Structural analysis (CH-314)

Week 3

Problems and Solutions

Problem 1. Consider a time-of-flight (TOF) mass spectrometer in which ions are accelerated by 10 kV into a two-meter drift tube. Calculate the flight time of the fullerene molecular ion, $C_{60}^{+\cdot}$.

Solution:

The mass of the fullerene ion is

$$m = 60 \cdot 12\ \text{Da} - 0.000549\ \text{Da} \approx 720\ \text{Da} \approx 720 \cdot 1.66 \cdot 10^{-27}\ \text{kg} \approx 1.2 \cdot 10^{-24}\ \text{kg}$$

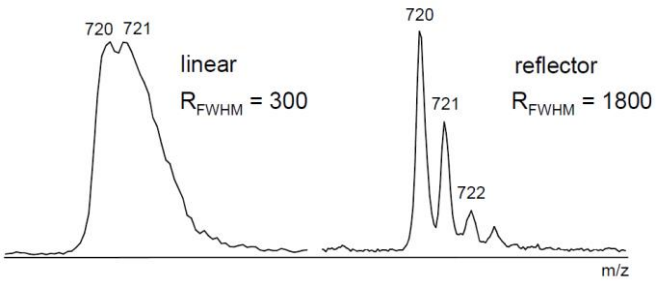
Velocity of ions leaving the acceleration region is calculated as follows:

$$v = \sqrt{\frac{2qU}{m}} = \sqrt{\frac{2 \cdot 10^4\ \text{eV}}{720\ \text{Da}}} = \sqrt{\frac{3.2 \cdot 10^{-15}\ \text{J}}{1.2 \cdot 10^{-24}\ \text{kg}}} \approx 5.2 \cdot 10^4\ \frac{\text{m}}{\text{s}}$$

Then, the flight time is

$$\tau = \frac{L}{v} = \frac{2\ \text{m}}{5.2 \cdot 10^4\ \frac{\text{m}}{\text{s}}} = 38.7\ \mu\text{s}$$

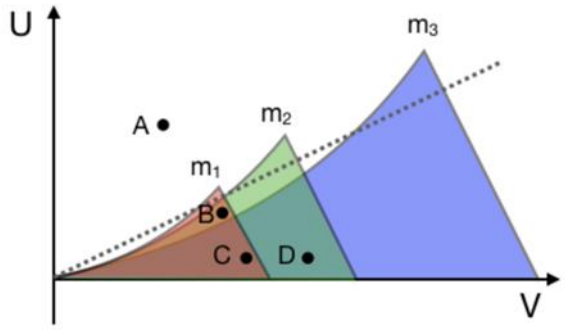
Problem 2. Shown below are the mass spectra of the fullerene molecular ion recorded on a linear TOF mass spectrometer and on a TOF with reflectron. Assuming the path length of the ions in both instruments are the same, which of the two spectra, do you think, was recorded on the instrument with reflectron?



Solution:

Reflectron compensates for the initial energy spread of ions, which results in an increased resolving power of TOF. Therefore, the mass spectrum with resolved isotopic distribution (right panel) can be assigned to TOF with reflectron.

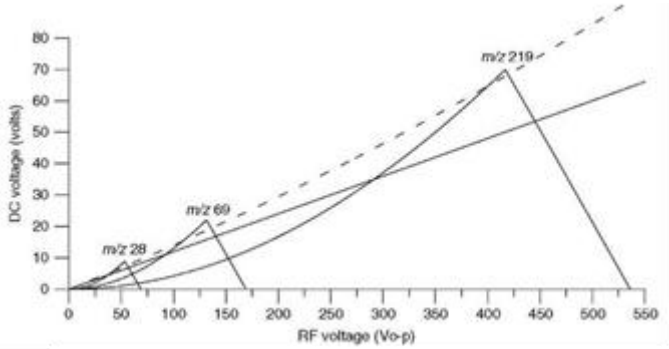
Problem 3. Consider the figure below representing the quadrupole stability diagram for three ions of mass-to-charge ratios m_1, m_2, and m_3. Explain which ions will be transmitted through the quadrupole when the U and V voltages are set to those represented by the points A-D in the figure.



Solution:

Trajectories of ions of a certain mass-to-charge ratio are stable only when the applied DC and RF voltages lie within the respective "triangle of stability". Therefore, when the applied DC and RF voltages correspond to point A, the trajectories of all the ions will be unstable. At point B, both m_1 and m_2 will be transmitted while m_3 ions will have unstable trajectories. Point C lies within all the three triangles; thus, all the ions will be transmitted. At point D, both m_2 and m_3 will be transmitted while m_1 ions will have unstable trajectories.

Problem 4. Consider the figure below representing the quadrupole stability diagram with two scan lines, solid and dashed. Which of the two lines, do you think, corresponds to a higher quadrupole resolution?



Solution:

For each DC and RF voltages, only ions within a certain m/z window are transmitted. The resolution is $R = {m/z}\Big/{\Delta(m/z)}$. Therefore, the narrower the transmittance window the higher the resolution. The width of the window is determined by the slope of the scan line, and it is larger in the case of the solid scan line. Thus, the dashed scan line results in a higher quadrupole resolution.

Problem 5. Find the cyclotron frequency (in Hz) of ions with m/z = 500 Th in a 12 Tesla ion cyclotron resonance (ICR) mass spectrometer.

Solution:

The cyclotron frequency (in Hz) is calculated as follows:

$$f = \frac{qB}{2\pi m} = \frac{1.6 \cdot 10^{-19}\text{C} \cdot 12\ \text{T}}{2 \cdot 3.14 \cdot 500 \cdot 1.66 \cdot 10^{-27}\ \text{kg}} = 3.7 \cdot 10^{5}\ \text{Hz} = 0.37\ \text{MHz}$$