Interference and Fourier Transform Spectroscopy

❑ Coherence and Interference

❑ Interferometry and Interferograms

❑ Fourier components

- time-dependence of a signal

- resolution

❑ Fourier Transform Spectroscopy

- Advantages

- Spectrometers

❑ Conclusions

Phase and Amplitude

Any oscillating quantity $\mathbf{A(t) = A_o \cos(\omega t - \underline{k} \cdot \underline{r} + \phi)}$ (for electro-magnetic waves the electric field vector and the magnetic field vector) is characterized by :
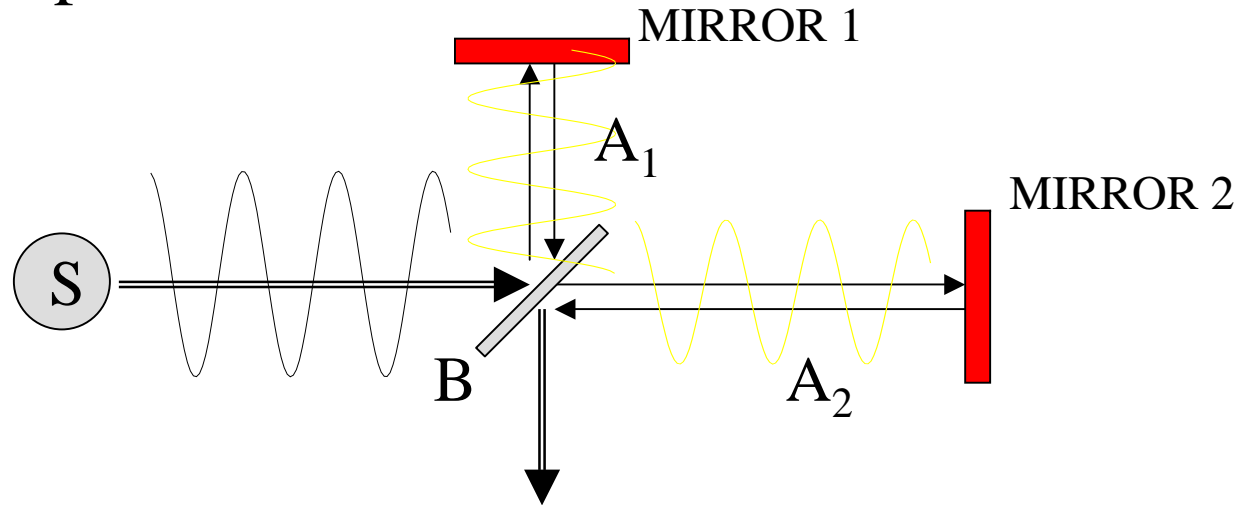
- the oscillation frequency ω

- the wavelength, $\lambda = 2\pi/|k| = 2\pi \, v/\omega$

Once the frequency has been fixed (monochromatic wave) and the velocity of propagation "v" is given

- the amplitude = the maximum value A_o

- the phase of the wave ϕ

Of course, the phase definition related to a reference e.g. a second component of the same beam

Let us consider a wave travelling from a source S to a beam splitter B

The two wave components (A_1, A_2) recombine at the exit of the interferometer and sum their instantaneous amplitudes: the eventual phase delay of one wave with respect to the other must be taken into account.

Phase modulation : Interferogram
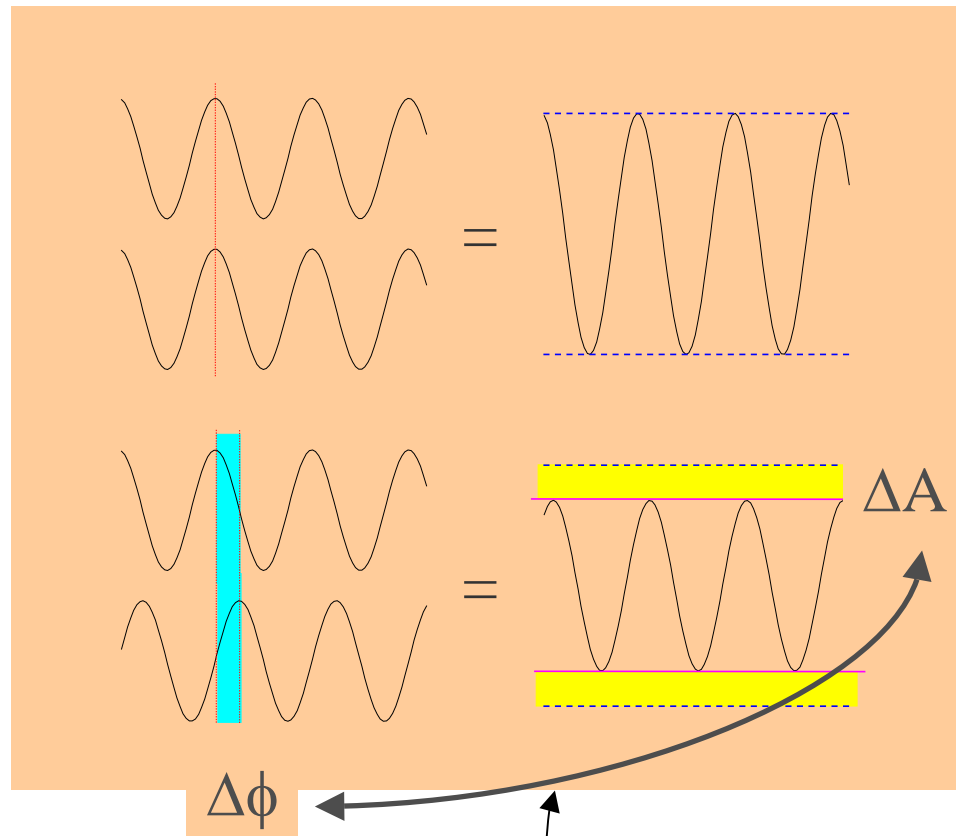
- The final amplitude of the out-coming wave is then modulated by the relative phase shift of the two wave components.

- When the phase shift (or the delay) of one of the compo-nents is changed (e.g.: by changing the optical path, moving a mirror or intro-ducing a different medium) the amplitude, and then the intensity of the outcoming wave is correspondingly changed.

Interferogram

$$A_1(\omega, t) = E_o e^{i(\omega t - \vec{k}_z \cdot \vec{z} + \varphi_1)}$$

$$A_2(\omega, t) = E_o e^{i(\omega t - \vec{k}_z \cdot (\vec{z} + \Delta\vec{z} + \varphi_2))}$$

$$A_T(\omega, t) = A_1(\omega, t) + A_2(\omega, t) =$$

$$= E_o(e^{i(\omega t - \vec{k}_z \cdot \vec{z} + \varphi_1)} + e^{i(\omega t - \vec{k}_z \cdot (\vec{z} + \Delta\vec{z} + \varphi_2))}) =$$

$$= E_o e^{i(\omega t - \vec{k}_z \cdot \vec{z} + \varphi_1)}(1 + e^{i(\varphi_2 - \varphi_1 - \vec{k}_z \cdot \Delta\vec{z})})$$

$$I(t) = \left| \tilde{A}_T(\omega, t) \cdot \tilde{A}_T^*(\omega, t) \right| =$$

$$= E_o^2(2 + e^{i(\varphi_2 - \varphi_1 - \vec{k}_z \cdot \Delta\vec{z})} + e^{-i(\varphi_2 - \varphi_1 - \vec{k}_z \cdot \Delta\vec{z})}) =$$

$$= E_o^2(2 + 2\cos(\Delta\varphi - \vec{k}_z \cdot \Delta\vec{z}))$$

Interferogram

- Each component with frequency ω and wavevector $k = \omega/c$ is then modulated by the spatial delay Δz;

- The whole beam can be described by the sum (the integral) of all the components;

- By considering the intensity of each component (and of the whole beam) one is obtaining a sum of a constant term and a modulated one.

Interferogram

$$A_1(\omega,t) = \int_{-\infty}^{+\infty} E_k e^{i(\omega t - k \cdot z + \varphi_{k1})} d\omega$$

$$A_2(\omega,t) = \int_{-\infty}^{+\infty} E_k e^{i(\omega t - k \cdot (z + \Delta z) + \varphi_{k2})} d\omega$$

$$A_T(\omega,t) = A_1(\omega,t) + A_2(\omega,t) =$$

$$= \int_{-\infty}^{+\infty} E_k e^{i(\omega t - k \cdot z + \varphi_{k1})} (1 + e^{i(-k \cdot \Delta z + \varphi_{k2} - \varphi_{k1})}) d\omega$$

$$\boxed{\omega = ck \qquad \Delta z = vt}$$

$$\Downarrow$$

$$I(t) = \left| \tilde{A}_T(\omega,t) \cdot \tilde{A}_T^*(\omega,t) \right| =$$

$$= \int_{-\infty}^{+\infty} E_k^2 \left(2 + 2\cos(\Delta\varphi - \frac{v}{c}\omega \cdot t)\right) d\omega$$

When the delay Δz is described as a continuous, linear function of time, one can show that the resulting intensity is also time dependent and corresponds to the Fourier transform of its spectral function.

Interferogram

- The function of time (interferogram) obtained is different depending on the spectral content of the light beam:

- A single frequency beam will be modulated as a continuous cosine function;

- A spectrum extended over a frequency region will approximate a delta function (pinned at $\Delta z=0$) as better as the frequency region is larger.

Interferogram and resolution
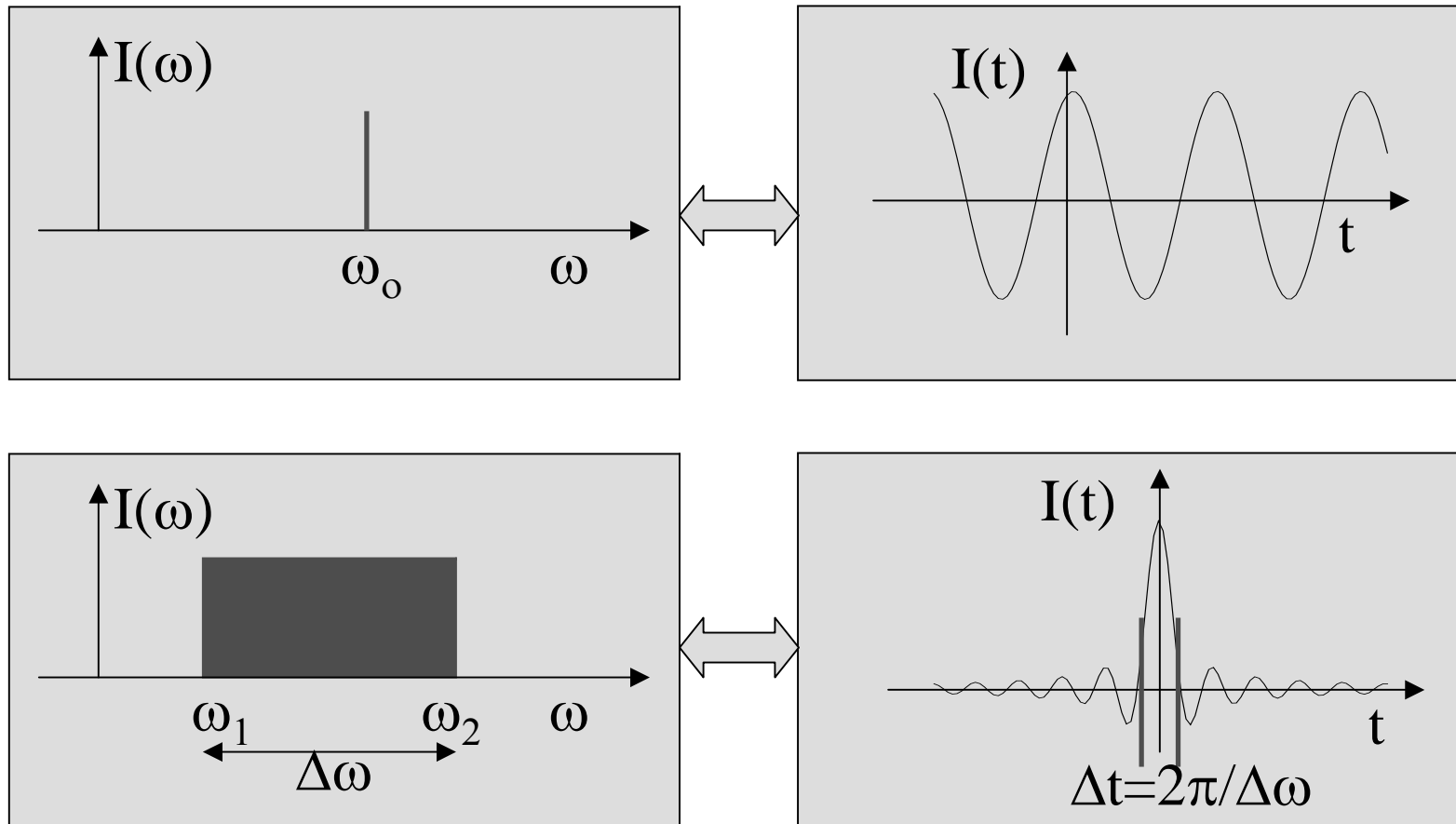
Interferogram and resolution

<u>Problem</u>: it is obviously impossible to measure an interferogram developing in time from -∞ to ∞.

What is then the effect of taking a limited portion of signal (let us say from t=-τ to t=τ)?

<u>Answer</u>: there is a kind of inverse symmetry between the two conjugated spaces. As shown in the pictures above, inasmuch a structure is narrow on one side, as much its transformed counterpart is extended.

This also means that we can only distinguish among different spectral components close one to the other if the corresponding interferogram is wide enough.
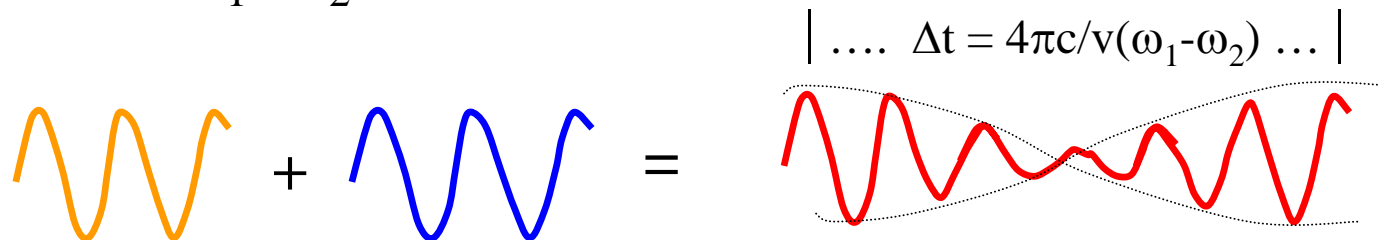
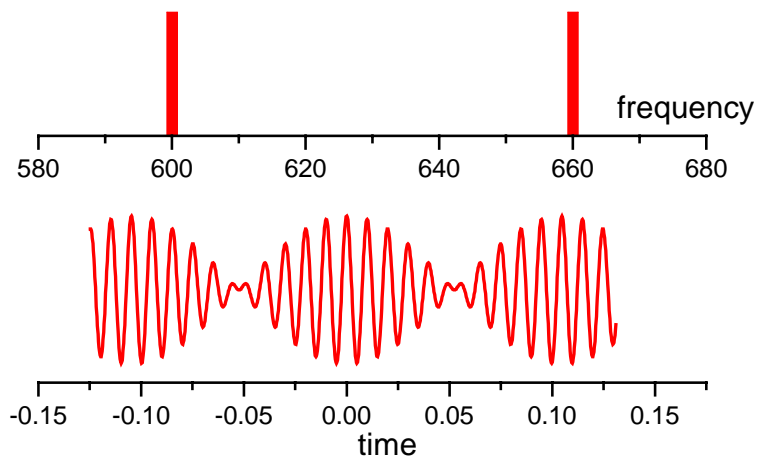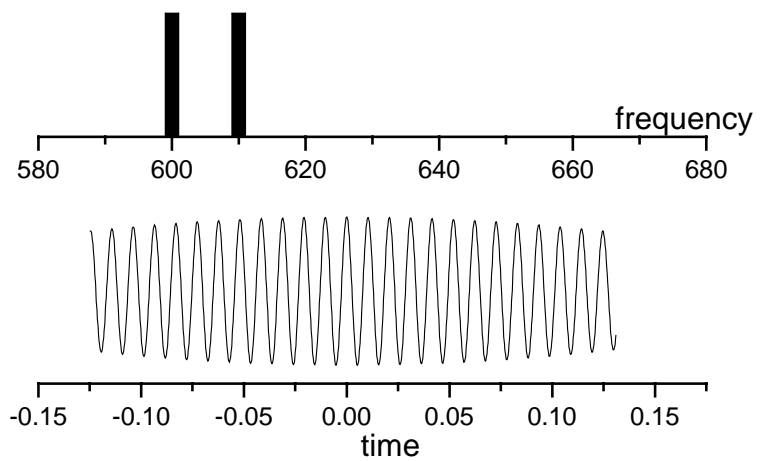**Resolution depends on the length of the interferogram**

Interferogram and resolution

As an example let us consider the interferogram obtained by the sum of two components at frequency ω_1 and ω_2, respectively. It will consist of the product of two cosine function: one of frequency $[v(\omega_1+\omega_2)/2c]$ and the other one of frequency $[v(\omega_1-\omega_2)/2c]$.

The first one is a rapidly varying function corresponding to the interferogram of a single component spectrum with an average frequency between ω_1 and ω_2.

In order to discriminate between ω_1 and ω_2 one has to wait a time corresponding to the period of the second, slowly varying function, which bring the information about the difference $\omega_1 - \omega_2$.

$$\left| \;\dots\; \Delta t = 4\pi c / v(\omega_1-\omega_2) \; \dots \right|$$

frequency

580   600   620   640   660   680

-0.15   -0.10   -0.05   0.00   0.05   0.10   0.15

time

frequency

580   600   620   640   660   680

-0.15   -0.10   -0.05   0.00   0.05   0.10   0.15

time

Resolution and Apodization

The truncation of the interferogram at the limits $-\tau$ and $+\tau$ can be viewed as the multiplication of the interferogram by a *boxcar* function having the same limits.

According to the convolution theorem and considering that the Fourier transform of a *boxcar* function is the *sinc* function, the resulting Fourier transform of the considered interferogram is the convolution of the Fourier transform of the whole spectrum with the *sinc* function with argument $(\pi t/\tau)$.

Since the sinc function introduces some lobes in the spectra of narrow lines, it is sometimes preferred to multiply the interferogram by a function which reduces the intensity to zero at the limits $-\tau$ and $+\tau$. This can be a triangular function, or an exponential decay, or a combination of function. The effect is the reduction of the lobes, payed by a loss of resolution.

Such an operation is called Apodization.

1.7 Useful functions

There are some functions which occur again and again in physics, and whose properties should be learned. They are extremely useful in the manipulation and general taming of other functions which would otherwise be almost unmanageable. Chief among these are:

1.7.1 The 'top-hat' function†, $\Pi_a(x)$

This has the property that:

$$
\begin{aligned}
\Pi_a(x) &= 0, -\infty < x < -a/2 \\
&= 1, -a/2 < x < a/2 \\
&= 0, a/2 < x < \infty
\end{aligned}
$$

and the symbol Π is chosen as an obvious aid to memory.

Its Fourier pair is obtained by integration:

$$
\begin{aligned}
\Phi(p) &= \int_{-\infty}^{\infty} \Pi_a(x)e^{2\pi ipx}dx \\
&= \int_{-a/2}^{a/2} e^{2\pi ipx}dx \\
&= \frac{1}{2\pi ip}[e^{\pi ipa} - e^{-\pi ipa}] \\
&= a\left\{\frac{\sin \pi pa}{\pi pa}\right\} \\
&= a \cdot \text{sinc}(\pi pa)
\end{aligned}
$$

and the 'sinc-function', defined‡ by $\text{sinc}(x) = \sin x/x$ is one which recurs throughout physics. As before, we write symbolically:

$$
\Pi_a(x) \rightleftharpoons a \cdot \text{sinc}(\pi pa)
$$

† In the USA, this is called a 'box-car' or 'rect' function.
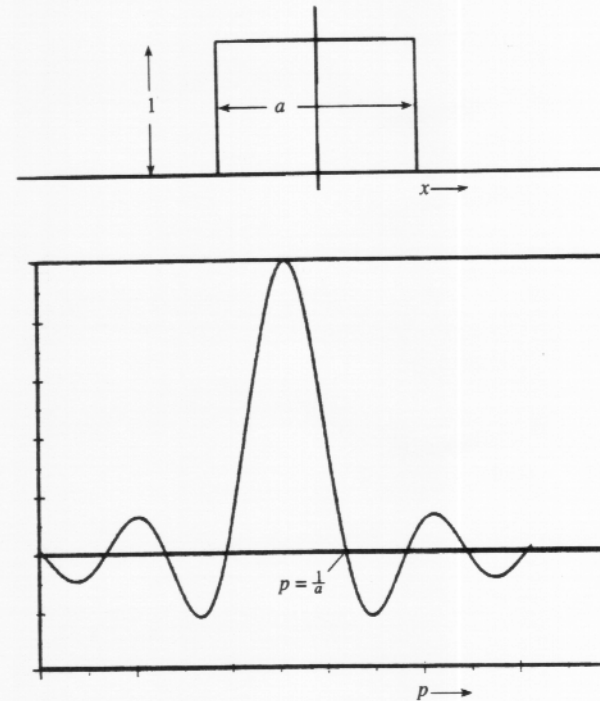‡ Caution: some people define $\text{sinc}(x)$ as $\sin(\pi x)/(\pi x)$.

Fig. 1.5. The top-hat function and its transform, the sinc-function.

1.7.2 The sinc-function

$$
\text{sinc}(x) = \sin x/x
$$

Has the value unity at $x = 0$, and has zeros whenever $x = n\pi$. The function $\text{sinc}(x)$ above, the most common form, has zeros when $p = 1/a, 2/a, 3/a \dots$

ere are several theorems which are of great use in manipulating urier-pairs, and they should be memorised. For the most part the oofs are elementary. The art of practical Fourier-transforming is in : manipulation of functions using these theorems, rather than in doing ensive and tedious elementary integrations. It is this, as much as ything, which makes Fourier theory such a powerful tool for the actical working scientist.

In what follows, we assume:

$$F_1(x) \rightleftharpoons \Phi_1(p) \; ; \; F_2(x) \rightleftharpoons \Phi_2(p)$$

iere '$\rightleftharpoons$' implies that F_1 and Φ_1 are a Fourier pair.

The Addition Theorem:

$$F_1(x) + F_2(x) \rightleftharpoons \Phi_1(p) + \Phi_2(p) \tag{2.1}$$

The Shift Theorems:

$$F_1(x + a) \rightleftharpoons \Phi_1(p)e^{2\pi i p a}$$

$$F_1(x - a) \rightleftharpoons \Phi_1(p)e^{-2\pi i p a} \tag{2.2}$$

$$F_1(x - a) + F_1(x + a) \rightleftharpoons 2\Phi_1(p) \cos 2\pi p a$$

The third of these theorems can be illustrated: In particular, notice that if $F_1(x)$ is the δ-function, the shift theorems are:

$$\delta(x + a) \rightleftharpoons e^{-2\pi i p a}$$

$$\delta(x - a) \rightleftharpoons e^{2\pi i p a} \tag{2.3}$$

$$\delta(x - a) + \delta(x + a) \rightleftharpoons 2 \cos 2\pi p a$$

The convolution theorem

$$C(x) = \int\limits_{-\infty}^{\infty} F_1(x')F_2(x-x')dx' = F_1(x) \otimes F_2(x)$$

La trasformata di Fouroier della convoluzione di 2 funzioni è uguale al prodotto delle trasformate di Fourier delle 2 funzioni

$$F_1(x) \otimes F_2(x) \Leftrightarrow \Phi_1(p)\Phi_2(p)$$

2.5.3 Parseval's Theorem

This is met under various guises. It is sometimes called 'Rayleigh's Theorem' or simply the 'Power Theorem'. In general it states:

$$\int_{-\infty}^{\infty} F_1(x)F_2^*(x)dx = \int_{-\infty}^{\infty} \Phi_1(p)\Phi_2^*(p)dp \qquad (2.11)$$

where * denotes a complex conjugate.
The proof of the theorem is in the appendix.

Two special cases of particular interest are :

$$\frac{1}{P}\int_0^P |F(x)|^2 \, dx = \sum_{-\infty}^{\infty}(a_n^2 + b_n^2) = \frac{A_0^2}{4} + \frac{1}{2}\sum_1^{\infty}[A_n^2 + B_n^2] \qquad (2.12)$$

which is used for finding the power in a periodic waveform, and

$$\int_{-\infty}^{\infty} |F(x)|^2 \, dx = \int_{-\infty}^{\infty} |\Phi(p)|^2 \, dp \qquad (2.13)$$

for non-periodic Fourier pairs.

2.5.4 The Sampling Theorem

This is also known as the 'Cardinal Theorem' of interpolary function theory, and originated with Whittaker[†], who asked and answered the question: How often must a signal be measured (sampled) in order that all the frequencies present should be detected? The answer is: the sampling interval must be the reciprocal of twice the highest frequency present.

The theorem is best illustrated with a diagram. This highest frequency is sometimes called the 'folding frequency', or alternatively the 'Nyquist' frequency, and is given the symbol v_f.

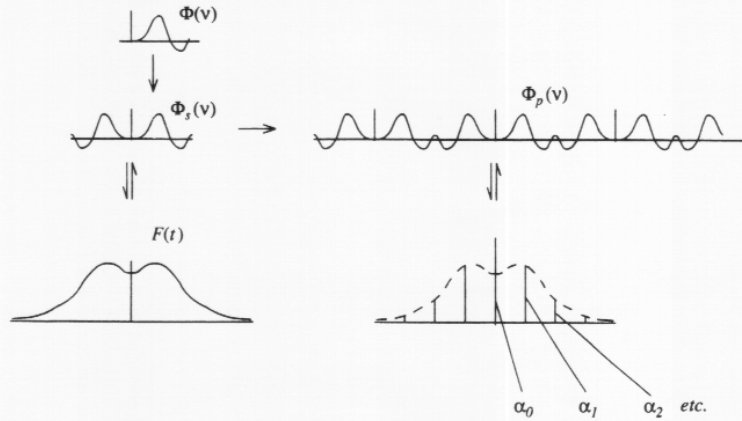† J. M. Whittaker, *Interpolary Function Theory*, Cambridge University Press, 1935.

Fig. 2.7. The Sampling Theorem.

Suppose that the frequency spectrum, $\Phi(v)$, of the signal is $F(t)$ and that it contains frequencies from 0 to v_f. From its frequency spectrum $\Phi(v)$ we construct a function $\Phi_s(v)$ which is the original spectrum plus its mirror image. This is symmetrical about the origin and stretches from $-v_f$ to v_f. The convolution of $\Phi_s(v)$ with a Dirac comb of period $2v_f$ provides a periodic function $\Phi_p(v)$ and the Fourier transform of this periodic function is the *product* of a Dirac comb with $\Phi_s(v)$: in other words it is the set of Fourier coefficients representing the series. This is because the Fourier transform of $\Phi_s(v)$ has the same values – apart from a constant – as the coefficients of its periodic counterpart at points $t = 0, 1/2v_f, 2/2v_f, 3/2v_f, \ldots$ Thus the periodic function is always known provided that the coefficients are known, and the coefficients are the values of the original signal $F(t)$, multiplied by a constant, at intervals of time $1/2v_f$. As more coeffcients become known, that is, as more samples are taken, more harmonics can be added to make the spectrum and more detail can be seen in the function when it is reconstructed.

Formally, the process can be written, with $F(t)$ and $\Phi(v)$ a Fourier pair as usual. The Fourier transform of $F(t)III_a(t)$ is:

$$\int_{-\infty}^{\infty} F(t)III_a(t)e^{-2\pi ivt}\,dt = \Phi(v) * III_{1/a}(v)$$

rewrite the left hand side as:

$$\int_{-\infty}^{\infty} F(t) \sum_{n=-\infty}^{\infty} \delta(t - na)e^{-2\pi ivt}\,dt = \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} F(t)\delta(t - na)e^{-2\pi ivt}\,dt$$

$$= \sum_{n=-\infty}^{\infty} F(na)e^{-2\pi ivna} = \Phi'(v)$$

The left hand side is now a Fourier series, so that $\Phi'(v)$ is a periodic function, the convolution of $\Phi(v)$ with a Dirac comb of period $1/a$. The constraint is that $\Phi(v)$ must occupy the interval $-1/2a$ to $1/2a$ only; in other words, $1/a$ is twice the highest frequency in the function $F(t)$, in accordance with the sampling theorem.
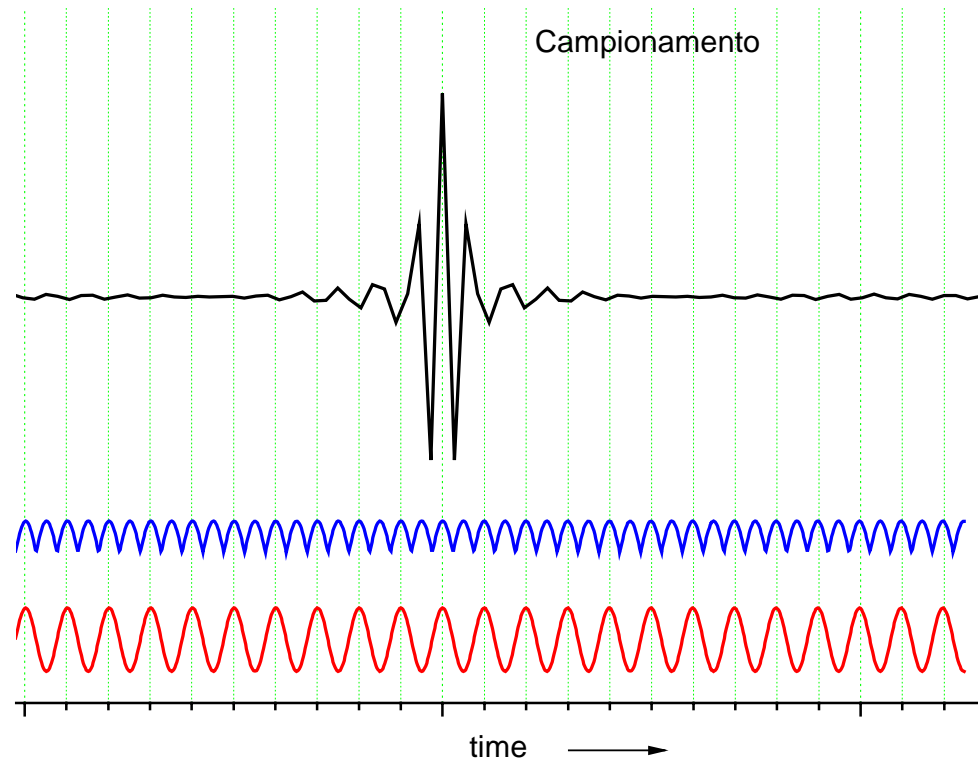
$$F(\nu_k) = \frac{2}{\pi} \sum_{n=0}^{N} A(t_n) e^{2\pi i \nu_k \cdot t_n}$$

Campionamento

$$t_n = t_0 + n\Delta t$$

$$\frac{1}{\Delta t} = \nu_s = \text{sampling frequency}$$

time

$$\nu_k = \nu_0 + k\Delta\nu$$

$$F(\nu_k) = \frac{2}{\pi} \sum_{n=0}^{N} A(t_0 + n\Delta t) e^{2\pi i(\nu_0 + k\Delta\nu)\cdot(t_0 + n\Delta t)}$$

DFFT
Discrete Fast Fourier Transform

- The need of a discrete sampling of the interferogram data allows the use of a computer and fast algoritmes to make the transformation.

- Nevertheless the discrete character of the data introduces some further problems and requires some caution in producing and evaluating the results.

DFFT
Aliasing

- The sampling theorem says that the sampling frequency must be the double of the largest frequency ν_{max} of the signal. That means that, in order to avoid spurious contributions (aliasing), one needs some kind of low pass filter (optical or electrical) which cut the spectrum above ν_{max}.

- Due to the discrete character of the sum, the Fourier transformed function results to be a symmetrical and periodic function in the frequency space, with period $1/2\nu_{max}$. (this is way a component with frequency larger than ν_{max} should be folded and superimposed to the lower frequencies, leading to a wrong spectrum)

Phase correction

- All the components of an interferometer introduce, in general, both an intensity correction and a phase contribution to the interference beam. The amplitude (intensity) effects are similar to the ones introduced by any optical device in a spectroscopic experiment, and call for the need of a reference measurement.

- The phase effects are peculiar of the use of an interferometer. In general, the phase shift introduced by the optics (mirrors, beam splitter, retardation plates) is a function of the wavelenght and of the experimental geometry (since one has to do with several different optical paths when the light beam is not perfectly collimated) and is adding to the modulation shift intentionally created in the experiment.

- The effect of such a situation is that each component is added to form the interferogram with a different phase shift; in other words, both *cos*-(symmetrical) and *sin*- (antisymmetrical) functions contribute to the interferogram. It means that both real- and imaginary- components are obtained after inverse FT.

Phase correction

- Since the experiment result is usually an intensity value, just the power spectrum is actually interesting. Nevertheless, the calculation of the phase correction is a necessary step in the process.

- Phase spectrum is, in general, a slowly varying function of the frequency; then a low resolution evaluation is enough to have a good correction. Such a spectrum can be interpolated in order to be used for the correction of a high resolution spectrum.

- This way of proceeding has two advantages:

  A more efficient averaging of the noise in the spectrum can be achieved using $P(\omega) = \mathrm{Re}(\omega) / \cos(\phi(\omega))$ with respect to $P(\omega) = \sqrt{\mathrm{Re}^2(\omega) + \mathrm{Im}^2(\omega)}$

  The possibility of dealing with an interferogram not symmetrically displaced around its maximum (which is the ordinary case in the experiments)

How is Working a Fourier Transform Spectrometer
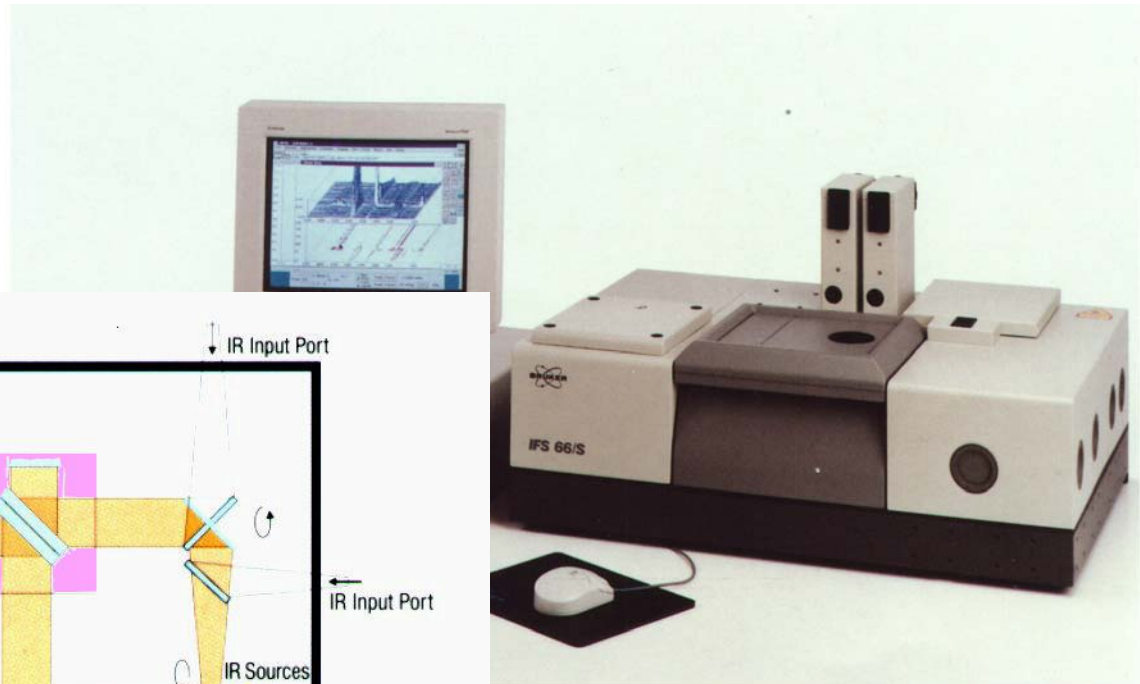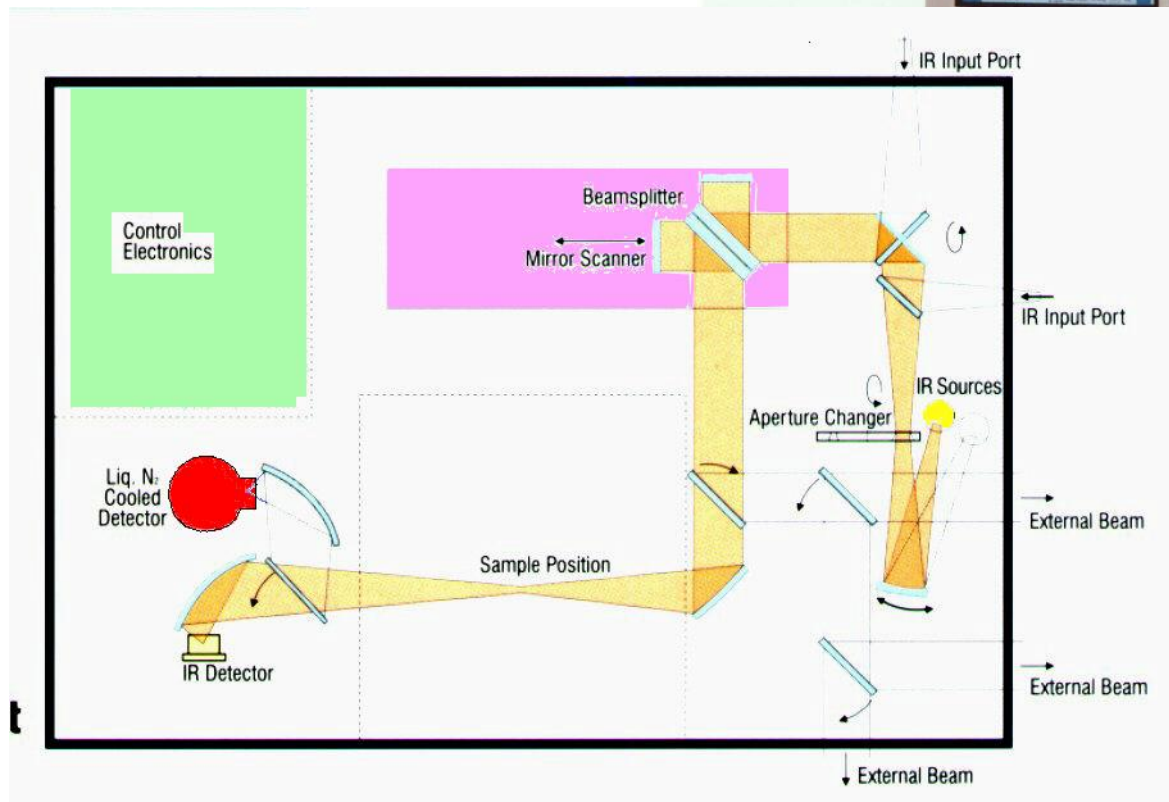
Main features of a Fourier Transform Spectrometer

Besides the necessary lamp and detector, the key features of a FTIR instrument are:

- An interpherometer moving mirror whose position can be controlled to a high accuracy (usually such a control is obtained with the help of a laser);

- A sampling and acquisition system which allows to obtain the correct time dependence of the interferogram;

- An analysis system which can perform the FFT (fast Fourier Transformations) and correctly evaluate the corrections (intensity, phase and noise effects introduced by the experimental setup).
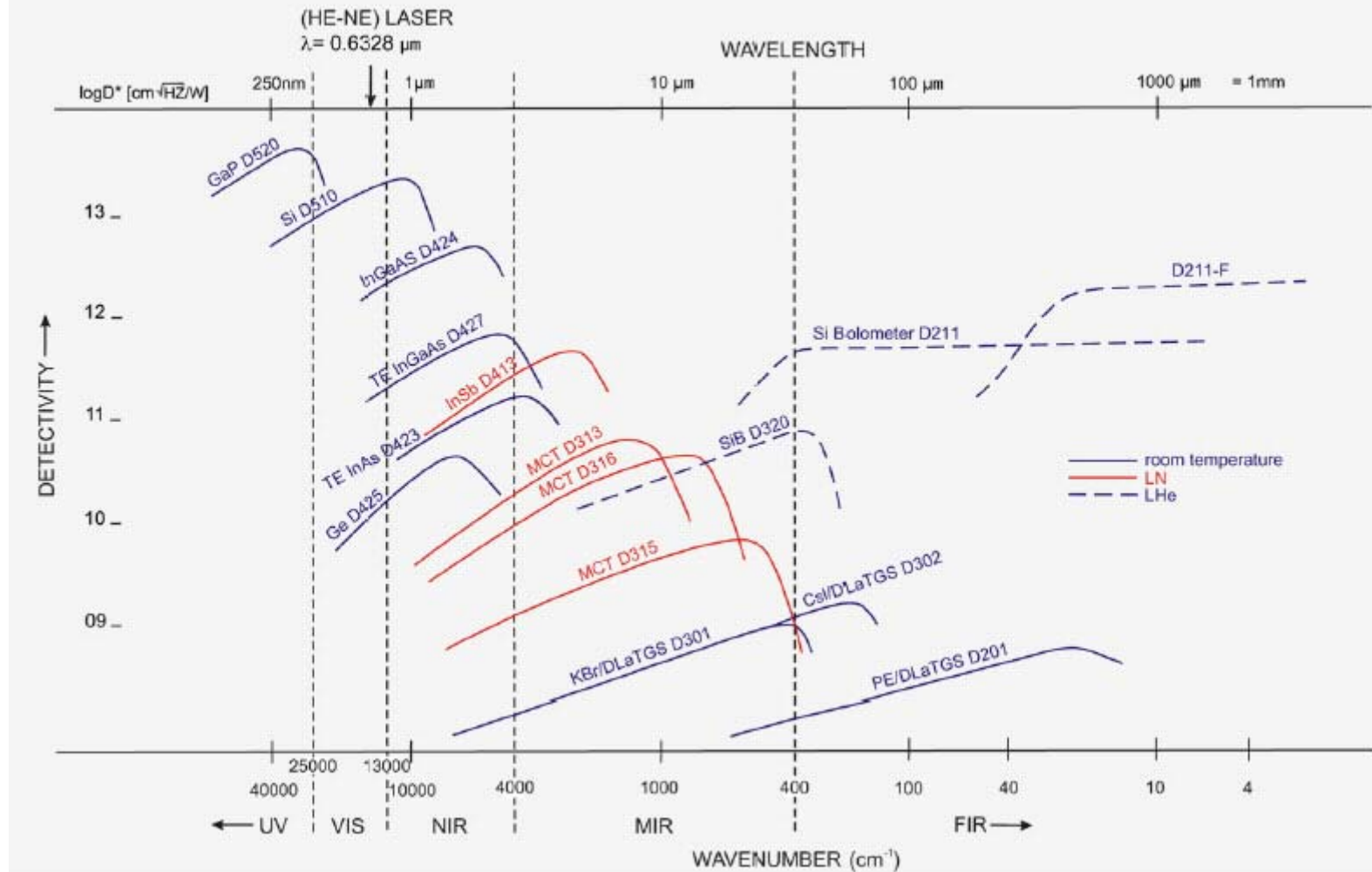
Main features of a Fourier Transform Spectrometer

- The interference signal of a laser beam colinear to the light path in the interferometer is used to control the position of the moving mirror with a precision of less than 1 nm;

- The same interference fringes of the laser are used for the sampling of the data: according to the Nyquist theorem, one must sample the data at a frequency (at least) double of the maximum frequency of phase modulation;

- An usual PC is nowadays enough to perform the mathematical data treatment (and also to control the whole experiment)
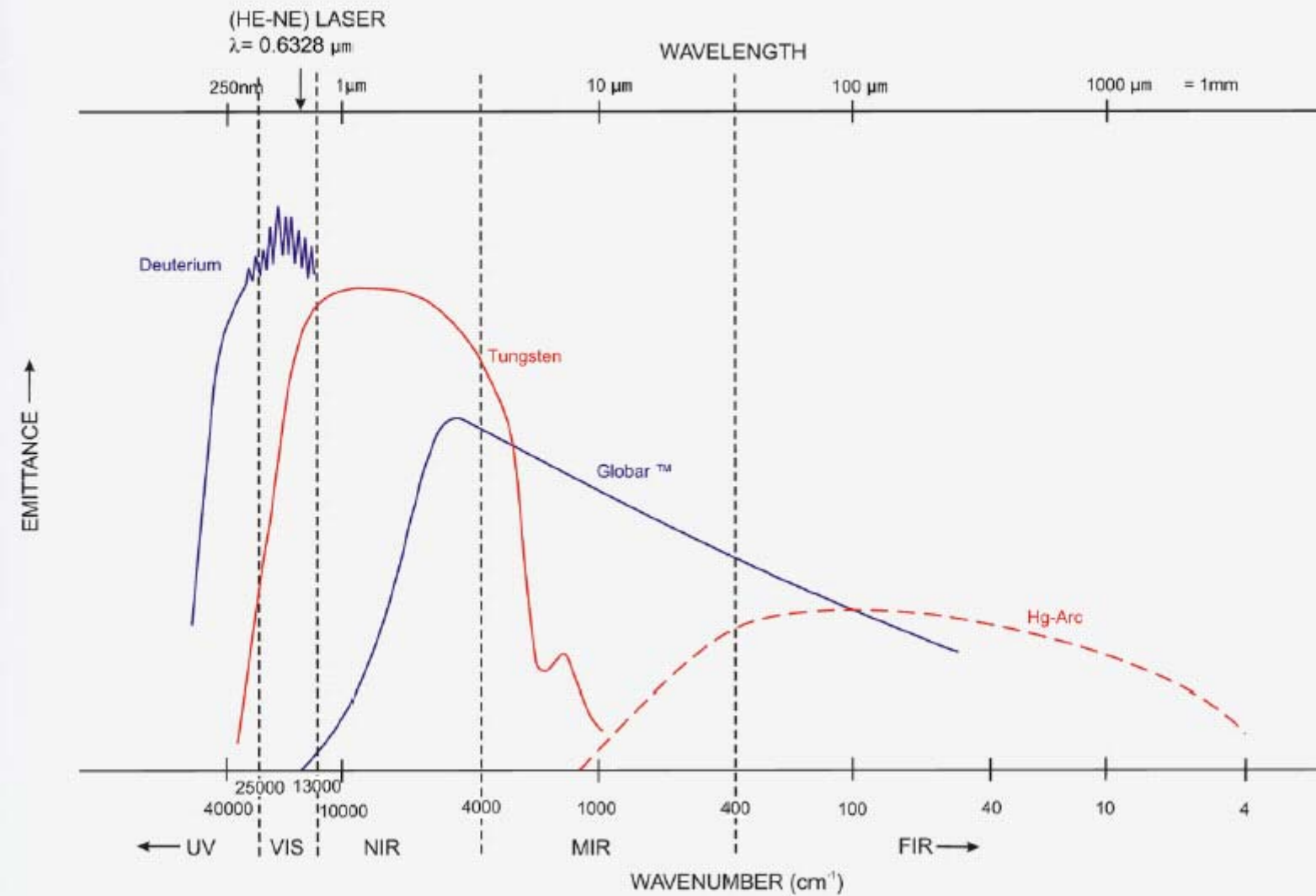
Advantages of FTIR Spectroscopy

❑ The so-called Jaquinot advantage: there is no need of slits which limit the throughput of radiation, so one can have a large signal without affecting the resolution;

❑ The Fellget (multiplex) advantage: the whole spectrum is obtained simultaneously for all the frequencies from a single interpherogram;

❑ Because of the two features above, it is possible to obtain instruments with a much higher resolving power than in dispersive instruments, even when the beam energy is low;

❑ Since mirror mouvements can be very fast (and/or very precise), time resolution is easily implemented.

DETECTORS

WAVELENGTH

(HE-NE) LASER
λ = 0.6328 μm

logD* [cm√HZ/W]   250nm   1μm   10 μm   100 μm   1000 μm   = 1mm

DETECTIVITY

GaP D520
Si D510
InGaAS D424
TE InGaAS D427
InSb D413
TE InAs D423
Ge D425
MCT D313
MCT D316
MCT D315
SiB D320
Si Bolometer D211
D211-F
CsI/DLaTGS D302
KBr/DLaTGS D301
PE/DLaTGS D201

13
12
11
10
09

room temperature
LN
LHe

40000   25000   13000   10000   4000   1000   400   100   40   10   4

← UV   VIS   NIR   MIR   FIR →

WAVENUMBER (cm⁻¹)

BEAMSPLITTERS
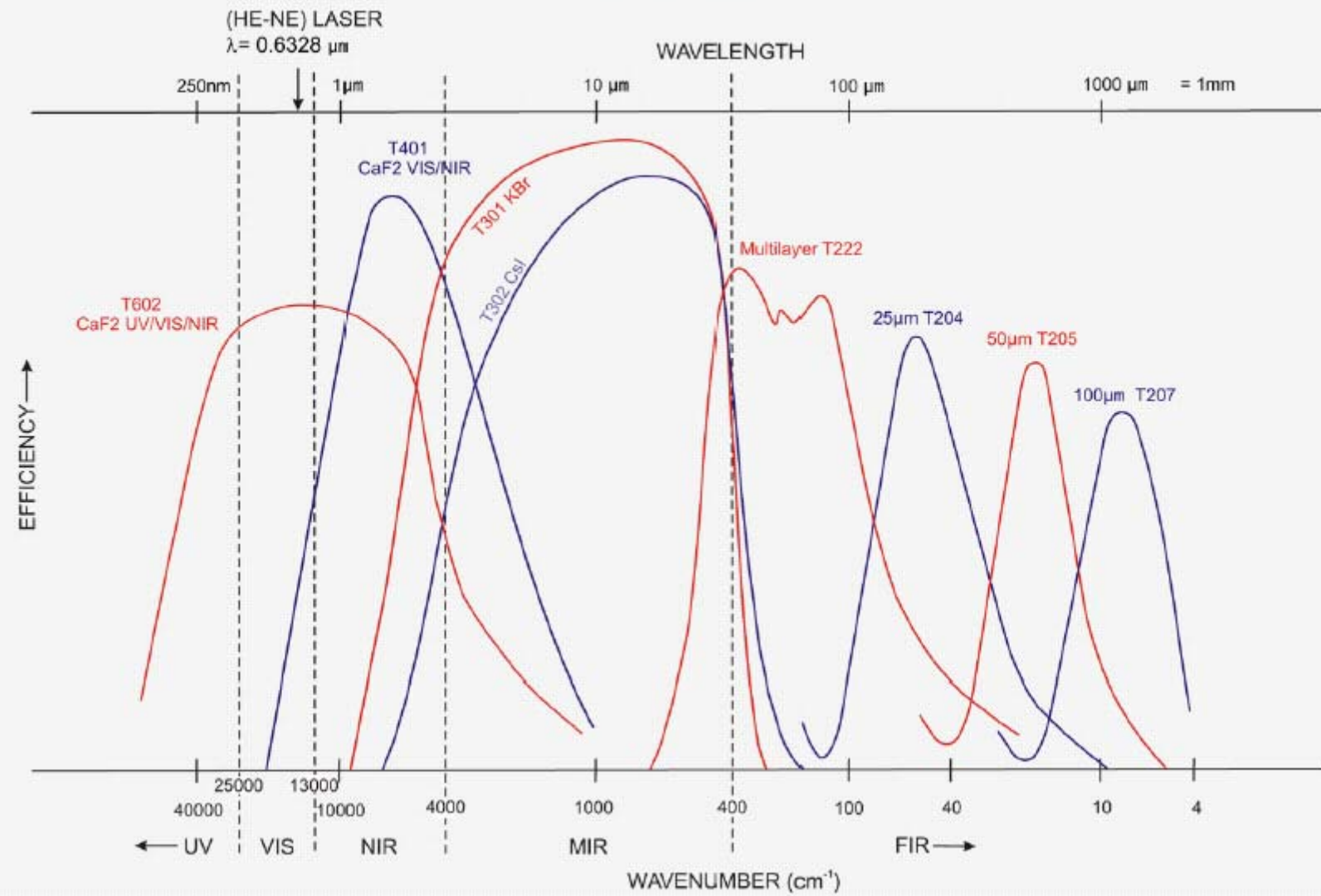
Material	Transmission Range [cm^{-1}] ([micrometers])	Refractive Index n at 2000 cm^{-1}	Reflectance loss per surface	Hardness (Knoop)	Chemical Properties
Infrasil SiO$_2$	57,000-2,800 (0.175-3.6)	1.46	~ 3.3 %	461	Insoluble in water; soluble in HF.
UV Sapphire AL$_2$O$_3$	66,000-2,000 (0.15-5.0)	1.75	~ 7.3 %	1370	Very slightly soluble in acids and bases.
Silicon Si	10,000-100 (1.0-100)	3.42	~ 30 %	1150	Insoluble in most acids and bases; soluble in HF and HNO$_3$.
Calcium Fluoride CaF$_2$	66,000-1,200 (0.15-8.0)	1.40	~ 2.8%	158	Insoluble in water; resists most acids and bases; soluble in NH$_4$ salts.
Barium Fluoride BaF$_2$	50,000-900 (0.2-11)	1.45	~ 3.3%	82	Low water solubility; soluble in acid and NH$_4$Cl.
Zinc Sulfide, Cleartran ZnS	22,000-750 (0.45-13.0)	2.25	~ 15%	355	Soluble in acid; insoluble in water.
Germanium Ge	5,000-600 (2.0-17)	4.01	~ 36%	550	Insoluble in water; soluble in hot H$_2$SO$_4$ and aqua regia.
Sodium Chloride NaCl	28,000-700 (0.35-15)	1.52	~ 4.5%	15	Hygroscopic; slightly soluble in alcohol and NH$_3$.
AMTIR GeAsSe Glass	11,000-900 (0.9-11)	2.50	~ 18%	170	Insoluble in water. Soluble in bases.
Zinc Selenide ZnSe	20,000-500 (0.5-20)	2.43	~ 17%	150	Soluble in strong acids; dissolves in HNO$_3$.
Silver Chloride AgCl	23,000-400 (0.42-25)	2.00	~ 11%	10	Insoluble in water; soluble in NH$_4$OH.
Potassium Bromide KBr	33,000-400 (0.3-25)	1.54	~ 4.5 %	7	Soluble in water, alcohol, and glycerine; hygroscopic.
Cesium Iodide CsI	33,000-150 (0.3-70)	1.74	~ 7.3%	20	Soluble in water and alcohol; hygroscopic.
KRS-5 TlBr/I	16,000-200 (0.6-60)	2.38	~ 17%	40	Soluble in warm water; soluble in bases; insoluble in acids.
Polyethylene PE (high density)	600-10 (16-1,000)	1.52	~ 4.5%	5	Resistant to most solvents.
Diamond C	45,000-10 (0.22-1,000)	2.40	~ 17%	7000	Insoluble in water, acids, and bases.
TPX$^{(TM)}$ Methylpentene Resin	350-10 (28-1,000)	1,43	~ 3.3%		Similar to PE but transparent and more rigid