Quantification of multifunctional molecules in chamber and ambient air using GC-CIMS

John Crounse
Caltech

ACM 2018

Gas-phase RO_2 chemistry

oxidant + VOC $\xrightarrow{O_2}$ RO_2

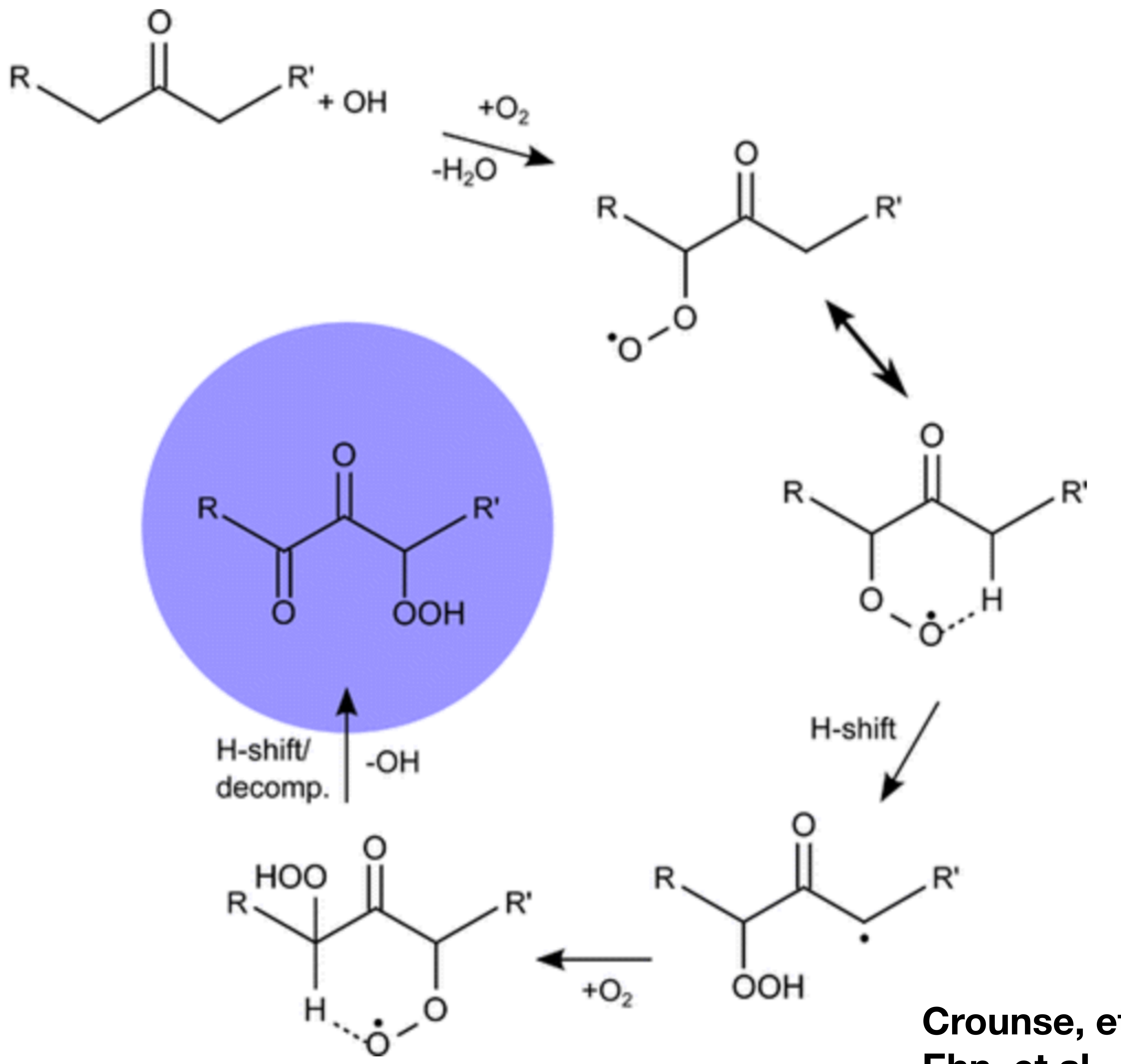
(OH, NO_3, O_3, Cl)

$\xrightarrow{NO}$ $RO^{\bullet}$ (alkoxy) + NO_2 $RONO_2$

$\xrightarrow{HO_2}$ $ROOH + O_2$ $R(O) + OH + HO_2$

$\xrightarrow{RO_2}$ $2RO^{\bullet}$ (alkoxy) + O_2 $ROH + R(O) + O_2$ ROOR

Autoxidation



Crounse, et al., *J Phys Chem Lett,* 2013
Ehn, et al., *Nature*, 2014

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$$RO_2 \xrightarrow{NO} RO^{\bullet}\ (\text{alkoxy}) + NO_2 \qquad RONO_2$$

$$RO_2 \xrightarrow{HO_2} ROOH + O_2 \qquad R(O) + OH + HO_2$$

$$RO_2 \xrightarrow{RO_2} 2RO^{\bullet}\ (\text{alkoxy}) + O_2 \qquad ROH + R(O) + O_2 \qquad ROOR$$

$$RO_2 \xrightarrow[+O_2]{\text{Isom}} HOORO_2 \quad (\text{autoxidation})$$

Gas-phase RO_2 chemistry

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$\xrightarrow{k_{NO}[NO]}$ $RO^{\bullet}$ (alkoxy) + NO_2 $RONO_2$

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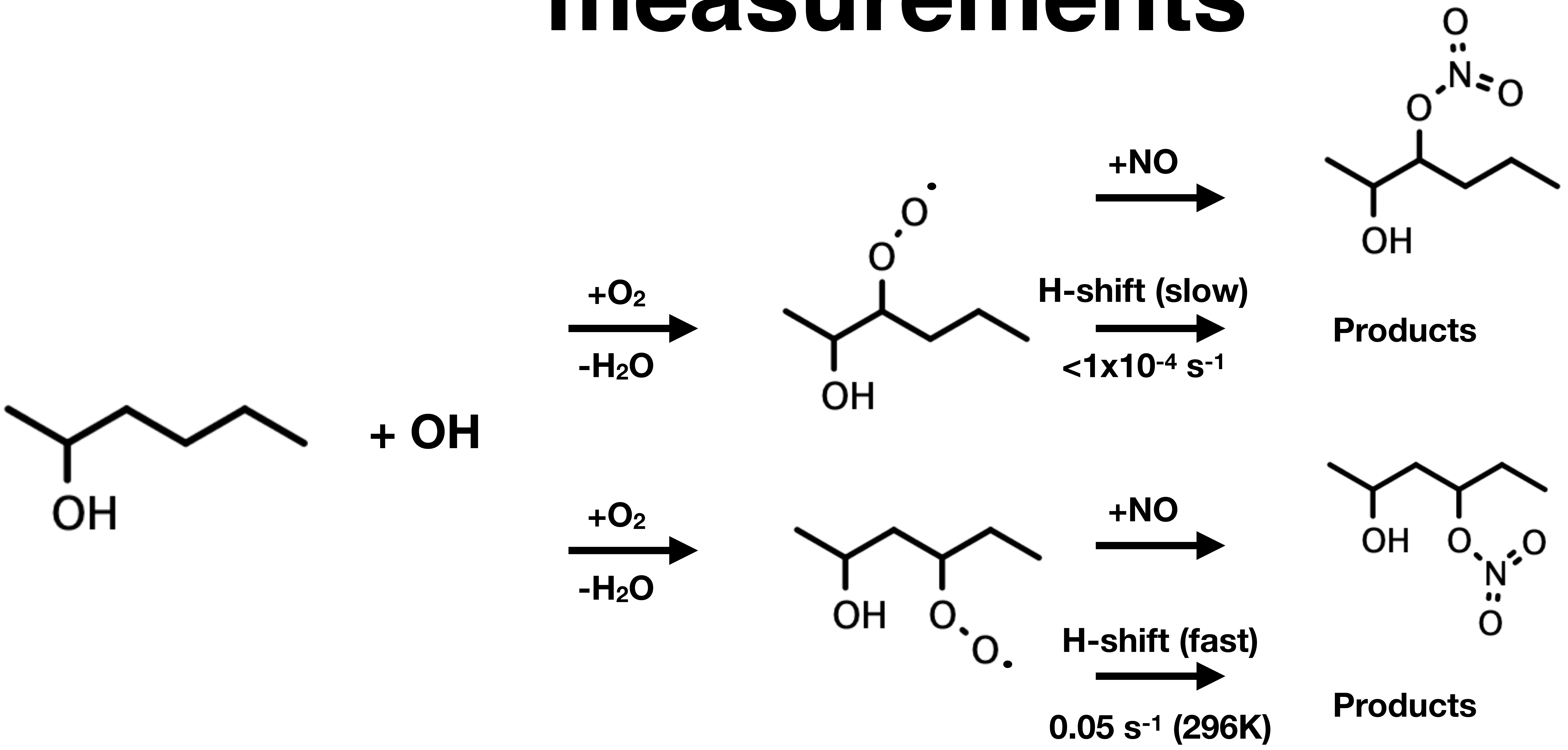
$\xrightarrow{k_{RO2}[RO_2]}$ $2RO^{\bullet}$ (alkoxy) + O_2 $ROH + R(O) + O_2$ ROOR

$\xrightarrow[+O_2]{k_{isom}}$ $HOORO_2$ (autoxidation)

The need for isomer resolved measurements



Praske, et al., PNAS, 2018

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$\xrightarrow[+O_2]{k_{isom}}$ $HOORO_2$ (autoxidation)

Isomer-resolved measurements are needed to understand the chemistry of RO_2+RO_2 and autoxidation reaction channels.

Gas-phase RO_2 chemistry

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$RO_2 \xrightarrow[+O_2]{k_{isom}}$ $HOORO_2$ (autoxidation)

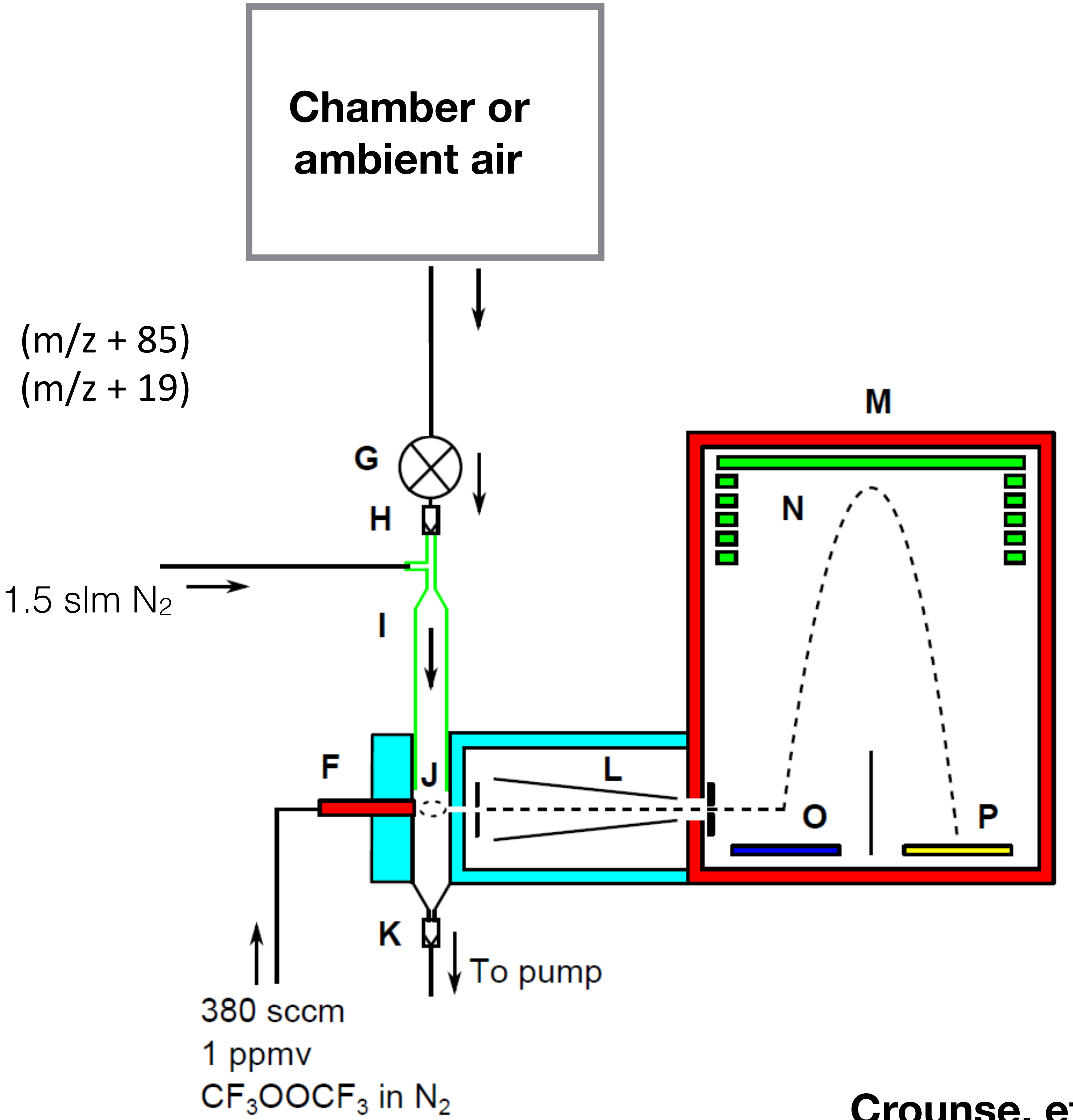
Approach: Use isomer specific observations of the stable closed-shell products [$RONO_2$, ROOH, ROH, R(O)] to make inferences [e.g., branching fractions and relative rates] about the RO_2 chemistry.

Tool for measurement

CF_3O^- ion chemistry:

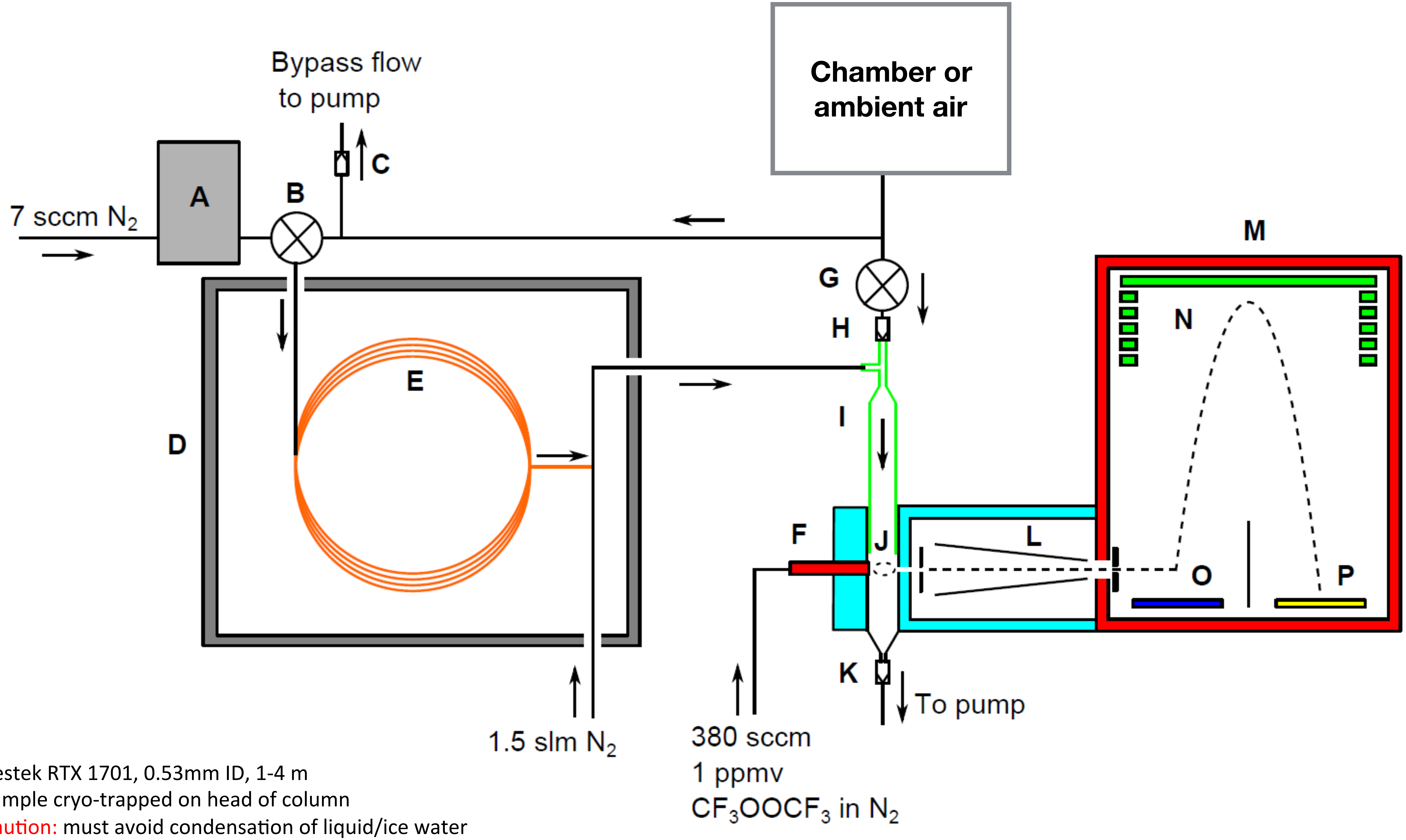
A) CF_3O^- + HB → $CF_3O^-{\bullet}HB$ (m/z + 85)
B) CF_3O^- + HA → CF_2O + $HF{\bullet}A^-$ (m/z + 19)

Sensitivity from authentic calibrations or through calculation of ion-molecule collision rates.



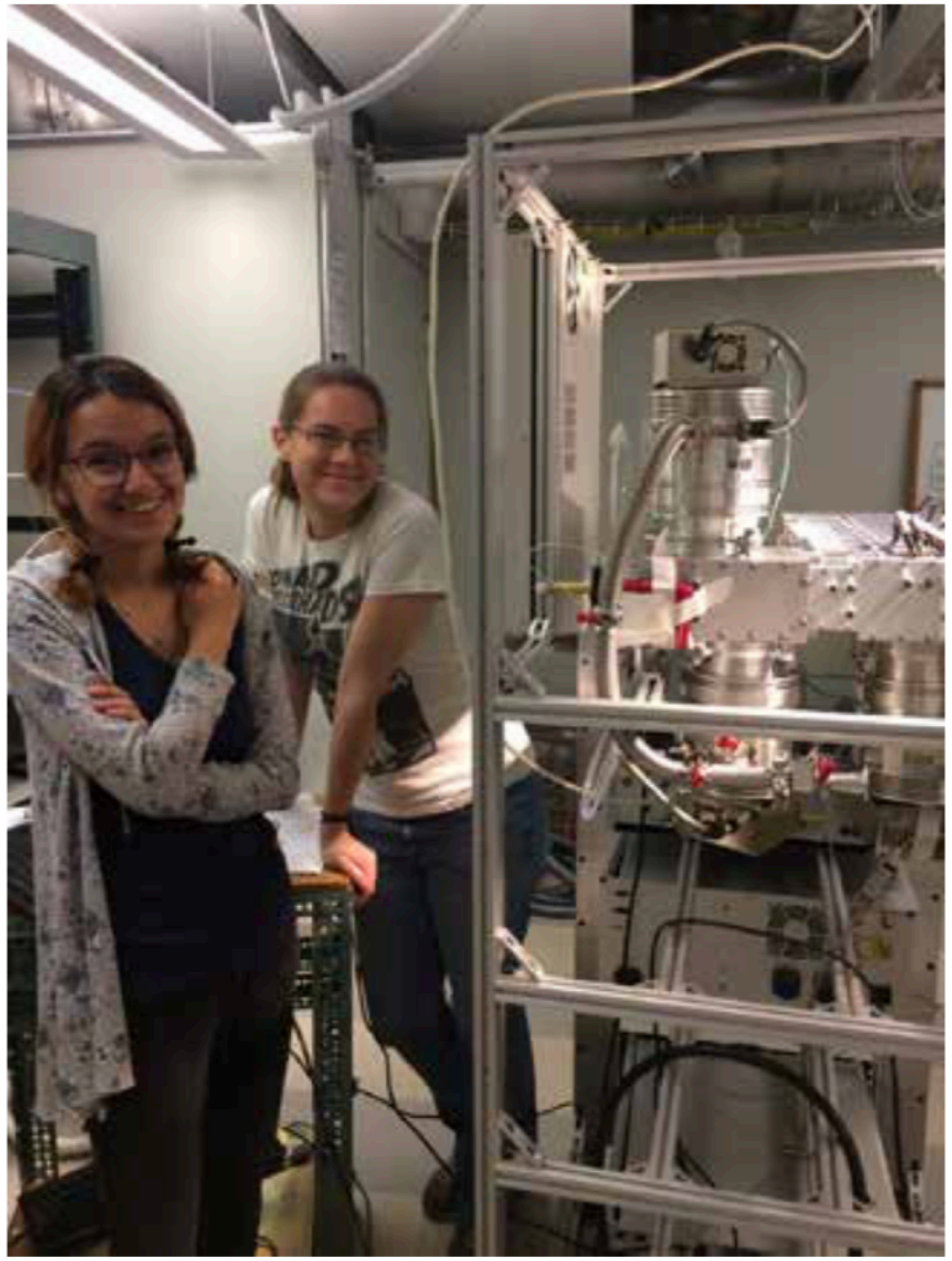
Crounse, et al., *Anal. Chem.*, 2006

Addition of gas-chromatograph



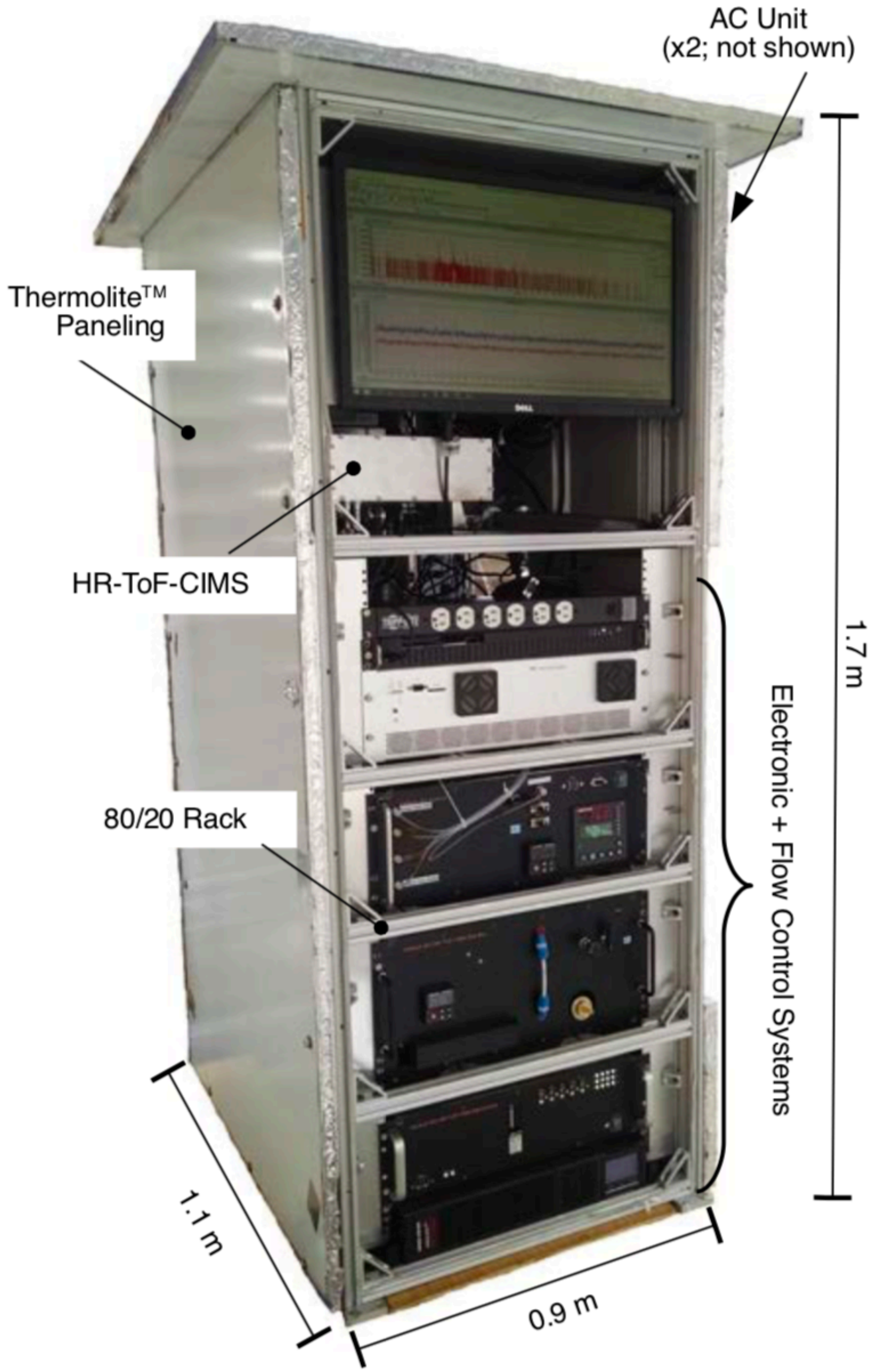
Restek RTX 1701, 0.53mm ID, 1-4 m
Sample cryo-trapped on head of column
Caution: must avoid condensation of liquid/ice water

Fully automated GC-CIMS



Krystal Vasquez   Hannah Allen

Eric Praske



Vasquez, et al., AMTD, 2018

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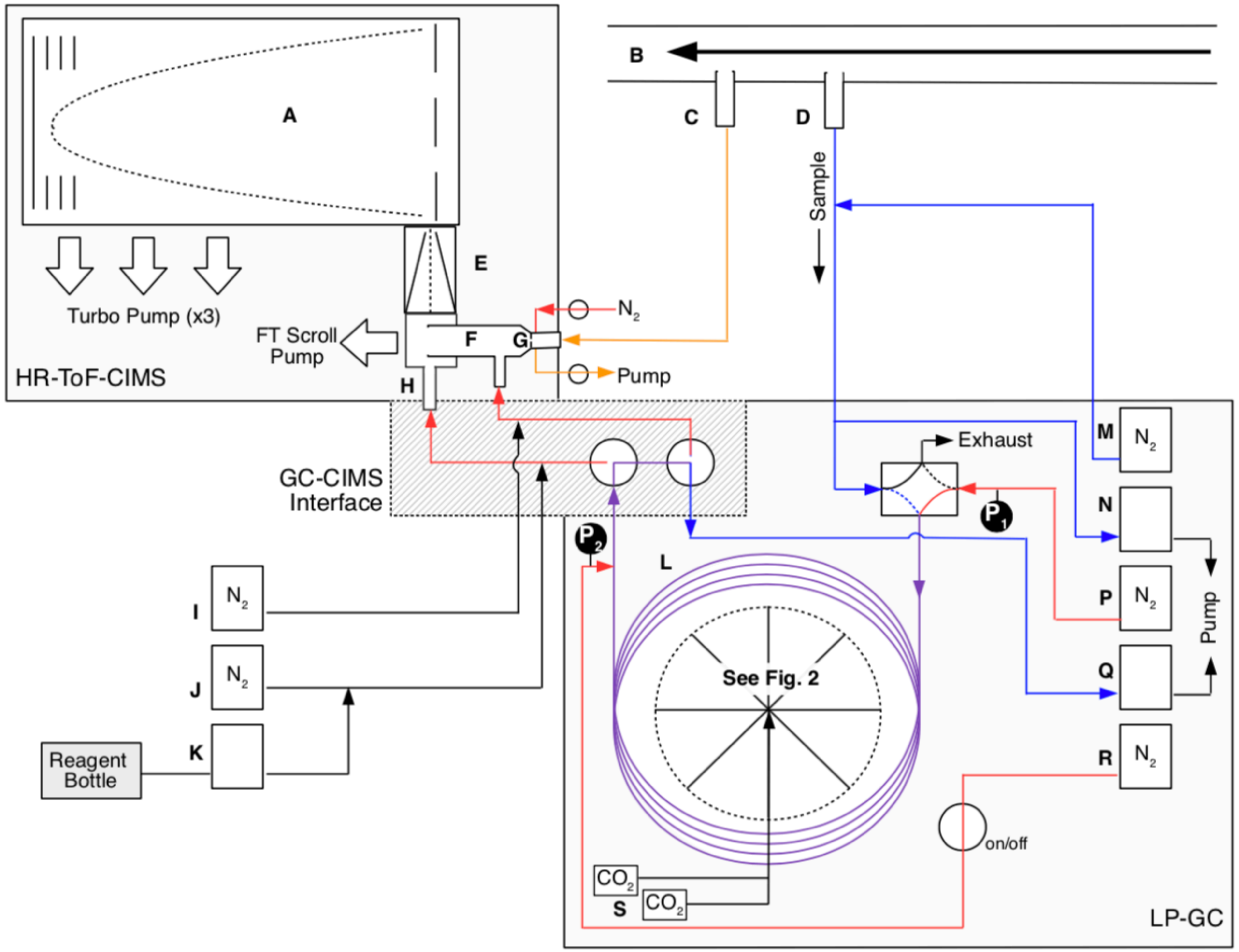
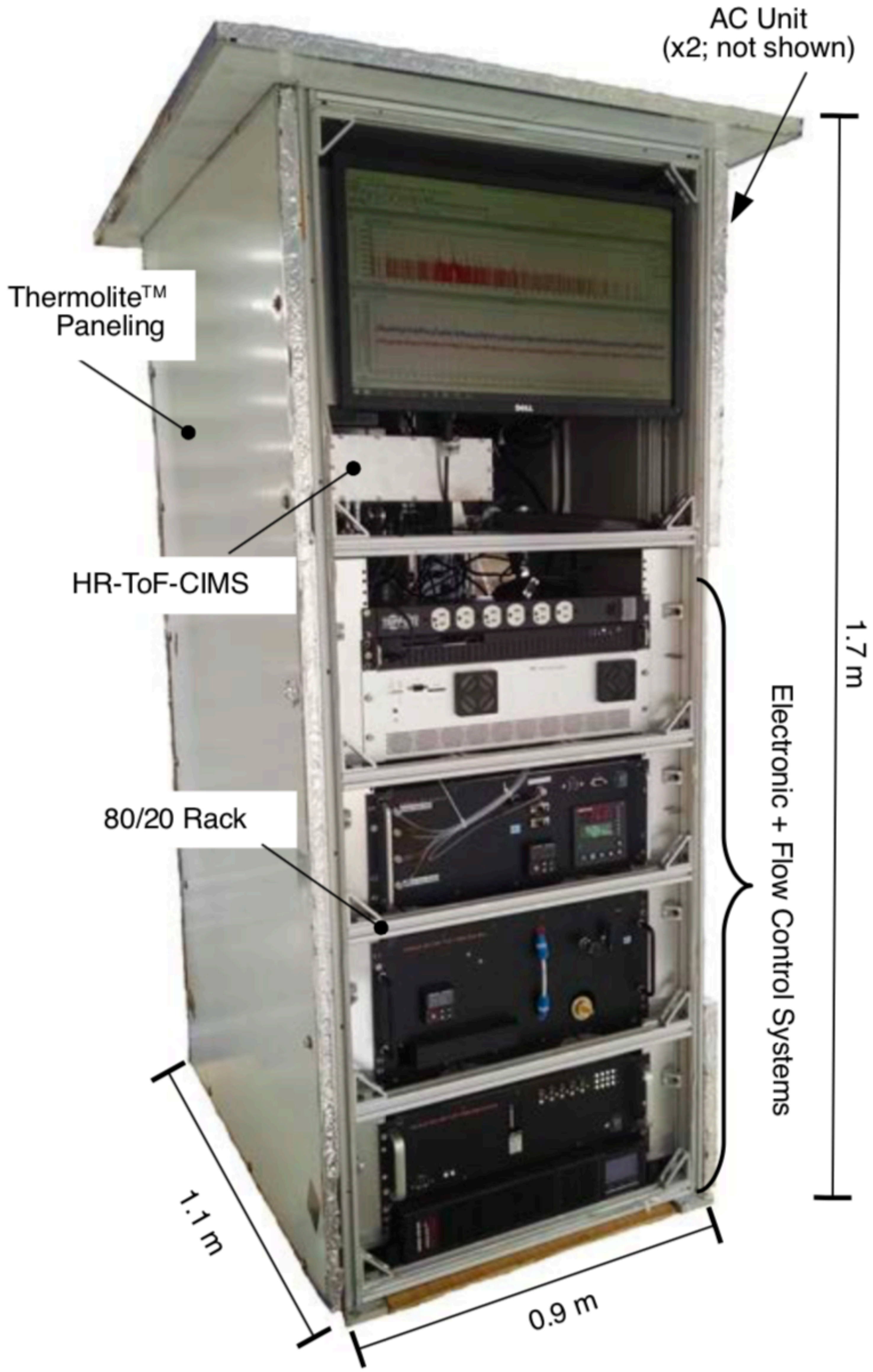
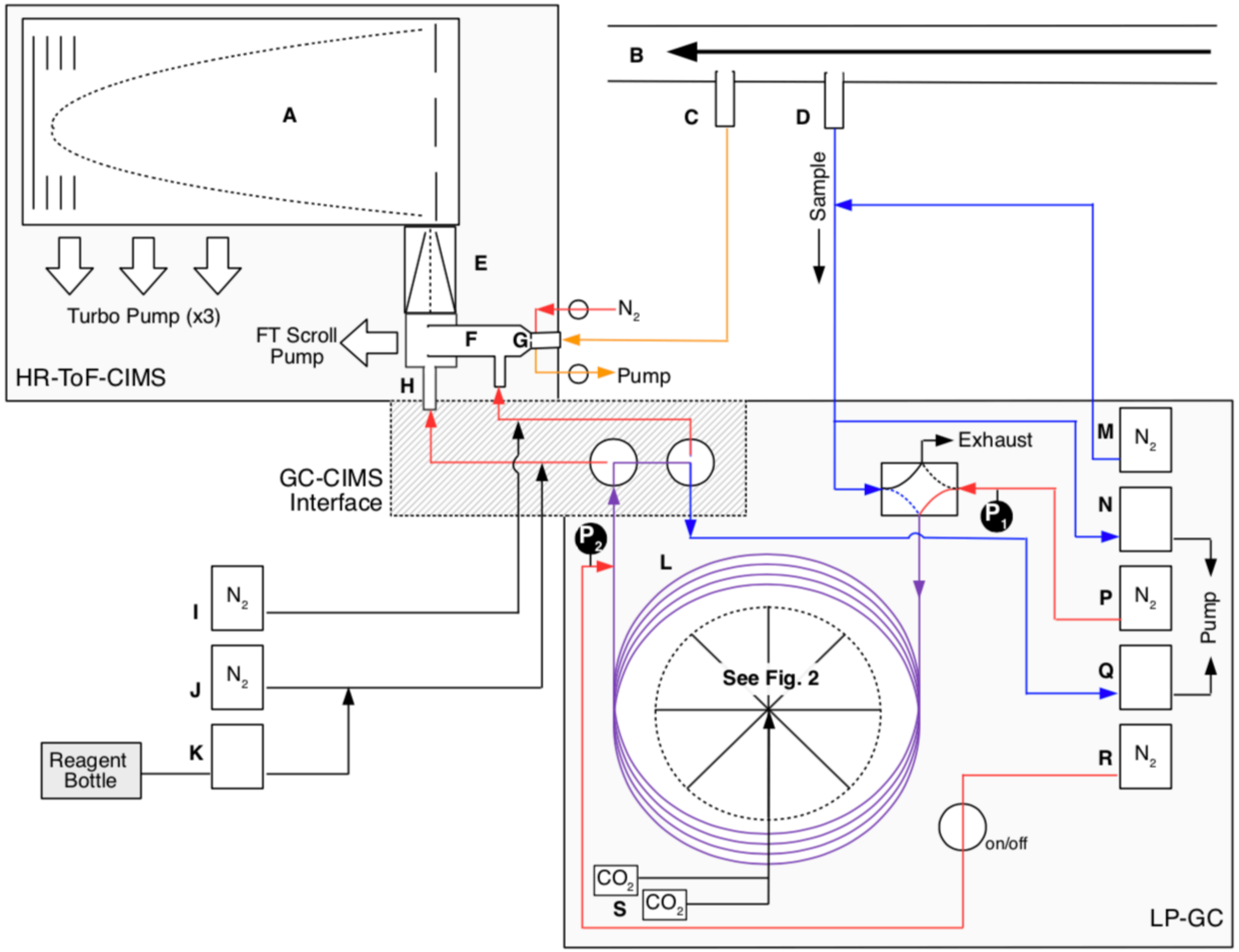




Field deployable / weatherproof / air conditioned
Weight: 500 kg
Power: ~2.5kVA

Vasquez, et al., AMTD, 2018

Fully automated GC-CIMS



Direct sampling:

- **High time resolution (10Hz)**
- **Concentration data**
- **Flux data**

GC sampling:

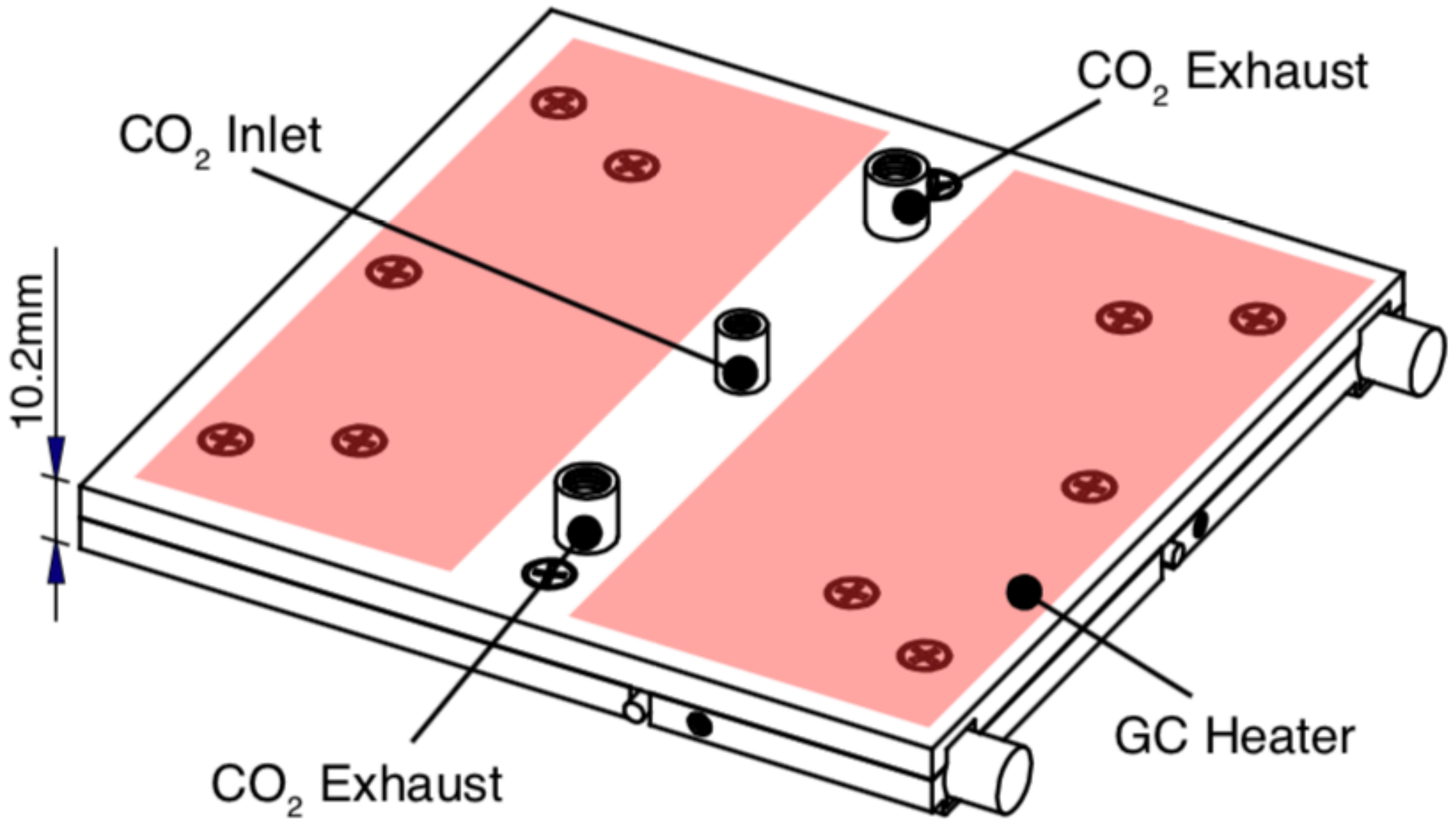
- **Metal free flow path**
- **Analytes collected on column head**
- **Elution under reduced pressure**
- **~1 hr cycle time**
- **Isomer resolved data**

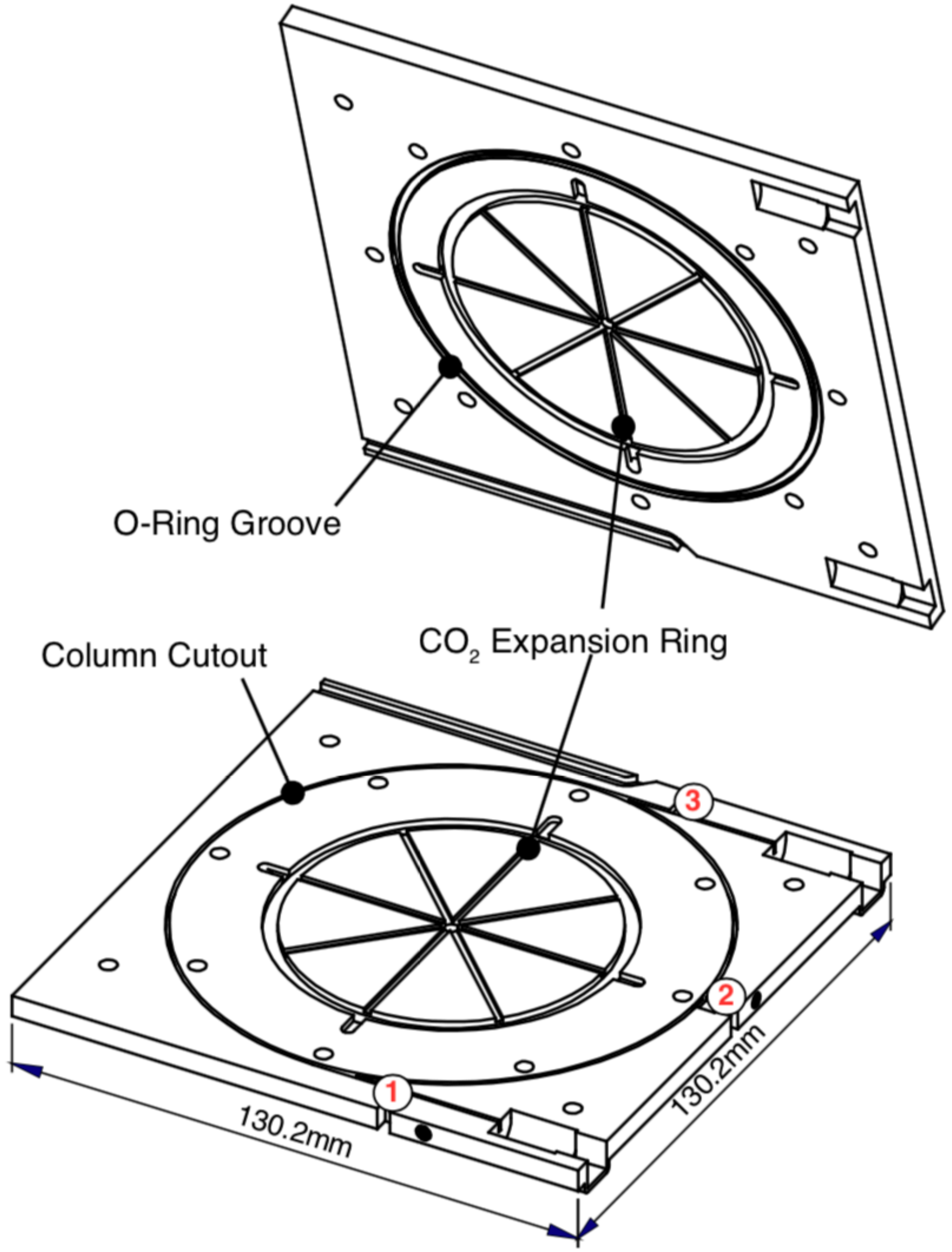
GC sample collected concurrently with direct sampling — allows for transmission calculation

Field deployable / weatherproof
Weight: 500 kg
Power: ~2.5kVA

Vasquez, et al., AMTD, 2018

Custom GC Oven

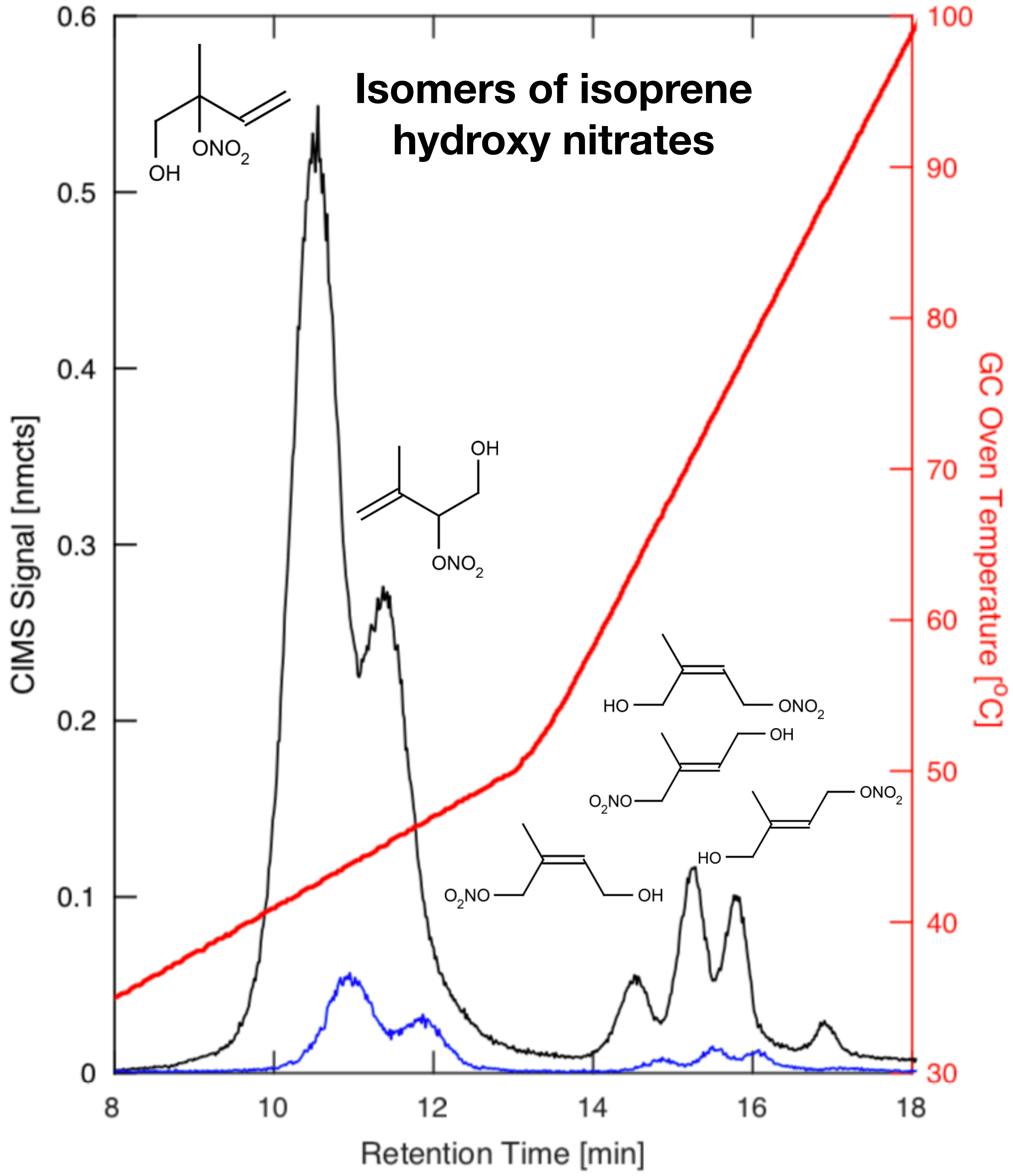


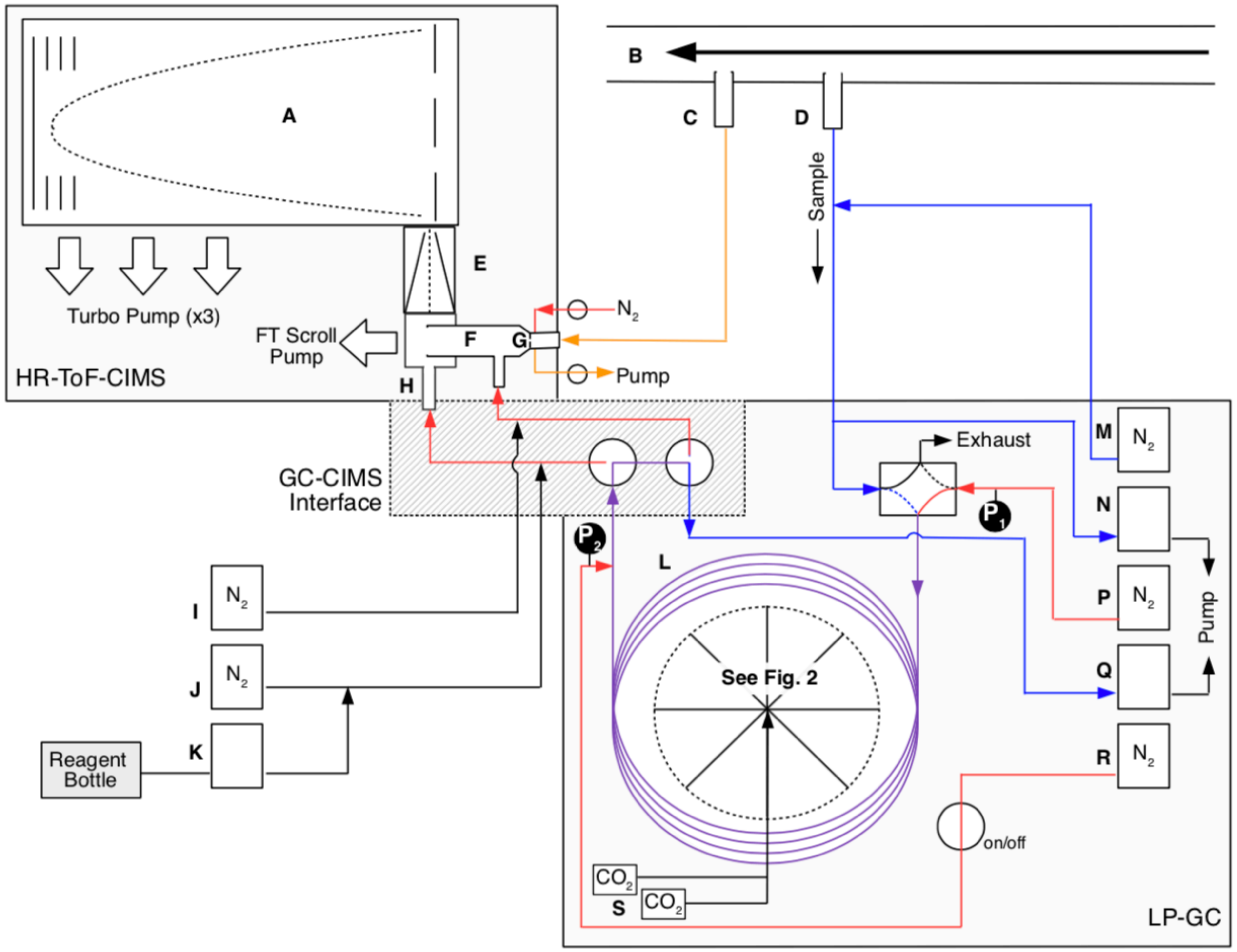


Machined aluminum plates — 470 g
Holds ~1 m 0.53 mm OD column
Cooled using expansion of CO_2
1/16” PEEK capillary tubing allows for easy control of CO_2 flow rate
Kapton heaters (400 watts) allow for ramping T up to 40 C/min

Vasquez, et al., AMTD, 2018

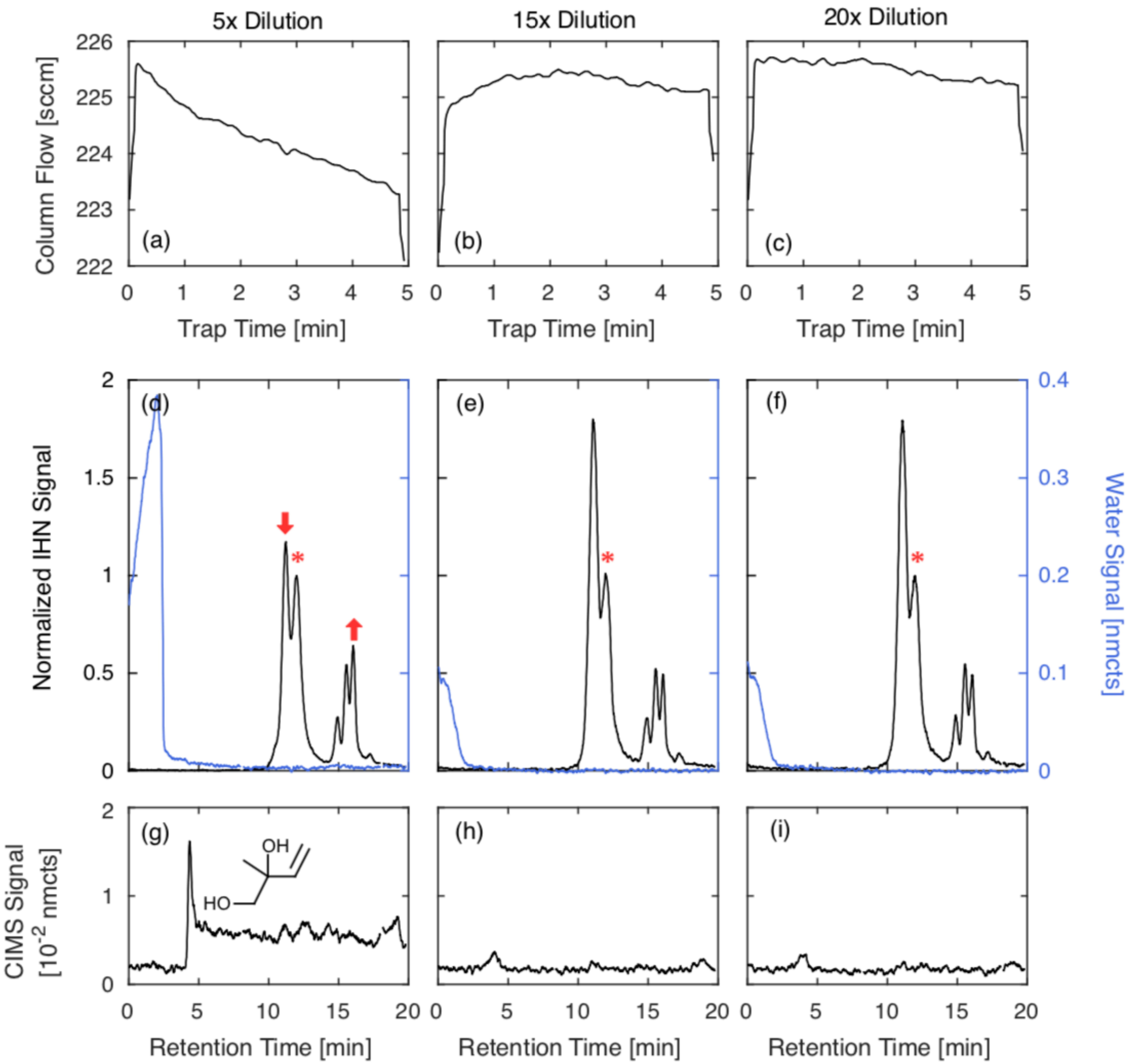
Modes of Analysis





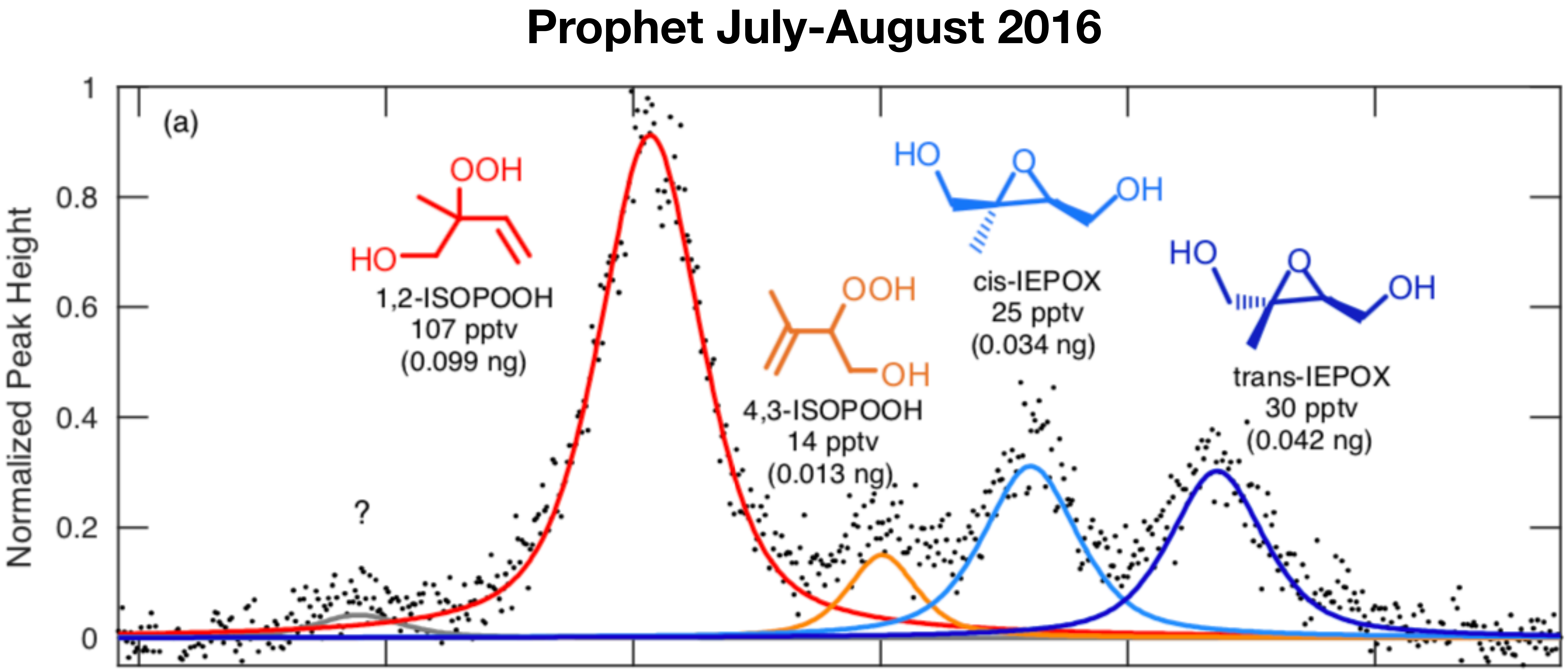
Vasquez, et al., AMTD, 2018

Problem: High humidity
Solution: Dilution



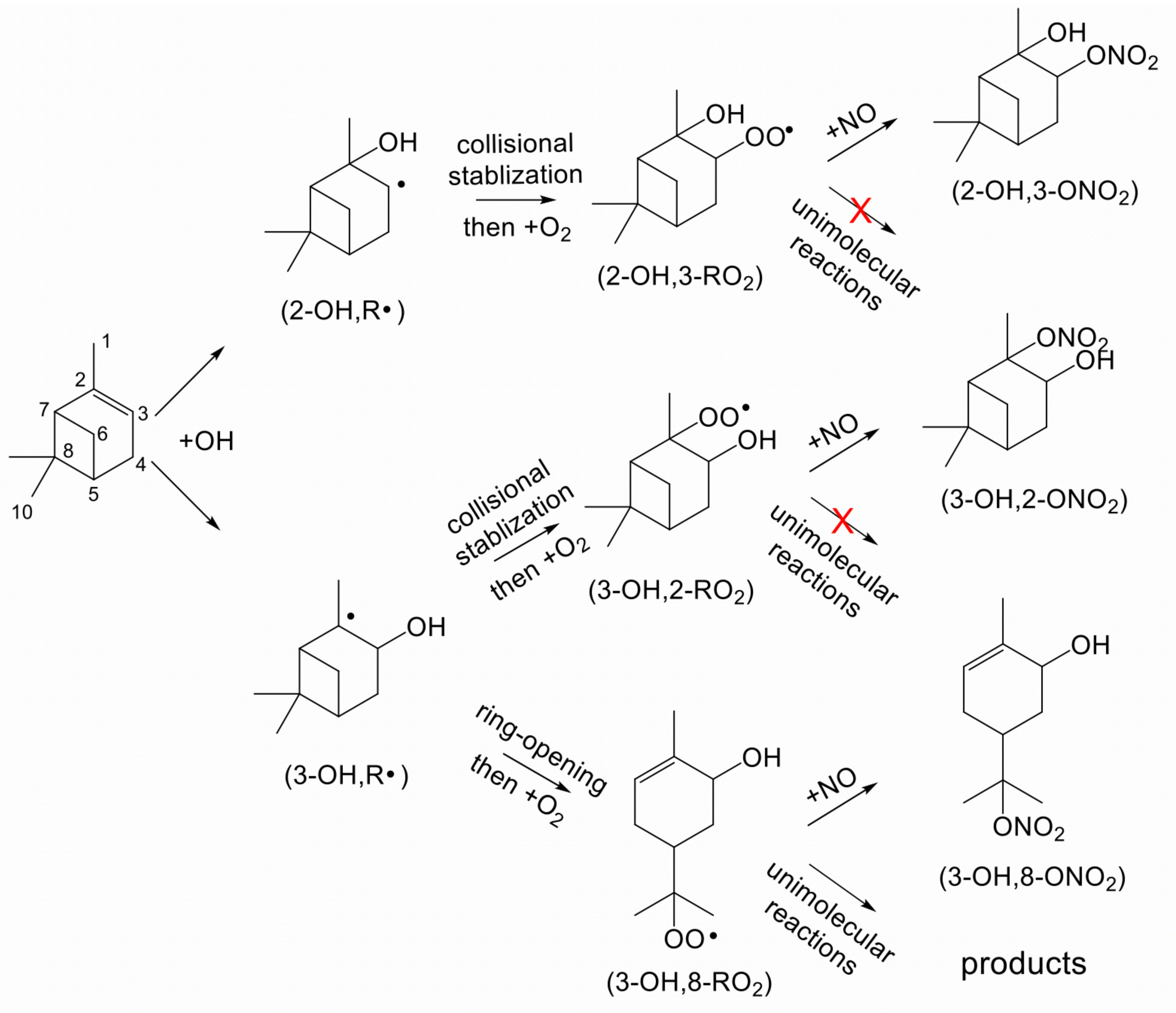
Vasquez, et al., AMTD, 2018

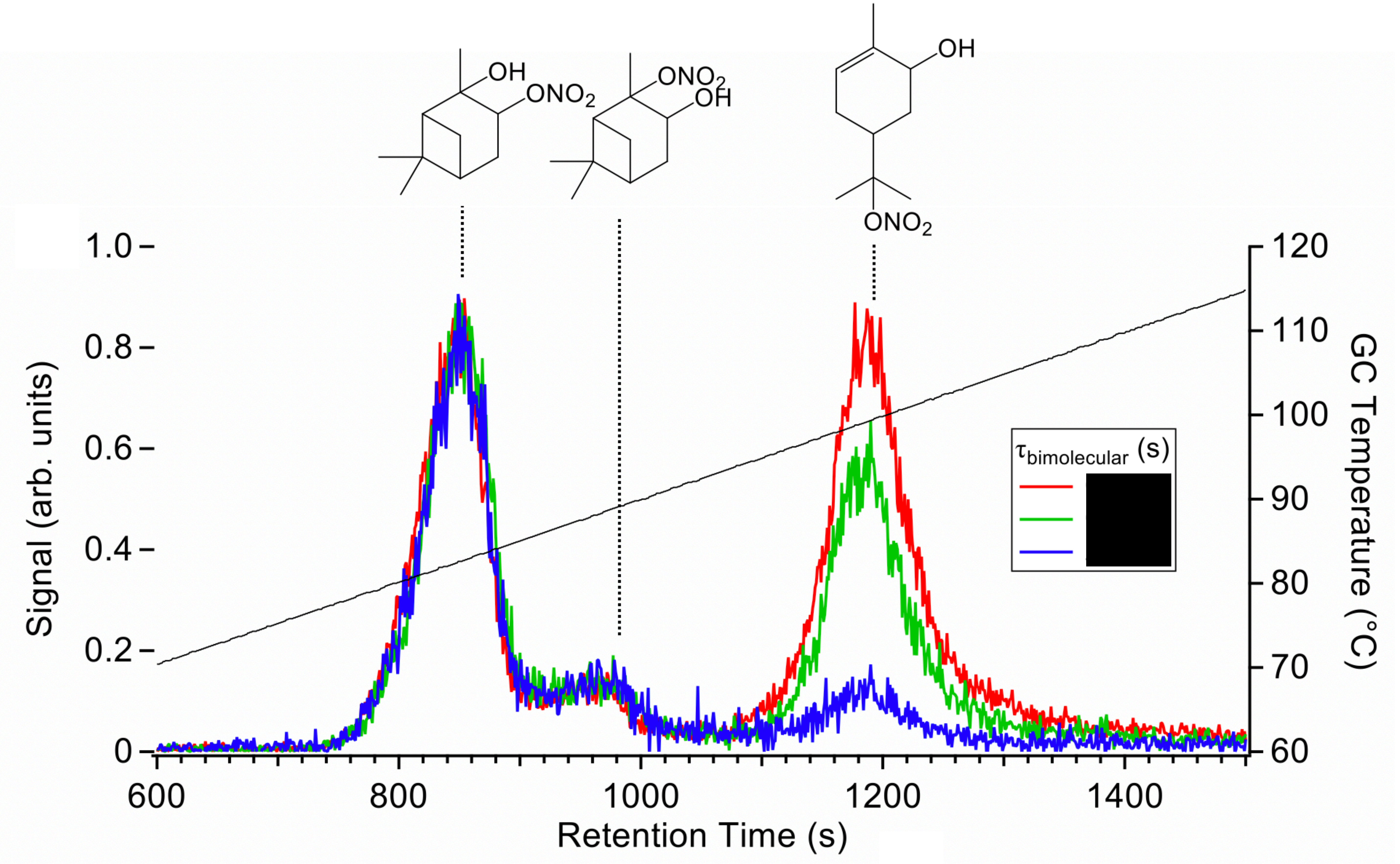
Isomer-specific observations from the field



Vasquez, et al., AMTD, 2018

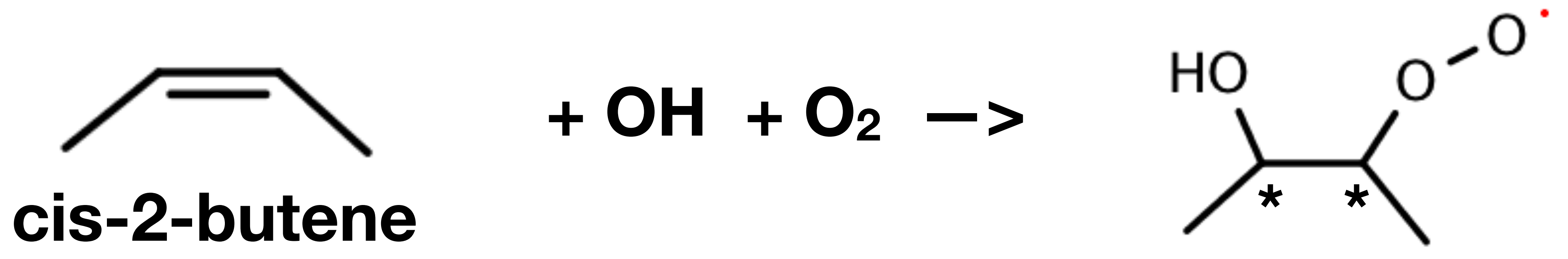
Autoxidation in the OH oxidation of terpenes



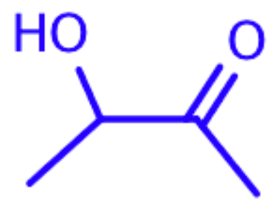


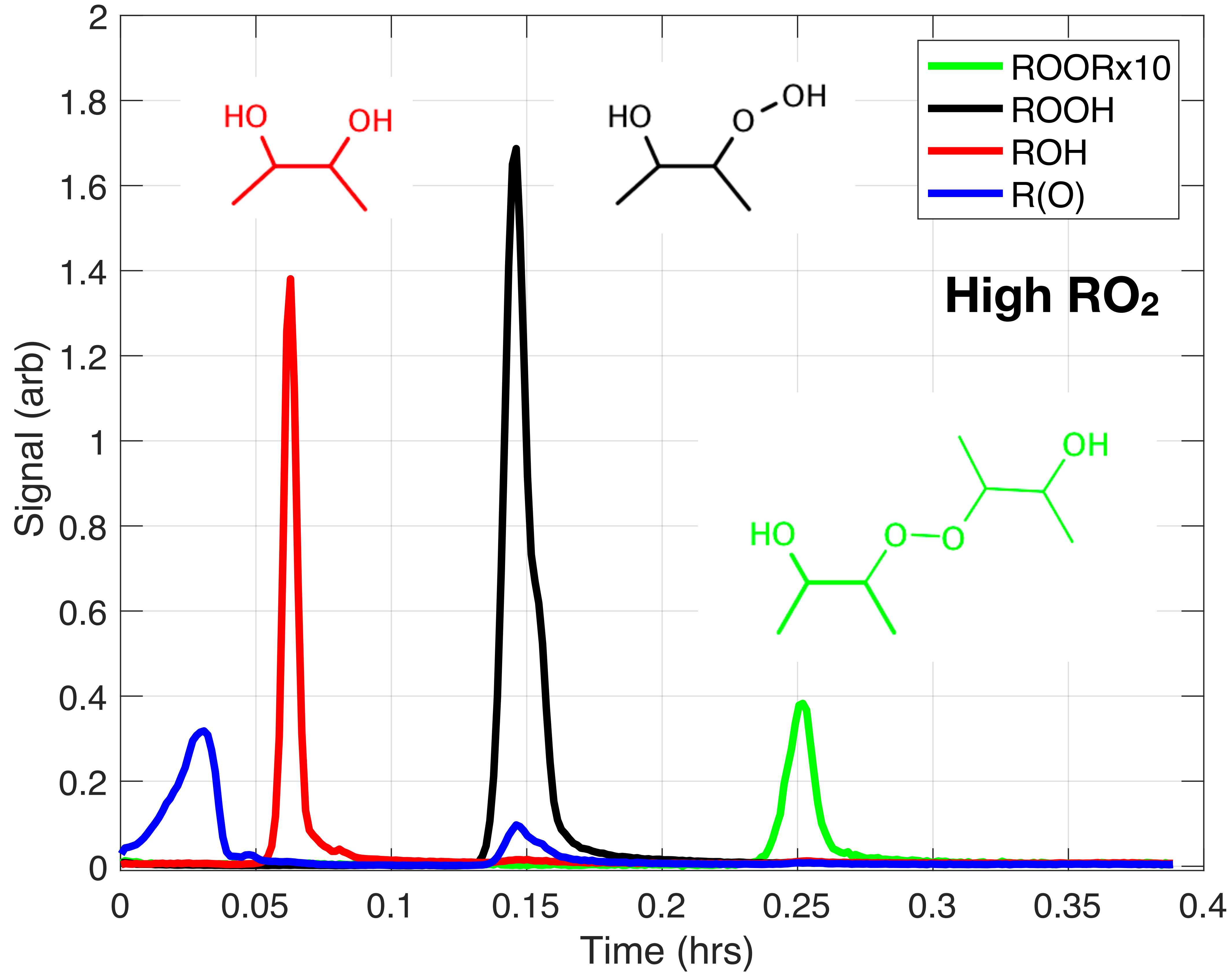
Xu, et al., submitted, 2018

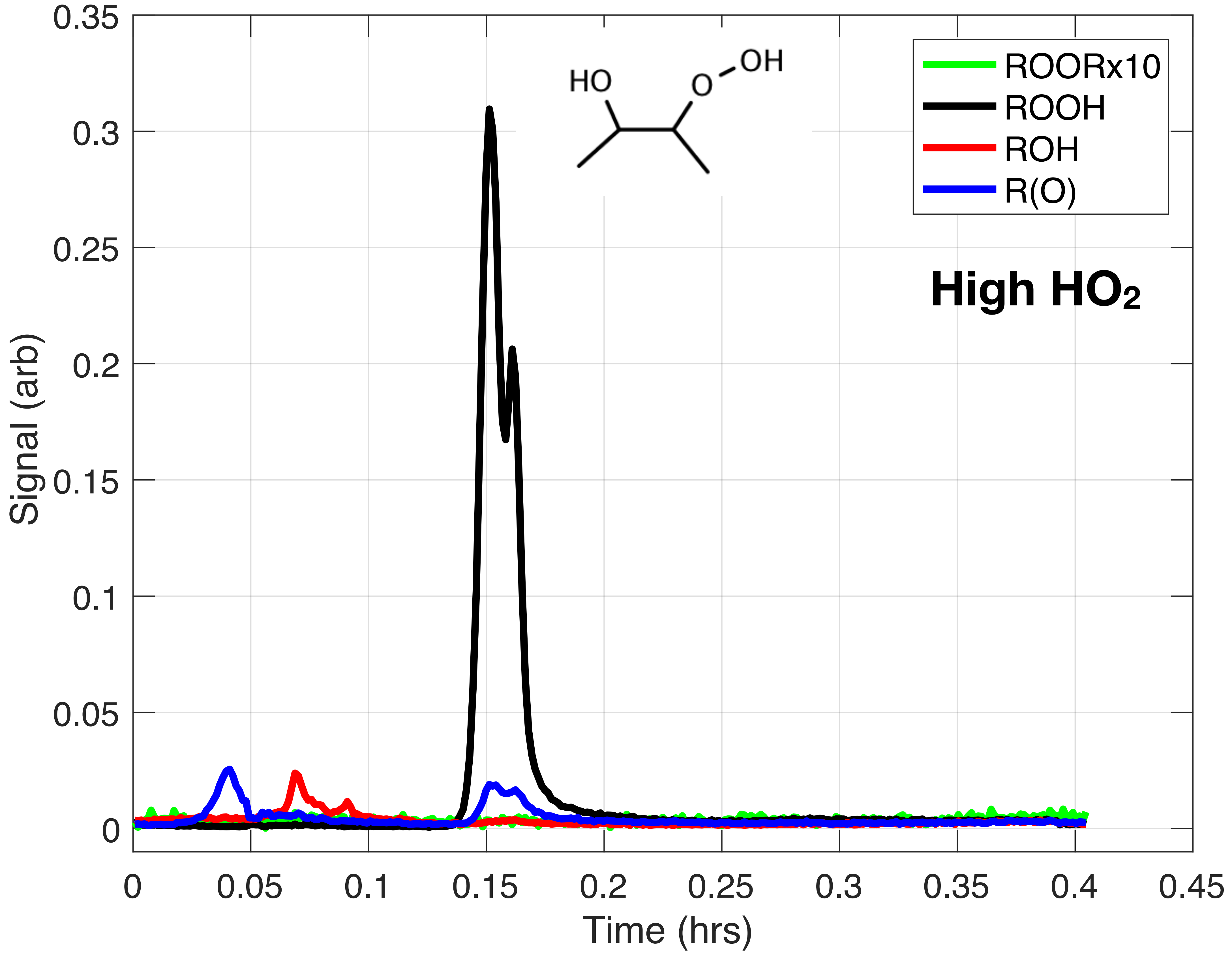
RO_2 + RO_2 Chemistry



(R,R) /(S,S) and (R,S)/(S,R)







Conclusions

Automated GC-CIMS allows for sensitive, isomer-specific measurements of multifunctional compounds in laboratory and ambient environments.

Isomer-specific measurements provide a powerful tool for understanding autoxidation and RO_2 + RO_2 mechanisms within the laboratory and the ambient atmosphere.

Acknowledgments

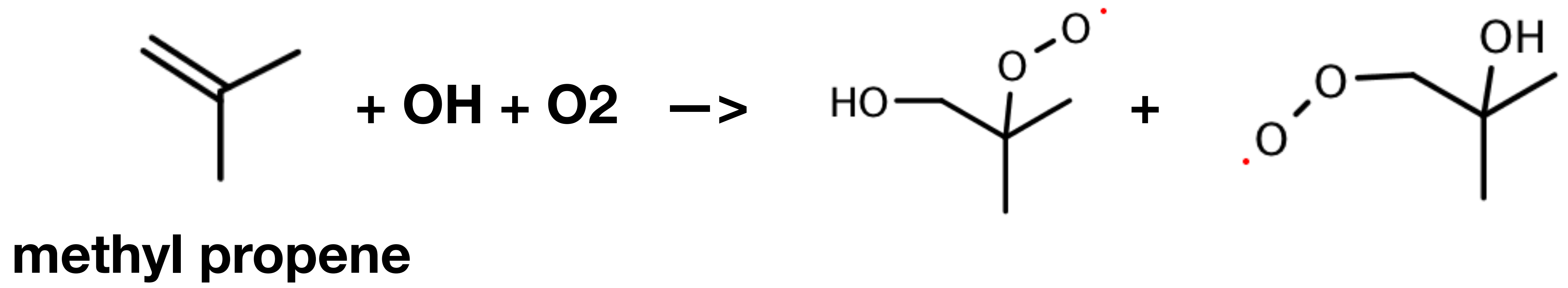
Krystal Vasquez
Hannah Allen
Eric Praske
Lu Xu
Paul Wennberg

RO_2 + RO_2 Experiments

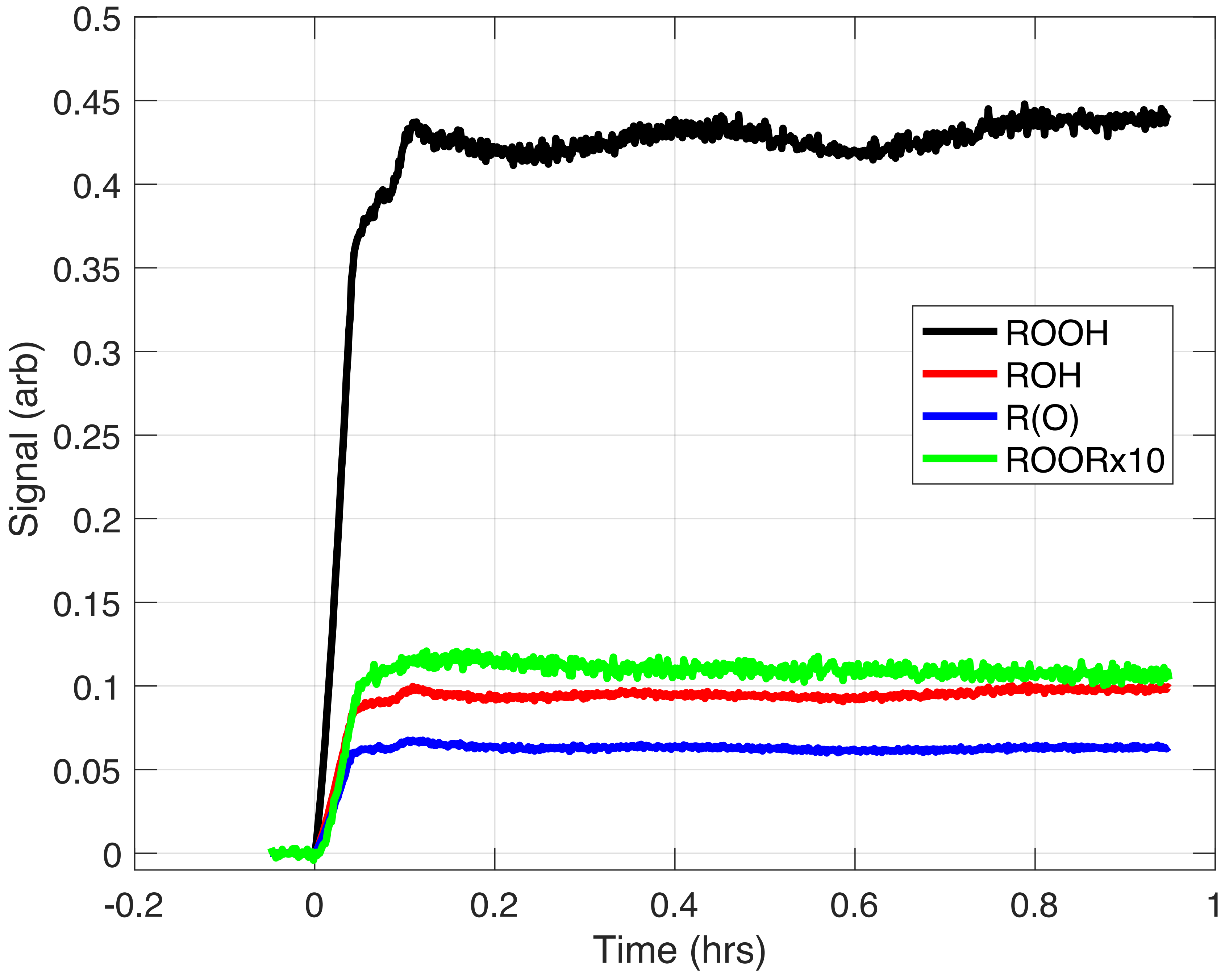
- H_2O_2, alkene in teflon bag, room temperture, atmospheric pressure
- 254 nm UV lights to initiate chemistry
- Vary initial [alkene] : [H_2O_2] to vary P(RO_2) to P(HO_2)
- Measure products using CF_3O^- CIMS direct sampling and gas chromatography

H_2O_2 + hv —> 2 OH
OH + alkene + O_2 —> RO_2
OH + H_2O_2 —> HO_2 + H_2O
RO_2 + RO_2 —> products
RO_2 + HO_2 —> ROOH + O_2

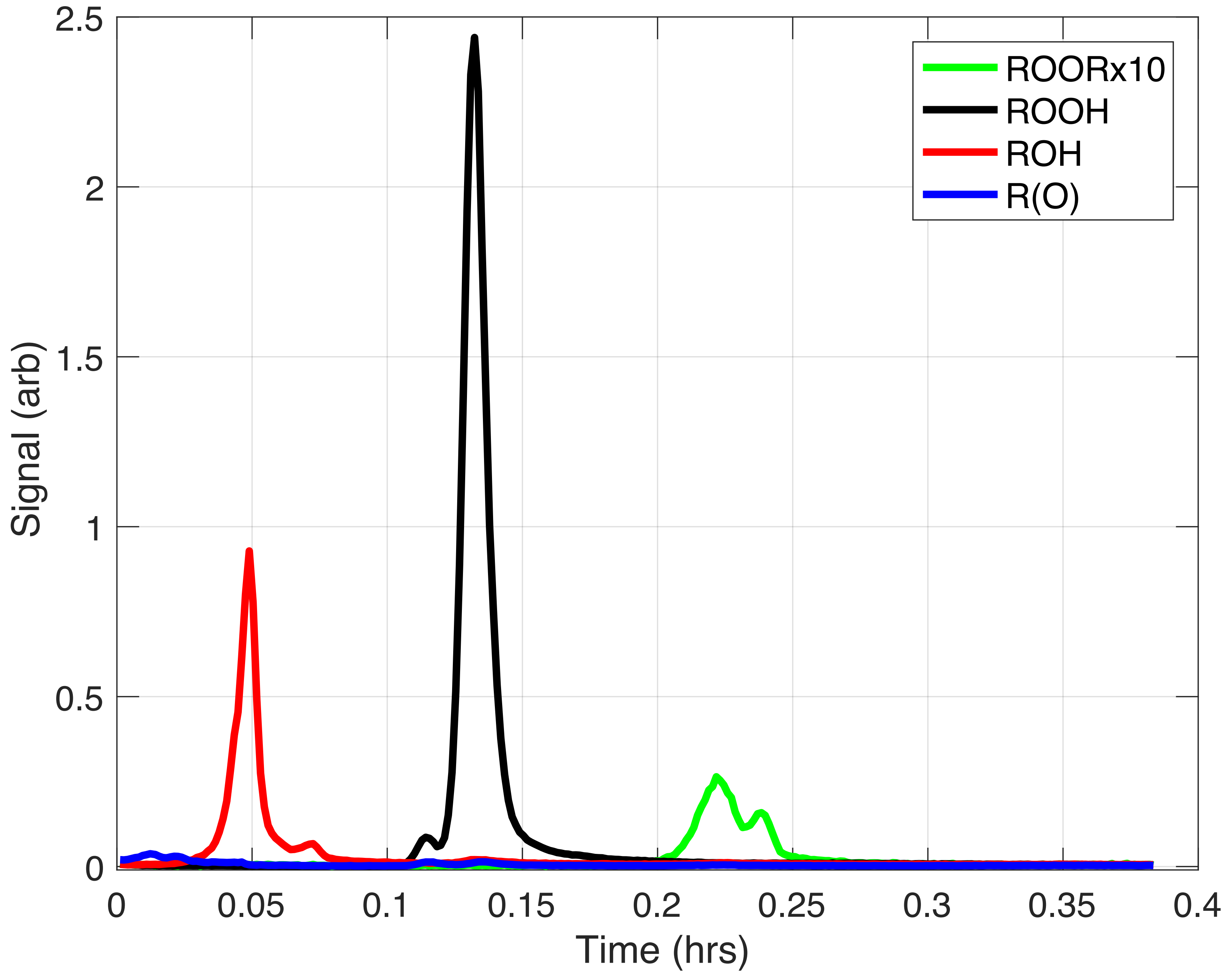
Methyl propene: RO_2 + RO_2 experiments



High RO2



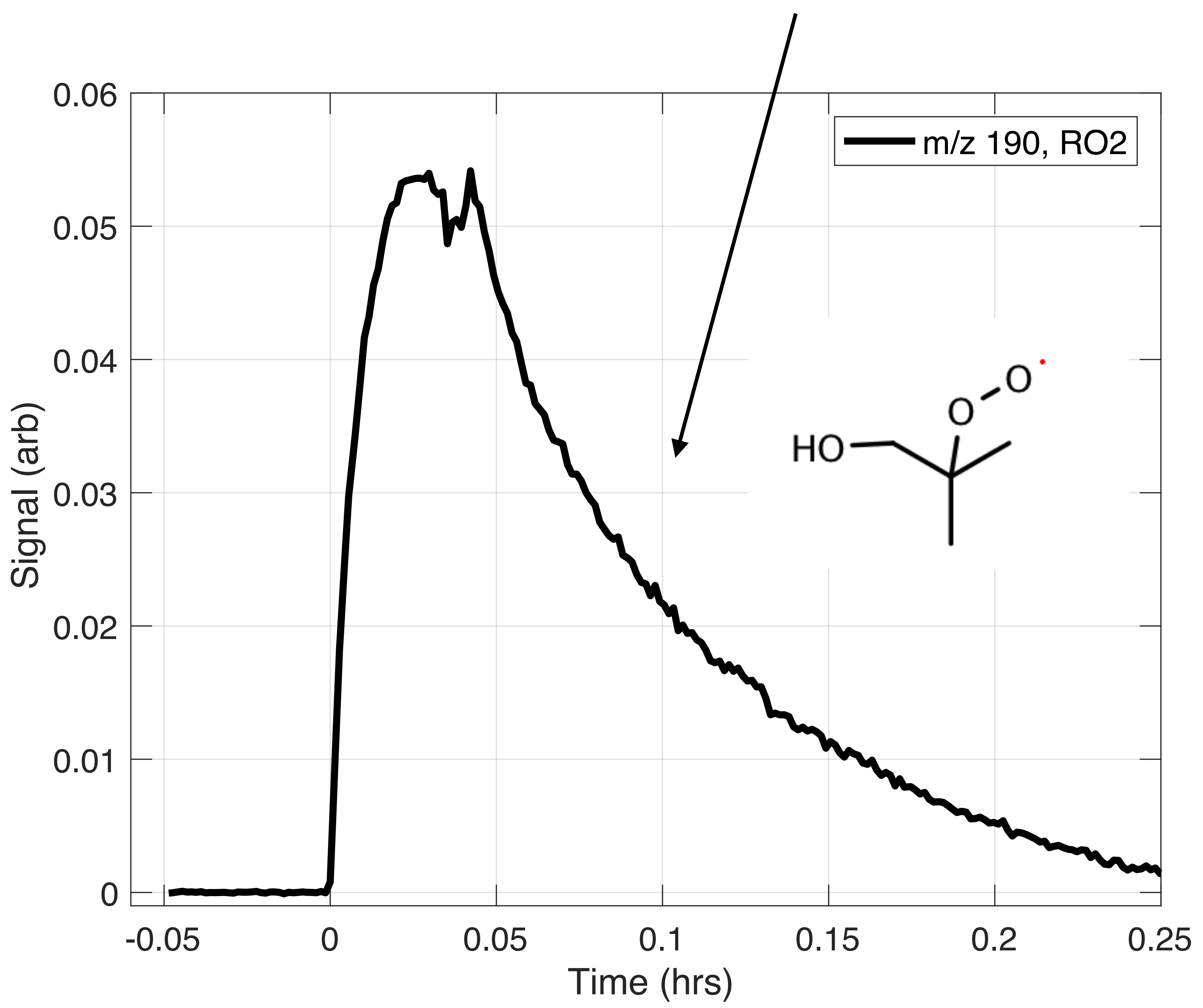
Should be 3 ROOR isomers



Methyl propene: RO_2 + RO_2 experiments

Interesting signals

Lifetime ~4 min @ 296K



Lifetime ~20 min @ 296K