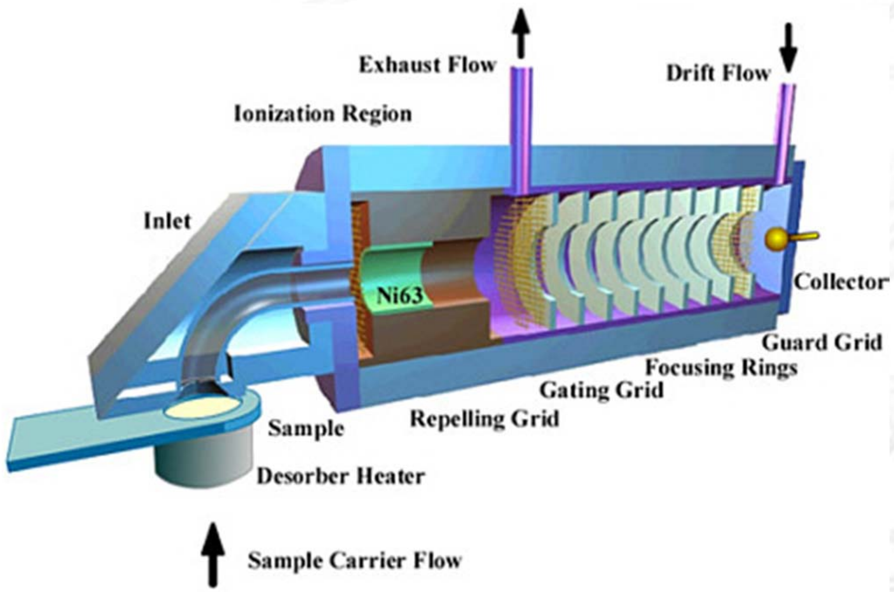
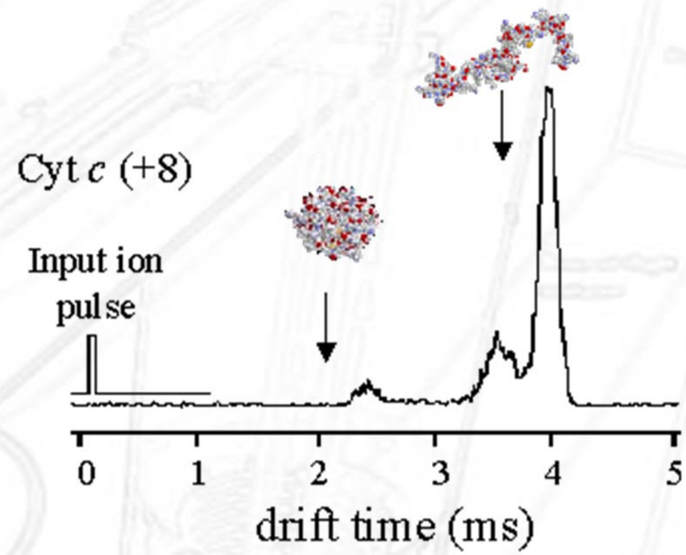
Week 7: Ion Mobility





Last Time…

- Vacuum Systems

What is ion mobility?

- Ion mobility is a bit like electrophoresis in the gas phase

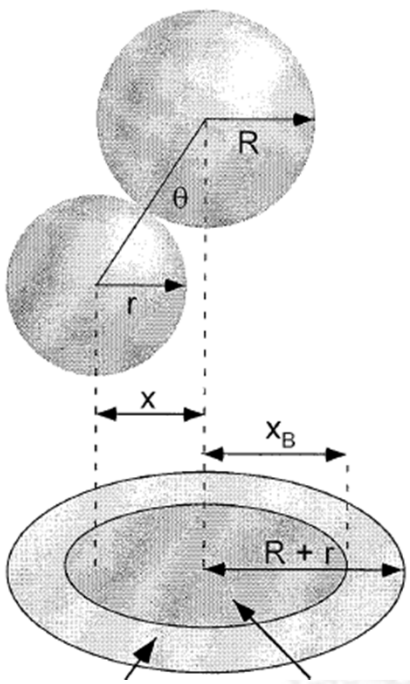
- If we have a packet of ions traveling down a drift tube across which there is a potential, the progress of those ions will be hampered by collisions with background gas.

- And here's the key: The extent to which progress is hampered depends on the size of the ion.

- Thus, by measuring the amount of time that it takes to get from one side of the drift tube to the other t_d, we can learn something about the collision cross section of the molecule.

What is the Collision Cross Section?

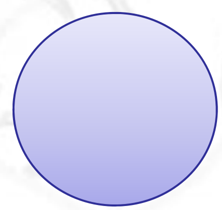
• We've seen collision cross section before (last week in fact) when we were talking about the Mean Free Path:



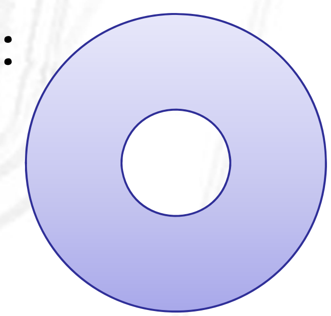
• It is a two dimensional projection of a three dimensional object.

• It assumes that the object is spherical (i.e. that the radius in one direction is the same as the radius in all other directions.

• That makes it hard to tell the difference between this:



And this:



Cross Section from Drift Time

- Getting to cross section from drift time involves a big scary equation, however, there's only one variable!

- So, let's take our ion $[DEREK + H]^+$ on an ion mobility rig that's 0.01 m wide and 0.2 m long and a pressure of 1 Torr. We measure a drift time of 5 ms with a 50 V accelerating voltage across the flight tube using a helium bath gas at 298 K.

Collisional Cross Section, Example:

- Lets start by calculating the particle density:

- And the masses of gas and analyte in kg:

Collision Cross Section Example

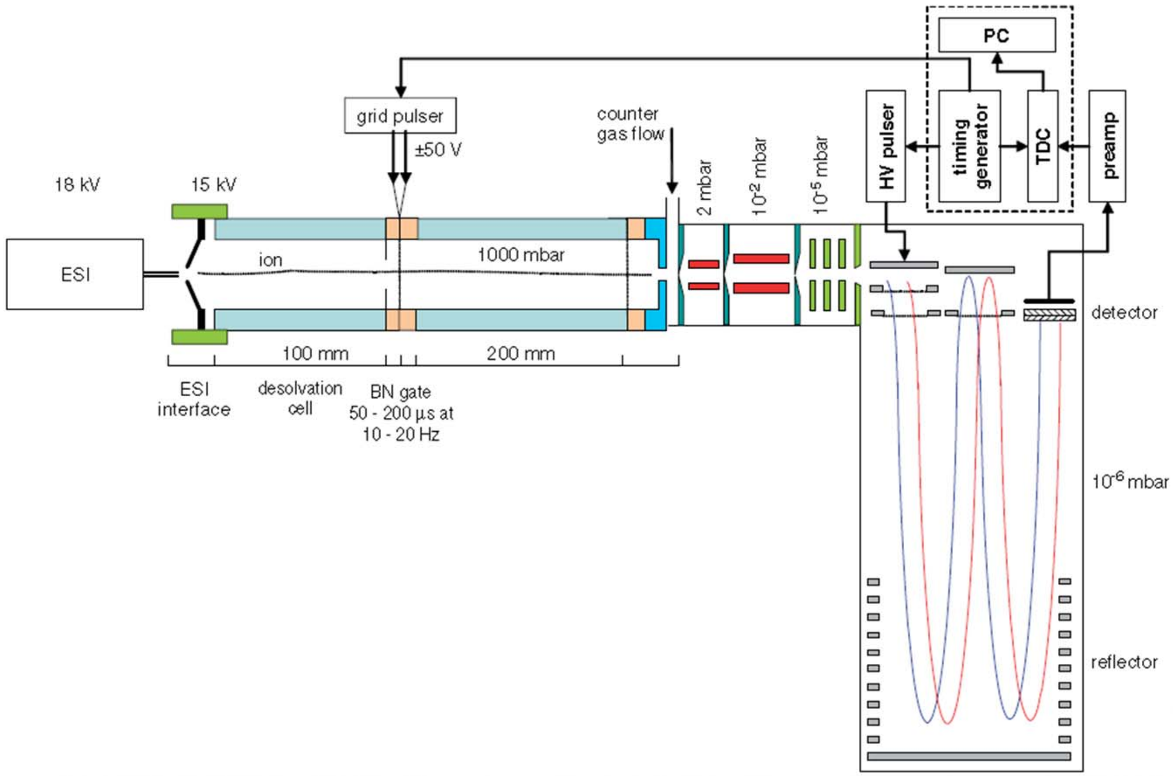
- Now we just have to plug our numbers in!

- This cross section is a little big for [DEREK + H]$^+$, could be the drift time that I made up (5 ms) was too long...

- Just for fun, lets calculate the mean free path:

Types of Ion mobility Analyzers

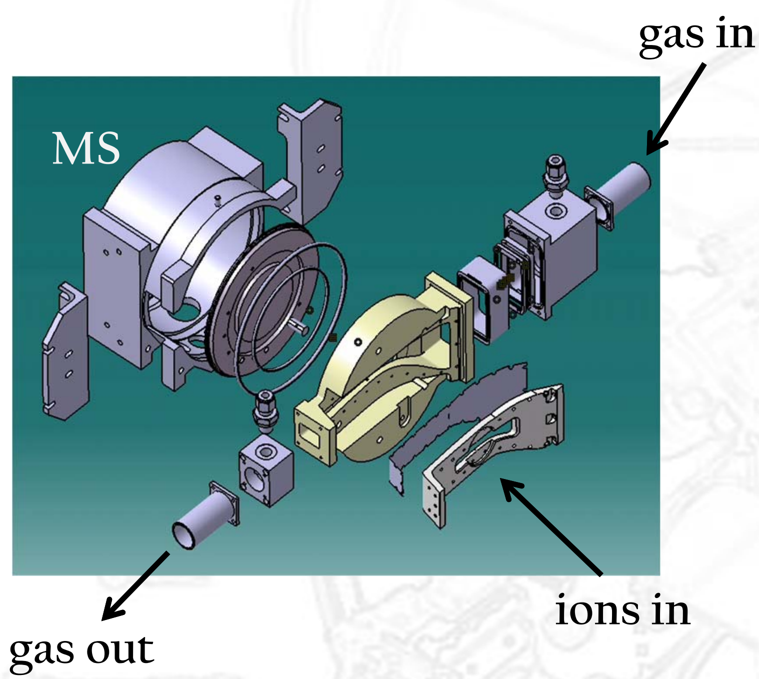
• The example we were just looking at was the simplest ‘drift tube’ case

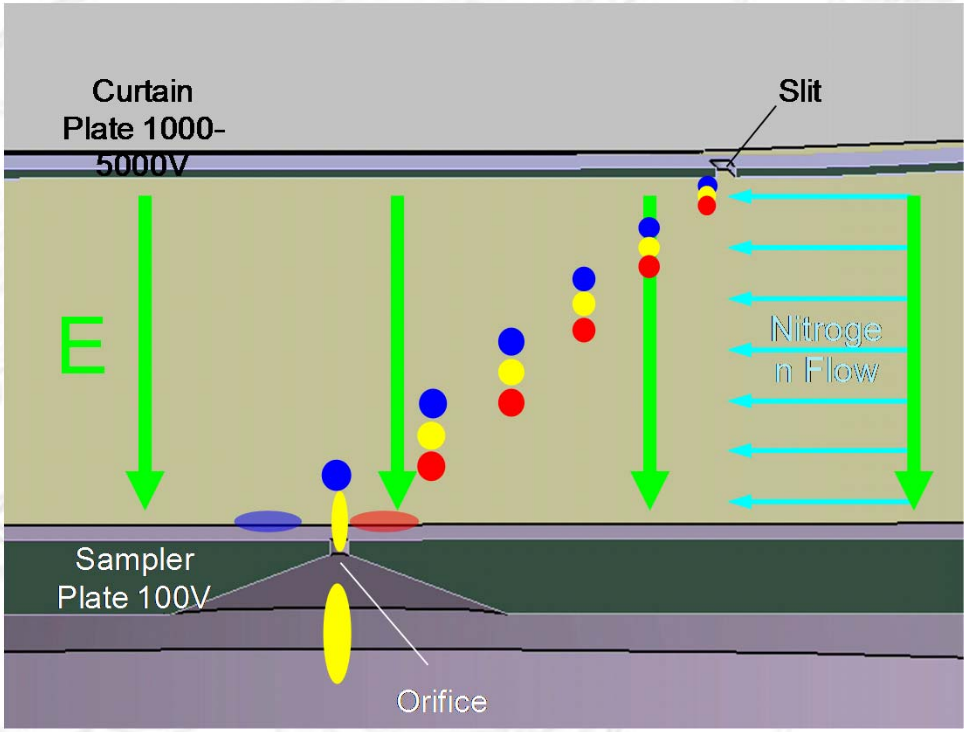


• It is important that the ions are ‘pulsed’ in as packets where the pulse time (maybe 10 µs) is much sorter than the drift time.

Differential Mobility Analyzers

• Differential Mobility Analyzers (DMAs) are front end, ion mobility-based size filters.





Differential Mobility Analyzers Cont.

- DMAs use high pressure, laminar Nitrogen flows to push ions towards (or past) entrance slit.

- The result is that we cannot reliably measure a cross section because:

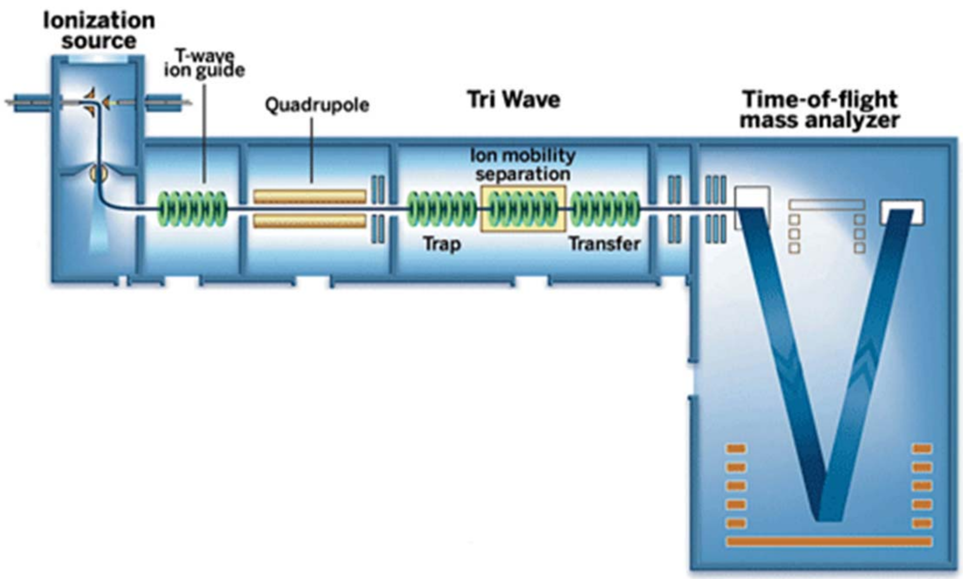
    - Our 'drift tube' formula assumes single elastic collisions. The high pressure gas means simultaneous collisions are likely.

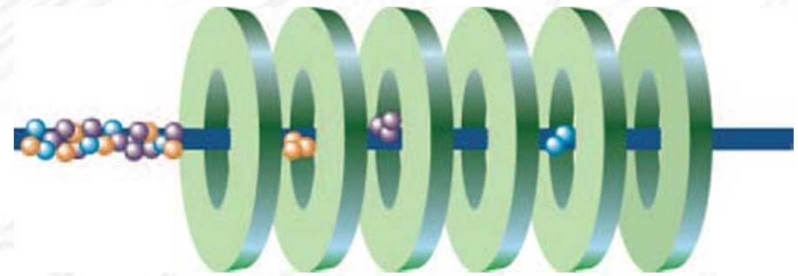
    - DMAs use high electric potentials to draw ions towards the entrance slit. This potential interacts badly with Nitrogen gas, which is polarizable. Effectively this causes more collisions than one would expect based solely on the mean free path.

- The inventors of the DMA, Juan de la Mora (Yale), still argue (probably correctly) that Ω can be measured with more advanced theory.

Traveling Wave Mobility Analyzers

• This is the only form of ion mobility that has been incorporated into a commercial instrument.

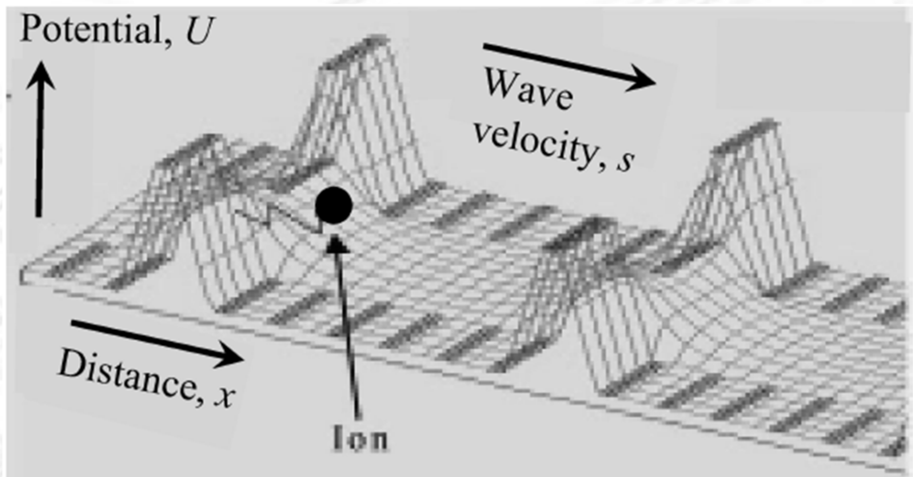




• In this device, ions are 'swept' along by a travelling wave going through the 'rings' of an ion funnel in a He bath gas.

Travelling Wave Mobility Analyzers Cont.

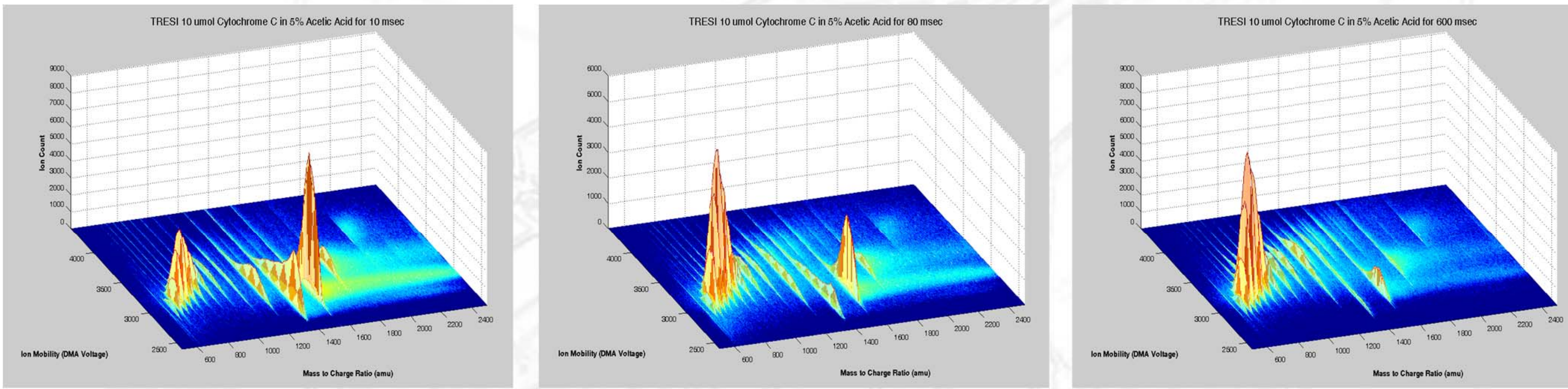
- Of course, we can't calculate cross section as easily here as we could for a drift tube because it depends on the shape, intensity and frequency of the travelling wave.



- Nonetheless, using some fancy math and external calibration (from drift-tube ion mobility), it is possible to calculate cross sections.

What Does Ion Mobility-MS Look Like?

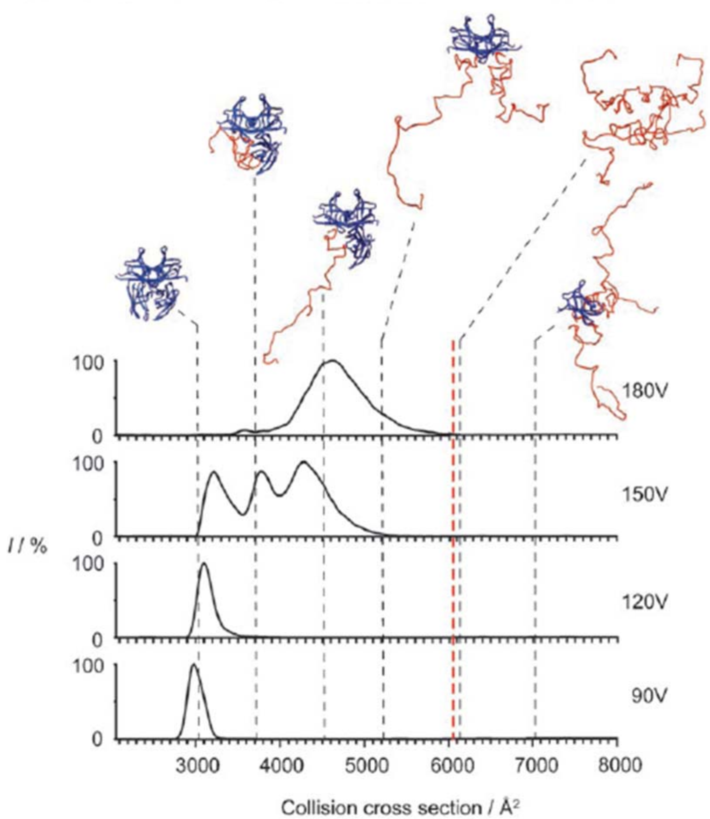
• When you combine Ion Mobility with MS, you get a 2D analysis where species separated by m/z are further separated by size:

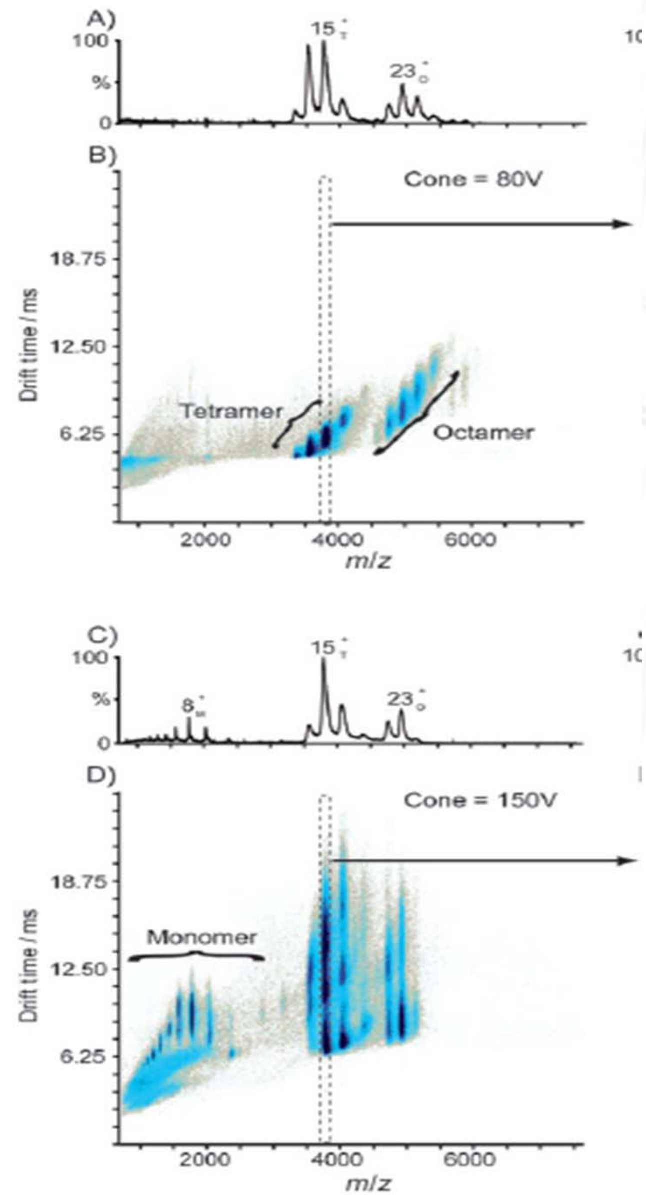


Figures 5 a,b,c: cytochrome c mixed with 5% Acetic Acid using Time Resolved-ESI (10, 80 and 200 msec)

Ion Mobility MS

- Here's an example where a protein is unfolded after it is ionized, so that the m/z peaks are 'split up' into different mobilities:

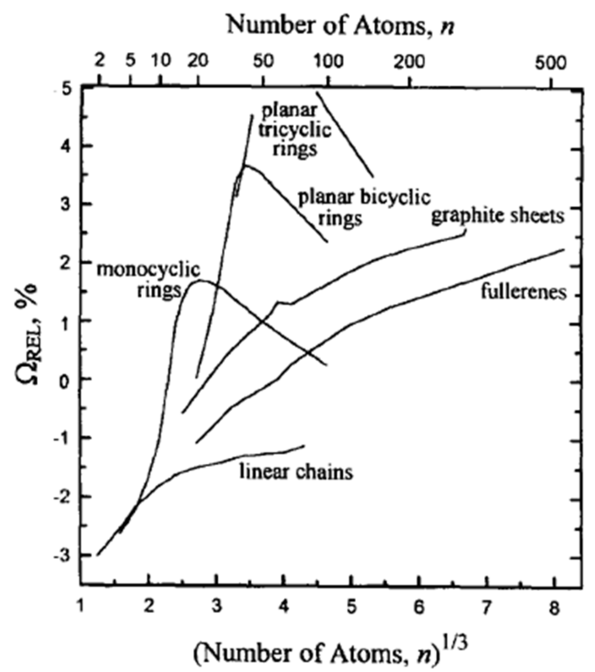




Ion Mobility and Computer Modeling

- But how do we know what these molecules look like?

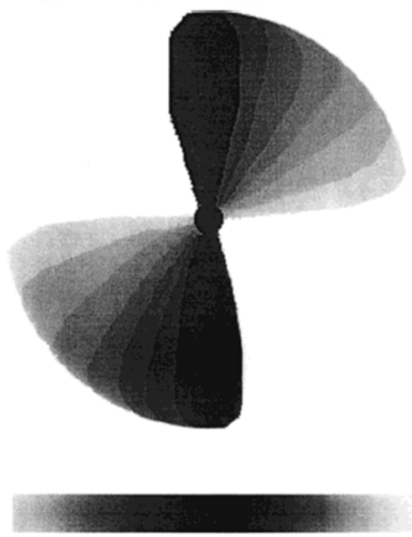
- We can use computer modeling to predict cross sections for specific shapes



- Turns out that different shapes result in different cross sections relative to their size

Computer Modeling: Projection

• The other computational method is to imagine the cross section as the weighted average of all 2D projections of the object.



• Here is the wieghted average 2D projection from an airplane propeller

• This kind of modeling is not unlike how people reconstruct 3D images from Cryo-EM experiments…