mass or because the molecules became bigger or more thermally stable?
- Are highly oxygenated molecules more apt to thermally decompose?
- What about more hygroscopic molecules?

More outstanding questions



1. Do delayed particles have the same thermal fragmentation as prompt particles?
In general, are there multiple volatilization temperatures?
2. Do particles in a valley in the vaporizer decompose the same as those on a hill?
3. When organics thermally decompose, is any mass left behind as char?
4. There is competition between evaporation and decomposition. Is there any dependence on particle size?
5. Has thermal decomposition been at times confounded with bounce?
6. Are there implications for factor analysis?
7. Any “Aha” moments with your data?

Summary

- The sensitivity of the AMS depends on the molecular weight of the gas-phase species being ionized.
- Thermal decomposition becomes very important: small fragments (formed prior to electron impact) can have a factor of 4 lower sensitivity than large, intact molecules.
Comparable to bounce
- Thermal decomposition opens up the possibility of some very complex behavior.
- Thermal decomposition isn't intuitive to me.
apparently NH_4NO_3 mostly stays together but citric acid almost totally falls apart
- A paradigm change for quantitation: molecular form needs to be considered.

Some ways forward:

- Calibrations
There are no peer-reviewed papers on AMS organic sensitivity.
- Need light scattering or other method to separate sensitivity and bounce
- Vaporizer temperature changes may be informative.
- Rick Flagan suggested organics chosen to parse vaporizer effects.
- Measure particle pulse lengths-> upper bound on residence time.
- Is $m/z=44$ a marker for low organic sensitivity?

With this information, when do details matter most?

More eyes can sometimes help – I'm happy to help