The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

2328-10

Preparatory School to the Winter College on Optics and the Winter College on Optics: Advances in Nano-Optics and Plasmonics

6 - 17 February, 2012

Spectra of Molecules - Vibrational nanospectroscopy for biomolecules and nanomaterials

Z. BenLakhdar
Universite de Tunis
Tunis
Tunisia

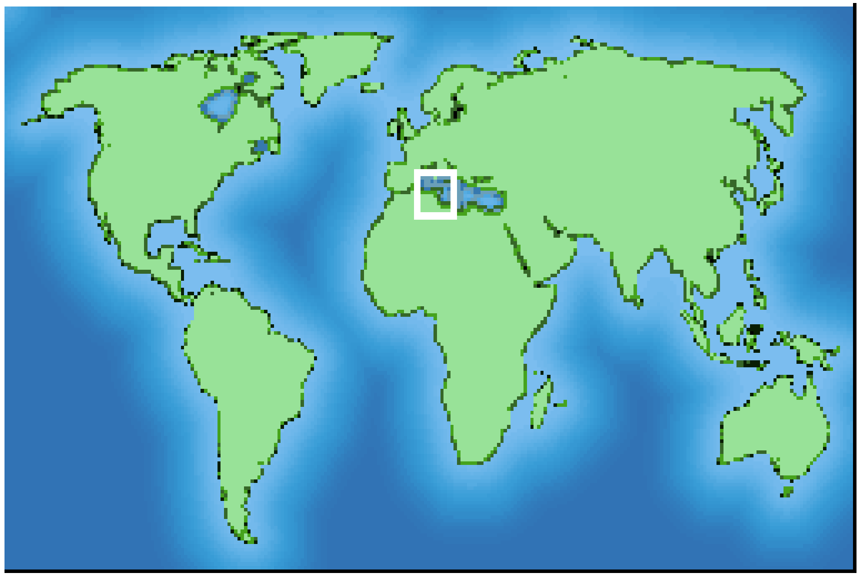
كلية العلوم بتونس
FACULTE DES SCIENCES DE TUNIS

الجمعية التونسية للبصريات
Société Tunisienne d'Optique

Winter College on Optics
Advances in Nano-Optics and Plasmonics
ICTP-Trieste-Italy 6-17 February 2012

Raman & Fluorescence Spectroscopy coupled with scanning tunnelling microscopy

Zohra Ben Lakhdar
Dep. of Physics-Faculty of Sciences-Tunis-Tunisia



I come from Tunisia, from a revolution ,
A new kind of revolution- It is conducted by new technology!
Using radiation as messenger!
as atoms & molecules

Through radiation, they communicate their state of energy, describe their situation, their environment,….

Topics

-Atoms and molecules behaviour

-Scales for molecules studies

-Example of Molecular structure and dynamics-
    Spectroscopy of Atoms and molecules
    Energy states-spectra-
    environment and spectra
    Structures & symetry

-Nanoplasmonics

-STM and Raman & fluorescence spectroscopy

Atoms and Molecules behavior

Atoms and molecules as human
sometimes like or attract each other sometimes don't?
This love and hate dynamic in atoms , molecules society

→ Why substances in different shapes and phases
→ How substances transform to other substances.
→ Atoms and Molecules behavior?

&

We have to understand their language, their spectra
To analyse radiation-interaction, collisions,..
&
To access to this Behavior, to this Functioning
How??

“If you want to understand function, study structure”
(Francis Crick)

Function??

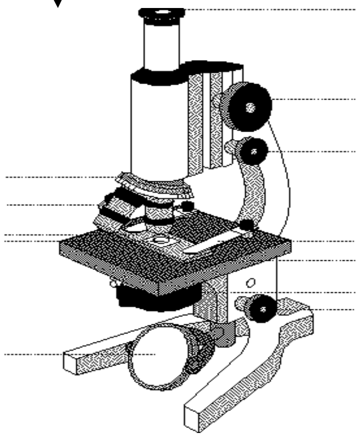
Function= sequence of events over time, characterized by structural modifications

“If you want to understand function,
study time-dependent structures”

How??

Observation structure

↓



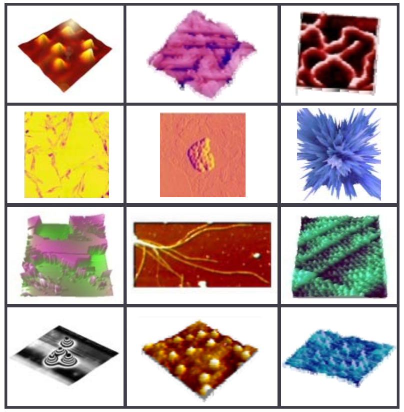
Microscope

XVIIéme. C

to studying the living cells

↓

Molecular biology and genetics



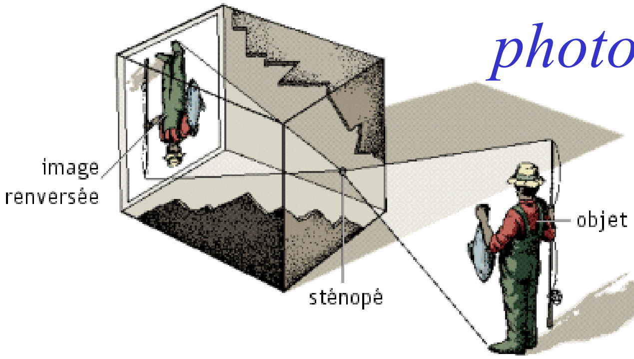
Telescope

Begining of XVIIème.C

Telescope approaches the very far

Registration events Functionning

photography

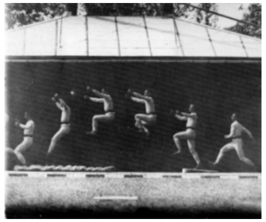


Camera obscura

Xeme.C

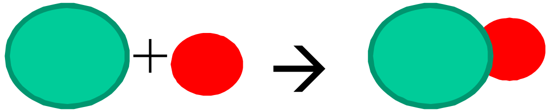
Registration of ephemeral phenomena

Chronophotography



E.J.Marey (1886)
(~7 positions /photo)

How Chronophotography molecule-reation??



There is a need to bring the world of atoms and molecules

- very close for observation

but also

- to freeze them in time so we can take snapshots in chemical reactions ,

atoms move along ~ fewÅ–

Spatial resolution needed~ 0,1Å

atoms move at $\sim 10^{6}$m/s

(0,1Å)/ (10^{6}m/s) = 10^{-14} s=10 fs

Time resolution needed ~ 1fs

Scale for molecules studies

Spatial

nanoscale

Time

femtoscale

Nanoplasmonics at atomic scale

Raman & Fluorescence Spectroscopy coupled with Scanning Tunnelling Microscopy

Increasing Importance of Molecular Physics

Dev. of New Experimental Technology

increase in

-Sensitivity

-Spectral resolution(space, times cale)

Measurement of structure of molecules & dynamics even for large molecules

Studies of chemical reactions and biological process on molecular level---→ **New Technolgies**

Dev. of Fast Computer & Sophisticated Software

- structure

-Dynamics +

-Kinetic of reaction , ….

with

-Visualization on computer in slow mov.

⇄ **Understanding**

Molecular structure and Dynamics spectroscopy

Spectroscopy

Spectroscopy: analysis of various types of e.m radiation (abs. or em. by the atom or molecule → understanding of the system

The spectroscopic information can be in various kind of the energy analysis-

The choice of spectroscopic method is primarily determined by **the energy range** of the phenomenon to be studied

Radio & microwaves	**IR**	**Visible - UV**	**X rays**
Molecular rotations Hyperfine structure Isotopic shifts	Molec.Vibrations Fine structure	outer electron transition	inner electron transition
MHz, cm^{-1}	µm, cm^{-1}	nm, Å	keV

Spectroscopic phenomena and Energy scales

Energy $\Delta E = h\nu = (h/2\pi)\omega = hc/\lambda$

Wavelength $\lambda = c/\nu$

Wavenumber $1/\lambda = \nu/c$

Frequency $\nu = c/\lambda$

1eV $\longleftrightarrow$ 8000cm^{-1} $\longleftrightarrow$ 12000Å)

Atoms

Nucleus (neutrons+protons), electrons; Mn/Me~ 2000
size of the atom~10^5 size of the nucleus

Electron Distribution on orbitals (s, p, d,.. …) filled by
a maximum of (2, 6, 10,..) electrons

- ^{1}H ^{2}He
- ^{3}Li ^{4}Be ^{5}B ^{6}C ^{7}N ^{8}O ^{9}F ^{10}Ne
- ^{11}Na ^{12}Mg ^{13}Al ^{14}Si ^{15}P ^{16}S ^{17}Cl ^{18}Ar

^{19}K ^{20}Ca ^{21}Sc ^{22}Ti ^{23}V ^{24}Cr ^{25}Mn ^{26}Fe ^{27}Co ^{28}Ni ^{29}Cu ^{30}Zn ^{31}Ga ^{32}Ge ^{33}As ^{34}Se ^{35}Br ^{6}Kr

- ^{37}Rb ^{38}Sr ^{39}Y ^{40}Zr ^{41}Nb ^{42}Mo ^{43}Tc ^{44}Ru ^{45}Rh ^{46}Pd ^{47}Ag ^{48}Cd ^{49}In ^{50}Sn ^{51}Sb ^{52}Te ^{53}I ^{54}Xe
- ^{55}Cs ^{56}Ba * ^{72}Hf ^{73}Ta ^{74}W ^{75}Re ^{76}Os ^{77}Ir ^{78}Pt ^{79}Au ^{80}Hg ^{81}Tl ^{82}Pb ^{83}Bi ^{84}Po ^{85}At ^{86}Rn
- ^{87}Fr ^{88}Ra +
- Lanthanides ^{57}La ^{58}Ce ^{59}Pr ^{60}Nd ^{61}Pm ^{62}Sm ^{63}Eu ^{64}Gd ^{65}Tb ^{66}Dy ^{67}Ho ^{68}Er ^{69}Tm ^{70}Yb ^{71}Lu
- $^{+}$Actinides ^{89}Ac ^{90}Th ^{91}Pa ^{92}U ^{93}Np ^{94}Pu ^{95}Am ^{96}Cm ^{97}Bk ^{98}Cf ^{99}Es
-

Structure of Atoms

Cu I Ground State $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s$

Ag I Ground State $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s$

Au I Ground State $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s$

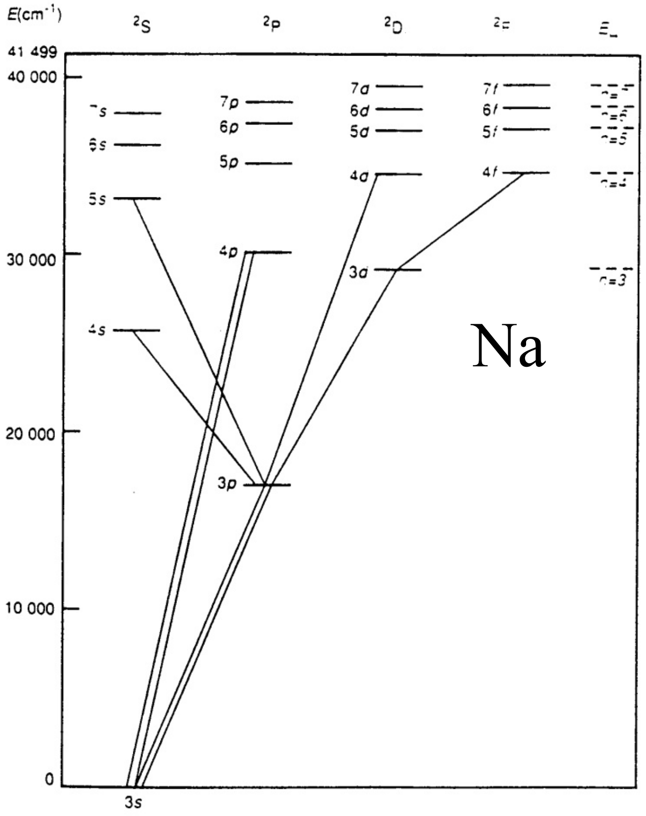
Ex: in plasmonics , Metal atom Cu, Ag, Au as alcalin

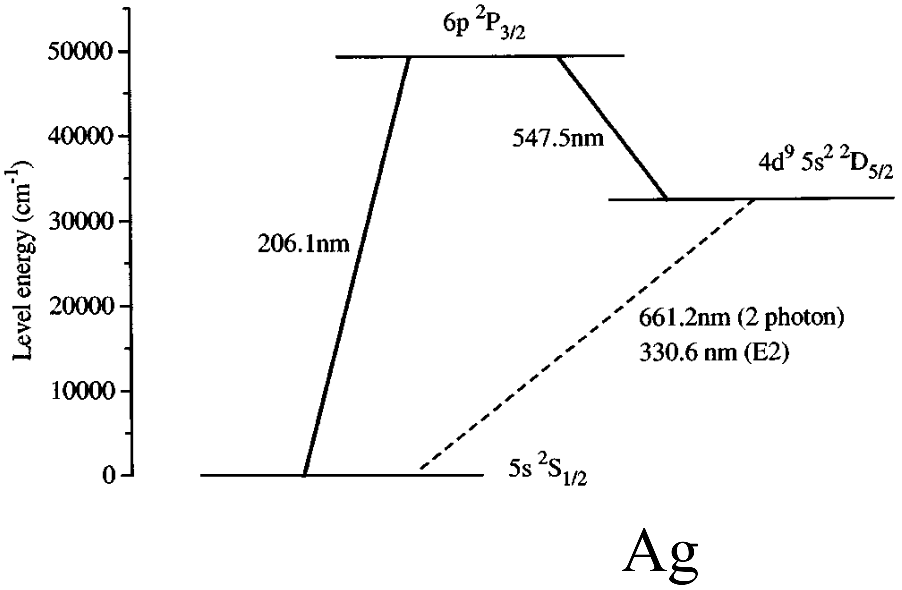
•	Isotope	Mass	Abundance	Spin	Magn Moment	Ionization energy
•	$_{29}$Cu	63	69,1%	3/2	2,22	7,72638 **eV**
		65	30,1	3/2	2,38	
•	$_{47}$Ag	106.905092	51.84%	1/2	-0.1135	7.57623 eV
		108.904757	48.16%	1/2	-0.1305	
•	$_{79}$ Au	196.966543	100%	3/2	0,14	9.22553 eV

Atomic energy states

Different energy levels- Each energy state has a precise dynamic due to orbital moment **L**, spin **S** and **L,S** Interaction

Interaction with an electric field will be with the outer electrons first





Molecule

A molecule is formed by the binding of 2 or more atoms in such a way that the total energy is lower than the sum of the energies of the constituants. The bonds are normally of ionic or covalent nature. Particularly weak bonds occur in van der Waals molecules

Classically light is emitted by a system only if **its electric dipole moment is changed**-This rule valid classically for atoms is also valid by QM and is also valid for molecule

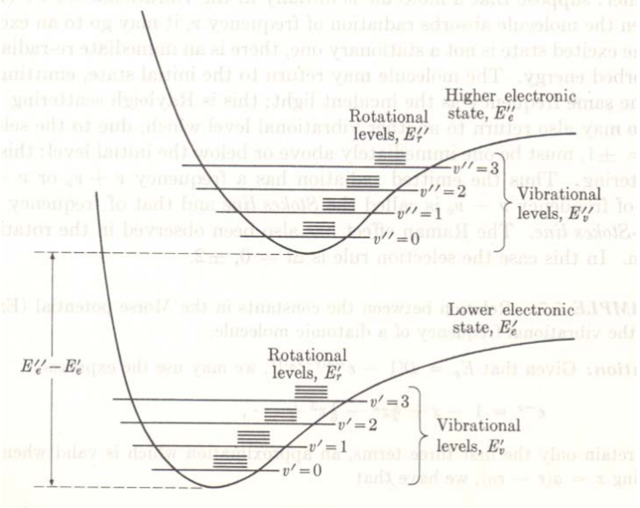
The dynamic of a molecule is connected to movement of electrons and nucleus with E_e, E_v,E_r ,

Molecular energy states

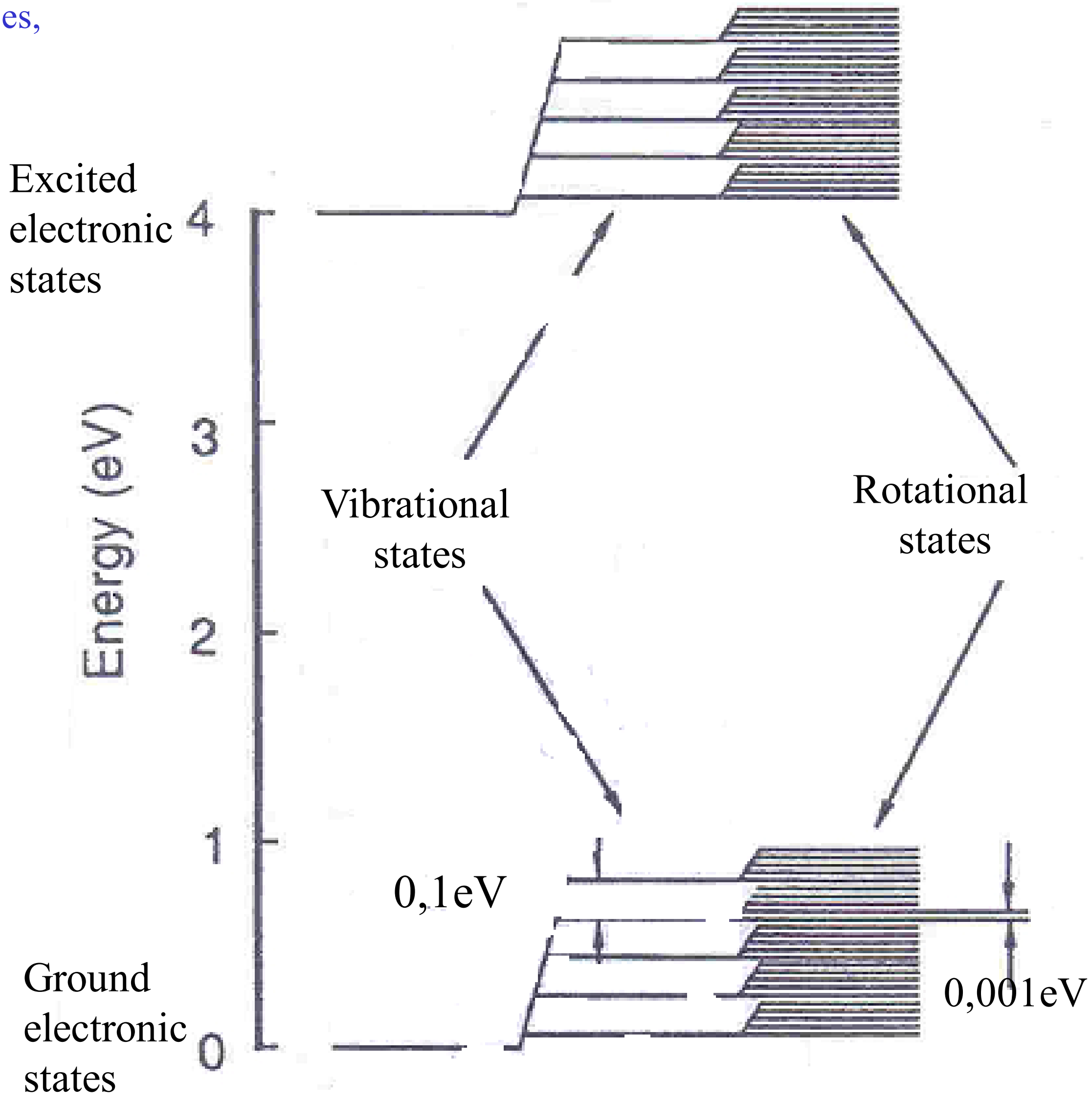
In all chemical, biological and physical processes,

primary events: Electronic structure change

geometric structural changes,
i.e.
nuclear motion



**Diatomic molecule
Energy States**



Excited electronic states

Vibrational states

Rotational states

0,1eV

0,001eV

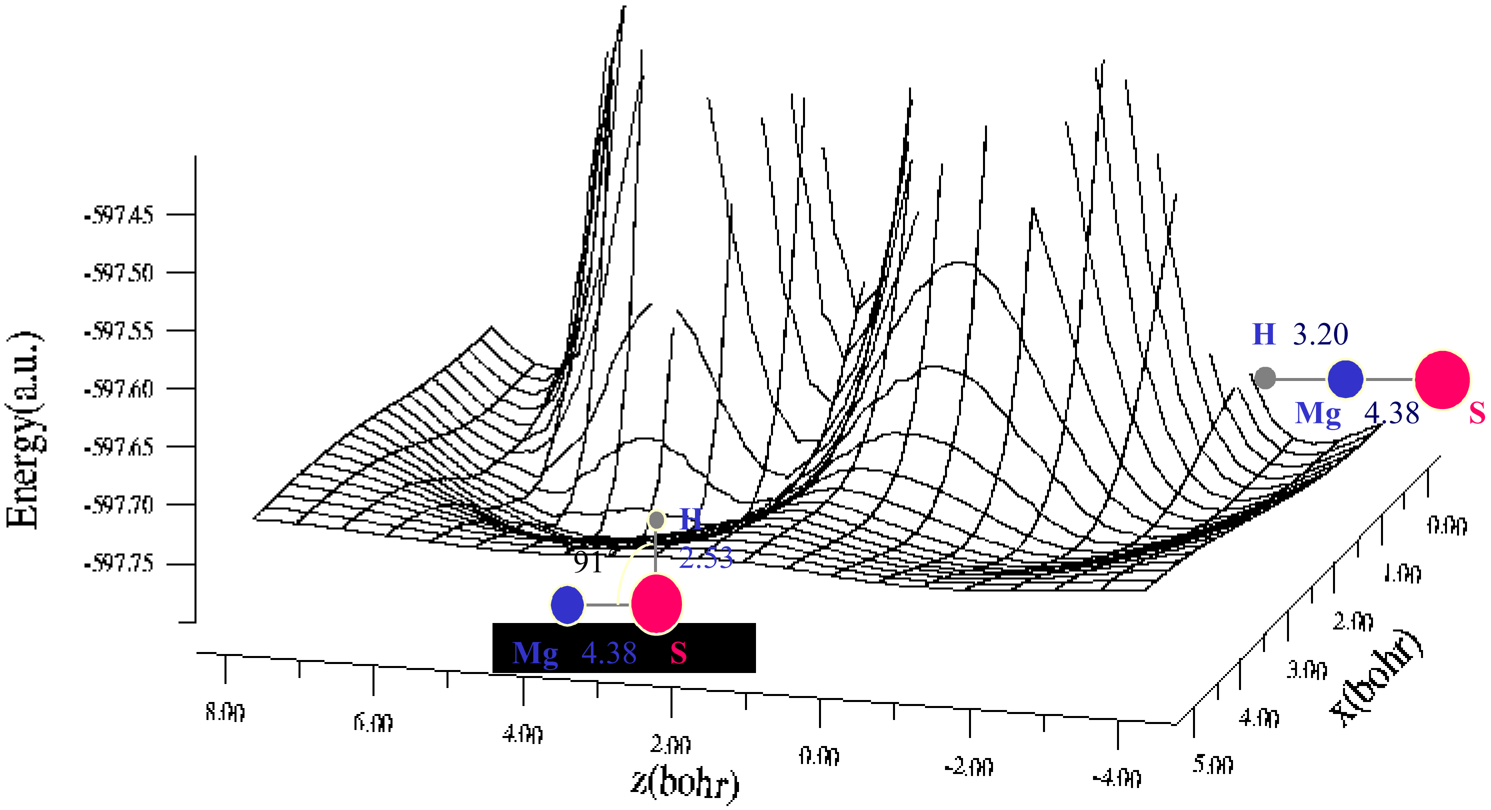
Ground electronic states

with $E_e >> E_v >> E_r$

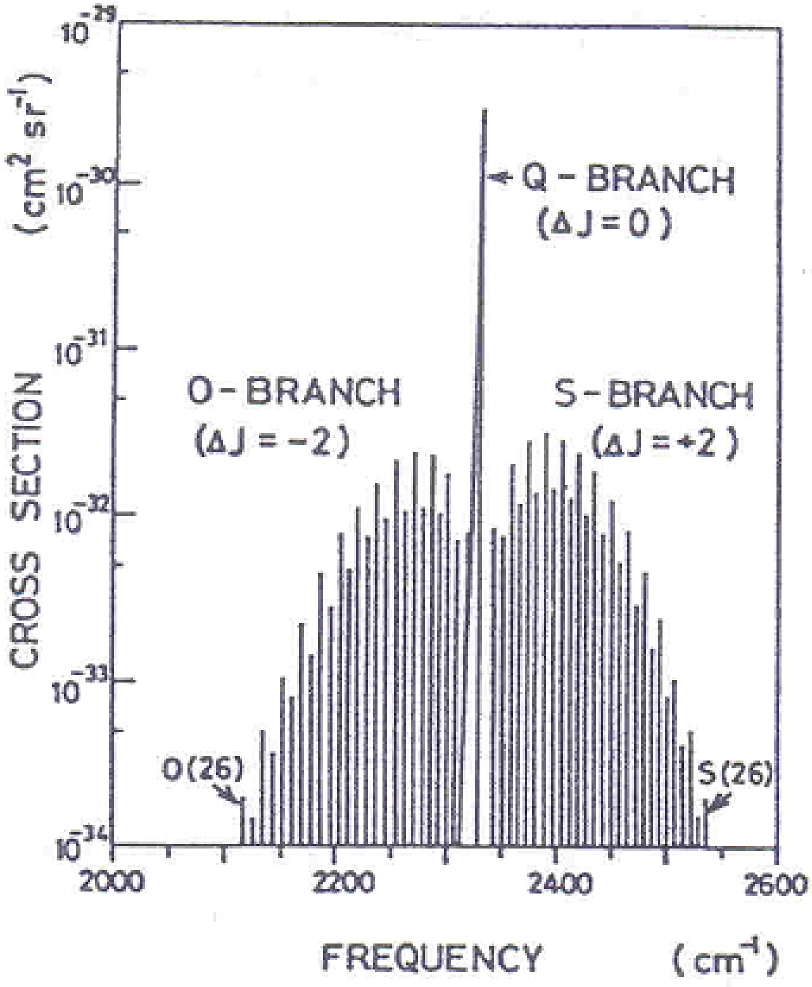
Example of Energy State for 3 atomic- molecule

Surface for X ^{2}A' State

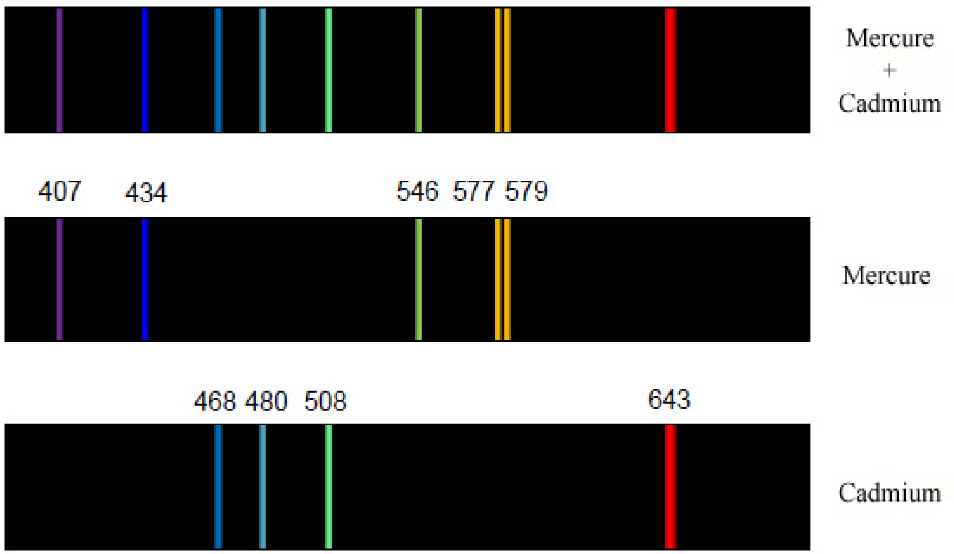
molecule MgSH



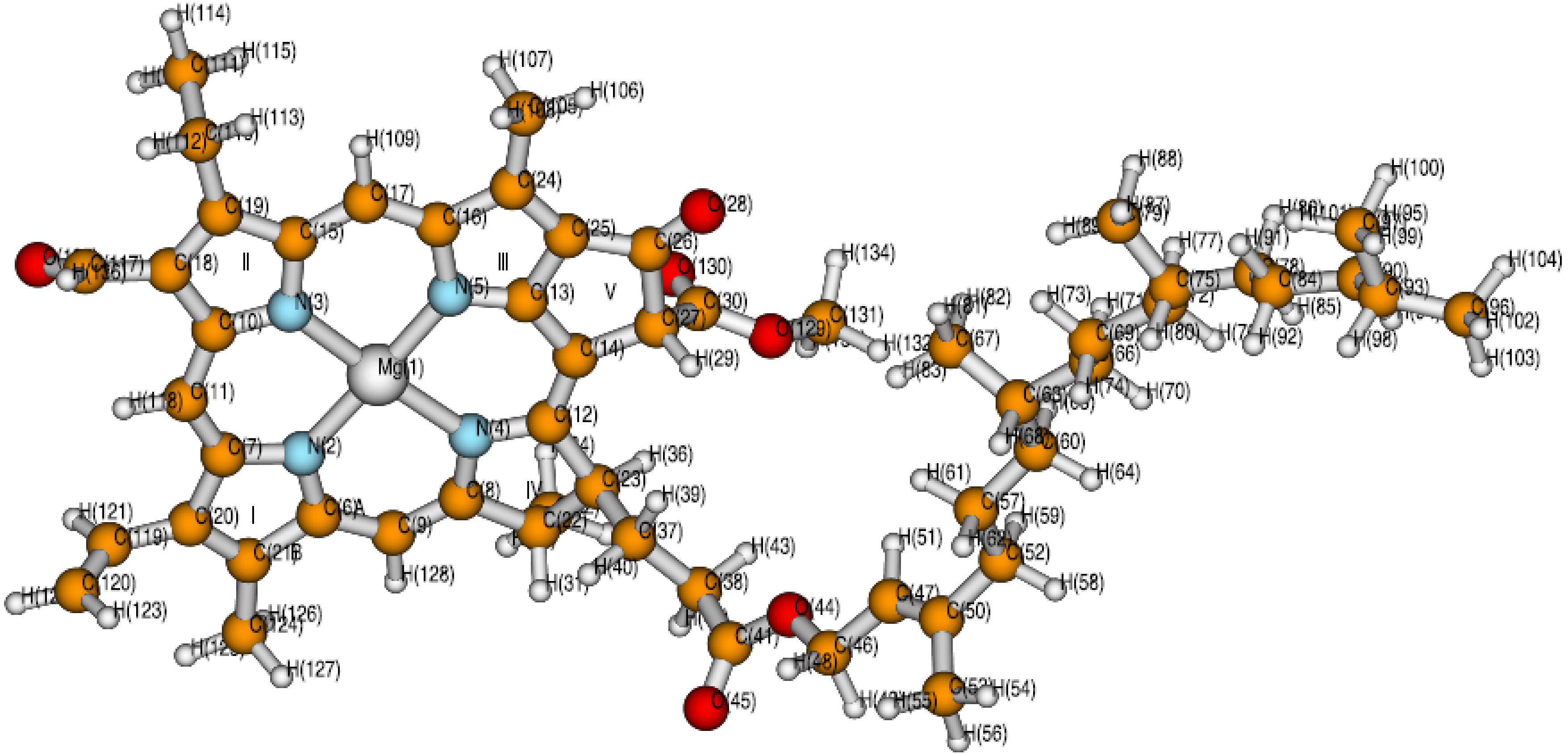
Ex of molecular & atomic Spectra



Vibrational-rotational raman spectrum of N2



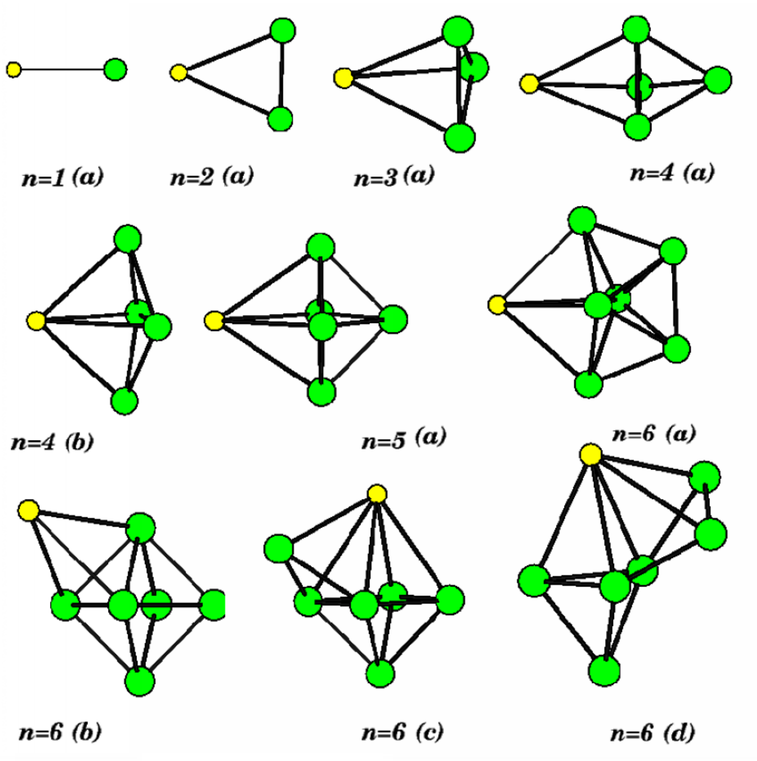
Structure

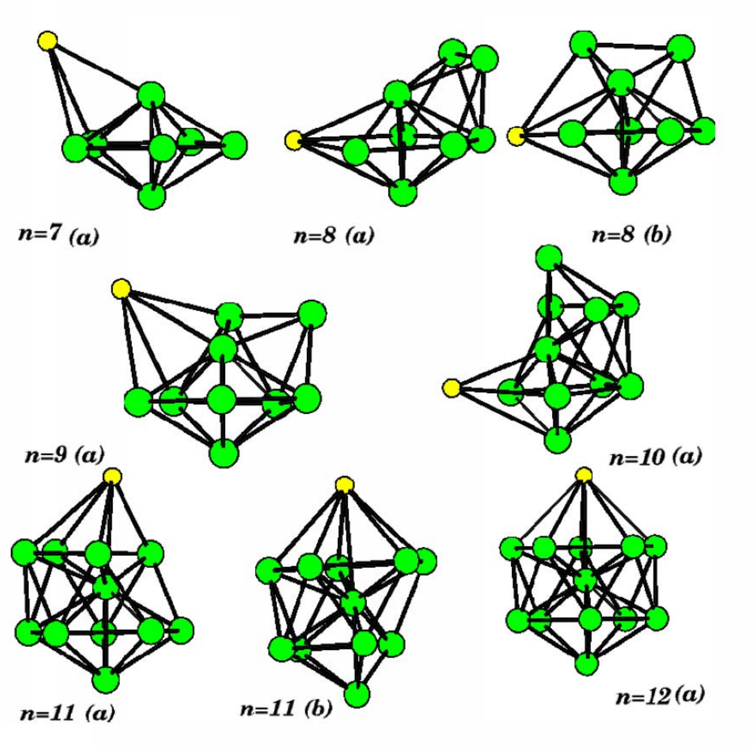


chlorophyll

Journal of Molecular Structure: THEOCHEM 726 (2005) 245–251

Isomers' Structures of $NaAr_n$ Agregates

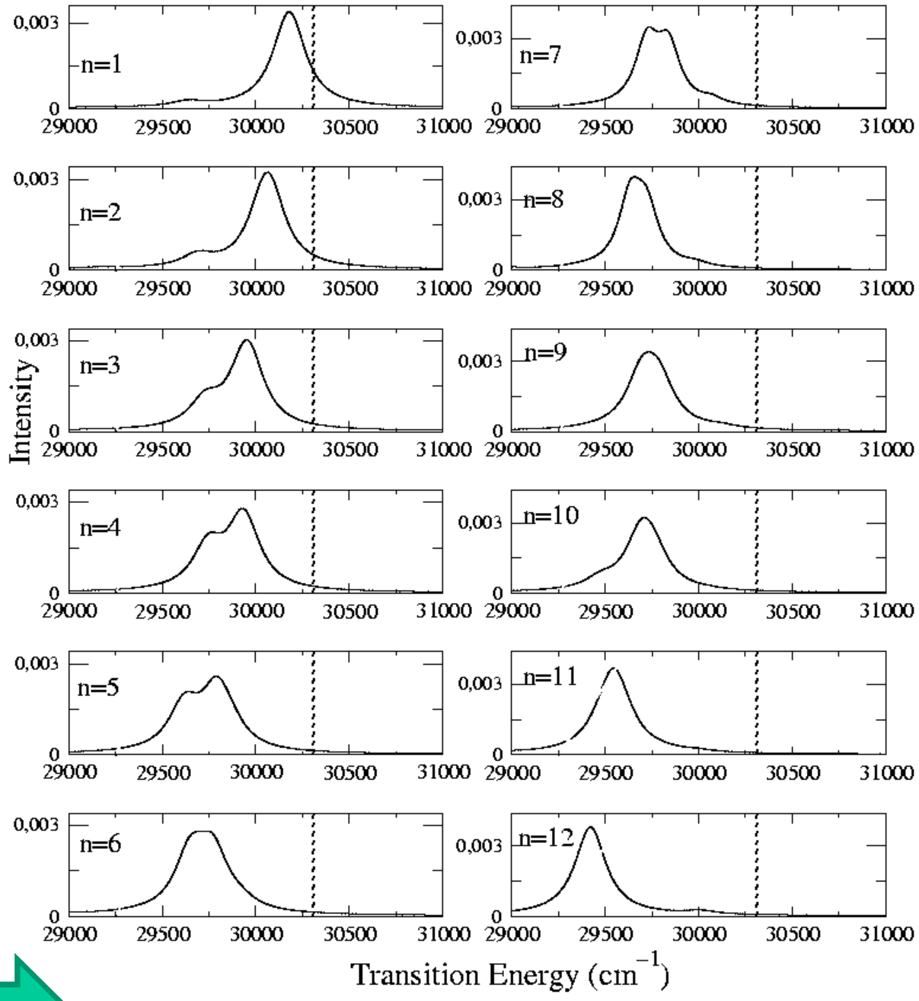


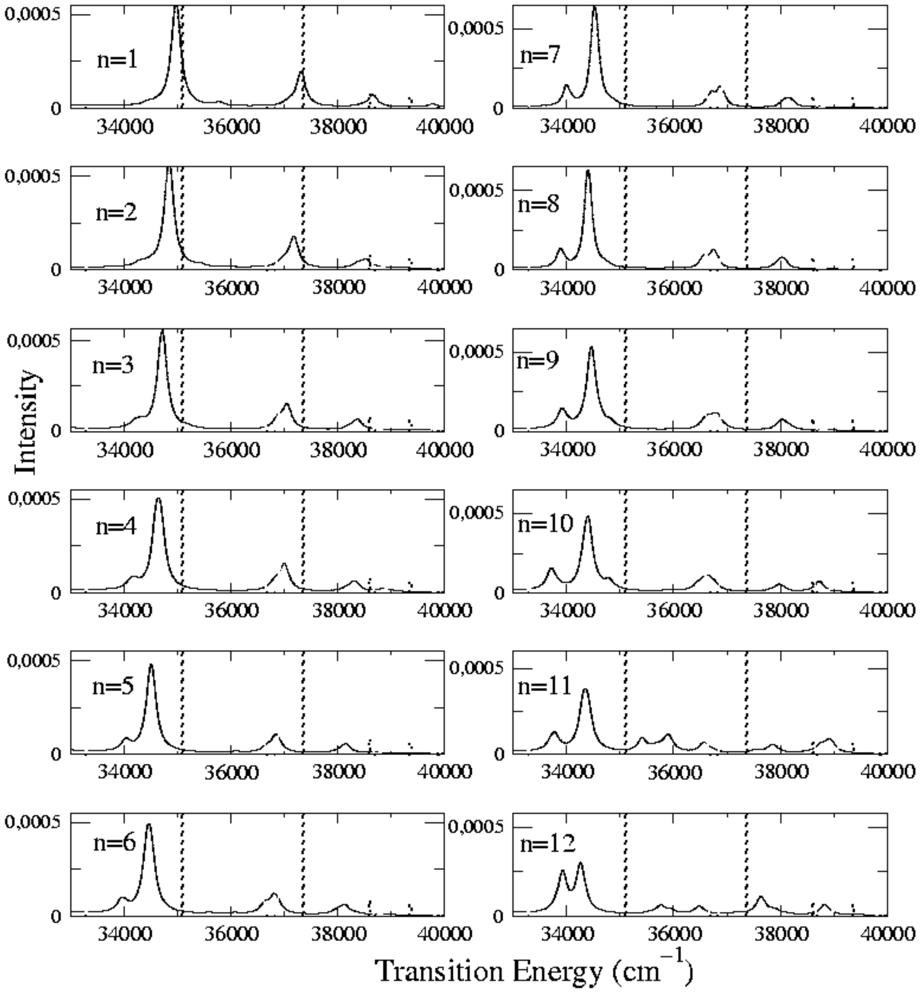


Na on the surface of the Ar aggregate

$$E_{NaAr} = 40\ cm^{-1} < E_{Ar-Ar} = 100\ cm^{-1}$$

Transition Spectra to 4p et 5p of $NaAr_n$

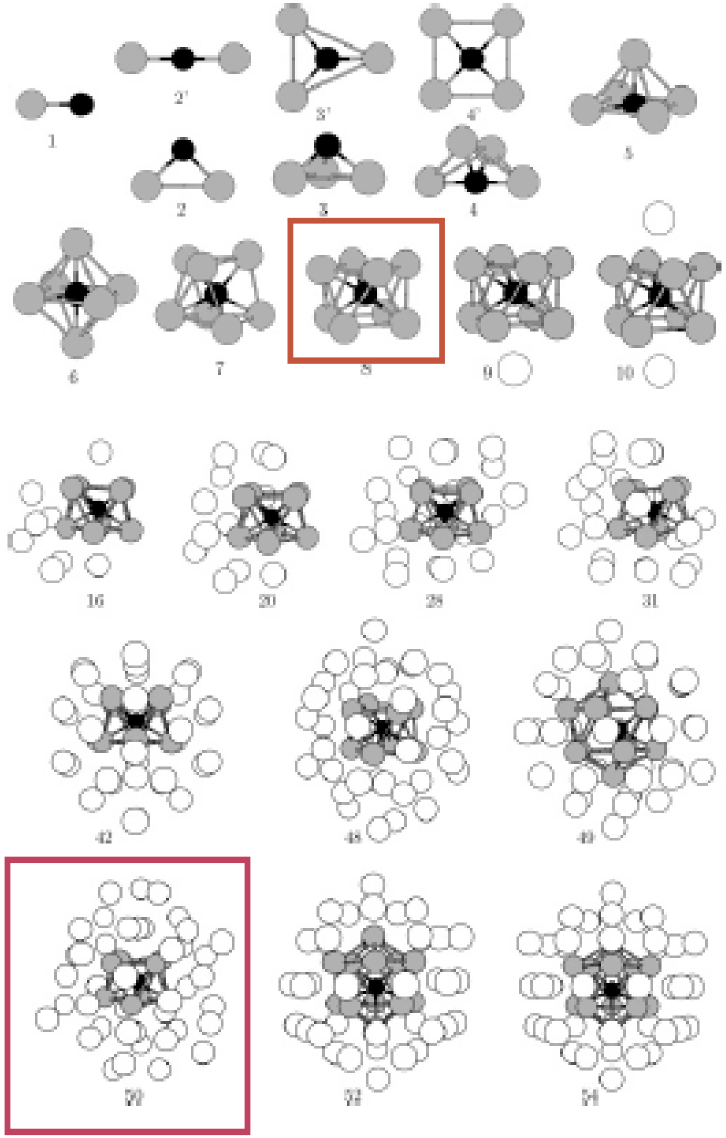


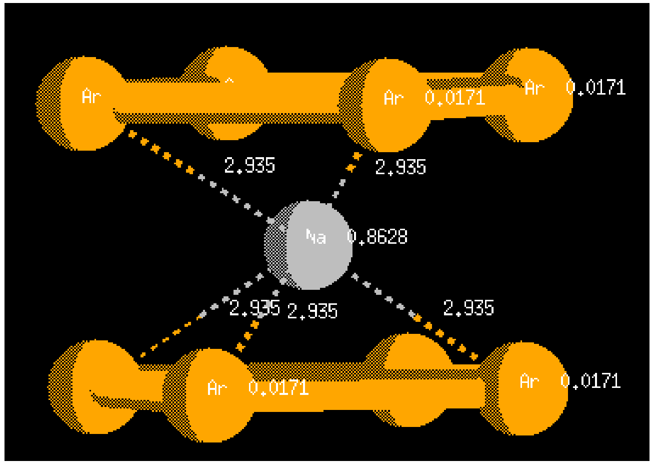


transitions to excited states 4p et 5p depend on the structure of agregates

agregate Na^+Ar_n

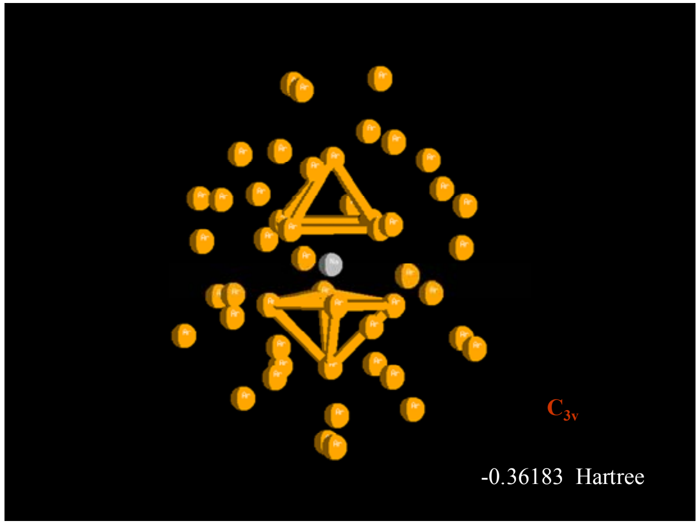
confinement change and symetry group change for increasing n in the from n=8 (first confinement) to the second confinement (n=50)





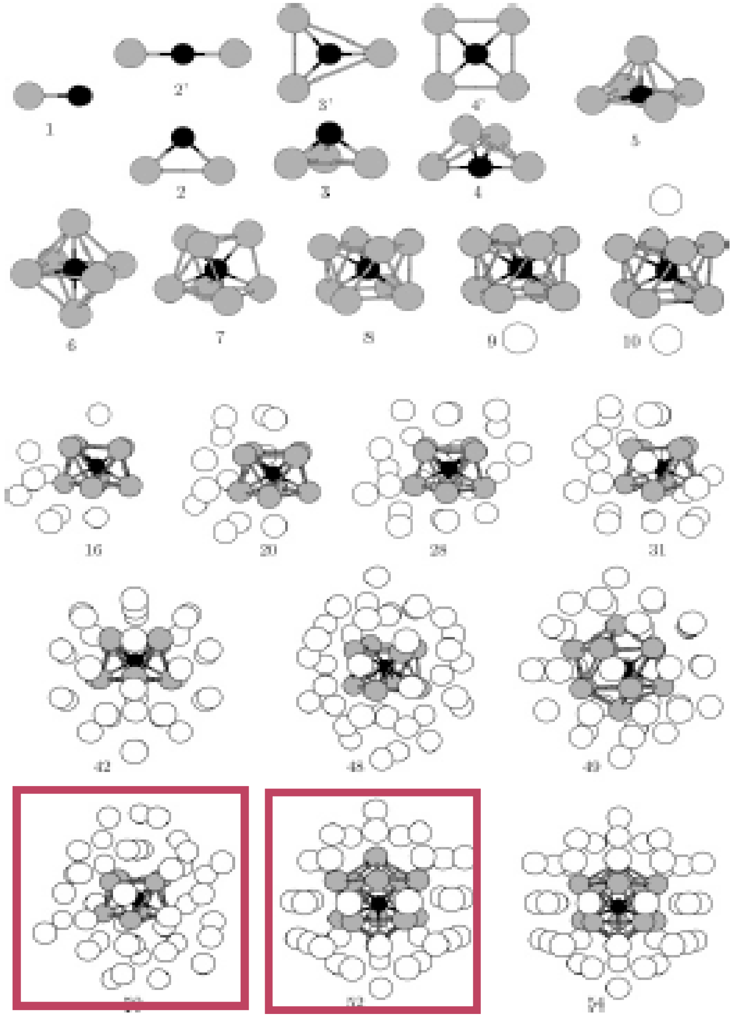
D_{4d}

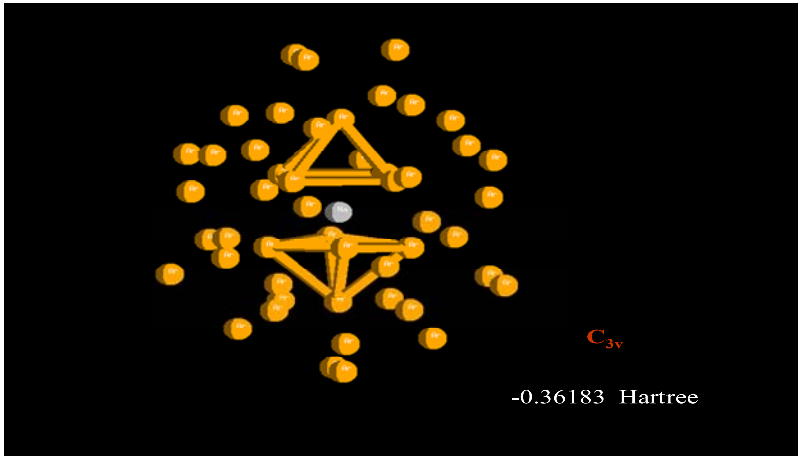
n=8

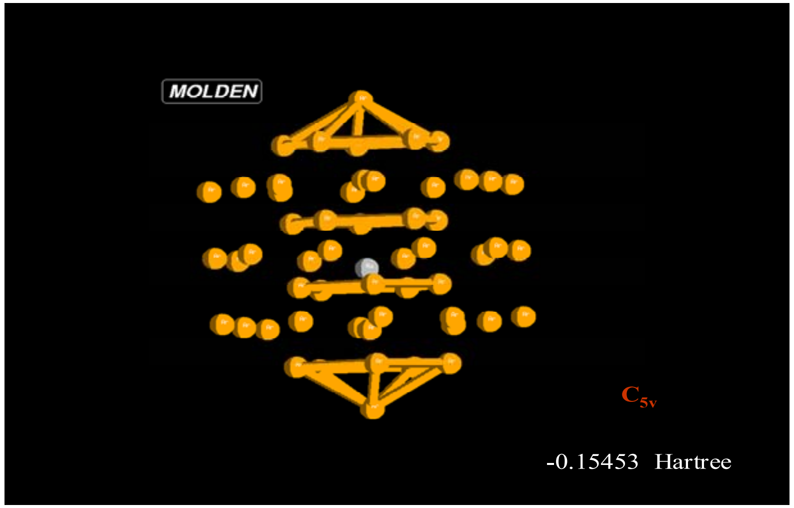


C_{3V}

PhaseTransition from square antiprism to new confinment (icosaedric) for n=51 .

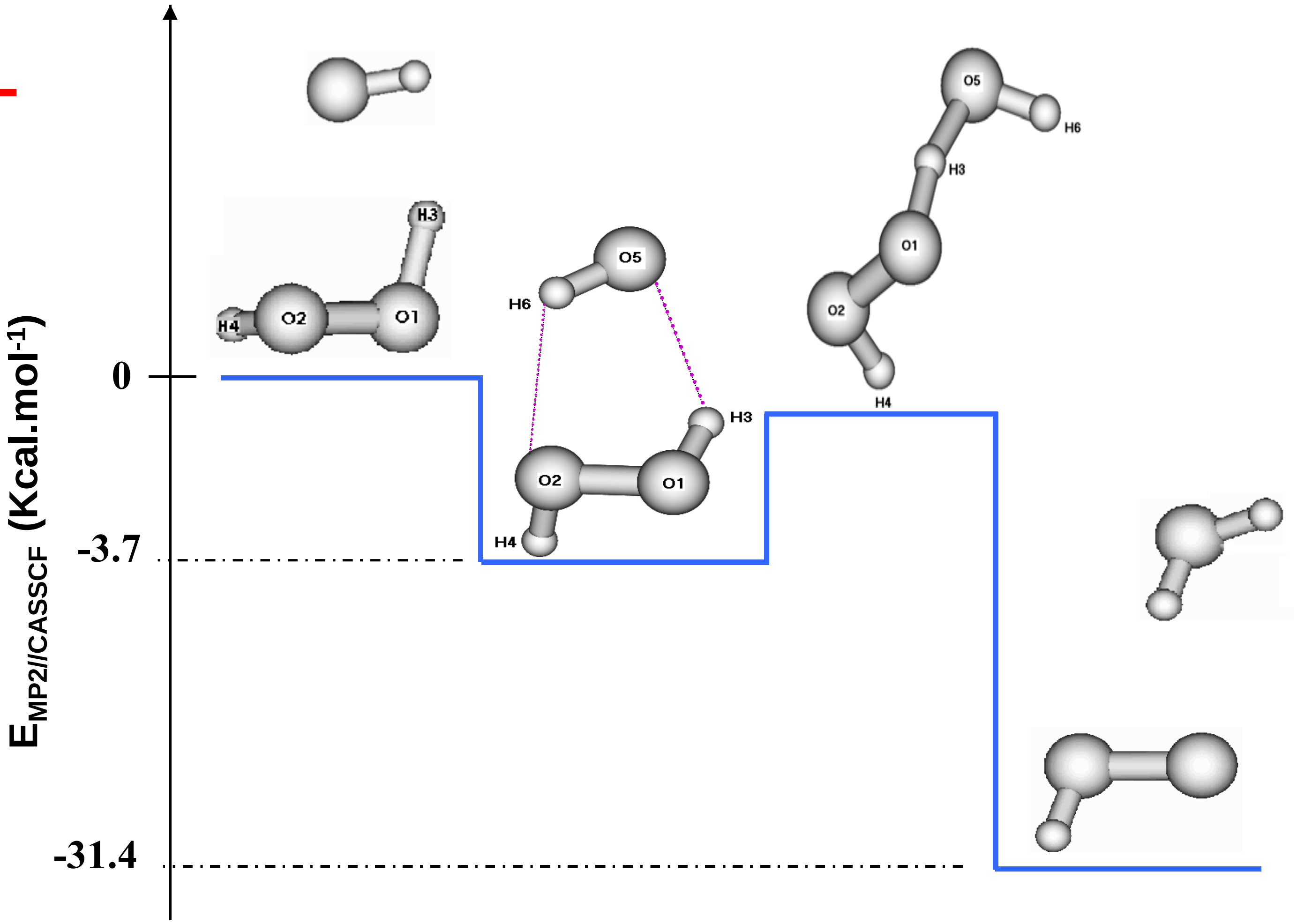






When the number of Ar atoms increases, Ar-Ar interactions lead to stable structures (poly-icosaedric), energy decreases

Reaction



Direct Reaction

OH + H_2O_2

$HO_2 + H_2O$

Independant of Température

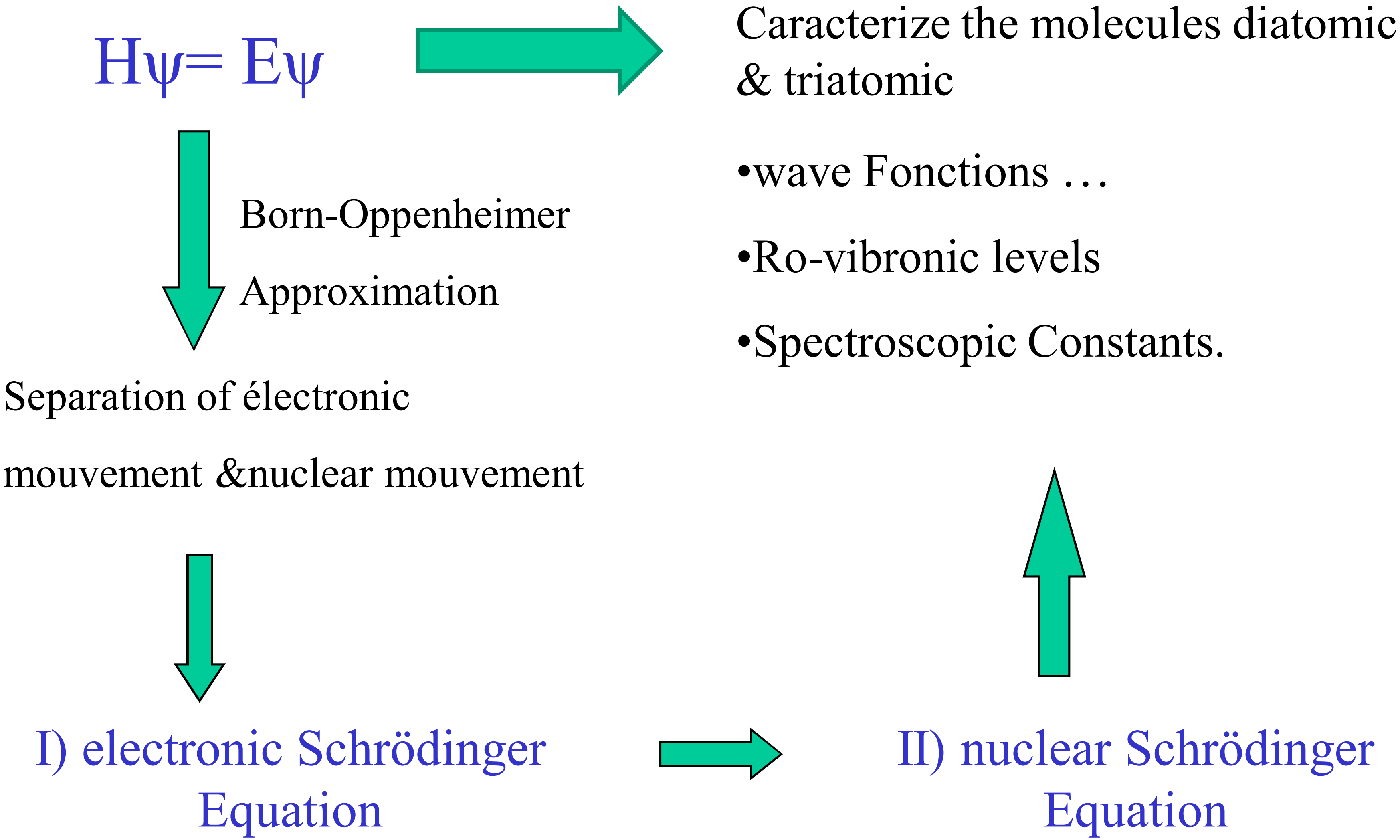
réorientation

OH-H_2O_2

H_3O_3

Journal of Molecular Structure: THEOCHEM 770 (2006) 149–156

Process for analysis: potential calculation



$H\psi = E\psi$

Caracterize the molecules diatomic & triatomic

- wave Fonctions …
- Ro-vibronic levels
- Spectroscopic Constants.

Born-Oppenheimer

Approximation

Separation of électronic

mouvement &nuclear mouvement

I) electronic Schrödinger Equation

II) nuclear Schrödinger Equation

Résolution de l’équation de Schrödinger électronique par des méthodes de calcul ab-initio

$$\hat{H}_{el}\Psi_{el,n}(\vec{r},\vec{R}) = E_{nn}(\vec{R})\Psi_{el,n}(\vec{r},\vec{R})$$

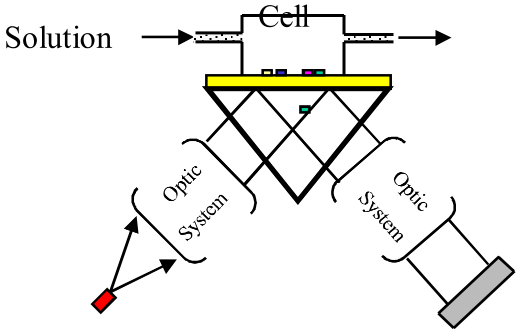
- Method HF-SCF (Hartree-Fock Self Consistent Field)

  Approximation monoelectronic

⇓

- Traitment of electronic correlation
  - Interaction of configuration (IC)
  - Couples Clusters (CC)
  - Multiconfiguration Self Consistent Field (MCSCF)
  - Multireference Configuration Interaction (MRCI)

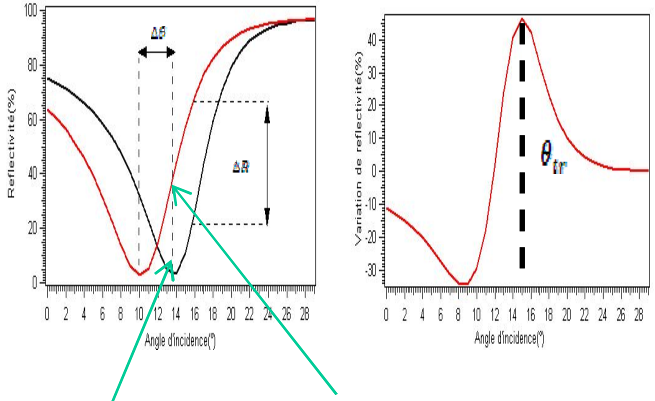
Nanoplasmonics



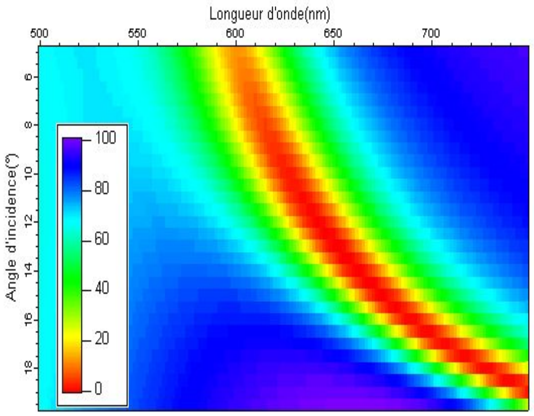
?

A device for preparation and
molecule analysis

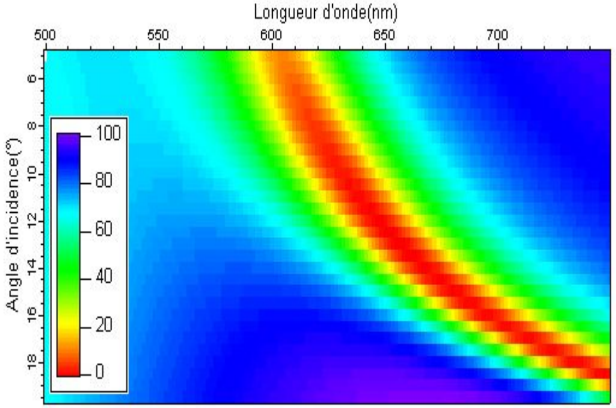
Simulation: of reflectivity & its variation for 3 layers :



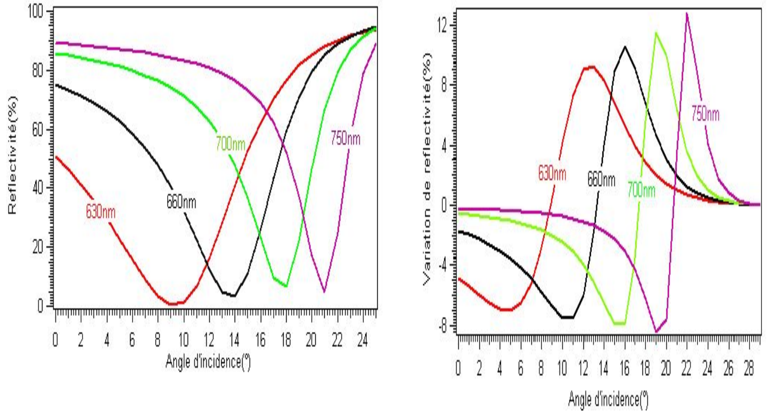
prism BK7; Au(47 nm) water +10 nm diélectric (DNA=1.46)
& water at λ = 660 nm for # angles



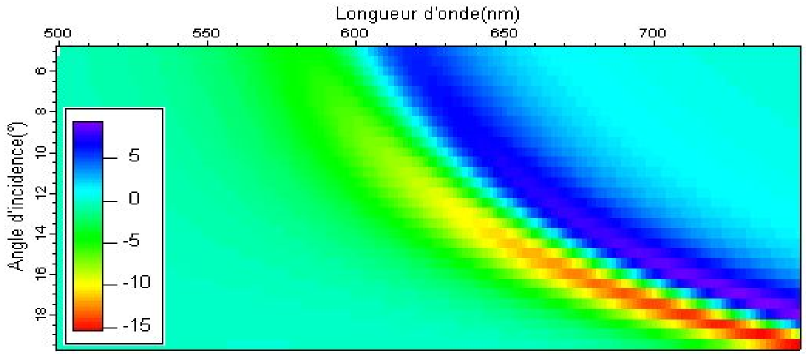
prismBK7+(2nmChr
& 47 nm Au) +water



prismBK7+chip(2nmChr
&47 nm Au)+ DNA (2 nm, n=1.46)
+water



prism BK7; Au(47 nm) water +10 nm diélectric (DNA=1.46)
& water at # λ & for # angles

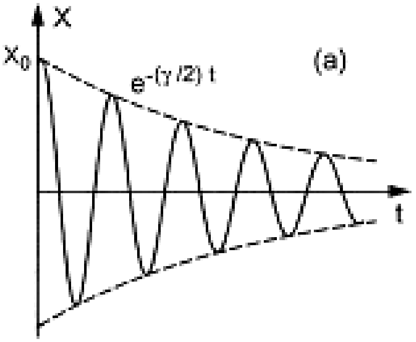


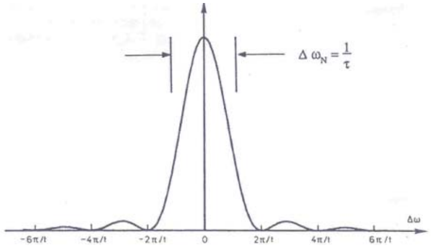
Difference in reflectivitéy for addition of the biological layer DNA (e=2 nm , n=1.46)

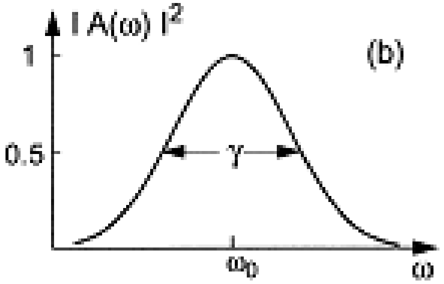
The central problem of nanoplasmonics is

-controlling and monitoring (based on resonance)

- the localization of optical energy in the plasmonic region on the nanometer scale







Damped oscillation τ

-τ =1/2γ , time localization, on the femto-second scale.(ultra fast plasmonics)

(τ calculated is in the range 10-60fsfor silver
1-10fs for gold

various applications, especially :

ultrafast computations, data control & storage on the nanoscale,
fs pulsed light source
biomolecular structures, dynamics, kinetik reactions…medical science, …

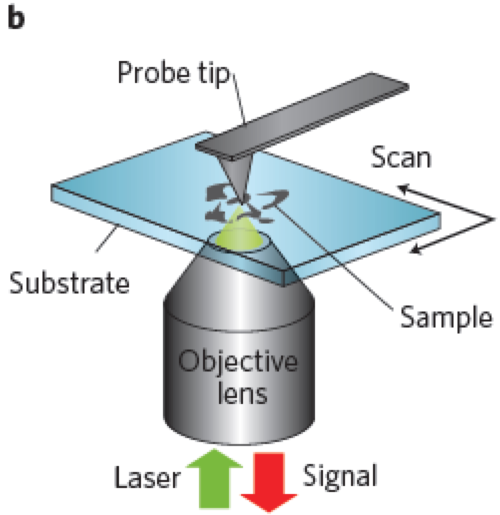
Atoms-Molecules
energy states, spectra, reactions
Plasmonic

STM coupled with spectroscopy

Raman and fluorescence spectroscopy

Sub diffraction limit

- For conventional microscope, the resolution is about half of the observation wavelength, resolution is limited because of the diffraction limit of light (250nm for 500*nm- in the case of VIS)*
- to overcome the diffraction limit



⬇

-(SNOM)+Raman spectr.

spatial resolution defined by the

aperture tip. →spatial resolution ~*50nm*

-(AFM) + Raman spectr. When the light is radiated on tip metal & surface→ large enhancement of Raman scattering with spatial resolution→~15nm

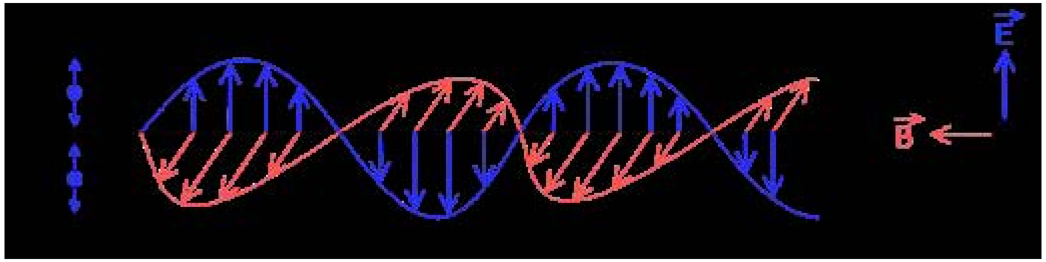
-(STM)+ spectroscpy →Resolution at ultimate atomic scale

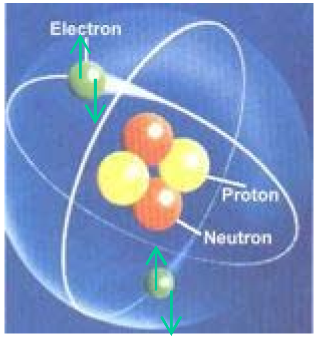
Scattering light by atoms, molecules

The electric field on atom or molecule *leads to oscillations of electrons –

-Atom as microscopic antenna

Scatter





extinction

(light+light)=No light, interference

Rayleigh Scattering

Raman Spectroscopy

Light is ***inelastically scattered*** by molecules and, owing to molecular vibration excitation or de-excitation, light with higher or lower energy is observed.

Raman scattering is emitted together with a vast amount of elastically scattered light , the Rayleigh scattering, which generally makes the measurement of Raman spectra difficult.

With a Raman intensity ~1/1000 intensity of Rayleigh line

Raman spectra are, however, very valuable because we can obtain directly the vibration frequencies of bonds contained in matter by using visible light.

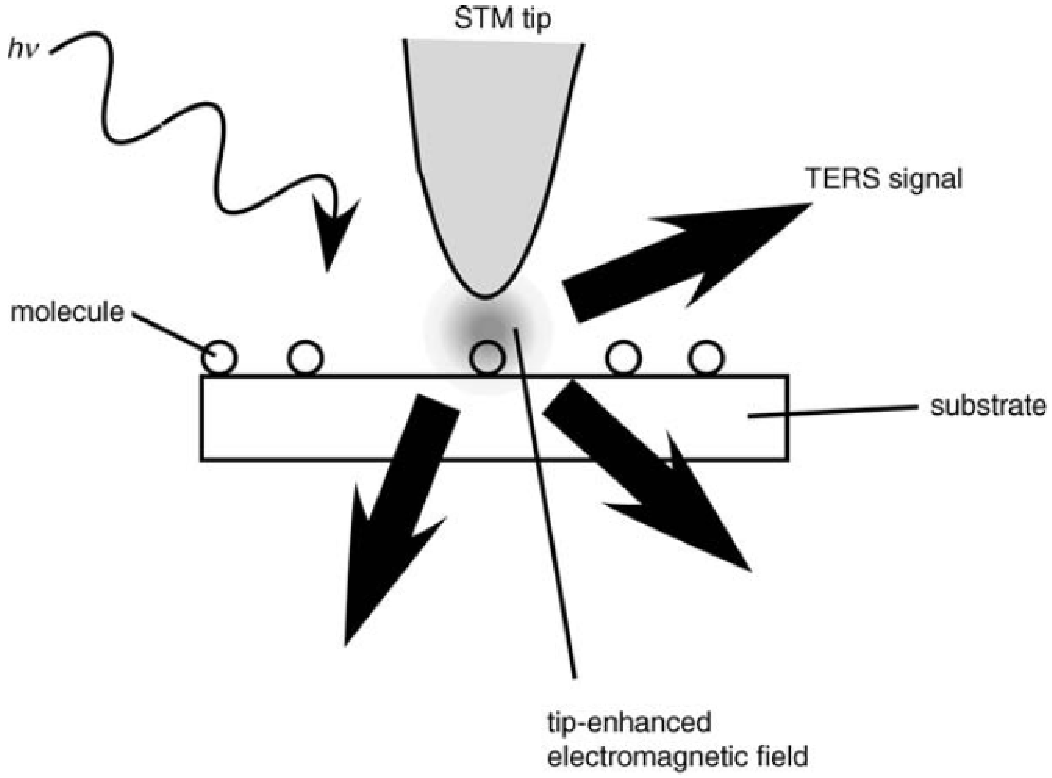
surface enhanced Raman scattering(SERS) provide a far greater detection sensitivity than conventional Raman spectroscopy –

it is further shown that under special conditions nanoparticulate silver films allow for fine rearrangement of their local structure under protein deposition

⇩

new way to perform protein sensing and can be applied in micro arrays protein.

STM-Raman spectroscopy



STM Raman spectroscopy process

The enhancement factor of Raman intensity isM^4, where M factor indicating by how much the electric field is enhanced by nanostructure

By changement of shape, size, material, surrounding medium→ the wavelength dependence of the enhancement efficiency changes

for silver, enhancement x~10^6

--------- with a single molecule x~10^{14}

Fundamentals of Raman Scattering-R.S

R.S. originates from a change in the polarizability of molecules
or the susceptibility of crystals by the excited quasi-particles.
The optical phonons are the most often investigated species.

In contrast to absorption spectroscopy it **is the modulation of the response by the vibrations which is important**, rather than the contribution of the vibronic oscillators themselves.

Resonant transitions can be obtained if an atomic or molecular system
is irradiated by light with an energy corresponding to a transition between two levels

Even if the light is not of a resonant frequency , weak scattering effects are still obtained : **Rayleigh scattering and Raman scattering**

This scattering can be explained classically as well as quatum mecanically

If a molecule is subject to an electric field E → an electric dipole is induced

$$\mathbf{P} = \alpha\mathbf{E}$$

P is not directly //**E** , the molecule is generally asymetric and α is then a polarization tensor

For $E = E_0\sin 2\pi\nu t$, the polarization will vary at the frequency ν

resulting in a re-radiation of light at the same frequency →

Rayleigh scattering (elastic nature)

For the total radiated energy from the oscillating dipole

$I = 2/3c^3 \langle (d^2P/dt^2) \rangle$ -→ $I = [(16\pi^4 c)/(3\lambda^4)]\ \alpha^2 E^2$

If a molecule vibrates, its polarisability varies. Further it depends of the orientation of the molecule with regard to the field-

Thus polarizabity varies as the molecule rotates.

We can write:

$$\alpha = \alpha_0 + \alpha_{1v} \sin 2\pi\nu_{vib} t \qquad \alpha_{1v} << \alpha_0$$

$$\alpha = \alpha_0 + \alpha_{1r} \sin 2\pi\nu_{rot} t \qquad \alpha_{1r} << \alpha_0$$

There will be coupling between the applied and the internal oscillation

For *vibrational motion*

$$P = \alpha_0\, E_0 \sin 2\pi\nu t + (\ ½\ )\ \alpha_{1v}\, E_0[\cos 2\pi(\nu - \nu_{vib} t) - \cos 2\pi\ (\nu + \nu_{vib} t)]$$

For *rotational motion*

$$P = \alpha_0\, E_0 \sin 2\pi\nu t + (½)\ \ \alpha_{1r}\, E_0[\cos 2\pi(\nu - 2\nu_{rot} t) - \cos 2\pi(\nu + 2\nu_{rot} t)]$$

↕ ↕ ↕

Rayleigh Stokes Anti-Stokes

⬇

A side band appear on both sides of the Raleigh line. The side bands are shifted from the rayleigh frequency by

-the vibrational frequency

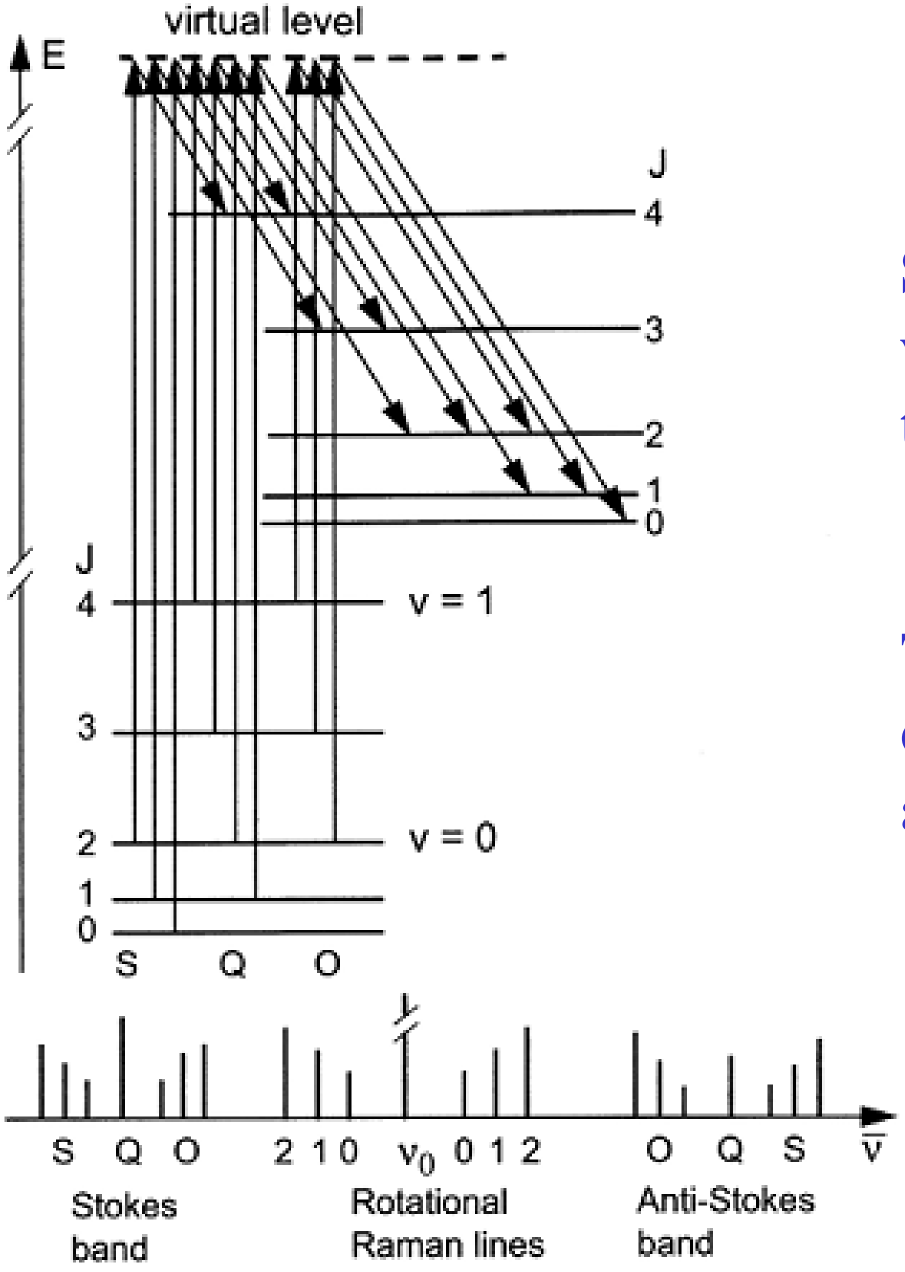
-twice the rotational frequency

The intensity of the stokes & antistokes lies are ~1/1000 intensity of Rayleigh line

The phenomen is called **Raman effect and was first observed by C.V Raman (Nobel price 1930)**

The Raman effect represent inelastic scattering.

In the quantum mechanics theory on Raman scattering, virtual levels are introduced which mediate the scattering



Stokes Raman spectrum of vibration – rotation transitions

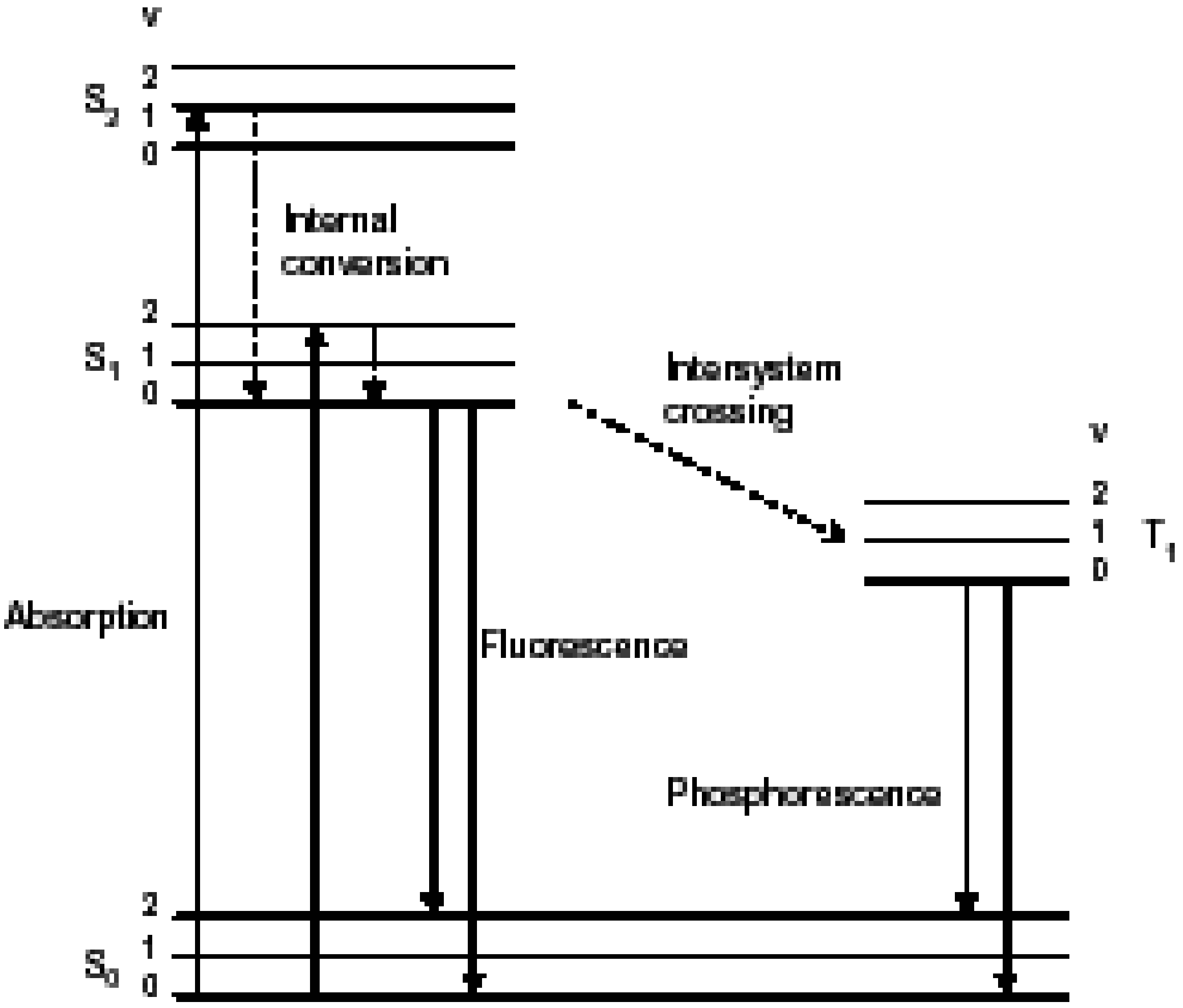
The antistokes transitions are obtained by reversing all arrow directions

Fluorescence spectroscopy

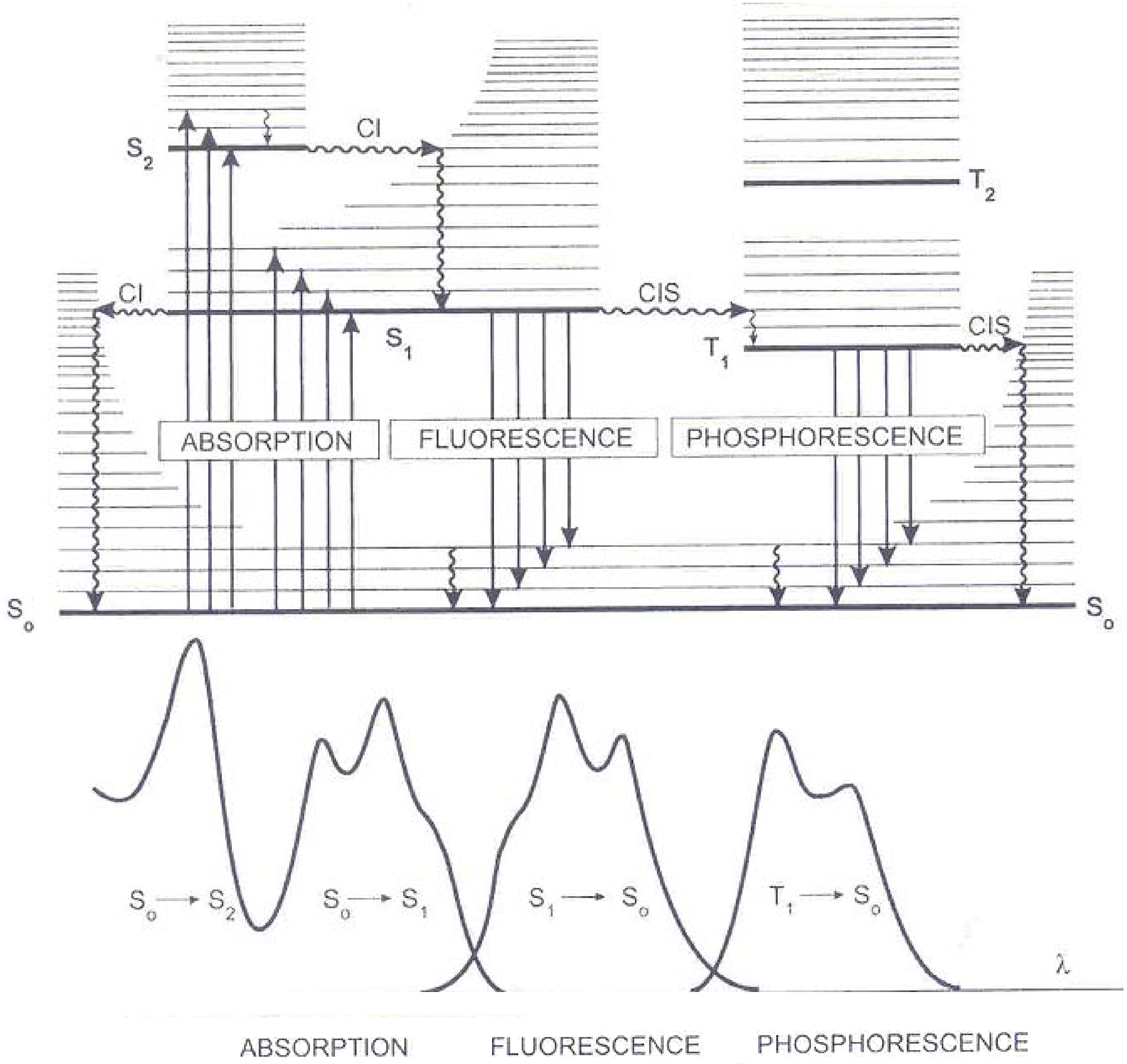
Light is absorbed by molecules and the molecules are excited to the electronically excited state, resulting in the emission of fluorescence when the molecules relax to the ground state.

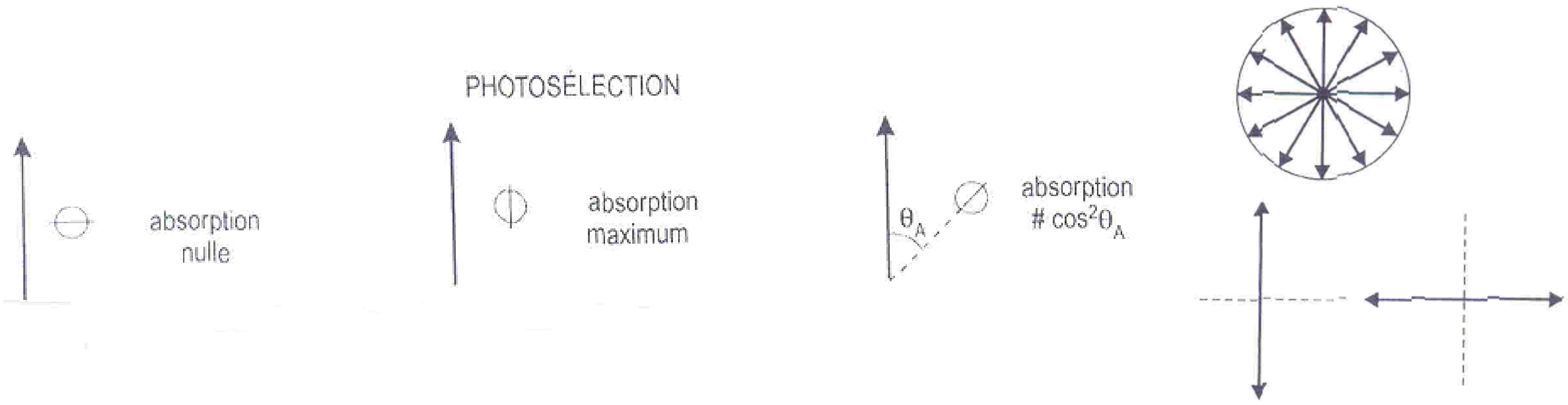
Fluorescence spectra and decay processes are generally sensitive to intermolecular interactions in excited states.
By the use of such optical spectroscopy,

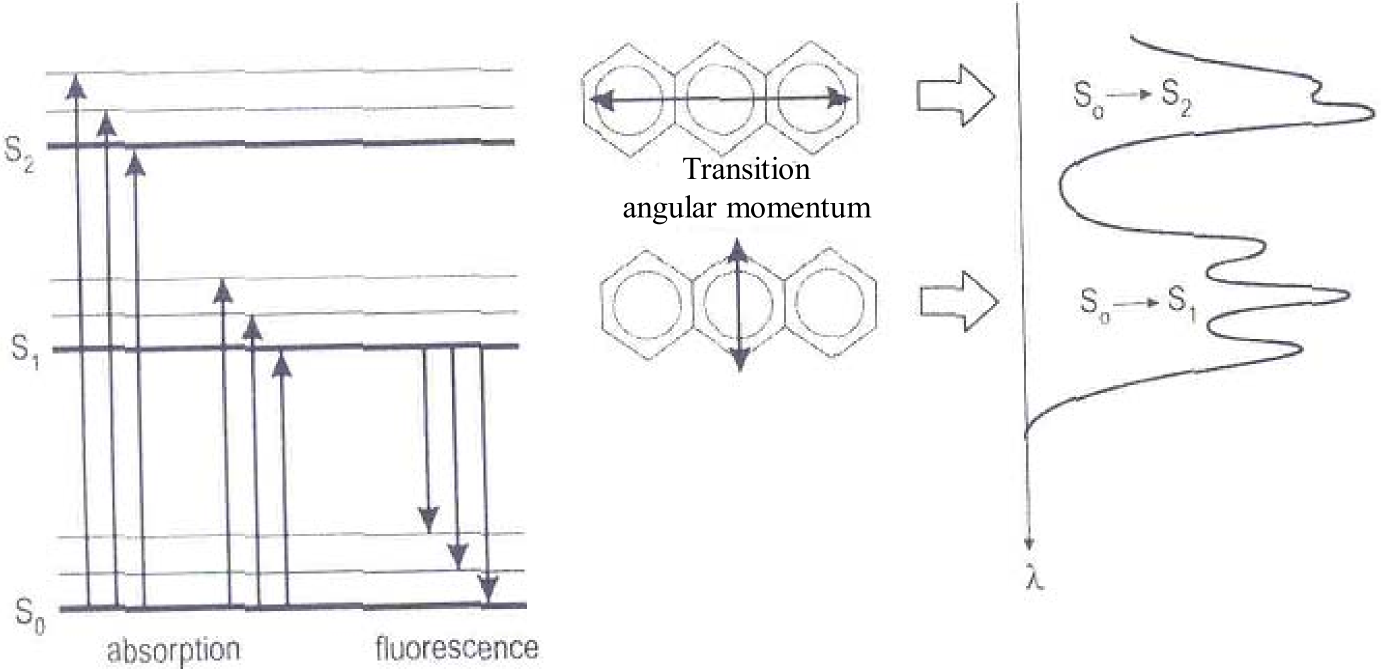
- chemical species can be identified and
- the average environment surrounding target molecules can be deduced.



Jablonski Diagram


S$_2$
CI
T$_2$
CI
CIS
S$_1$
T$_1$
CIS
ABSORPTION
FLUORESCENCE
PHOSPHORESCENCE
S$_o$
S$_o$
S$_o$ → S$_2$
S$_o$ → S$_1$
S$_1$ → S$_o$
T$_1$ → S$_o$
λ
ABSORPTION
FLUORESCENCE
PHOSPHORESCENCE

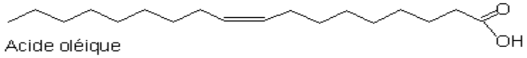

PHOTOSÉLECTION
absorption
nulle
absorption
maximum
θ_A
absorption
$\cos^2\theta_A$


S_2
S_1
S_0
absorption
fluorescence
Transition
angular momentum
$S_0 \rightarrow S_2$
$S_0 \rightarrow S_1$
λ

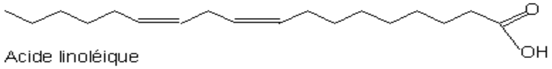
Ex of Fluorescence application:

Analysis of oils oxydation

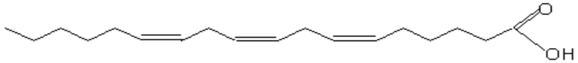
Which molecule(s) is(are) more sensible to oxydation?



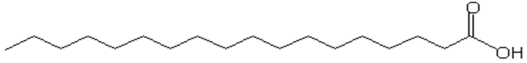
Acide oléique



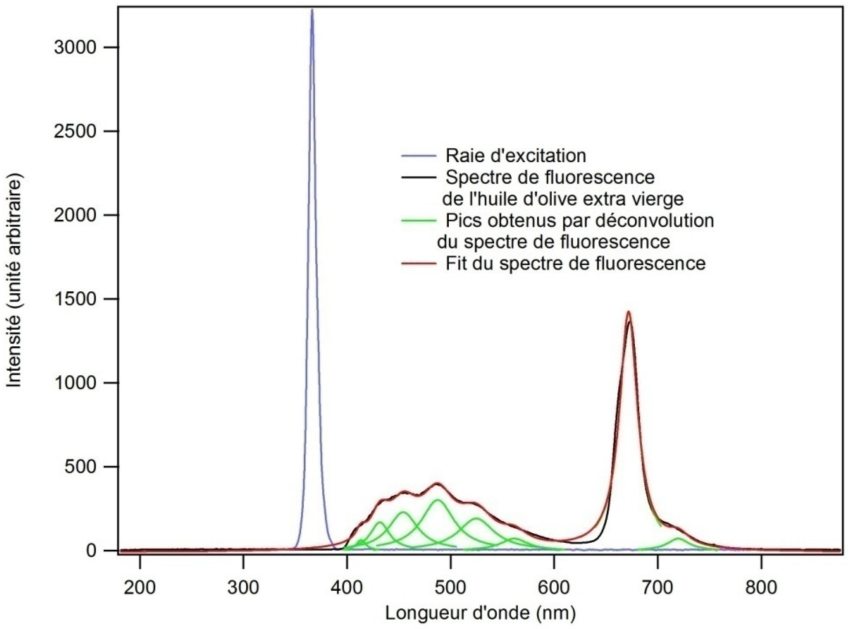
Acide linoléique

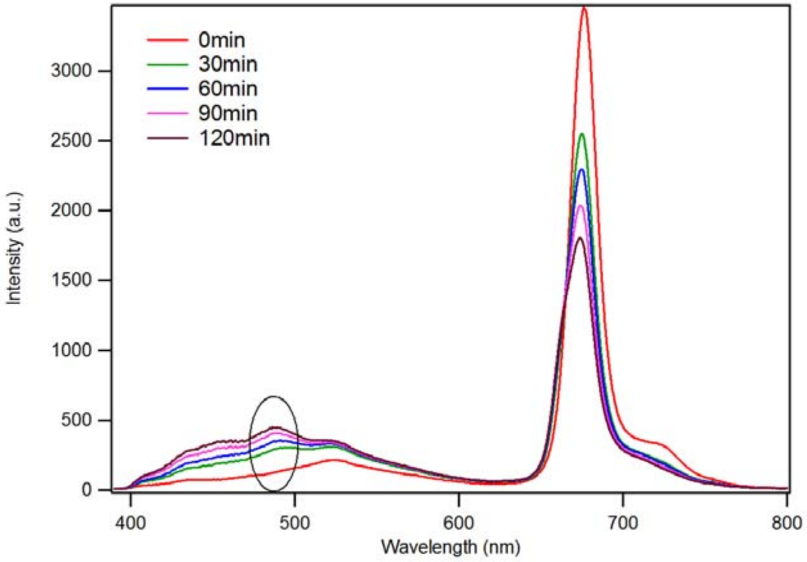


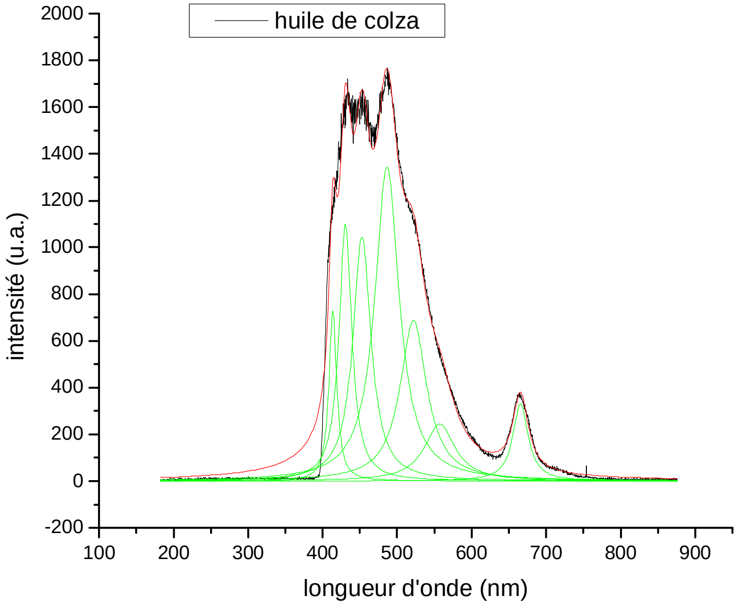
Acide linolénique



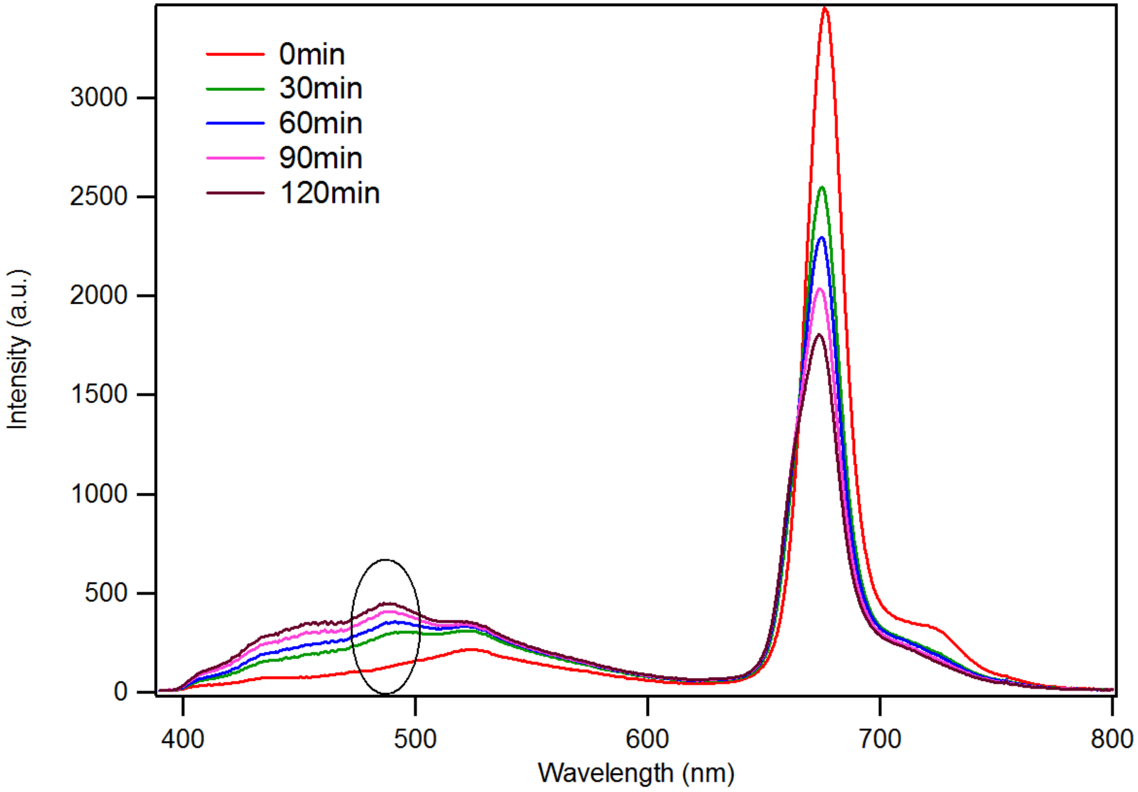
Acide stéarique



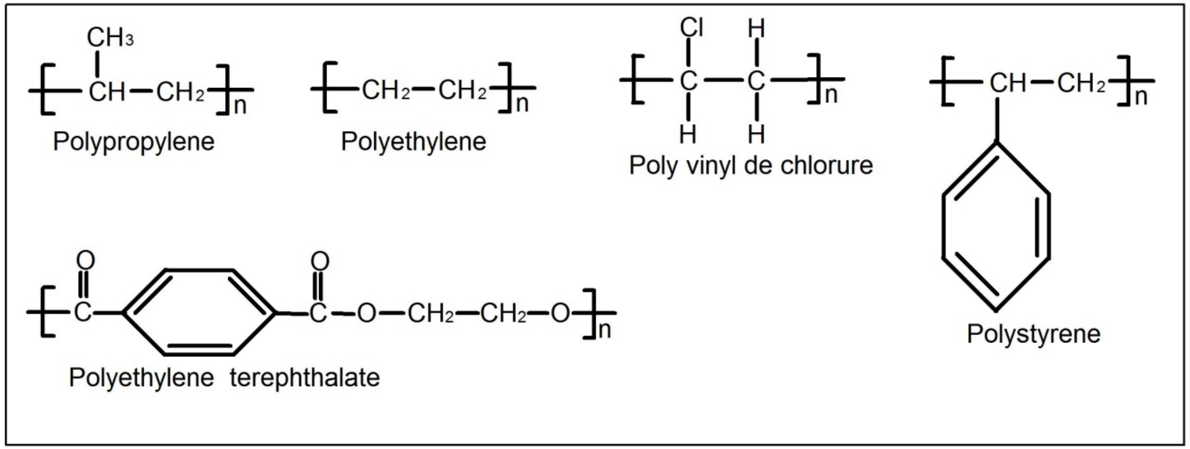




fluorescence



Increase of olive oil oxydation with T=180°C at different time



Polypropylene

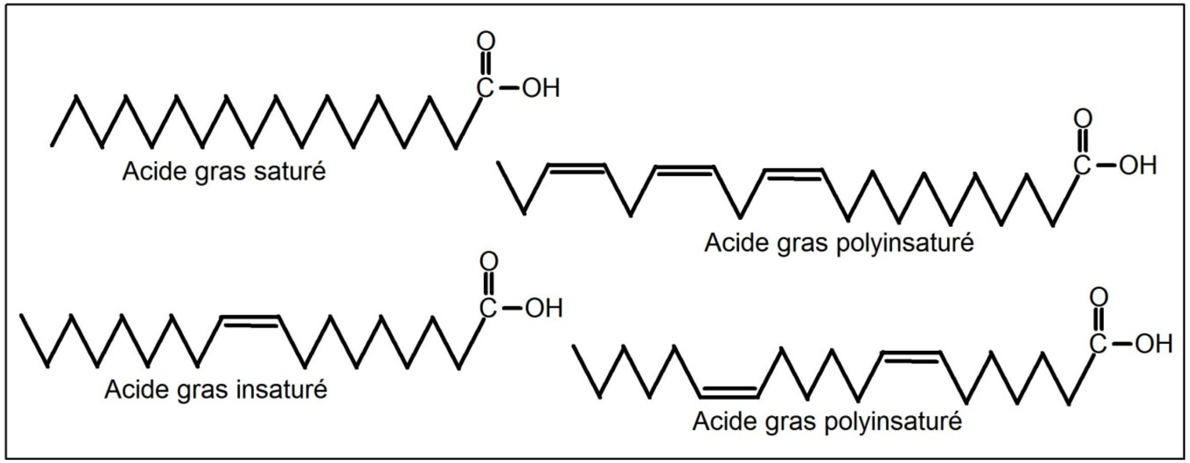
Polyethylene

Poly vinyl de chlorure

Polystyrene

Polyethylene terephthalate

Polymers



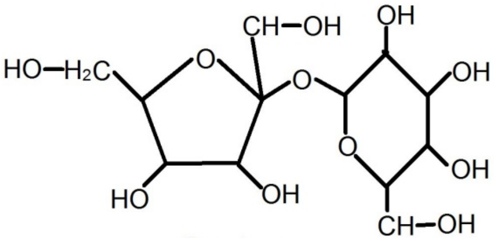
Acide gras saturé

Acide gras polyinsaturé

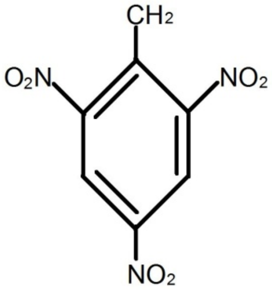
Acide gras insaturé

Acide gras polyinsaturé

Constituants d'huiles végétales



Saccharose



Trinitrotoluene

STM-Fluorescence spectroscopy

The effect of tunneling tip on fluorescence is complicated:

-there is a quenching of fluorescence in the region close to tip,by approaching or in contact the tip; but enhancement stay important at distance > 5nm

With

↓

Possible origin of quenching of fluorescence:

-energy transfer

(at ~5nm tip-molecul

-electron transfer

(~1nm, tip-molecule)

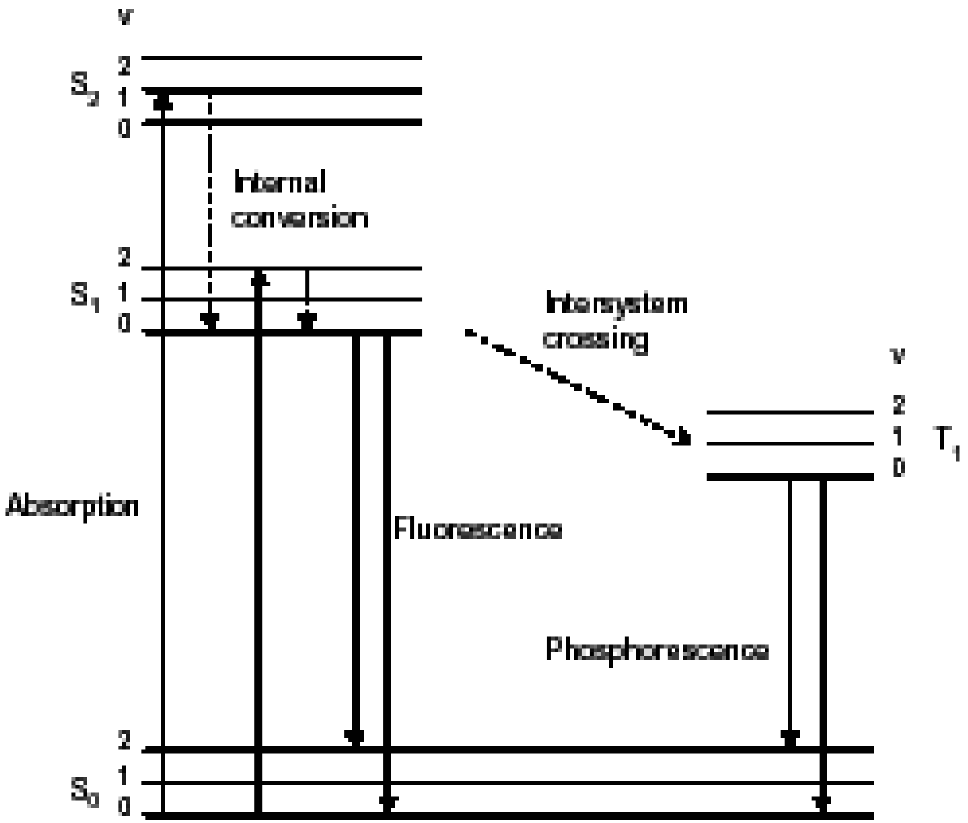
-intersystem crossing

(triplet-singulet)

by approaching heavy atoms

to singulet states molecule

-internal conversion



Conclusions

-Atoms and molecules behaviour

-Scales for molecules studies

-Example of Molecular structure and dynamics-
  Spectroscopy of Atoms and molecules
  Energy states-spectra-
  environment and spectra
  Structures & symetry

-Nanoplasmonics

-STM and Raman & fluorescence spectroscopy

Question

– What can be learned about molecular structure, and interaction with environment from spectra & spectral line shapes analysis?

Thank you

References

-I. Pockrand, J.D. Swalen, J.G. Gordon, M.R. Philpott, Surface plasmon spectroscopy of organic monolayer assemblies, Surface Sci. 74 (1978) 237–244.
-J.G. Gordon II, S. Ernst, Surface plasmons as a probe of the electrochemical interface, Surface Sci. 101 (1980) 499–506.
-C. Nylander, B. Liedberg, T. Lind, Gas detection by means of surface plasmons resonance, Sensors and Actuators 3 (1982) 79–88.
-B. Liedberg, C. Nylander, I. Lundstro¨m, Surface plasmons resonance for gas detection and biosensing, -Sensors and Actuators 4 (1983) 299–304.
-B. Liedberg, C. Nylander, I. Lundstro¨m, Biosensing with surface plasmon resonance—how it all started, Biosensors Bioelectron. 10 (1995) i–ix.
-J.Homola et al. : Sensors and Actuators B 54 (1999) 3–15 5
-M.A. Ordal,et al , optical properties of metals Al, Co, Cu, Au, Fe, Pb, Ni, Pd, Pt, Ag, Ti, and W in the infrared and far infrared, Appl. Opt. 11 (1983) 1099–1119
-Wei-Yin Chien-thesis . Photonic Systems Group-Department of Electrical and Computer Engineering-Faculty of Engineering-McGill University-June, 2008
-M.N. Weiss, R. Srivastava, H. Groger, Experimental investigation of a surface plasmon-based integrated-optic humidity sensor, Electron. Lett. 32 (1996) 842–843.
-J. Homola, G. Schwotzer, H. Lehmann, R. Willsch, W. Ecke,H. Bartelt, A new optical fiber sensor for humidity measurement, Photonics' 95, Prague, Czech Republic, August 1995, EOS Annual Meeting Digest Series, 2A 245–248.
-B. Chadwick, M. Gal, An optical temperature sensor usingsurface plasmons, Japn. J. Appl. Phys. 32 (1993) 2716–2717.

-Detection of Heavy Metal Ions in Drinking Water Using a High-Resolution Differential SurfacePlasmon Resonance Sensor *(Erica s. Forzani et al, Environ. Sci. Technol. 2005, 39, 1257-1262).*

- Detection of arsenic in groundwater using a surface plasmon resonance sensor *(Erica S. Forzani a et al-Sensors and Actuators B 123 (2007) 82–88).*
- Shozo Miwa et al, Thin solid fim,281-282(1996)-466-468
- R.P.Podgorsek et al-Sensors & Actuators B 38-39(1997) 349-352
- A.Duval et M.Nakkache-Optique et vivant-n°35 • mai-juin 2008
- H.Ghalila, M.Chamtouri, workshop biophotonique- Tunis16-18 Jan.2008