Synapt G2 – ion mobility approach

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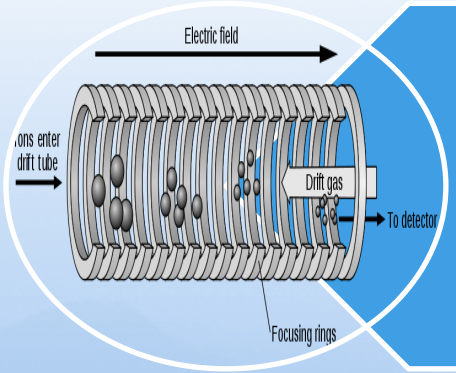
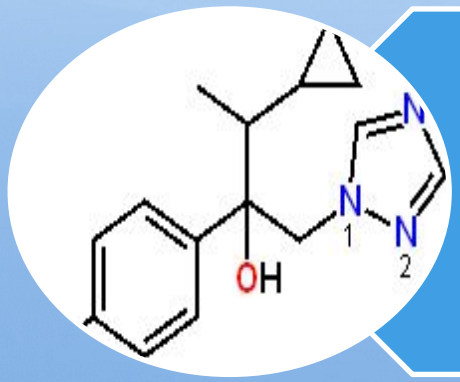
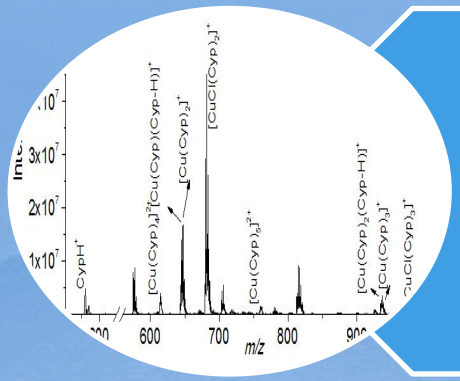
Miniškola hmotnostní spektrometrie



IMS theory

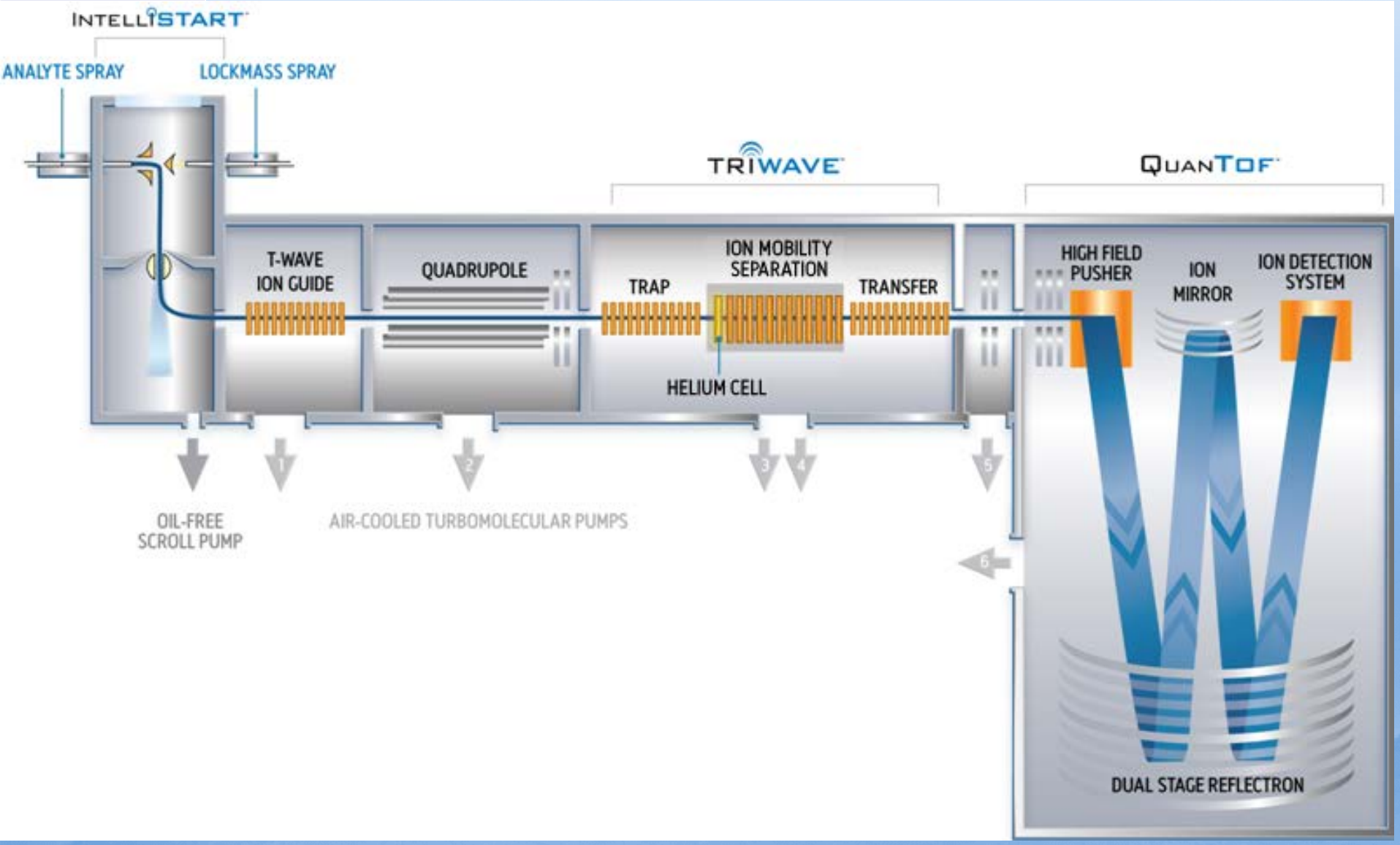


Separation of izobaric species

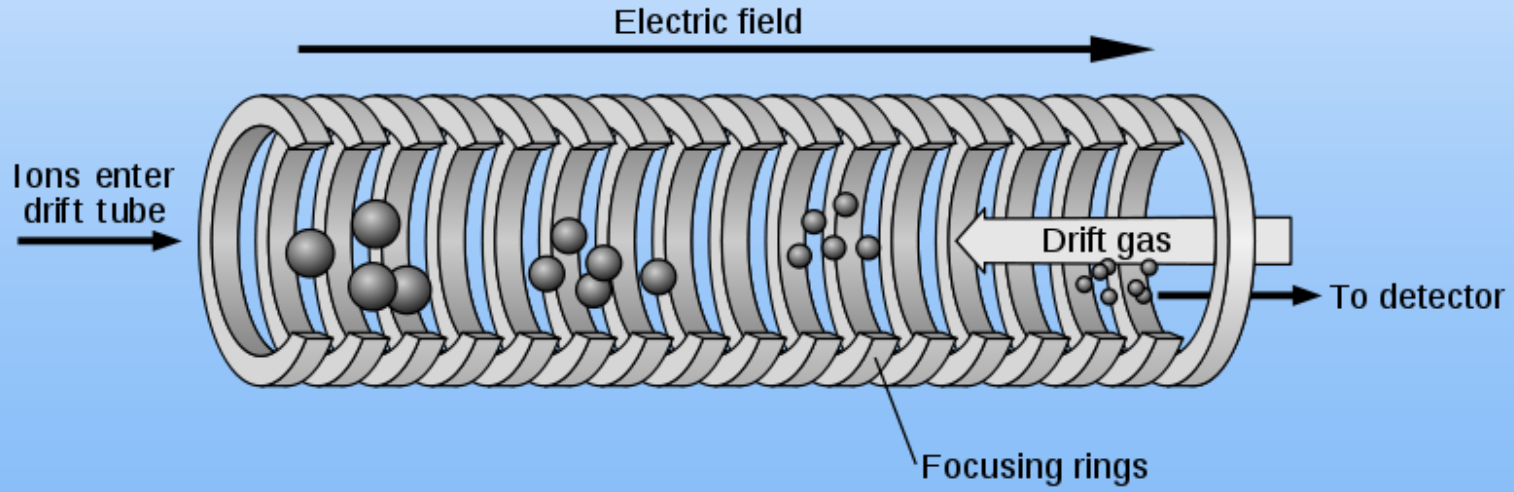


Determination of collision area

SYNAPT G2 Optics



The principle of IMS



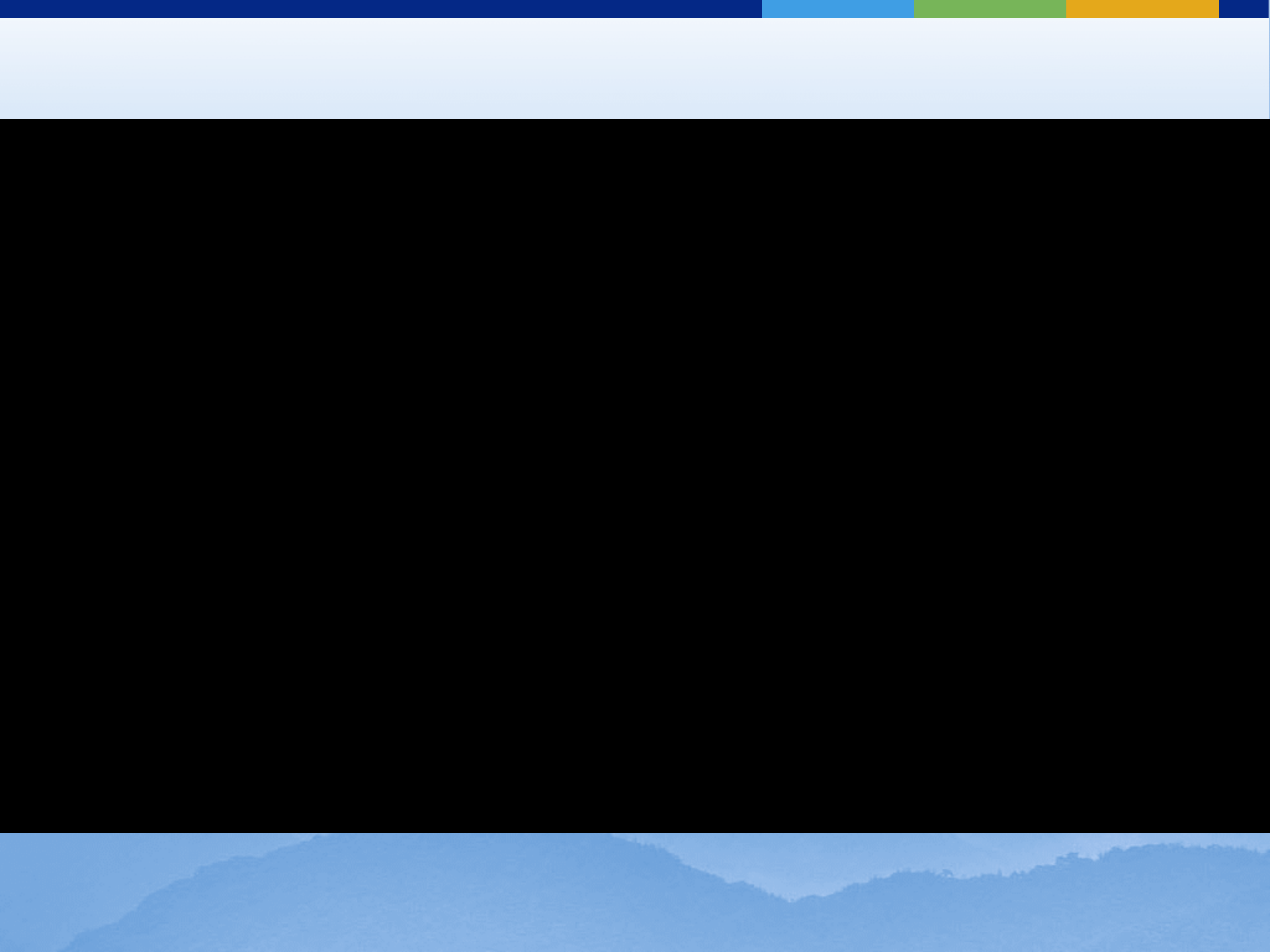
Chaotic sequence of accelerations and collisions

Molecular level

Constant ion velocity

Macroscopic distances

$$v = \frac{L}{t_D} = KE$$



The principle of IMS

$$K = \frac{3e}{16N}\sqrt{\frac{2\pi}{\mu k_B T}}\frac{1}{\Omega}$$

- e is the ion charge,
- N is the gas number density,
- μ is the reduced mass,
- k_B is Boltzmann's constant,
- T is the absolute temperature
- Ω is the collision cross section (also called collision momentum transfer integral), **Mason-Schamp** equation and is derived from the kinetic theory, more specifically from **Boltzmann transport equation**.

Mason E. A., Schamp H. W.: *Ann. Phys. 4, 233-270, (1958).*

approximation

$$K = \frac{3e}{16N}\sqrt{\frac{2\pi}{\mu k_B T}}\frac{1}{\Omega}$$

- The electric field is considered weak if the average energy gained by ions from this field is comparable to their thermal energy.
- The speed of the ion will be affected mainly by its size and charge.
- The acceleration gained by the electrical field depends on the mass of the ion and also on the mass of the buffer gas.
- The deceleration by collisions must be temperature dependent, because at different temperatures buffer gas molecules have different momentum.
- Also higher buffer gas density means larger deceleration effect.

- 1) low ion concentrations and thus negligible ion-ion interactions;
- 2) only two-particle collisions are considered;
- 3) the collisions are elastic;
- 4) ion-molecule force law is spherically symmetric;
- 5) quantum effects are neglected.

Structure of ions

$$\Omega = \frac{3e}{16N}\sqrt{\frac{2\pi}{\mu k_B T}}\frac{760}{p}\frac{T}{273.15}\frac{t_D E}{L},$$

$$K_0 = \frac{760}{p}\frac{T}{273.15}\cdot K$$

Ω_{exp} Ω_{calc}

Ω

The reduced mobility is used, because it is independent from the buffer gas number density.

DT IMS x FAIMS x TW IMS

Drift tube IMS

- Linear dependence of transit time on mobility
- Direct calculation

Field asymmetric IMS

- Non-linear dependence of transit time on mobility
- Spectral calibration

Traveling wave IMS

Calculation of Ω for TW IMS

$$\Omega = \frac{3e}{16N}\sqrt{\frac{2\pi}{\mu k_B T}}\frac{760}{p}\frac{T}{273.15}At_D{}^{B},$$

A …field parameters
B …nonlinear behaviour

Shvartsburg A. A., Smith R. D.: *Anal. Chem. 80, 9689-99, (2008)*
Giles K., Wildgoose J. L., Langridge D. J., Campuzano I.: *Int. J. Mass spectrom. 298, 10-16, (2010)*

modeling

The first order orientationlly-averaged collision integral?

$$\Omega_{avg}^{(1,1)} = \frac{1}{8\pi^2}\int_0^{2\pi} d\Theta \int_0^{\pi} d\phi \sin\phi \int_0^{2\pi} d\gamma \frac{\pi}{8}\left(\frac{\mu}{k_B T}\right)^3 \times \int_0^{\infty} dg\, e^{-\frac{\mu g^2}{2k_B T}} g^5 \int_0^{\infty} db\, 2b(1-\cos\chi(\theta,\phi,\gamma,g,b))$$

- Θ, Φ, γ are the angles defining the geometry between the ion and the buffering gas molecule/atom,
- g is the relative velocity,
- b is the impact parameter,
- χ is the scattering angle.

Modeling
1st approach

Projection Approximation (PA)

$$\Omega_{avg}^{(1,1)} = \frac{1}{4\pi}\int_0^{\pi} \mathrm{d}\phi \sin\phi \int_0^{2\pi} \mathrm{d}\gamma\, \Omega_{dir}(\phi,\gamma),$$

where the directional cross section is calculated as:

$$\Omega_{dir}(\phi,\gamma) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} M(\phi,\gamma,y,z)\mathrm{d}y\,\mathrm{d}z$$

$$M(\varphi,\gamma,y,z) = \begin{cases} 1 - collision \\ 0 - no\ collision \end{cases}$$

- The integral Ω_{dir} is usually obtained by Monte Carlo integration.
- The PA method differs from experimental values significantly when the ion of interest is partially concave or when the Van der Waals forces are strong.

von Helden G., Hsu M. T., Gotts N., Bowers M. T.: *J. Phys. Chem. 97, 8182-8192, (1993).*

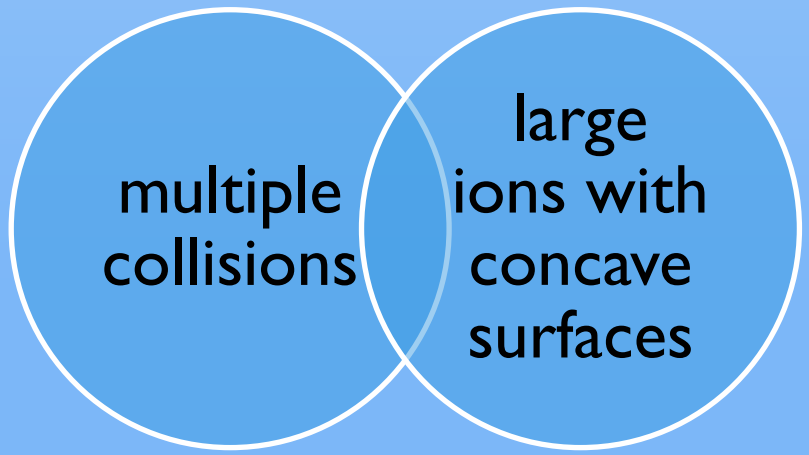
Modeling 2nd approach

Hard Sphere Scattering Model (EHSS)

$$\Omega_{avg}^{(1,1)} = \frac{1}{4\pi}\int_0^{\pi} d\phi \sin\phi \int_0^{2\pi} d\gamma\, \Omega_{dir}(\phi,\gamma),$$

where the directional cross section is calculated as:

$$\Omega_{dir}(\phi,\gamma) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}[1 - \cos\,\chi(\varphi,\gamma,y,z)]dy\,dz$$



Shvartsburg A. A., Jarrold M. F.: *Chem. Phys. Lett. 261, 86-91, (1996).*

Modeling 3rd approach

Trajectory Method (TM)

- The calculation of trajectories in realistic potential model is made by numerical integration of the **equations of motion**.
- The potential model used is usually an extension of **Lennard-Jones potential** by ion-induced dipole interaction.
  - In case of nitrogen as a buffer gas, ion-induced quadrupole interaction should be also considered.
- This approach is implemented in freely available software **MOBCAL**.

Jarrold M. F.: http://www.indiana.edu/~nano/software.html (accessed 29. 6. 2012).
Mesleh M. F., Hunter J. M., Shvartsburg A. A., Schatz G. C., Jarrold M. F.: *J. Phys. Chem. 100, 16082-16086, (1996).*

Examples

How to use Synapt?

4-butylalanin vs N-butylanilin

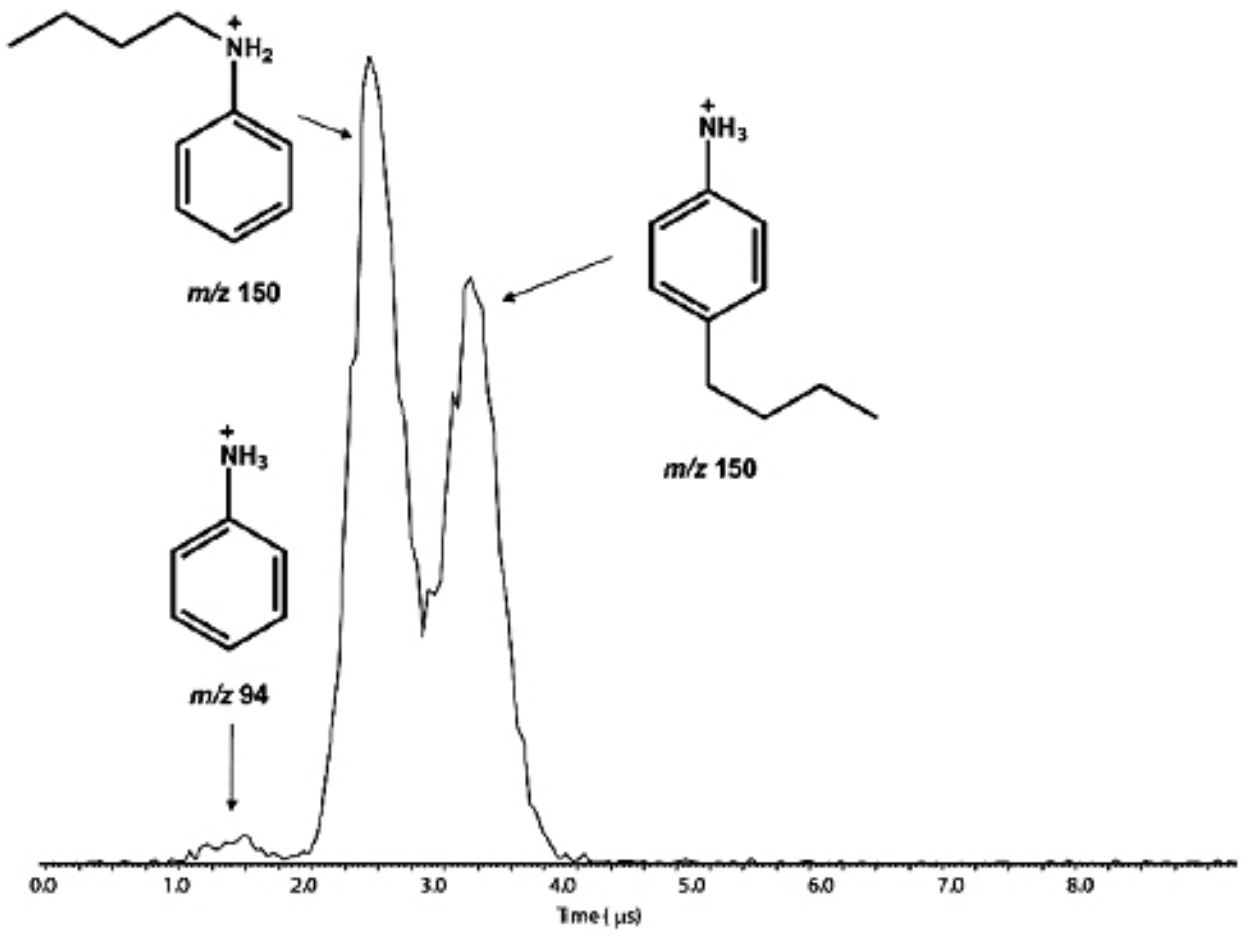
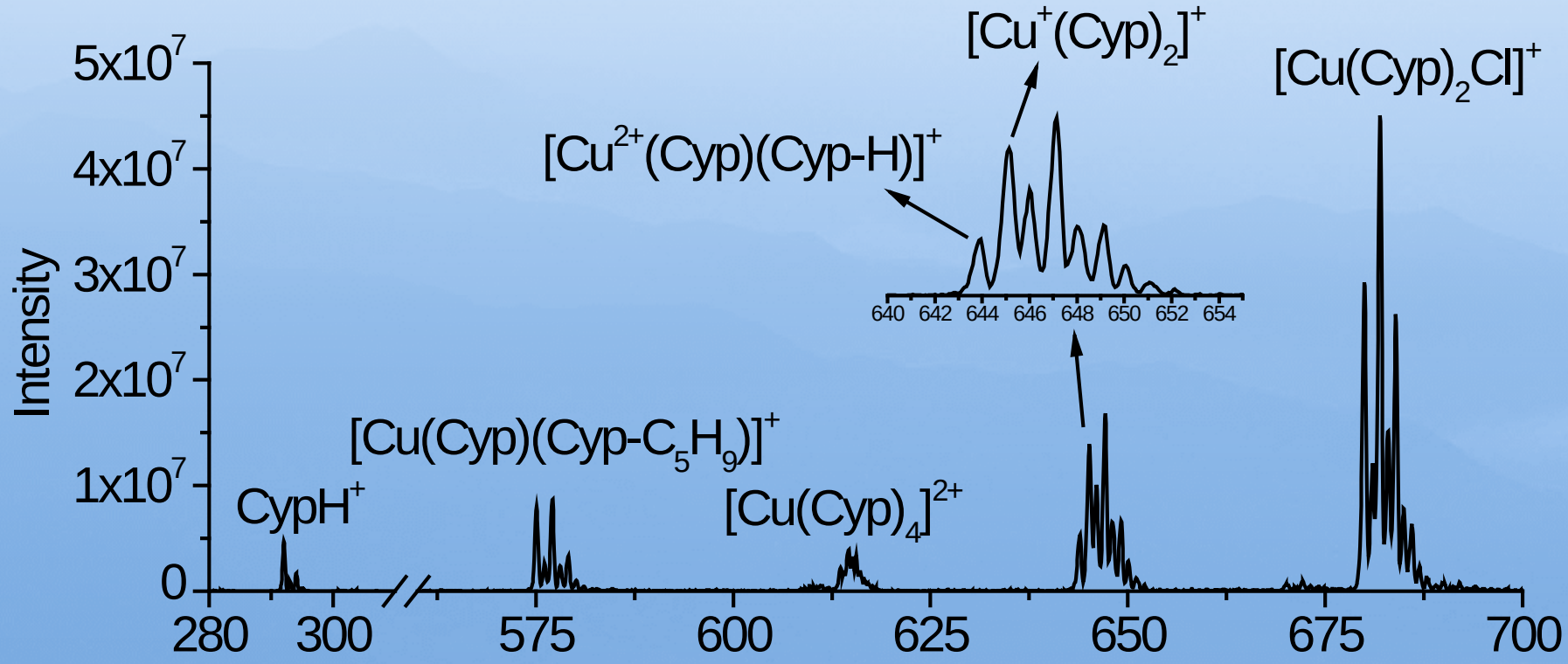
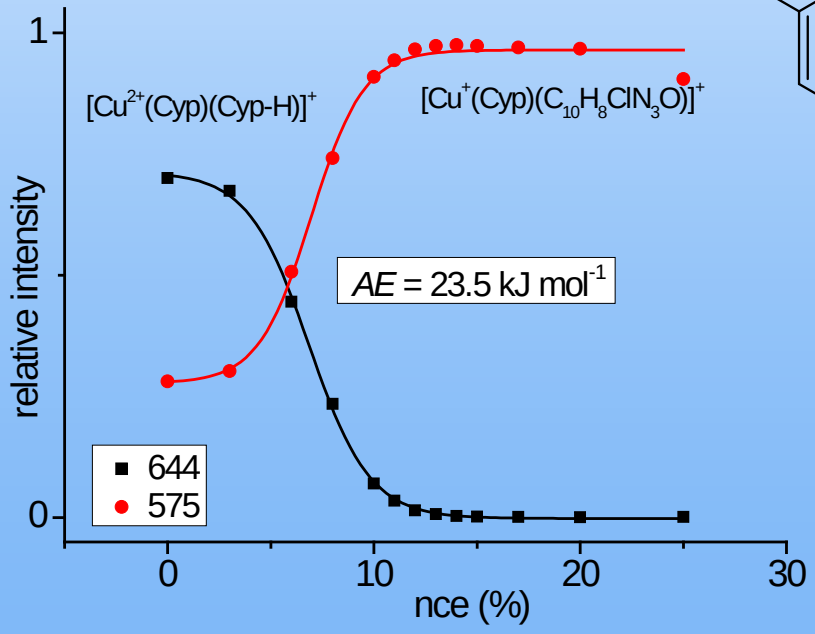


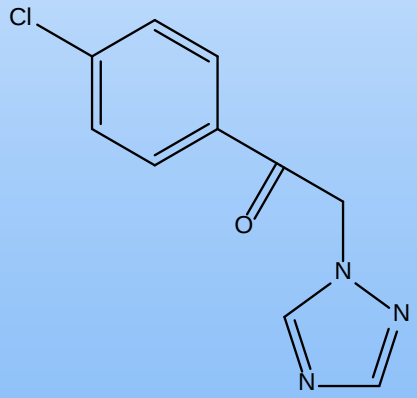
Figure 5. MS/TWIMS/MS chromatogram of a mixture of the protonated molecules of the isomeric 4-butylaniline and *N*-butylaniline of *m/z* 106.

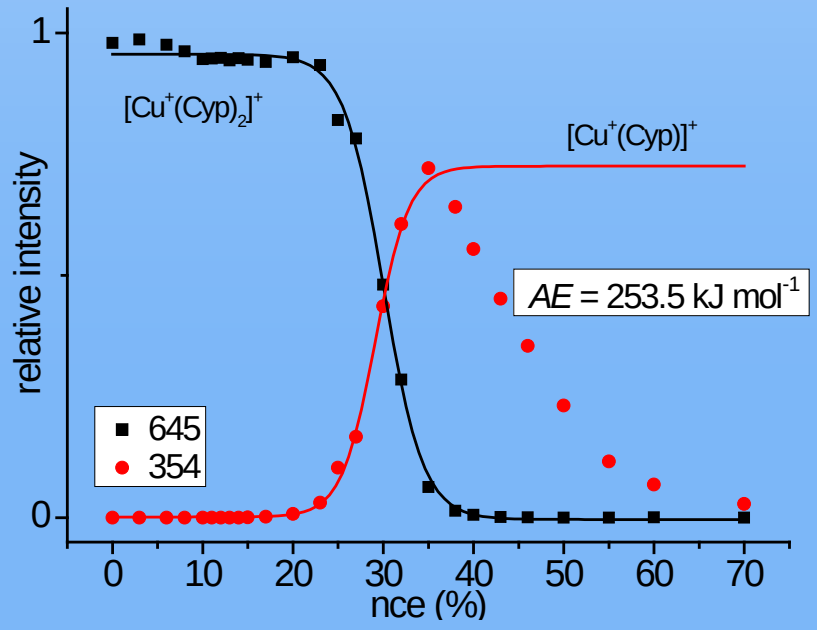


Positive mode ESI mass spectrum in the range from *m/z* 280 to 700 of an equimolar mixture of cyproconazole (Cyp) and $CuCl_2$ (both $5 \cdot 10^{-5}$ mol L^{-1}) methanol/water (1:1). The mixed isotope pattern $[Cu^{2+}(Cyp)(Cyp\text{-}H)]^+$ and $[Cu^{+}(Cyp)_2]^+$ is shown in an expanded mass scale.

Collision experiments







Cross section (Ω)

complex	m/z	Ω_{exp} (Å)	Ω_{calc} (Å)
$CypH^+$	291.93	125.37	117.68
$[Cu^+(Cyp)(C_{10}H_8ClN_3O)]^+$	575.05	208.48	192.12
$[Cu^+(Cyp)_2]^+$	645.18	221.57	205.61

Conclusion

Exact mass measurement

Separation of isobaric species

Cross section area – structure assessment