

Contents

1	Light-matter interaction	1
1.1	Introduction	1
1.2	Raman Scattering	1
1.3	Fluorescence	2
1.4	Raman and Fluorescence set-up	2
1.5	Angle resolved and transmittance uvVis set-up	2
2	Plasmonic exciton strong coupling on gold nanostructured surfaces covered with porphyrin layer	3
2.1	Introduction	3
2.2	Metallic nanostructures	3
2.3	Applications	3
2.4	Optical measurements	4
2.5	The dielectric constant	5
2.6	Drude approximation	5
2.7	dielectric function, refractive index and extinction coefficient	7
2.8	Noble metals interaction with electromagnetic waves at visible spectral range	8
2.9	Surface plasmons	9
2.10	Theoretical explanation of nanostructures optical response .	9
2.11	Polaritons	11
2.12	Coupling Surface Plasmon Polariton	11
2.13	Fano Resonance	12
3	Strong coupling in molecular exciton-plasmon Au nanorod array systems	13
3.1	Sample preparation	13
3.2	Strong coupling regime	13
4	TMPyP porphyrin	15
4.1	Sample preparation	16
4.2	Strong coupling regime	17
4.3	Main Section 2	17
5	TMPyP porphyrin	19
A	Appendix Title Here	21

List of Figures

2.1	A simple caption	4
2.2	Fano Resonance line shape at $Q = 0$, $Q = 1$ and $Q = 3$ respectively	12
4.1	TMPyP uvVis absorption spectrum in water solution with HCl ($pH = 1.0$ and j-aggregate) and without HCl	15
4.2	TMPyP chemical formula	16
4.3	TMPyP uvVis absorption spectrum in water solution with HCl ($pH = 1.0$ and j-aggregate) and without HCl	16

List of Tables

List of Abbreviations

LAH List Abbreviations Here
WSF What (it) Stands For

Physical Constants

Speed of Light $c_0 = 2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$ (exact)

List of Symbols

a	distance	m
P	power	W (J s ⁻¹)
ω	angular frequency	rad

For/Dedicated to/To my...

Chapter 1

Light-matter interaction

1.1 Introduction

Light-matter interaction phenomena can be distinguished into two wide different categories: **resonances** and **scattering**. In the first case light photons have specific energies that correspond to the energy difference of two different states in the system, a photon is absorbed by the system and a successive decay to a stationary state is responsible for light re-emission.

An example of scattering is reflection: what we see of the objects around us is the light reflected by them to our eyes. Reflection is an **elastic scattering** that means energy is conserved. An example of **inelastic scattering**, in which photon energy is not conserved is **Raman scattering**, a phenomenon widely used for matter investigation

1.2 Raman Scattering

A monochromatic light impinging on a sample brings an electric and magnetic field. At first approximation, molecules on the samples act as a receiving and emitting antenna because they can be thought as a dipole generated by the light itself

$$\mathbf{p} = \alpha \mathbf{E} \quad (1.1)$$

that resonate with the incoming light and with its vibration generate an electromagnetic signal of the same frequency of the impinging one.

Raman spectrum is related to the change in polarizability of the molecules due to thermal vibronic motions of the molecules themselves.

If we think about the polarizability α as a function of the intermolecular distance $\alpha(R)$ and we develop this function in Taylor series

$$\alpha(\mathbf{R}) \approx \alpha(\mathbf{R}_0) + \frac{\partial \alpha}{\partial \mathbf{R}} (\mathbf{R} - \mathbf{R}_0) \quad (1.2)$$

Light at visible spectral range has a frequency that resonates with the uppermost electrons in the atomic shells, in molecular and metallic bonds. When an electron absorbs a photon it moves to an excited state, the successive decay back to the ground state can take place in several different ways, that can be distinguished into two different categories: radiative (such as photon to phonon decay) and non-radiative.

In a radiative decay energy can be conserved and the outcoming electron from the excited material has the same wavelength as compared to the

incoming one. It is the most probable type of material-light interaction and even the less interesting for material investigation.

On the other hand, when the incoming light has an energy that corresponds to the energy difference between the ground state and the excited one, a resonance phenomenon is possible, in which the electron absorbs the photon and jumps to the excited level. Different decay mechanisms (both radioactive and non-radioactive) back to the ground state are possible. **Fluorescence** is a phenomenon that takes place on a wide range of materials. When a material is excited by a monochromatic incoming light and it emits photons with a continuum range of different wavelengths greater than the incoming one, then a fluorescence phenomenon is taking place.

Fluorescence is a resonance phenomenon followed by a radioactive and non-radioactive decay, while phenomena such as reflection and Raman are classified as scattering phenomena. Reflection is an elastic scattering, in which the energy of the outcoming electron is not varied, it is the most probable and so the most intense one, while Raman is a non-linear effect due to the change of polarizability of molecules, the outcoming wavelength can be both greater or lesser than the incoming one and it is classified as an inelastic resonance.

. In the case of fluorescence, electrons jump to an excited molecular level, while in the case of Raman there is no resonance phenomenon as it does not depend on the wavelength of the incoming light.

Electrons jump to a so-called virtual level and then they decay back to the ground state

1.3 Fluorescence

1.4 Raman and Fluorescence set-up

The set-up used is a home-made fluorescence microscope with a set of visible lasers at different wavelengths (532 nm, 475 nm and 600 nm)

1.5 Angle resolved and transmittance uvVis set-up

The spectrophotometer is a *Thorlabs cs200-M*

Chapter 2

Plasmonic exciton strong coupling on gold nanostructured surfaces covered with porphyrin layer

2.1 Introduction

The first investigations of matter at atomic sizes took place with the electromagnetic theories of light: Fourier analysis of diffraction patterns of light of specific frequencies reflected or transmitted by crystalline samples made possible a wide understanding of material structure and properties. Today a wide range of different technologies are growing up in order to further develop and investigate materials at nanoscales.

Nanotechnology is the investigation and implementation of devices and structures at dimensions comparable to the atomic sizes. A wide range of different techniques are available today.

2.2 Metallic nanostructures

Metallic nanostructures can have different dimensions and different sizes and can be made of different materials, all those properties strongly change their optical response. Nanoparticles can be in suspension or ordered on flat surfaces.

Probably the simplest structures are nanospheres that can be placed in liquid suspension and can be deposited on surfaces with the aim of changing their optical properties

Self standing gold structures are fabricated via anodized aluminium oxide (AAO) or via electrodeposition of gold into nanoporous alumina.

2.3 Applications

Gold nanostructured surfaces are promising interacting with electromagnetic waves of visible spectral range exhibits plasmonic effects that can interact with excitonic effects on porphyrin molecules [1].

A wide range of different applications in different disciplines such as

electro-chemistry, catalysis, wetting, thin organic condensates, biosensing, gas or chemical sensing, non-linear optics etc.



FIGURE 2.1: A simple caption

2.4 Optical measurements

When a beam of light reach the surface of separation between two different materials three different phenomena take place:

- *absorption*: light is converted in another form of energy
- *refraction*: light pass through the medium, but with a different angle
- *reflection*: light is reflected back to the previous medium, it can be thought as a particular type of absorption by electrical charges in the medium that behave as scattered oscillating dipoles (Rayleigh scattering) generating a new wave with some frequency and some wave-length λ .

In an experiment in which light is scattered from a sample two different types of measurements can be done: measurements in transmission mode and in reflectance mode. In the first case the detector collect light passing through the sample, in the second case the detector collect light reflected by the samples.

By definition, extinction is the amount of light that doesn't reach the detector, from which when an experiment is performed in **reflectance mode** than

$$extinction = transmittance + absorption \quad (2.1)$$

while in the case in which the experiment is performed in **transmission mode**

$$extinction = scattering + absorption \quad (2.2)$$

The extinction cross section in trasmission mode of N polarizable particles is [3]

$$C_{ext} = \frac{4\pi k}{|\mathbf{E}_{inc}|^2} \sum_{j=1}^N Im(\mathbf{E}_{inc,j}^* \cdot \mathbf{P}_j) \quad (2.3)$$

It is interesting to remember that in electromagnetism the product $-\mathbf{p} \cdot \mathbf{E}$ is the energy of the electric dipole

2.5 The dielectric constant

The medium polarization induced by an out-coming electric fields generates a new and opposite electric field that variate over the time until a new stationary state of the medium charges take place. The time variation of the total electric field can be expressed by a time varying dielectric constant $\epsilon(t)$ of the medium until the new stationary state take place.

When the time necessary to the system to relocate to its stationary state is of the some order of magnitude of the time variation of the electric field, resonance phenomena are possible and a frequency dependent dielectric function $\tilde{\epsilon}(\omega)$ has to be considered.

When light pass from one material to another, a discontinuity of the incoming electric and magnetic field take place. When the two medium are non-magnetic, that is the most common case that happen in nature, then *only* the electric field and *only* the perpendicular component to the surface will experience a discontinuity. This discontinuity depends on the frequency dependent dielectric constants of the two materials ($\tilde{\epsilon}_1(\omega)$ and $\tilde{\epsilon}_2(\omega)$ respectively).

Light is composed by photons with momentum $\hbar k$, if they imping a surface separation they impart a momentum perpendicular to the surface itself. The reflection of elastically scattered waves at an angle $-\theta$ is a consequence of the fact that momentum is conserved.

The net momentum transferred from the electromagnetic wave to the surface is due to the magnetic field, as the time average momentum transferred by the field due to the electric field is zero.

As shown later in this thesis, there is a special case in which the momentum transferred from the incoming light to the surface separation between two medium is parallel. This is the case of plasmonic waves

2.6 Drude approximation

The interaction between electromagnetic waves at visible spectral ranges and matter is mainly due to electrons in the last atomic shells and in crystal bonds. This interaction could be described as a many-body system constituted by atomic cores fixed at their equilibrium configuration and electrons strongly interacting with electromagnetic waves (Born Oppenheimer approximation).

Although this is already a huge simplification, the task of solving such a many body problem is still a formidable one. When the volume concentration of conduction electrons is sufficiently high, then each electron interact with ion cores strongly screened by other conduction electrons and a response of the total system to an out coming electromagnetic perturbation can be described as constituted by a set of classical particles with an effective mass m_{eff} (quasiparticles) different from the well known electron mass.

Under those considerations the classical Drude model, in which conduction electrons are supposed to be a gas of classical charged particles, gives

rise an accurate description of the metal **response function**. According to this model, this interaction is expressed by a second order non homogeneous linear equation

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = F_0 e^{i\omega t} \quad (2.4)$$

in which

- \ddot{x} is the particle acceleration
- $\gamma\dot{x}$ is the damping factor related to the excitement lifetime
- $\omega_0^2 x$ is the harmonic term related to any particle confinement
- $F_0 e^{i\omega t}$ is the external perturbation

Eq. 2.4 together with

$$\mathbf{P} = n\mathbf{x} \quad (2.5)$$

$$\mathbf{D} = \epsilon\mathbf{E} + \mathbf{P} \quad (2.6)$$

gives rise the mathematical expression of the frequency dependent dielectric constant $\tilde{\epsilon}(\omega)$

in the case of conduction electron the zero order term $\omega_0^2 x$ is zero and the dielectric response of the system coming from eq. 2.4 is

$$\tilde{\epsilon}_D(\omega) = \tilde{\epsilon}_1(\omega) + j\tilde{\epsilon}_2(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + j\gamma\omega} \quad (2.7)$$

where $\omega_p = ne^2/\epsilon_0 m_{eff}$ is known as the *plasma frequency* and it can be interpreted as the frequency of which the metal stop to behave as a conductor and start to behave as a dielectric, n is the density conduction electrons of the medium, ϵ_0 the vacuum dielectric constant, γ as the harmonic damping factor, that is related to the plasmon bandwidth Γ .

We can explicit the real and imaginary part of eq. 2.7

$$\tilde{\epsilon}_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \quad (2.8)$$

$$\tilde{\epsilon}_2(\omega) = \frac{\gamma/\omega}{\omega^2 + \gamma^2} \quad (2.9)$$

and observe that the real part of the frequency dependent dielectric constant 2.9 can have both positive and negative values while the imaginary part 2.9 can be only positive.

In the case in which electrons are bounded, such as d atomic shells in gold, the zero order term $\omega_0^2 x$ has to be considered, an inter-band transition to the conduction band take place and the Drude-Sommerfield approximation gives rise a dielectric function with a resonance peak at a frequency

ω_0

$$\epsilon_{interband} = 1 + \frac{\tilde{\omega}_p^2}{(\omega_0^2 - \omega^2) - i\gamma\omega} \quad (2.10)$$

ω_p is a limiting frequency above which the metal is no longer metallic

The (longitudinal?) dielectric constant is complex expression that is linearly related to the longitudinal conductivity function $\sigma(\omega)$

$$\tilde{\epsilon}(\omega) = 1 + 4\pi i\sigma(\omega)/\omega \quad (2.11)$$

The extinction cross section in trasmission mode of N polarizable particles is [3]

$$C_{ext} = \frac{4\pi k}{|\mathbf{E}_{inc}|^2} \sum_{j=1}^N \text{Im}(\mathbf{E}_{inc,j}^* \cdot \mathbf{P}_j) \quad (2.12)$$

It is interesting to remember that in electromagnetism the product $-\mathbf{p} \cdot \mathbf{E}$ is the energy of the electric dipole

2.7 dielectric function, refractive index and extinction coefficient

The medium refractive index is well known to be related to the dielectric constant ϵ and diamagnetic constant μ the last one being equal to 1 in non-magnetic materials

$$n(\omega) + i\kappa(\omega) \approx \sqrt{\tilde{\epsilon}(\omega)} = \sqrt{\tilde{\epsilon}_1(\omega) + j\tilde{\epsilon}_2(\omega)} \quad (2.13)$$

Eq. 2.13 can be readjusted in order to explicit the real and imaginary part

$$n^2 - \kappa^2 = \tilde{\epsilon}_1(\omega) \quad (2.14)$$

$$2n\kappa = \tilde{\epsilon}_2(\omega) \quad (2.15)$$

both n and κ have to be positive and even $\tilde{\epsilon}_2(\omega)$ has to be positive, while $\tilde{\epsilon}_1(\omega)$ has to be negative

A plane wave travelling inside a medium with a complex refractive index $n + i\kappa$ increases its momentum k of a factor n and undergoes to an exponential damping expressed by the imaginary part κ of the refractive index

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{x} n - \omega t) - \mathbf{k} \cdot \mathbf{x} \kappa} \quad (2.16)$$

the imaginary part is known as **extinction coefficient**, and it can be calculated from the absorbance spectrum in trasmission mode

$$T = \frac{\text{signal}}{\text{background}} = e^{-\tau} = 10^{-A} \quad (2.17)$$

where T is the transmittance, τ is known as optical depth and A is the Absorbance.

from the 2.16 it can be easily seen that

$$E = E_0 e^{-2\pi\kappa z\lambda} \quad (2.18)$$

$$\kappa = \frac{\lambda \log T}{2\pi z} \quad (2.19)$$

where c is the molar concentration of the absorbing material and d the distance that the light has to travel in that given material.

Kramers-Kronig are two integral equations that connect the real part of the refractive index to the imaginary part and vice versa. The frequency response of the dielectric constant is the Fourier Transform $\tilde{\epsilon}(\omega)$ (Laplace?) of the time dependent dielectric constant $\epsilon(t)$ that is a quantity positively defined

$$\tilde{\epsilon}(\omega) = \int_{-\infty}^{+\infty} \epsilon(t) e^{i\omega t} dt \quad (2.20)$$

$$\epsilon(t) > 0 \quad (2.21)$$

from which it can easily be deduced that

$$\tilde{\epsilon}(-\omega) = \tilde{\epsilon}^*(\omega) \quad (2.22)$$

while the real part of the refractive index $\tilde{\epsilon}_1(\omega)$ is even for sign inversion, the imaginary part is $\tilde{\epsilon}_2(\omega)$ odd

Real and imaginary parts of the dielectric function are related between each other via the **Kramers-Kronig** relation, that follow from the assumption that n is an analytical function of ω and from mathematical symmetries

$$n = \frac{2}{\pi} P \int_0^\infty \frac{\omega' k(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (2.23)$$

$$k = -\frac{2\omega}{\pi} P \int_0^\infty \frac{k(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (2.24)$$

2.8 Noble metals interaction with electromagnetic waves at visible spectral range

In an ideal conductor the charge relocation instantaneously completely damp the electric field inside the medium, the dielectric constant ϵ tends to infinity and the electric field inside the medium is zero. In a real conductor the charge relocation on the medium surface requires a finite time and the damping is not always complete. The Silver and Gold electronic configuration are $[Kr]4d^{10}5s^1$ and $[Xe]4f^{14}5s^{10}6s^1$ respectively and they are

known as noble metals as their d shell completely filled up. Once they aggregate in crystal, the uppermost electrons s^1 of each atom generate the metallic bound, that constitute the conduction electron band of the crystal itself, while the d and f electrons remain almost unperturbed at their atomic shells.

In the case of Silver, visible light interact only with conduction electrons, and eq. 2.7 is greatly satisfied, while in the case of Gold interband transition from d electrons take place at a wavelength of 450 nm and the measured imaginary part of the dielectric function increases much more strongly as predicted by the Drude-Sommerfeld theory. The dielectric function is the sum of the Drude dielectric function with an interband factor ϵ_{IB} [2]

$$\tilde{\epsilon}(\omega) = \tilde{\epsilon}_{IB}(\omega) + \tilde{\epsilon}_D(\omega) \quad (2.25)$$

2.9 Surface plasmons

Surface Plasmons are collective motion of charges at metal surfaces that take place when an electromagnetic wave of proper frequency interact with the surface itself. They are waves that propagates along the surface: the perturbation is going to a collective charge motion perpendicular to the direction of propagation and to the surface itself and they transfer a momentum along the surface.

Setting the $x - z$ so that x is along the metallic surface and z is perpendicular to it and the origin is on the surface itself, in order to have a wave that propagates along the surface it is necessary that

$$\frac{k_{z1}}{\tilde{\epsilon}_1(\omega)} + \frac{k_{z2}}{\tilde{\epsilon}_2(\omega)} = 0 \quad (2.26)$$

it is evident that to have an in plane wave it is necessary that both k_{z1} and k_{z2} are two decaying factor of the wave, it means that they have to be of opposite sign, so even $\tilde{\epsilon}_1$ and $\tilde{\epsilon}_2$ have to be of opposite sign.

A necessary condition to have plasmonic effects on metallic surface is that the surface has a *negative* dielectric function.

The momentum transferred from the electromagnetic wave to the plasmonic surface has to be in-planar, time average of the out of plane component of the momentum is zero.

The electromagnetic wave interacting with the surface has to match both the energy and the in-plane momentum. While the first one is easy to be realized, the second one can be hard, and for this reason plasmons on metal surfaces can be generated only at particular configurations.

2.10 Theoretical explanation of nanostructures optical response

The theory to be used to investigate light scattering to particles depends mostly on the size of the particle as compared to the electromagnetic wavelength. When the particles are much smaller than the light wavelength,

then the Rayleigh scattering has to be used.

The quasi-electrostatic approximation in which the field is considered constant all over the nanoparticle is available in all that cases in which the nanoparticle sizes are much less than the electromagnetic wavelength $d \ll \lambda$. In this case the scattering process can be described via the Mie Theory that calculate the light scattered by metallic spherical nanoparticles in colloidal form by using the absorption and scattering of electromagnetic radiation [2]. Today this theory is widely used to calculate extinction spectra.

$$\kappa = \frac{18\pi NV\epsilon_m^{3/2}}{\lambda} \frac{\epsilon_2}{[\epsilon_1 + 2\epsilon_m]^2 + \epsilon_2^2} \quad (2.27)$$

where

- N is the number of particles
- V is the volume
- ϵ_m is the dielectric constant of the medium
- ϵ_1 and ϵ_2 are the real and imaginary part of the dielectric constant
- λ the electromagnetic wavelength

Today different shaped nanoparticles are available, particularly gold nanorod are studied in the present thesis, their extinction spectra can be theoretically calculated from the Maxwell-Garnett Theory, that is an extension of the Mie theory

$$\kappa = \frac{2\pi N\epsilon_m^{3/2}}{3\lambda} \sum_{j=1}^3 \frac{\epsilon_2/P_j^2}{\left(\epsilon_1 + \frac{1-P_j}{P_j}\epsilon_m\right)^2 + \epsilon_2^2} \quad (2.28)$$

where P_j are the **depolarization factors** for the three axes.

For gold nanorods the plasmon resonance splits into two modes: one longitudinal mode along the axis of the rod and a transverse mode perpendicular to the first.

The shape of the particle can be included into the extinction formula as a screening parameter, the optical absorption spectrum shows only one plasmon band, which **blueshift** with increasing aspect ratio.

In our experiment in which angle resolved uvVis reflectance is performed, we can argue that a redshift of the dip position take place when the angle is increased, as increasing the angle is equivalent in decreasing the aspect ratio.

The main difference in the extinction spectrum, as compared to the gold nanospheres, is the presence of not only one peak but two peaks, one related to the plasmonic resonance at the top of the nanostructure, the other to the plasmonic resonance by side of the nanostructure.

2.11 Polaritons

The electromagnetic coupling between a radiation field and a quasiparticle such as a **plasmon**, a **phonon** and an **exciton** leads to the concept of a new quasiparticle that is the **polariton**

Lattice vibrations on semiconductors crystals such as GaAs, or AlAs are properly understood in terms of quantum theory of harmonic crystals. dispersion relation of longitudinal and transverse modes exhibit a trend

The quantum of the oscillatory movement of atoms in crystals, known as phonon, exhibit a dispersion relation that can be coupled with phonons at specific frequencies, giving rise to coupling phenomena known as polaritons (?)

2.12 Coupling Surface Plasmon Polariton

Surface Plasmon Polariton can be generated via electromagnetic coupling, typical spectral range is in the visible range although studies of plasmonic coupling in the infrared range are present in the literature.

Surface plasmon polaritons can be generated in different ways

- Grating coupling method
- Metallic nanostructured surfaces
- Prism coupling (Otto configuration)

Excitons are electron-hole couples that can be generated in molecules and they are responsible for physical effects widely used in technological applications such as photovoltaic cells and photodiodes.

When molecular exciton and Surface Plasmon Polaritons are generated from the same electromagnetic wavelength λ , a further coupling between polaritons and excitons can take place. This phenomena intensively studied in the scientific literature is promising for material optical response optimization and successive technological applications. A further coupling phenomena between

A problem that take place in plasmonic coupling is that energy and momentum coupling can not take place in the same time without any proper physical adjustment of the gold surface. One way to couple both energy and momentum is implementing proper metallic nanostructures.

The peaks position in uvVis trasmission spectra of nanoparticles depends on the dielectric constant of the environment.

$$k_{SPP} = \frac{\omega}{c} \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \quad (2.29)$$

Surface plasmonic effects take place only on that type of materials that have the real part of the refractive index ϵ_1 of opposite sign as compared to the real part of the medium refractive index ϵ_m .

2.13 Fano Resonance

The asymmetric spectral shape of a spectral structure can be the fingerprint of a *Fano* like resonance spectra, in which the perturbation from the external probe generate a coupling between a discrete energy level and a continuum one. The first experimental derivation of this type of interaction was in 1957, in which an Electron Energy Loss Spectroscopy was performed on an *He* gas and an asymmetric peak appeared at energies around 60 eV.

This type of resonance can be derived via the Green's Function

$$G(\omega) = (\omega - H + i\delta)^{-1} \quad (2.30)$$

now if we call $|0\rangle$ the isolated state and $|\lambda\rangle$ the continuous one, we can expand the Local Green's Function of the unperturbed system on the isolated state $G_{00} = \langle 0| G(\omega) |0\rangle$

$$G_{00} = \langle 0| G(\omega) |0\rangle = \sum_{\lambda} \frac{|\langle 0|\lambda\rangle|^2}{\omega - \epsilon_{\lambda} + i\delta} \quad (2.31)$$

This is a type of spectrum that can be theoretically resolved via the use of Green's function and the spectral shape is expressed by the following formula

$$f(E) = \frac{(q + E^2)^2}{1 + E^2} \quad (2.32)$$

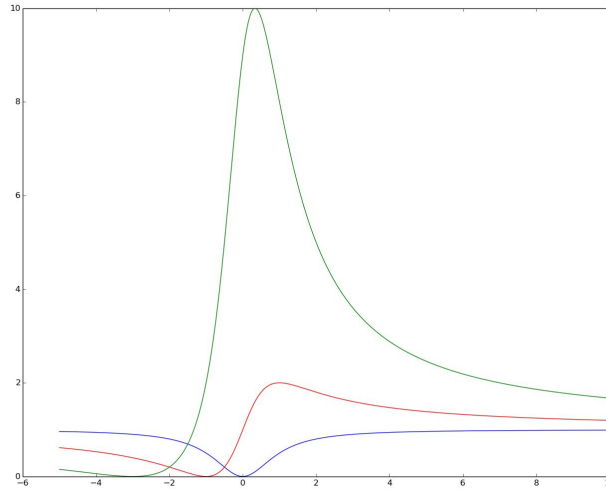


FIGURE 2.2: Fano Resonance line shape at $Q = 0$, $Q = 1$ and $Q = 3$ respectively

Fano Resonance is asymmetric

Chapter 3

Strong coupling in molecular exciton-plasmon Au nanorod array systems

3.1 Sample preparation

In order to find the volume of solvent necessary to get a concentration 10^{-5} mol/l we have to use the following formula

$$SolventVolume = \frac{powderweight(gr)}{molecularweight(gr/moles)} \cdot \frac{1}{10^{-5}} \quad (3.1)$$

and the solution will be expressed in *ml*

The biological and chemical importance of porphyrins is well established in the current research, those materials are going to be studied in order to find further applications in fields related to light-current transduction; for those purposes a wide range of different porphyrins are synthesized. as they are involved in processes such as photosynthesis, metabolic redox reactions and oxygen transport.

Self-assembled structures of porphyrines such as J-aggregate and H-aggregate, provide the possibility inter-molecular transport of excitons with a wide range of potential applications. The fingerprint of such molecular aggregations is provided by the uvVis absorption spectrum, that exhibit red-shift and blue-shift respectively in the Q bands.

Typically the porphyrin absorption spectrum in uvVis is characterized by an intense peak at values around 400 and 500 nm named **Soret band** and three smaller bands named **Q band**.

3.2 Strong coupling regime

In general light can be thought as a superposition of different wavelengths that can be expressed using an integral

$$\mathbf{E}(\omega, (\kappa)) = \int d\mathbf{k} \frac{\partial E}{\partial \mathbf{k}} e^{-i(\mathbf{k} \cdot \mathbf{x} - \omega(\mathbf{k})t)} \quad (3.2)$$

Where $\omega(\mathbf{k})$ is the the dispersion relation, its derivative $d\omega(\mathbf{k})/d\mathbf{k}$ provides the **group velocity** and the number of points in the ω \mathbf{k} space for each value of ω provides the **Density of States** of the system.

In the present work strong coupling between surface plasmon on metallic nanostructured surfaces and molecular exciton was investigated.

The nanostructured surface was constituted by a set of self-standing gold nanorod with a diameter of 70 nm , the optically active molecule was a type of porphyrin called TMPyP in acid solution

Chapter 4

TMPyP porphyrin

TMPyP is a particular type of porphyrin that exhibit a typical absorption spectrum like that one reported in 4.1. Four peaks are clearly visible in this spectrum (black line) at 425 nm, 530 nm 610 nm and 660 nm respectively; those peaks were explained via the *Gouterman's four orbital model*.

In this model, two energy levels $1e_u$ are generated.

The first one is the most intense and is known as *Soret* band and it is due to $S_0 \rightarrow S_2$ transition (π to π^* transition ?). The difference between the Q band and the Soret band are related to the electronic transition from singlet to singlet and from singlet to triplet.

while the other three less intense at higher wavelengths are called *Q bands* and they come from S_0 to S_1 transition. In acid environment (*HCl* at $pH = 1.0$) the external π bonds of different TMPyP molecule bound each other, giving rise a molecular arrangement in a "head to tail" configuration known as *J aggregate* that exhibit a red-shift of the four peaks mentioned before; as reported in the red line in fig. 4.1

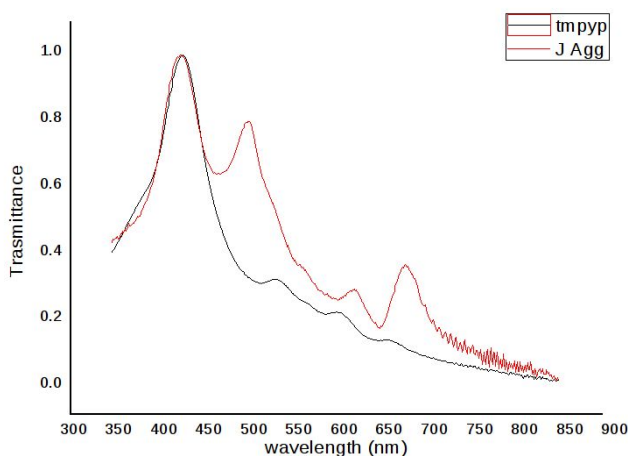


FIGURE 4.1: TMPyP uvVis absorption spectrum in water solution with *HCl* ($pH = 1.0$ and j-aggregate) and without *HCl*

In fig. 4.3 Reflectance spectra at different angles of TMPyP j-aggregate on gold nanorod are reported. A dip splitting, representing a Fano perturbation is changes is shape as function of the angle

TMPyP aggregates as microrods when it's not j-aggregate and as microsquares when it is aggregated

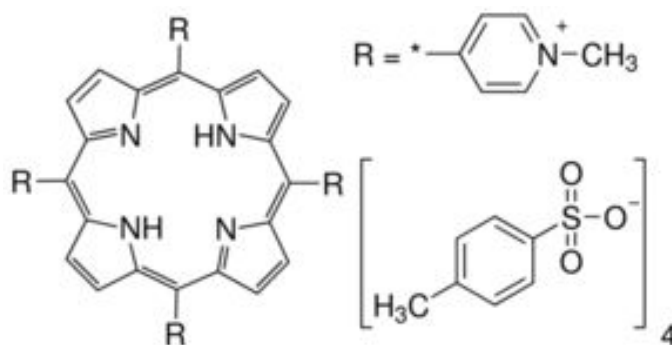
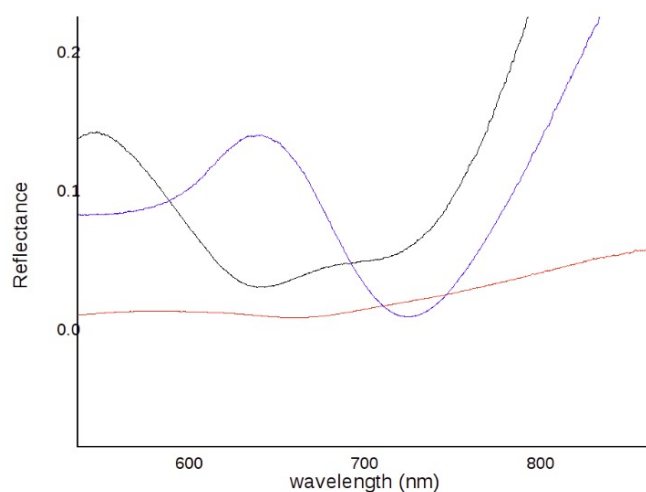


FIGURE 4.2: TMPyP chemical formula

FIGURE 4.3: TMPyP uvVis absorption spectrum in water solution with HCl ($pH = 1.0$ and j-aggregate) and without HCl

4.1 Sample preparation

In order to find the volume of solvent necessary to get a concentration 10^{-5} mol/l we have to use the following formula

$$SolventVolume = \frac{powderweight(gr)}{molecularweight(gr/moles)} \cdot \frac{1}{10^{-5}} \quad (4.1)$$

and the solution will be expressed in ml

The biological and chemical importance of porphyrins is well established in the current research, those materials are going to be studied in order to find further applications in fields related to light-current transduction; for those purposes a wide range of different porphyrins are synthesized. as they are involved in processes such as photosynthesis, metabolic redox reactions and oxygen transport.

Self-assembled structures of porphyrines such as J-aggregate and H-aggregate, provide the possibility inter-molecular transport of excitons with a wide range of potential applications. The fingerprint of such molecular aggregations is provided by the uvVis absorption spectrum, that exhibit red-shift and blue-shift respectively in the Q bands.

Typically the porphyrin absorption spectrum in uvVis is characterized by an intense peak at values around 400 and 500 nm named **Soret band** and three smaller bands named **Q band**.

4.2 Strong coupling regime

In general light can be thought as a superposition of different wavelengths that can be expressed using an integral

$$E(\omega, (\kappa)) = \int d\mathbf{k} \frac{\partial E}{\partial \mathbf{k}} e^{-i(\mathbf{k} \cdot \mathbf{x} - \omega(\mathbf{k})t)} \quad (4.2)$$

Where $\omega(\mathbf{k})$ is the the dispersion relation, its derivative $d\omega(\mathbf{k})/d\mathbf{k}$ provides the **group velocity** and the number of points in the ω \mathbf{k} space for each value of ω provides the **Density of States** of the system.

In the present work strong coupling between surface plasmon on metallic nanostructured surfaces and molecular exciton was investigated.

The nanostructured surface was constituted by a set of self-standing gold nanorod with a diameter of 70 nm , the optically active molecule was a type of porphyrin called TMPyP in acid solution

4.3 Main Section 2

Sed ullamcorper quam eu nisl interdum at interdum enim egestas. Aliquam placerat justo sed lectus lobortis ut porta nisl porttitor. Vestibulum mi dolor, lacinia molestie gravida at, tempus vitae ligula. Donec eget quam sapien, in viverra eros. Donec pellentesque justo a massa fringilla non vestibulum metus vestibulum. Vestibulum in orci quis felis tempor lacinia. Vivamus ornare ultrices facilisis. Ut hendrerit volutpat vulputate. Morbi condimentum venenatis augue, id porta ipsum vulputate in. Curabitur luctus tempus justo. Vestibulum risus lectus, adipiscing nec condimentum quis, condimentum nec nisl. Aliquam dictum sagittis velit sed iaculis. Morbi tristique augue sit amet nulla pulvinar id facilisis ligula mollis. Nam elit libero, tincidunt ut aliquam at, molestie in quam. Aenean rhoncus vehicula hendrerit.

Chapter 5

TMPyP porphyrin

This is a chapter in which results are present

Appendix A

Appendix Title Here

Write your Appendix content here.

Bibliography

- [1] P. Torma and W. L. Barnes "Strong Coupling between surface plasmon polariton and emitters: a review", Rep. Prog. Phys. 78, 1 (2015)
- [2] S. Link and M. A. El-Sayed "Spectral Properties and Relaxation Dynamics of Surface Plasmon Electronic Oscillations in Gold and Silver Nanodots and Nanorods", J. Phys. Chem. B, 103, 8410 (1999)
- [3] L. Zaho, K. L. Kelly and G. C. Schatz "The extinction Spectra of Silver Nanoparticle Arrays: Influence of Array Structure on Plasmon Resonance Wavelength and Width", J. Phys. Chem. B, 107, 7343 (2003)