COMBUSTION RESEARCH FACILITY

SAND2014-20361C

The Thermal Decomposition Chemistry of CL-20

J. D. Steill and J. J. Kay

Sandia National Laboratories, Livermore, CA

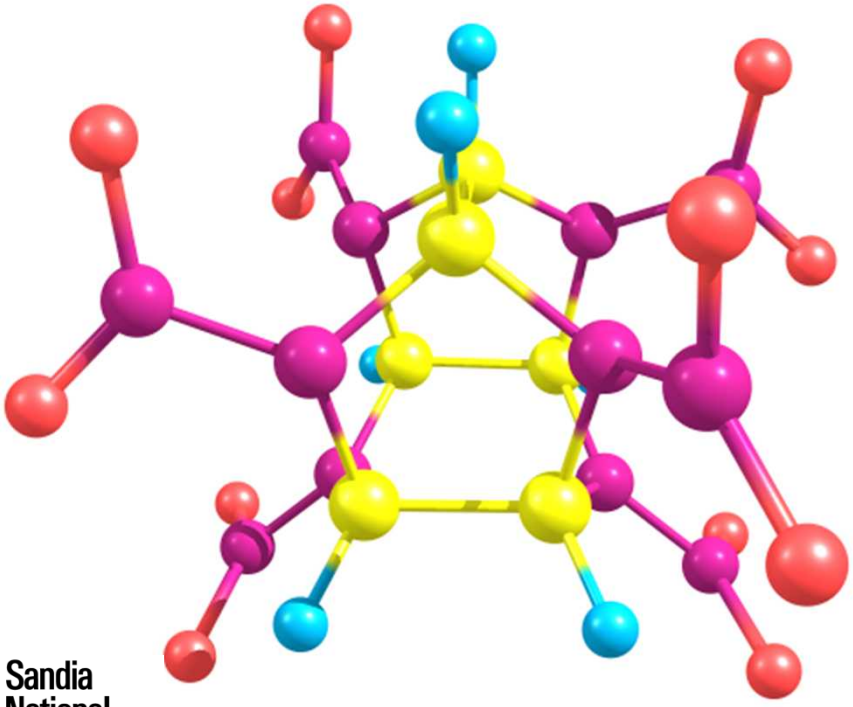
JANNAF Albuquerque, NM

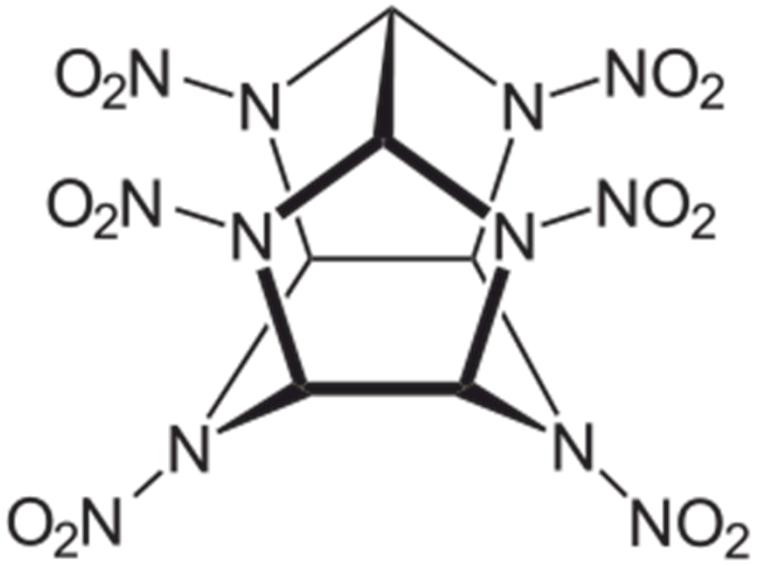
Dec. 9th, 2014

Sandia National Laboratories

CL-20 is a “relatively” new energetic material

- $C_6H_6N_{12}O_{12}$ synthesized at China Lake, CA in 80’s.
- High **O**,**N** and low **C** balance
- Relatively insensitive





- Caged structure leads to steric strain than increases energy
- Crystalline forms have very high density
- Overall *very high energy density*

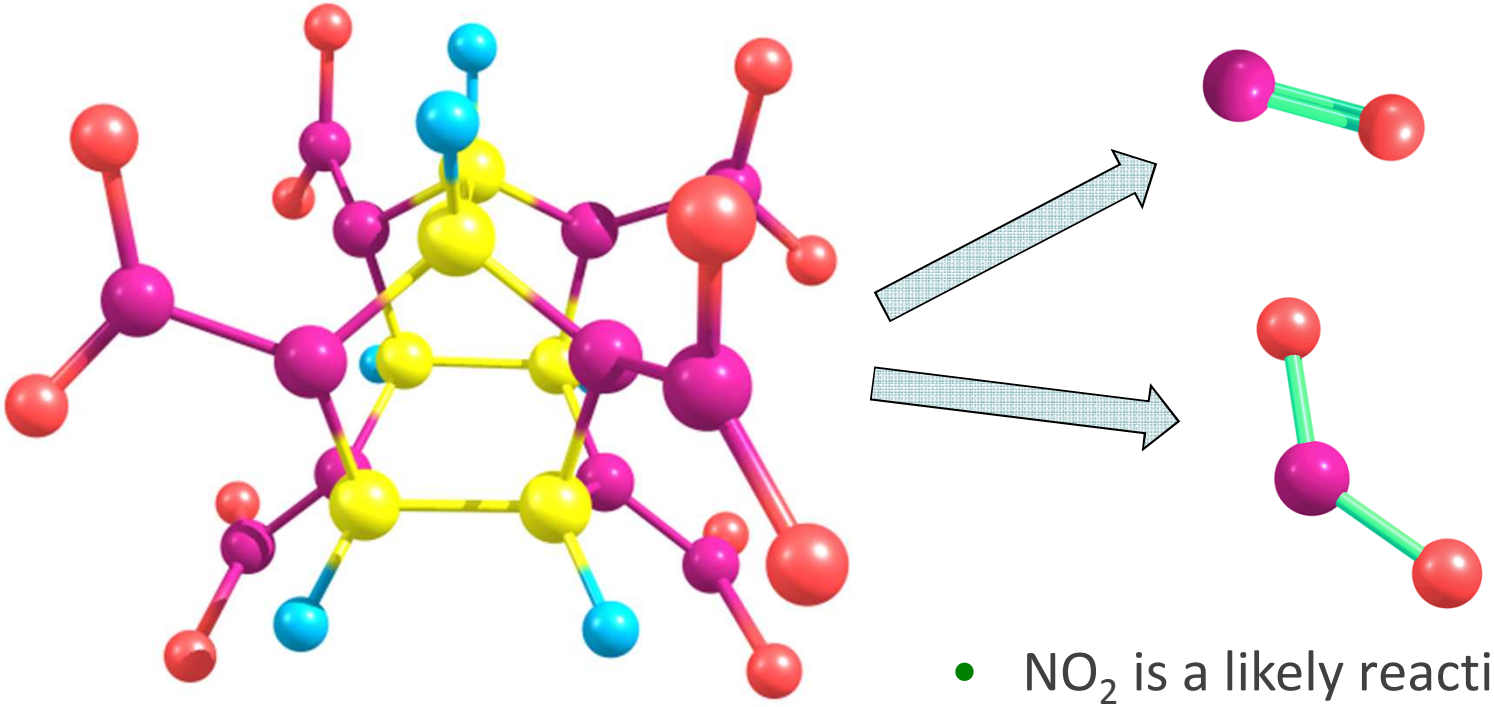
Sandia National Laboratories

We need to understand the decomposition chemistry of energetic materials

- *Pragmatically*, this is a crucial consideration for safety of use.
  - Decomposition chemistry determines the potential for violence from thermal stress
  - Thermal studies provide insight into chemical processes active (at a slower pace) in materials aging

- *Fundamentally*, it is essential science.
  - The chemical reactions that constitute the thermal breakdown of the material are very different from deflagration and detonation processes - *but we don't understand how*.
  - The observed decomposition chemistry is more complex than just unimolecular or bimolecular dissociation processes – we must meet the challenge posed by complex multi-scale systems.

What is the decomposition chemistry of CL-20?

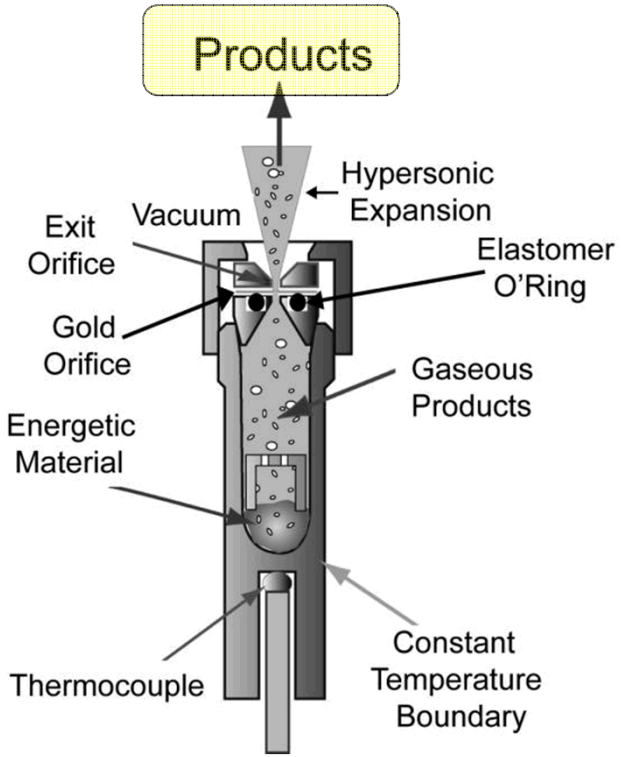


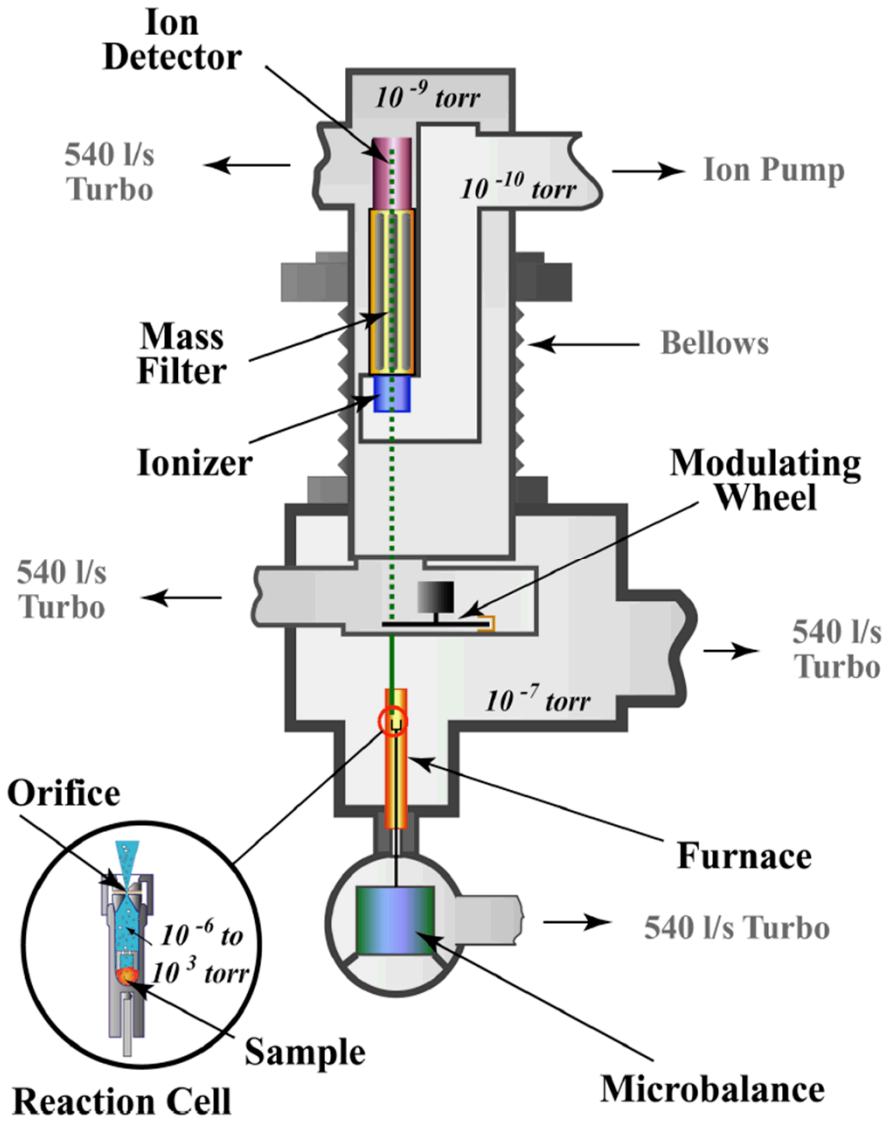
- Is NO loss a part of the initial decomposition steps of CL-20?
- NO_2 is a likely reaction product and may interact with system
  - Is NO_2 loss a part of the initial decomposition steps of CL-20?

Sandia National Laboratories

Experimental analysis of the thermal decomposition of energetic materials reveals the active chemistry

- Our approach is to identify the chemical species evolved from a sample while we control it's temperature.



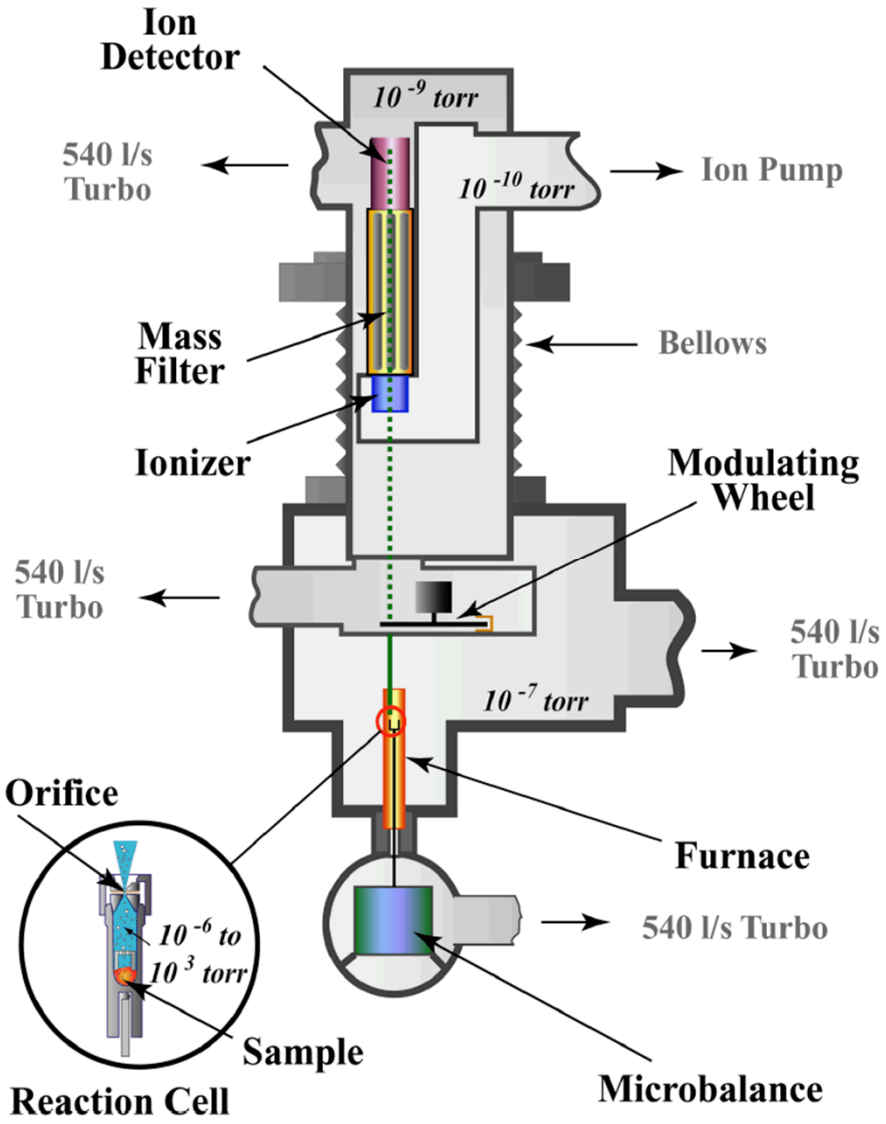


Sandia National Laboratories

Experimental analysis of the thermal decomposition of energetic materials reveals the active chemistry

- We measure the weight loss of the heated sample and thus can quantify the vapor pressure and relative chemical reaction yields.

Simultaneous Thermogravimetric and Modulated Molecular Beam Mass Spectrometry (STMBMS)



Sandia National Laboratories

CL-20 Thermal Decomposition: STMBMS Experiments

- Will describe the results of six experiments total, three “ramps” and three “isotherms”.

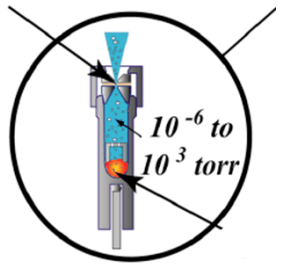
Description	Index	Notes
isotherm @ 175 °C	008	slow decomposition
isotherm @ 185 °C	004	slow decomposition
isotherm @ 195 °C	013	fast decomposition
ramp to 240 °C	001	very fast decomposition
ramp to 400 °C	012	very fast decomposition
ramp to 500 °C	011	very fast decomposition

- **Isotherms** produce varying results based upon the temperature of the sample. Relative cool isotherm experiments show very slow decomposition. Hotter isotherms can result in rapid decomposition.
- Temperature **ramps** often result in a quicker reaction once a particular temperature threshold is reached.

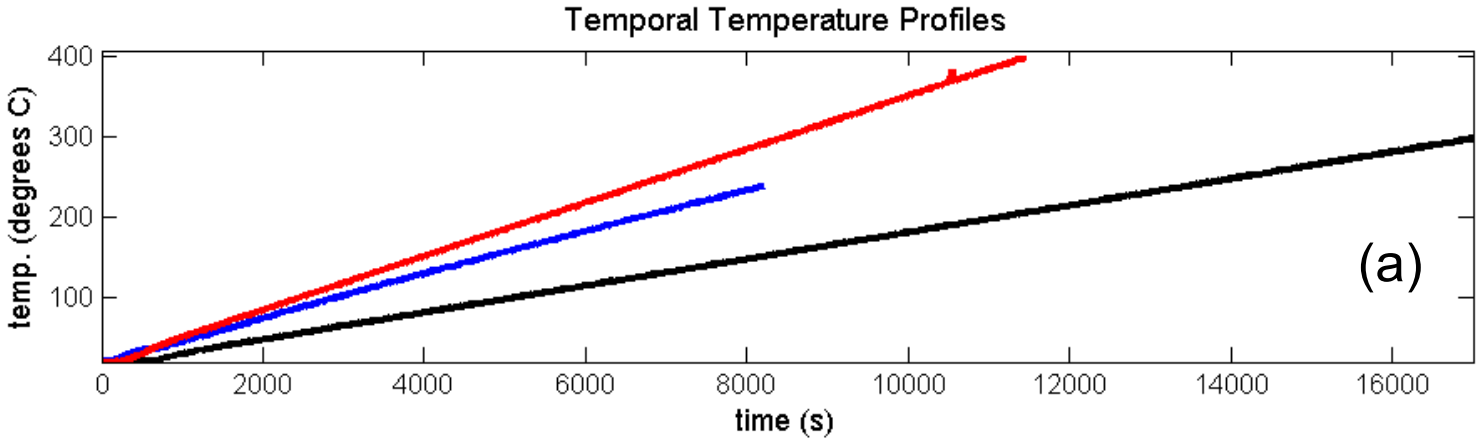
Sandia National Laboratories

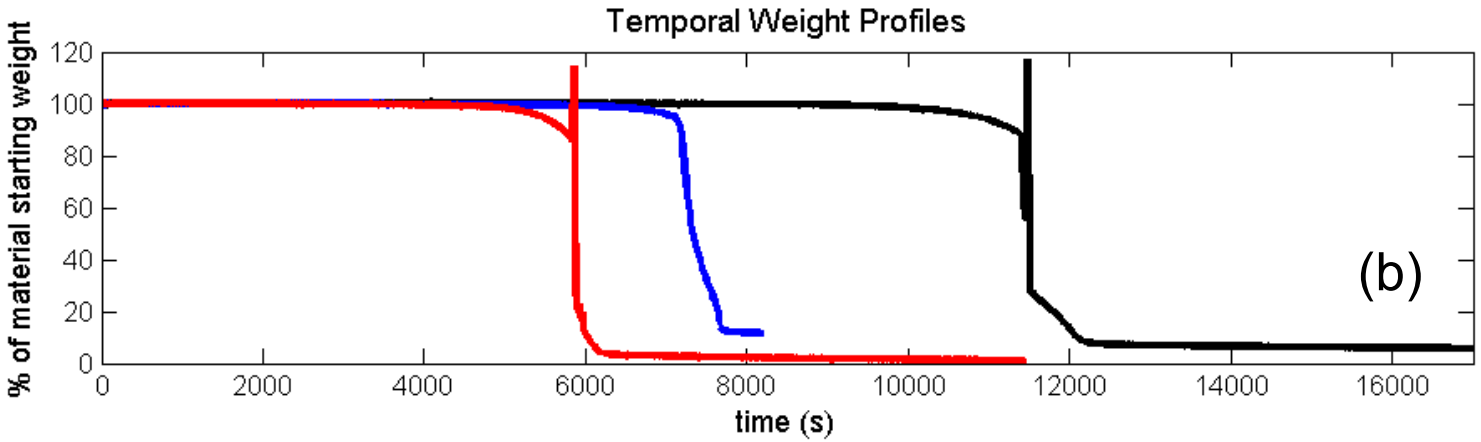
CL-20:

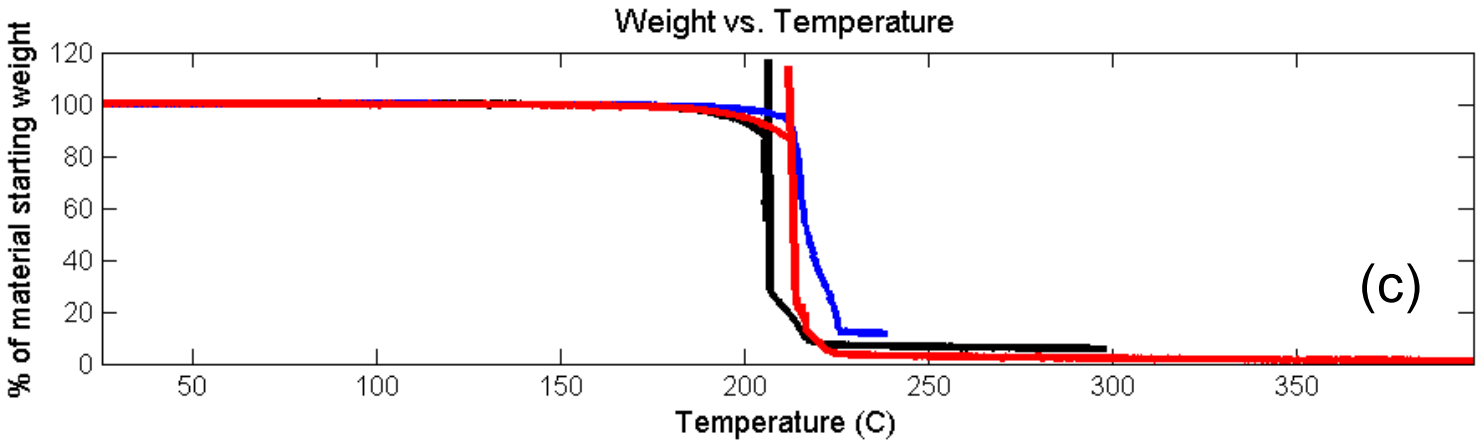
mass loss from heating ramps



Reaction Cell

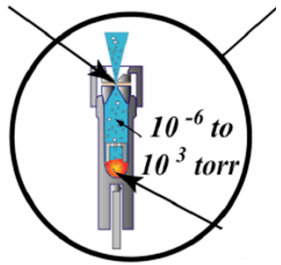




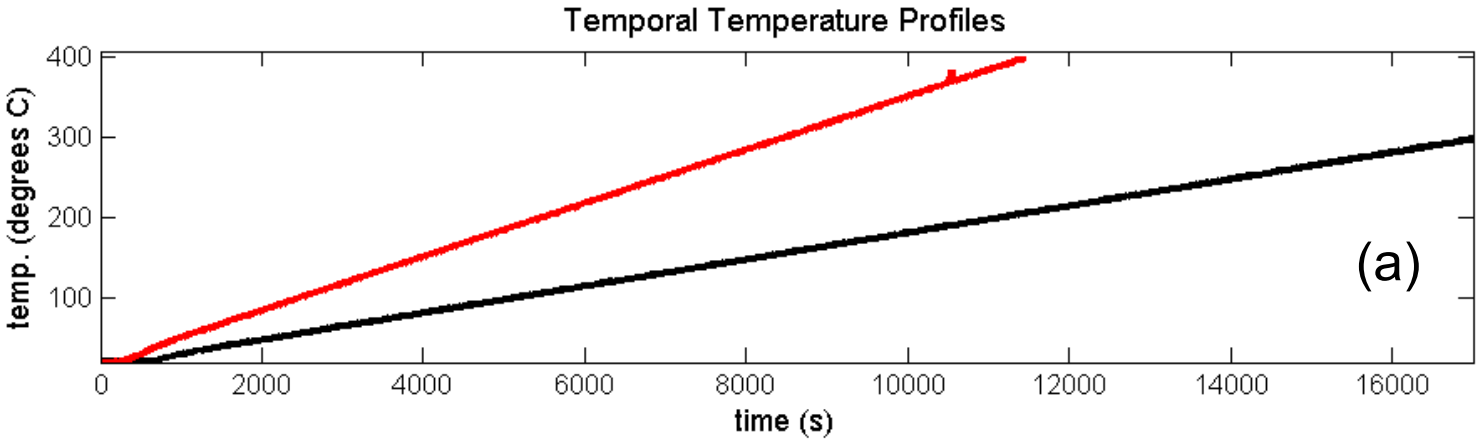


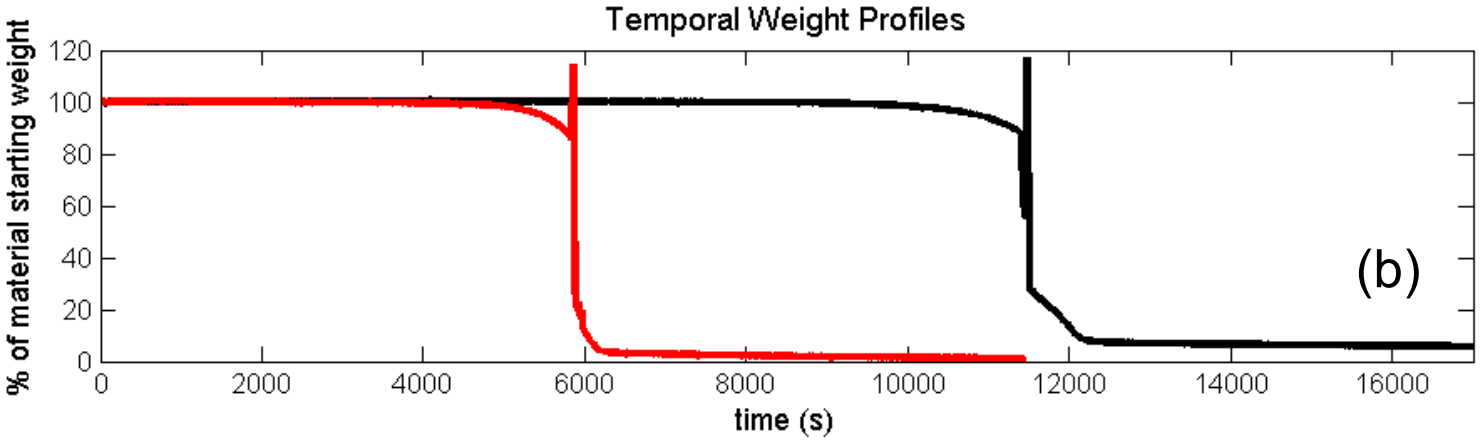
CL-20:

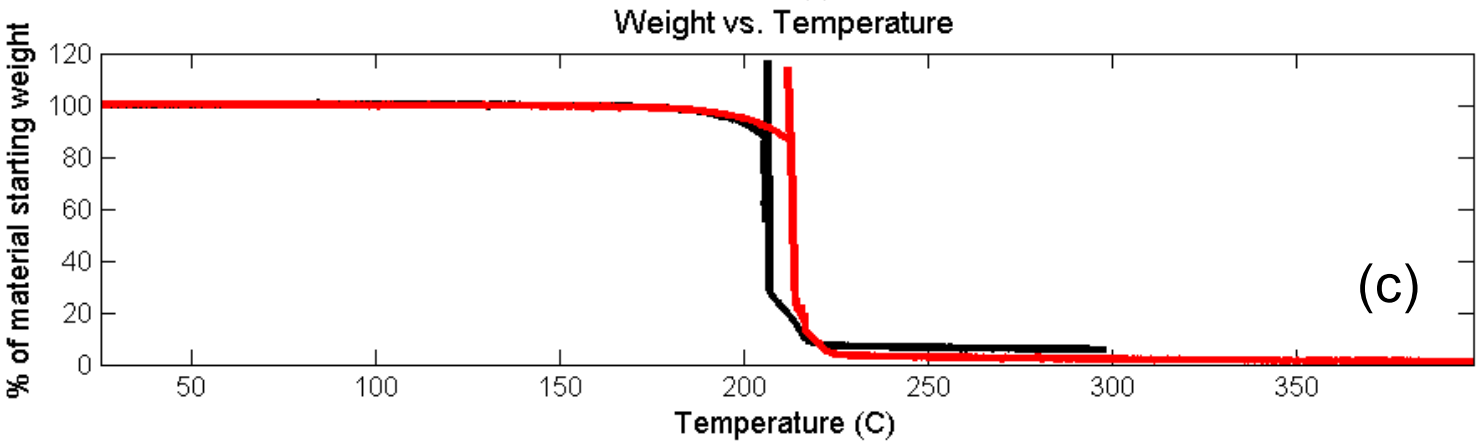
mass loss from heating ramps



Reaction Cell

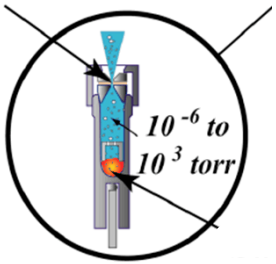




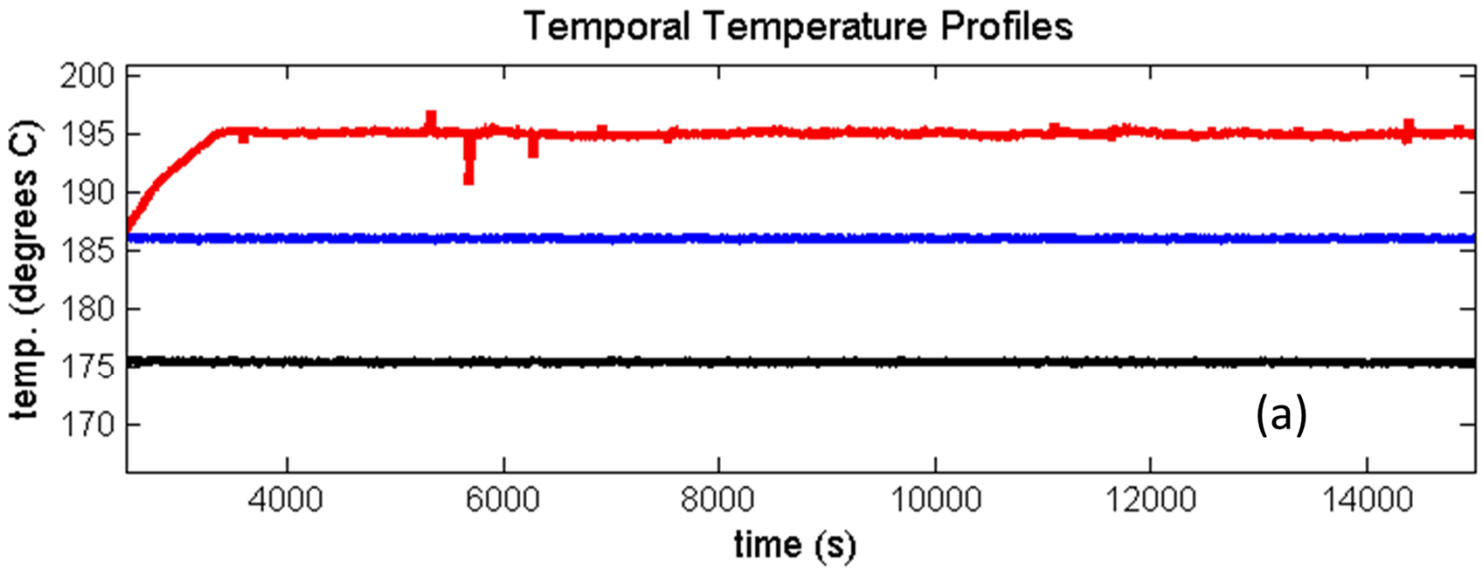


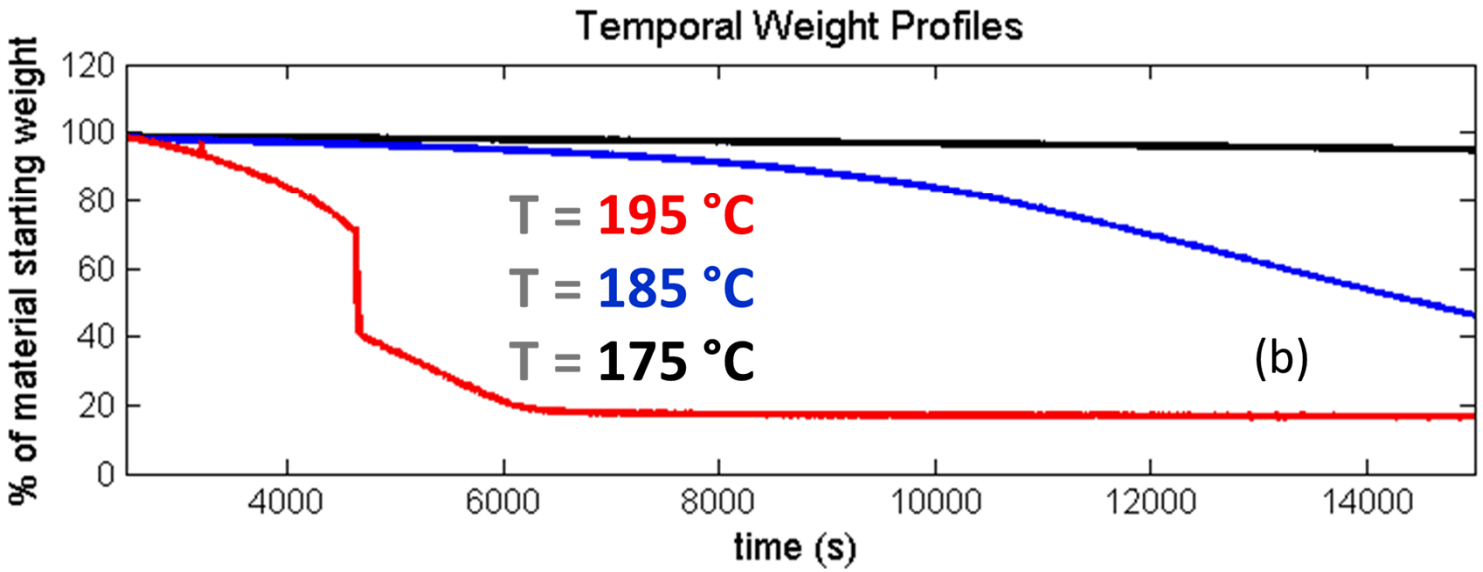
CL-20:

mass loss from heating isotherms

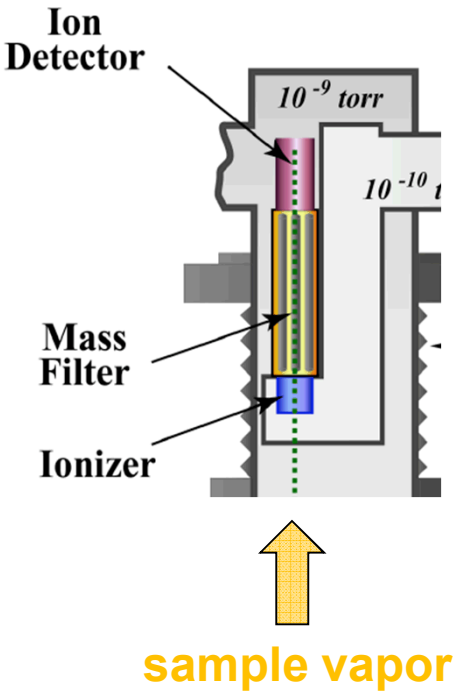


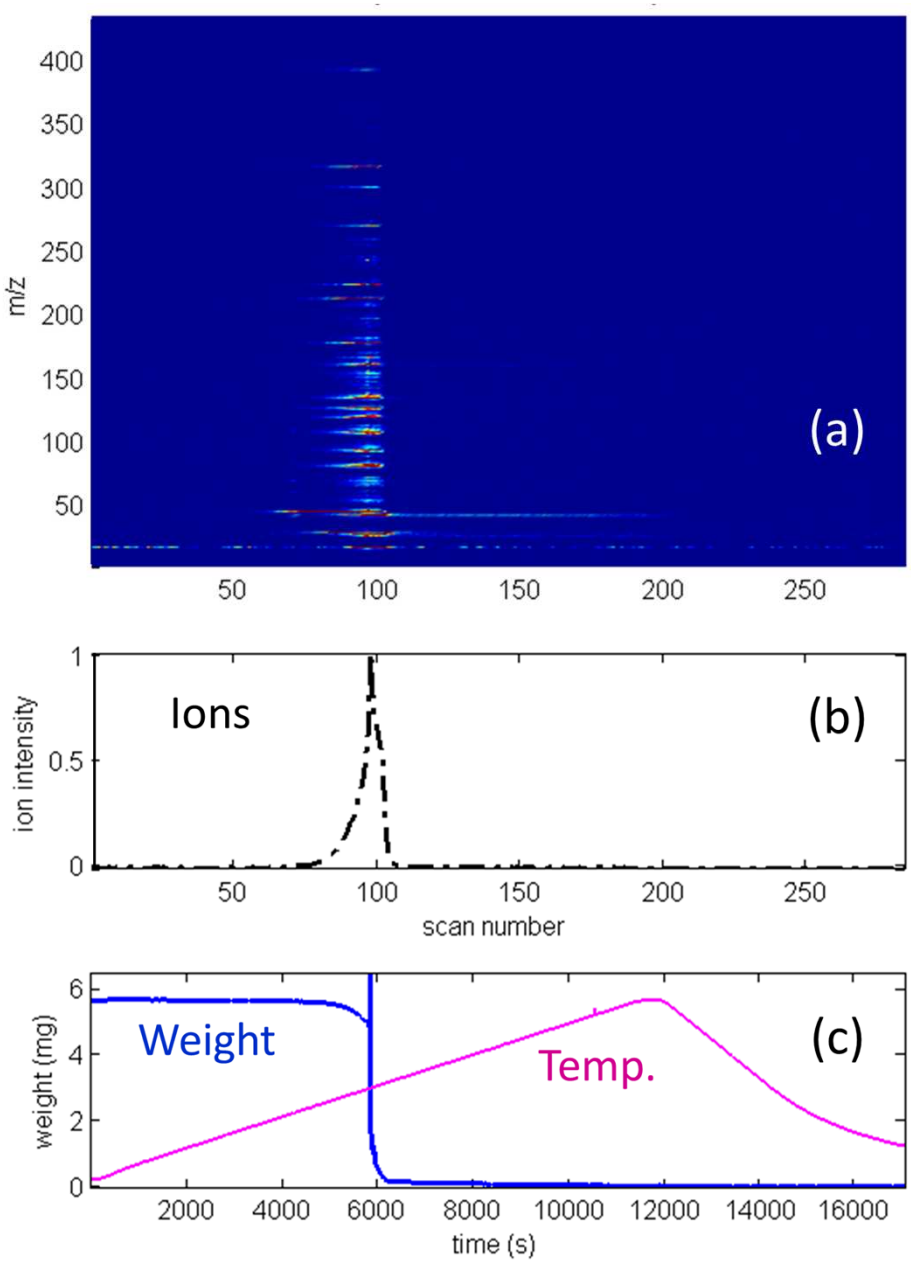
Reaction Cell





CL-20 Thermal Decomposition: STMBMS Experiment



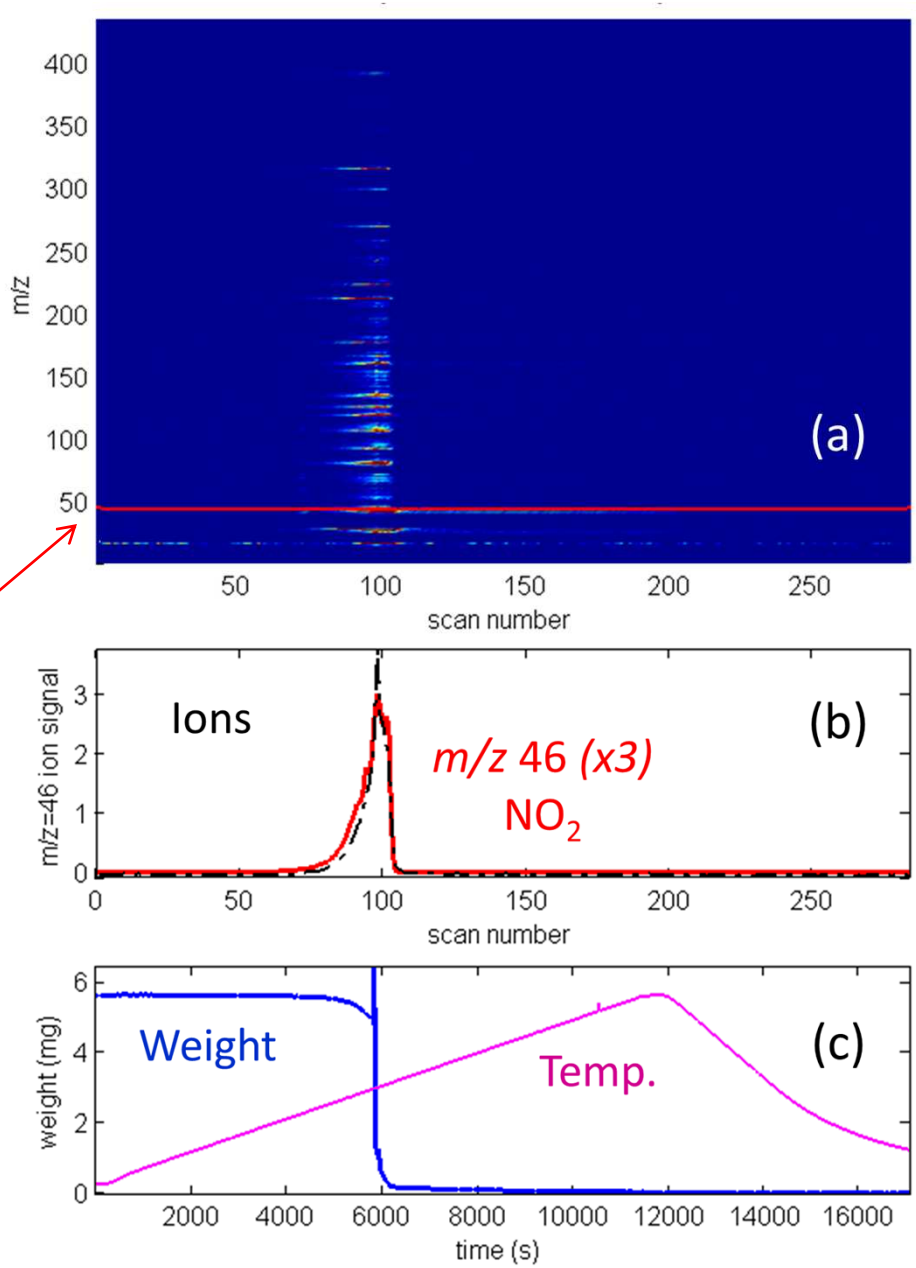


Mass spectra of sample

total ions from sample

weight loss from sample

CL-20 Thermal Decomposition: STMBMS Experiment



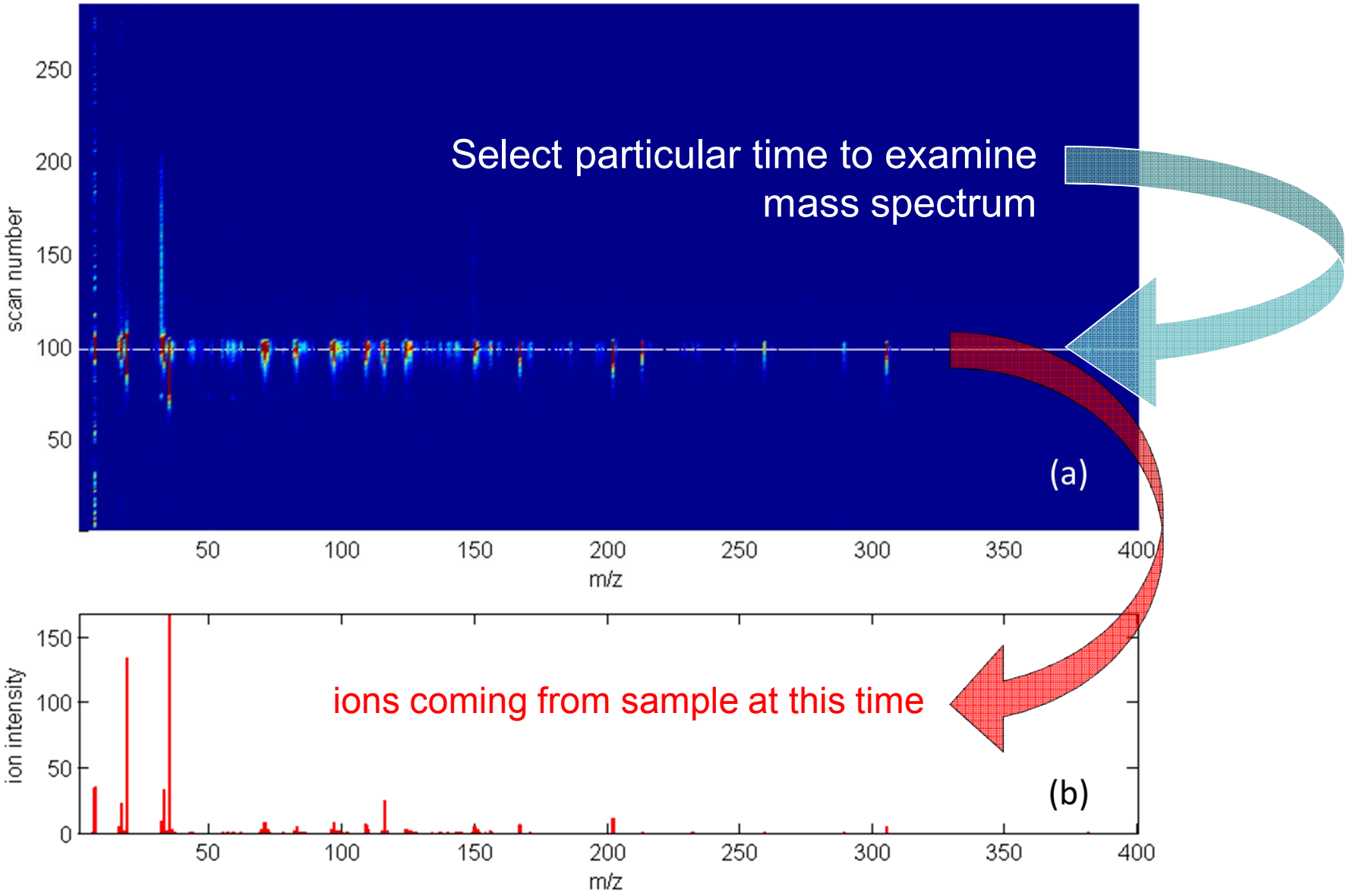
Select a particular m/z from mass spectrum, *e.g.* *m/z*=46 is NO_2.

Mass spectra of sample

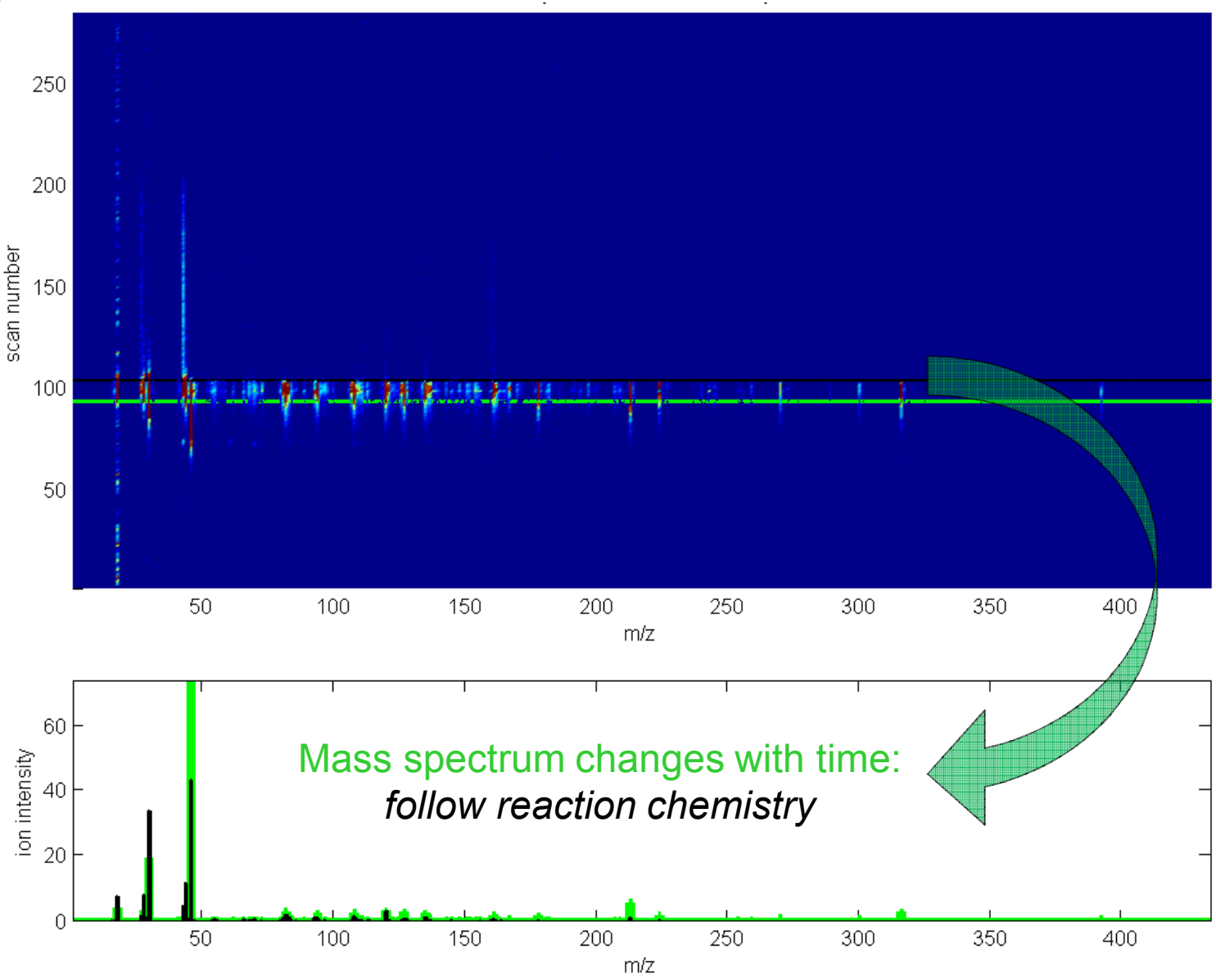
total ions from sample

weight loss from sample

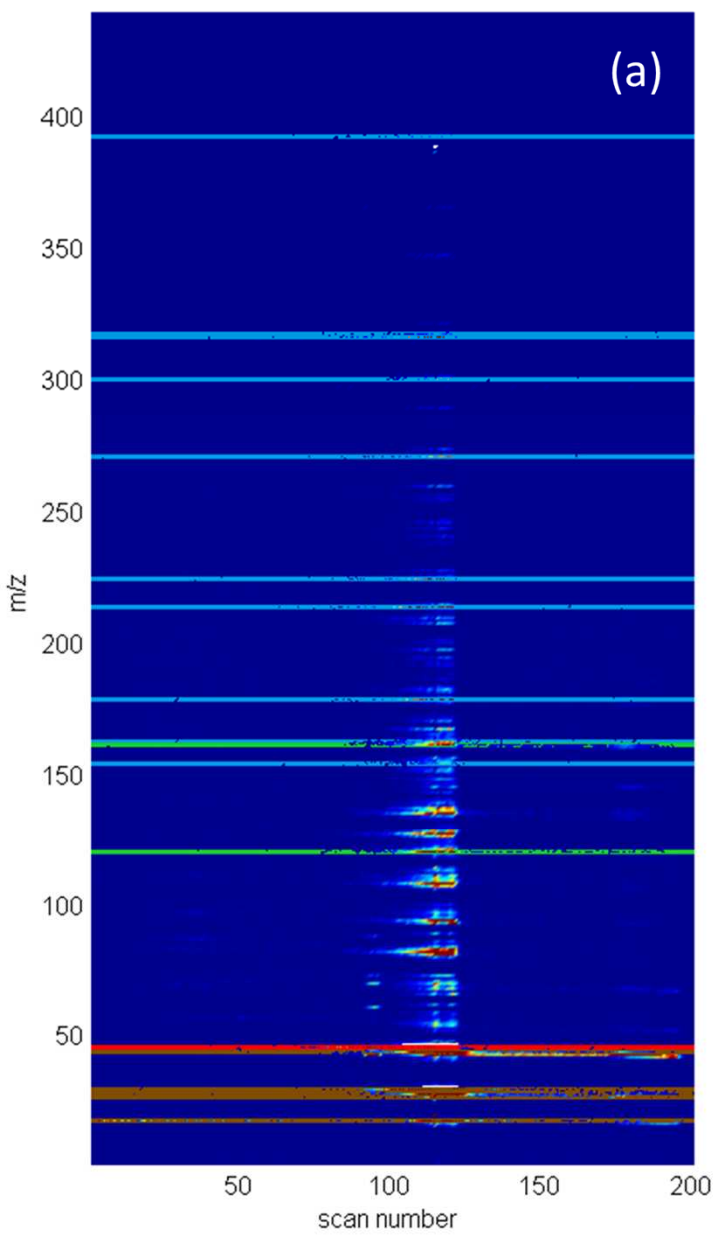
CL-20 Thermal Decomposition: STMBMS Data

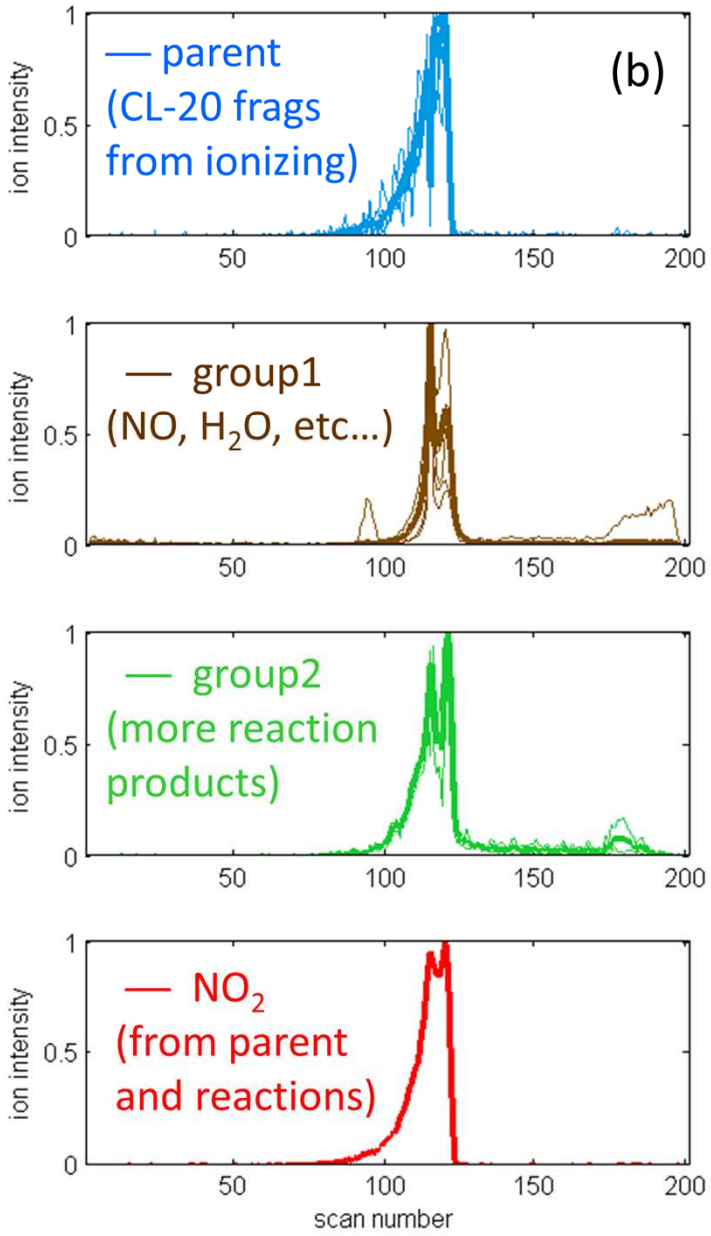


CL-20 Thermal Decomposition: STMBMS Data



CL-20 Thermal Decomposition: Chemical Reaction Groups





CL-20 Thermal Decomposition: Chemical Reaction Groups

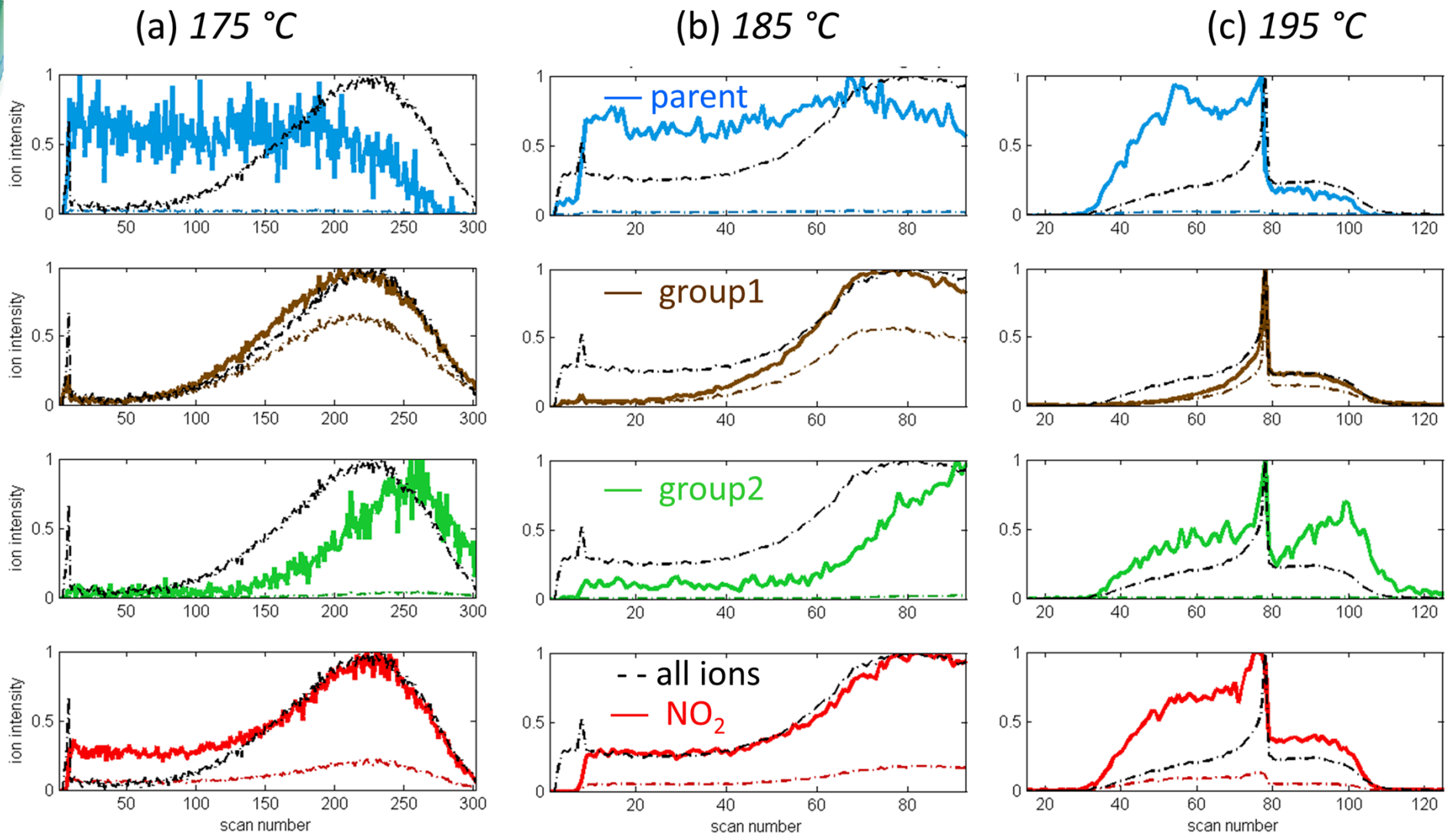
- **parent**: the CL-20 molecule fragments when it ionizes, producing a variety of ions, including *m/z* 46

parent	group1	group 2	NO_2
392	18	161	46
316	27	120	
300	28		
270	30		
224	44		
213	45		
178			
162			
154			
46			

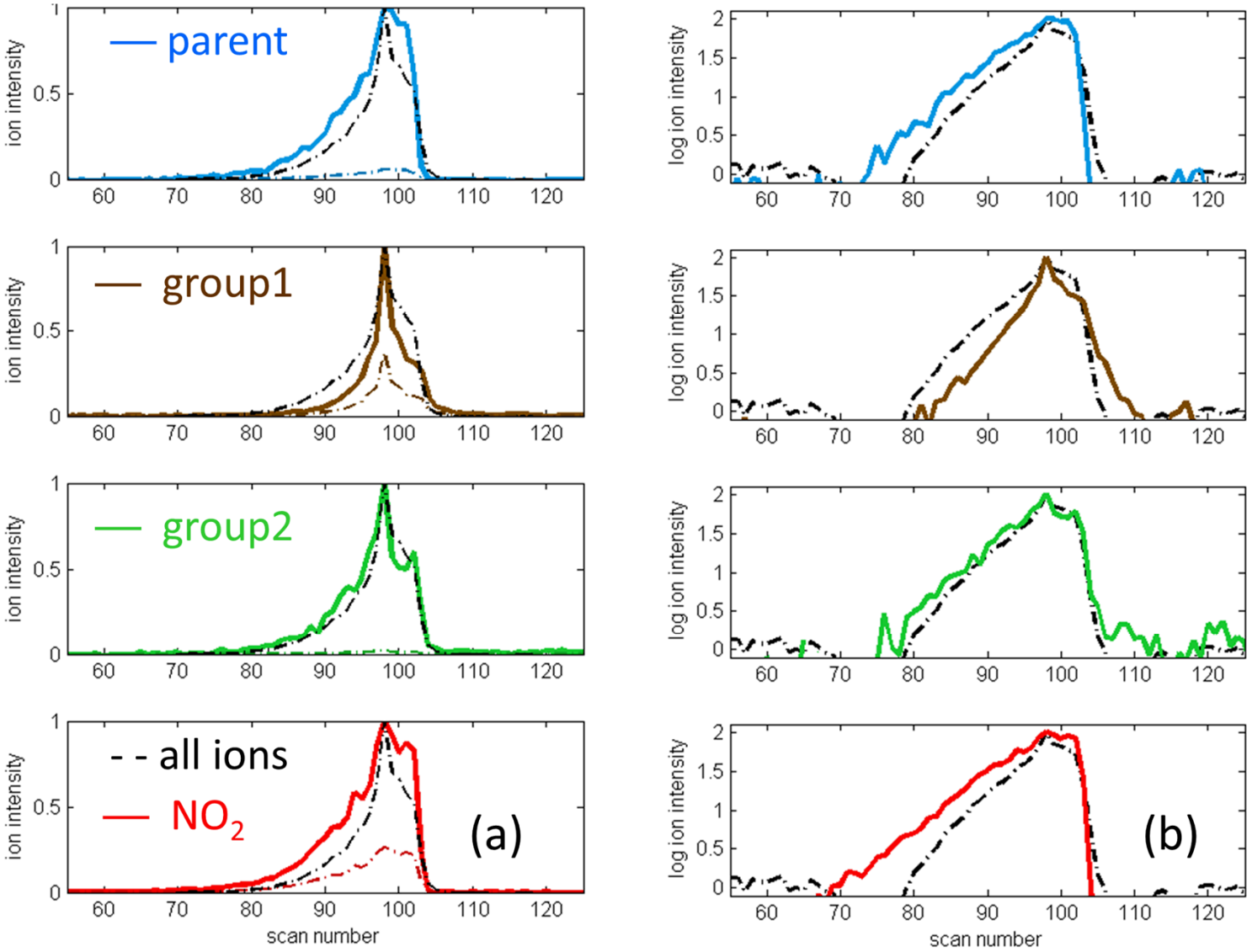
- **group1**: H_2O, NO, CO, etc…
- **NO_2** (*m/z* 46) is also a reaction product.

Sandia National Laboratories

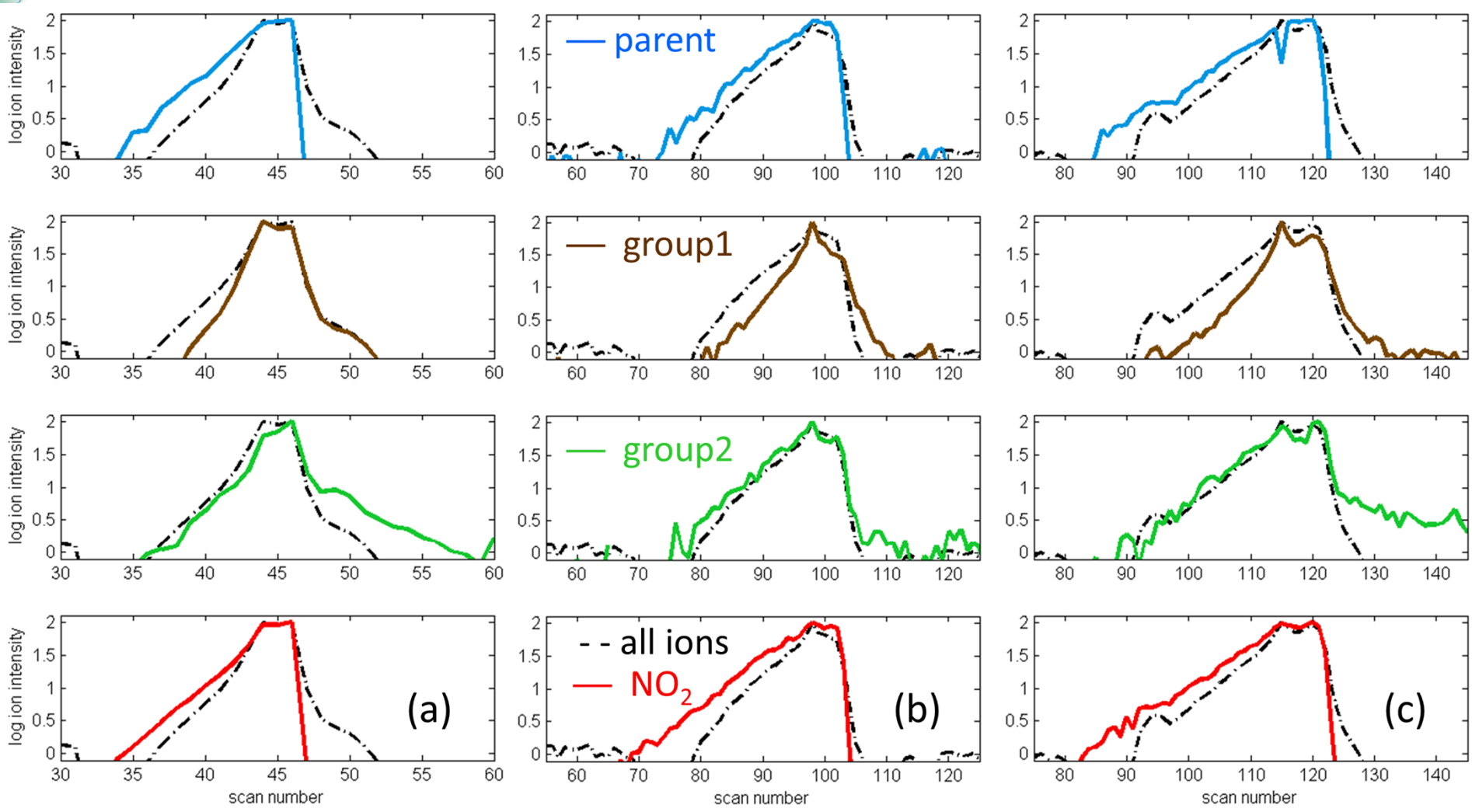
CL-20 Isotherms: Chemical Reaction Groups



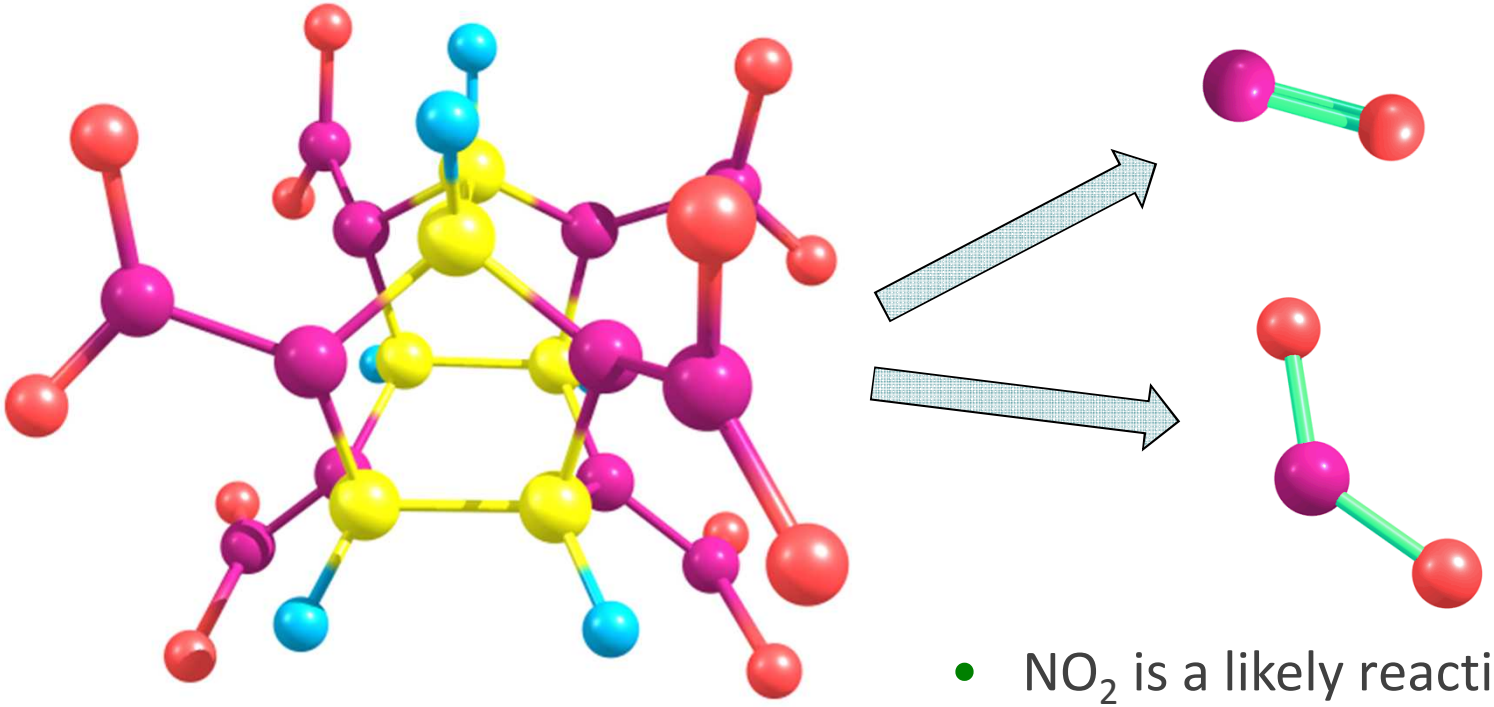
CL-20 Ramps: Chemical Reaction Group Log Plot



CL-20 Ramps: Chemical Reaction Groups



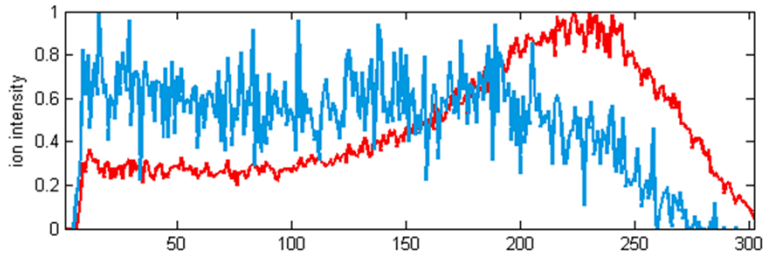
What is the decomposition chemistry of CL-20?

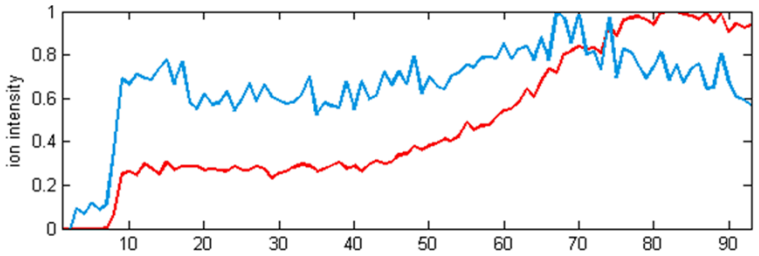


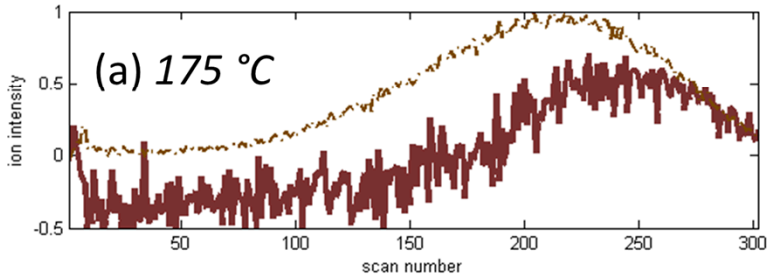
- Is NO loss a part of the initial decomposition steps of CL-20?
- NO_2 is a likely reaction product and may interact with system
  - Is NO_2 loss a part of the initial decomposition steps of CL-20?

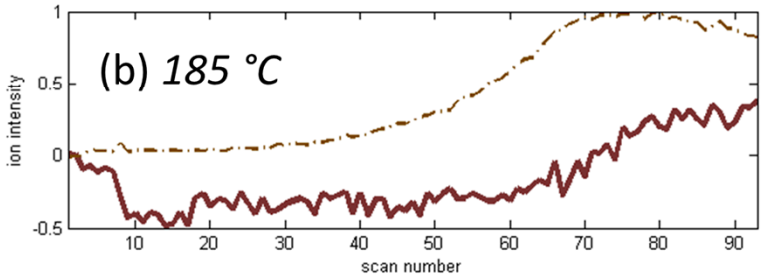
Sandia National Laboratories

CL-20 Isotherms: Is NO_2 a Reaction Product?







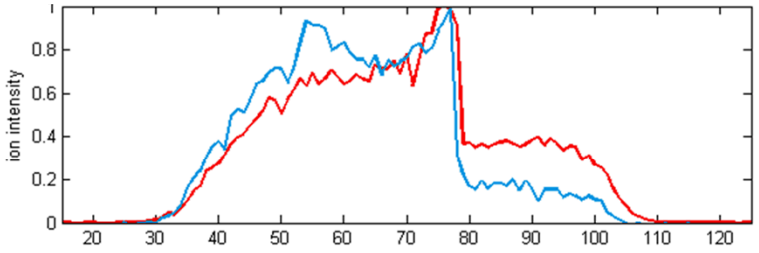


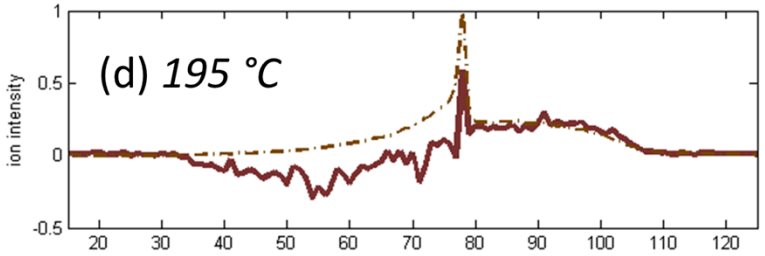
— parent frags

— NO_2

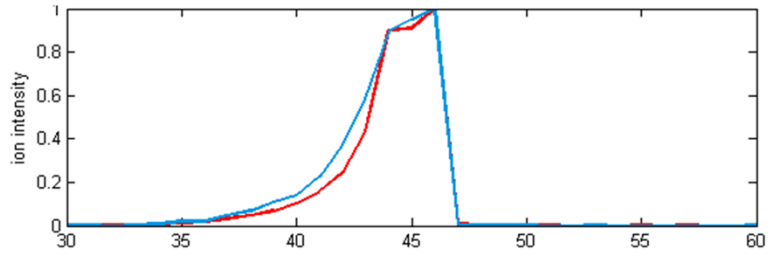
— **diff. (NO_2 – parent)**

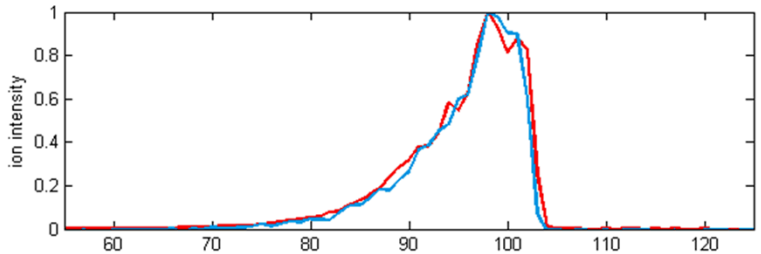
- - rxn. products (NO, H_2O, CO_2, etc…)

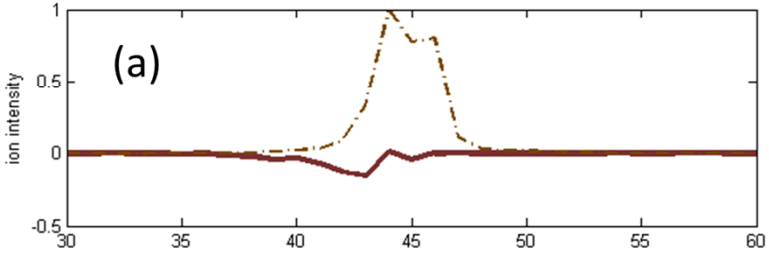


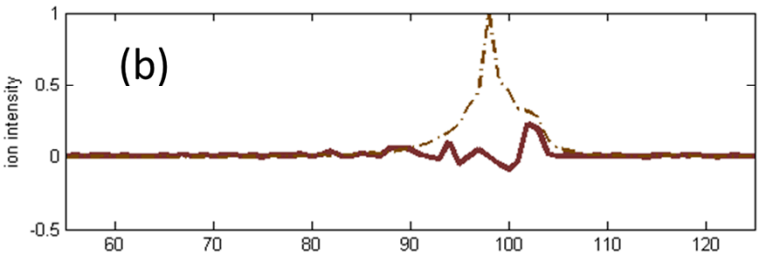


CL-20 Thermal Ramps: Is NO_2 a Reaction Product?







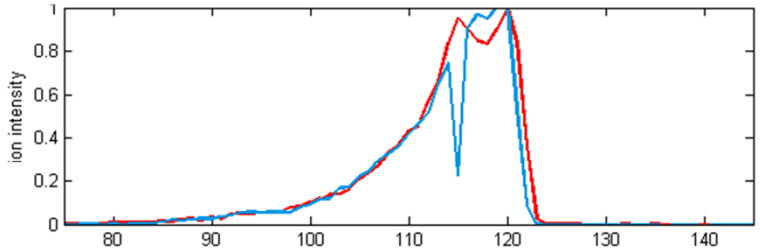


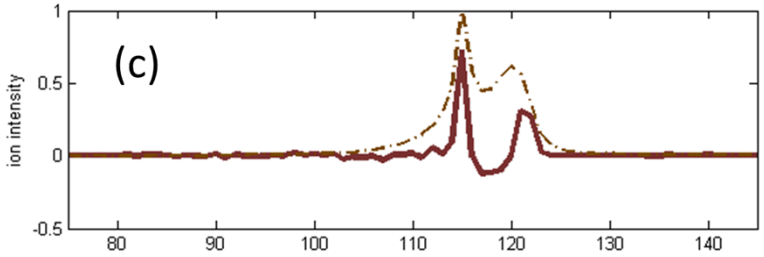
— parent frags

— NO_2

— **diff. (NO_2 – parent)**

- - rxn. products (NO, H_2O, CO_2, etc…)





Conclusions

- CL-20 shows a very rapid decomposition at temperatures above 190 degrees Celsius.
- The primary initial gaseous decomposition products observed are small molecules such as NO, H_2O, and CO_2.
- NO_2 is produced directly from CL-20 ionization, so accounting for this is required to address source of observed NO_2
- Analysis suggests that NO_2 is indeed directly evolved from sample but probably further reacts.

Acknowledgements

- Thank you for your attention
- Funding from DoD/DOE JMP
- Sandia colleagues: Richard Behrens, Deneille Wiese-Smith

Sandia National Laboratories