

Introduction

Here comes the sun...

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The demand of energy has dramatically increased since the start of the industrial revolution, in which the transformation of heat into motion began to be applied. This increase is the result not only of industrial development but also of population growth. Part of this energy is wasted by modern habits or life style, but since this is not the subject of the present thesis, it will not be discussed further. Nowadays, the majority of the energy sources are non-renewable, such as fossil fuels — coal, oil and natural gas, which provide over 80% of our energy — plus uranium. These sources are contaminating, dangerous, or produce a strong impact on the environment — especially the climate; hence, the world is in search of alternative renewable sources of energy. This includes solar, wind and wave energy, biomass (wood or crops such as sugar), geothermal energy, and hydro power [5]. These alternative sources are fast developing in some countries, e.g. eolic energy constitutes the 6% of the primary energy in the European Union, but less than 1% world-wide. Big expectations are related to fusion research (ITER), which is considered the energy source of the future.

Amongst the renewable energy sources, solar energy is one of the most promising. An immense amount of energy from the sun strikes the surface of the earth every day. This energy may be captured and used in the form of heat for some applications, or it may be converted directly into electricity using photovoltaic cells.

In the early 1950s, researchers at Bell Laboratories produced the first silicon-based solar cell that generated enough electricity to operate common electric devices. In 1958, the first Earth-orbiting satellite, Vanguard I, was powered with solar energy. Slowly, solar technology has become the standard method for generating energy in the space. But it was not until the 1970s that it has started to be commonly used on the Earth, in everyday-life devices. Since then, the prices of these cells have decreased but still this technology remains expensive compared with other energy sources.

Inorganic solar cells consist of a semiconductor (generally silicon) which has been doped with impurity atoms so that it contains positively charged (p-type) and negatively charged (n-type) regions. The semiconductor absorbs photons whose energies

are above its energy gap. These photons excite electrons from the valence band to the conduction band, producing electron-hole pairs near the interface between the two regions (p-n junction) which are separated by the potential difference across the interface. Electrons will migrate toward the positive side of the junction and holes toward the negative side leading to a flow of electric current. This type of solar cells can reach efficiencies of about 25% on the Earth and roughly 30% in space. But for optimum performance of these cells, large high-purity single crystals are needed and the crystal-growth processes required are highly demanding, which is finally reflected in the price. Therefore, cheaper solar cells have been searched for.

In 1991, O'Regan and Grätzel published an article entitled: "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films" [1] which opened up a new perspective in the world of solar energy. The authors presented the first dye-sensitized nanocrystalline solar cell with an announced conversion yield of 7.1%, which is presently claimed to be over 10% [6]. In contrast to conventional silicon cells, in dye-sensitized photovoltaic cells, light absorption and charge separation occur in separate molecular layers. This simplifies the cell design, thus leading to lower costs.

The dye-sensitized solar cells consists of a Ru-complex adsorbed on nanocrystalline layers of TiO_2 . This dye is often a member of the ruthenium-polypyridyl family. The molecules contain anchoring groups such as carboxylic acid, dihydroxy, and phosphonic acid, which serve to immobilize the dye on the nanocrystalline TiO_2 surface [7]. The dye absorbs the incoming light, and after photoexcitation, transfers an electron to the conduction band of the semiconductor (TiO_2). The injected electrons percolate in the nanocrystalline TiO_2 to the anode. The oxidized form of the dye is rapidly reduced by redox mediators. A good understanding of the phenomenon is necessary for further optimization of the performance of the cells and for enhancing their quantum yield.

In the present thesis, ruthenium bipyridyl complexes with ligands of different nature have been investigated in order to obtain a better understanding of the influence of the interactions between solvent, complex, and substrate. The dyes were the well-known $(\text{Bu}_4\text{N})_2[\text{Ru}(\text{dcbpyH})_2(\text{NCS})_2]$ photosensitizer with cyano ligands and a new dye, $[\text{Ru}(\text{dcbpyH}_2)_2(\text{bpy-TPA}_2)](\text{PF}_6)_2$, with triphenylamine (TPA) moieties.

For this purpose, UV-VIS, Raman, resonance Raman, SERS, FTIR, and ATR-FTIR spectroscopies have been used. UV-VIS spectroscopy provides information about the electronic transitions of the dye molecules, while the vibrational spectroscopies are able to offer structural information of the adsorption processes as well as the relevant changes induced by the chemisorption on the surface.

The fundamentals and the experimental setups of these techniques are described in the theoretical and experimental introductions, chapter 1 and 2, respectively.

The aim of chapter 3 is to characterize the samples using the different spectroscopic techniques. In addition, different TiO_2 substrates are described.

The adsorption of the complexes on silver and gold nanoparticles is investigated with surface-enhanced Raman spectroscopy (SERS) in chapter 4. SERS data provide highly sensitive information about the orientation of the adsorbate with respect to the metal surface and about the nature of the interaction of the molecule with the colloidal system.

In chapter 5, the adsorption of the dye on two different TiO_2 substrates, anatase paste films and anatase nanopowder, is studied which clarifies the role of the carboxylate groups in the anchoring process of the dyes on the semiconductor surface.

Finally, the results obtained in this thesis and an outlook to suggested future research activities are summarized in chapter 6.

Chapter 1

Theoretical Background

1.1 Interaction of Molecules with Electromagnetic Radiation

Using the Born-Oppenheimer approximation, the energy of a molecule in one of its eigenstates can be written as the sum of four terms which correspond to different motions of the molecule:

$$E = E_{transl} + E_{elec} + E_{vib} + E_{rot}, \quad (1.1)$$

where E_{transl} is the energy of the translation of the molecule, E_{elec} the electronic energy, E_{vib} the contribution of the vibrations of the atoms or atomic groups, and E_{rot} that of the rotation of the complete molecule. Since the translational motion is not of interest, the E_{transl} term will be neglected in the following. Also E_{rot} will be disregarded, since rotational transitions are not resolved in condensed matter.

Molecular spectroscopy is the study of the interaction of light with matter. The photons can interact with the molecules in three different ways: by absorption, emission and scattering (see Fig. 1.1).

Absorption takes place if the photon energy corresponds to the difference between two energy eigenlevels of the molecule. The molecules are excited to a higher energy level when they absorb light. The type of excitation depends on the wavelength of this light (λ). For example, with UV and visible light (200-700 nm) electrons are promoted to higher orbitals, with infrared light (1000 nm-2.5 μm) vibrations are excited, and with far-IR and microwaves (25 μm -2.5 cm) rotations are excited. An absorption spectrum represents the absorption as a function of wavelength.

Emission occurs when the excited molecules decay to lower energy levels emitting a photon whose energy corresponds to the difference between two energy

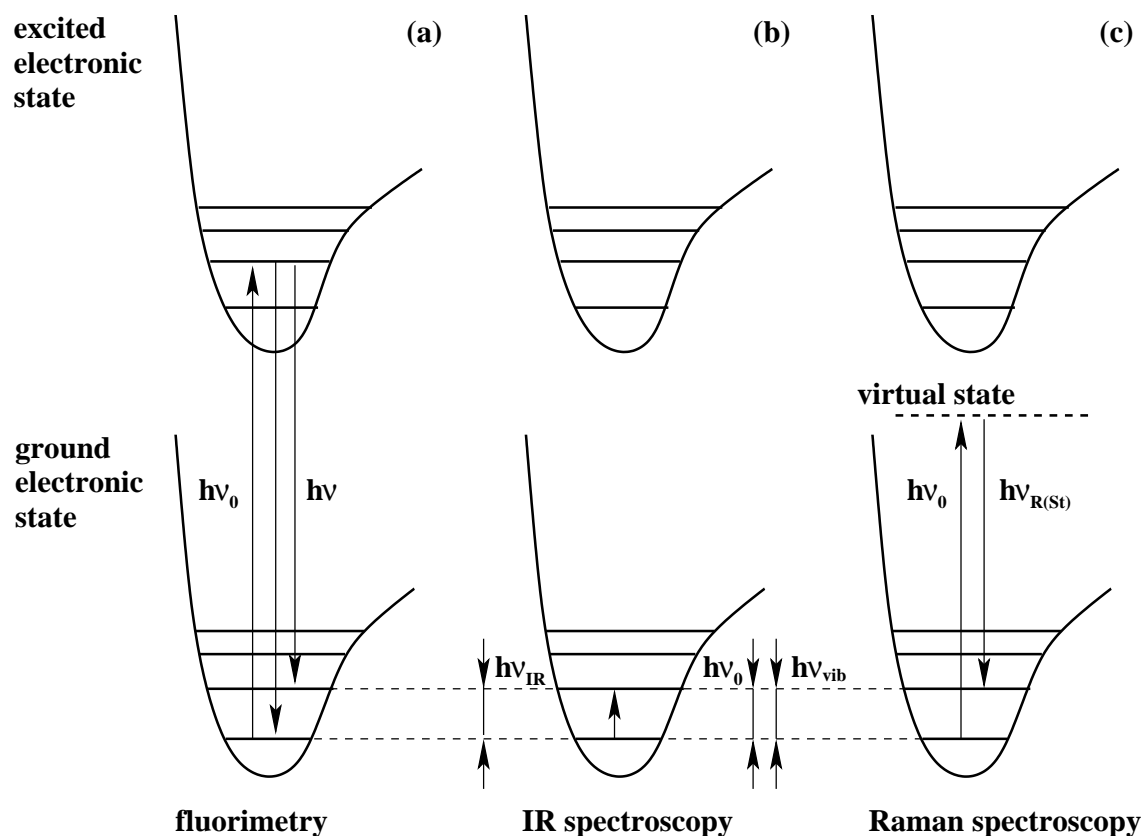


FIG. 1.1. Comparison of the different interactions of molecules with light: (a) UV-VIS absorption/emission, (b) IR absorption, and (c) Raman scattering; and the different spectroscopic techniques to study them.

levels of the molecule. If the transition is between states with the same spin, the emission is called fluorescence, if they have different spin, phosphorescence. Typical lifetimes of excited electronic states are several nanoseconds.

Also *scattering* of the irradiated light can occur but with less probability. The energy of the scattered photon does not correspond to the difference between two energy levels of the molecule. If the interaction is elastic, it is called Rayleigh scattering, if inelastic, Raman scattering. This process takes place instantaneously ($< 10^{-12}$ s).

In this chapter a theoretical description of the interaction of UV, visible, and infrared light with molecules is given. A partial quantum mechanical formulation is used: The radiation is treated classically and is regarded as the source of a perturbation of the molecular system which is treated quantum-mechanically. Transitions between energy levels of the molecular system can occur with absorption or emission of radiation, if the transition dipole moment between the initial and the final molecular state is non-zero. For light scattering, the polarizability of the molecule is the important quantity. Moreover a qualitative discussion of the selection rules and a general overview

of the band assignment of the different spectra are also included. The fundamentals of surface-enhanced Raman scattering (SERS) and its applications are summarized at the end of the chapter. Several books of molecular spectroscopy have been used for the formulation of this theoretical introduction [8–13].

1.1.1 Quantum Theory

A quantum mechanical system is described by the Schrödinger equation:

$$H_0\Psi_0 = -\frac{\hbar}{i}\frac{\partial\Psi_0}{\partial t}. \quad (1.2)$$

A perturbation to this state is described by introducing an additional term, the *interaction operator* H_{int} ,

$$(H_0 + H_{int})\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}. \quad (1.3)$$

The solution of the perturbed system can be written as a superposition of the eigenstates of the unperturbed one:

$$\Psi(\vec{r}, t) = -\sum_k a_k(t)\Psi_k(\vec{r}, t), \quad (1.4)$$

where the coefficients $a_k(t)$ are time-dependent weighting factors, and $a_k^*(t)a_k(t)$ gives the probability of finding the system in state k . From Eqs. 1.3 and 1.4 it follows that

$$(H_0 + H_{int})\sum_k a_k(t)\Psi_k(\vec{r}, t) = -\frac{\hbar}{i}\sum_k \dot{a}_k(t)\Psi_k(\vec{r}, t) - \frac{\hbar}{i}\sum_k a_k(t)\dot{\Psi}_k(\vec{r}, t). \quad (1.5)$$

Since $\Psi_k(\vec{r}, t)$ are the solutions of the Schrödinger equation for the system without perturbation, it follows that

$$H_{int}\sum_k a_k(t)\Psi_k(\vec{r}, t) = -\frac{\hbar}{i}\sum_k \dot{a}_k(t)\Psi_k(\vec{r}, t). \quad (1.6)$$

The wavefunctions $\Psi_k(\vec{r}, t)$ are orthonormal; so Eq. 1.6 after being multiplied with $\Psi_m^*(\vec{r}, t)$ from the left and integrated over all space gives

$$\dot{a}_m(t) = -\frac{i}{\hbar}\sum_k a_k(t)\int \Psi_m^*(\vec{r}, t)H_{int}\Psi_k(\vec{r}, t)d\vec{r}. \quad (1.7)$$

If the wavefunction $\Psi_k(\vec{r}, t)$ is written as the product of a time-dependent and a space-dependent term $\psi_k(\vec{r})\exp(-\frac{i}{\hbar}E_k t)$, it yields

$$\dot{a}_m(t) = -\frac{i}{\hbar}\sum_k a_k(t)\exp\left\{\frac{i}{\hbar}(E_m - E_k)t\right\}\int \psi_m^*(\vec{r})H_{int}\psi_k(\vec{r})d\vec{r}, \quad (1.8)$$

where

$$\int \psi_m^*(\vec{r}) H_{int} \psi_k(\vec{r}) d\vec{r} = \langle m | H_{int} | k \rangle \quad (1.9)$$

is the matrix element of the operator H_{int} between the states m and k . With the Dirac bra-ket notation, equation 1.8 is given by

$$\dot{a}_m(t) = -\frac{i}{\hbar} \sum_k a_k(t) \exp \left\{ \frac{i}{\hbar} (E_m - E_k) t \right\} \langle m | H_{int} | k \rangle. \quad (1.10)$$

Now, rewriting

$$a_k(t) = b_k(t) \exp \left(\frac{i}{\hbar} E_k t \right) \quad (1.11)$$

a set of homogeneous differential equations are obtained

$$\dot{b}_m(t) = -\frac{i}{\hbar} \left\{ E_m b_m(t) + \sum_k b_k(t) \langle m | H_{int} | k \rangle \right\}, \quad \text{with } m = 1, 2, \dots \quad (1.12)$$

Assuming that the time-dependent factor of H_{int} is either constant within an interval $0 \leq t \leq \theta$ or proportional to $\exp(i\omega t) + \exp(-i\omega t)$, this system can be solved by any standard method. Introducing $b_k = c_k \exp(\alpha t)$ yields

$$-\left(\frac{i}{\hbar} \alpha + E_m \right) c_m = \sum_k c_k \langle m | H_{int} | k \rangle, \quad \text{with } m = 1, 2, \dots \quad (1.13)$$

This system of equations can be solved if the determinant of the coefficients is equal to zero:

$$\begin{vmatrix} -E_1 - \frac{i}{\hbar} \alpha & \dots & \langle n | H_{int} | 1 \rangle \\ \langle 1 | H_{int} | 2 \rangle & \ddots & \\ \dots & -E_k - \frac{i}{\hbar} \alpha & \dots \\ & & \ddots & \\ \langle 1 | H_{int} | n \rangle & \dots & -E_n - \frac{i}{\hbar} \alpha \end{vmatrix} = 0. \quad (1.14)$$

Supposing that the perturbation caused by the interaction of the e.m. radiation with the molecule is small, Eq. 1.14 can be expanded up to second order in the matrix element of the operator H_{int} , resulting in

$$\frac{i}{\hbar} \alpha = -E_l + \sum_{k \neq l}^n \frac{\langle m | H_{int} | l \rangle \langle l | H_{int} | k \rangle}{E_k - E_l}, \quad \text{with } l = 1, 2, \dots \quad (1.15)$$

After determining c_k and b_k , an expression for a_k can be derived with the eigenvalues of Eq. 1.14:

$$a_k(t) = \frac{\langle m | H_{int} | k \rangle}{E_m - E_k} \left\{ 1 - \exp \left[\frac{i}{\hbar} (E_k - E_m) t \right] \right\} \quad (1.16a)$$

$$+ \frac{1}{E_m - E_k} \sum_{l > k}^n \frac{\langle m | H_{int} | l \rangle \langle l | H_{int} | k \rangle}{E_m - E_l} \left\{ 1 - \exp \left[\frac{i}{\hbar} (E_k - E_m) t \right] \right\} \quad (1.16b)$$

$$+ \sum_{l > k}^n \frac{\langle m | H_{int} | l \rangle \langle l | H_{int} | k \rangle}{(E_m - E_l)(E_l - E_k)} \left\{ 1 - \exp \left[\frac{i}{\hbar} (E_k - E_m) t \right] \right\}. \quad (1.16c)$$

The first term of equation 1.16 describes the transition from an initial state m to a final state k due to emission or absorption of radiation, respectively. The terms 1.16b and 1.16c contain transition matrix elements to all other electronic states (with index l). They are important, e.g., for Raman scattering.

1.1.2 Interaction with the Dipole Moment

In this subsection, direct absorption or emission is studied; hence, the transition dipole moment of the system and the first term of equation 1.16 which describes the transition from an initial state m to a final state k due to emission or absorption of a photon will be considered.

The interaction of the electric field of the light, $\vec{E} = \vec{E}_0[\exp(-i\omega t) + \exp(i\omega t)]$, with the dipole moment operator of the molecules, $\vec{\mu} = \sum_j e_j \vec{r}_j$ (j being an index for the electrons), can be expressed as

$$H_{int} = \vec{E} \vec{\mu} = \vec{E}_0 [\exp(-i\omega t) + \exp(i\omega t)] \vec{\mu}. \quad (1.17)$$

The maximum of H_{int} occurs when the electric-field vector is parallel to the dipole moment, and no light will be absorbed when \vec{E} is perpendicular to $\vec{\mu}$.

After the introduction of this H_{int} in Eq. 1.10 and separation of the time-dependent factor of \vec{E} , the term 1.16a can be rewritten as

$$\begin{aligned} a_k(t) = & \frac{\langle m | \vec{\mu} | k \rangle}{E_m - E_k + \hbar\omega} \left\{ 1 - \exp \left[\frac{i}{\hbar} (E_k - E_m + \hbar\omega) t \right] \right\} \vec{E}_0 \\ & + \frac{\langle m | \vec{\mu} | k \rangle}{E_m - E_k - \hbar\omega} \left\{ 1 - \exp \left[\frac{i}{\hbar} (E_k - E_m - \hbar\omega) t \right] \right\} \vec{E}_0. \end{aligned} \quad (1.18)$$

For the absorption of radiation, e.g. a transition from k to m , equation 1.18 simplifies to

$$a_k(t) = \langle m | \vec{\mu} | k \rangle \vec{E}_0 \frac{1 - \exp \left[\frac{i}{\hbar} (E_k - E_m - \hbar\omega) t \right]}{E_k - E_m - \hbar\omega}. \quad (1.19)$$

With $\exp(-i\omega t) + \exp(i\omega t) = 2 \cos \omega t$, the probability for the transition at a given frequency reads

$$a_k^*(t) a_k(t) = 4 |\langle m | \vec{\mu} | k \rangle|^2 \vec{E}_0^2 \frac{[\sin \frac{1}{2\hbar} (E_k - E_m - \hbar\omega) t]^2}{(E_k - E_m - \hbar\omega)^2}, \quad (1.20)$$

and integrating over the whole frequency range yields

$$a_k^*(t) a_k(t) = \frac{1}{\hbar^2} |\langle m | \vec{\mu} | k \rangle|^2 \vec{E}_0^2 t. \quad (1.21)$$