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NPTEL ONLINE
CERTIFICATION COURSE

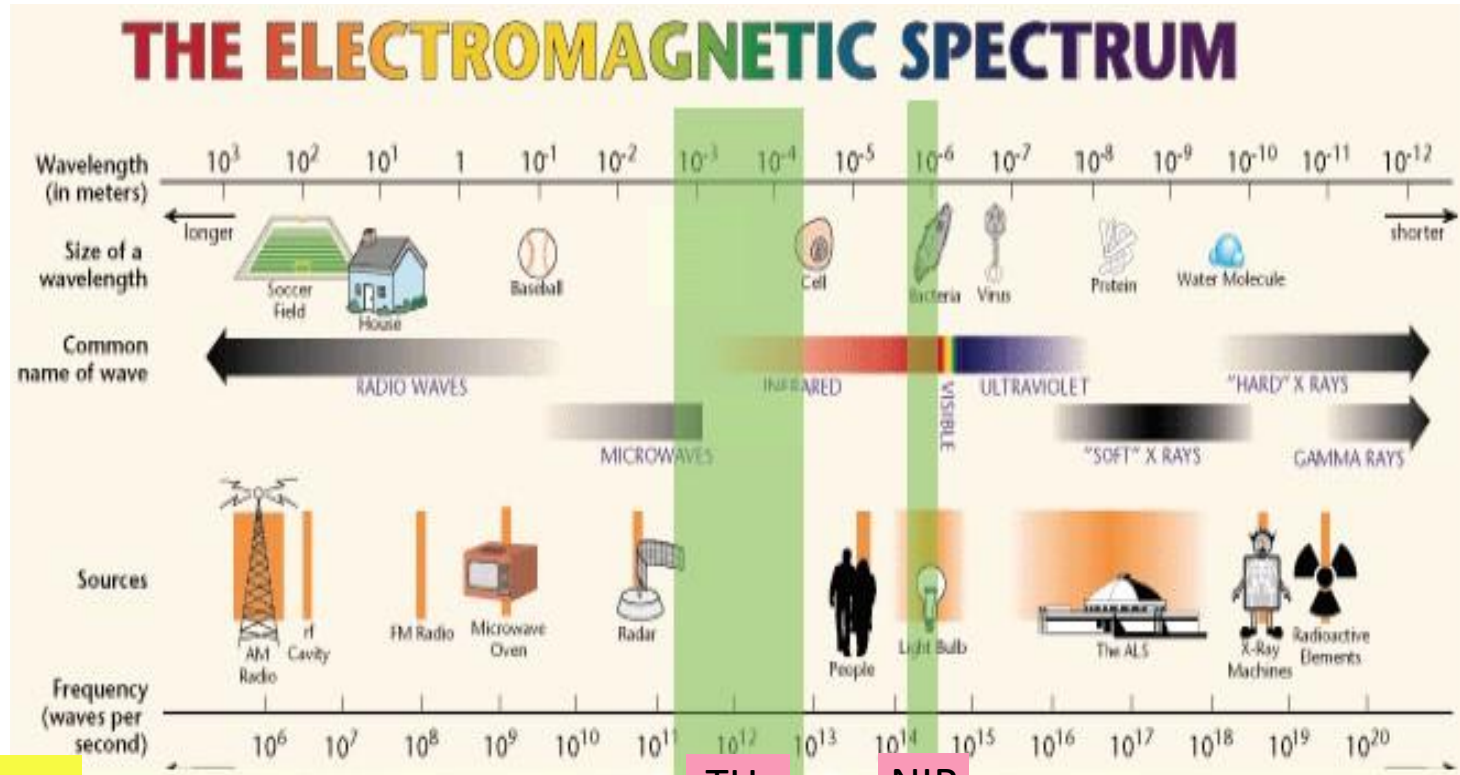
Lecture 20: Terahertz Based Detection, Circular Dichroism Terahertz Applications, Chirality, polarization rotation and dichroism

Sachin Kumar Srivastava

Department of Physics



The THz Range in the EM Spectrum

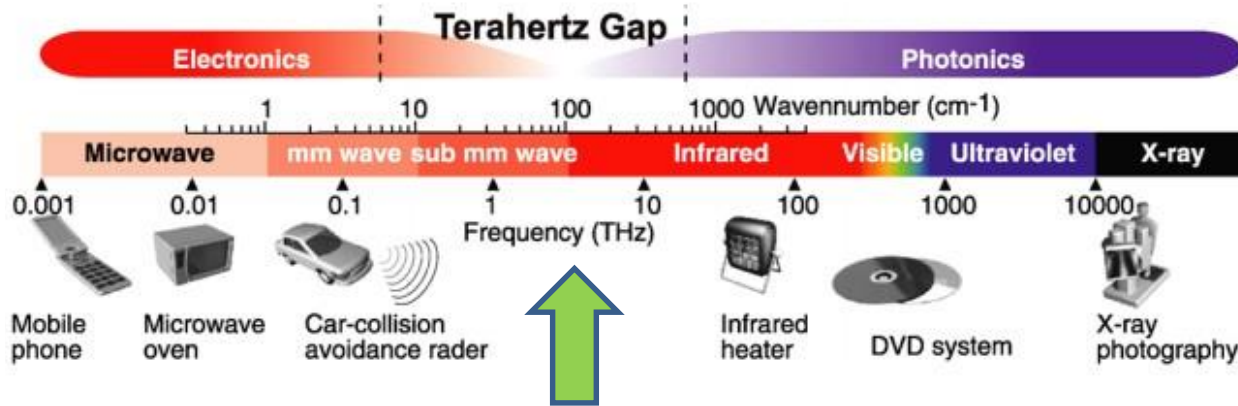


1THz=300 μ m

THz

NIR

What is Terahertz Gap?



- Range: 0.1 to 10THz
- $1\text{THz} = 10^{12}\text{ Hz}$
- Wavelength: 3 to 0.03mm
- Wave no.: 3.3 to 333.6 cm^{-1}
- Energy: 0.41 to 41 meV
- Temperature: 1 to 100K

- Non availability of THz generators and Detectors
- Non availability of stable femtosecond lasers

This restricts the application of THz in science and industry, offering complementary or even alternative methods of material characterization.

Appl. Phys. A, **2010**, 100, 591–597

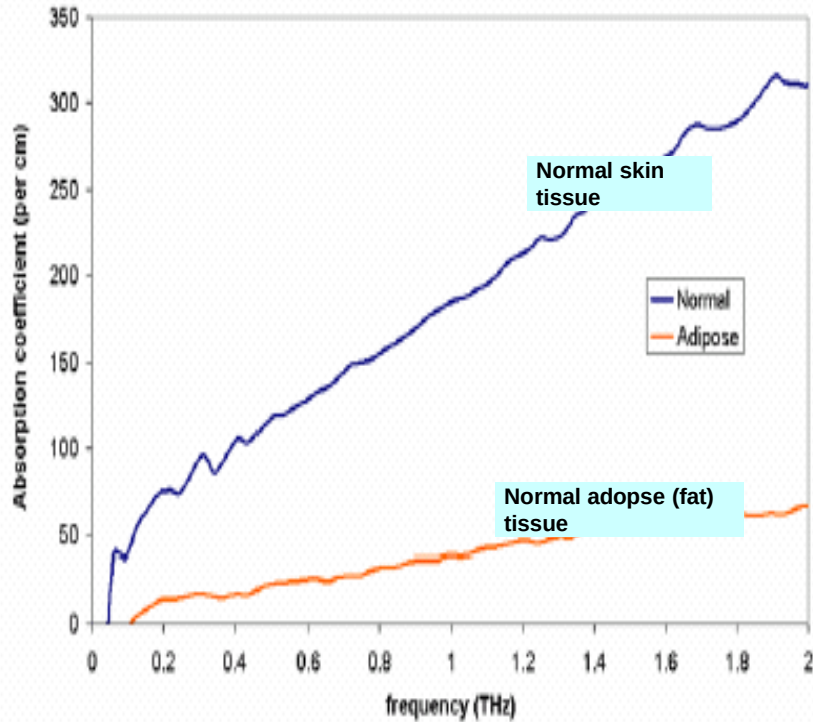
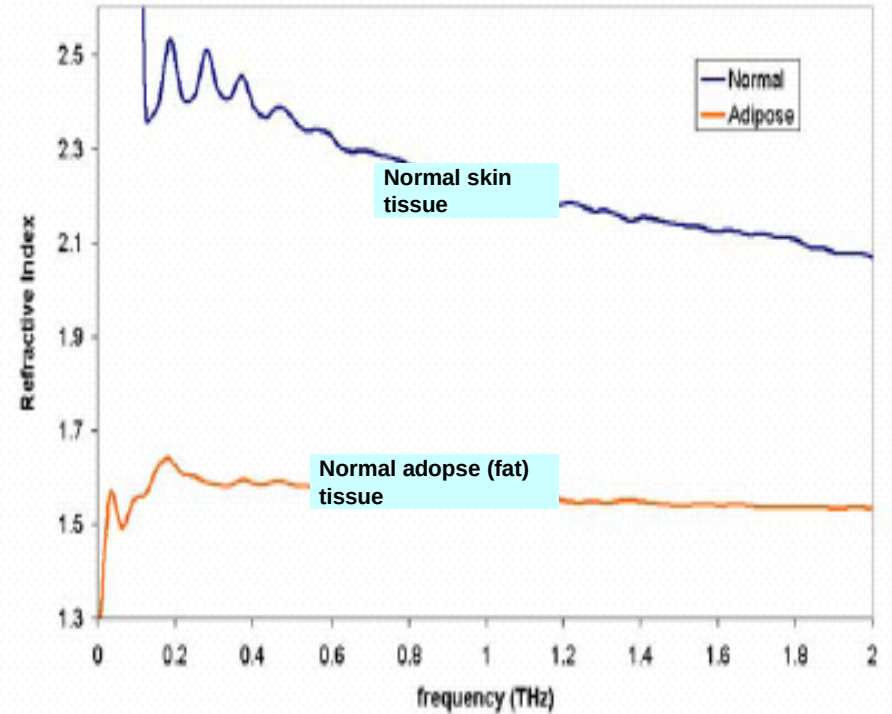
Properties of THz Radiation

- Terahertz waves can penetrate through materials opaque to other parts of the EM spectrum
- Packaging materials are transparent to some degree
- Does not make any chemical structure of the analytes, as compared to other
- Can be useful in communication
- It lies in such a region of the EM spectrum that it covers rotational transitions of many gases and vibrational transitions of weak bonds.



D. Clery, Science, **297**, 763 (2002)

THz Absorption Coefficient and Refractive Index of Tissue

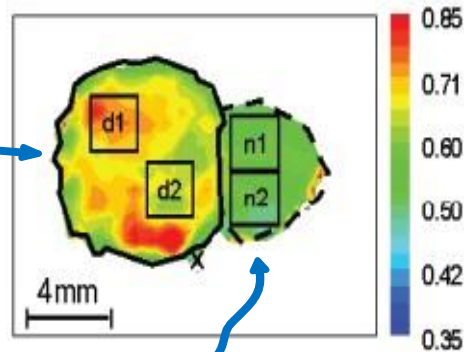


Biomedical Imaging with THz

Basal cell carcinoma (BCC), the most common form of skin cancer

Diseased tissue

Normal tissue



Melanoma In Transmission

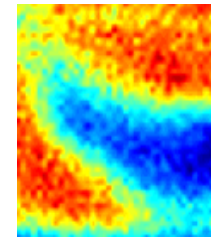
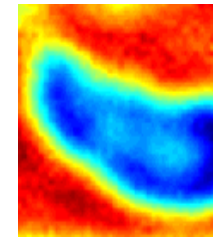
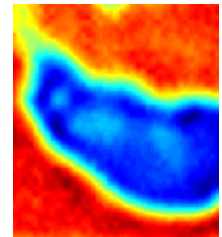
Terra View company



0.5THz

1.0THz

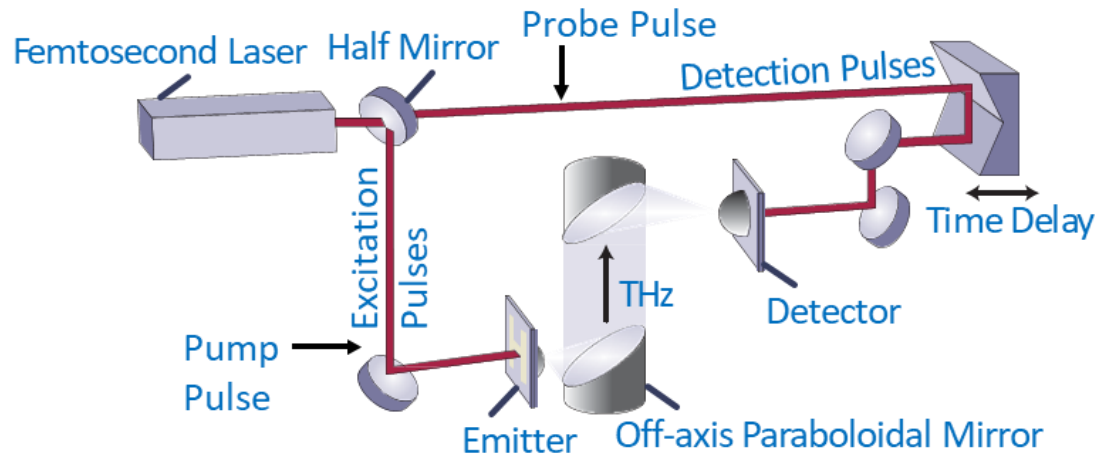
2.0THz



Woodward et.al.,The Society for Investigative Dermatology, **73**, (2003)

THz Time-domain Spectroscopy

It uses THz pulsed tradition and consists of an **Emitter** stimulated by femtosecond laser, a **beam forming optics** consisting of focuses lenses and mirrors, a sample holder and optical delay line and a **Detector** which uses a femtosecond laser.



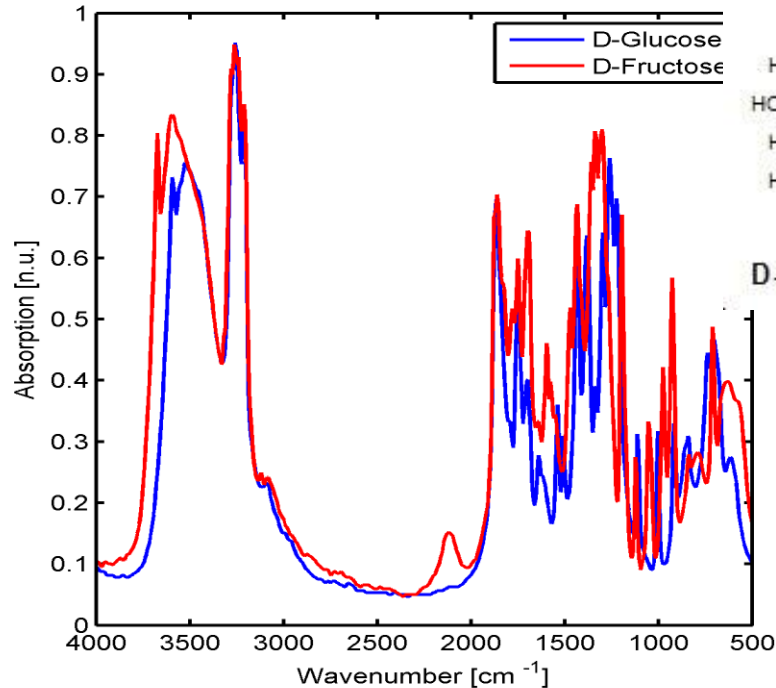
Schematic diagram of THz time domain spectrometer

- Difference absorption spectra technique, THz pulse is measured with and without the sample.
- The absorption and dispersion of the sample obtained by Fourier transformation.
- THz-TDS determines both the amplitude and the phase

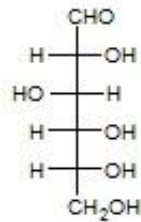
Nanotechnology, 2015, 26 (31), 5203

Chemical Analysis and Molecular Spectroscopy

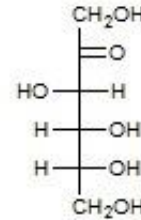
IR-Spectra



Differentiating the molecules

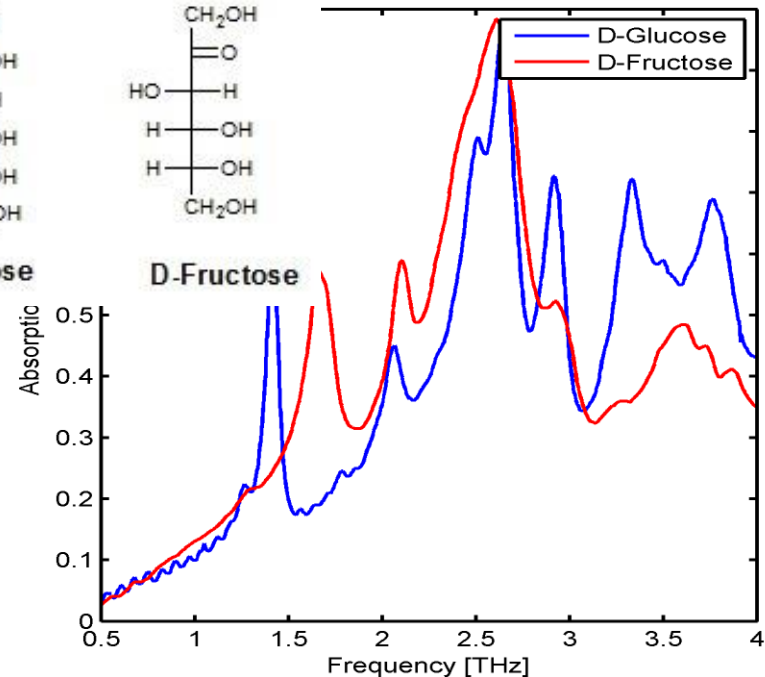


D-Glucose



D-Fructose

THz-Spectra

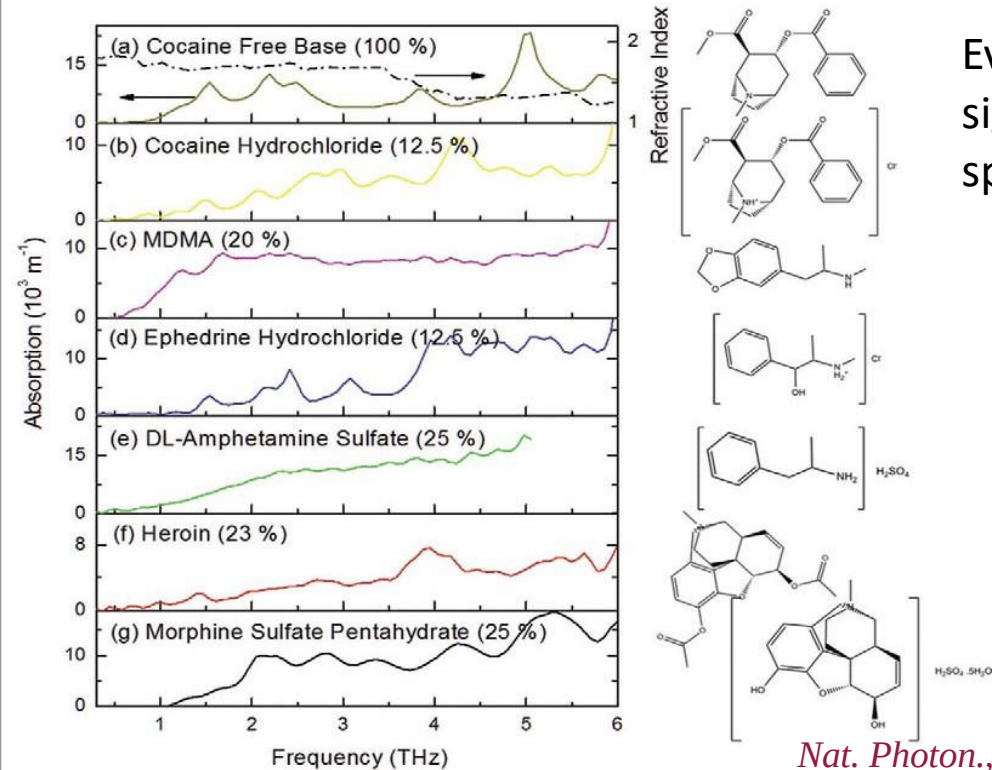


Zheng et al., Opt. Commun., **285**, 1868 (2012)

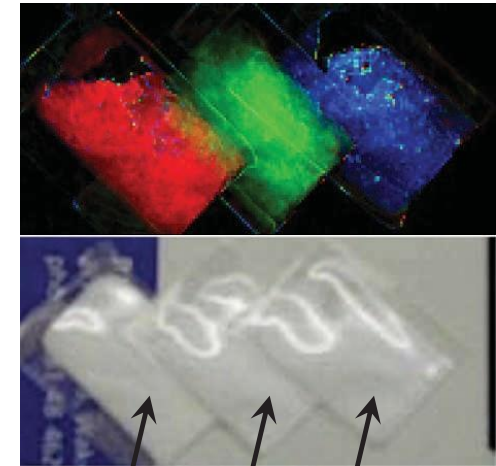


Tracing Illegal Drugs/ Narcotics

Due to low energy of THz radiation many vibrational and rotational modes fall within this region.



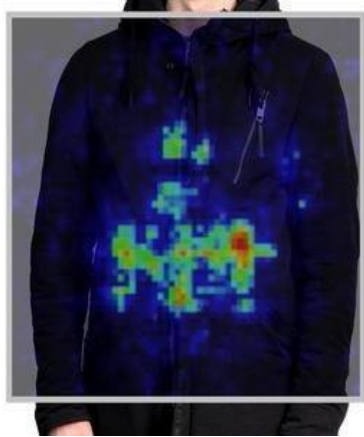
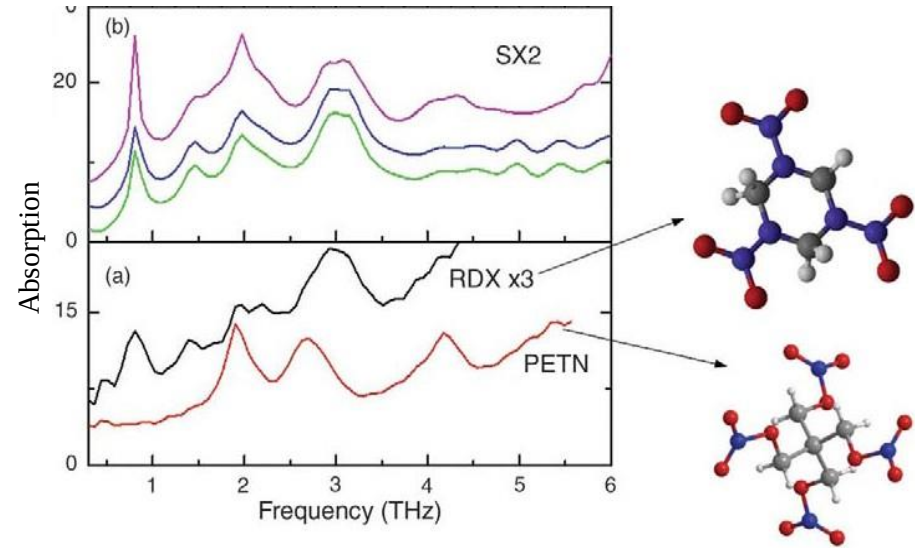
Every explosive and narcotic has a distinct signature in its THz spectra, making THz spectroscopy valuable for security applications.



Codeine Cocaine Sucrose

Nat. Photon., 2007, 1 97105

Tracing explosives

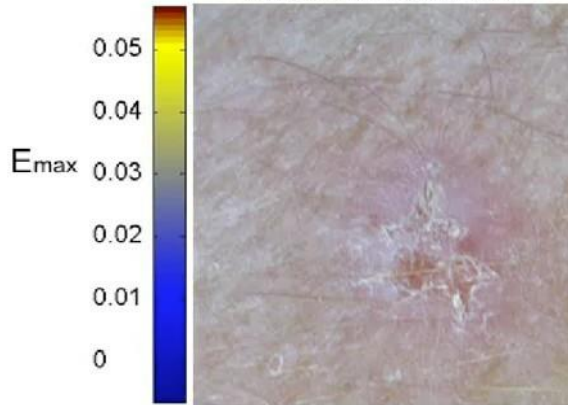


THz absorption spectra of a range of common explosives. The pure explosive samples (PETN and RDX) were diluted with PTFE powder to a 30:70 (explosive: PTFE) ratio by weight, and compressed into pellets

Sensesac and Thundat, Mater. Today, **11**, 28 (2008)

Applications in Biology and Medicine

Surface Features

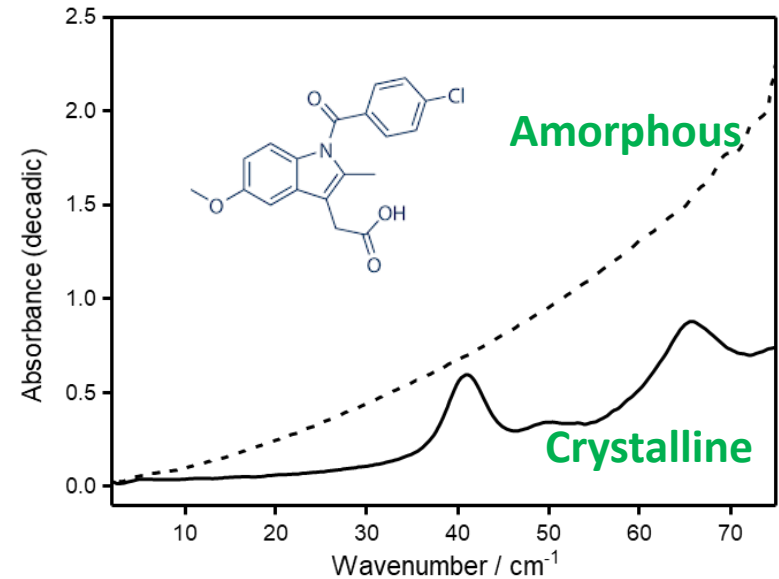


- Water has strong absorption in 1-3THz.
- So THz radiation can detect the difference in water content and density of a tissue.

teraview.com

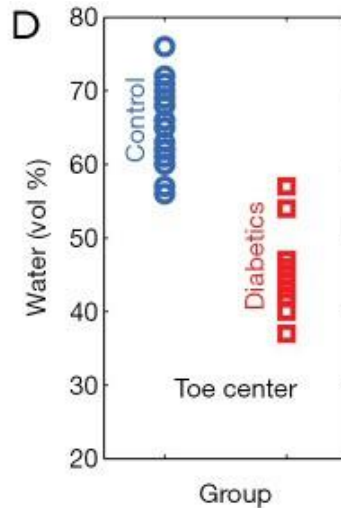
Pharmaceuticals:

Indomethacin (anti-inflammatory drug)



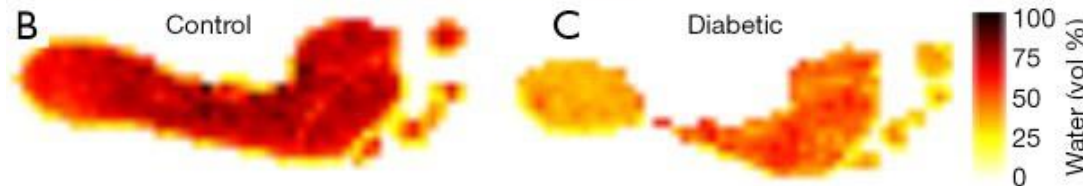
Strachan et al., Chem. Phy. Lett. 390, 20 (2004)

Confirmation of Diabetes Using THz Foot Measurement



(A) Photograph of the measurement set-up. THz images plotting the calculated water volume for (B) a control and (C) a diabetic patient. (D)

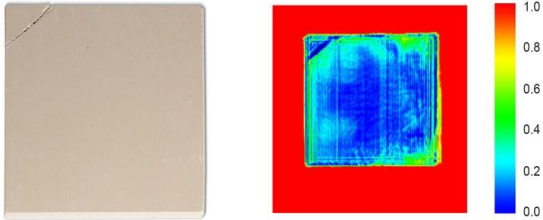
Calculated water volume for control and diabetic patients using data from the centre of the big toe.



Sun et al., Quant Imaging Med. Surg., 7, 345 (2017)

THz imaging

Crack in ceramic



Check before you buy next time..



Concealed knife under the sole of shoe



Visible image of an IC



THz image

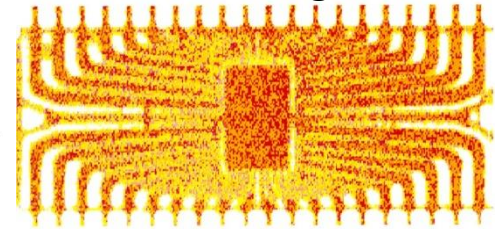
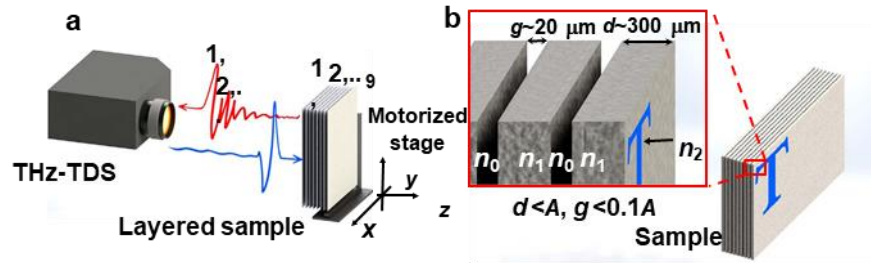


Plate 1. THz image of a packaged semiconductor integrated circuit (plastic packaging).

Terasense and Teraview

Hu and Nuss, Opt. Lett., **20**, 1716 (1995)

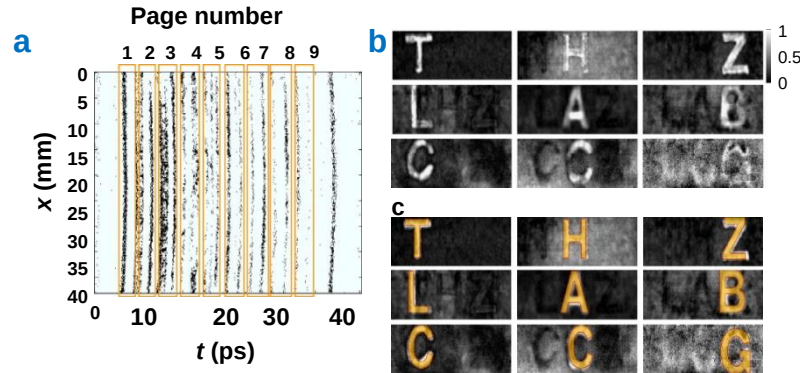
Read through a book without opening it..



Nine roman letters T, H, Z, L, A, B, C, C and G are written on nine pages

Page 1	Page 2	Page 3
T	H	Z
Page 4	Page 5	Page 6
L	A	B
Page 7	Page 8	Page 9
C	C	G

- THz-TDS measurement in reflection geometry
- Layered Sample: Nine packed paper layers of uniform thickness



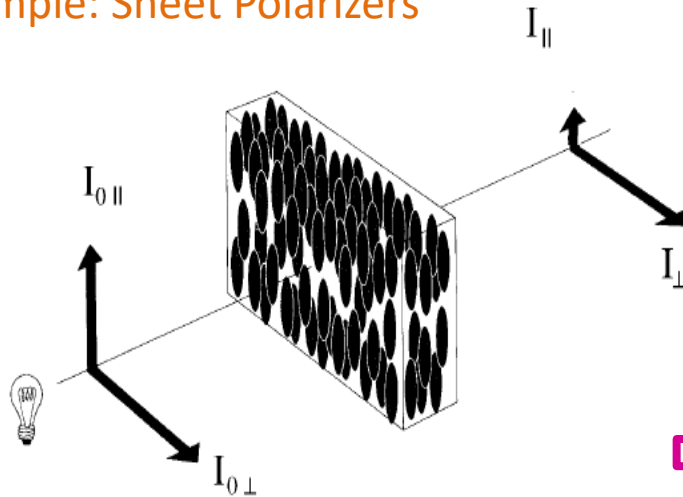
- Layers are identified in time based on the statistics of the reflected bipolar THz field signal
- Then converted the time-gated Fourier transform to contrast the content.
- Convex cardinal shape composition algorithm extracts the occluded characters through THz noise down to page 9.

Aghasi et al., Nat. Comm. **7**, 12665 (2016)

Linear Dichroism

Absorption of one of two plane-polarized components of transmitted light more strongly than the other

Example: Sheet Polarizers

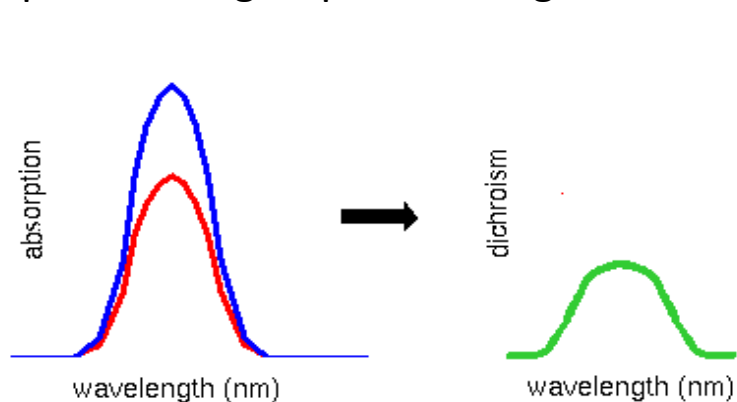


$$LD = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} \quad \text{A-absorbance}$$

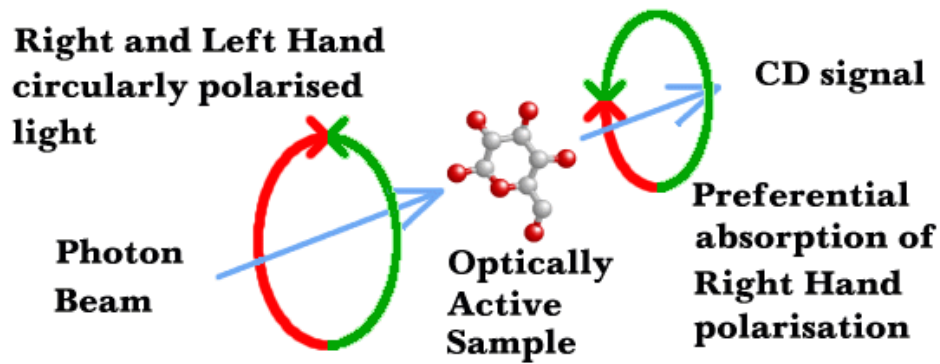
Similarly for circular dichroism and circularly polarized light

Circular Dichroism

CD measures the **difference** between the absorption of **left** and **right** handed circularly-polarized light. polarized light:



http://www.cryst.bbk.ac.uk/BBS/whatis/cd_website.html



$$\Delta A(\lambda) = A_R(\lambda) - A_L(\lambda) = [\epsilon_R(\lambda) - \epsilon_L(\lambda)]/c$$

or

$$\Delta A(\lambda) = \Delta \epsilon(\lambda)/c$$

staff.bath.ac.uk/bssmdb/cd_lecture.ppt

If linearly polarized light passes through an optically active substance, it is possible that not only the speeds of the two circularly polarized components are different, but also the absorption coefficients, ϵ_L and ϵ_R . The difference in the absorption coefficient is determined. Since the absorptions of the left circularly polarized light and the right circularly polarized light are different, elliptically polarized light emerges from the sample. In practice of CD spectroscopy the ellipticity is determined from the difference of the absorption coefficients:

$$\Theta_\lambda = \text{const} \cdot (\epsilon_L - \epsilon_R) \cdot c \cdot d \quad (\text{Grad})$$

where d is the thickness and c the concentration of the sample. Const is given by $\text{const} = \frac{180}{4\pi} \ln(10) \approx 33$

The molar ellipticity is then given by $[\theta]_\lambda = \frac{M_r \Theta_\lambda}{10 \cdot d \cdot c} \quad \left(\frac{\text{Grad} \cdot \text{cm}^2}{\text{mol}} \right)$ 1grad=0.9deg

M_r is the molar mass in $\text{g} \cdot \text{mol}^{-1}$. If the molar extinction coefficients of the left and right circularly polarized light are known, the molar ellipticity can be expressed as

$$[\theta]_\lambda = 3300 \cdot \Delta\epsilon$$

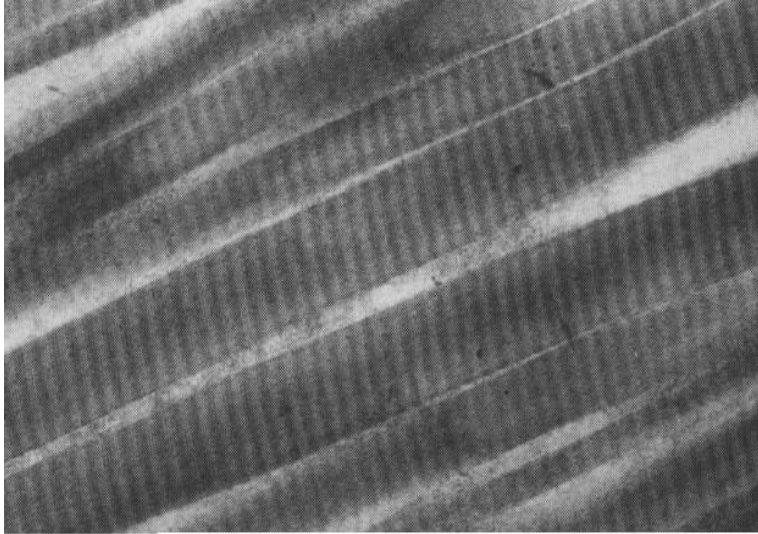
Show this!

The sign of the CD is different in the two sides of the absorption band

$$\begin{aligned} CD &= A_l - A_r \\ CD &= \epsilon_l - \epsilon_r \\ \tan \theta &= \tanh \left(\frac{\pi d (n'_l - n'_r)}{\lambda} \right) \\ \theta &\approx \frac{\pi d (n'_l - n'_r)}{\lambda} [\text{rads}] \end{aligned}$$



Birefringence



Collagen fibers (about 2-3 μm in diameter) are composed of bundles of smaller **collagen fibrils** about 0.3 μm in diameter

Orientational order



Form Birefringence

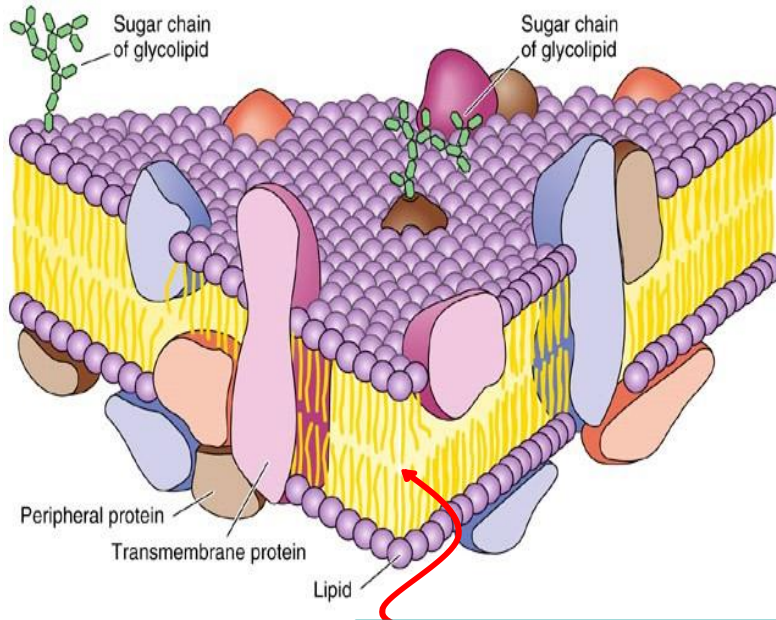


Polarization dependence

Birefringence in Cell Membrane

Fluid mosaic model of membrane structure

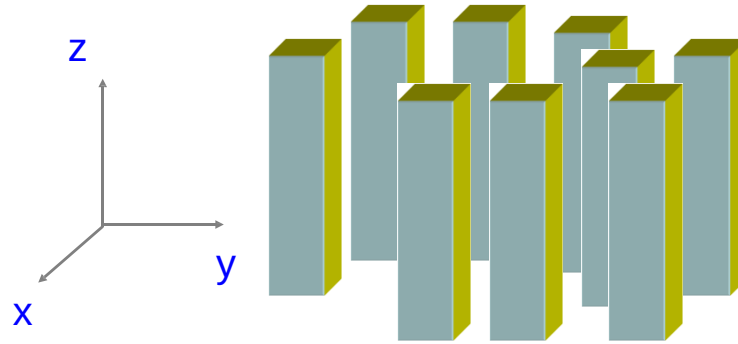
A Carbohydrate chains bound to lipids and proteins



Lyotropic liquid crystals

The membrane consists of a phospholipid double layer with proteins inserted in it (integral proteins) or bound to the cytoplasmic surface (peripheral proteins). Some of these proteins completely span the bilayer and are called transmembrane proteins, whereas others are embedded in either the outer or inner leaflet of the lipid bilayer. The dotted line in the integral membrane protein is the region where hydrophobic amino acids interact with the hydrophobic portions of the membrane..(from Krstić RV: Ultrastructure of the Mammalian Cell. Springer- Verlag, 1979.)

Form Birefringence

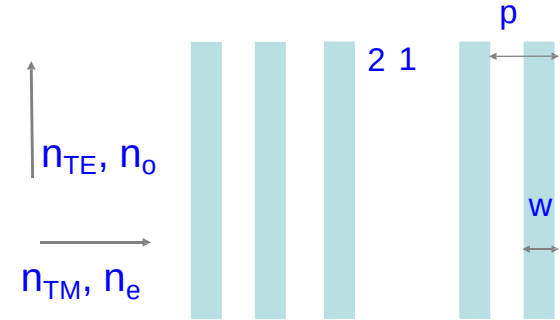


Response in
x, y and z is
different

Periodic gratings behave as negative index uniaxial film with optic axis along the gratings vector

$$n_{TM} = \frac{n_1 n_2}{\sqrt{n_1^2(1-f) + f n_2^2}}$$

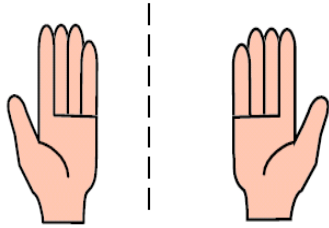
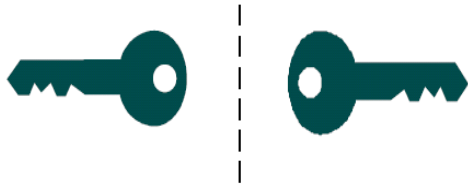
$$n_{TE} = \sqrt{n_2^2(1-f) + f n_1^2}$$



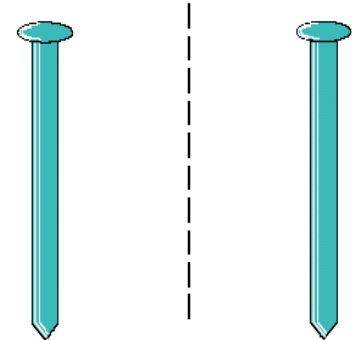
Principles of Optics, Born & Wolf page 730

Chirality

A **chiral** object is not superimposable on its mirror image. Examples include hands, screws, propellers, and keys

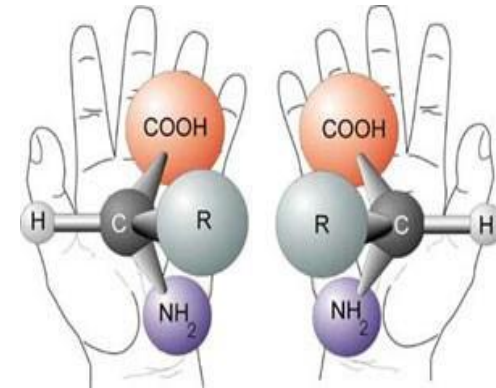


Achiral objects



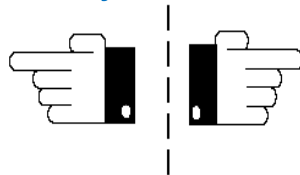
Chirality and Symmetry

- Whether or not a molecule or crystal is chiral is determined by its *symmetry*. A molecule is *achiral* (non-chiral) if and only if it has an *axis of improper rotation*, that is, an **n-fold rotation** (rotation by $360^\circ/n$) followed by a reflection in the plane perpendicular to this axis maps the molecule on to itself. Thus a molecule is chiral if and only if it *lacks* such an axis.
- Because chiral molecules lack this type of symmetry, they are called **dissymmetric**. They are not necessarily **asymmetric** (i.e. without symmetry), because they can have other types of symmetry. However, all **amino acids** (except glycine) and many **sugars** are indeed asymmetric as well as dissymmetric.

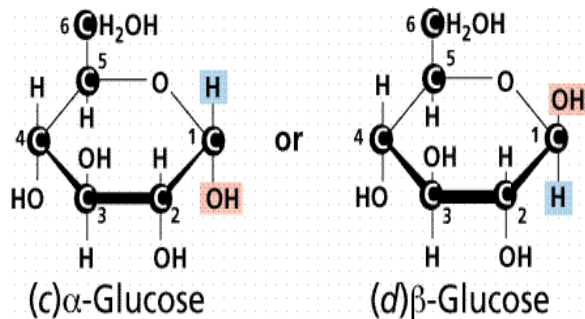
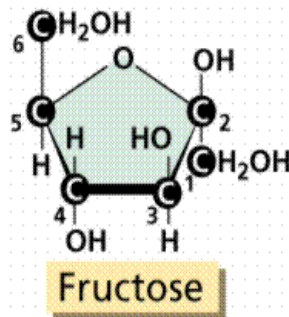


Enantiomers

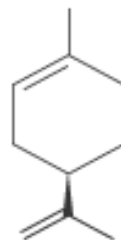
The two forms of a chiral object are known as **Enantiomers**



Unlike other stereoisomers, enantiomers have **identical physical properties** and consequently are difficult to separate and quantitate.

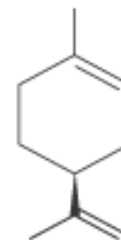


Smells like oranges



(*R*)-limonene

Smells like lemons

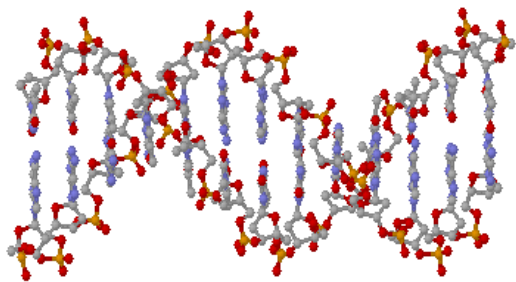


(*S*)-limonene

mirror plane

Optical Rotation

- *Enantiomers can rotate the plane of polarization of plane-polarized light.*
- **Dextrorotatory (+)** enantiomer giving a positive optical rotation
Levorotatory (-) enantiomer giving a negative optical rotation
- The “dl” nomenclature system previously used to designate the sign of optical rotation is no longer used, (+) and (-) symbols are now preferred.



L. Pasteur, Ann. Chim. Phys., Series 3, 24, 442 (1848).

Circular Modes and Optical Activity

$$\left. \begin{aligned} \hat{R} &= \frac{1}{\sqrt{2}} (\hat{x} - i\hat{y}) \\ \hat{L} &= \frac{1}{\sqrt{2}} (\hat{x} + i\hat{y}) \end{aligned} \right\} \Rightarrow \begin{aligned} \hat{x} &= \frac{1}{\sqrt{2}} (\hat{R} + \hat{L}) \\ \hat{y} &= \frac{i}{\sqrt{2}} (\hat{R} - \hat{L}) \end{aligned}$$

The two circular polarizations propagate with different wavevectors: $k_{r,l} = \frac{2\pi n_{r,l}}{\lambda}$

$$\left. \begin{aligned} E_R &= \hat{R} e^{i(\omega t - k_r z)} \\ E_L &= \hat{L} e^{i(\omega t - k_l z)} \end{aligned} \right\} \Rightarrow E = \exp \left[i(\omega t - k_{av} z) \right] \left\{ \hat{x} \cos \left(\frac{k_l - k_r}{2} z \right) + \hat{y} \right\} \sin \left(\frac{k_l - k_r}{2} z \right)$$

Hence the total field is linearly polarized rotating counterclockwise with a rate:

$$\rho = \pi(n_l - n_r) / \lambda$$

- the optical rotatory power. RH when

$$n_l > n_r$$

Specific Rotatory Power

Optical Rotation Angle: $\alpha_\lambda = 180(n_i - n_r)d / \lambda [\text{deg.}]$

Specific Rotation: $[\alpha]_\lambda = \frac{\alpha_\lambda}{c.d} \left[\frac{\text{deg.cm}^2}{g} \right]$

With respect to molar mass M_r in g.mole^{-1} :

$$[\alpha]_\lambda = \frac{\alpha_\lambda M_r}{c.d} \left[\frac{\text{deg.cm}^2}{\text{mole}} \right]$$

For normal blood the glucose concentration is $c=100\text{mg/dL}$ which gives rise to rotation of polarization of $\alpha=0.004^\circ$ for sample thickness of $d=1\text{cm}$ at visible wavelengths ($\sim 550\text{nm}$).

What is $[\alpha]$?



Comparison of Absorbance and CD

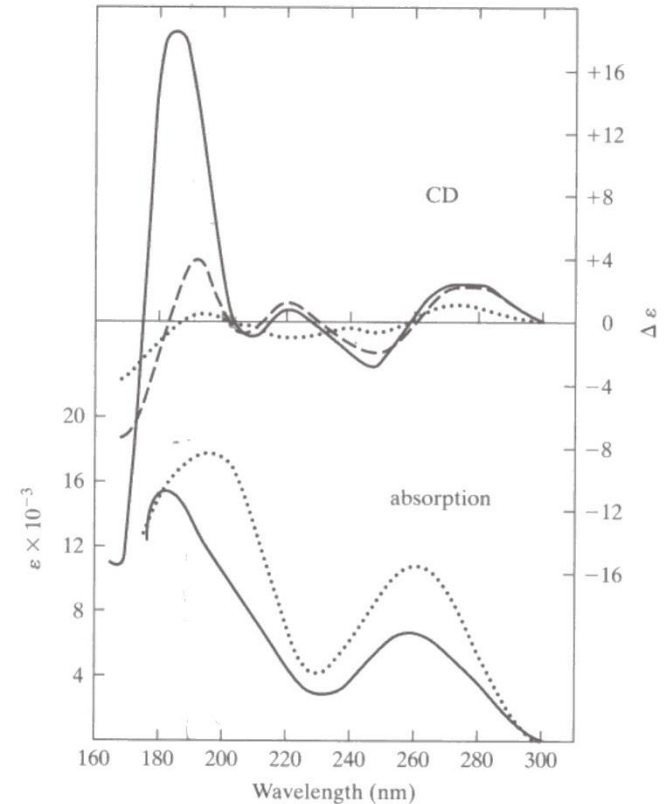
Example: Native (—) versus denatured (...) DNA

- Extinction coefficient at 260 nm:

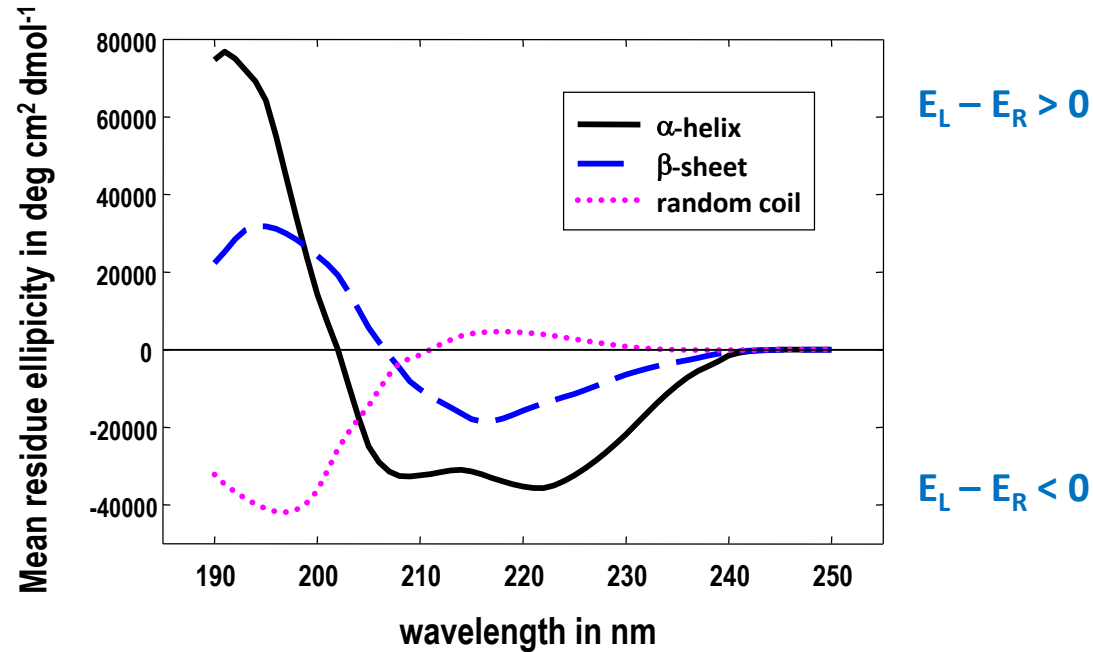
$$\Delta\epsilon = \sim 3 \text{ M}^{-1}\text{cm}^{-1}$$

$$\epsilon = \sim 6000 \text{ M}^{-1}\text{cm}^{-1}$$

The CD signal is 0.05% of the absorbance signal.

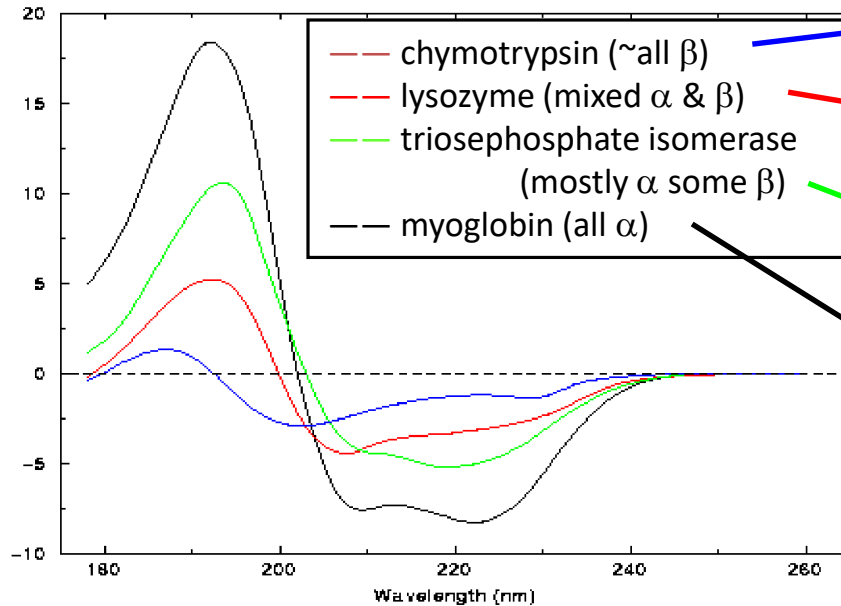
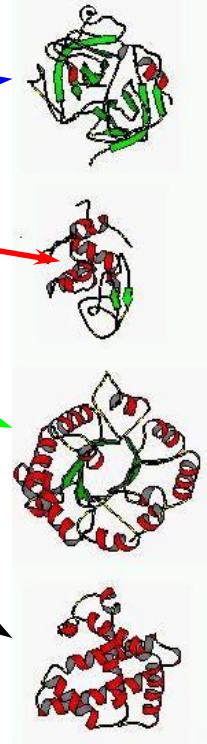


Fasman Standard Curves for Polylysine



staff.bath.ac.uk/bssmdb/cd_lecture.ppt

Real CD Spectra of Example Proteins



staff.bath.ac.uk/bssmdb/cd_lecture.ppt

Summary

1. Basics of THz spectroscopy and its applications were discussed
2. Circular Dichroism was discussed for the analysis of biomolecules.

Thank You







