You are invited to the

Department of Chemistry

Chemistry Majors BBQ Lunch 2024

Thursday 29th February
12:30pm – 1:30pm

Outside Mellor Labs

(between Biochemistry and Mellor Laboratories)

CHEM202

Organic Chemistry

Nick Green

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Module 1: Spectroscopy and Characterisation

Lecture 1: General Principles of Spectroscopy

The word **spectroscopy** comes from the Latin word *spectrum*, which means "image", and the Greek word *skopia*, which means "observation". Spectroscopy is the study of the interaction between matter and light.

CHEM202: Organic Chemistry

Course Convenor:
Bill Hawkins, bhawkins@chemistry.otago.ac.nz , 4n10

Lectures: Mon 9am OBS117
                  Tue 9am BIG13
                  Wed 11am RMOOT

Attendance strongly recommended, strong correlation with final grade.

Labs start this week 2pm. If you miss a lab, contact Bill urgently to make it up.

Tutorials start next week. If you miss a tutorial, just come to a different one. Very useful for exam.

Blackboard: familiarise yourself now, check in now and then

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Class Reps Wanted!

Are you...

Proactive, friendly and keen to contribute to your learning environment?

A great communicator who can represent your peers?

What's in it for you?

FREE support

A reference letter from OUSA for your CV

Professional development training to boost your CV

FREE food

OUSA student support

Organic Synthesis; Structural Characterisation and Analysis

Spectroscopy and Structural Elucidation
General Principles
Data Collection   Continuous wave spectrometers
                   Fourier transform spectrometers

NMR Spectroscopy
nmr visible nuclei, spin half nuclei.
Principles of nmr.
Sensitivity. Relaxation.

^{1}H-nmr; Spectral Features.
Chemical Shift, shielding, deshielding. inductive effects, anisotropic effects, mesomeric effects.
Coupling, geminal, vicinal, long range.
Obtaining data from spectra.
First order analysis, non first order analysis.
Decoupling. COSY, 2D-NMR. NOE, NOESY

^{13}C-nmr; Spectral Features
Comparison with ^{1}H-nmr. Relative sensitivity, proton decoupling.
DEPT, APT, HETCOR

Identification of Organic Compounds Problems

The need to identify and characterise compounds

The identification of an organic compound is typically made from the correlation of data from several spectroscopic techniques.

Spectroscopy	Information
Mass spectrometry	Molar mass Atomic groupings in a molecule
Ultraviolet and visible (UV-vis) spectroscopy	Identification of chromophoric groups
Infrared (IR) spectroscopy	Functional group identification "Fingerprint" region for unique comparison with authentic sample
^{1}H nuclear magnetic resonance spectroscopy (^{1}H nmr)	Number of protons Proton environments Number of protons adjacent to a particular proton Functional group identification
^{13}C nuclear magnetic resonance spectroscopy (^{13}C nmr)	Number of carbon atoms Number of different carbon types Carbon environments Functional group identification

Spectroscopic Methods

Absorption spectroscopy

- measurement of interactions between molecules, ions or atoms and electromagnetic (EM) radiation.
- all involve absorption of specific energies of EM radiation, corresponding to specific excitations (transitions) within a molecule
    - ultraviolet
    - infrared
    - nuclear magnetic resonance
- Specific techniques based on specific interactions allow specific interrogations of structure
- for each technique vast libraries of spectral data for known compounds
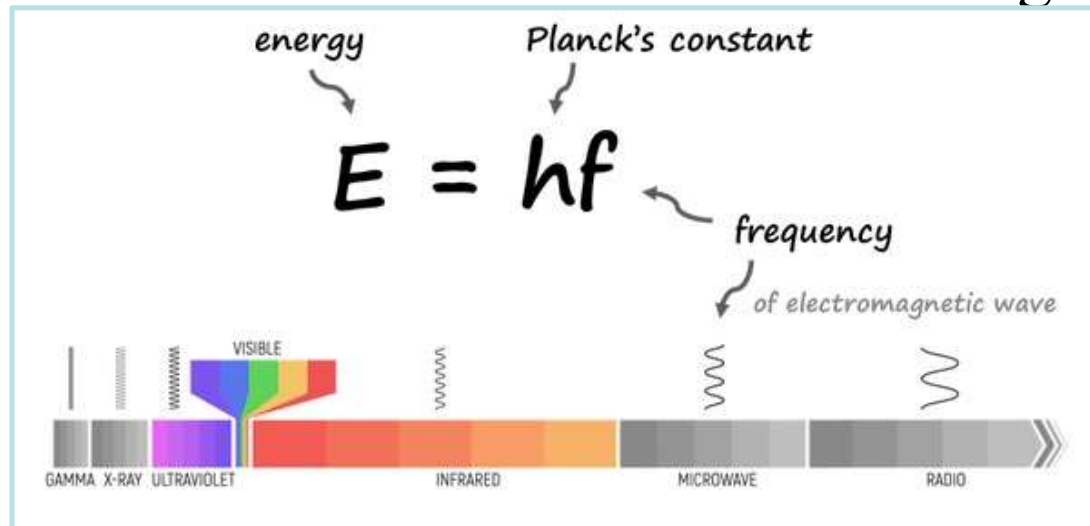
Absorption Spectra

Absorbance
% Transmission   **Vs**   **Energy (E, λ, ν, $\tilde{\nu}$)**
Intensity

- frequency reflects ΔE, the difference in energy between the higher and lower states of the absorbing species

- Intensity reflects
  - the relative populations of the respective states
  - the probability of a transition (can have allowed and forbidden transitions)
  - the amount and concentration of the absorbing species
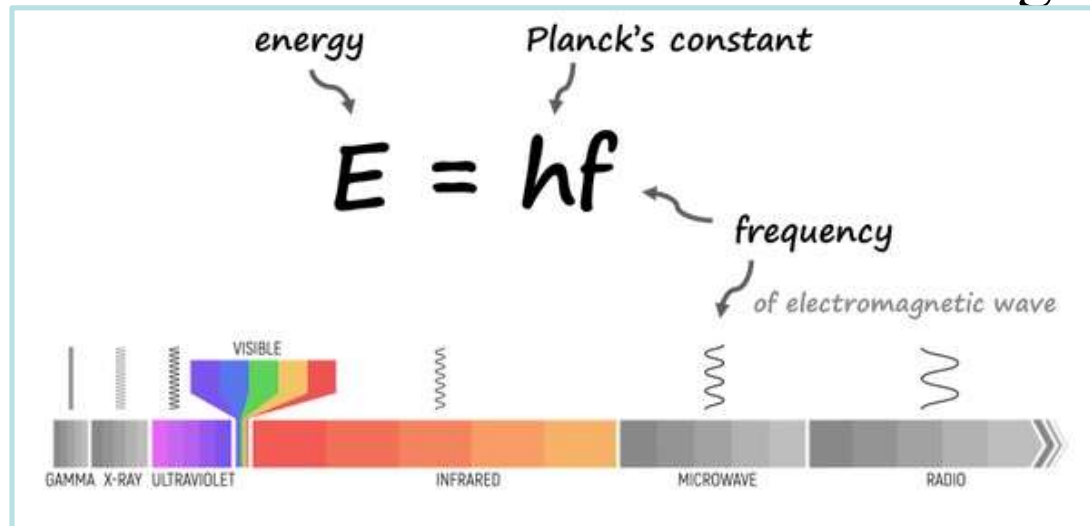
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EM Radiation

electric component

direction of wave propagation

magnetic component
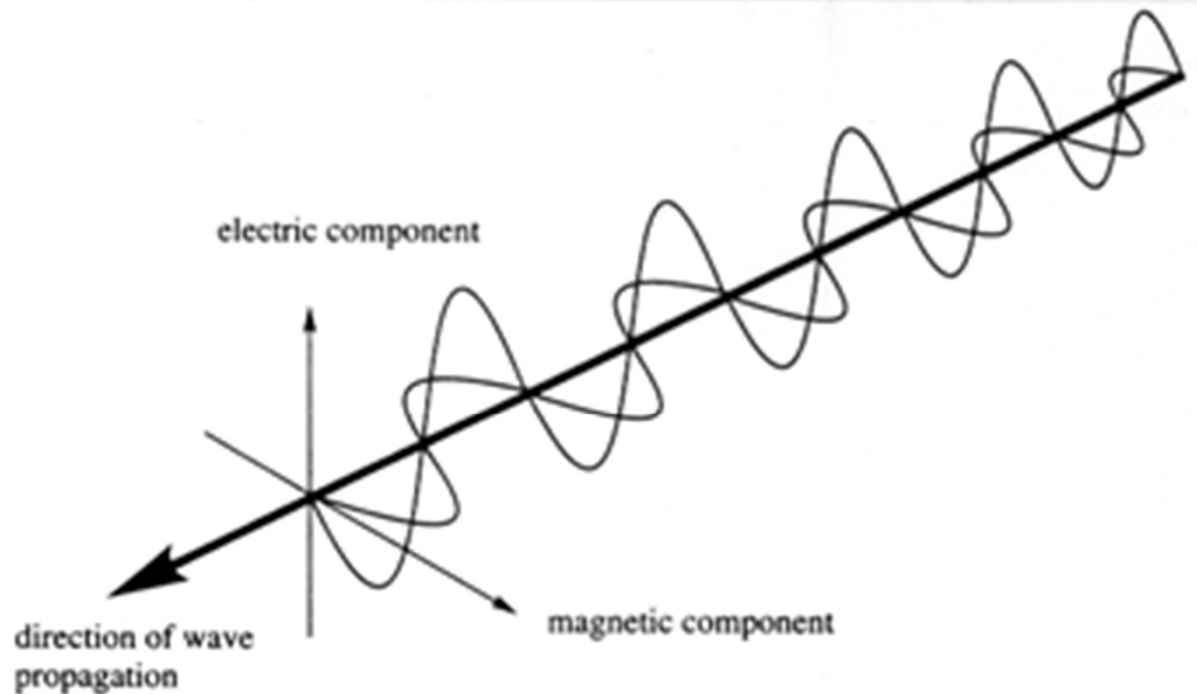
The classical wave form depiction of electromagnetic radiation.

EM wave consists of orthogonal electric and magnetic fields oscillating in phase at the same frequency

- can be defined by either
- wavelength (λ)
- wavenumber ($\tilde{v}$)
- frequency (v)
- (Different styles of presenting)

$$v = c/\lambda = c\,\tilde{v}$$

v : frequency (Hz, note 1 Hz = 1 s^{-1})

c: speed of light, 3 x 10^8 m s^{-1} or 3 x 10^{10} cm s^{-1}

λ : wavelength
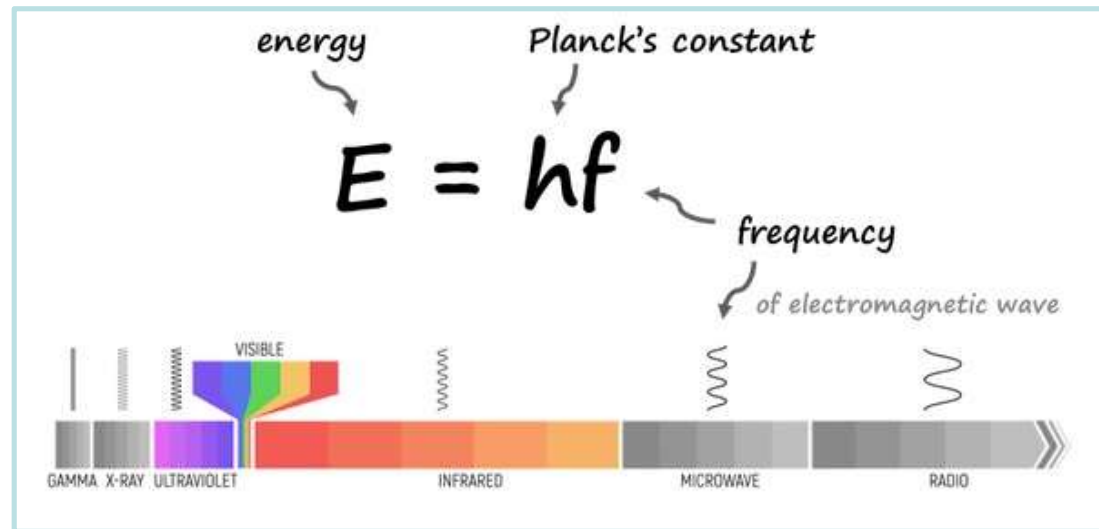
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Velocity = c = νλ, => $\nu = c/\lambda = c \tilde{\nu}$

$\tilde{\nu}$: wavenumber of light (cm^{-1})

Inverse wavelength, $\tilde{\nu} = 1/\lambda$.

cycles of the EM radiation in 1 cm.

$E = h\nu$

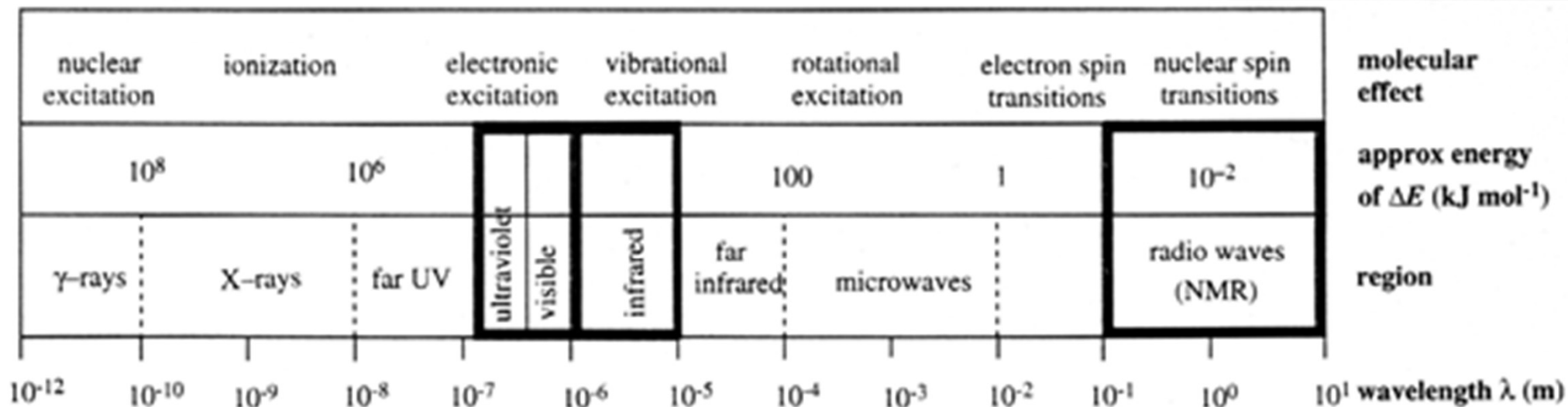$E = h(c/\lambda) = hc \tilde{\nu}$

Energy is proportional to frequency

    Inversely proportional to wavelength

    Proportional to wavenumber

E: energy (J)

h: Planck's constant 6.63 x 10^{-34} (J s)

Electromagnetic Spectrum

molecular effect	nuclear excitation	ionization	electronic excitation	vibrational excitation	rotational excitation	electron spin transitions	nuclear spin transitions
approx energy of ΔE (kJ mol^{-1})	10^8	10^6			100	1	10^{-2}
region	γ-rays	X-rays	far UV / ultraviolet / visible	infrared / far infrared	microwaves		radio waves (NMR)
wavelength λ (m)	10^{-12} 10^{-10} 10^{-9} 10^{-8}		10^{-7} 10^{-6}	10^{-5}	10^{-4} 10^{-3} 10^{-2}	10^{-1}	10^0 10^1

The electromagnetic spectrum. **Note** the wavelength scale is logarithmic.
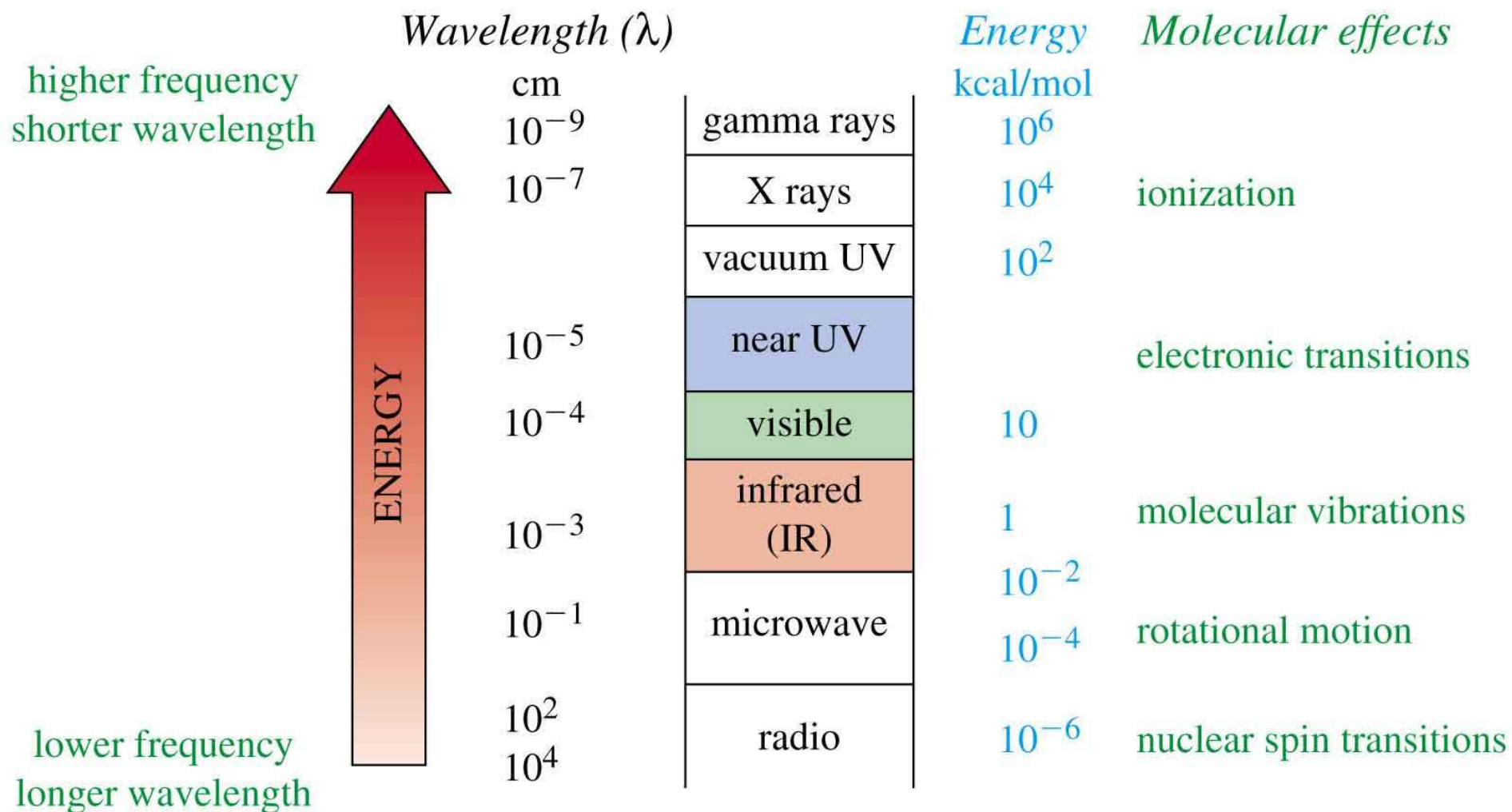
Sensitivity is influenced by ΔE
UV and higher is destructive
Molecular effect determines what structural information can be interrogated

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Absorption Spectroscopy

Wavelength (λ)

higher frequency shorter wavelength			Energy	Molecular effects
	cm		kcal/mol	
	10^{-9}	gamma rays	10^6	
	10^{-7}	X rays	10^4	ionization
		vacuum UV	10^2	
	10^{-5}	near UV		electronic transitions
	10^{-4}	visible	10	
	10^{-3}	infrared (IR)	1	molecular vibrations
			10^{-2}	
	10^{-1}	microwave	10^{-4}	rotational motion
	10^2 10^4	radio	10^{-6}	nuclear spin transitions

lower frequency longer wavelength

ENERGY

• non-destructive techniques often preferred

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Spectrometers

Continuous Wave

- First generation instrument.

- Simplest way of recording absorption frequency involves irradiating the sample by sweeping/scanning through the wavelength range, recording I_0-I vs frequency

Fourier Transform (FT)

- the development of FT IR/NMR spectrometers has made their CW equivalents obsolete, due to their superior sensitivity and speed of operation.
- the sample is irradiated over the entire bandwidth ie all frequencies, and then detecting all frequencies simultaneously as a complex interference pattern.

Fourier Transform (FT)

The FT is a mathematical manipulation a time domain spectrum (the interference signal) to a frequency domain spectrum.

Time Domain
$s(t)$

FT

Frequency Domain
$S(\omega)$
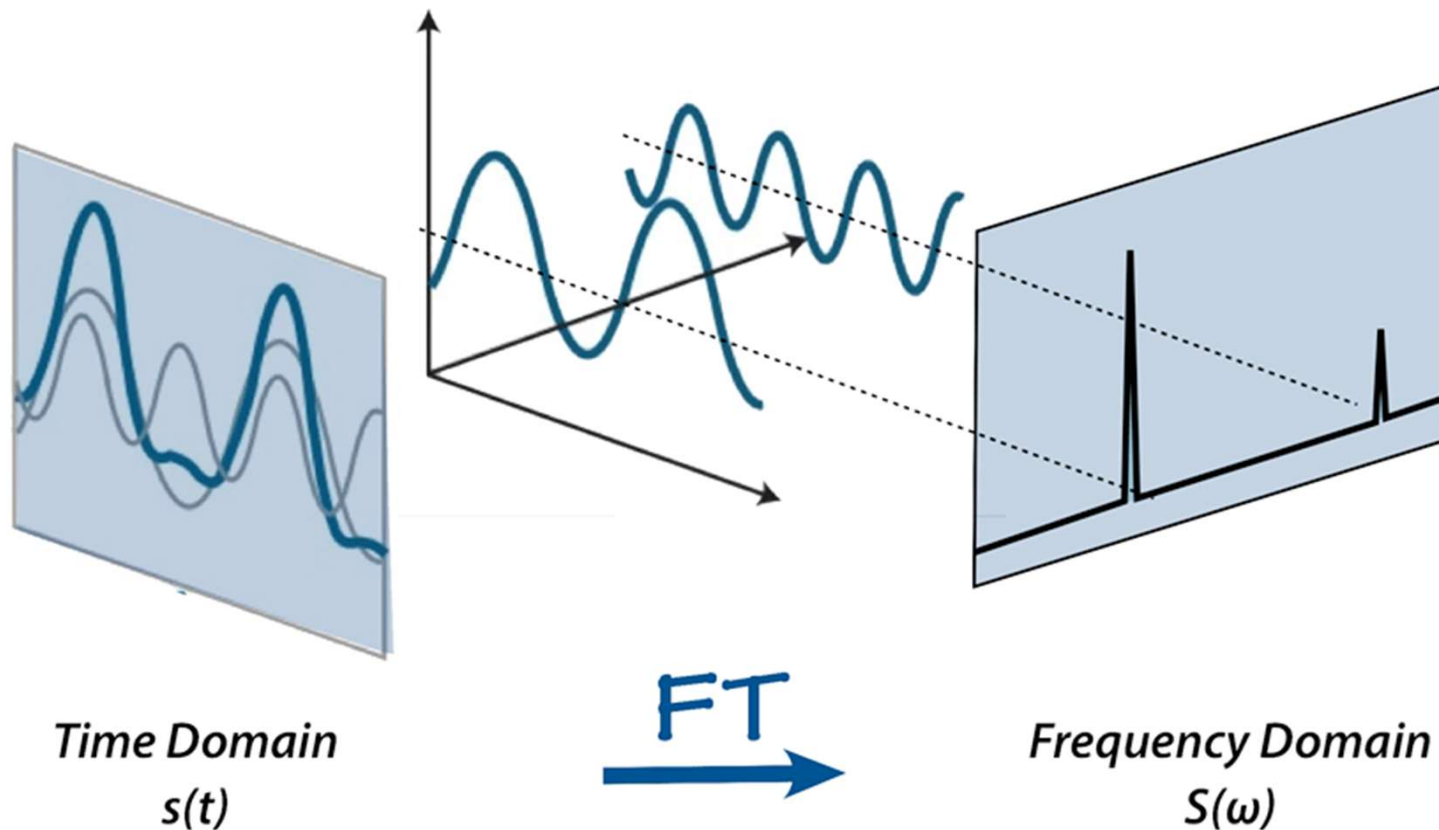
Complex overlapping waves →

'List' of constituent waves and their relative intensity and phase

Fourier Transform (FT) Spectrometers

- **FT-IR**   the resulting interferogram corresponds to the frequencies that pass through the sample and are not absorbed. This 'transmission' spectrum is usually converted to a 'absorbance' spectrum (how?).

- **FT-NMR**   the detected signal, known as the free induction decay (FID) arises from the excited species re-emitting the absorbed frequencies as they return to their ground state (relaxation).

Reverse Fourier Transforms.

(a)

(b)

$\tilde{v}$

(c)
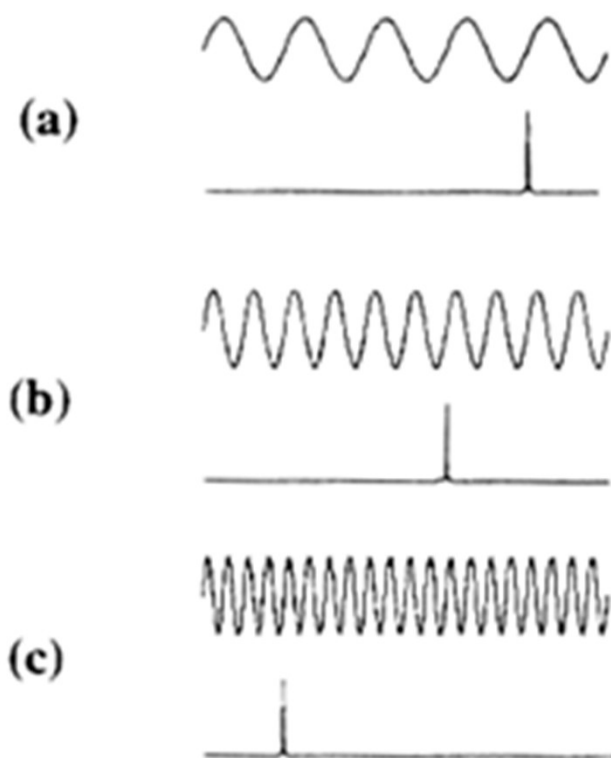
Effects of carrying out Fourier
transforms on sine waves having
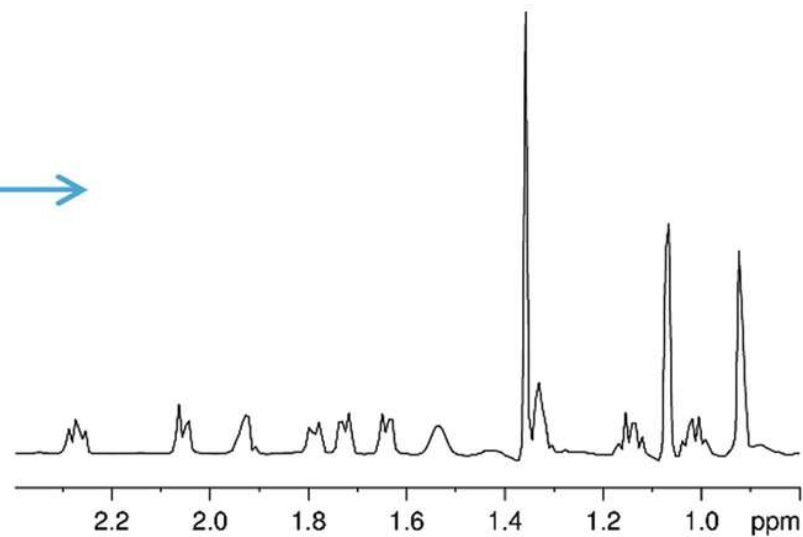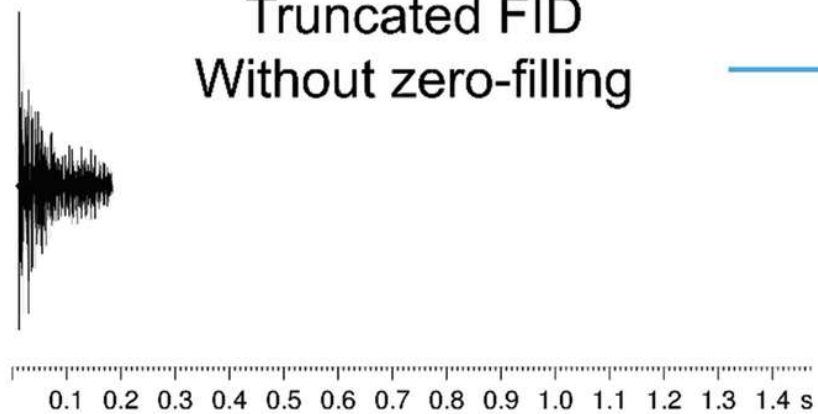frequencies (a) 50 Hz (b) 100 Hz
(c) 200 Hz.

(a)

(b)

(c)
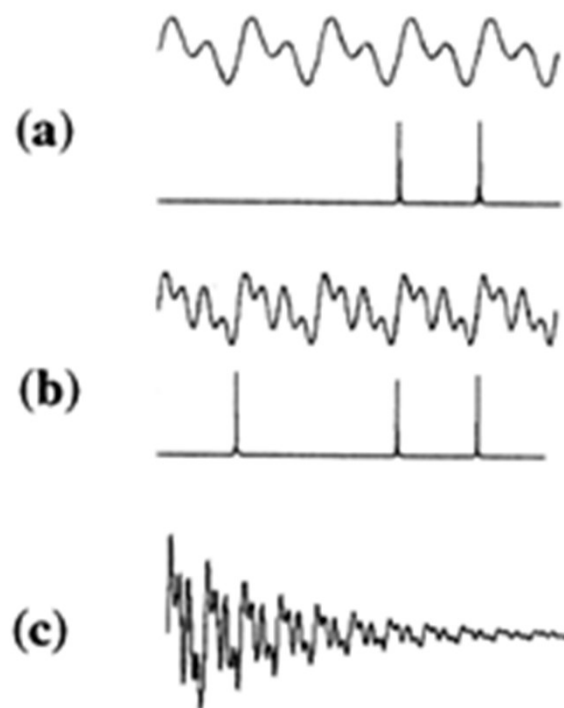
Effects of carrying out Fourier
transforms on progressively more
complex interference patterns.
(a) 50 + 100 Hz (b) 50 + 100 + 200 Hz
(c) 50 + 100 + 200 Hz FID.

Signal decays in amplitude as relaxation occurs

Real FID