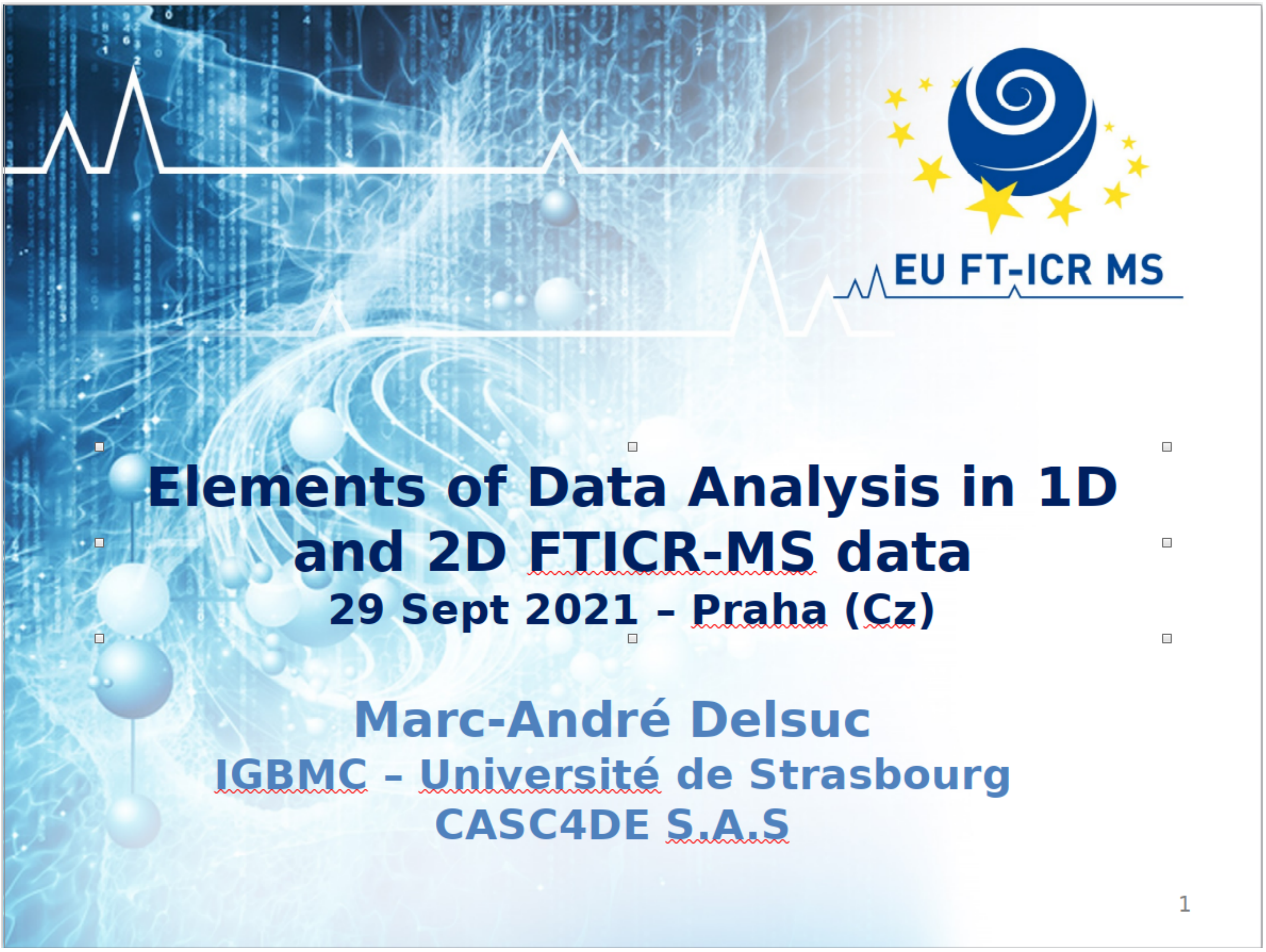


This presentation relies on several tools and set-up available in jupyter notebooks

- a complex scientific python stack
- the spike processing library installed
- choosing to view the cell slideshow support will help
- the "Hide imput" nb extension to hide the python code
- the RISE nbextension to run the slideshow

In [1]:

```
%matplotlib inline
%autosave 60
```

executed in 512ms, finished 09:41:32 2021-09-30

```
Autosaving every 60 seconds
```

In [2]:

```
#import spike
#from spike.Interactive import INTER as I
#I.hidecode(message="")
import matplotlib
import matplotlib.pyplot as plt
from matplotlib.pyplot import scatter, plot, figure, text, title, xlabel, ylabe
import numpy as np
from numpy import exp, cos, sin, arctan2, pi, linspace, arange

from ipywidgets import Button, interactive
import ipywidgets as widgets
from IPython.display import display, HTML, Javascript, Markdown, Image

matplotlib.style.use("fivethirtyeight")
for i in ('font.size','axes.labelsize','legend.fontsize','legend.title_fontsize
    matplotlib.rcParams[i]=24
for i in ('xtick.labelsize', 'ytick.labelsize'):
    matplotlib.rcParams[i]=18

#matplotlib.style.available
```

executed in 108ms, finished 09:41:32 2021-09-30

Elements of Data Analysis in 1D

and 2D FTICR-MS data

Marc-André Delsuc - 2nd Advanced User School, Prague, Sept 2021

---

3 parts

- **The Fourier Transform - the basic aspects**
  - some theory
- **The basic FT-ICR experiment**
  - playing with real data
  - some more theory
- **more advanced aspects**
  - big datasets
  - even more theory

1. The Fourier Transform - the basic aspects

2nd-AUS-FTICR

Marc-André Delsuc - Prague 26-30 Sept 2021

a developed content of this part can be found on github.com/delsuc (https://github.com/delsuc/Fourier_Transform/blob/master/Definition_Properties.ipynb)

FT-MS - Fourier Transform Mass Spectrometry

You know it !

FT-ICR - indeed

Orbitrap - of course

also Charge Detection MS

and other more "exotic" approaches

they have in common

- very high resolving power
- slow...

BUT what is Fourier transform ?

Fourier Transform Definition

Fourier Transform is defined on continuous functions:

for a function $f(x)\ x \in \mathbb{R} \rightarrow f(x) \in \mathbb{C}$

the **Fourier transform** of f is another function F

$F(X)\ X \in \mathbb{R} \rightarrow F(X) \in \mathbb{C}$

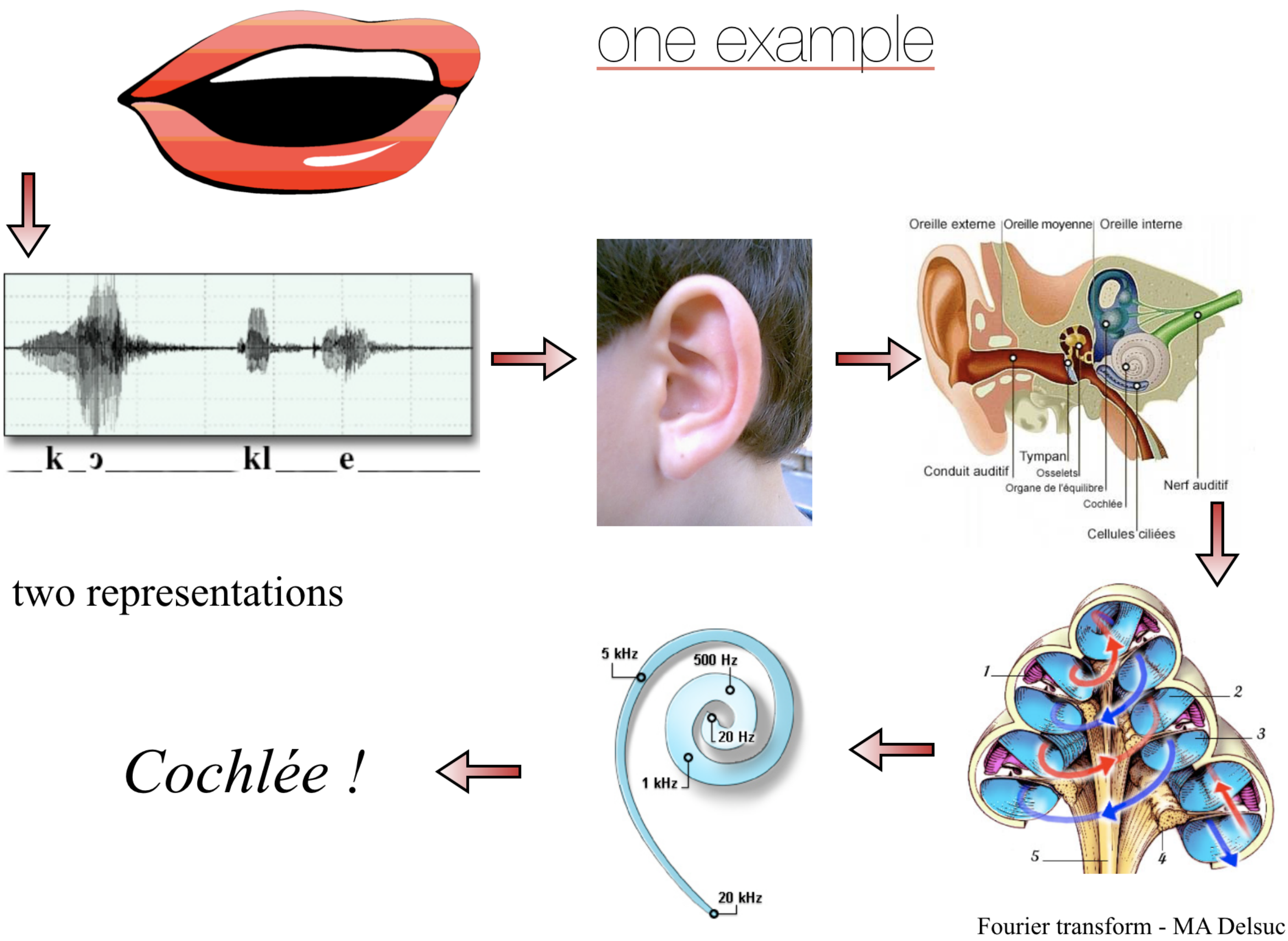
$$f \xrightarrow{FT} F$$

$$F(X) = \int_{-\infty}^{+\infty} f(x) e^{-2i\pi xX} dx$$

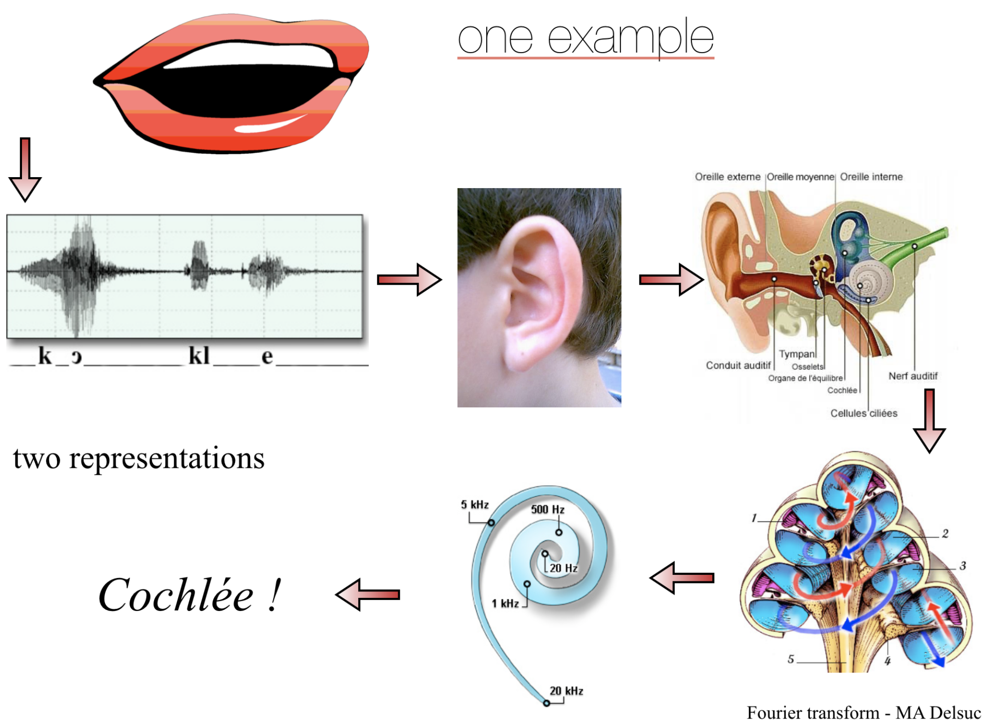
❓

😭 **or** 🤣

Time vs Frequency - One example



Time vs Frequency - One example



- $f(t)$ pressure wave / function of time.

- ear-drum vibrate with the same pattern $\rightarrow$ standing wave in the cochlea $\rightarrow$ *position F(frequency)*
  - $\Rightarrow$ a mechanical Fourier transform !
- phonetic pattern is somehow the time-dependent **Fourier transform** of the inital pressure wave.
- They both carry somehow the same information, but in a very different way.
- 2 point of views for the same information

Fourier Transform Definition (2)

using $x \rightarrow t$ as time

and $X \rightarrow \omega$ as frequency

$$\text{the expression} \qquad \int_{-\infty}^{+\infty} f(t) e^{-2i\pi\omega t} dt$$

is just a way to **weigh** in $f(t)$ the presence of a given frequency ω : $e^{-2i\pi\omega t}$

x and X represent two different reciproqual quantitites, and can be found in many domains

x	X
t : time (sec)	ω : frequency (Hz)
x : space (Å)	k : spatial frequency (Å^{-1})
λ : wavelength (cm)	k : spatial frequency (cm^{-1})
etc...	

exemple on a real data-set !

ECD fragmentation of a mixture of 4 histone peptides with various PTM *from M. van Agthoven - Innsbruck*

In [3]:

```
import spike
from spike.File import BrukerMS as bkMS
d = bkMS.Import_1D("files/histonepeptide_ms2_000002.d/fid")
```

executed in 3.75s, finished 09:41:36 2021-09-30

```
    ========================
          SPIKE
    ========================
    Version     : 0.99.29
    Date        : 20-09-2021
    Revision Id : 529
    ========================
*** zoom3D not loaded ***
plugins loaded:
Fitter,  Linear_prediction,  Peaks,  bcorr,  fastclean,  gaussenh,  re
m_ridge,  sane,  sg,  test,  urQRd,
plugins loaded:
msapmin,

spike.plugins.report() for a short description of each plugins
spike.plugins.report('module_name') for complete documentation on one
plugin
plugins loaded:
FTMS_calib,  PhaseMS,  diagonal_2DMS,
*** PALMA not loaded ***
plugins loaded:
Bruker_NMR_FT,  Bucketing,  Integrate,  apmin,
Using 3 parameters calibration,  Warning calibB is -ML2
```

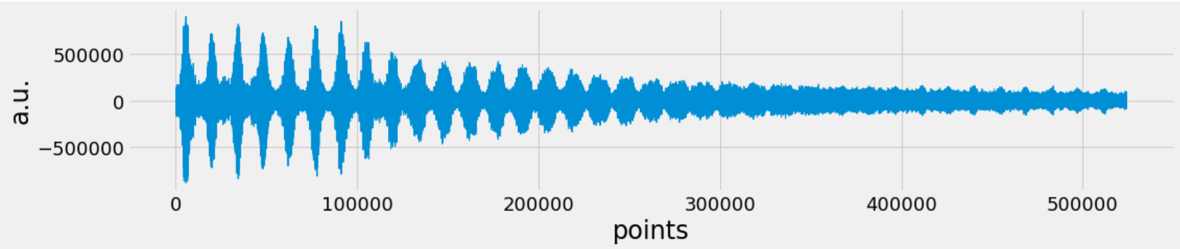
In [4]:

```
figure(figsize=(16, 3))
d.display(new_fig=False)
```

executed in 325ms, finished 09:41:36 2021-09-30

Out[4]:

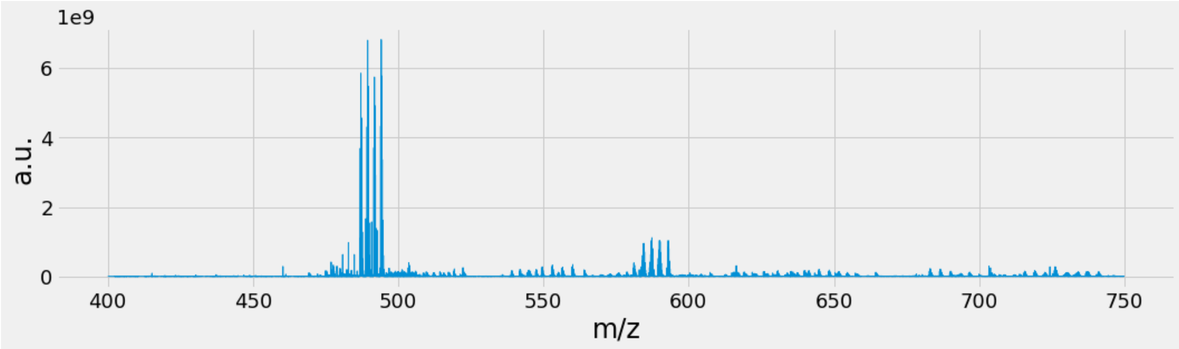
```
FTICR data-set
Bo: 7.05
Single Spectrum data-set
FT-ICR axis at 535.714286 kHz,  524288 real points,  from physical mz
=  202.203   to m/z = 1450.000  R max (M=400) = 265036
```



In [5]:

```
figure(figsize=(16,4))
D = d.copy().center().kaiser(4).zf(2).rfft().modulus()
D.set_unit('m/z').display(zoom=(400,750),new_fig=False);
```

executed in 332ms, finished 09:41:37 2021-09-30

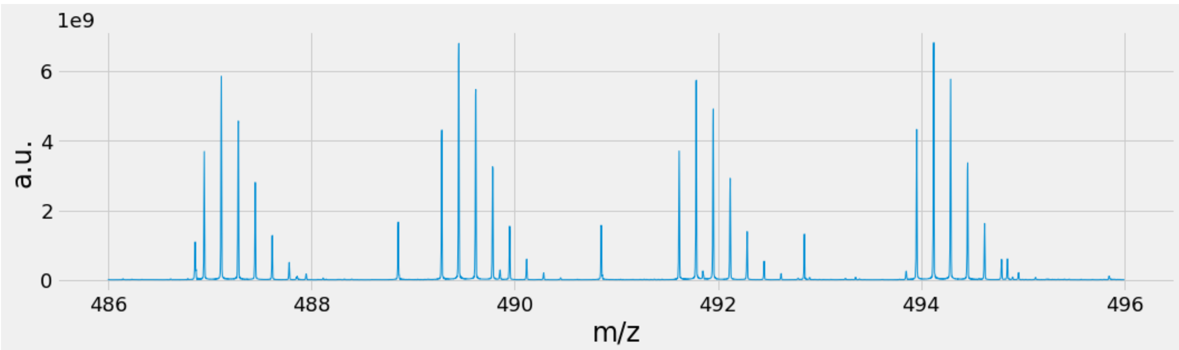


In [6]:

```
display(Markdown("**zooming on the main peptides** *(10 Thomson wide)*"))
figure(figsize=(16,4))
D.display(zoom=(486, 496),new_fig=False);
```

executed in 148ms, finished 09:41:37 2021-09-30

zooming on the main peptides *(10 Thomson wide)*

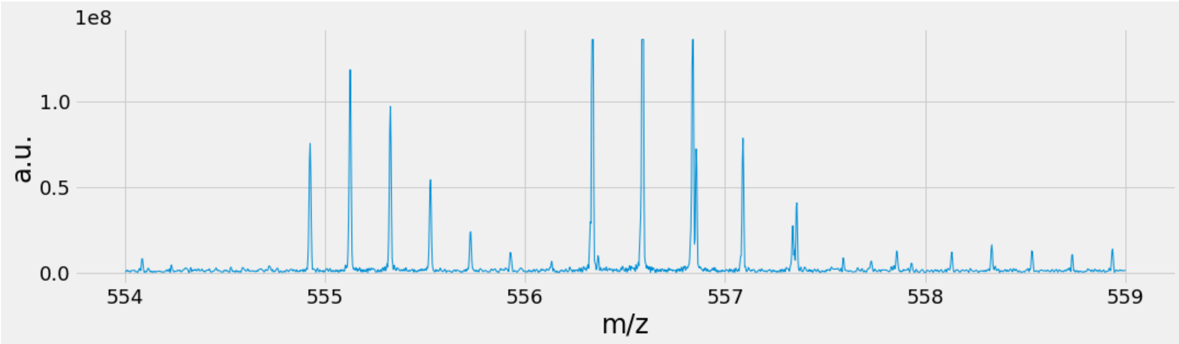


In [7]:

```
display(Markdown(r"**zooming on smaller fragments** *( 5 Thomson wide - $\times
figure(figsize=(16,4))
D.display(zoom=(554, 559),scale=50,new_fig=False);
```

executed in 147ms, finished 09:41:37 2021-09-30

zooming on smaller fragments *(5 Thomson wide - $\times 50$)*



a brief reminder on complex numbers.

- *complex numbers are central to Fourier analysis, and their understanding is needed to fully comprehend the beauty of Fourier analysis*

Real numbers are *regular* numbers, going from $-\infty$ to $+\infty$.

- They belong to $\mathbb{R}$, the set of all real numbers
- $\mathbb{R}$ can be seen as a line, going from $-\infty$ to $+\infty$.

If Reals are on a line, Complex numbers are on a plane.

As any plane, the coordinates are defined on two axes, the horizontal axis is the $\mathbb{R}$ line, the vertical one is the *Imaginary* axis, also holding real numbers, and labeled with i. This plane is called $\mathbb{C}$ the complex plane.

A complex number z (a point in this plane) is thus described with two numbers, a and b:

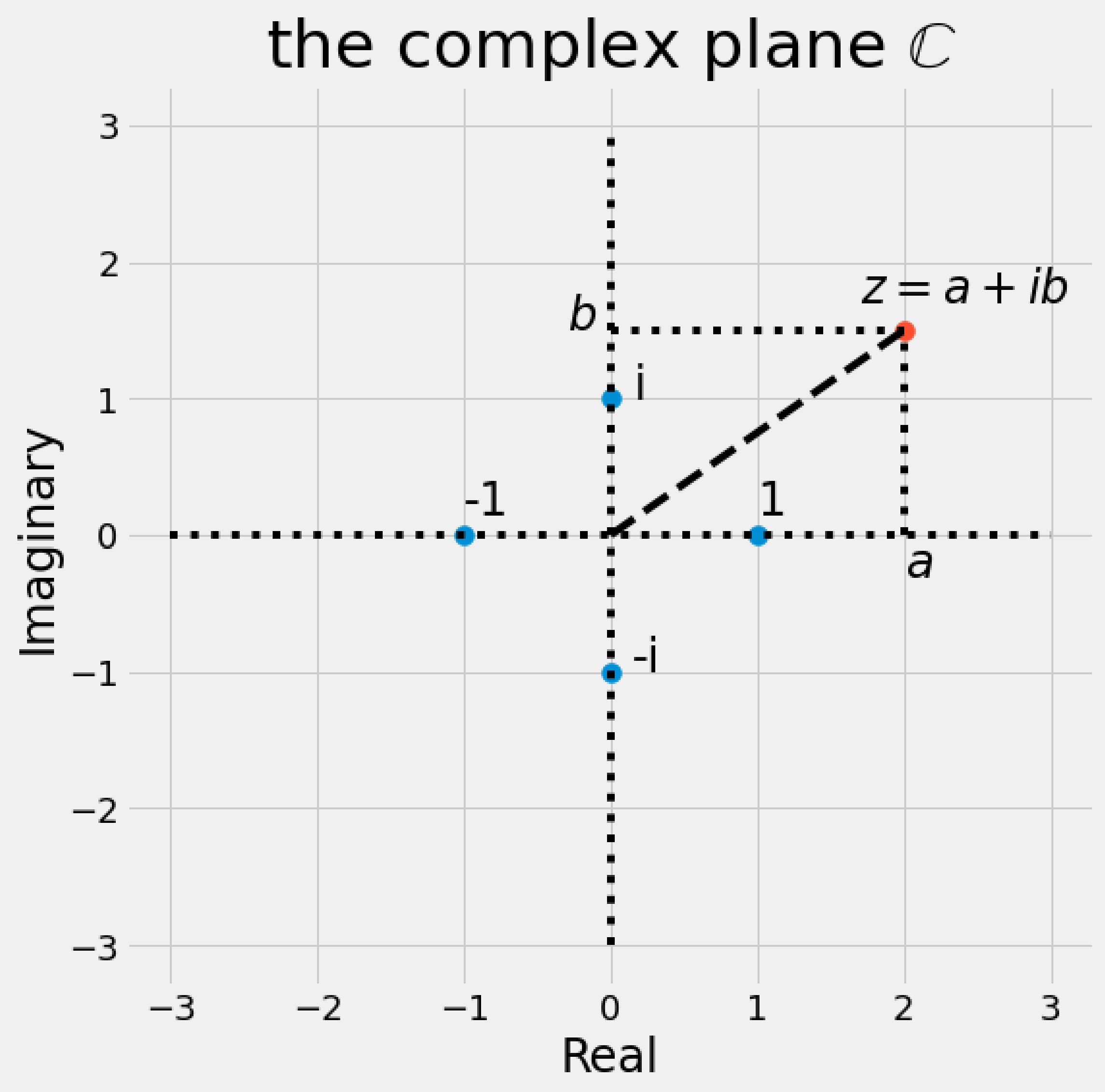
$$z = a + ib$$

a is the real part, and b the imaginary part.

In [8]:

```
# let's draw this
figure(figsize=(8,8))
plot([-3,3],[0,0],':k') # the real axis
plot([0,0],[-3,3],':k') # the imaginary axis
scatter([1,0,-1,0],[0,1,0,-1], 100)
text(1,0.15,'1')
text(-1,0.15,'-1')
text(0.15,1,'i')
text(0.15,-1,'-i')
title('the complex plane $\mathbb{C}$')
a = 2
b = 1.5
z = a + 1j*b             #  i is noted j in python
scatter(z.real, z.imag, 100)
plot([0,z.real],[0,z.imag],'--k')
plot([z.real,z.real],[0,z.imag],':k')
plot([0,z.real],[z.imag,z.imag],':k')
xlabel("Real")
ylabel("Imaginary")

text(a, -0.3, '$a$')
text(-0.3, b,'$b$')
text(a-0.3,b+0.2,'$z = a +ib$');

```

executed in 416ms, finished 09:41:37 2021-09-30



modulus

$$|z| = R = \sqrt{a^2 + b^2}$$

argument (*usually noted with a greek letter*)

$$arg(z) = \arctan\left(\frac{b}{a}\right) = \theta$$

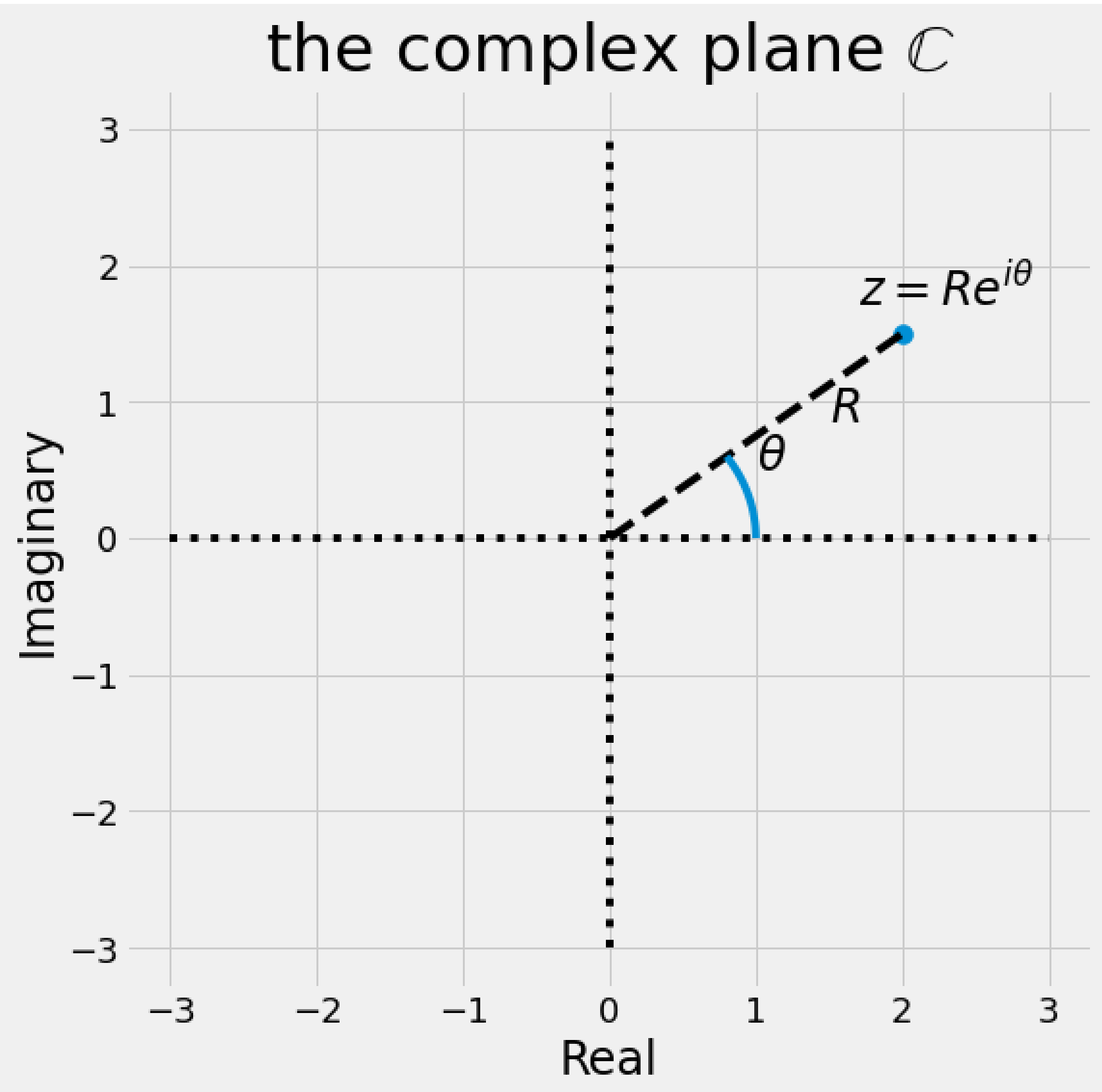
This is noted using the *Euler* notation:

$$z = a + ib$$
$$z = Re^{i\,\arg(z)} = Re^{i\theta}$$

In [9]:

```
# let's draw this
figure(figsize=(8,8))
plot([-3,3],[0,0],':k') # the real axis
plot([0,0],[-3,3],':k') # the imaginary axis
title('the complex plane $\mathbb{C}$')
a = 2
b = 1.5
z = a + 1j*b              #  i is noted j in python
scatter(z.real, z.imag, 100)
plot([0,z.real],[0,z.imag],'--k')

xlabel("Real")
ylabel("Imaginary")

text(a-0.3,b+0.2,r'$z = R e^{i \theta}$');

t = linspace(0, np.arctan2(b,a),30)
plot(cos(t),sin(t))
text(a-0.5, b/2+0.1, '$R$')

text(1,0.5, r'$\theta$');
```

executed in 223ms, finished 09:41:37 2021-09-30



Complex numbers can be added and multiplied, they form an **algebra**.

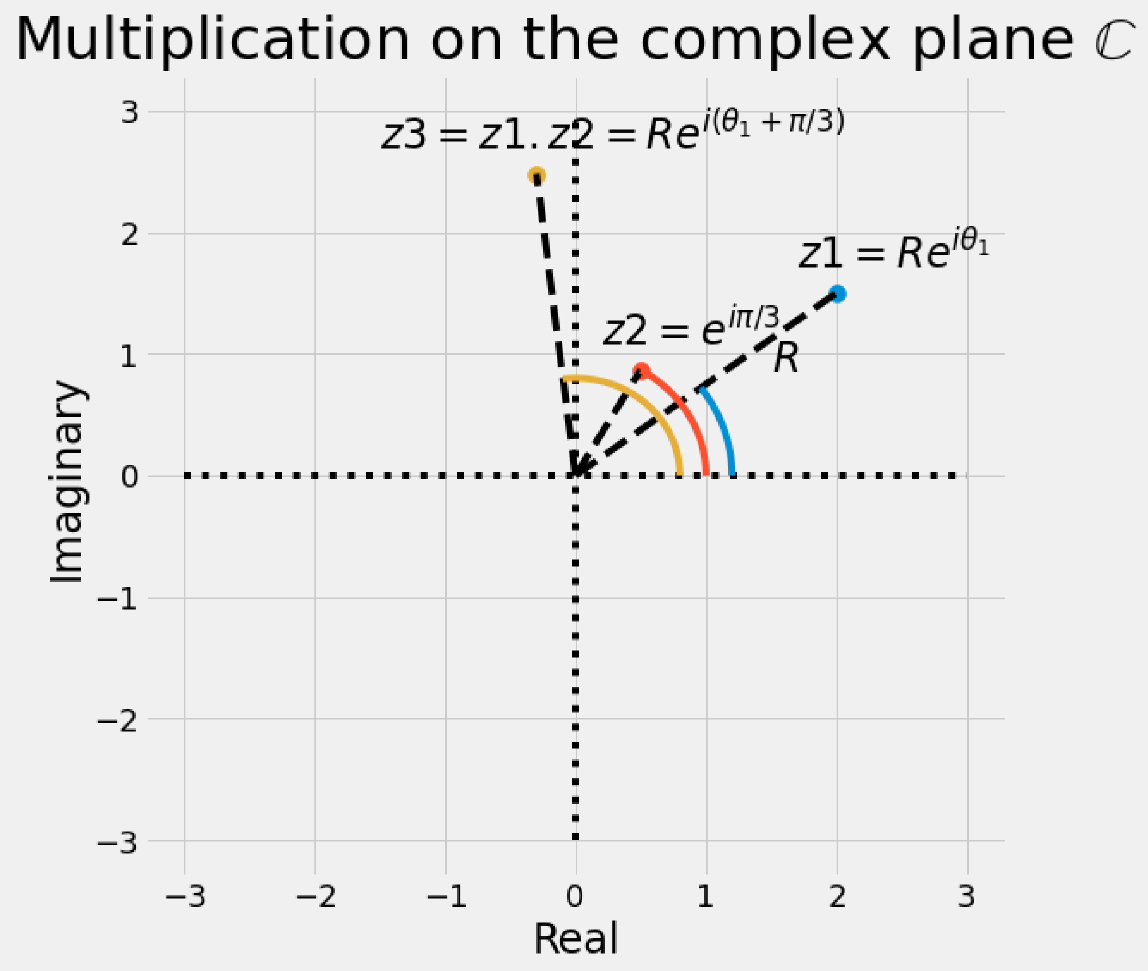
The Euler Notation stresses the multiplicative rules, where **modulus** are multiplied, and **angles** are added.

$$z_1 . z_2 = R_1 e^{i\theta_1} . R_2 e^{i\theta_2}$$
$$z_1 . z_2 = R_1 R_2 e^{i(\theta_1 + \theta_2)}$$

In [10]:

```python
# let's draw this
figure(figsize=(8,8))
plot([-3,3],[0,0],':k') # the real axis
plot([0,0],[-3,3],':k') # the imaginary axis
title('Multiplication on the complex plane $\mathbb{C}$')
z1 = a + 1j*b                                   #  i is noted j in python
c = cos(pi/3)
d = sin(pi/3)
z2 = c + 1j*d
xp = (z1*z2).real
yp = (z1*z2).imag
scatter(a, b, 100)
scatter(c, d, 100)
scatter(xp, yp, 100)

plot([0,a],[0,b],'--k')
plot([0,c],[0,d],'--k')
plot([0,xp],[0,yp],'--k')

xlabel("Real")
ylabel("Imaginary")

text(a-0.3,b+0.2,r'$z1 = R e^{i \theta_1}$');
text(c-0.3,d+0.2,r'$z2 = e^{i \pi / 3}$');
text(xp-1.2, yp+0.2, r'$z3 = z1 . z2 = R e^{i (\theta_1 + \pi/3)}$');

text(a-0.5, b/2+0.1, '$R$')

t1 = linspace(0, arctan2(b,a),30)
plot(1.2*cos(t1), 1.2*sin(t1))

t2 = linspace(0, pi/3,30)
plot(cos(t2), sin(t2))

t3 = linspace(0, arctan2(yp,xp),30)
plot(0.8*cos(t3), 0.8*sin(t3));

```

executed in 374ms, finished 09:41:38 2021-09-30



You have a more detailed (in interactive) presentation in [the complex_reminder (https://github.com/delsuc/Fourier_Transform/blob/master/Definition_Properties.ipynb)](https://github.com/delsuc/Fourier_Transform/blob/master/Definition_Properties.ipynb) on `github`
see also: [Wikipedia:Complex_plane (https://en.wikipedia.org/wiki/Complex_plane)](https://en.wikipedia.org/wiki/Complex_plane)

some useful properties of FT

Linearity

- $FT(A + B) = FT(A) + FT(B)$ FT of sum = sum of FT
- $\Rightarrow$ FT of a composite signal is just the sum of the FT of each component

Invertible

- $f \xrightarrow{FT} F \qquad F \xrightarrow{FT^{-1}} f$
- actually $F^{-1} = F^3$
- 2 different points of view of the SAME information ! *(~ rotating by 90° in information space)*

Unitary

- *if F is the FT of f* $\int |f(t)|^2 dt = \int |F(\omega)|^2 d\omega$ $\Rightarrow$ signal power is conserved

some useful properties of FT *(2)*

integrals

$F_o = \int f(t)dt \qquad f_o = \int F(\omega)d\omega$

compaction theorem

convolution theorem

- both are central !
- so important we shall see them later on !

FT vs DFT

Fourier Transform

- This Fourier transform is analytic, defined on continuous, infinite functions

Digital Fourier Transform

- the counter part for **regularly** sampled data $\quad x_n \rightarrow X_n \quad$ (with $n \in \{1 \cdots N\}$)

$$X_n = \sum_{k=1}^{N} x_k e^{-2\pi \frac{kn}{N}}$$

This is the operation which is used *nearly* everywhere - and in particular in most FT-ICR processing.

The elements

$$e^{\frac{2\pi k}{N}}$$

are the k roots of 1 of order N

so

$$e^{\frac{2\pi kn}{N}} = (e^{\frac{2\pi k}{N}})^n$$

are these roots at the power n

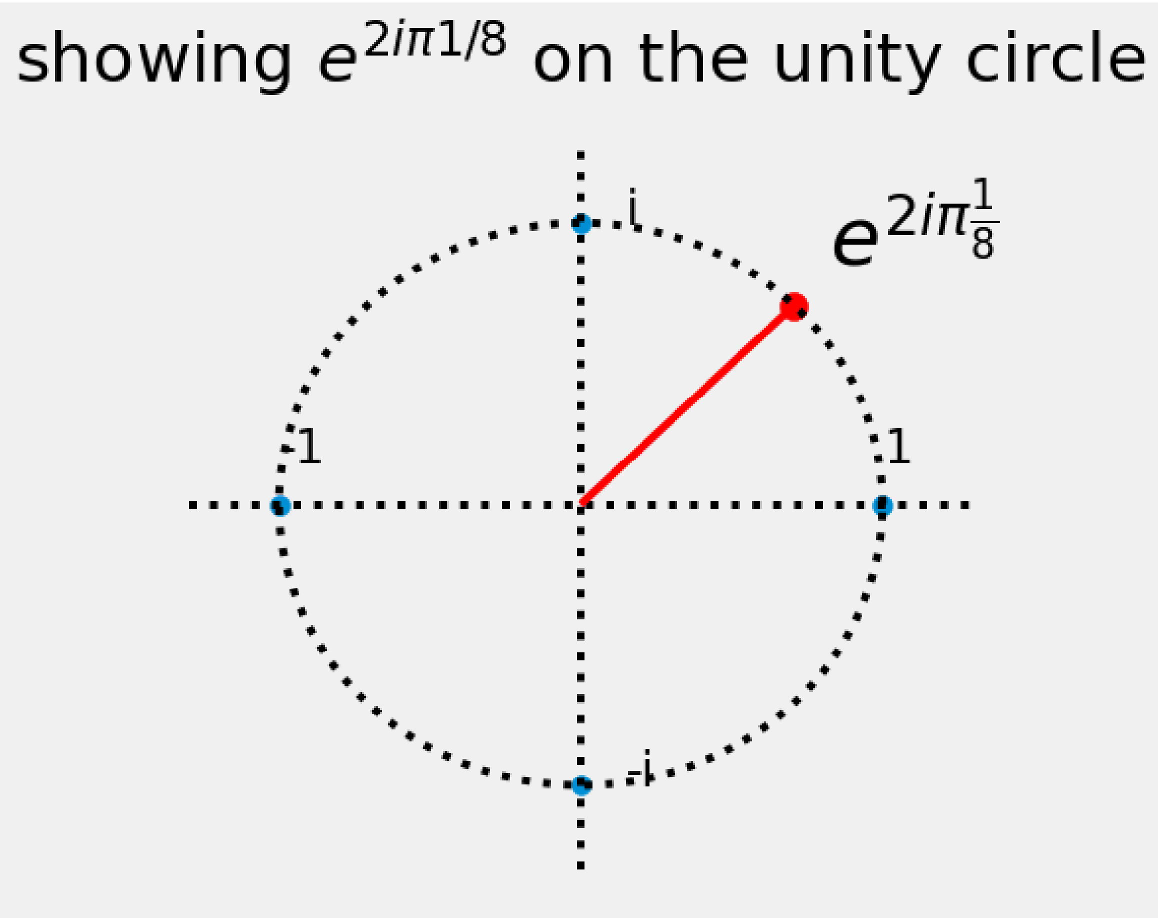
In [11]:

```
# let's make it interactive
def Nroot(k=1,N=8):
    f,(ax) = subplots(figsize=(7,7))
    t = linspace(0, 2*pi,100)
    ax.plot([-1.3,1.3],[0,0],':k') # the real axis
    ax.plot([0,0],[-1.3,1.3],':k') # the imaginary axis
    ax.plot(np.cos(t), np.sin(t),':k')   # the unity circle
    scatter([1,0,-1,0],[0,1,0,-1], 100)
    text(1,0.15,'1')
    text(-1,0.15,'-1')
    text(0.15,1,'i')
    text(0.15,-1,'-i')

    z = exp(2j * pi /N)          # e^(2 i pi / N)
    zk = z**k
    ax.scatter(zk.real, zk.imag, 200, c='r',edgecolors='r')   # draw roots
    ax.plot([0,zk.real],[0,zk.imag],'r')
    ax.text(1.3*zk.real-0.1, 1.2*zk.imag, r"$e^{2 i \pi \frac{%d}{%d}}$"%(k,N),
    ax.set_axis_off()
    ax.set_title(r'showing $e^{2i\pi %d/%d}$ on the unity circle'%(k,N));
interactive(Nroot, k=(0,16), N=(2,16))
```

executed in 179ms, finished 09:41:38 2021-09-30

k 1

N 8



DFT / FT fundamental difference

analytical Fourier	digital Fourier
infinite signal	finite signal
	time bounded signal
continuous signal	sampled signal
	missing information
infinite spectrum	finite spectrum
	frequency bounded signal
continuous spectrum	sampled spectrum
	missing information

Nyquist relation

$$\Delta t = \frac{1}{2F_{max}} \qquad \text{or} \qquad F_{max} = \frac{1}{2\Delta t}$$

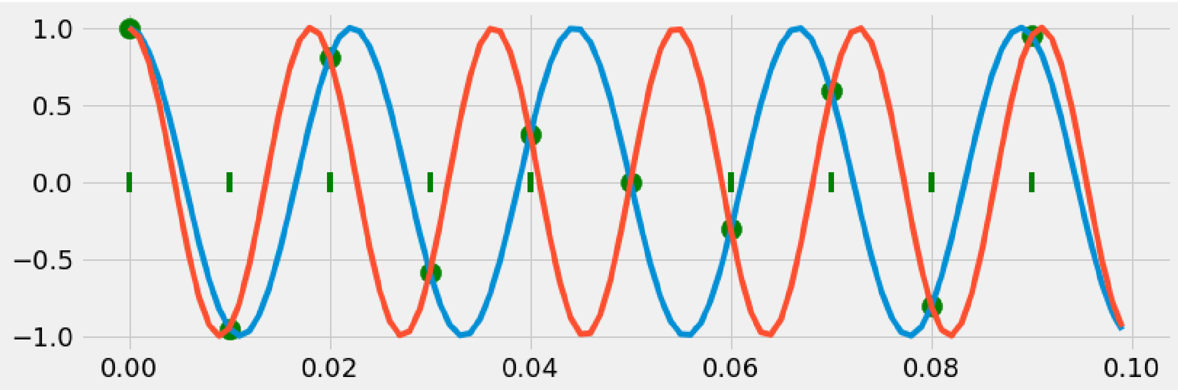
sampling = 0.01 => Fmax = 50 Hz

- F1 (blue) = 45 Hz
- F2 (red) = 55 Hz

In [12]:

```
deltat = 0.01   # 10 msec => Fmax = 50Hz
t = 0.1*deltat * np.arange(100)   # oversampling x10 to draw
F1 = 45
F2 = 55
figure(figsize=(12,4))
plot(t, np.cos(2*pi*F1*t))
plot(t, np.cos(2*pi*F2*t))
for i in range(10):
    scatter(i*deltat, 0, 200, 'g', marker="|")
    scatter(i*deltat, np.cos(2*pi*F1*i*deltat), 200, 'g')

```

executed in 294ms, finished 09:41:38 2021-09-30



aliasing

sampling $\Rightarrow$ periodisation of the reciprocal space

- time sampling $\Rightarrow$ frequency periodisation
    - aliasing / folding
- frequency sampling $\Rightarrow$ time periodisation
    - time shifting

fundamental relationships

N points, acquired at sampling rate Δt $\Rightarrow$ N point spectrum sampled at ΔF.

Time domain

- Δt
- $t_{max} = N \Delta t$
- $\Delta t = \frac{1}{2 F_{max}}$
- $t_{max} = \frac{1}{2 \Delta F}$

Frequency domain

- ΔF
- $F_{max} = N \Delta F$
- $\Delta F = \frac{1}{2 t_{max}}$
- $F_{max} = \frac{1}{2 \Delta t}$

And a general relation: $N = 2F_{max}t_{max} \quad = \frac{1}{2\Delta t \Delta F}$

fundamental relationships

N points, acquired at sampling rate $\Delta t \Rightarrow N$ point spectrum sampled at ΔF.

Time domain

- Δt
- $t_{max} = N\Delta t$
- $\Delta t = \frac{1}{2F_{max}}$ Nyquist-Shanon theorem
- $t_{max} = \frac{1}{2\Delta F}$

Frequency domain

- ΔF
- $F_{max} = N\Delta F$
- $\Delta F = \frac{1}{2t_{max}}$ Heisenberg uncertainty
- $F_{max} = \frac{1}{2\Delta t}$

And a general relation: $N = 2F_{max}t_{max} \quad = \frac{1}{2\Delta t \Delta F} \quad \Delta t \Delta F = \frac{2}{N}$ Gabor theorem

	Time domain	Frequency domain
	Δt	ΔF
$t_{max} = N\Delta t$		$F_{max} = N\Delta F$
	$\Delta t = \frac{1}{2F_{max}}$	$\Delta F = \frac{1}{2t_{max}}$
	$t_{max} = \frac{1}{2\Delta F}$	$F_{max} = \frac{1}{2\Delta t}$

some algorithmic

DFT can be seen as the product of the signal series $\mathbf{x} = x_n$ of length N, by a $N \times N$ square matrix $\mathcal{M}$:

$$\mathbf{X} = \mathcal{M}\mathbf{x}$$

$$X_n = \sum_{k=1}^{N} x_k e^{2\pi \frac{kn}{N}}$$

so $\mathcal{M}_{ij} = e^{2\pi \frac{ij}{N}}$ is the matrix of the power of the N roots of 1 we have seen earlier.

As a matrix product, we expect the processing time to be $\propto N^2$.

HOWEVER, there is a fast algorithm, (*Cooley & Tuckey 1965*) called **FFT**

- $\propto N \log_2(N)$ *much* faster for large data-sets.
- does not require matrix expression (*a $512k \times 512k$ matrix is not easy to handle on a computer*)
- faster if N used

Comparing FFT and DFT

In [13]:

```
figure(figsize=(12,8))
P = np.arange(1,20)                     # power of 2
N = 1024*(2**P)                        # size of vectors, starting at 1k points
base = 1e-6/(N[0]**2)                  # assume 1μsec processing for 1k vector ( my la
DFT = base*(N**2)
plt.loglog(N, DFT, label='DFT')                 # draw both
text(N[-1], DFT[-1], 'DFT')
FFT = 2*1024*base*N*P
plt.loglog(N, FFT, label='FFT')
text(N[-1], FFT[-1], 'FFT')
# some annotations
plt.title('processing time simulation')
plt.xlabel('Size of vector')
plt.ylabel('processing time in sec')
#plt.legend(loc=4)
plt.plot(N, [1E-3]*19, '--k'); plt.text(2*1024, 2E-3, '1 msec')
plt.plot(N, [1]*19, '--k');    plt.text(2*1024, 2, '1 sec')
plt.plot(N, [60]*19, '--k');   plt.text(2*1024, 120, '1 min')
plt.plot(N, [3600]*19, '--k'); plt.text(2*1024, 2*3600, '1 hour')
plt.plot(N, [24*3600]*19, '--k'); plt.text(2*1024, 50*3600, '1 day');
```

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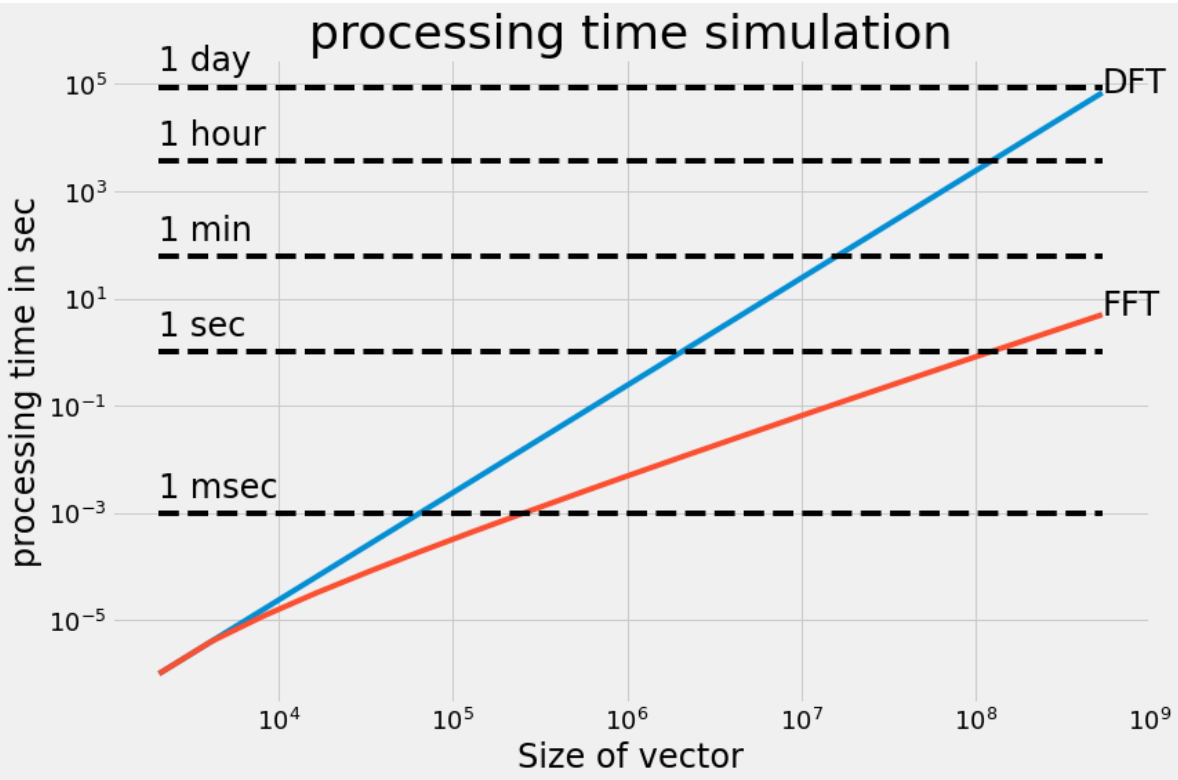

26 slides

In [ ]:

```

```