OPTICAL PROPERTIES OF SOLIDS

OPTICAL SPECTROSCOPY ↔ **THEORY**

(1950-1960)

Mainly R and T

- Band structure calculations
- One-electron approximation
- Semi-empirical models

Microscopic interpretation of the fundamental characteristics of the optical response in solids

after 1960

- Modulation spectroscopy (TR, ER, WLM, PR, PZR, ,,,)
- Spectroscopic ellipsometry (SE)
- Photoluminescence spectr. (PL)
- Raman spectr. (RS)
- Photoemission spectr. (PES)
- Electron spectroscopies (EELS, Auger)
- New growth and processing techniques (epitaxy ⇨ Q-size structures)
- New light sources (synchrotron, laser CW and pulsed,…)
- Microprobes (HRTEM, STM, AFM, SNOM, …)

- Self-consistent methods
- Ab-initio calc. (total energy , density functional….)
- Surface and interface prop.
- Many-bodies, correlations
- Molecular dynamics

Interaction of electro-magnetic field with matter

In linear materials, the polarization density $\mathbf{P}$ (in coulombs per square meter) and magnetization density $\mathbf{M}$ (in amperes per meter) are given by:

$$\mathbf{P} = \chi_e \varepsilon_0 \mathbf{E}$$

$$\mathbf{M} = \chi_m \mathbf{H}$$

and the $\mathbf{D}$ and $\mathbf{B}$ fields are related to $\mathbf{E}$ and $\mathbf{H}$ by:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = (1 + \chi_e) \varepsilon_0 \mathbf{E} = \varepsilon \mathbf{E}$$

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = (1 + \chi_m) \mu_0 \mathbf{H} = \mu \mathbf{H}$$

where:

χ_e is the electrical susceptibility of the material,

χ_m is the magnetic susceptibility of the material,

ε is the electrical permittivity of the material, and

μ is the magnetic permeability of the material

Maxwell Equations

In non-dispersive, isotropic media, ε and μ are time-independent scalars, and Maxwell's equations reduce to

$$\nabla \cdot \varepsilon \mathbf{E} = \rho$$

$$\nabla \cdot \mu \mathbf{H} = 0$$

$$\nabla \times \mathbf{E} = -\mu \frac{\partial \mathbf{H}}{\partial t}$$

$$\nabla \times \mathbf{H} = \mathbf{J} + \varepsilon \frac{\partial \mathbf{E}}{\partial t}$$

In a uniform (homogeneous) medium, ε and μ are constants independent of position, and can thus be furthermore interchanged with the spatial derivatives.

More generally, ε and μ can be rank-2 tensors (3×3 matrices) describing birefringent (anisotropic) materials.

REAL AND COMPLEX FORMALISM

In the case of time-dependent e.m. fields, there will generally be a phase shift between the motion of the charge carriers and the electric field **E** (similarly to what happens in A.C. circuits). In such cases the complex formalism is particularly convenient to describe phase shifts, and in addition to describe dispersion and absorption effects at the same time. Complex fields are usually defined, the real parts of which have physical meaning and are the ones involved in Maxwell's eqs.

REAL FORMALISM

$$E = E_O \cos \omega t \quad \Longrightarrow \quad x = C\, E_O \cos(\omega t + \varphi) \quad \Longrightarrow \quad x' = -\, C\, \omega\, E_O \,\mathrm{sen}\,(\omega t + \varphi)$$

$$J = eNx' = -\, eNC\omega\, E_O\,(\mathrm{sen}\,\omega t\ \cos\varphi + \cos\omega t\ \mathrm{sen}\,\varphi)$$

90° out of phase vs E
(polarization current - no dissipation)

in phase with E
(conduction current – dissipation)

COMPLEX FORMALISM

$$\tilde{E} = E_o\, e^{i\omega t} \quad \Longrightarrow \quad \tilde{x} = CE_o\, e^{i(\omega t + \varphi)} \quad \Longrightarrow \quad \tilde{x}' = i\omega\tilde{x} = Ci\omega\, e^{i\varphi}\tilde{E}$$

$$\tilde{J} = e\,N\,\tilde{x}' = eNC\, i\omega\, e^{i\varphi}\,\tilde{E} = \tilde{\sigma}\,\tilde{E}$$

$$\tilde{\sigma} = \sigma_1 + i\sigma_2$$

$$\sigma_1 = -\, eNC\,\omega\,\mathrm{sen}\,\varphi \equiv \sigma$$

$$\sigma_2 = eNC\,\omega\cos\varphi$$

Similarly

$$\tilde{P} = e\ N\ \tilde{x} = \tilde{\chi}\ \tilde{E} \qquad \tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2 = 1 + 4\pi\tilde{\chi} \qquad \tilde{\sigma} = -\,i\ \omega\ \tilde{\chi}$$

In order to elucidate the meaning of ε_1 and ε_2 let us consider the Maxwell eqs.:

$$c\,(\nabla \times \mathbf{H}) = 4\pi \mathbf{J}_{cond} + \partial \mathbf{D} / \partial t = 4\pi\sigma\,\mathbf{E} + \varepsilon\,\partial \mathbf{E} / \partial t = 4\pi\,Re\left[\left(\sigma - \frac{i\omega\,\varepsilon}{4\pi}\right)\tilde{\mathbf{E}}\right] =$$

$$= Re\left[-i\omega\left(\varepsilon + \frac{4\pi\,\sigma}{\omega}\right)\tilde{\mathbf{E}}\right]$$

➡ $\tilde{\mathbf{J}} = \tilde{\sigma}\,\tilde{\mathbf{E}}$ with $\tilde{\sigma} \equiv \sigma_1 + i\,\sigma_2 = \sigma - i\,\omega\,\varepsilon$ complex optical conductivity

$\tilde{\mathbf{D}} = \tilde{\varepsilon}\,\tilde{\mathbf{E}}$ with $\tilde{\varepsilon} \equiv \varepsilon_1 + i\,\varepsilon_2 = \varepsilon + i\,4\,\pi\,\sigma/\omega$ complex dielectric function

$\varepsilon_1(\omega) \equiv \varepsilon\,(\omega)$ describes the dispersion processes, *i.e.* the displacement **r** of the charges in-phase with **E** ➡ $\mathbf{p} = e\,\mathbf{r} = \chi\,\mathbf{E}$

$\varepsilon_2(\omega) \equiv 4\,\pi\sigma\,(\omega)/\omega$ describes the energy absorption, *i.e.* the velocity **v** of the charges in-phase with **E**

$$W = <\mathbf{J}\cdot\mathbf{E}> = \sigma < E^2 > + \varepsilon_1 < \partial E/\partial t\ \cdot E > = \sigma < E^2 > + 0$$

Only for $\omega = 0$ (static field) $\sigma \equiv \sigma_0$ is due to free-carriers (conductor) and $\varepsilon_1 \equiv \varepsilon$ to bound-carriers (dielectric). For $\omega > 0$ the distinction between free- and bound-carriers is meaningless (for $\omega \rightarrow \infty$ the charges are all “free”).

- $\tilde{\mathbf{E}}$, $\tilde{\varepsilon}(\omega)$, $\tilde{\sigma}(\omega)$ appearing in the Maxwell eqs. are macroscopic quantities, average on volume elements ΔV (with $\lambda >> \Delta V >> a^3$) of microscopic quantities which vary rapidly on the atomic scale.

- The displacement of one point-charge does not depend on **E** but on $\mathbf{E}_{loc}$, which can differ greatly from **E** and which should be generally calculated in a self-consistent way.

- In an anisotropic medium

$$\tilde{\varepsilon}(\omega) \Longrightarrow \tilde{\tilde{\varepsilon}}(\omega) \qquad \text{complex dielectric tensor}$$

$\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are always symmetric tensors $\Longrightarrow$ they can be diagonalized with respect to principal axes, depending on ω. Generally the directions of the principal axes are different for $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, but they do coincide for crystals with symmetry at least as high as orthorhombic. In a cubic crystal ε_{ij} reduces to a scalar quantity.

- In a nonlinear dielectric medium, it is possible to expand the relation between **P** and **E** in a Taylor series about **E** = 0. Thus

$$\mathbf{P} = (\chi\,\mathbf{E} + \chi^{(2)}\,\mathbf{E}^2 + \chi^{(3)}\,\mathbf{E}^3 + \ldots)$$

where the $\chi^{(n)}$ coefficient describes the *n*-th order nonlinear effect. The D'Alembert equation is not applicable to e.m. waves in nonlinear media. However, Maxwell's equations can be used to derive a nonlinear partial differential equation that these waves obey.

KRAMERS-KRONIG RELATIONS

$\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are not independent quantities, being related one to the other by the integral relations, the so called *Kramers-Kronig relations*. These relations follow rigorously from the requirement of causality (*i.e.*, *there can be no effect before the cause*) and apply to the real and imaginary part of whatever linear response function. Thus, the complex dielectric function obeys the following relations

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$

$$\varepsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega'$$

where P stands for the principal part of the integral.

Also the Fresnel coefficient $\tilde{r} = |\tilde{r}| e^{i\theta}$ expresses the linear relation between incident and reflected electric field amplitudes which obey causality → a dispersion relation exists which connects its real and imaginary parts. Using the normal incidence reflectivity $R = |\tilde{r}|^2$, the dispersion relation between the absolute value R and the phase angle θ should be written as:

$$\theta(\omega) = -\frac{\omega}{\pi} P \int_0^\infty \frac{\ln R(\omega')}{\omega'^2 - \omega^2} d\omega'$$

DIELECTRIC RESPONSE OF SOLIDS

Homogeneous, isotropic, non-magnetic, charge-free medium → Complex dielectric function $\tilde{\varepsilon}(\omega,\mathbf{q})$ with $\mathbf{q}=2\pi\mathbf{u}/\lambda$

From the Maxwell's eqs. → the wave equation (d'Alembert eq.)

$$\nabla^2 \mathbf{E} = \frac{\varepsilon}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{4\pi\sigma}{c^2}\frac{\partial \mathbf{E}}{\partial t} = \frac{\tilde{\varepsilon}}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2}$$

e.m. wave propagating in a absorbing medium

→ attenuation of wave amplitude + dephasing between field and medium response

→ (*i.e.*: A.C. circuits) usefulness of complex formalism.

A solution of the d'Alembert eq. Is a monochromatic plane wave (transverse, because $\nabla\cdot\mathbf{E}=0$):

$$\tilde{\mathbf{E}}(\mathbf{r},t) = \tilde{\mathbf{E}}_0\, e^{i(\tilde{\mathbf{q}}\mathbf{r}-\omega t)}$$

amplitude, polarization and initial phase

complex wavevector $\mathbf{q} = \mathbf{q}_1 + i\,\mathbf{q}_2$

$$\tilde{\mathbf{D}} = \tilde{\varepsilon}(\omega,\mathbf{q})\tilde{\mathbf{E}}$$ linear response

$$\tilde{\varepsilon}(\omega,\mathbf{q}) = \varepsilon_1(\omega,\mathbf{q}) + i\,\varepsilon_2(\omega,\mathbf{q})$$

dispersion

absorption

By inserting the plane-wave complex solution in the Maxwell eqs., we obtain:

$$\tilde{\varepsilon}(\omega,\tilde{\mathbf{q}})\,\omega^2 = c^2\,\tilde{\mathbf{q}}\;\tilde{\mathbf{q}}$$ dispersion relation

The ω and $\mathbf{q}$ dependence of $\varepsilon\ (\omega,\mathbf{q})$ (or $\sigma\ (\omega,\mathbf{q})$) describe the time and the spatial dispersion of the material, respectively. If $\lambda >> a$ (where a is a natural length in the medium, i.e. atomic dimension or lattice parameter) the space variation of ε can be neglected ➡ $\varepsilon\ (\omega,\mathbf{q}) = \varepsilon\ (\omega)$ (this is not possible at X-ray wavelengths).

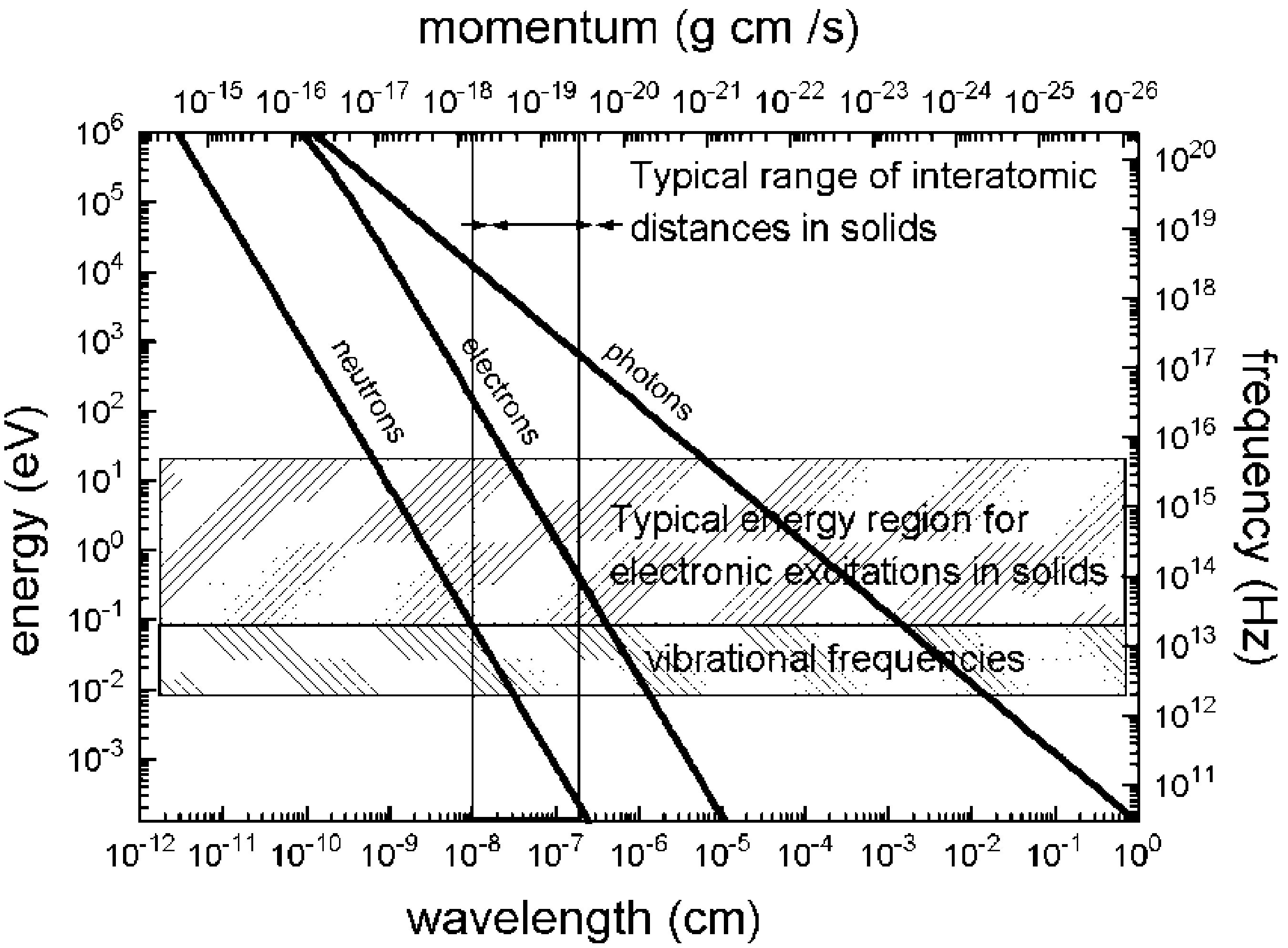
Moreover, for $q \cong 0$ $(\lambda \rightarrow \infty)$ the transverse and longitudinal response coincide, *i.e.* the medium cannot distinguish between electric fields parallel or perpendicular to $\mathbf{q}$

➡ direct comparison between EELS spectroscopy and optical spectroscopy

We note that the wave dispersion relation **does not imply in general** a connection between time-dispersion and spatial-dispersion. In principle, it is possible to investigate separately the temporal response of a medium (and hence the time-dispersion in ω) by subjecting it to a spatially uniform field that oscillates in time, or the spatial response (and hence the spatial dispersion in $\mathbf{q}$) with a static field that is spatially periodic.

Una funzione d’onda è caratterizzata da due grandezze coniugate: frequenza e lunghezza d’onda.

La relazione tra queste due grandezze dipende dalla natura della radiazione



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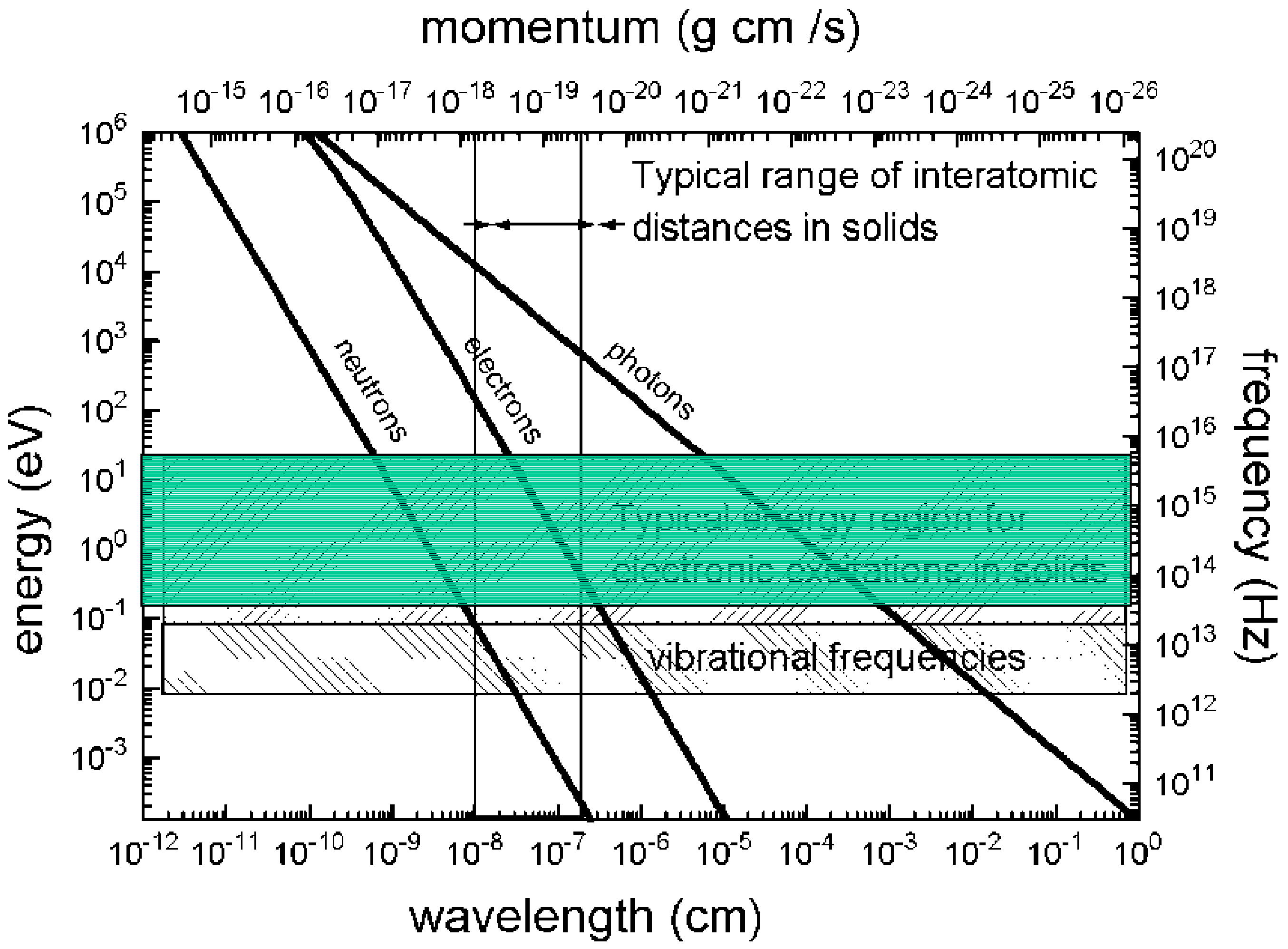

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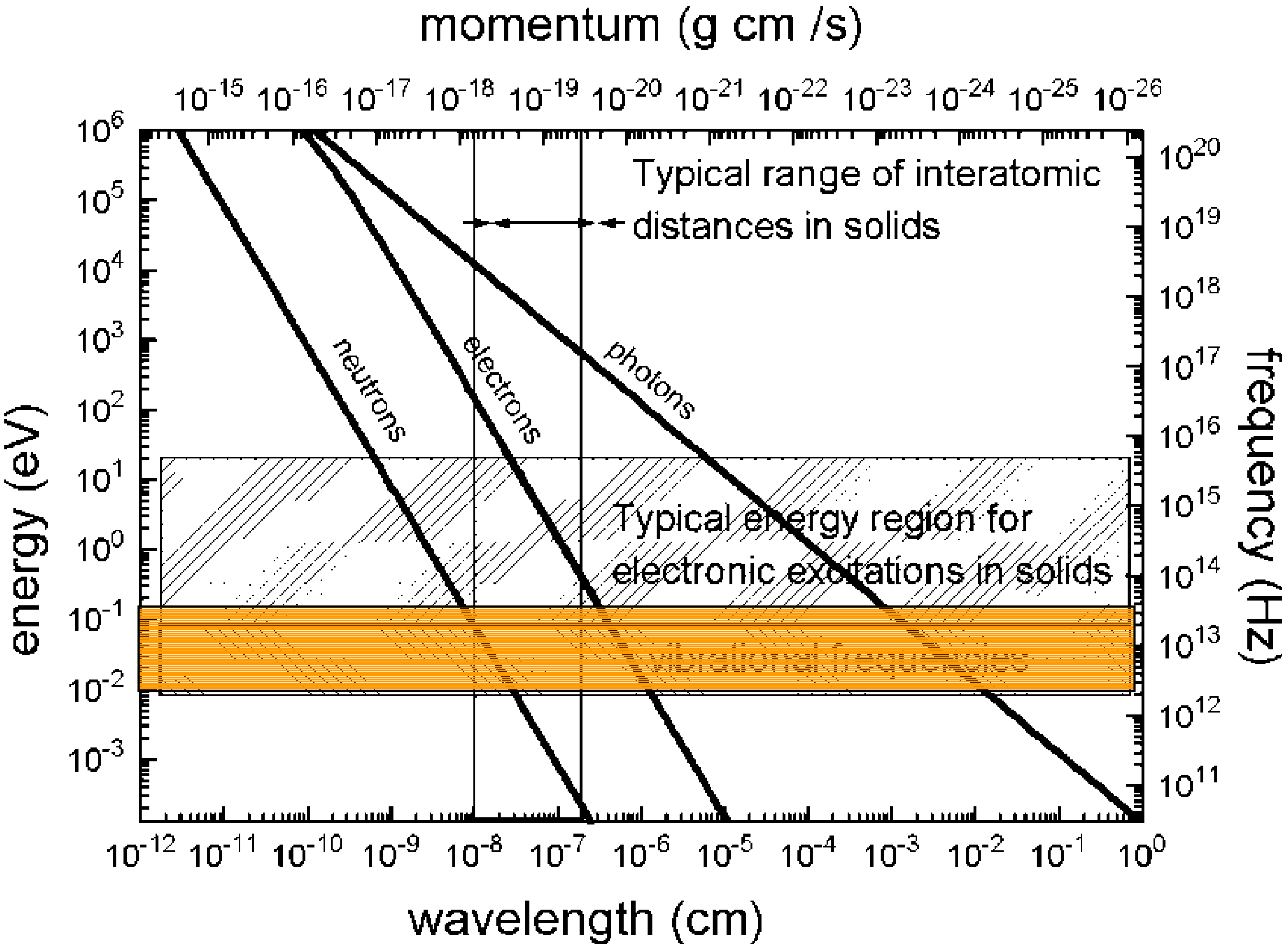

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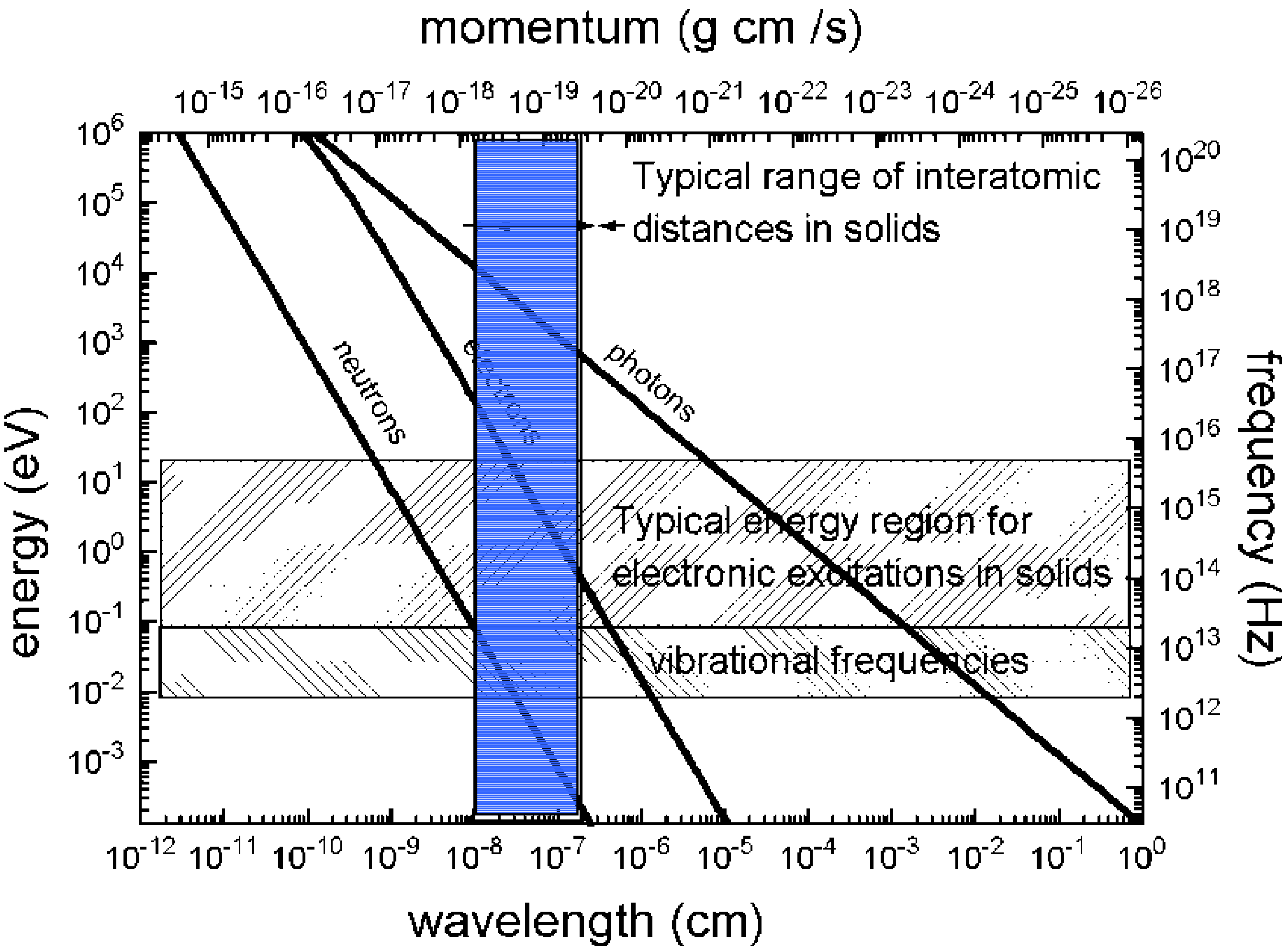

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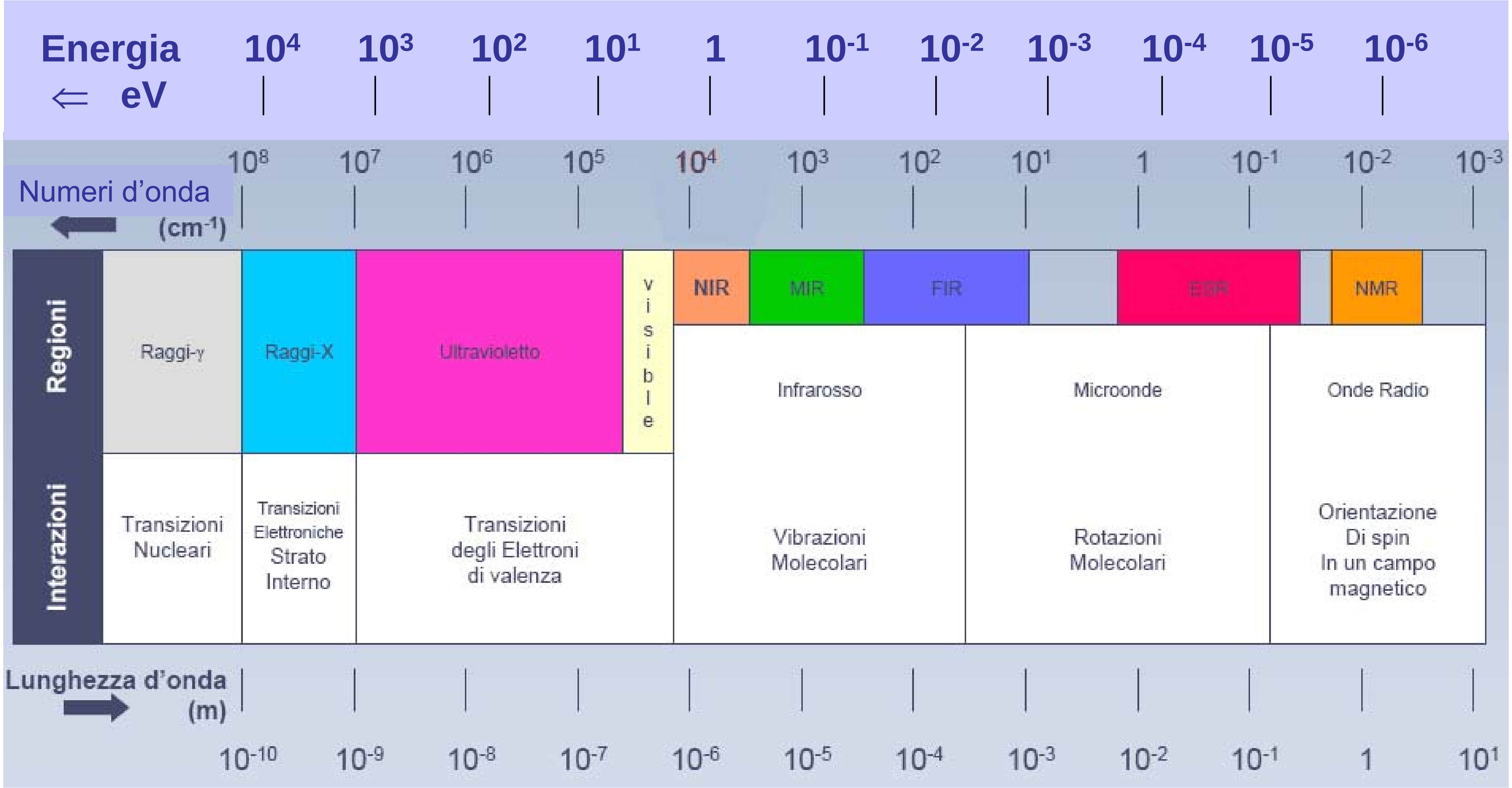
SPETTROSCOPIA (e spettroscopie)

Con il termine spettroscopia si intende una grande varietà di tecniche. Se pure il primo riferimento (anche dal punto di vista storico) va alla spettroscopia ottica e agli spettri di emissione o di assorbimento dei gas nel visibile e nel vicino ultravioletto, che per primi hanno evidenziato una struttura discreta dei livelli atomici, si parla oggigiorno di spettroscopia NMR così come di spettroscopia di neutroni.

Si intende come spettroscopia ogni tecnica che fornisce una grandezza risolta spettralmente, ovvero separando le sue componenti a diversa frequenza.

L'esempio più comune è dato dalla radiazione elettromagnetica e dalla sua decomposizione nei diversi colori del visibile, ma il discorso può essere esteso senza salti concettuali a tutte le frequenze e a tutte le grandezze per le quali è possibile definire una frequenza e/o una lunghezza d'onda.

Ogni grandezza in grado di propagarsi nello spazio (radiazione) e che possieda un carattere ondulatorio può essere impiegata per uno studio spettroscopico; nella fattispecie le stesse particelle (quali gli elettroni, i neutroni o i muoni) che possono essere associate ad una funzione d'onda (di De Broglie).


Energia
⇐ eV
10^{4}
10^{3}
10^{2}
10^{1}
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
Numeri d'onda
(cm^{-1})
10^{8}
10^{7}
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
1
10^{-1}
10^{-2}
10^{-3}
Regioni
Raggi-γ
Raggi-X
Ultravioletto
visible
NIR
MIR
FIR
ESR
NMR
Infrarosso
Microonde
Onde Radio
Interazioni
Transizioni Nucleari
Transizioni Elettroniche Strato Interno
Transizioni degli Elettroni di valenza
Vibrazioni Molecolari
Rotazioni Molecolari
Orientazione Di spin In un campo magnetico
Lunghezza d'onda
(m)
10^{-10}
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1
10^{1}

$$\lambda\,[\mu m] = \frac{1.24}{h\nu\,[eV]}$$

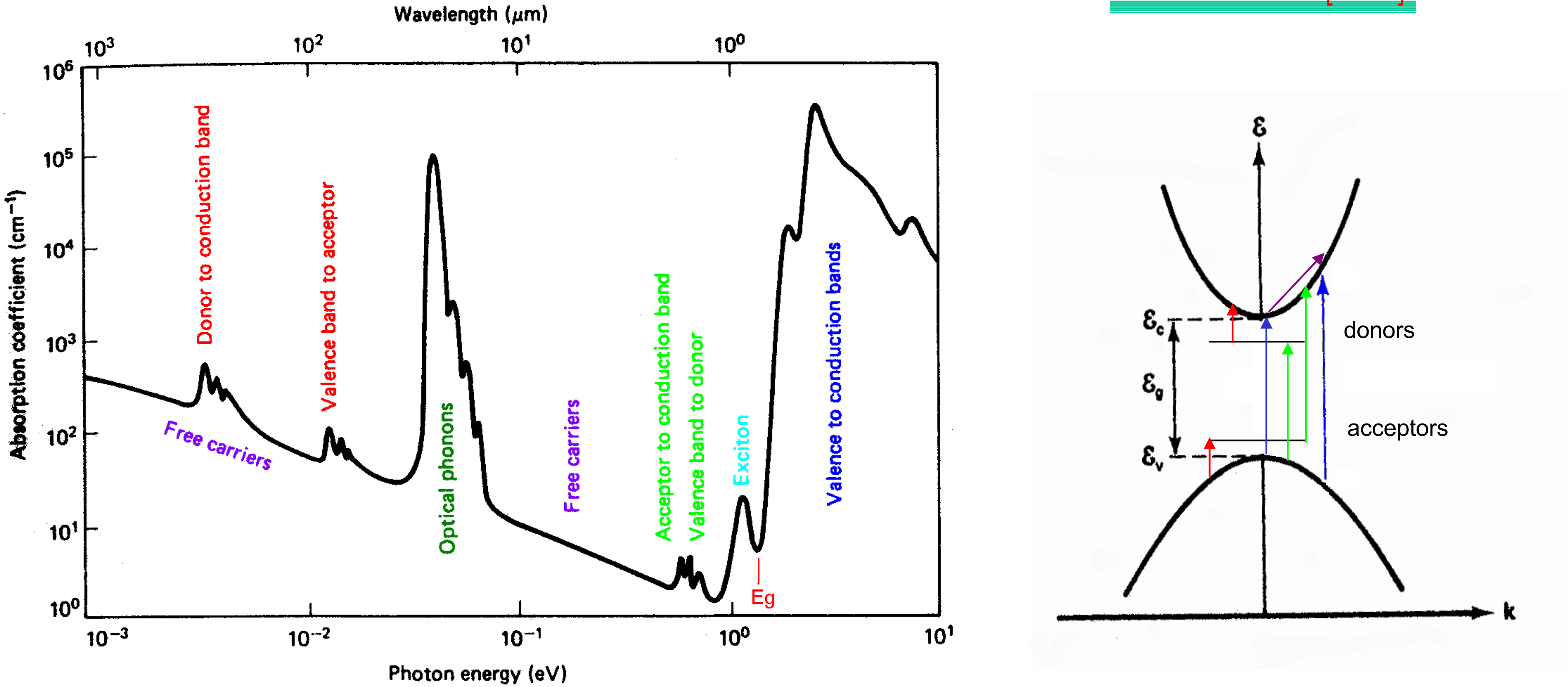


Fig. 2 Hypothetical absorption spectrum for a typical doped semiconductor and related electronic optical transitions.

OPTICAL SPECTRA

(R, T, SE, modulation spectroscopy, polarimetry)

↓

complex dielectric function $\tilde{\varepsilon}(\omega)$

↓

direct map of the elementary excitations in solids,
weighted with JDOS and transition probabilities

↓

- optical gaps
- interband critical points
- effective masses m*
- vibrational structure
- effects of external perturbations on electronic states
(temperature, **E**, **H**, doping, structural and compositional disorder, size,...)

↓

OPTICAL CHARACTERIZATION

OPTICAL CHARACTERIZATION

- $n(\omega)$, $k(\omega)$, $\alpha(\omega)$ optical functions
- N, m^*, τ of free-carriers
- Spatial homogeneity (range 1-1000 nm) and thickness of films and multilayers
- Surfaces and interfaces (roughness, planarity, anisotropy, traps, transition regions, oxides, overlayers,…)
- Compositional (impuritirs or dopants) and structural defects
- Structural disorder (single-crystal, polycrystal, amorphous,…)
- Phase transitions (structural, magnetic, conductor-insulator, superconductors)
- Dynamical processes associated to the growth (*in situ* measurements)
- Radiation effects and damages (light, ion and electron beams)

ADVANTAGES OF OPTICAL SPECTROSCOPY

- It can be used *in situ*, during growth, fabrication or testing
- It does not require special environments, such as ultrahigh vacuum (UHV), and may even be useful in hostile environments
- It is nonintrusive and noncontact (➡ repeatability)
- It may achieve submicron lateral resolution (SNOM ≈ 20 nm)
- It can be used to acquire data in real time (*i.e*., as growth or processing takes place)
- It offers the possibility of depth probe (depending on α)
- It presents a wide array of techniques, capable of measuring different properties and parameters (*e.g*.:optical functions, electronic properties, crystal order, thickness, impurities,composition, surface and interface quality, etc.)
- It has high spectral resolution $\Delta\lambda / \lambda$ ($\leq 10^{-3}$ vis-UV, $\leq 10^{-5}$ FFT- FIR) and high sensitivity to spectral details (derivative techniques)
- It has high sensitivity to the long-range order (disorder), to the thickness ($\leq$ 1 monolayer), to impurities ($< 1/10^9$)

LIMITS OF OPTICAL SPECTROSCOPY

- It does not give information on the absolute positions of the electron energy-levels

- It probes typically more than 10 nm in depth

⬇

average response in depth

⬇

no detailed information on electronic bonds,
surface structure, short-range effects

- It needs a “model” of the examined sample
(particularly relevant in films and multilayer structures)

Infrared Spectroscopy

Infrared spectroscopy studies vibrational frequencies of molecules.

The vibrations of molecules are what can help a researcher to determine a specific molecule. The most direct way to obtain the vibrational frequencies is with infrared radiation. A molecule that is said to be "IR active" has a change in its dipole moment as a result of the absorbance of infrared radiation.

A non-linear polyatomic molecule would use the 3N-6 formula to determine the number of vibrational modes. Water, H_2O, would therefore have 3 vibrational modes.

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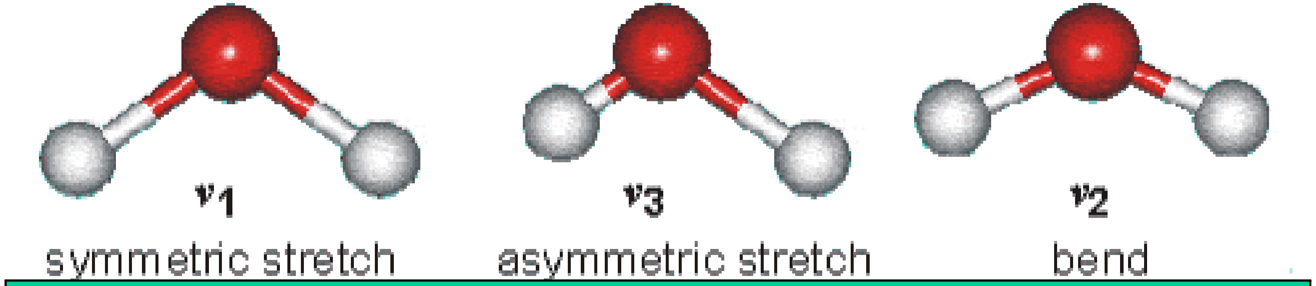

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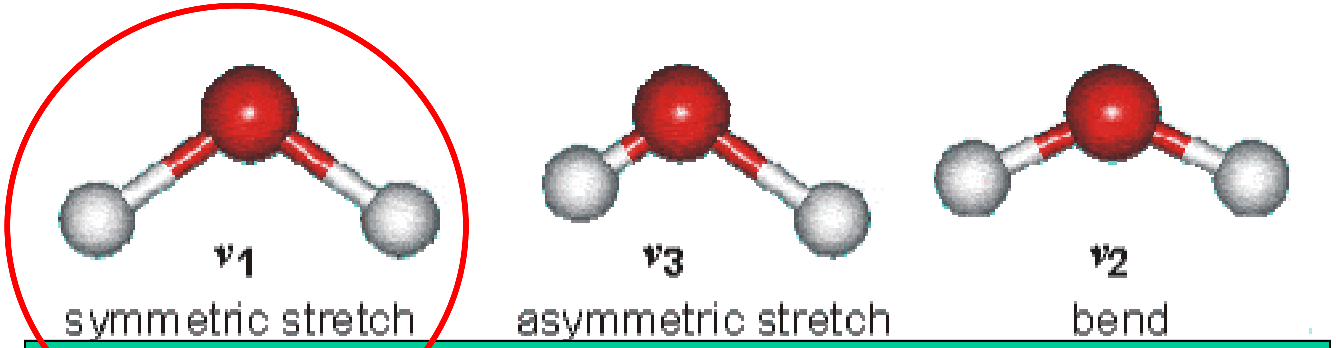
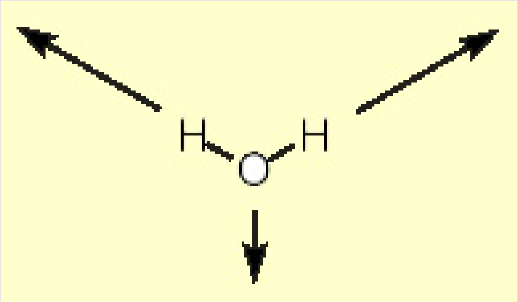
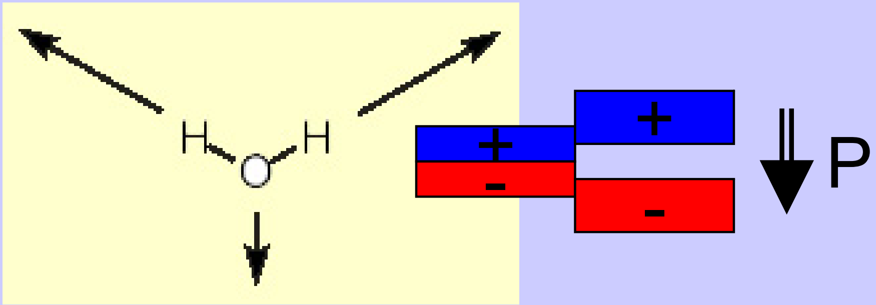




This is a symmetrical stretch. As you can see, the magnitudes of the arrows indicate that the stretch causes an increase in the dipole moment, pulling the oxygen away from the two hydrogen atoms. Although there is no change in the direction of the dipole moment, there is a change in its magnitude.

This vibrational mode is IR active and would be observed on a spectrum around 3650 cm^{-1}.



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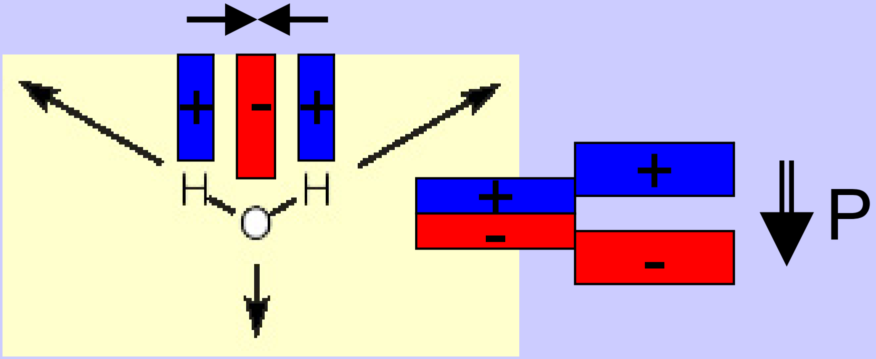

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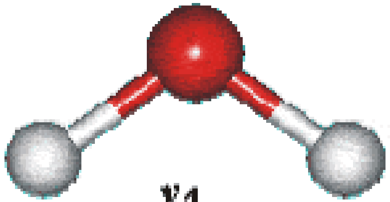
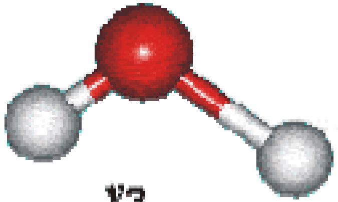


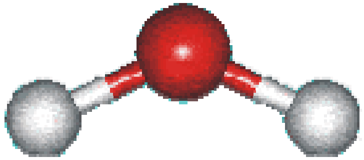
ν_1

symmetric stretch



ν_3

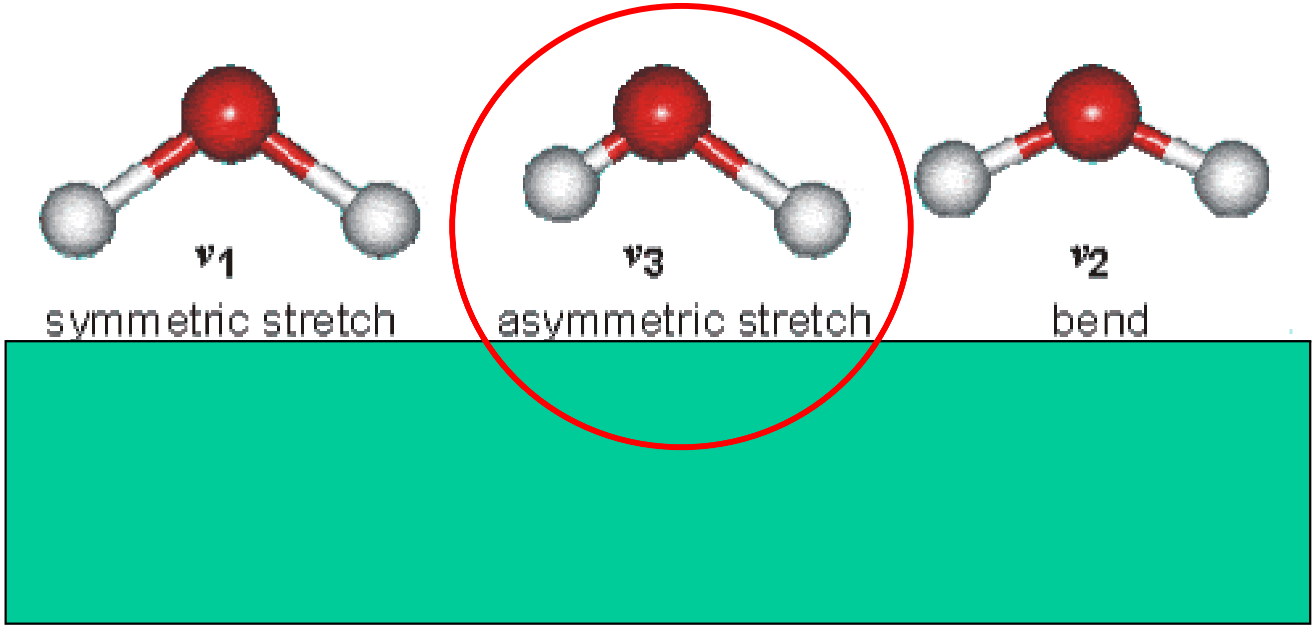
asymmetric stretch

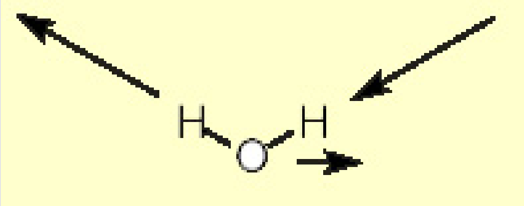


ν_2

bend

Water, H_2O, would therefore have 3 vibrational modes.





This is an asymmetrical stretch. This is more difficult to see, however, there is a change both in the magnitude and the direction of the dipole moment.

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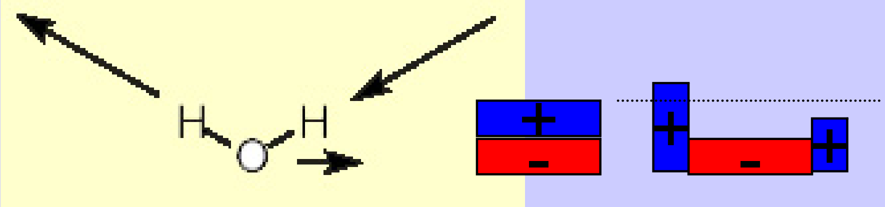

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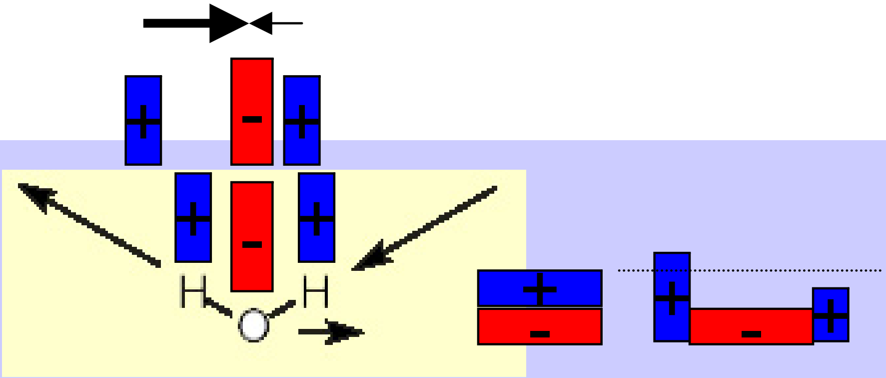

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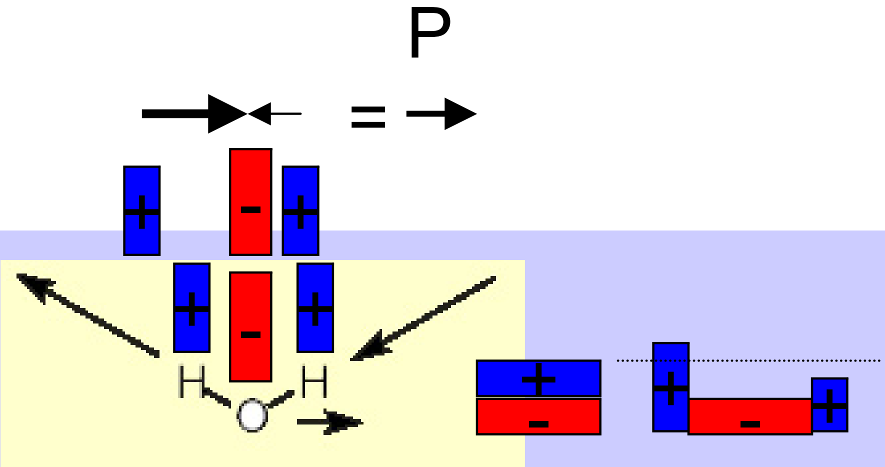

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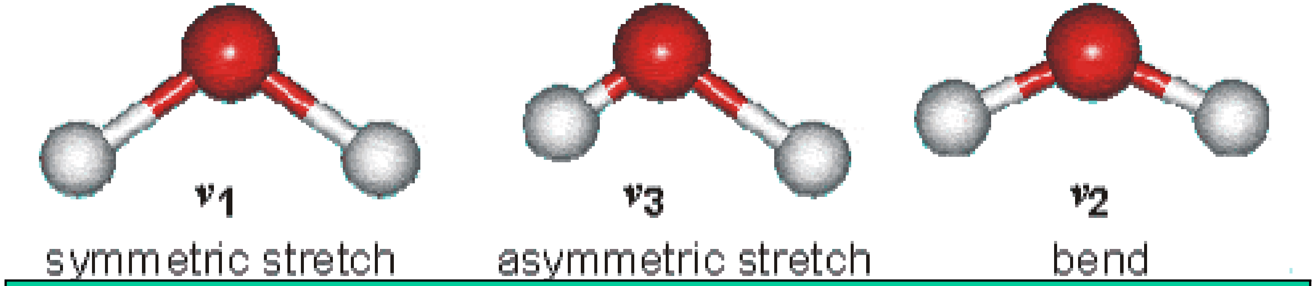
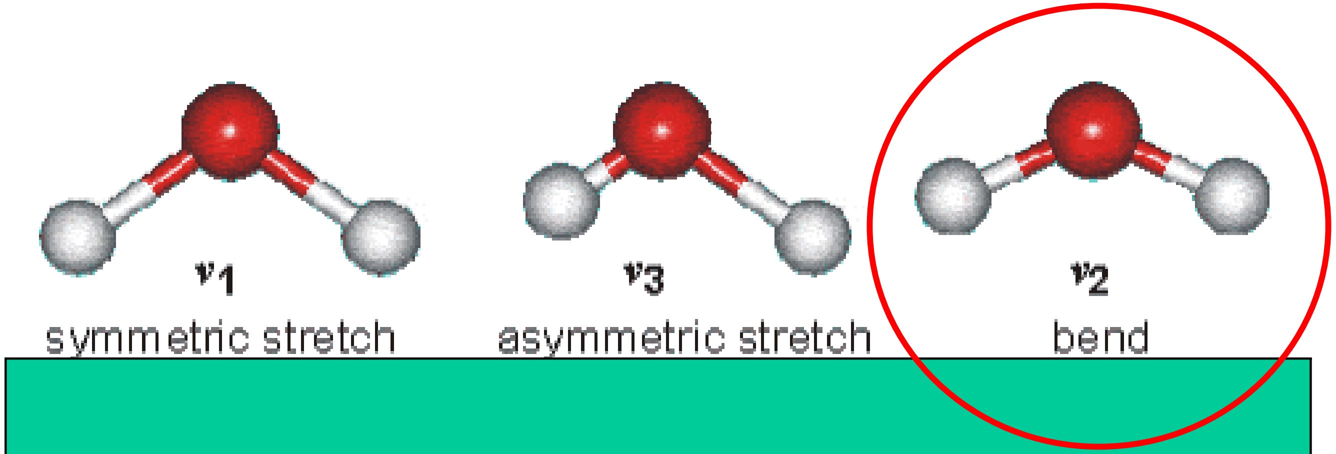
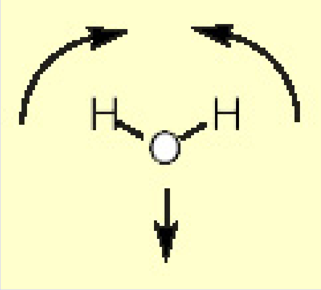


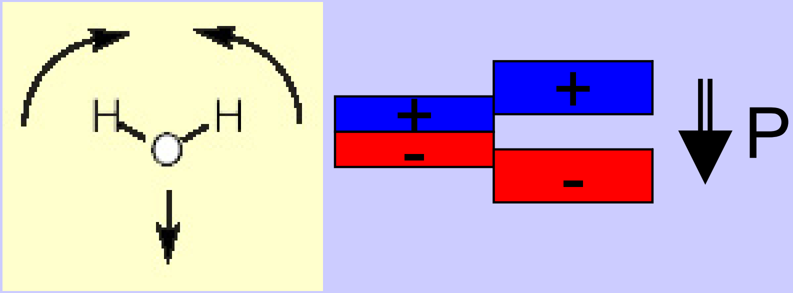
Water, H_2O, would therefore have 3 vibrational modes.





This is the one bending mode of water. In this mode the direction is unchanged, however as with the symmetrical stretch, the magnitude is changed.

This vibrational mode is IR active and would be observed on a spectrum around 3750 cm^{-1}.



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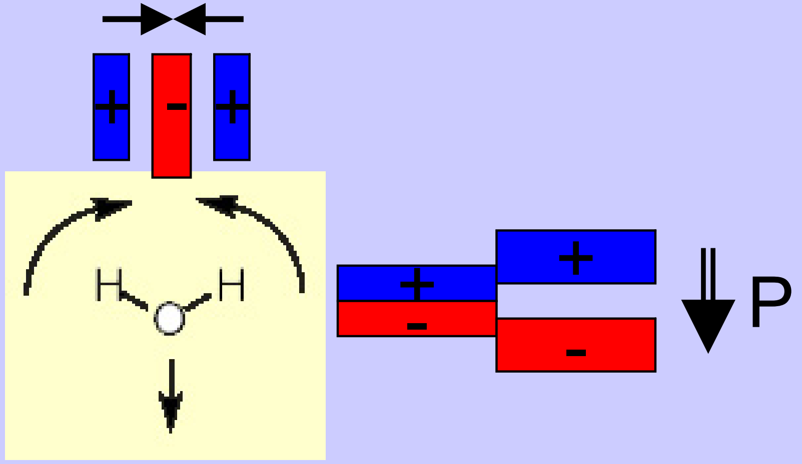

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This vibrational mode is IR active and would be observed on a spectrum around 3750 cm^{-1}.

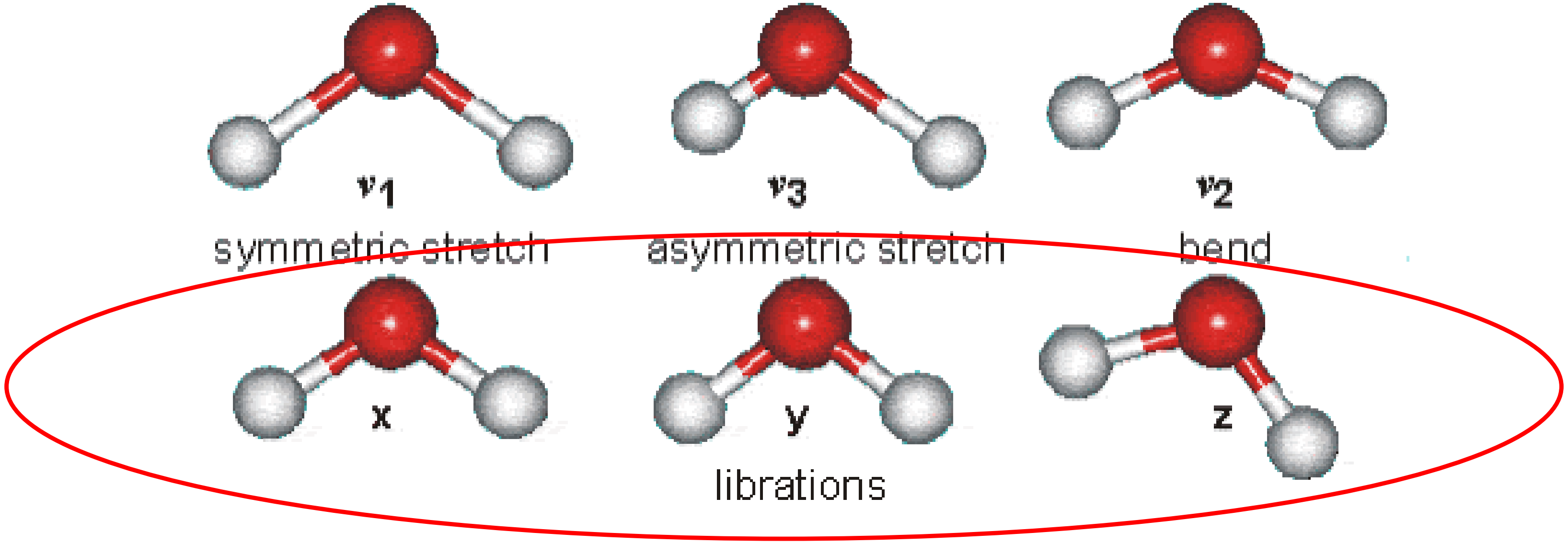
absorption intensity ratio ($H_2{}^{16}O$)

$v_1;v_2;v_3 = 0.07;1.47;1.00$

Main vibrations of water isotopologues

Gas	v_1, cm^{-1}	v_2, cm^{-1}	v_3, cm^{-1}
$H_2{}^{16}O$	3657.05	1594.75	3755.93
$H_2{}^{17}O$	3653.15	1591.32	3748.32
$H_2{}^{18}O$	3649.69	1588.26	3741.57
$HD^{16}O$	2723.68	1403.48	3707.47
$D_2{}^{16}O$	2669.40	1178.38	2787.92
$T_2{}^{16}O$	2233.9	995.37	2366.61

Moreover, 3 libration modes also exist.



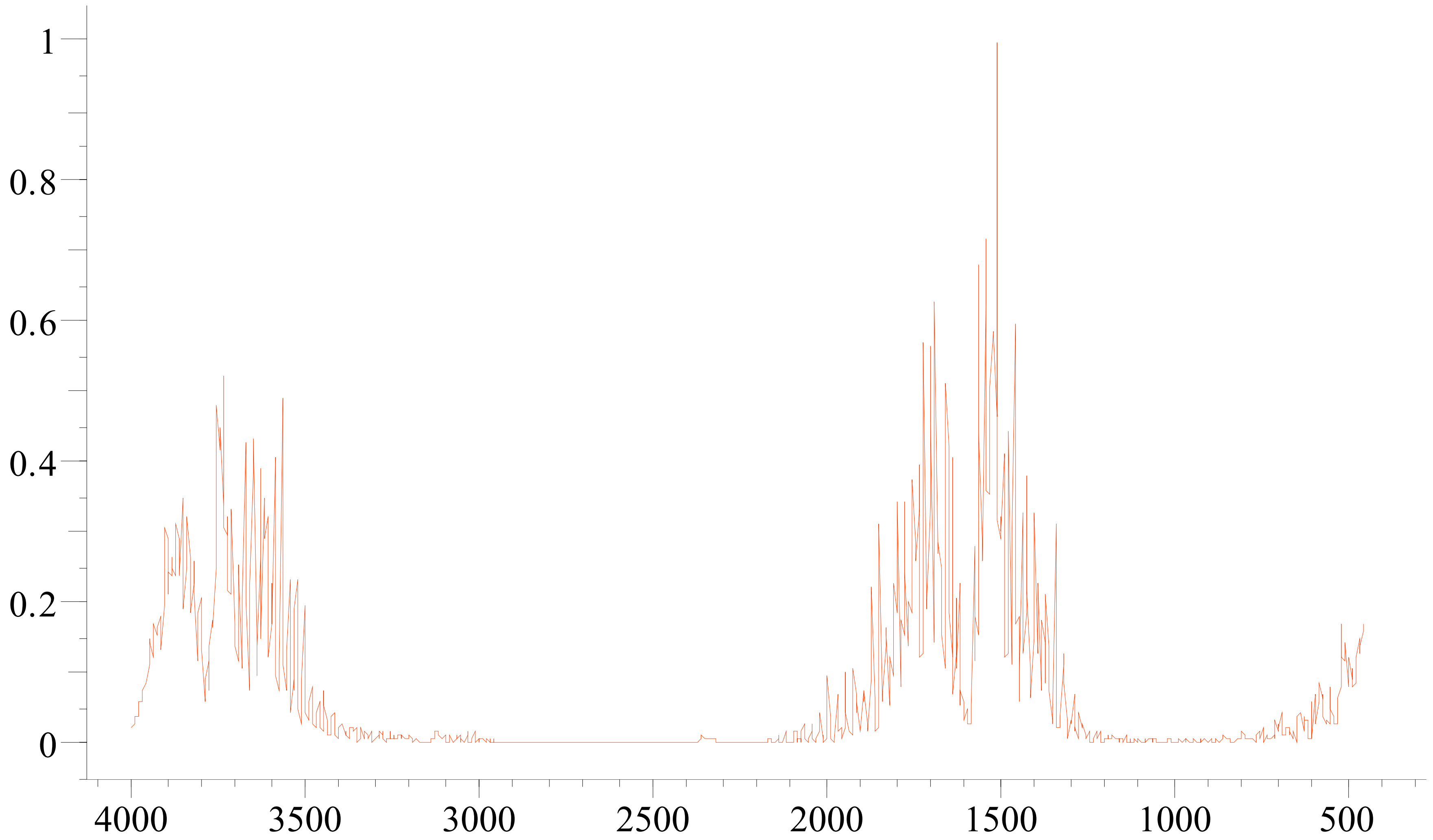
The main stretching band in liquid water is shifted to a lower frequency (v_3, 3490 cm^{-1} and v_1, 3280 cm^{-1}) and the bending frequency increased (v_2, 1644 cm^{-1}) by hydrogen bonding.

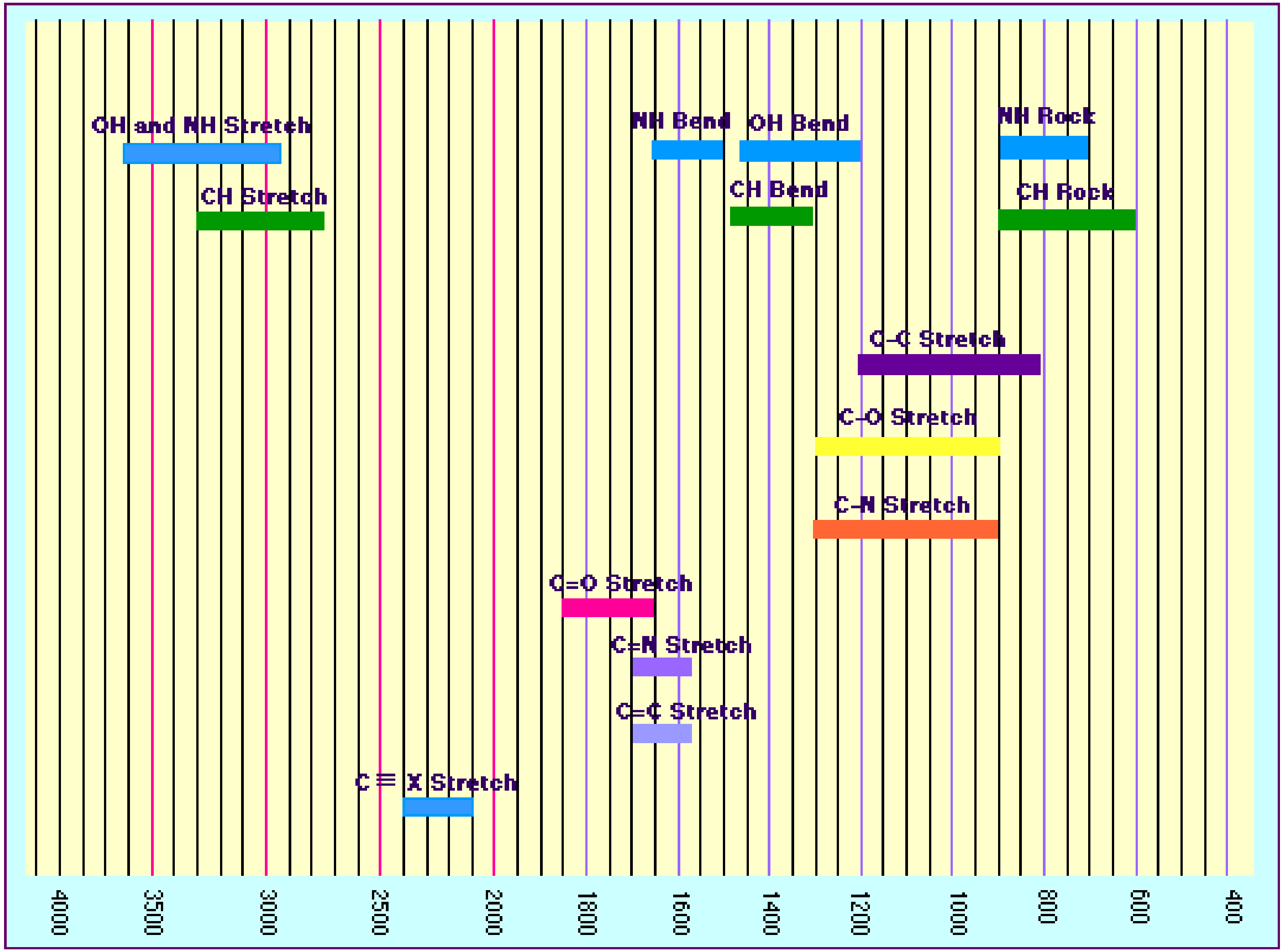
In liquid water and ice the infrared and Raman spectra are far more complex than the vapor due to vibrational overtones and combinations with librations (restricted rotations; *i.e.* rocking motions). These librations are due to the restrictions imposed by hydrogen bonding (minor L_1 band 395.5 cm^{-1}; major L_2 band 686.3 cm^{-1}

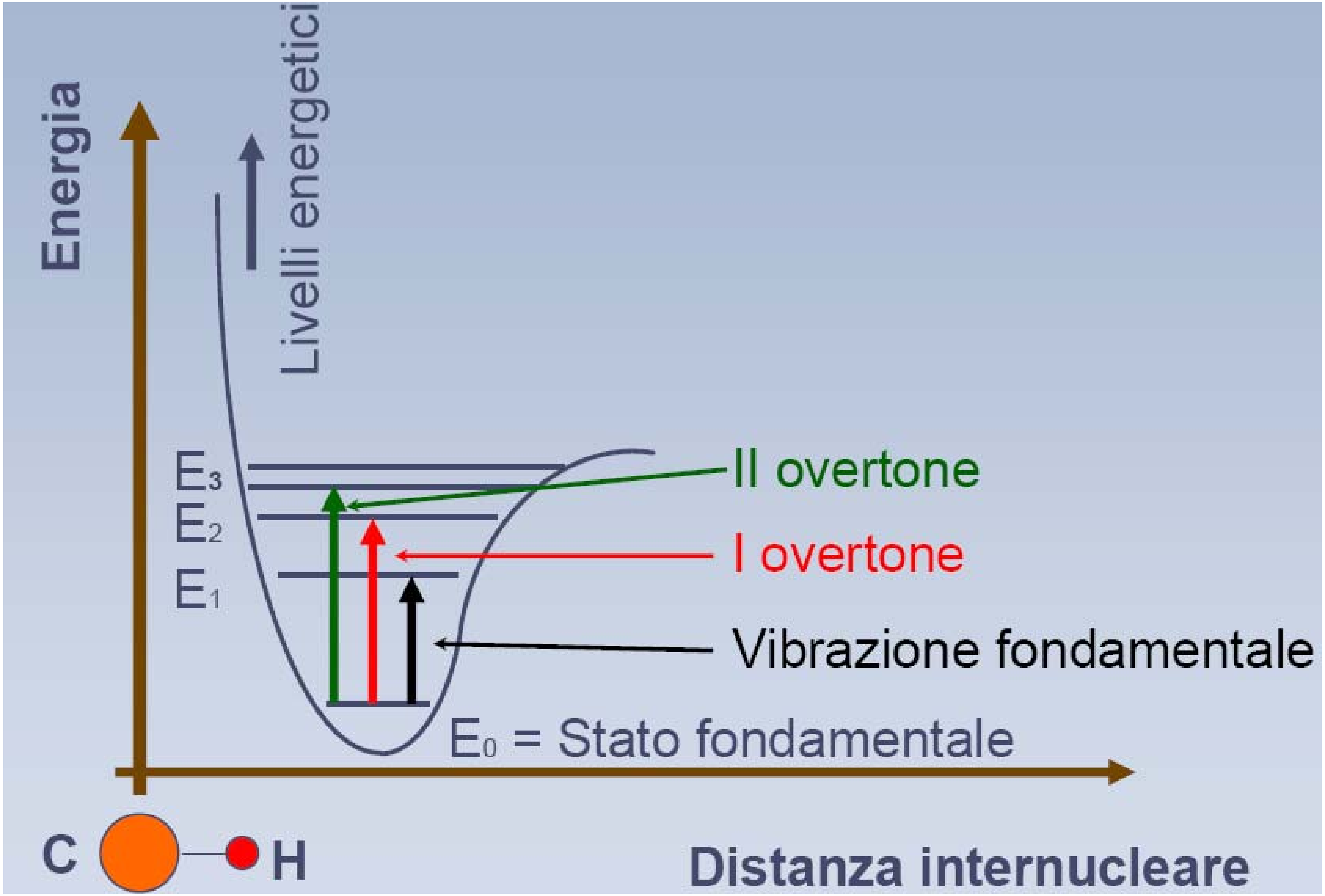
Variations in the environment around each liquid water molecule gives rise to considerable line broadening with vibration shifts in a hydrogen-bond-donating water molecule being greater than in a hydrogen-bond accepting molecule but both acting in the same direction, and accumulating with the number of hydrogen bonds.

Assignment of the IR vibrational absorption spectrum of liquid water[*]

Wavelength	cm^{-1}	Assignment	Wavelength	cm^{-1}	Assignment
0.2 mm	50	intermolecular bend	1470 nm	6800	$a\nu_1 + b\nu_3$; $a+b=2$
55 µm	183.4	intermolecular stretch	1200 nm	8330	$a\nu_1 + \nu_2 + b\nu_3$; $a+b=2$
25 µm	395.5	L_1, librations	970 nm	10310	$a\nu_1 + b\nu_3$; $a+b=3$
15 µm	686.3	L_2, librations	836 nm	11960	$a\nu_1 + \nu_2 + b\nu_3$; $a+b=3$
6.08 µm	1645	ν_2, bend	739 nm	13530	$a\nu_1 + b\nu_3$; $a+b=4$
4.65 µm	2150	$\nu_2 + L_2$ [a]	660 nm	15150	$a\nu_1 + \nu_2 + b\nu_3$; $a+b=4$
3.05 µm	3277	ν_1, symmetric stretch	606 nm	16500	$a\nu_1 + b\nu_3$; $a+b=5$ [526]
2.87 µm	3490	ν_3, asymmetric stretch	514 nm	19460	$a\nu_1 + b\nu_3$; $a+b=6$ [526]
1900 nm	5260	$a\nu_1 + \nu_2 + b\nu_3$; $a+b=1$	Note that a and b are integers, ≥ 0 ms.		


1
0.8
0.6
0.4
0.2
0
4000
3500
3000
2500
2000
1500
1000
500


OH and NH Stretch
CH Stretch
NH Bend
OH Bend
CH Bend
NH Rock
CH Rock
C-C Stretch
C-O Stretch
C-N Stretch
C=O Stretch
C=N Stretch
C=C Stretch
C ≡ X Stretch
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400



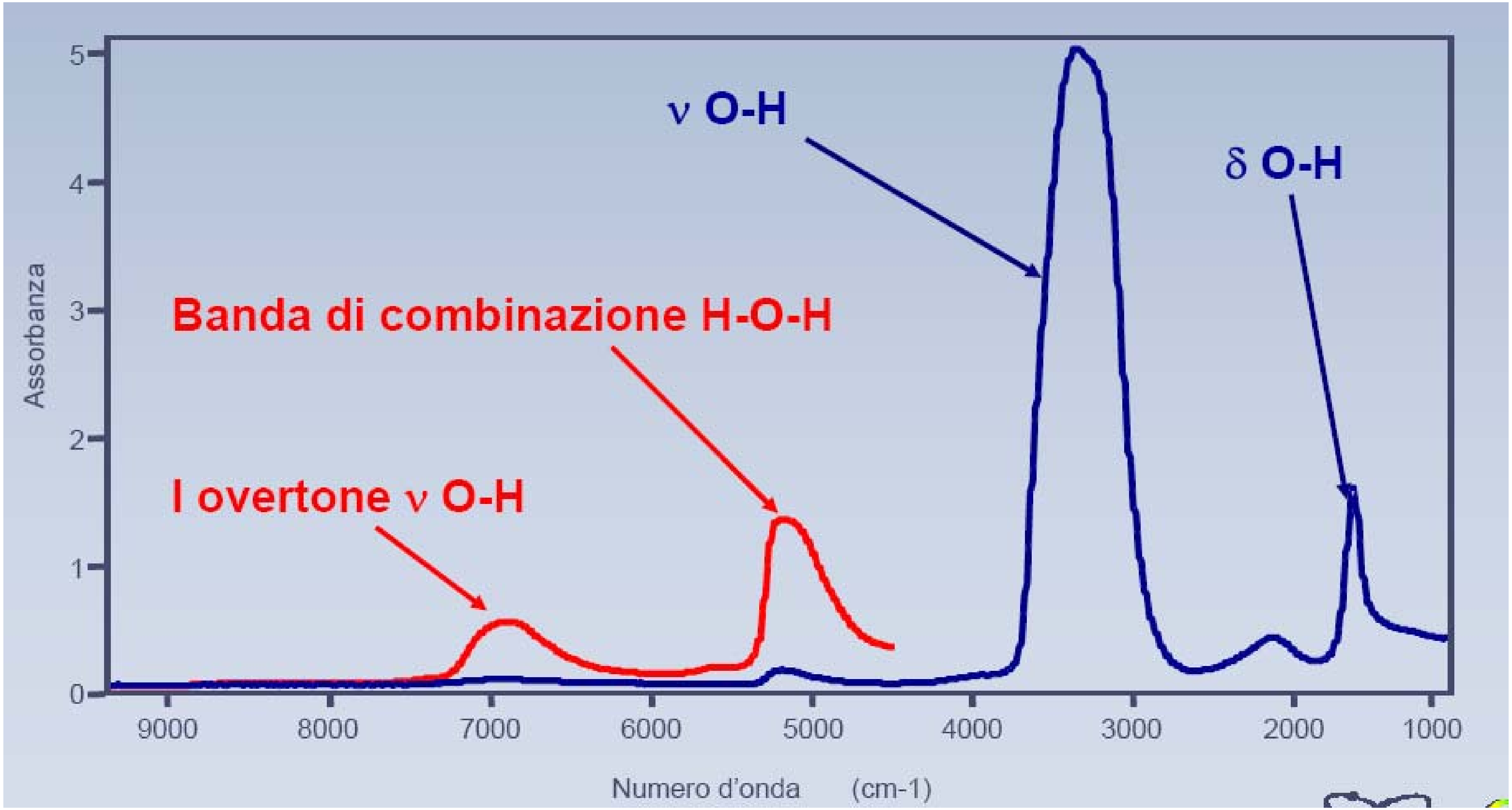
II overtone

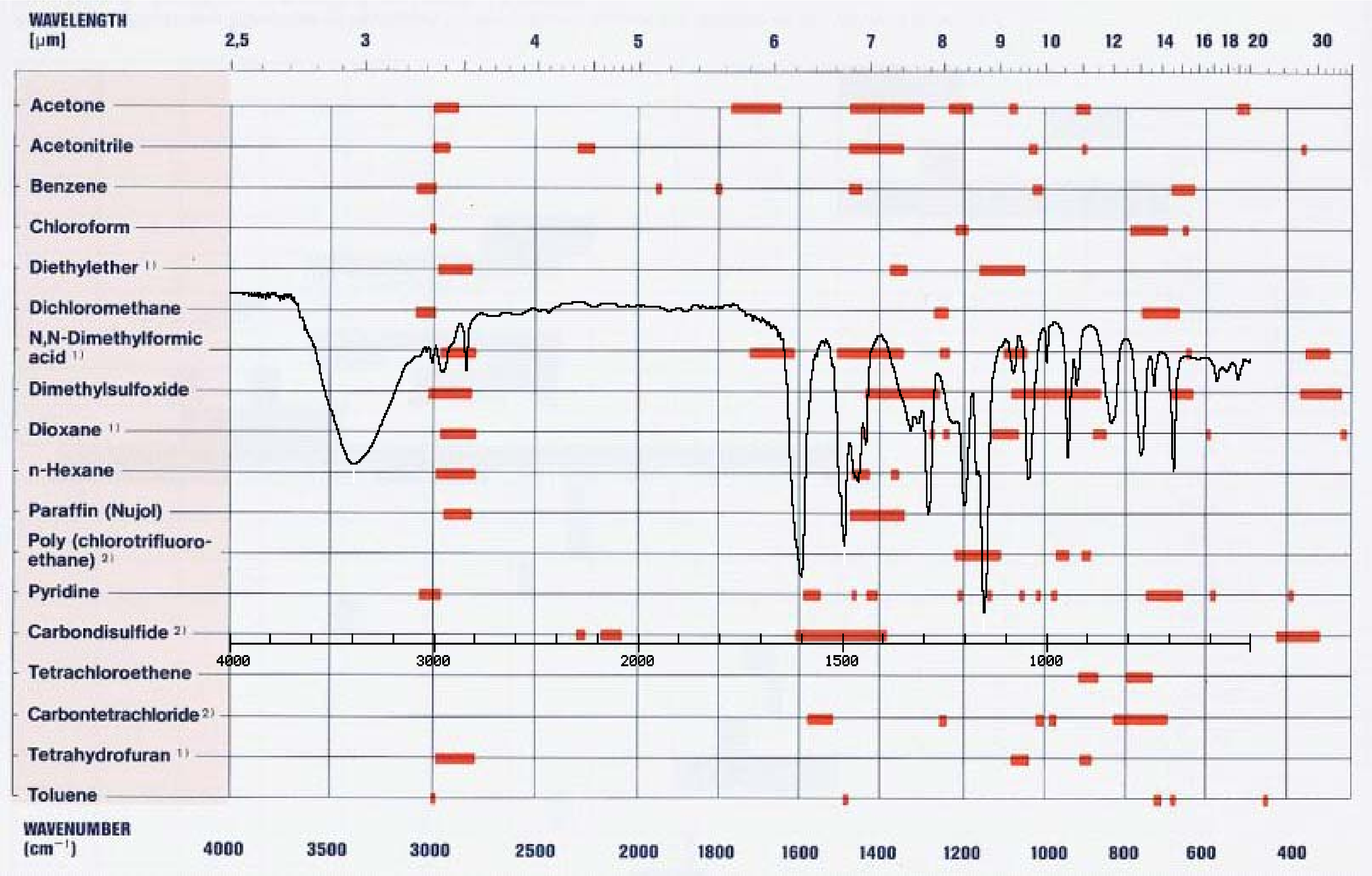
I overtone

Vibrazione fondamentale

E_0 = Stato fondamentale

Distanza internucleare


ν O-H
δ O-H
Banda di combinazione H-O-H
I overtone ν O-H
Assorbanza
5
4
3
2
1
0
9000
8000
7000
6000
5000
4000
3000
2000
1000
Numero d'onda (cm-1)


WAVELENGTH [µm]
2,5
3
4
5
6
7
8
9
10
12
14
16
18
20
30
Acetone
Acetonitrile
Benzene
Chloroform
Diethylether 1)
Dichloromethane
N,N-Dimethylformic acid 1)
Dimethylsulfoxide
Dioxane 1)
n-Hexane
Paraffin (Nujol)
Poly (chlorotrifluoro-ethane) 2)
Pyridine
Carbondisulfide 2)
Tetrachloroethene
Carbontetrachloride 2)
Tetrahydrofuran 1)
Toluene
4000
3000
2000
1500
1000
WAVENUMBER (cm⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400

From $c^2\tilde{q}^2 = \tilde{\varepsilon}\,\omega^2 \longrightarrow \tilde{q} = \frac{\omega}{c}\sqrt{\tilde{\varepsilon}} = \frac{\omega}{c}\tilde{n}$

where $\tilde{n}$ is the complex refractive index such that

$$\tilde{n}(\omega) = n(\omega) + ik(\omega) = \sqrt{\tilde{\varepsilon}(\omega)}$$

n is the usual refractive index ; k is the extinction coefficient. Thus

$$\varepsilon_1 = \varepsilon = n^2 - k^2 \qquad\qquad \varepsilon_2 = 4\pi\sigma/\omega = 2nk$$

If the wave is homogeneous, *i.e.* $\mathbf{q}_1 // \mathbf{q}_2$, it holds $\tilde{\mathbf{q}} = \frac{\omega}{c}\tilde{n}\,\mathbf{u}_q$, where $\mathbf{u}_q$ is the unit vector parallel to $\tilde{\mathbf{q}}$ and then

$$\mathbf{q}_1 = \frac{\omega}{c} n\,\mathbf{u}_q \qquad\qquad \mathbf{q}_2 = \frac{\omega}{c} k\,\mathbf{u}_q$$

Thus the wave plane solution should be written as

$$\tilde{\mathbf{E}}(\mathbf{r},t) = \tilde{\mathbf{E}}_0\, exp\left[-\frac{\omega}{c}k\,\mathbf{u_q}\cdot\mathbf{r}\right]\cdot exp\left[i\left(\frac{\omega}{c}n\,\mathbf{u_q}\cdot\mathbf{r} - \omega t\right)\right]$$

n determines the phase velocity c/n of the wave in the medium

k measures the attenuation of the wave amplitude with the propagation distance inside the medium

The classical skin depth δ , defined as the distance at which the field amplitude drops of $1/e$, is $\delta = c/(\omega k)$

ABSORPTION COEFFICIENT

An additional important macroscopic quantity of the medium is the absorption coefficient α , which describes the relative decrease in the wave intensity I with unit distance (in the propagation direction, *i.e.* $\mathbf{u}_q$ // d**r**). Since the wave intensity (*i.e.* the power which is incident on the unit area perpendicular to $\mathbf{u}_q$) is $I = nc\,E^2/2$ from the plane-wave solution it follows

$$\boxed{\alpha(\omega) = \frac{2k\omega}{c} = \frac{4\pi k}{\lambda} = \frac{\omega \varepsilon_2}{nc}}$$

The exponential attenuation of I after a propagating distance d accounts for the phenomenological Lambert-Beer law :

$$I = I_0 e^{-\alpha d}$$

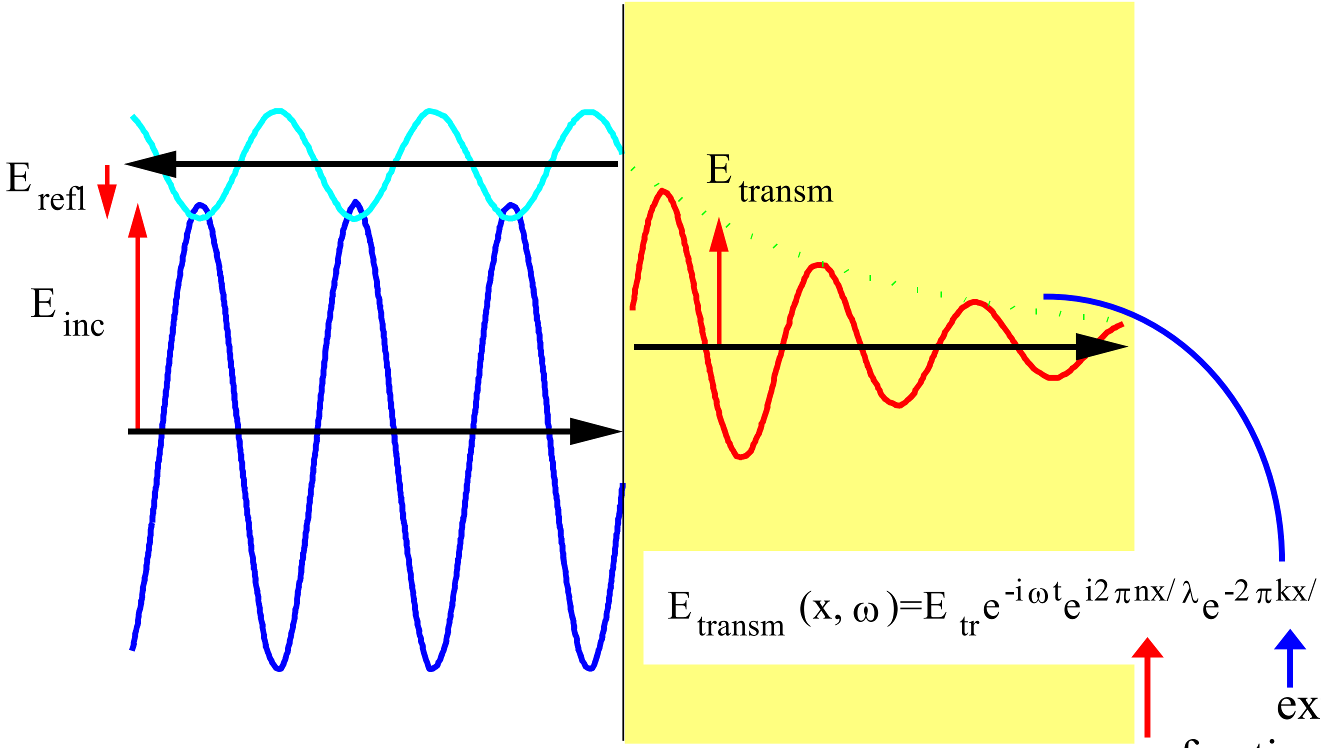
I_0 = incident wave intensity.

α is usually measured in cm^{-1} (n and k, instead, are dimensionless) . α^{-1} is the penetration depth.

αd = optical density (it reflects both the physical chemical properties and the geometry of the medium)

OPTICAL MEASUREMENTS OF SILICIDES

The optical response of a material is related to its dielectric function



$$E_{transm}(x,\omega)=E_{tr}e^{-i\omega t}e^{i2\pi nx/\lambda}e^{-2\pi kx/\lambda}$$

extinction coefficient

refractive index

from Maxwell equations:

$$\begin{cases} E_{inc}+E_{refl}=E_{transm} \\ E_{inc}-E_{refl}=\sqrt{\varepsilon}\,E_{transm} \quad (E_x=\sqrt{\mu\varepsilon}\,H_y) \end{cases}$$

$$\tilde{n}=n+ik=\sqrt{\tilde{\varepsilon}}=\sqrt{\varepsilon_1+i\varepsilon_2}$$

$$r=\frac{E_{refl}}{E_{inc}}=\frac{\tilde{n}-1}{\tilde{n}+1}$$

$$\alpha=\frac{4\pi}{\lambda}k=\frac{2\pi\varepsilon_2}{\lambda n}=\text{absorption\_ coefficient}$$

REFLECTION AND TRANSMISSION

At the interface between two media, the reflected (I_r) and transmitted (I_t) wave intensities relative to the incident one (I_0) are called reflectivity R and transmittivity T. At normal incidence they are given by

$$R = \frac{I_r}{I_0} = \left|\frac{\tilde{n}_0 - \tilde{n}}{\tilde{n}_0 + \tilde{n}}\right|^2 = \frac{(n-n_0)^2 + (k-k_0)^2}{(n+n_0)^2 + (k+k_0)^2}$$

$$T = \frac{I_t}{I_0} = \mathrm{Re}\left(\frac{\tilde{n}}{\tilde{n}_0}\right)\left|\frac{2\tilde{n}_0}{\tilde{n}_0 + \tilde{n}}\right|^2$$

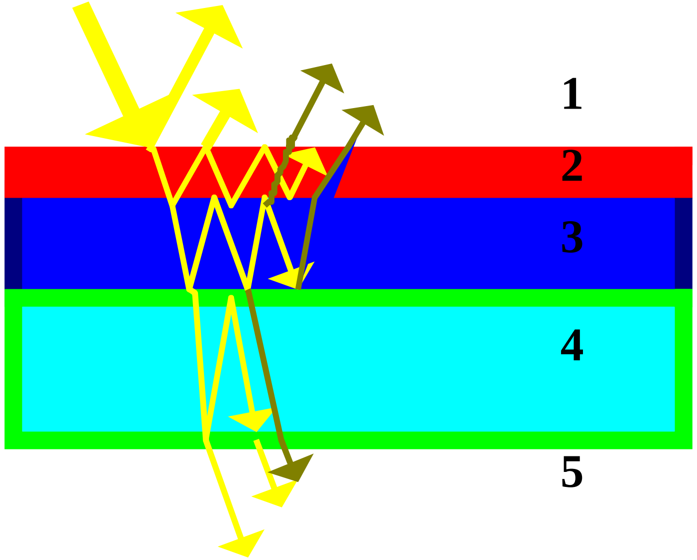
→

$$R + T = 1$$

(energy conservation)

Let us consider a sample of material with $\tilde{n}$ and thickness d, immersed in air ($\tilde{n}_0 = 1$) as shown in **Figure 1**. Coming from air, the near-normally incident beam is split into reflected and transmitted fractions (as determined by R and T) at each interface, giving rise to secondary beams: by summing up all the multiple-reflected and multiple-transmitted elements, which account also for light absorption along the thickness d, we obtain the total intensity reflected from the front surface:

Surface and Interface Effects



$$
\begin{aligned}
r_{tot} = {} & r_{12} + \\
& + t_{12} r_{23} t_{21} + t_{12} r_{23} r_{21} r_{23} t_{21} + \dots \\
& + t_{12} t_{23} r_{34} t_{32} t_{21} + t_{12} t_{23} r_{34} \; r_{32} \; r_{43} t_{32} t_{21} + \dots \\
& + t_{12} t_{23} t_{34} r_{45} t_{43} t_{32} t_{21} + t_{12} t_{23} t_{34} r_{45} r_{43} r_{45} t_{43} t_{32} t_{21} + \dots \\
& + \dots \\
& + t_{12} t_{23} r_{34} \; r_{32} \; t_{34} r_{45} r_{43} r_{45} t_{43} t_{32} t_{21} + \dots
\end{aligned}
$$

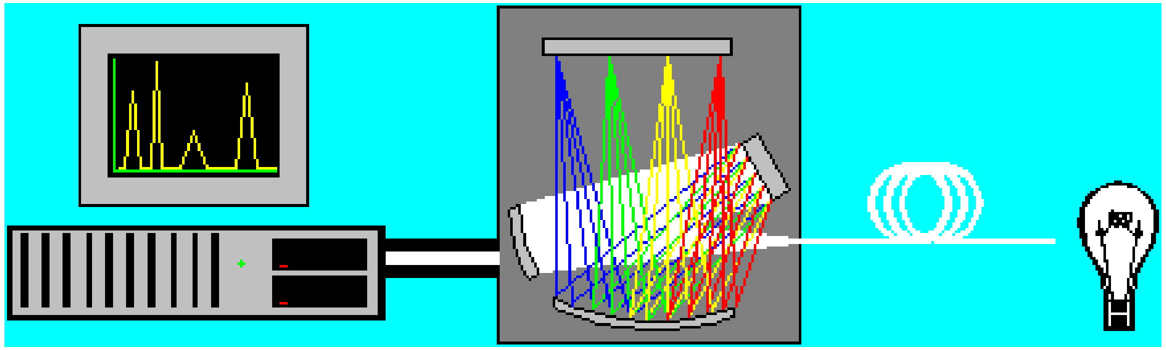
$$
\begin{aligned}
t_{tot} = {} & t_{12} t_{23} t_{34} t_{45} + \\
& + t_{12} r_{23} r_{21} t_{23} t_{34} t_{45} + t_{12} r_{23} r_{21} r_{23} r_{21} t_{23} t_{34} t_{45} + \dots \\
& + t_{12} t_{23} r_{34} r_{32} t_{34} t_{45} + t_{12} t_{23} r_{34} r_{32} r_{34} r_{32} t_{34} t_{45} + \dots \\
& + t_{12} t_{23} t_{34} r_{45} r_{43} t_{45} + t_{12} t_{23} t_{34} r_{45} r_{43} r_{45} r_{43} t_{45} + \dots \\
& + \dots \\
& + t_{12} t_{23} r_{34} \; r_{32} \; t_{34} r_{45} r_{43} t_{45} + \dots
\end{aligned}
$$

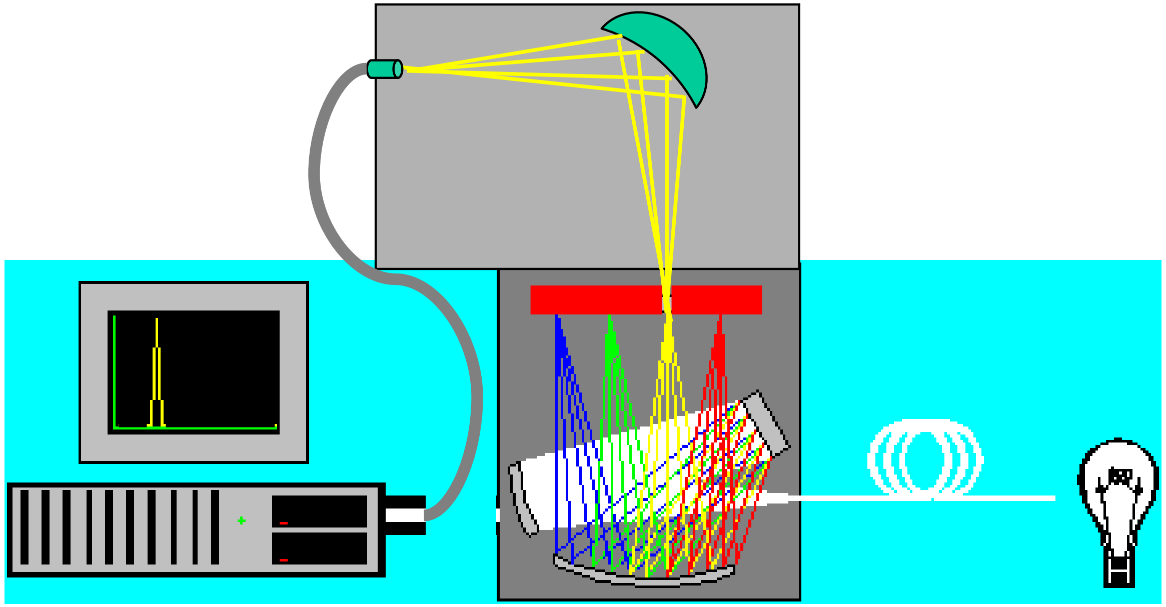
Multiple reflection is a common behaviour of thin (transparent) films and concerns:

⇒ film deposition
⇒ coatings
⇒ oxide layers
⇒ multilayered systems

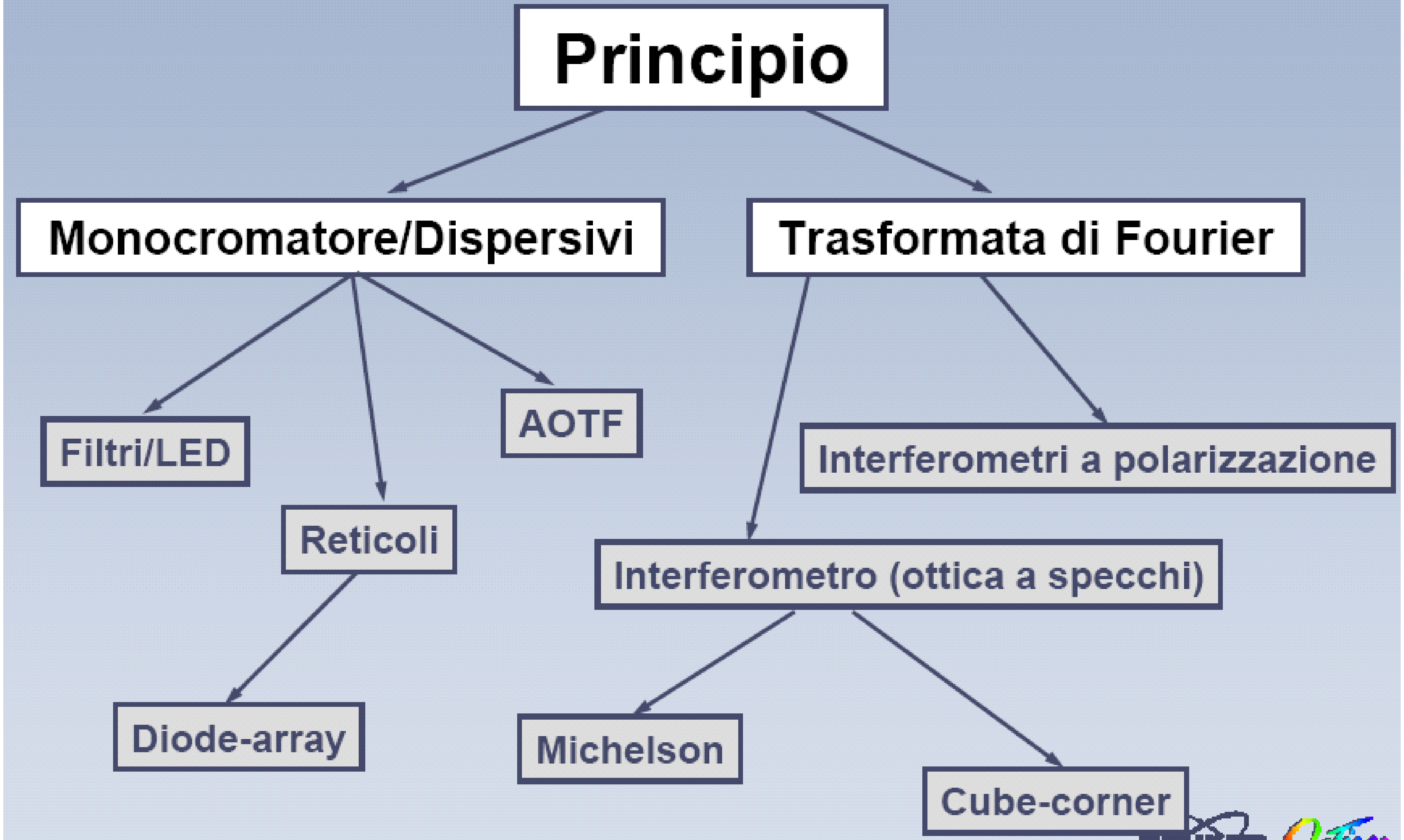
In multireflection, interference has to be considered and one can observe interference fringes.

Important parameters are: thickness, parallelism and homogeneity of the film, smoothness of interfaces





Tecnologia NIR: gli strumenti



Principio

Monocromatore/Dispersivi

Trasformata di Fourier

Filtri/LED

Reticoli

AOTF

Diode-array

Interferometri a polarizzazione

Interferometro (ottica a specchi)

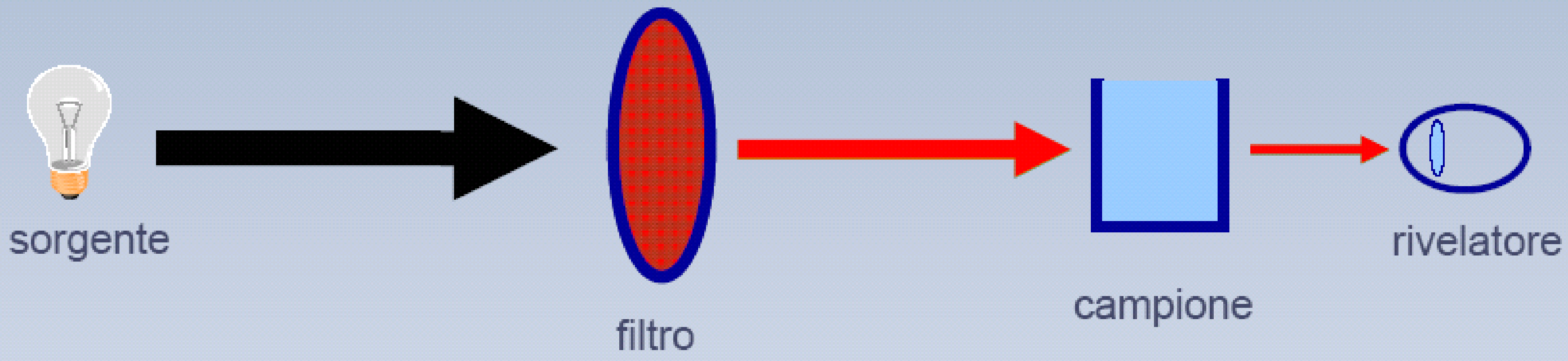
Michelson

Cube-corner

Tecnologia NIR: monocromatore/dispersivi

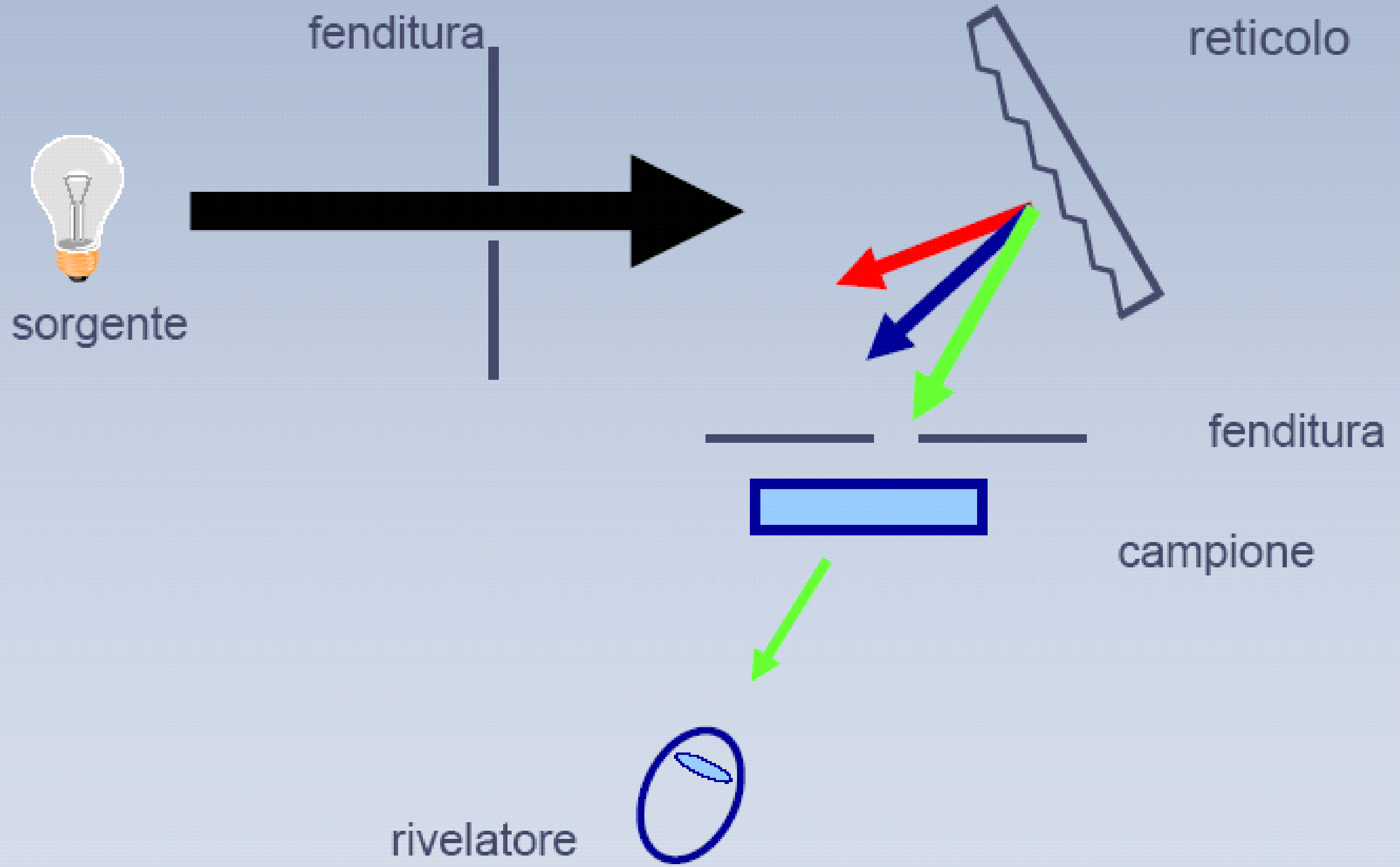
Monocromatore: filtri

filtri/LED



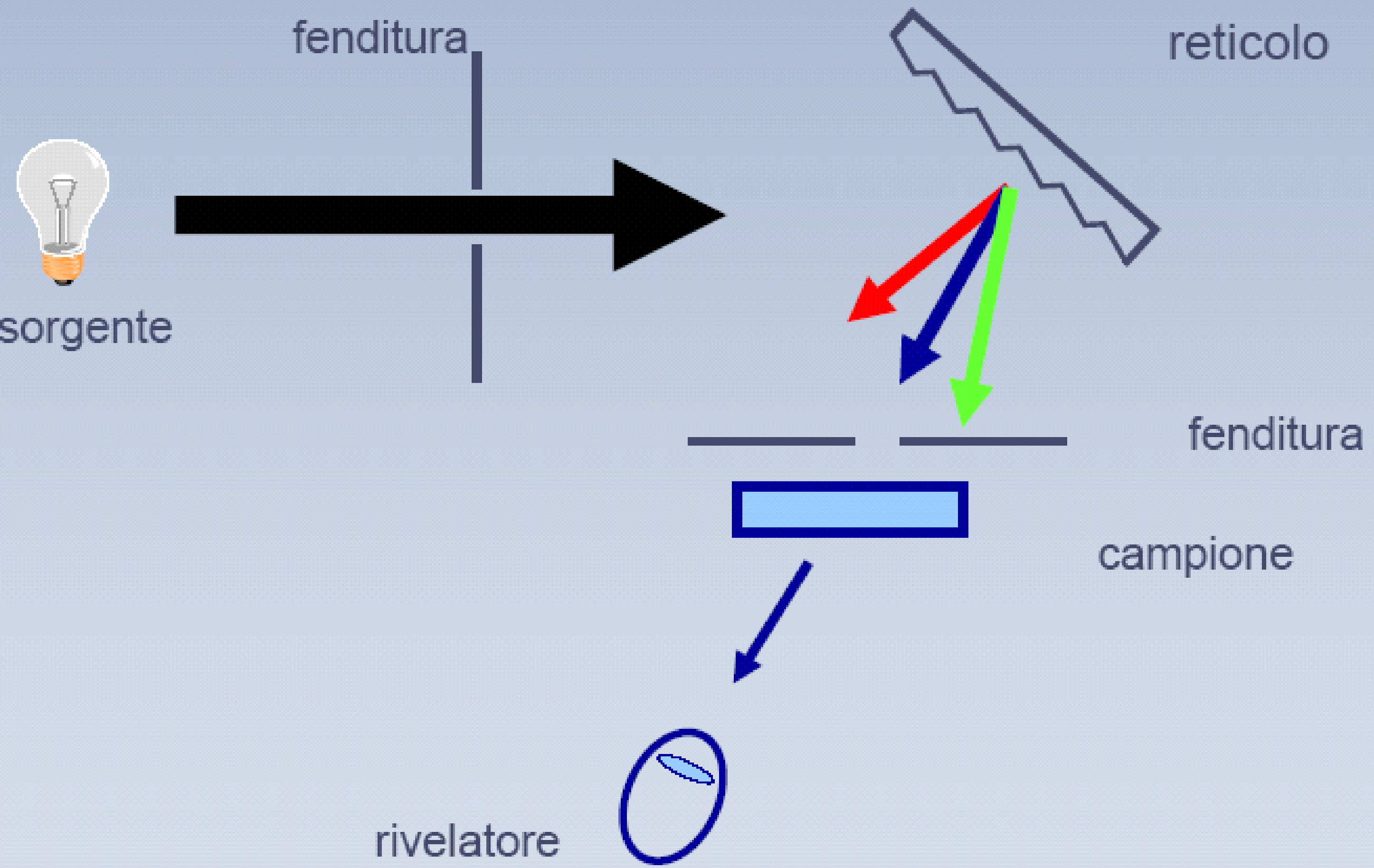
Tecnologia NIR: monocromatore/dispersivi

Monocromatore: reticoli



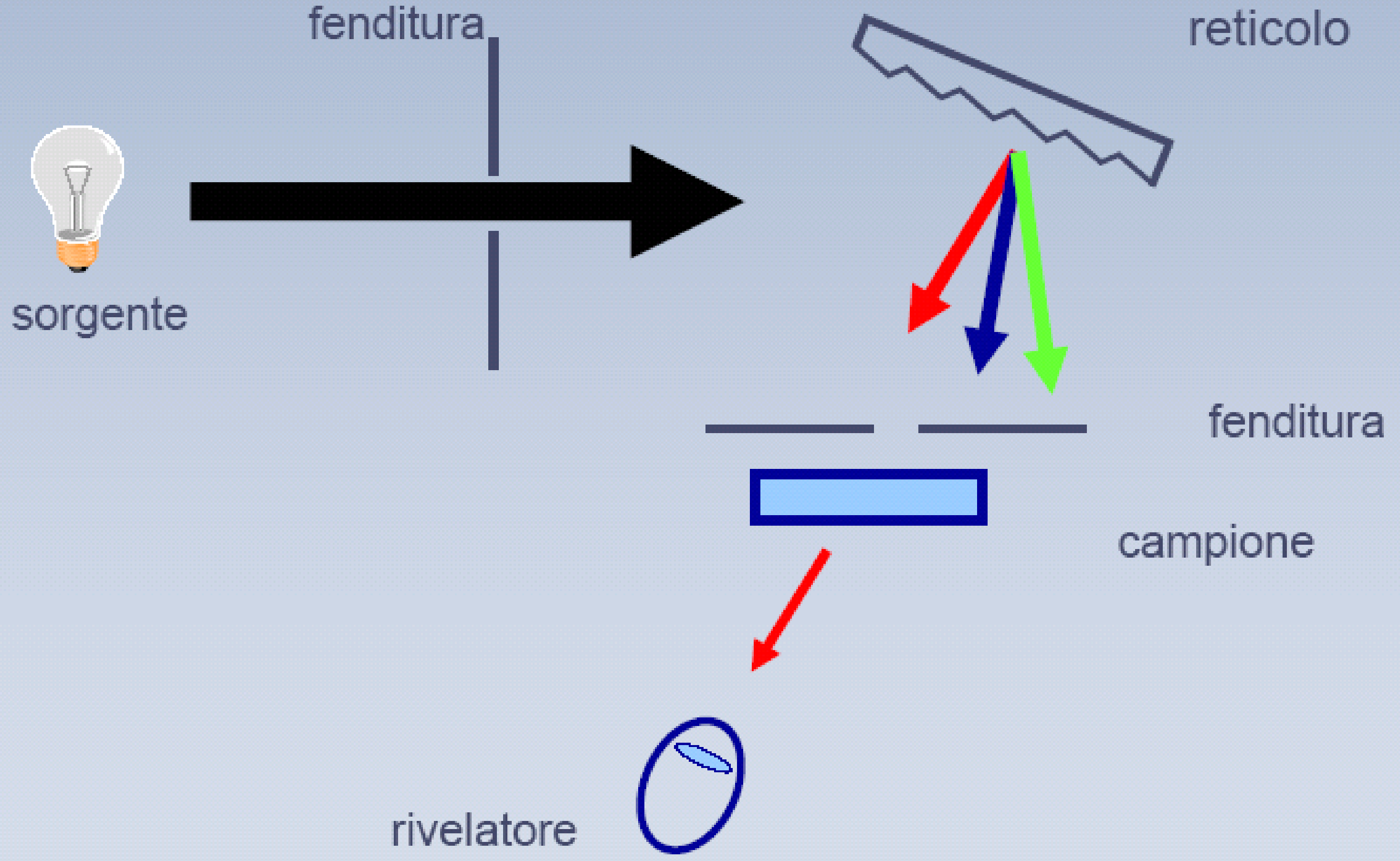
Tecnologia NIR: monocromatore/dispersivi

Monocromatore: reticoli



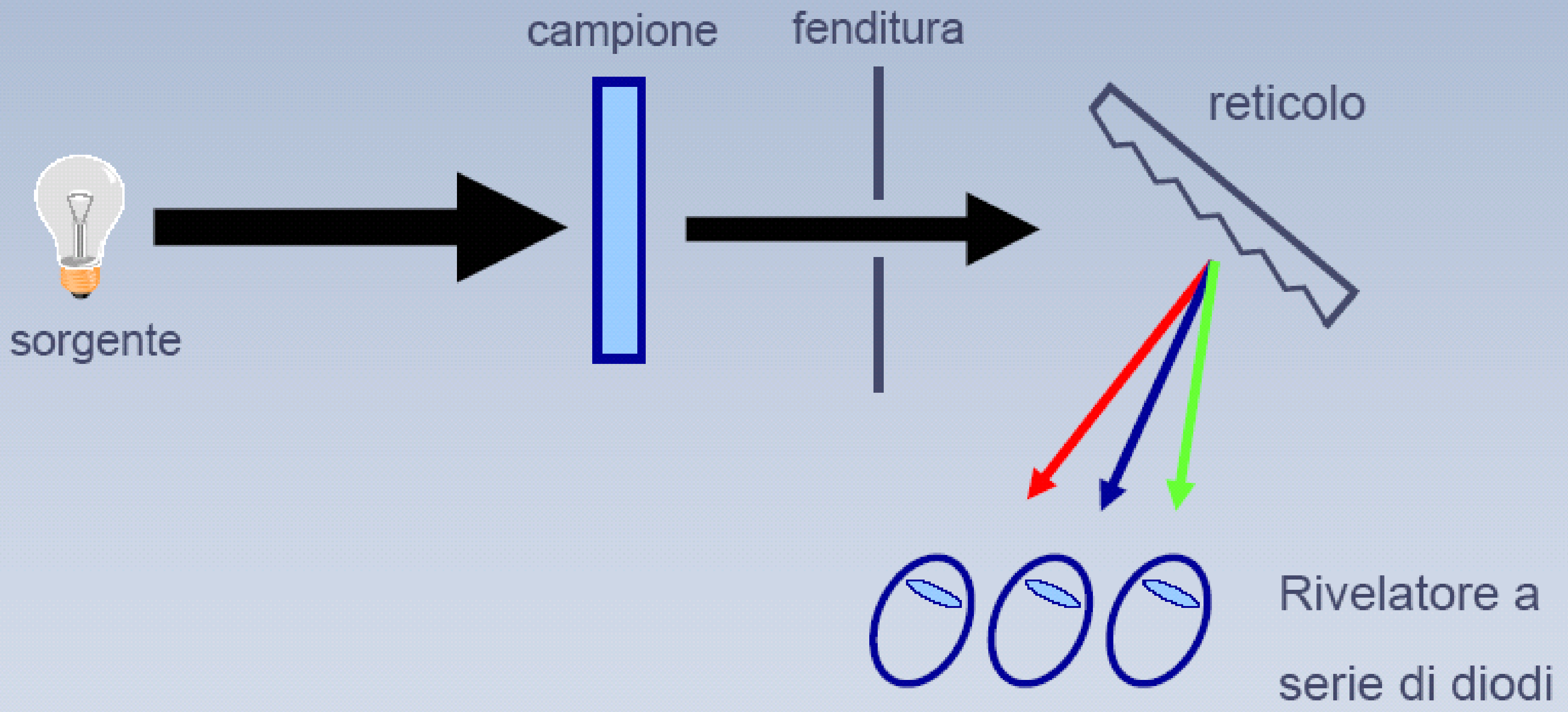
Tecnologia NIR: monocromatore/dispersivi

Monocromatore: reticoli



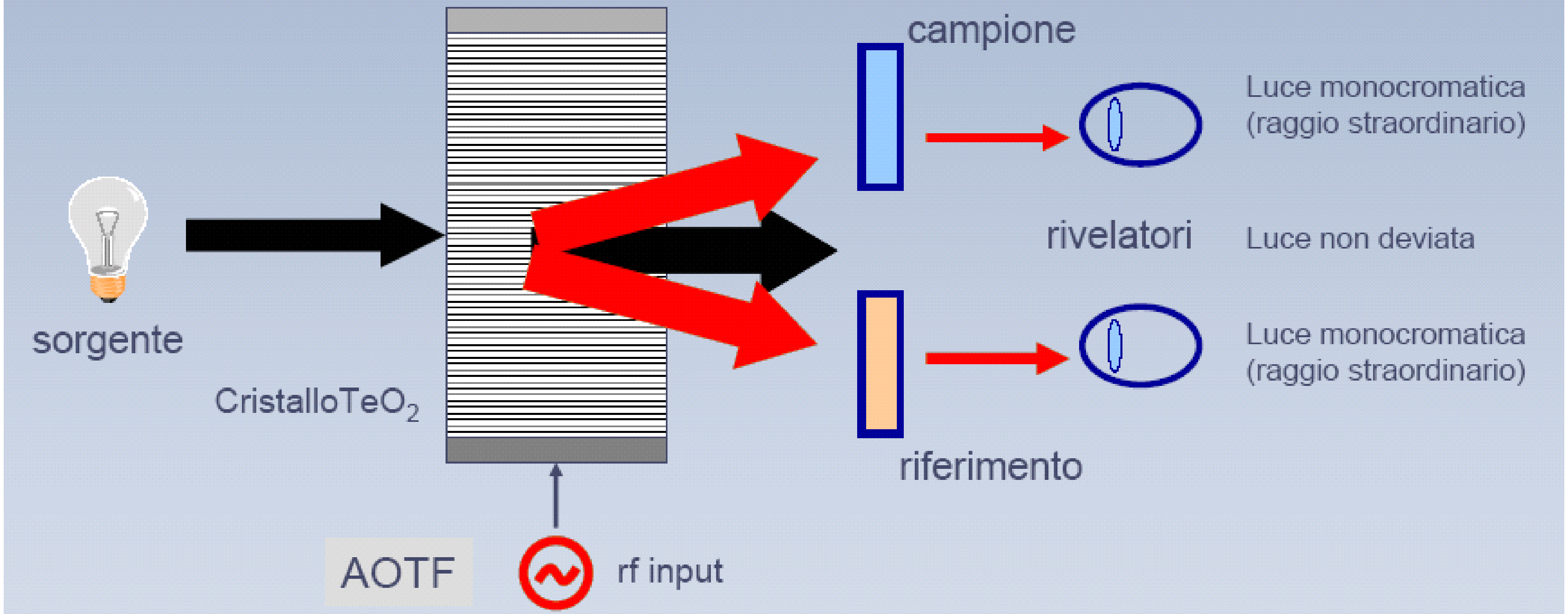
Tecnologia NIR: monocromatore/dispersivi

Monocromatore: reticoli e rivelatori a serie di diodi



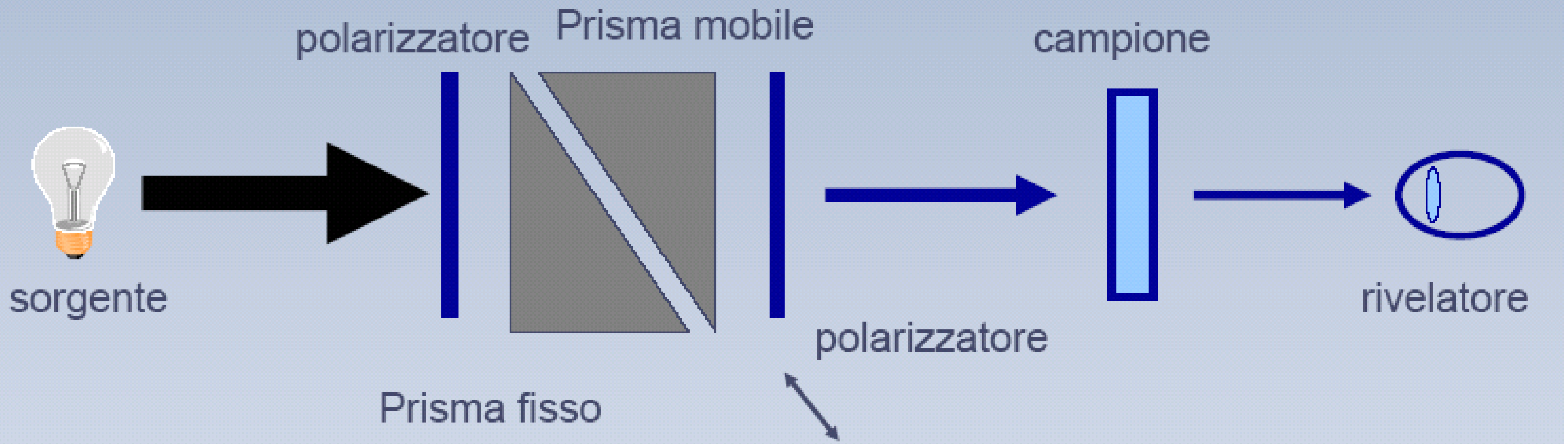
Tecnologia NIR: monocromatore/dispersivi

Monocromatore: Filtri AOTF (filtri Acusto ottici)



Tecnologia NIR: FT

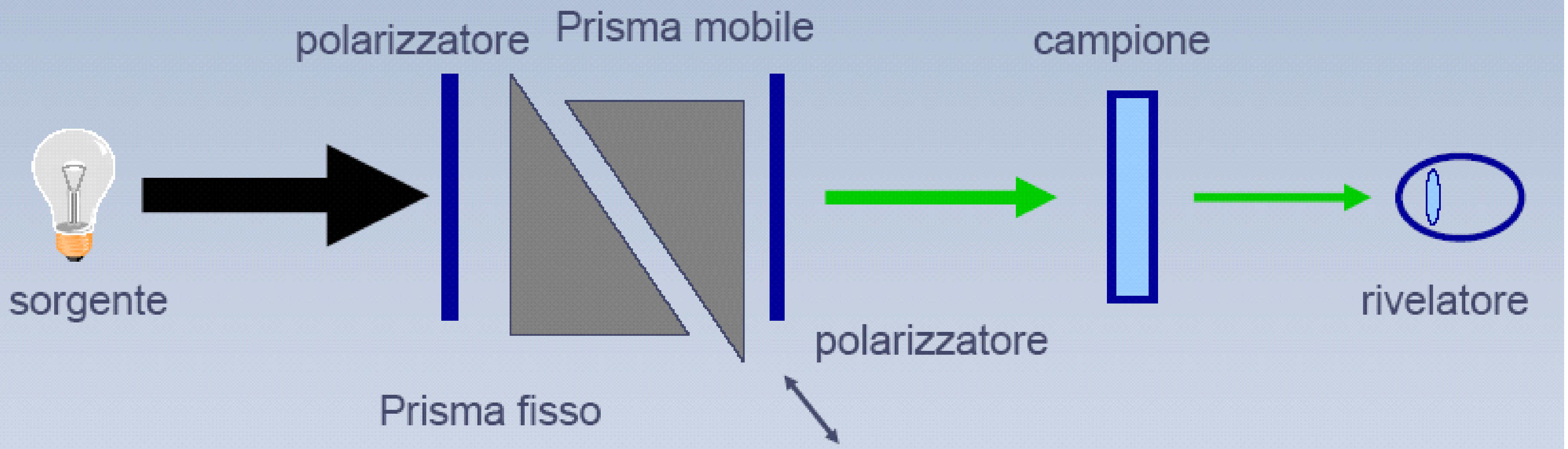
Tecniche a trasformata di Fourier: **Interferometro a Polarizzazione**



Interferometro a Polarizzazione

Tecnologia NIR: FT

Tecniche a trasformata di Fourier: **Interferometro a Polarizzazione**

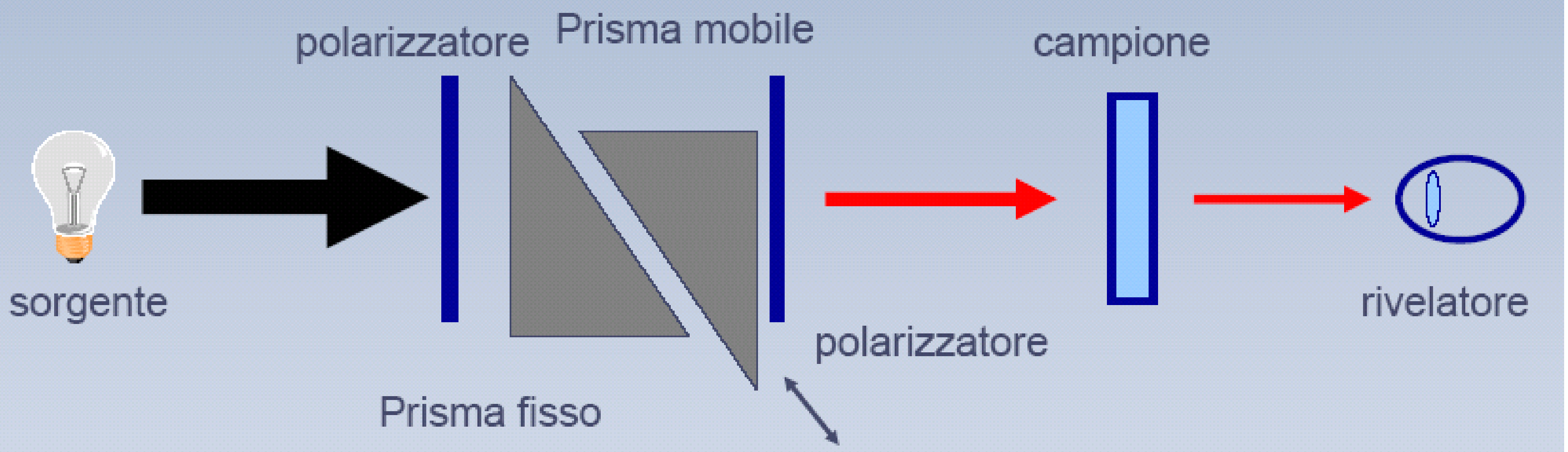


Interferometro a Polarizzazione

Tecnologia NIR: FT

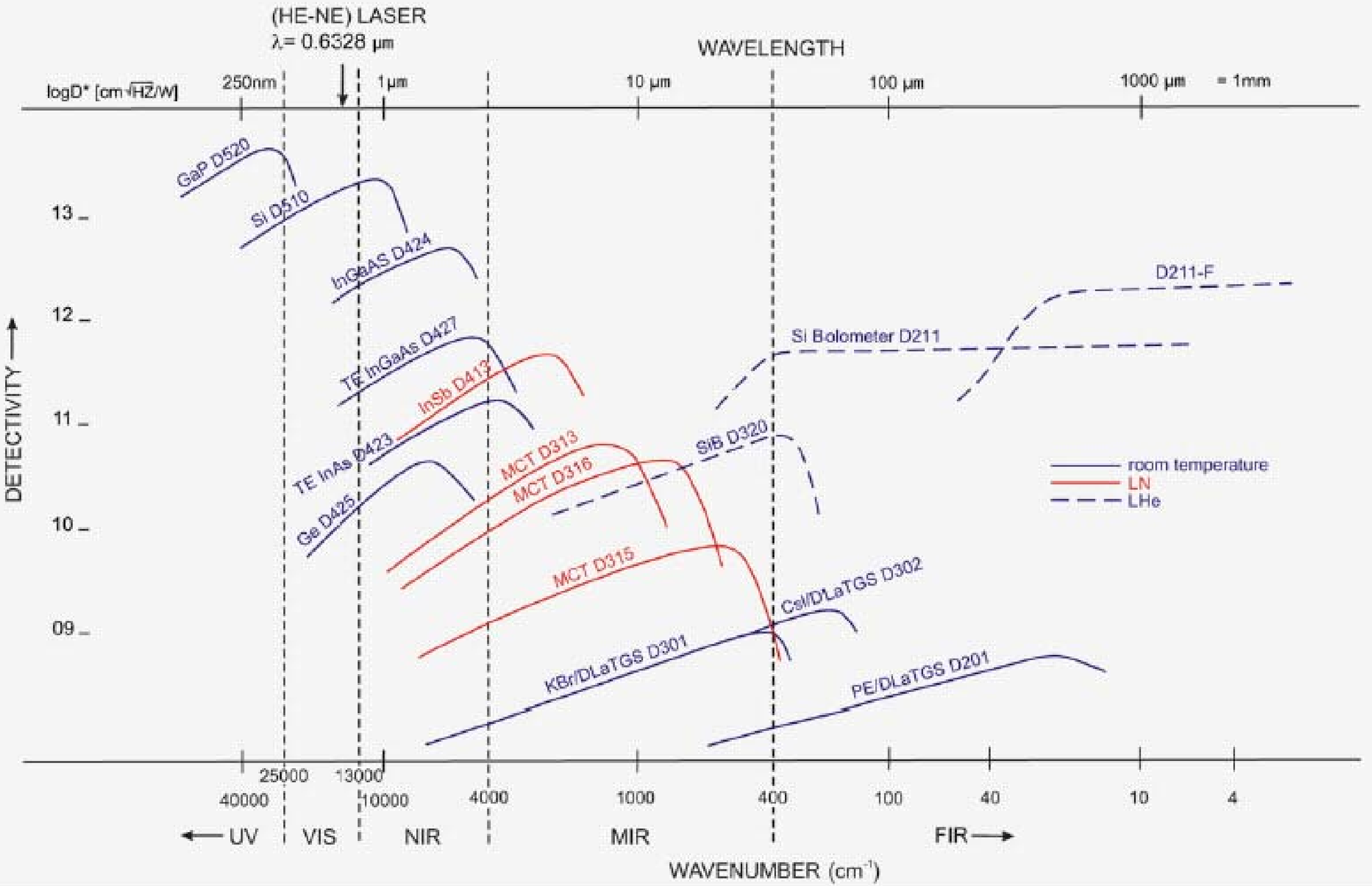
Tecniche a trasformata di Fourier:

Interferometro a Polarizzazione



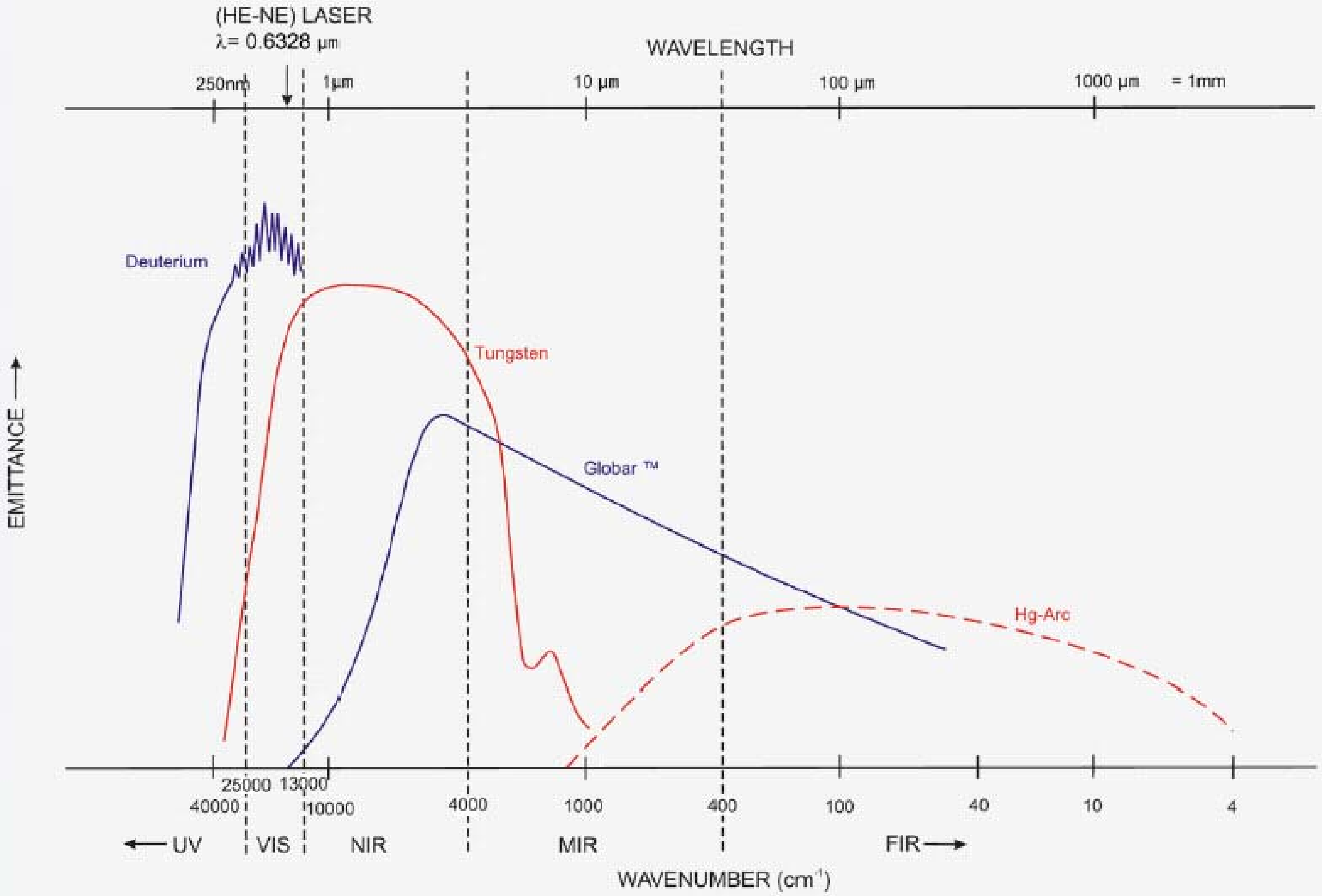
Interferometro a Polarizzazione

DETECTORS



(HE-NE) LASER
λ= 0.6328 µm
WAVELENGTH
logD* [cm √HZ/W]
250nm
1 µm
10 µm
100 µm
1000 µm
= 1mm
DETECTIVITY
13
12
11
10
09
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
room temperature
LN
LHe
25000
13000
40000
10000
4000
1000
400
100
40
10
4
UV
VIS
NIR
MIR
FIR
WAVENUMBER (cm⁻¹)

SOURCES


(HE-NE) LASER
λ= 0.6328 μm
WAVELENGTH
250nm
1μm
10 μm
100 μm
1000 μm
= 1mm
Deuterium
Tungsten
Globar ™
Hg-Arc
EMITTANCE
25000
13000
40000
10000
4000
1000
400
100
40
10
4
UV
VIS
NIR
MIR
FIR
WAVENUMBER (cm⁻¹)

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

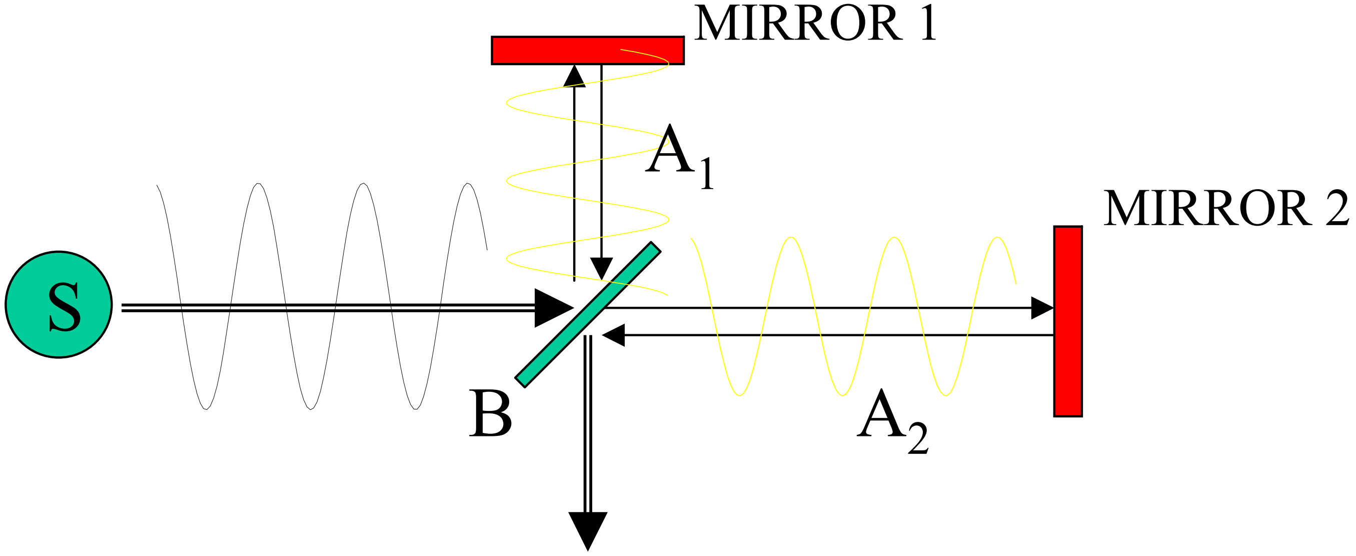
- the oscillation frequency ω
- the wavelength, $\lambda = 2\pi/|k| = 2\pi\, v/\omega$

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

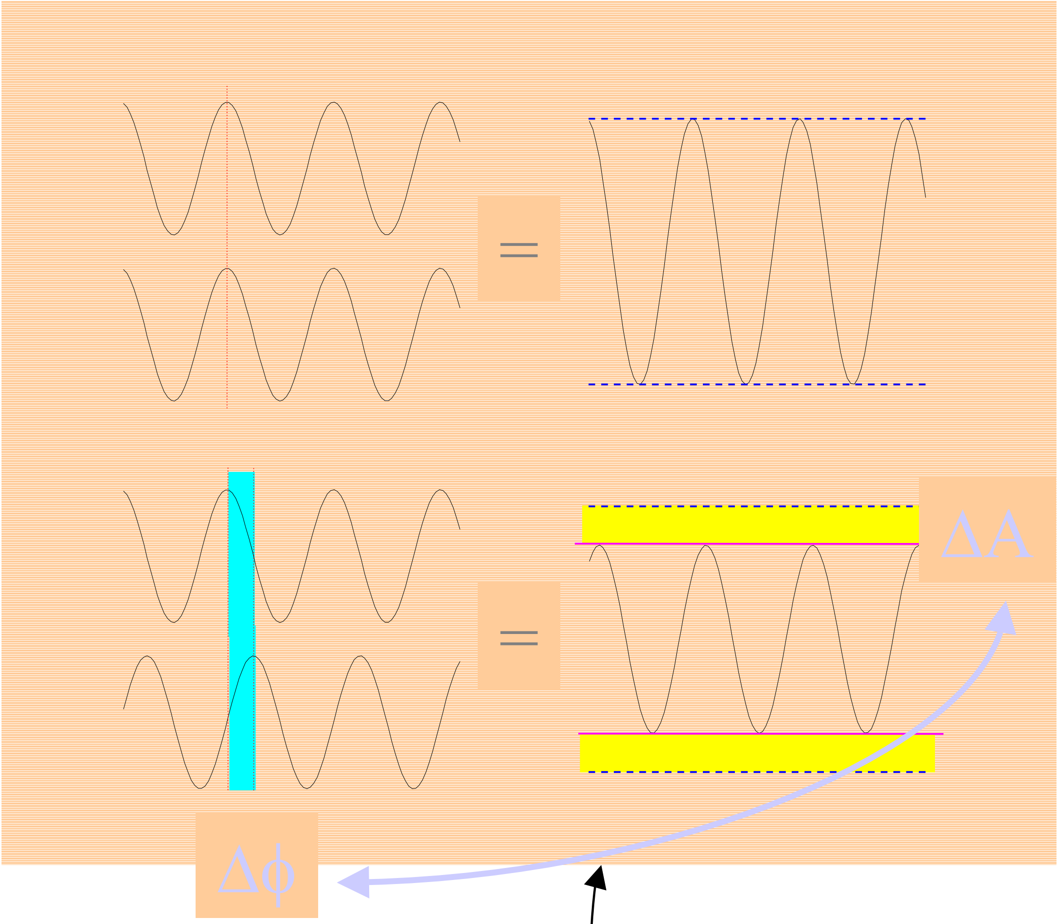
Of course, the phase definition related to a reference e.g. a second component of the same beam

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 components is changed (e.g.: by changing the optical path, moving a mirror or introducing a different medium) the amplitude, and then the intensity of the outcoming wave is correspondingly changed.

Interferogram

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\Downarrow$$

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

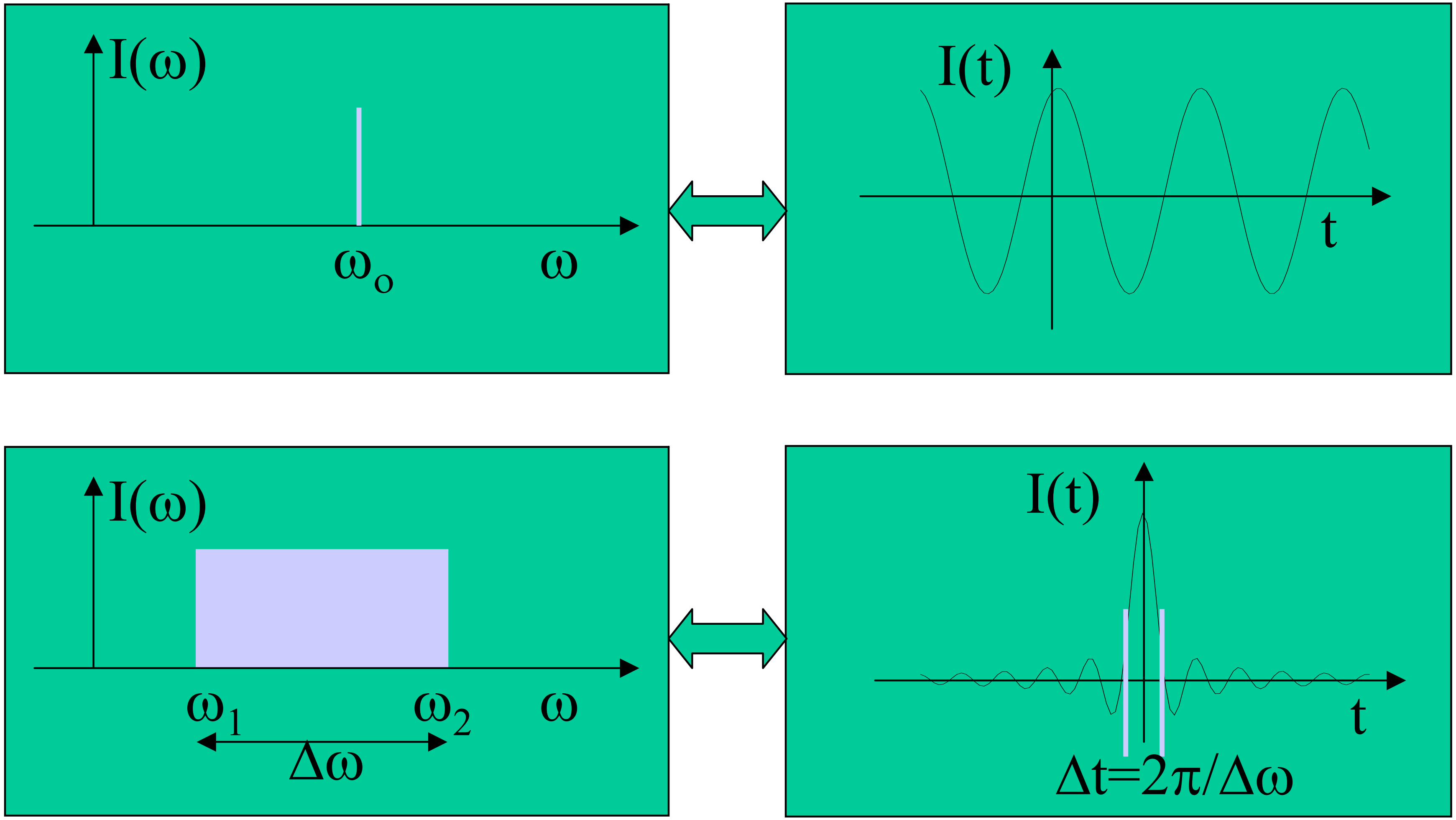
$$= \int_{-\infty}^{+\infty} E_k^2 (2 + 2\cos(\Delta\varphi - \frac{v}{c}\omega \cdot t)) d\omega$$

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.

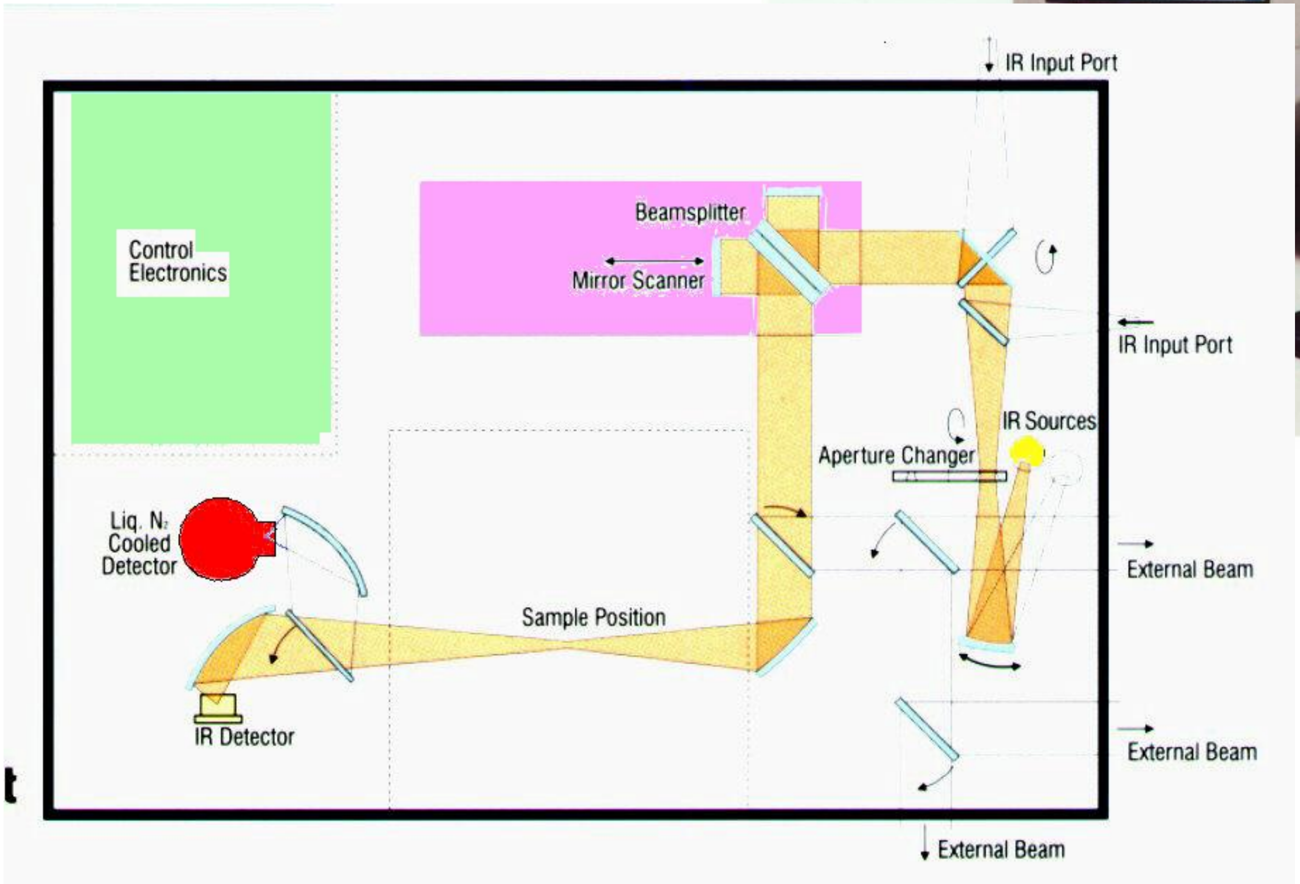
Interferogram

- 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



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.

Vantaggi dell’FT

- ☐ Eccellente rapporto segnale/Rumore
- ☐ Intervallo spettrale completo
- ☐ Alta risoluzione
- ☐ Elevata accuratezza nelle lunghezze d’onda
- ☐ Precisione fotometrica
- ☐ Velocità

MEDIO INFRAROSSO	VICINO INFRAROSSO	RAMAN
Economico	Costoso	Molto costoso
Materiali ottici speciali	Quarzo/Zaffiro	Quarzo/zaffiro
Trasmissione/Riflessione	Trasmissione/Riflessione	Scattering
Cammino ottico 5-50 μ	Cammino ottico 1-10 mm	N/A
Spettri interpretabili	Spettri non interpretabili	Spettri interpretabili
Bassa capacità di lavoro a distanza (< 5 metri)	Eccellente capacità di lavoro a distanza (> 200 metri)	Buona capacità di lavoro a distanza (fino a 30 metri)
Alta sensibilità	Media sensibilità	Bassa sensibilità
Adatto per campioni neri	inadatto per campioni neri	inadatto per campioni neri
Adatto per campioni disomogenei	Adatto per campioni disomogenei	Inadatto per campioni disomogenei
Ottimo per campioni gassosi	Buono per campioni gassosi	Limitato per campioni gassosi
Buono per campioni inorganici	Inadatto per campioni inorganici	Ottimo per campioni inorganici
Identificazione tarmite ricerca in libreria	Identificazione con tecniche chemiometriche	Identificazione tramite ricerca in libreria

Interferogram and resolution

Problem: 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)?

Answer: 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.

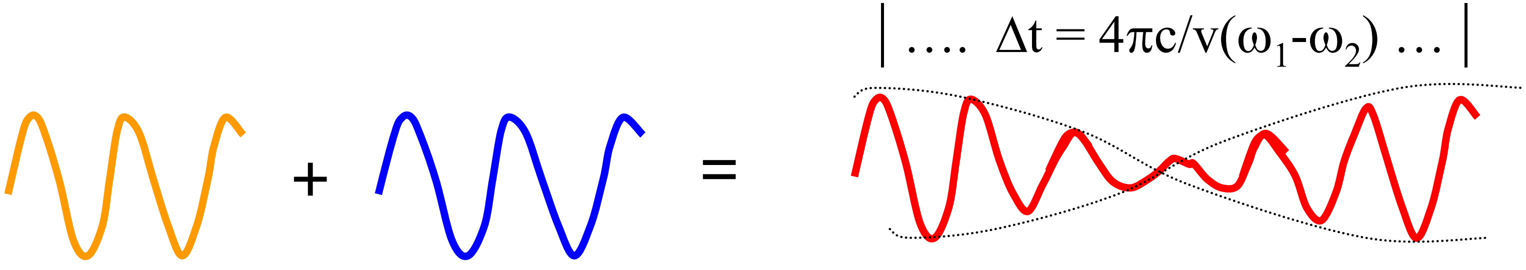
Resolution depends on the length of the interferogram

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 ω_1- ω_2.



Resolution and Apodization

The truncation of the interferogram at the limits –τ and +τ 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 –τ and +τ. 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.

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)

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)

$$F(\nu_k) = \frac{2}{\pi}\sum_{n=0}^{N} A(t_n)e^{2\pi i \nu_k \cdot t_n}$$

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

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

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

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