

Collision Cross Section:

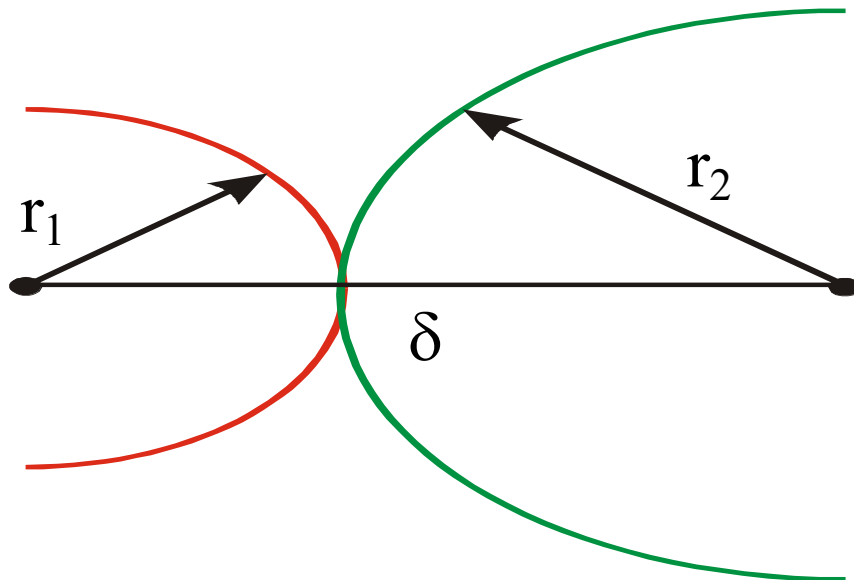
Ideal elastic hard sphere collision:

$$\Omega = \pi (r_1 + r_2)^2$$

Where Ω is the collision cross-section

$$\delta = r_1 + r_2 = \left(\frac{\Omega}{\pi} \right)^{\frac{1}{2}}$$

Where δ is the collision distance



These equations neglect potential interactions between the two molecules (atoms), attractive and repulsive, and assume spherical geometry.

Mean Free Path (λ):

#collisions per unit time:

$$Z_1 = \pi d^2 \langle v \rangle N$$

Mean free path (length b/w collisions)

$$\lambda = \frac{\langle v \rangle}{Z_1} = \frac{\langle v \rangle}{\pi (r_1 + r_2)^2 \sqrt{2} \langle v \rangle N}$$

$$\lambda = \frac{1}{\pi (r_1 + r_2)^2 \sqrt{2} N}$$

Motion in an Applied Field

(Maxwellian ions)

$$v_d = KE$$

v_d =drift velocity(cm/sec)

K =mobility(cm^2/Vsec)

E =applied field (V/cm)

Langevin Equation:

$$K = \frac{e\lambda}{m v}$$

e =ionic charge(Volts)

λ =mean free path(m)

Assumptions: ignoring coulombic interaction,
Low field limit, close to thermal equilibrium.

Deriving the Nernst-Townsend-Einstein Relation (Einstein Relation):

At equilibrium, the space distributions of ions is given by the Boltzman distribution:

$$n = n_o e^{\frac{eEr}{kT}}$$

Differentiating yields:

$$\frac{1}{n} \nabla n = \frac{eE}{kT}$$

Substitution into the linear transport equation and setting $J=0$ gives the Einstein relation:

$$K = \frac{eD}{kT}$$

Particle Parameters:

B = Mechanical mobility

D = Diffusion coefficient

K = Electric mobility

Relation:

$$D = kTB$$

$$K = qB$$

Nernst-Townsend-Einstein Relation:

$$K = eD/kT$$

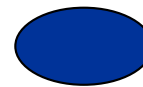
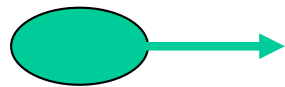
Once again, this only holds true at low fields. We make the assumption that ion's temperature is thermal.

Number Density (N) and Applied Field (E)

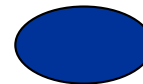
Dependency:

Both K and D are inversely proportional to N at these low fields.

However, at higher applied fields, E is now a factor.

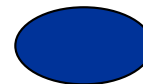


$$\frac{E}{N}$$



$$\frac{2E}{N}$$

Arrives at the buffer gas faster with more collision energy



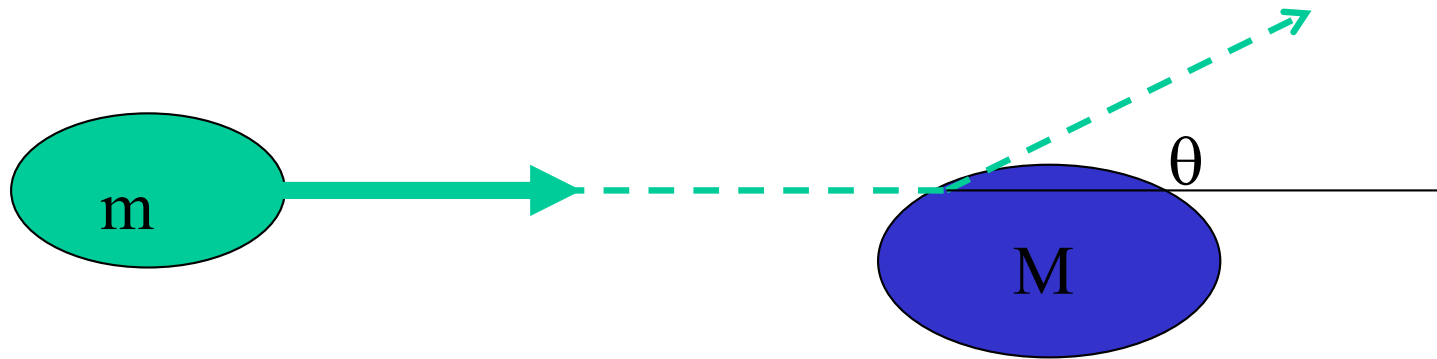
$$\frac{2E}{2N}$$

Now arrives at the buffer gas at half the distance with the same speed and collision energy as the first E/N.

At all fields, we can see that drift velocity, mobility, and diffusion are better characterized with the E/N ratio.

Momentum:

$$p = mv \quad (\text{kgm/s})$$



$$\delta = \mu v_{rel} (1 - \cos(\theta))$$

Where, δ is the momentum transferred, v_{rel} is the relative velocity b/w collision bodies, and θ is deflection angle.

$$\mu = \frac{mM}{m + M}$$

Where, μ is the reduced mass.

Collision Frequency:

Spherical:

$$Z_{12} = \pi b_{\max}^2 \langle \mathbf{v}_r \rangle N$$

Adding Momentum Transfer:

$$Z_{12} = Q_D(\varepsilon) \langle \mathbf{v}_r \rangle N$$

At low fields this is an easy calculation because the velocity of the ion (v) and the bath gas (V) are thermal. However, the field contributes to the velocity of the ion at higher fields.

Wannier equations for Diffusion in high E/N:

Weak Field $D(0)$:

Einstein Relation:

$$K = \frac{eD}{kT}$$

Mobility Equation:

$$v_d = KE$$

So,

$$D(0) = \frac{v_d kT}{eE}$$

Wannier equations for Diffusion in high E/N:

High Field D:

$$D_{T,L}(E) = D(0) + \xi_{T,L} \left(\frac{mM}{m+M} \right) \frac{v_d^3}{eE}$$

$$\xi_T = \frac{1}{3} \frac{(M+m)^2}{m(M+2m)}$$

$$\xi_L = \frac{1}{3} \frac{(M+m)(M+4m)}{m(M+2m)}$$

Representative Mobility Equations

$$v_d = KE_o$$

Mobility is Defined
As:

$$K_o = \frac{p}{760} \frac{273.15}{T} K$$

Where the reduced
mobility is:

$$K = \frac{e}{N} \left(\frac{1}{3\mu k_b T} \right)^{\frac{1}{2}} \frac{1}{\Omega}$$

The celebrated mobility
Equation:

Representative Mobility Equations

$$v_{rel}^2 \gg \frac{3kT}{\mu}$$

What happens when the relative velocity is greater than thermal?

$$v_{rel}^2 = \frac{eE_o}{N\mu\Omega} \left(\frac{2m}{\lambda\mu} \right)^{\frac{1}{2}}$$

Field induced relative velocity.

Where λ is the relative energy loss for the collision event.

$$K = \left[\frac{e}{E_o N \Omega} \frac{M + m}{M^2} \right]$$

High field mobility equation:

Resolution

So the variance is:

$$\sigma = \sqrt{2Dt_d}$$

HWHM (half width at half max) is 1.17σ , and
FWHM (full width at half max) is 2.35σ .

$$FWHM = W_{1/2} = 2.35\sigma = 3.32\sqrt{Dt_d}$$

Resolution is defined as the ratio of the traveled distance (L) to the peak width at half height ($W_{1/2}$).

$$R = \frac{L}{W_{1/2}}$$

Resolution

Using the drift velocity equation:

$$v_d = KE_o = \frac{L}{t_d}$$

Substituting in the resolution equation for L:

$$R = \frac{t_d KE_o}{3.32 \sqrt{Dt_d}}$$

And simplify:

$$R = \frac{KE_o t_d^{\frac{1}{2}}}{3.32 D^{\frac{1}{2}}}$$

Resolution

We then arrive at the Nernst-Townsend-Einstein Equation, sometimes referred to as the Einstein relation:

$$K = \frac{qD}{k_b T}$$

The main assumption of the Einstein relation is that mobility theory (motion acting on one species, but not the other) and diffusion theory are at equilibrium. Wannier no longer assumed that the applied field was weak and the ion mass was small.

$$D_{\perp} = K \frac{k_b T}{q} + \frac{m}{3} \frac{m + M}{m + 1.908M} \frac{E^2 K^3}{q}$$

$$D_{\parallel} = K \frac{k_b T}{q} + \frac{m}{3} \frac{m + 3.72M}{m + 1.908M} \frac{E^2 K^3}{q}$$

Resolution

At this point we can solve the resolution using either the Einstein relation or Wannier's relation. We will see from some of the future results that the maximum resolution is attained from systems that fit the Einstein relation. So, if we solve the resolution equation in terms of the Nernst-Townsend-Einstein equation:

$$R = \frac{L}{3.32 \sqrt{\frac{Kk_bT}{q} \frac{L}{KE_o}}} \quad (2.8)$$

Simplifies to for single charges ions:

$$R = 32.33 \sqrt{\frac{LE_o}{T}} \quad (2.9)$$

Resolution

Taking Wannier's
relation in the z
direction:

$$D_z = K \frac{k_b T}{q} + \frac{m}{3} \frac{m + 3.72M}{m + 1.908M} \frac{E^2 K^3}{q}$$

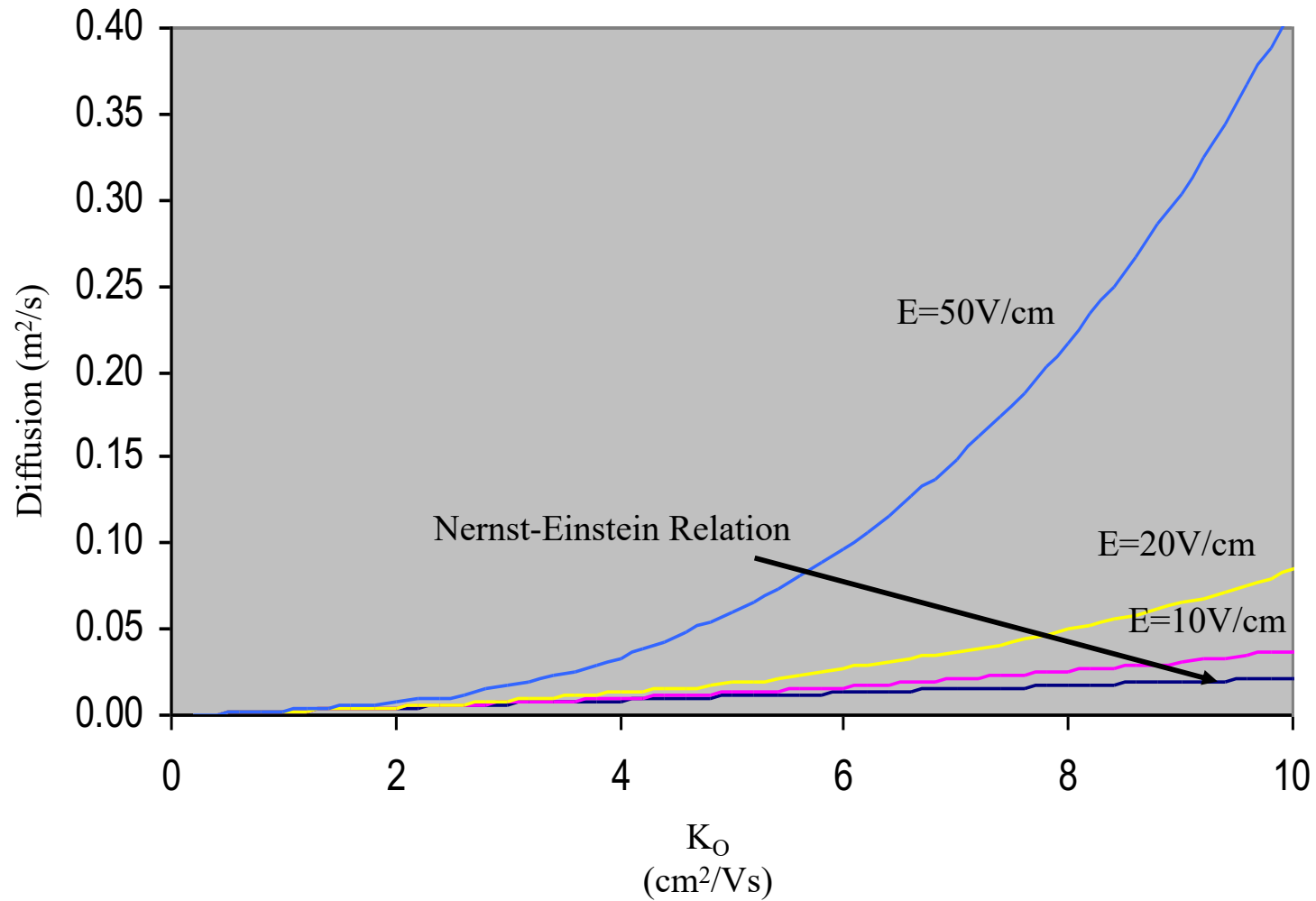
Simplify the mass
term in the relation:

$$\mu_w = \frac{m}{3} \frac{m + 3.2M}{m + 1.908M}$$

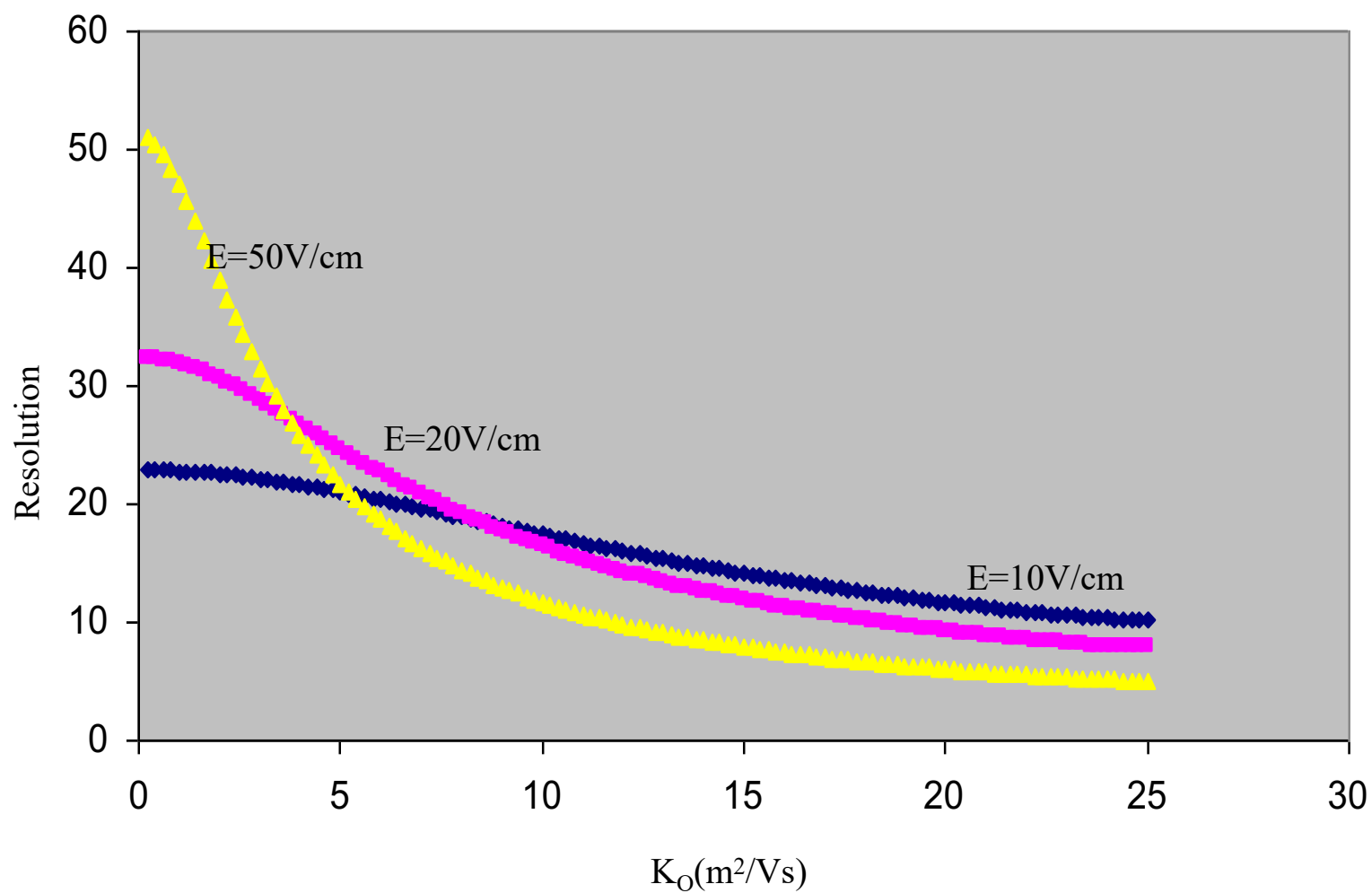
Resolution for a broader
range of fields:

$$R = \frac{E}{3.32} \sqrt{\frac{q K t_d}{k_b T + \mu_w E^2 K^2}}$$

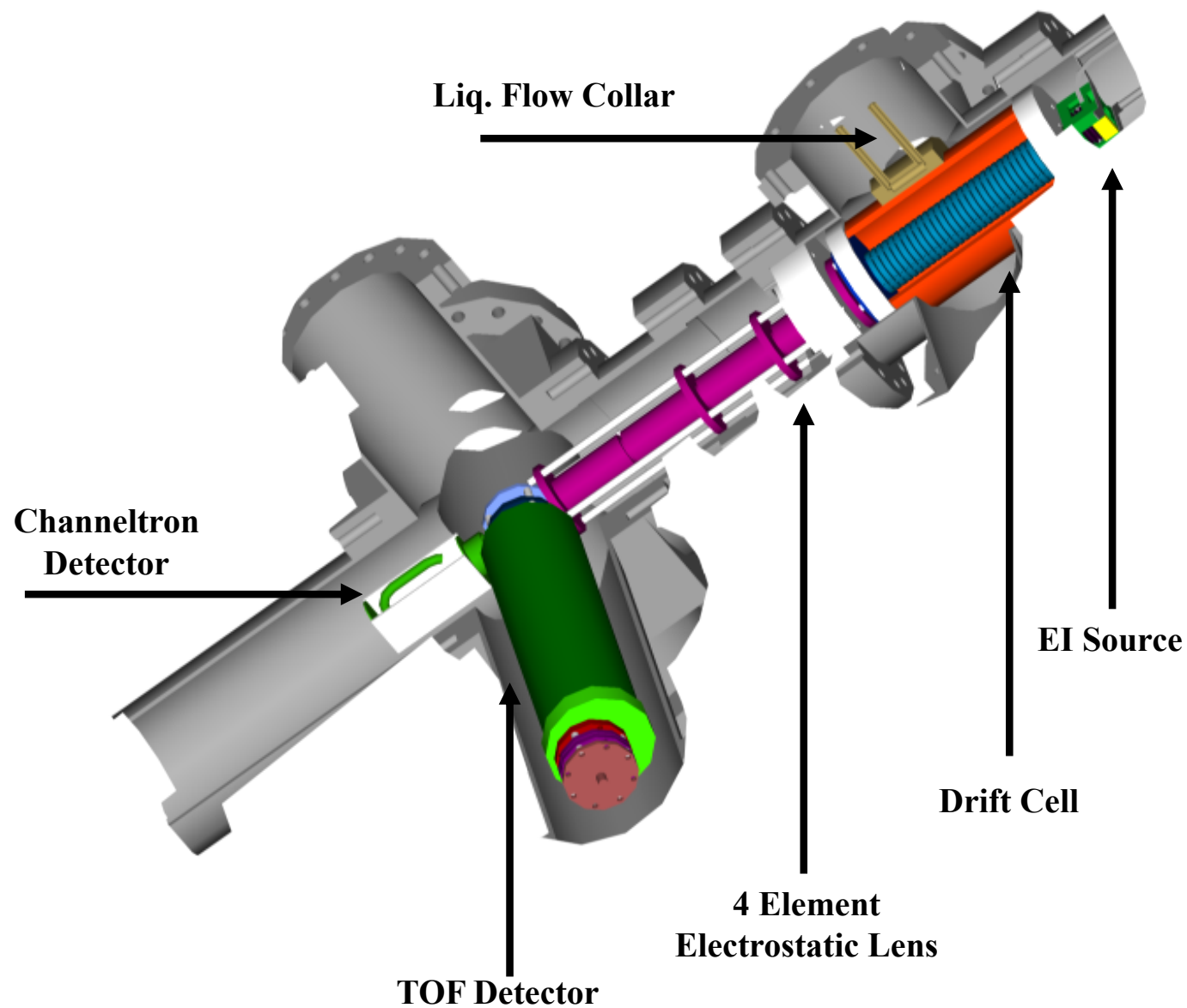
Wannier Relation, 15cm Drift Cell 1 Torr

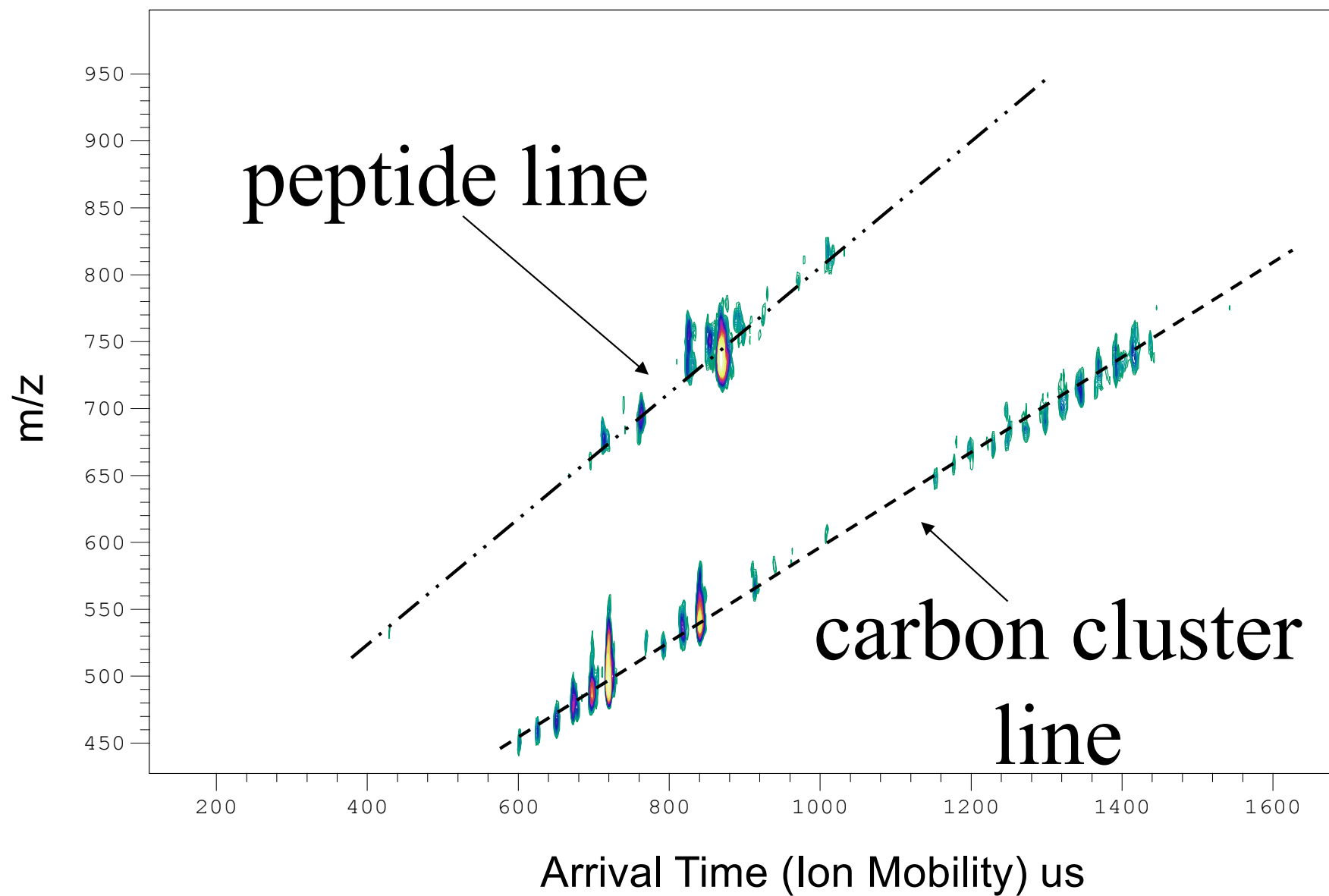


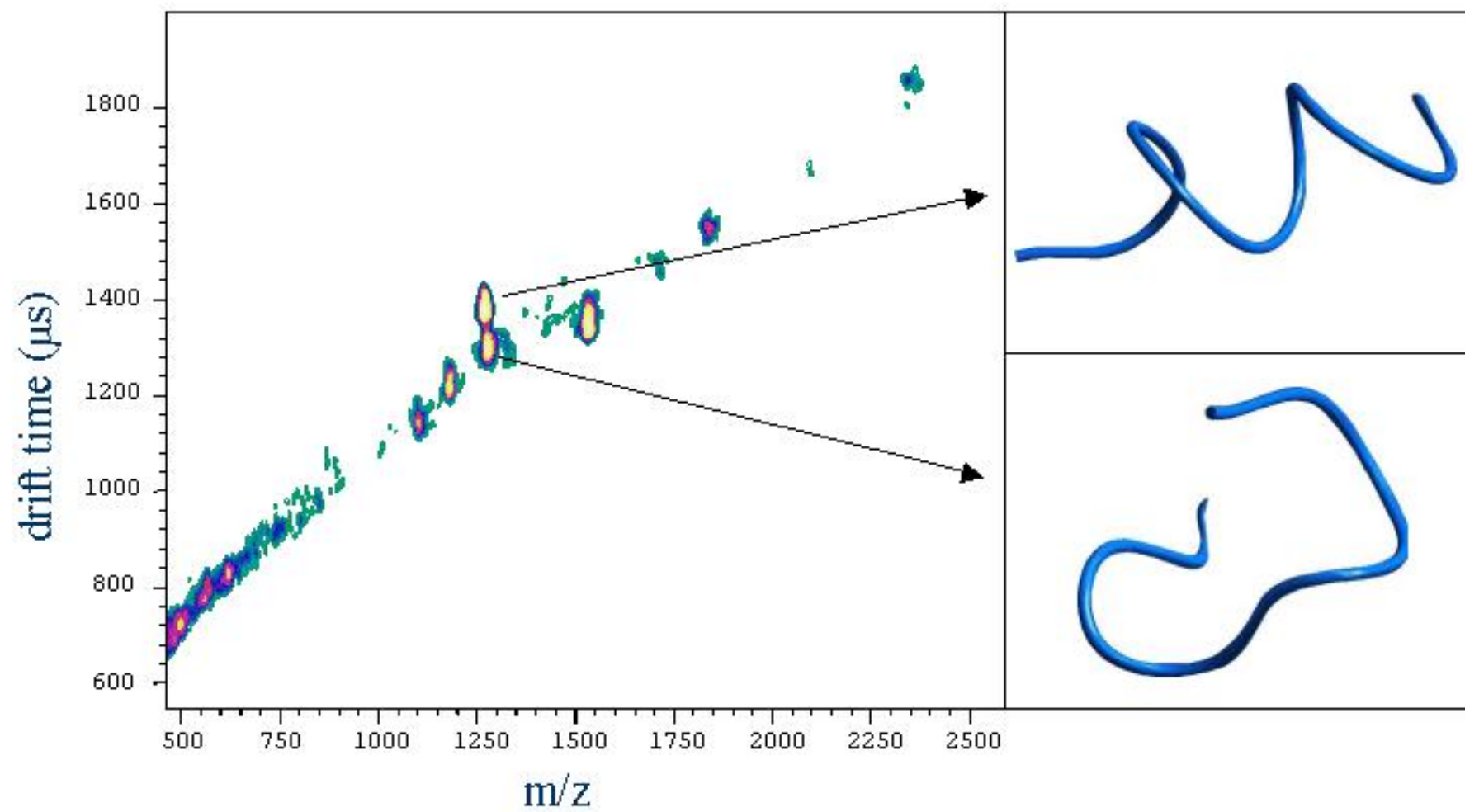
Comparison of Reduced Mobility vs. Resolution 1 Torr, 15cm Drift Cell

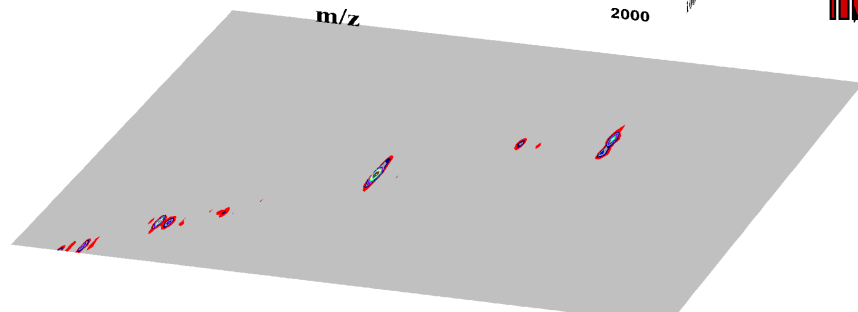
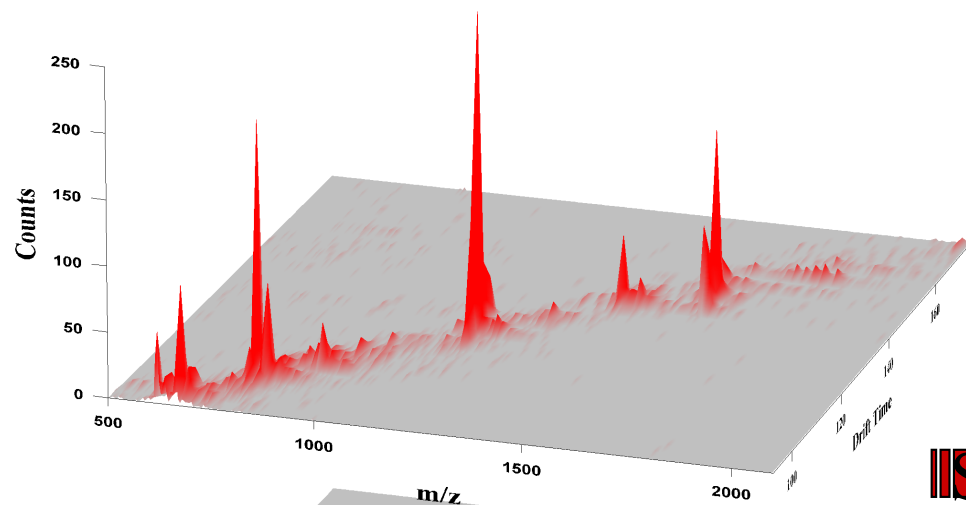


Instrumentation

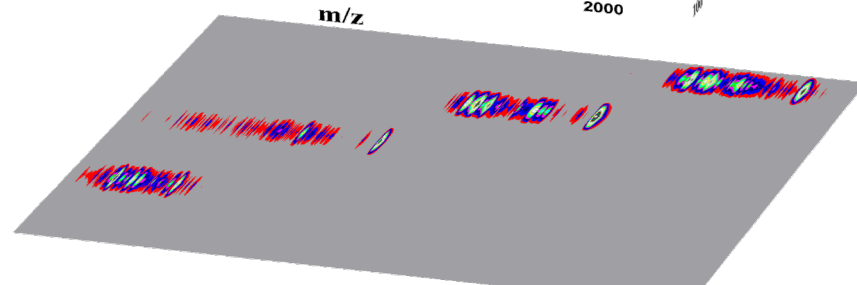
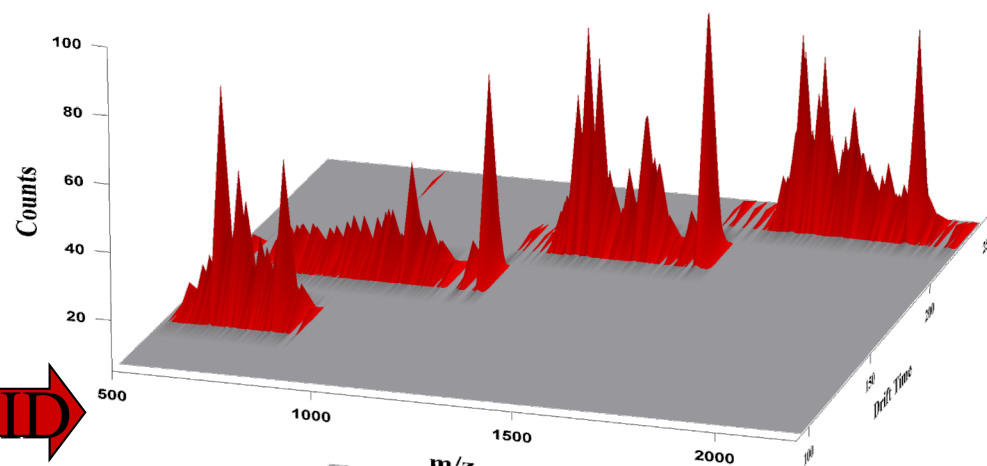


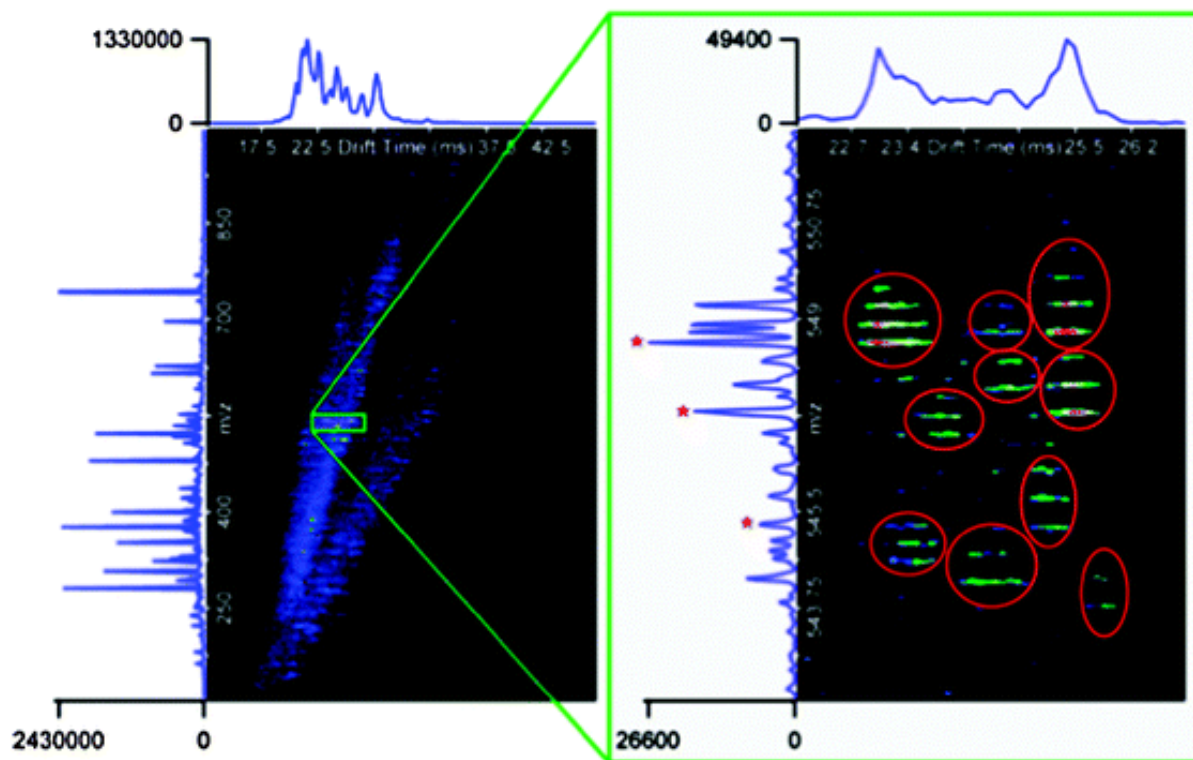






ISD





[Chem. Soc. Rev.](#), 2012, 41, 3912-3928