# IMS-MS for on- and offline analysis of atmospheric gas and aerosol compounds

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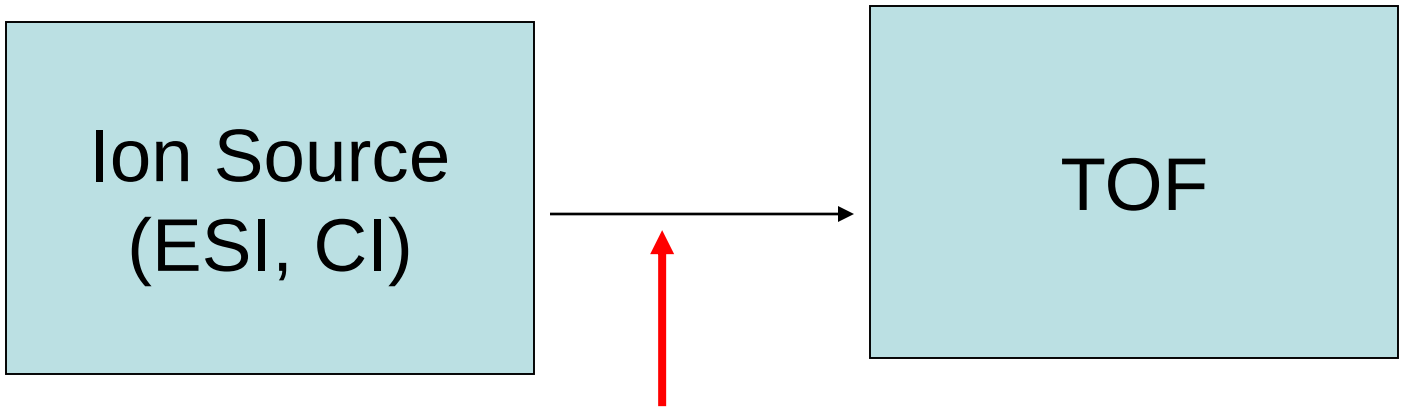
TOFWERK Time-of-Flight Mass Spectrometry

CIRES

# Background



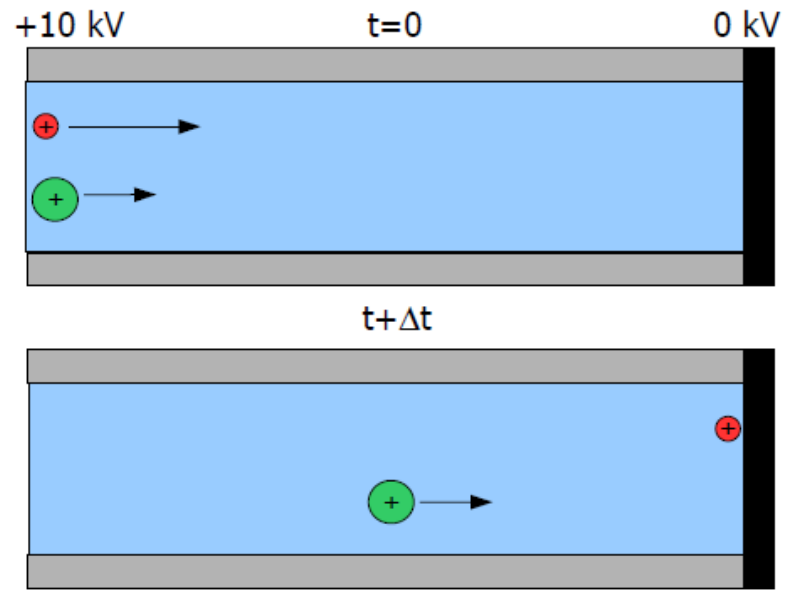

IMS

- Add in pre-separation of ions BEFORE they enter TOF
- Provide more chemical information about ions than possible with TOF alone

NOTE: Analogous to if you had LC or GC before TOF, but IMS-TOF has many advantages over these techniques

# Chemical Ionization +Ion Mobility Spectrometry (CI-IMS-TOF)

$NO_3^-$ Chemical Ionization → Ion Mobility Drift Tube → Time-of-Flight MS




Separate ions by their thermal collision cross section

Approximately proportional to $MW^{2/3}$

W.C. Röntgen, Nature v. 53, p. 274 (1895)

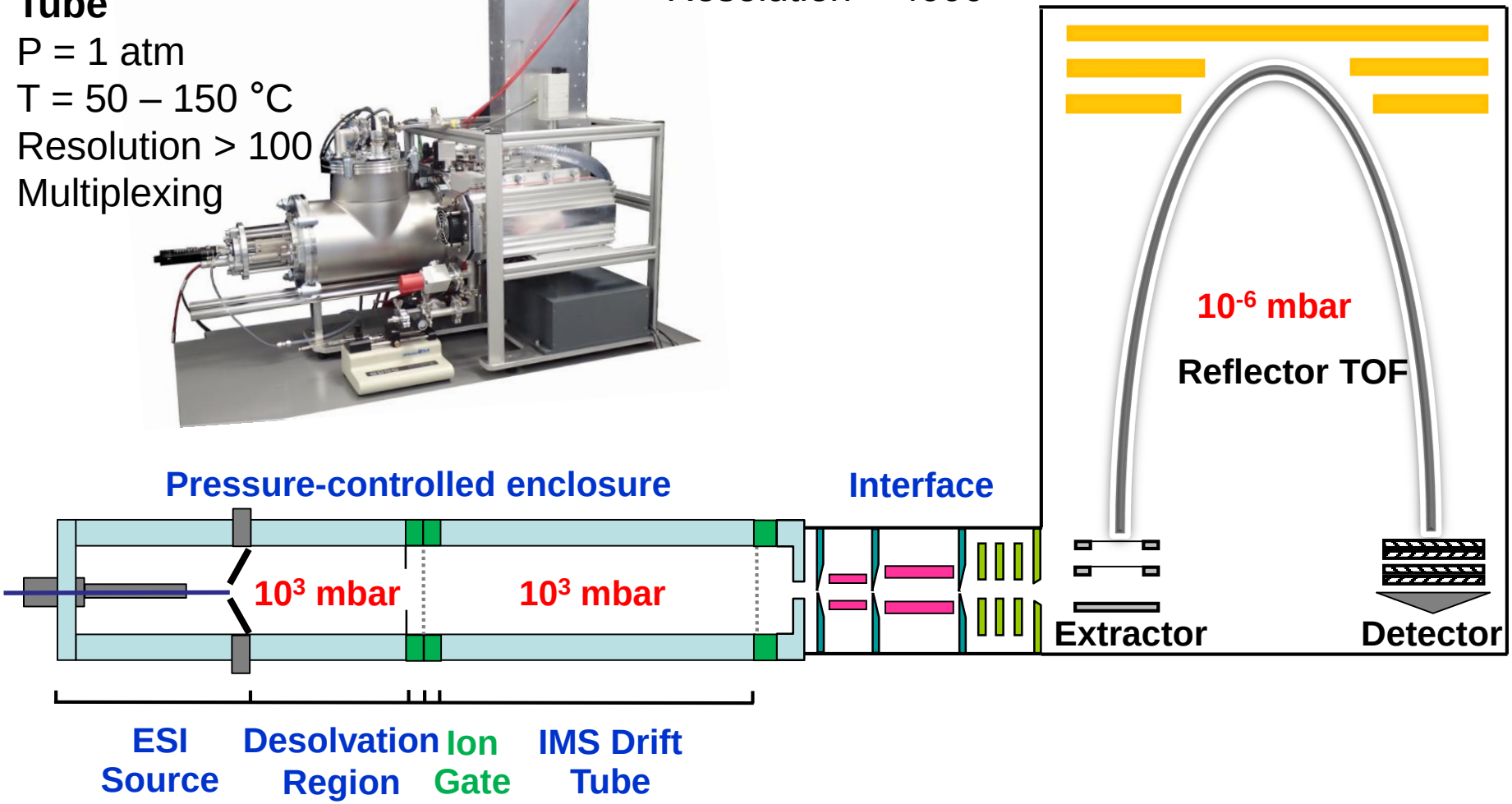
- Ions move through electric field while colliding with buffer gas (pressure= 1 atm)
- Separates ions according to differences in ion mobility

# IMS-TOF Instrument

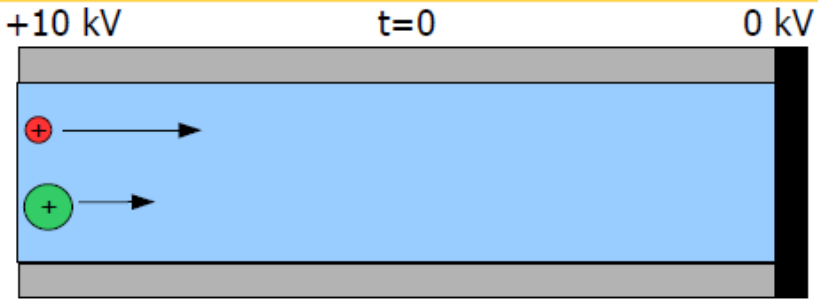
**Low field Drift Tube**
P = 1 atm
T = 50 – 150 °C
Resolution > 100
Multiplexing



**TOF-MS**
Mass accuracy ~ 2-7 ppm
Resolution > 4000



# Features of Tofwerk IMS-TOF




1) Pulse of ions into the drift tube to set t=0 is multiplexed (high sensitivity)

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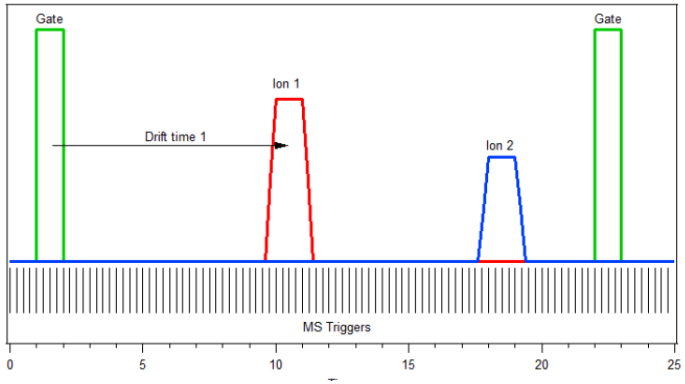
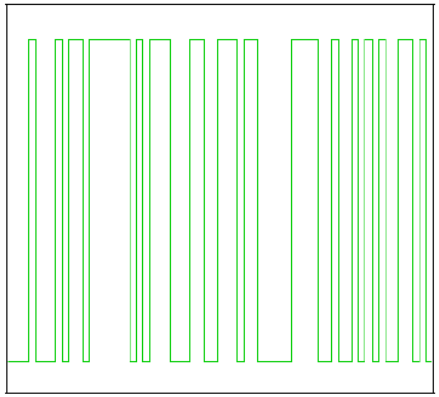



Low duty cycles



Duty cycle ~ 50%

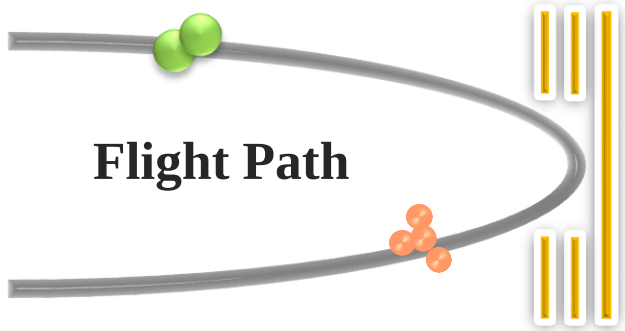
2) Drift tube operated at atmospheric pressure (<150 ms drift times)

Resolution $=t/\Delta t$

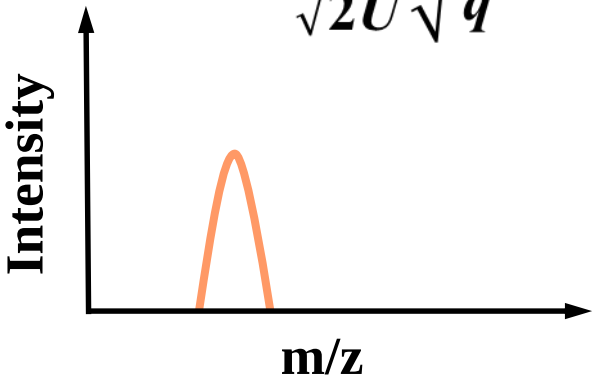
(resolution of 150 compared to typical low pressure values of 40)

# Ion separation Mechanism

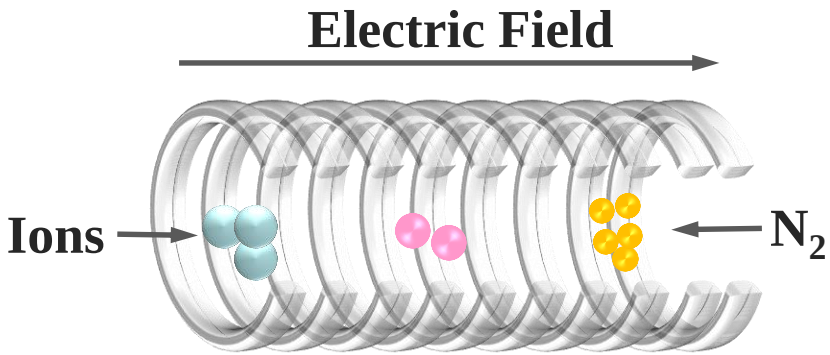
- **Based on Mass to Charge Ratio**



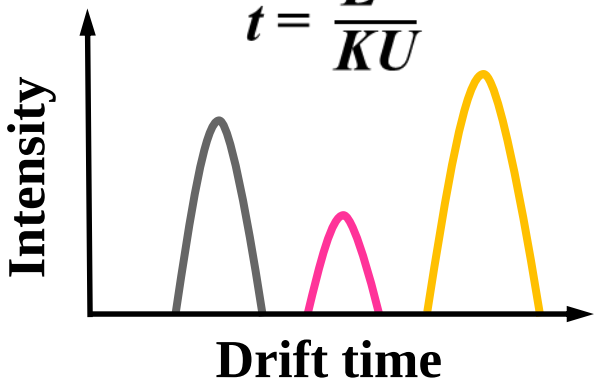

$$t = \frac{L}{\sqrt{2U}}\sqrt{\frac{m}{q}}$$



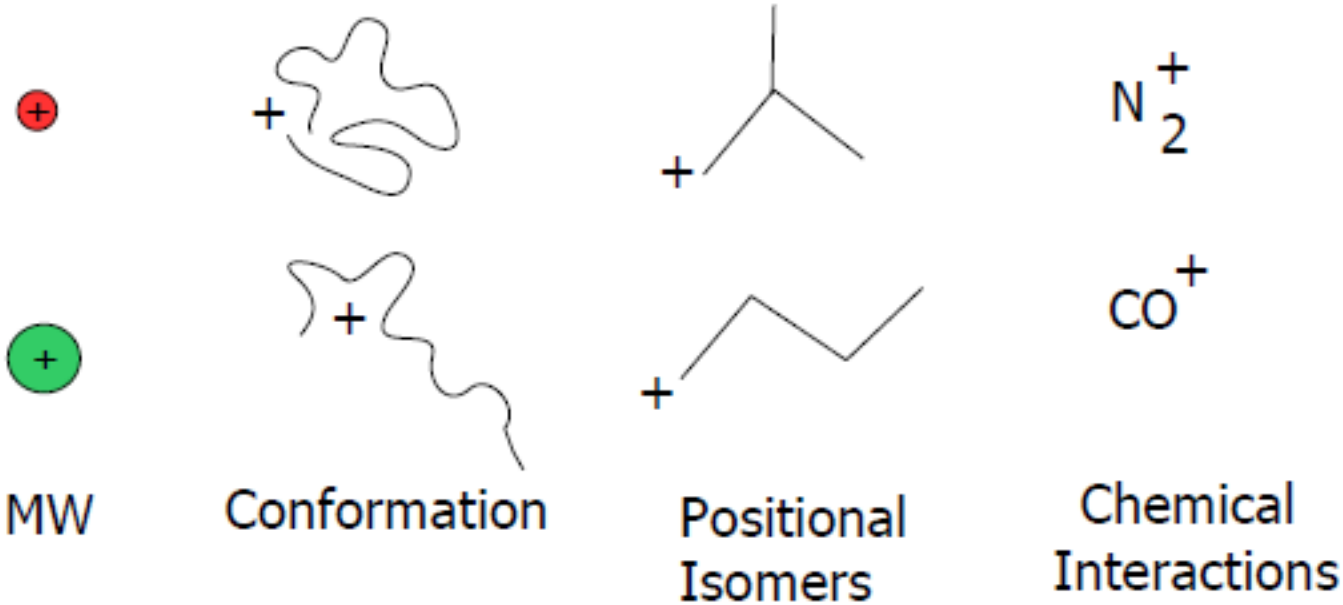

- **Based on Collision Cross Section**




$$t = \frac{L^2}{KU}$$



# Ion Mobility: what




Mobility depends on the ion and the drift gas.

Each ion/gas combination gives a characteristic mobility:

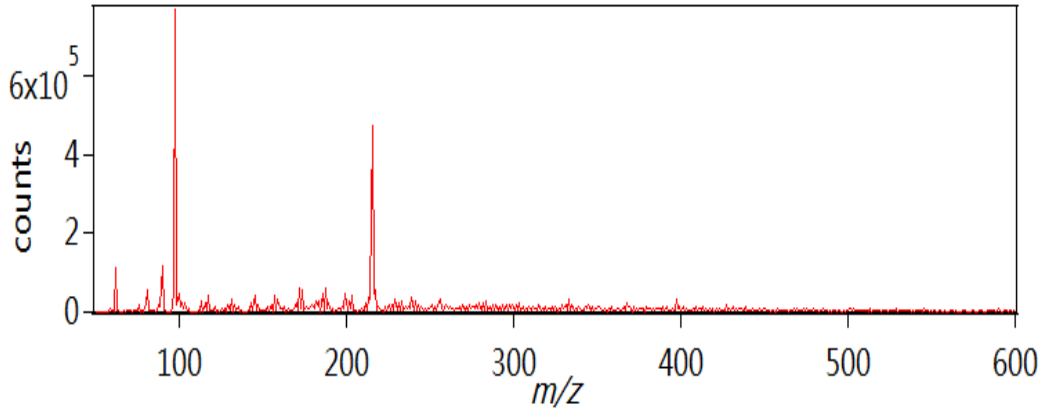
Cross section derived from measured mobility

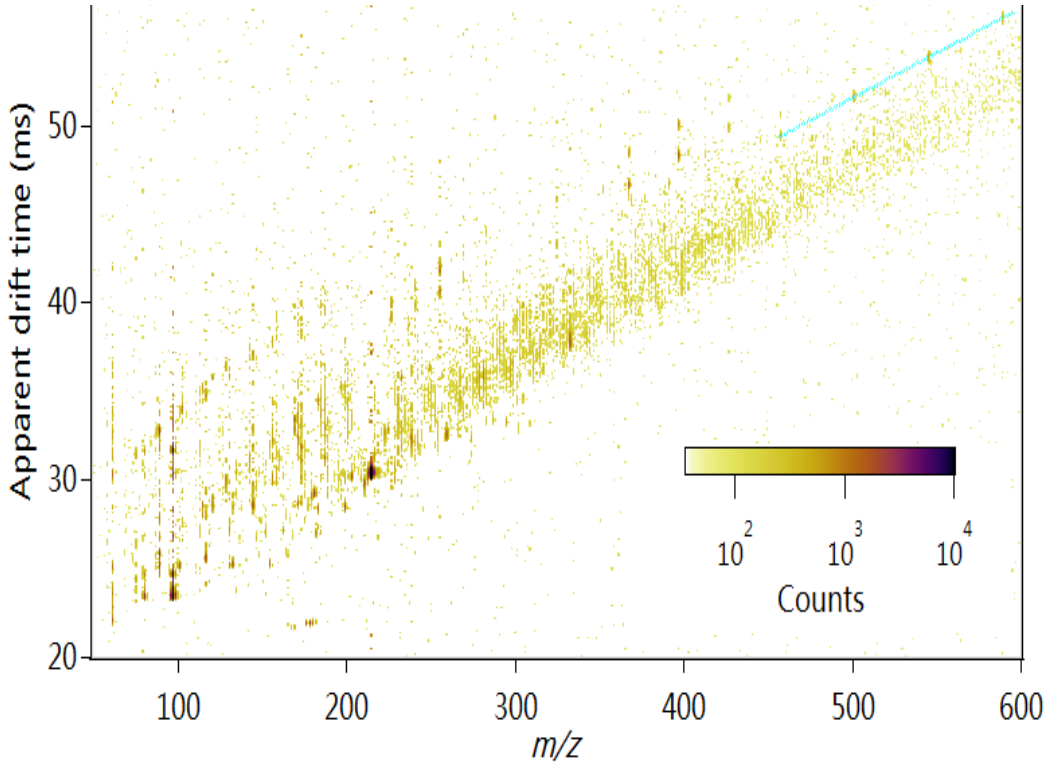
K=drift velocity / E field

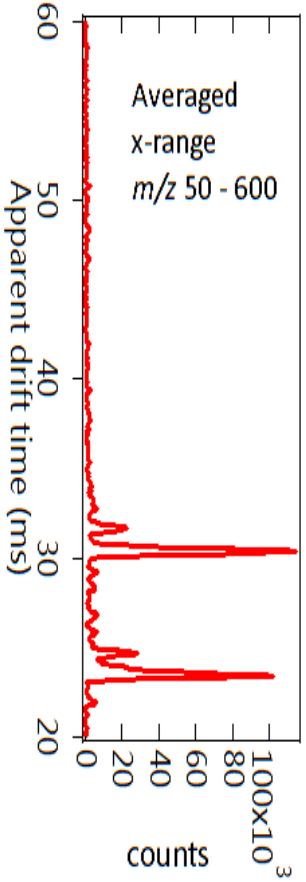
$$\Omega = \frac{3ze}{16N}\left(\frac{2\pi}{k_B \mu T}\right)^{1/2}\frac{1}{K}$$

***Measured mobilities calibrated against standards***

# 2D IMS spectrum

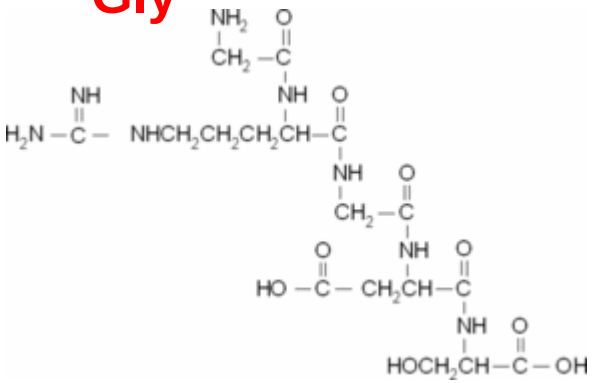


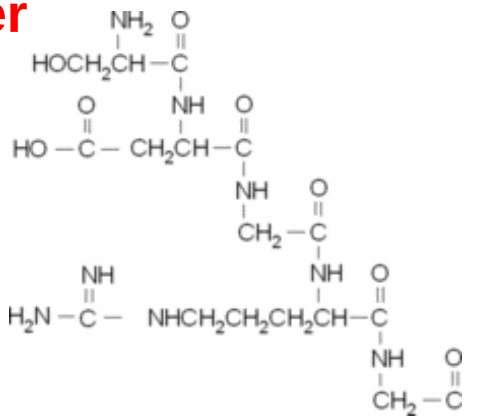



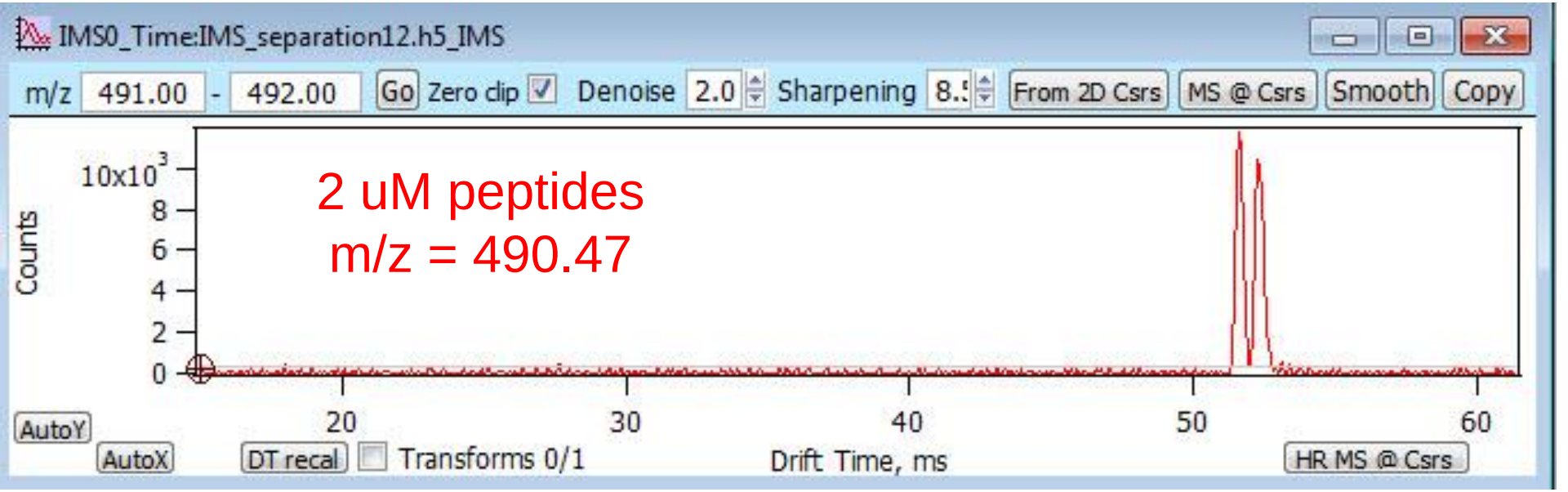
# IMS separation of Isomers

**Ser-Asp-Gly-Arg-Gly**



**Gly-Arg-Gly-Asp-Ser**





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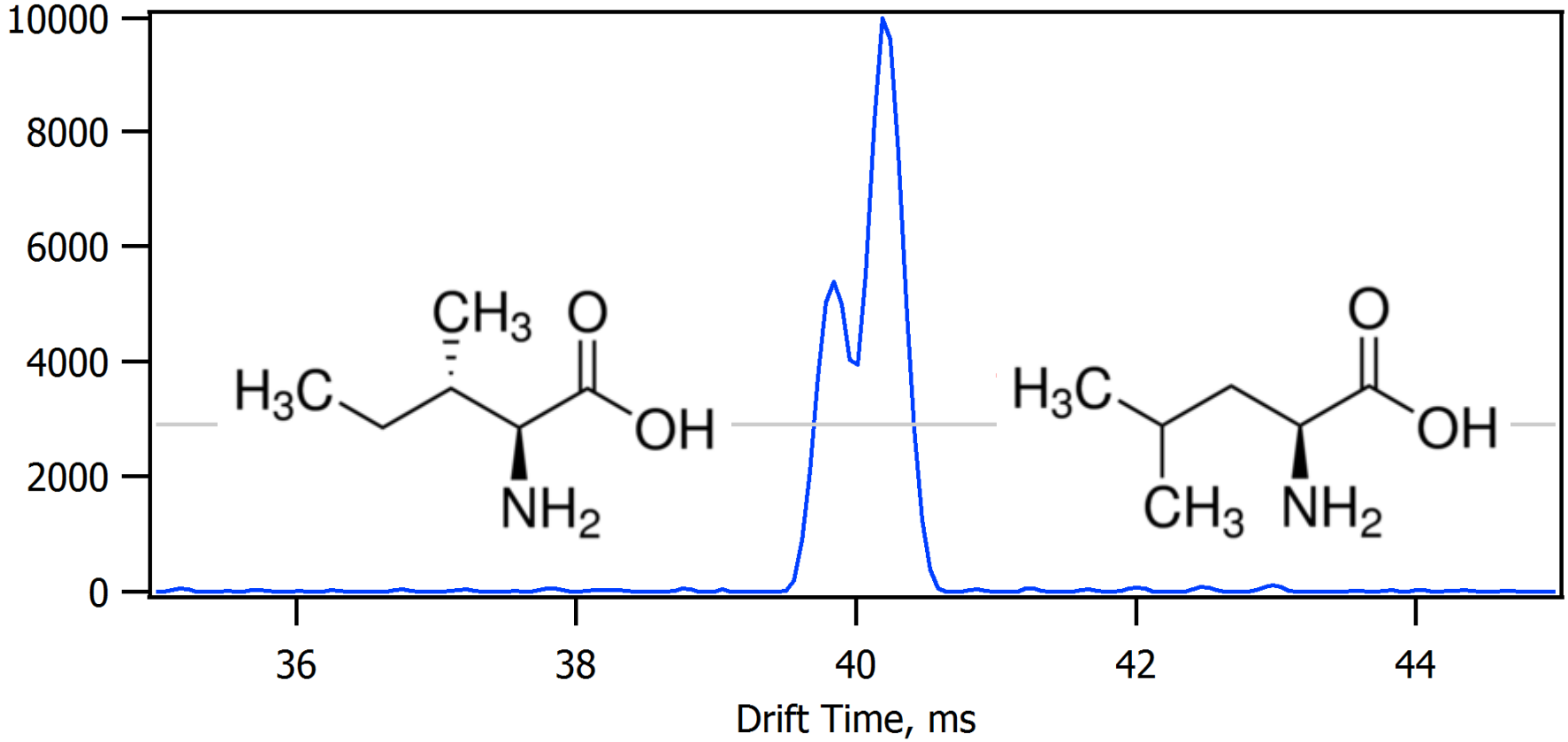
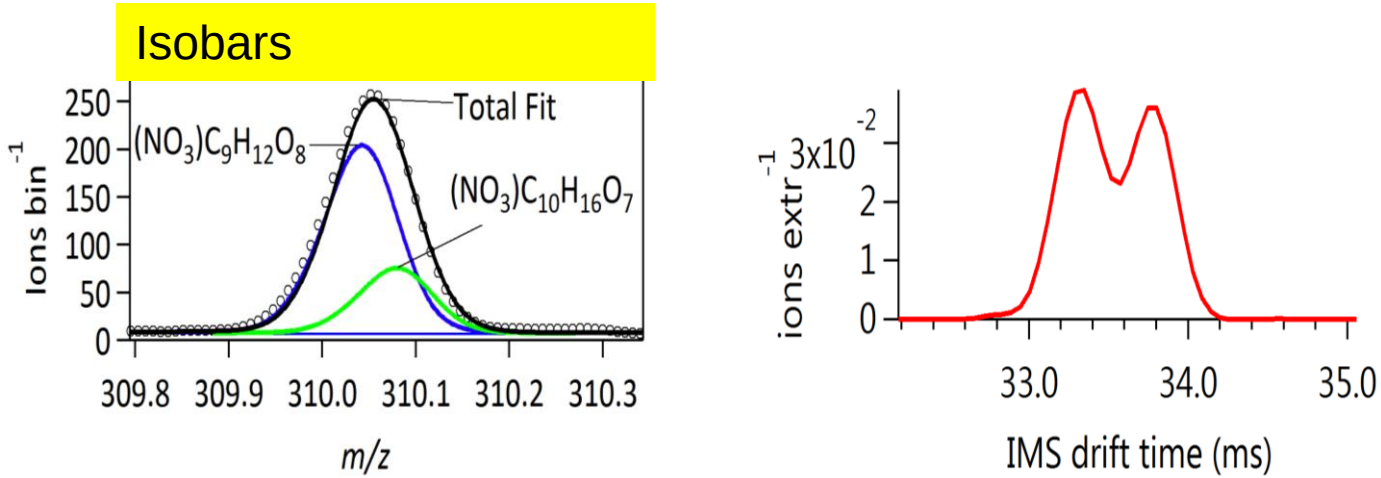



Zhang X. et al., A novel framework for molecular characterization of atmospherically relevant organic compounds based on collision cross section and mass-to-charge ratio, *Atmos. Chem. Phys.*,**16**, 12945–12959, 2016

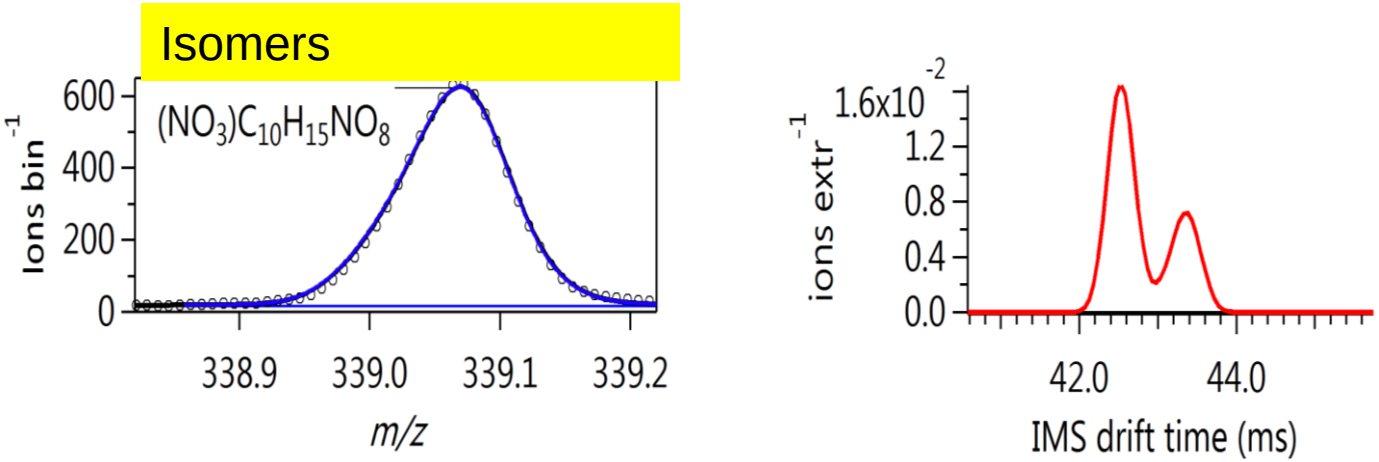
# IMS separation of Isobars and Isomers (CI-IMS)

CIMS Molecular-level identification limited by Isomeric and Isobaric species

*m/z* 310



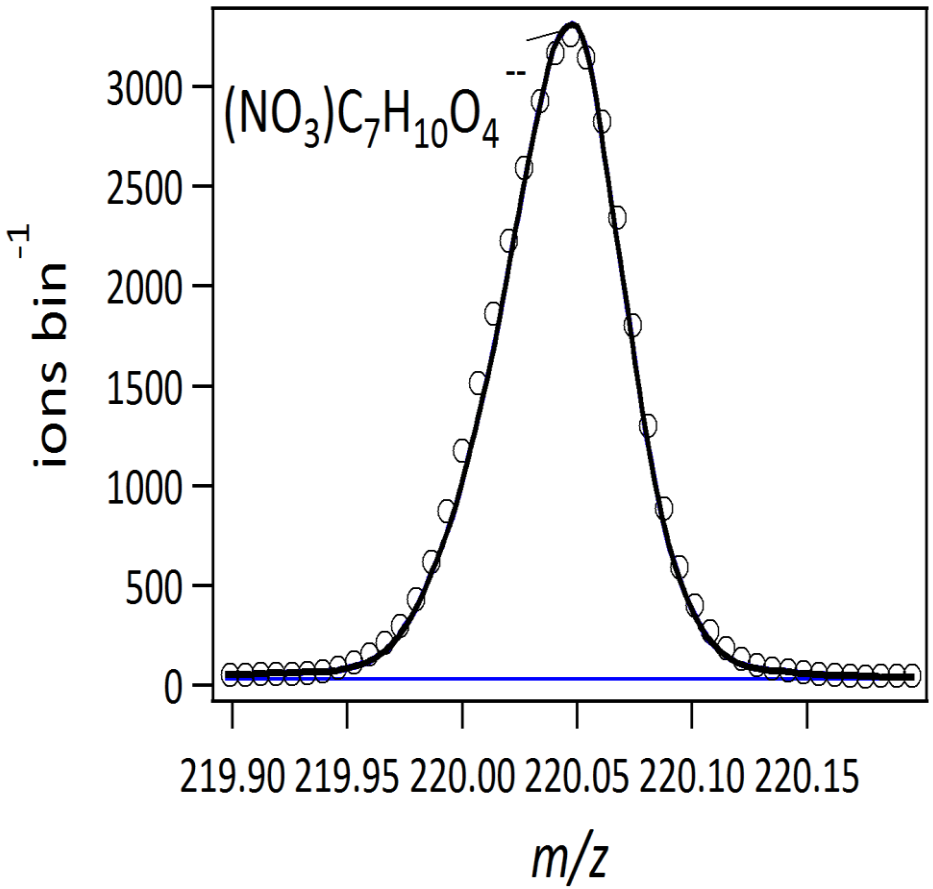

*m/z* 339

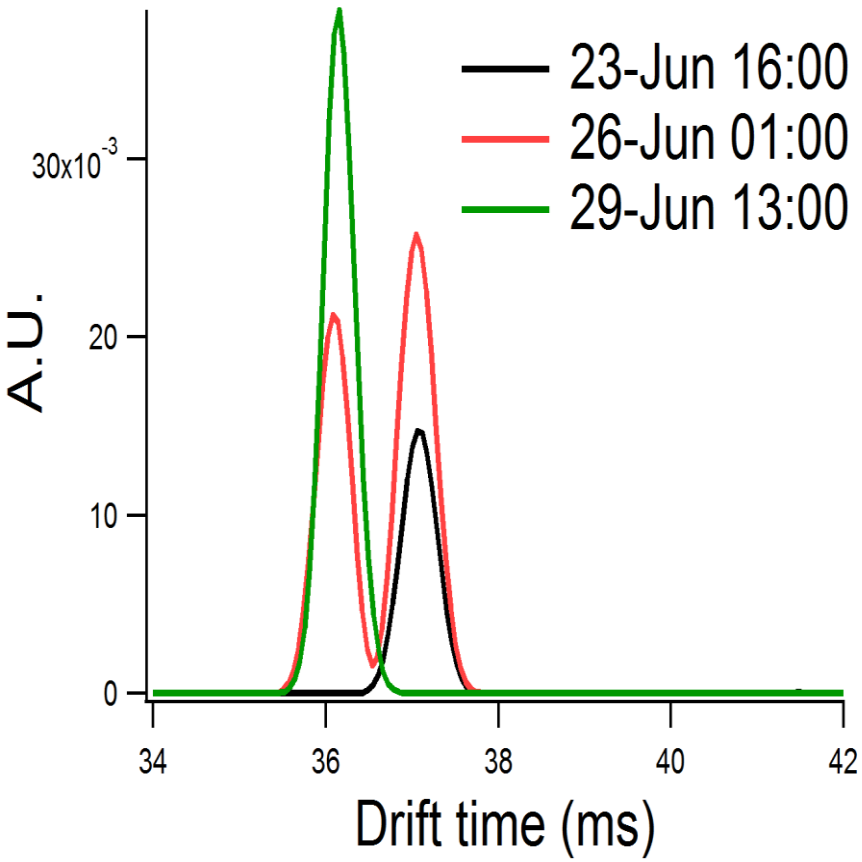



HOMs in ambient environment (SOAS 2013)

Krechmer et al., Atmos. Meas. Tech., 9, 3245–3262, 2016

# Time-resolved isomer trends (CI-IMS)



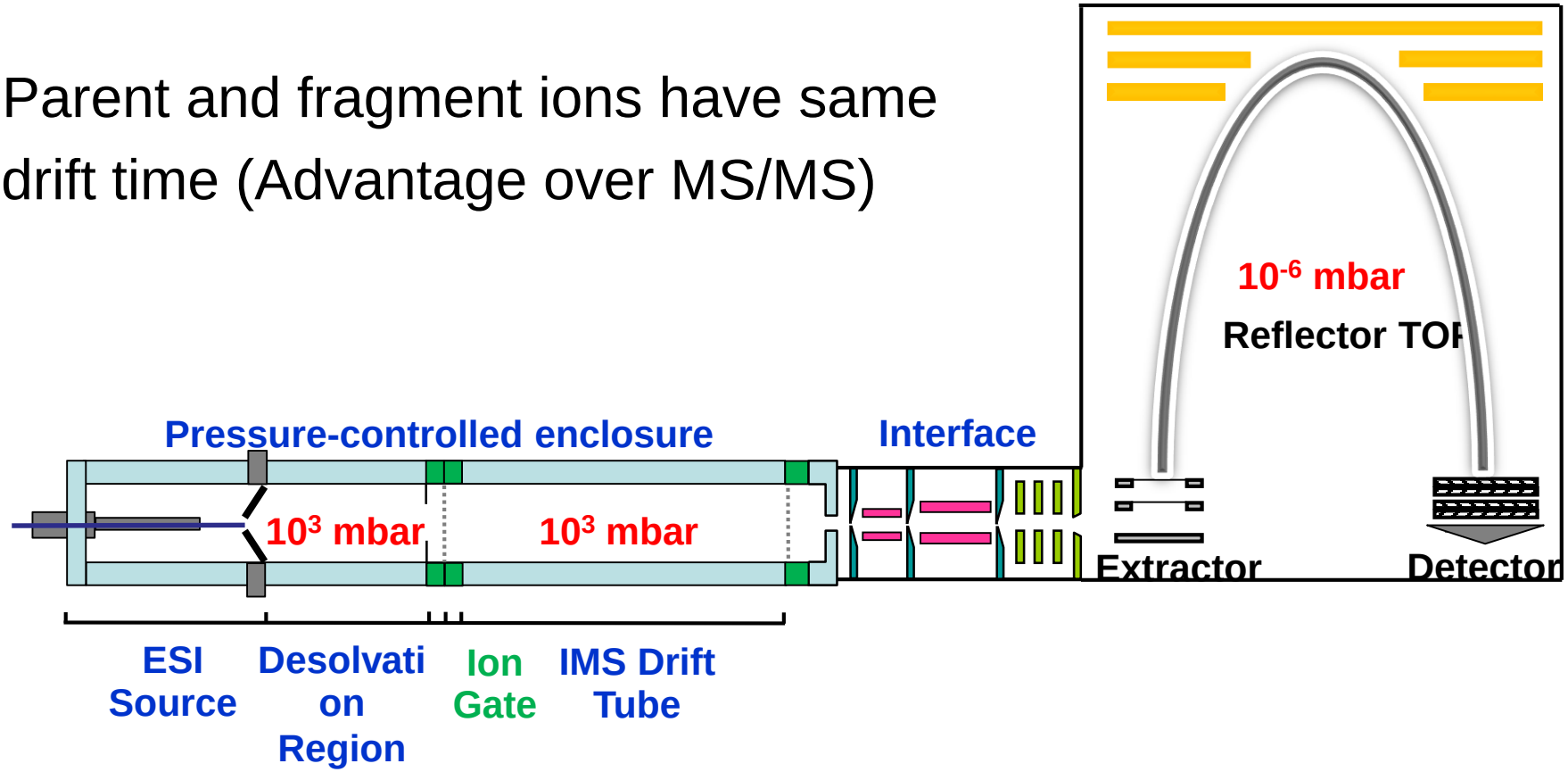

Ambient environment (SOAS 2013)

Krechmer et al., Atmos. Meas. Tech., 9, 3245–3262, 2016

# Collision Induced Dissociation

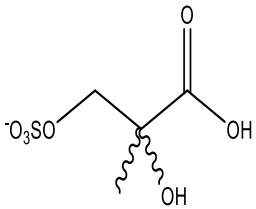
- Increase kinetic energy of ions exiting drift tube such that bonds within ion are broken during ion-molecule collisions with buffer gas in interface region.

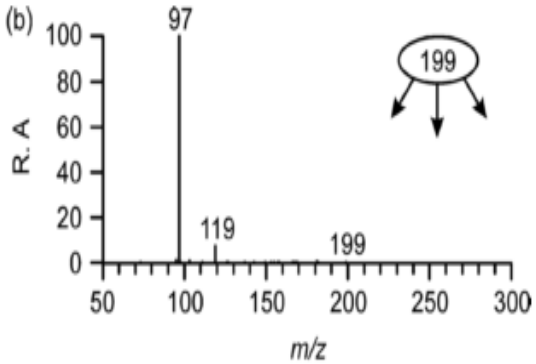
- Parent and fragment ions have same drift time (Advantage over MS/MS)

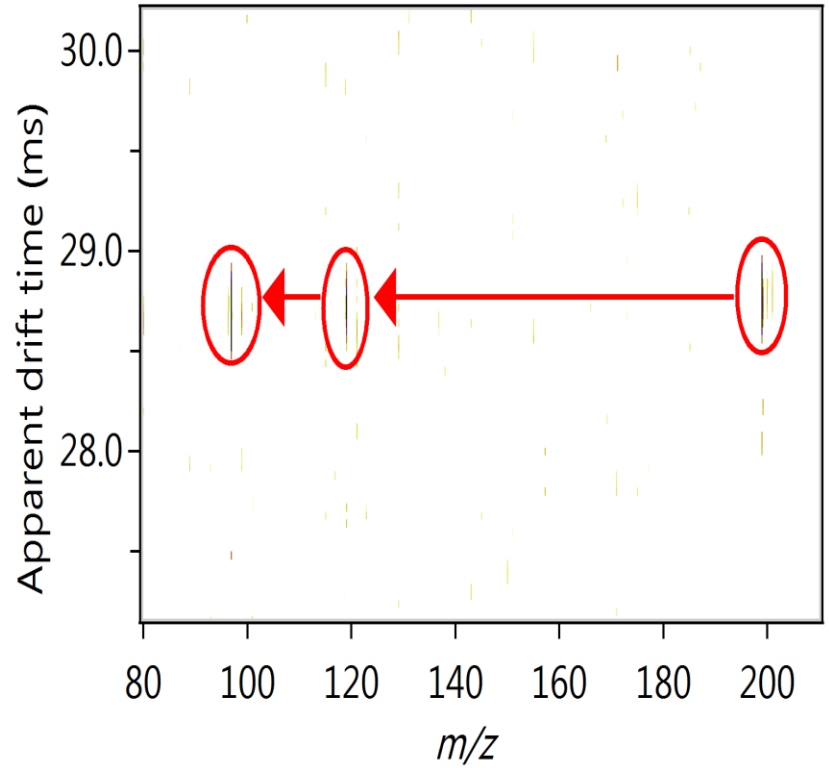


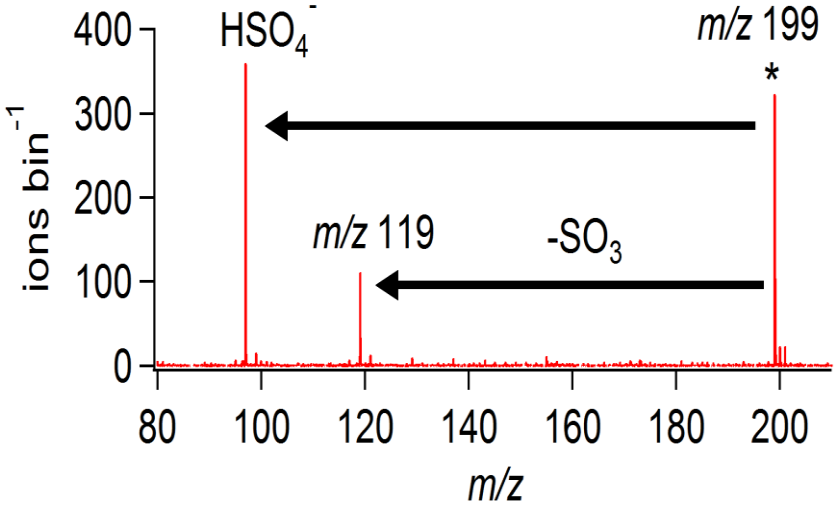
# CID for molecular structure (ESI-IMS)

sulfate ester of 2-methylglyeric acid



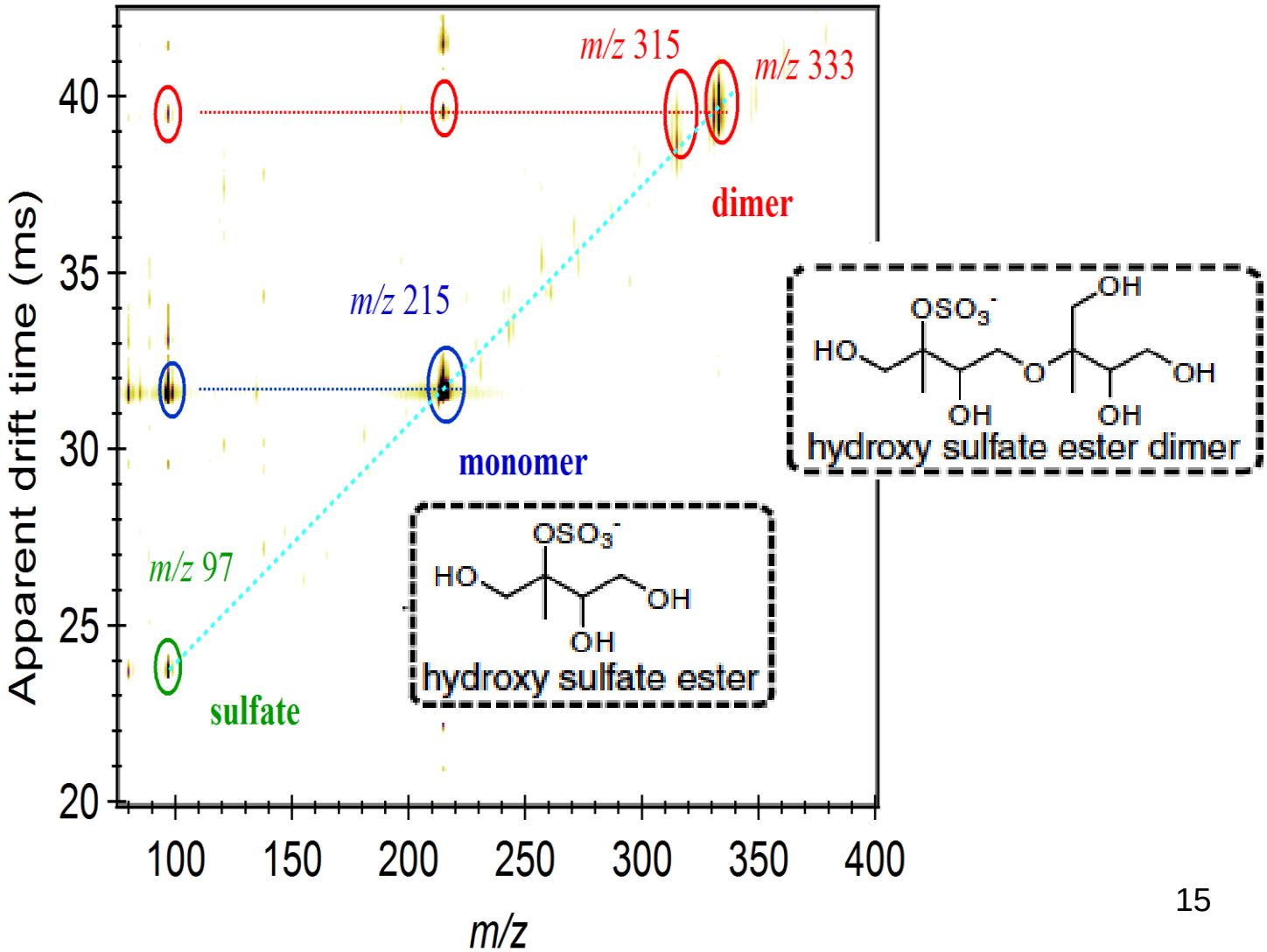



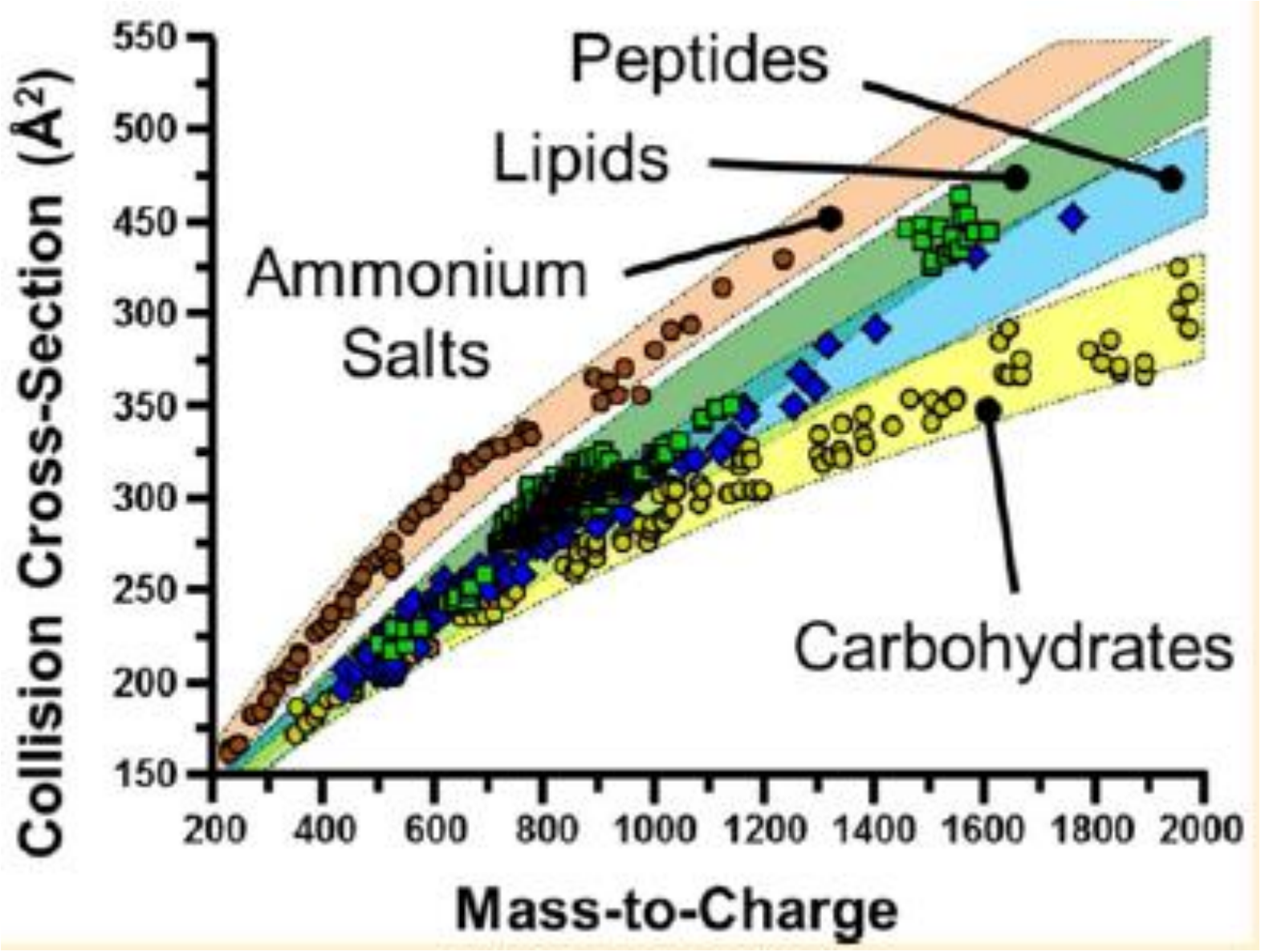




From: Gómez-González, et al. *J. Mass Spectrom.* **2008**, *43*, 371–382.

# CID for detecting oligomers (ESI-IMS)

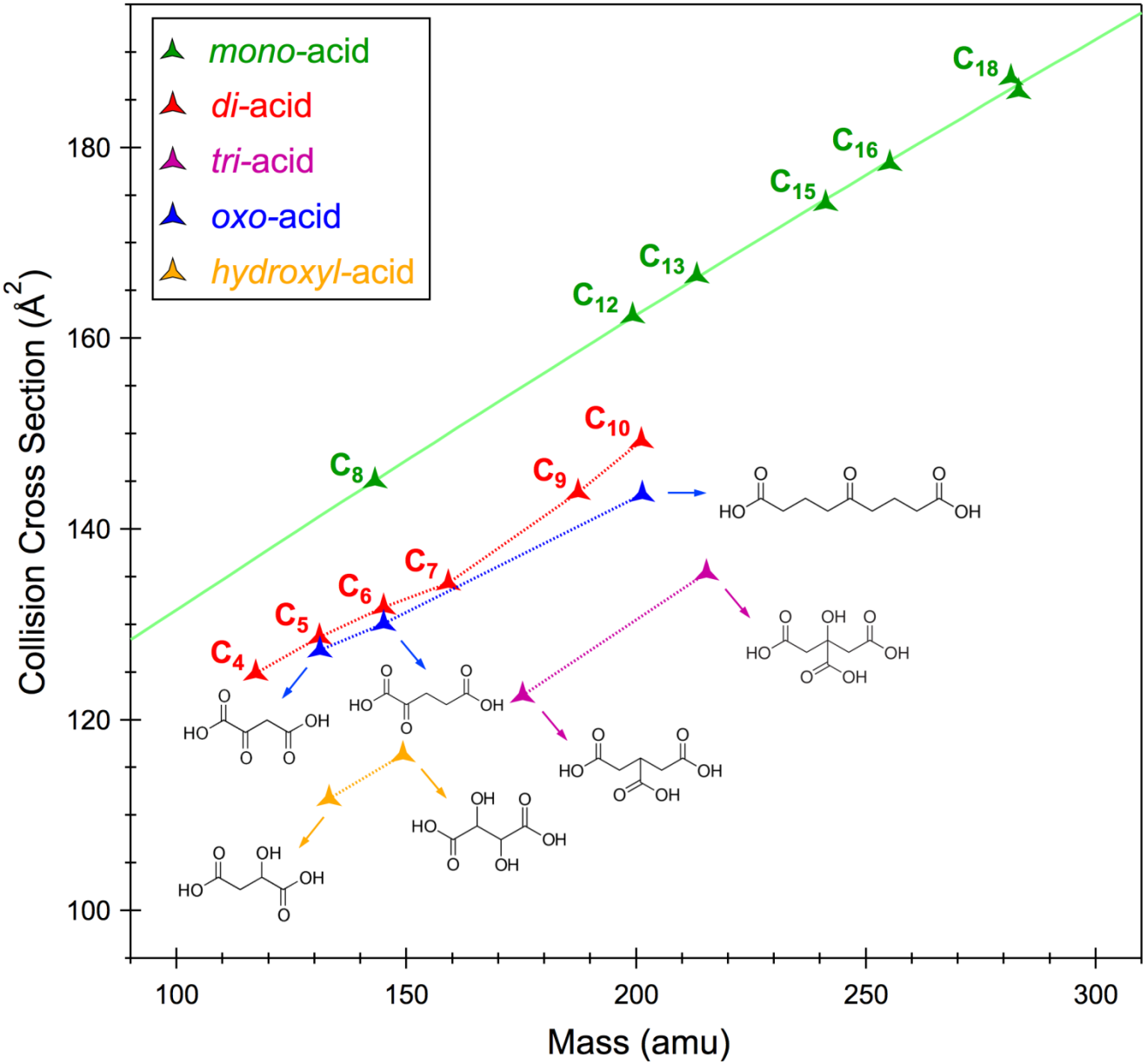


# 2D Trends for biomolecules




From
Ion Mobility Mass Spectrometry, By Eiceman and Karpas

# 2D Trends for small molecules




Clear separation in space according to molecular functionality

Zhang X., et al., Atmos. Chem. Phys., 16, 12945–12959, 2016

# Conclusions

- IMS-MS provides 2D (cross section vs. *m/z*) characterization of chemical composition.
- Can be used for gas (CIMS) and particle (ESI) characterization. Demonstrated for ambient real-time operation.
- Separates isobaric and isomeric species that correspond to an elemental formula
- CID allows for identification of molecules and for detection of oligomers
- Species with different chemical functionalities separate from each other in 2D space.

# Thank you for listening!

<u>References with more information</u>


- Krechmer et al., Ion mobility spectrometry–mass spectrometry (IMS–MS) for on- and offline analysis of atmospheric gas and aerosol species, *Atmos. Meas. Tech.*, **9**, 3245–3262, 2016
- Zhang X. et al., A novel framework for molecular characterization of atmospherically relevant organic compounds based on collision cross section and mass-to-charge ratio, *Atmos. Chem. Phys.*,**16**, 12945–12959, 2016
- Zhang X. et al., Highly Oxygenated Multifunctional Compounds in α-pinene Secondary Organic Aerosol, Env. Science and Technology, 2017