10.6 Fourier Transform Mass Spectrometry

- cyclotron frequency and thermal cyclotron motion
- absorption of rf radiation
- detection of coherent ion motion with the image current
- the ion cyclotron resonance cell
- the free-induction decay
- chirped and SWIFT excitation
- digitizing the FID with and without heterodyning
- a simple instrument block diagram
When an ion is placed in a magnetic field it travels in a circular orbit. The size of the orbit adjusts itself so the centrifugal force just offsets the magnetic force.

\[ qvB = \frac{m v^2}{r} \quad v = \frac{q}{m} Br \]

The time for an ion to travel one cycle of its orbit is given by the circumference divided by the velocity.

\[ t = \frac{2\pi r}{v} = \frac{m}{q} \frac{2\pi}{B} \quad f = \frac{1}{t} = \frac{q}{m} \frac{B}{2\pi} \]

For a molecular weight in amu and a magnetic field in Tesla, the cyclotron frequency is given by the following expression.

\[ f = 15.357 \times 10^6 \frac{B}{M} \]

For a 7 T magnet, the cyclotron frequency is 3.83 MHz at 28 amu, and 26.9 kHz at 4,000 amu. *The frequency range is large!*
Thermal Cyclotron Motion

The thermal velocity of gas phase ions is about 300 - 500 m s\(^{-1}\). The radius of cyclotron motion is given by the following expression.

\[
r = \frac{vm}{qB}
\]

For a singly-charged ion with a mass of 100 amu, the thermal radius will vary over the range of 45 - 74 \(\mu\)m. Although \(r\) varies from ion to ion, all ions of the same \(m/q\) have the same frequency.

The phase and the radius any particular ion are random due to collisions. The vector sum of the motion in the x,y-plane is zero. In the drawing the magnetic field is along the z-axis. The x,y-plane is the plane of the figure. Thus, the ions are trapped in the x,y-plane but free to move in the z-direction.
The radius of ion orbits can be increased by applying a voltage at the cyclotron frequency. While the rf field is present the ions will steadily accelerate into larger orbits,

\[ r = \frac{Vt}{2dB} \]

where \( V \) is the applied voltage, \( t \) the time of application, and \( d \) the separation between the two plates applying the voltage.

- although the phases of the thermal portion of the cyclotron motion are random, the applied voltage creates a coherent component to the motion of all ions
- ions with a cyclotron motion at a different frequency than the applied rf voltage do not have their orbits increased
- it is possible to apply sufficient voltage to drive the ions into the walls where they are neutralized
- ions of different \( m/z \) can be sequentially excited by sweeping the frequency of the applied voltage.
Detection of Coherent Ion Motion

Because a moving ion is a moving charge, its motion can be detected by its image current in two electrically conducting plates.

In the figure above, a single positive charge is shown. It induces a net negative charge in the plate closest to it. By attaching an rf voltmeter to the two plates the magnitude of the signal can be related to the number of ions having a specific $m/z$. The spectrum is obtained by taking the Fourier transform of the temporal change in current.

For a collection of ions it is the average current which is measured. Because of random phases, thermally excited ions will not contribute to the signal. Incoherent image current creates noise.
The image current is given by the following equation,

\[ i = \frac{Nqv}{d} \]

where \( N \) is the number of ions, \( q \) is the charge per ion, \( v \) is the velocity and \( d \) is the plate separation.

For \( 10^3 \) ions moving at \( 10^4 \) m s\(^{-1} \) between two plates separated by 2 cm, the image current is \( 8 \times 10^{-11} \) A. This is reasonably easy to measure.
A complete ICR cell is shown at the right. The cell is 1-2 cm on a side.

The magnetic field is shown by the B arrow. The front and rear plates have a +1 V potential applied to trap the ions in the z-direction.

The ions are added or removed by adjusting dc potentials on the plates and using holes in the z-plates.
The FID

If the excited ions undergo no collisions with the cell or other molecules in the gas phase they will continue to travel in the excited cyclotron orbit and produce an image current.

Excited ions have an energy in excess of the Boltzmann distribution. As they collide with thermal ions or neutrals, their excess energy and/or phase will be lost: the radius of coherent cyclotron motion will drop, decreasing the image current.

The exponential drop in amplitude of the coherent cyclotron motion creates a free-induction decay (FID). Like NMR, the Fourier transform of the FID yields a Lorentzian-shaped peak in the spectrum.

At low pressures it is not difficult to get cyclotron motion to last many minutes. This is why FTMS has the highest resolution of any mass spectrometry technique. If the signal-to-noise ratio is too low, a collision gas can be added to decrease the FID time constant and allow more FIDs to be averaged per unit time.
In NMR broadband excitation was achieved by pulsing the carrier. This was possible because the range of resonance frequencies was measured in ppm. With FTMS the range of frequencies is almost as large as the highest frequency. Under this condition pulsed excitation will not work because the width would have to be less than one cycle of rf.

The earliest FTMS instruments used chirped excitation. This is a method of varying the frequency across the duration of the excitation pulse.

As an example the frequency might start at 70 kHz and sweep to 3.6 MHz in 5 ms. The exact values depend upon the range of m/z to be examined.
Chirped excitation suffers from having each m/z start its FID at a different time. This complicates taking the Fourier transform.

In a Stored Waveform Inverse Fourier Transform (SWIFT) the range of masses to be excited is converted into a range of frequencies (rectangular shape). The Fourier transform of this range is then converted into a sinc function in the time domain. The frequency range is centered about half the upper frequency. Thus the sinc function is multiplied by a cosine of the center frequency.

Because the SWIFT waveform has an average amplitude which is low (due to the shape of the sinc function), the rf power has to be about a factor of 10 larger than that for chirped excitation.

Marshal and co-workers (J. Amer. Chem. Soc., 107, 7893, 1985) showed that randomly changing the phase in the frequency domain produced a more even excitation and required about the same amount of rf power as chirped excitation.
Constant phase rectangle in frequency

\[ \text{rect}_t := 1 \]

\[ \text{norm} := \sum \text{rect} \]

\[ a_j := \frac{1}{\text{norm}} \left( \sum \text{rect}_t \cdot \exp(\text{i} \cdot 2 \cdot \pi \cdot f_i \cdot t_j) \right) \]

\[ \text{amp}_j := \sqrt{a_j \cdot a_j \cdot \text{sign}(\text{Re}(a_j))} \quad \text{power}_j := a_j \cdot \overline{a_j} \]
Random phase rectangle in frequency.

\[
\text{rect}_t := \text{if}[(\text{rnd}(1) - 0.5) \cdot i > 0, 1, -1]
\]
Digitizing the FID

Direct digitization of a low-mass FID requires a very fast ADC and a very large memory. As an example, a 4 MHz signal requires at a minimum one data point every 0.125 μs. For one second of data collection time 8 million data points are collected. This would provide frequency resolution of 1 Hz.

To reduce the size of the data set and increase resolution, the signal can be heterodyned. Because of the large range of rf frequencies, heterodyning only works over limited ranges.

Suppose an ion has a nominal m/z = 1000. This corresponds to a cyclotron frequency of 107.5 kHz with a 7 T magnet. If you want to determine the mass to +0.01 amu, you would need to take data at 215 k samples per second for 100 seconds. This generates a 21.5 M sample vector of data that needs to be transformed. Instead heterodyne the rf signal against 107.4 kHz to generate a signal frequency at 100 Hz. This needs to be sampled at 200 Hz for 100 s, and produces 20,000 data points.
The instrument uses chirped excitation and can either directly measure an FID or use heterodyning to obtain high resolution.