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Stable single molecules for quantum optics and all-optical switches

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CHAPTER 1

1.1.Introduction

Over the history of computing hardware, the number of transistors in integrated circuits doubled every two years¹, as predicted by Gordon Moore, co-founder of Intel Co. His “law” has been also proven to be accurate in predicting the development of other fields of technology, such as: semiconductors, microprocessor prices related to number of transistors, memory capacity, sensors and even the number and size of pixels in digital screens. This development has dramatically enhanced the impact of digital electronics in nearly every segment of the world’s economy. However, after about 40 years, this technology is approaching its limit. On the one hand, the miniaturization of silicon transistors has a physical limit given by the finite size of atoms. On the other, the maximum frequency at which silicon transistors can be driven is determined by its size and shape.

Even though Moore’s law has been accurate, it has predicted its own end in a few years. However, the spectacular advances in nanosciences and nanooptics of the last 20 years have brought the realization of all-optical data processing near to us². Photonic circuits, quantum computing³ and quantum information processing⁴ have risen as the most promising emerging technologies. In principle, photonic circuits would be faster and easier to integrate with telecommunication networks than conventional electronic components. Photons are good candidates for transmitting information over large distances with minimal perturbation and losses⁵ because they hardly interact with each other. However, this “blessing” is at the same time a drawback when such interactions are needed to produce basic logic operations for further data manipulation.

The proposed photonic circuits will be composed of many different individual elements, each of them with a particular function. To replace the silicon chips of today by optical analogs, low-loss interconnect waveguides, optical transistors, power splitters,

optical amplifiers, optical modulators, filters, lasers and detectors have to be integrated on the same chip. Till now, just few of these devices have been realized independently⁶⁻⁸. Each of these reports required very particular experimental conditions, like low temperatures (1 K), ultra-high vacuums and/or nano lithographic fabrications. The main problem will be to integrate all the individual elements on the same chip while keeping the properties of each element unchanged.

The efforts in our research group are mostly focused in the development of all-optical transistors, amplifiers and modulators at the single molecule level. In order to develop such devices, the most fundamental element is a stable and high-efficient source of single photons with well-defined energies. Many single quantum emitters have been considered for quantum-optical applications because they produce photons in a stochastic way (one-by-one). The first isolated quantum systems were ions and neutral atoms trapped from the gas phase. But due to the experimental conditions, they might have problems for the assembly and integration on chips^{9,10}. So, condensed matter systems appear more attractive and promising in the long term. Quantum dots¹¹ (QD's) became very popular because of their room temperature performance and long photo-stability, together with a scalable preparation. However, due to their distribution in sizes their optical properties are also very broad distributed. In particular, they present very complex blinking dynamics which would limit their use as photon sources. Another promising quantum system in condense matter are the impurity-vacancy centers (IVC's) in diamond¹². Their robustness, photochemical stability, and room temperature operation are clear advantages, but at the same time, the very high chemical stability will make integration on chips very challenging. One disadvantage as single photon sources is the low monochromatic emission efficiencies (<1%)⁸.

In this thesis, we propose that single organic molecules could be used as high efficient single photon sources and non-linear elements for developing photonic circuits and even further, use their quantum properties to develop new information technologies⁵. The first advantage of using single organic molecules is that any kind of molecule can be

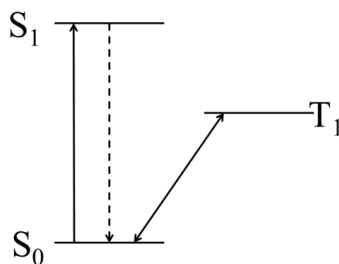
designed and chemically synthesized depending on the desired application. All the molecules obtained by synthetic methods are structurally the same and they have in principle, identical physico-chemical properties. Single organic molecules can be observed at room temperature if they are immobilized in a solid matrix (solvent) and if the concentration is set to about 1-10 nM. At these conditions, the stream of single photons from a single molecule is much more monochromatic (due to quantized transitions) and the emission rates are much higher than what can be obtained from QD's and/or IVC's. The main disadvantage for these molecules is their poor photostability at room temperature due to photochemical reactions induced by the presence of oxygen.

However, when the organic molecules are embedded in a solid medium and cooled to temperatures below 10 K many of these disadvantages can be overcome. The photostability is increased mainly because the absence of diffusing oxygen. The absorption cross section of a single molecule can be increased by many orders of magnitude compared to room temperature. The fluorescence quantum yield is enhanced by the decreased intersystem crossing (ISC) rate. When the solid medium surrounding the molecule is properly chosen such that it does not present active crystal modes at the experimental temperature, the electronic excitation occurs without creation or annihilation of phonons. As a result, the absorption and emission of photons occurs within a very narrow distribution of frequencies called the "zero-phonon line" (ZPL). The total number of photons per second that can be obtained within the ZPL from single molecules¹³ can be at least 10^3 times higher than what can be obtained from an IVC's or a QD¹¹. These photons could then be used to transport and process qubits⁵ without any need to constantly decode them into more manageable forms, such as charges. Different schemes to stochastically switch on and off the emission of photons have been also explored lately^{6,10,14}.

Furthermore, the non-linear response of the fluorescence of a single molecule (pump beam) to a second optical excitation (probe beam) could open the way to develop all-optical transistors¹⁵. However, the probability of occurrence of this non-linear optical

process is in particularly low in organic dyes. Therefore, these experiments require very high intensities of electromagnetic radiation. In order to reach such high intensities the work reported by Chang et. al made use of a surface plasmon to create a very high localized field near the quantum emitter^{16,16,17}. Another report by Hwang et. al described a modulation on the fluorescence of a single molecule when a second intense CW-radiation was applied on resonance with a higher vibroelectronic state¹⁸. The reported modulation was about 0.3%, and the effect was explained in terms of a population inversion.

Our proposed experiment can be described using scheme 1.1, which shows an energy diagram for a three-level system on a single organic molecule. First, we spectrally isolate the molecule at low temperature by exciting on-resonance the strongly-allowed optical transition (pump beam, transition $S_0 \rightarrow S_1$) while detecting the red-shifted fluorescent photons (Dashed arrow). At our conditions, the molecule behaves as a single two-level quantum system (TLS) that can be driven at any desired Rabi frequency (Ω). When the fluorescence state is optically saturated, the nonlinear response to the absorption of just one photon (Probe) into the dark triplet state (T_1) could switch-off the stream of photons with a very high efficiency.

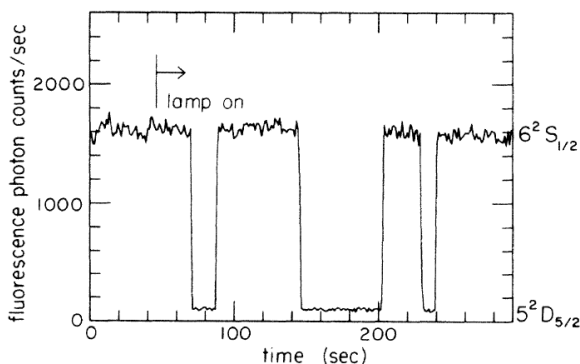


Scheme 1.1: Energy level diagram of a three-level system. The solid arrow is the resonant excitation (pump beam) and the dotted arrow is the fluorescence. The double arrow (probe beam) shows the resonant excitation of the transition to the triplet state

However, for the molecules studied in this thesis, the $S_0 \rightarrow T_1$ transition is strongly forbidden with an expected transition rate in the order of 10^{-10} s^{-1} . Even though

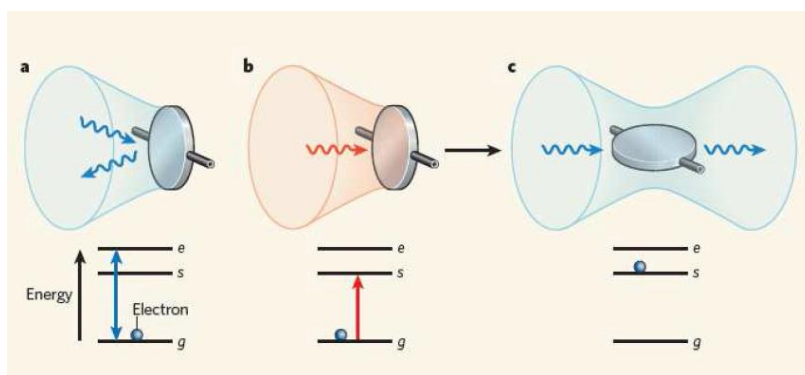
our proposed experiment is the optical response to the absorption of a single probe photon, we still need radiation intensities in the order of 1 kW cm^{-2} (I_{probe}) to populate this T_1 state. The control of such a non-linear process on an isolated molecule could be used in the development of new all-optical transistors with high optical gains. The transistor's gain that can be obtained from the ratio of the lifetimes of the two electronic states is 10^6 .

After the observation of such a non-linear effect in our single molecules, we could try to perform at least two experiments. The first idea resembles the observation made by Hans Dehmelt¹⁹, in 1986, which reported the experimental switching process of the fluorescence of a trapped Ba^{2+} ion (reproduced from ref.19, in scheme 1.2). The changes between the on and off states probed the existence of quantum jumps within the isolated quantum emitter. The photophysical process referred as “optical shelving”, corresponded to the random transition of the emissive state of the ion, into a “dark long-lived” state. This process was completely random, no active control was attempted.



Scheme 1.2: Fluorescence time trace of a trapped Ba^{2+} ion (As reported by Dehmelt, et.a ref.19). The fluorescence (in cps) is lost when the ion is shelved into a “dark” state and recovers after the lifetime of this state. The control beam is a continuous irradiation (lamp on).

The second operation that can be achieved on these two-color experiments is to make the molecule transparent to the pump beam (scheme 1.3, taken from ref 2). In this case, the molecule is continuously excited on resonance with the ground \rightarrow excited transition (pump, 1.3a). The excitation with the probe beam into the shelved state (“s”, 1.3b) prohibits the absorption of more pump photons. As a result, during the lifetime of this “shelved” state, the molecule becomes transparent to the pump beam (scheme 1.3c). The overall process is that one probe photon induces a huge change in the absorption of the single molecule, creating a non-linear optical response.



Scheme 1.3: The “mirror” represents a single quantum emitter that scatters light. a) Shows the excitation on resonance of the strong optical transition between ground (g) and excited (e) state. b) Excitation showing the transition to the shelved state (s). c) Shows that the system becomes transparent to the first beam when is in the s-state.

In our all-optical experiment we propose an active control of the population of the emissive state by pumping the molecule into its triplet state^{12,20}. In this way, we want to induce shelving of the fluorescent transition ($S_0 \rightarrow S_1$) after the absorption of just one photon into T_1 . The “off” times is related to the time the molecule resides on its triplet dark state (micro-milliseconds). During this time no fluorescence is expected, however, the signal is recovered after the decay of the triplet state into its ground state. These two beam experiments may lead to an optical triggered source of single photons^{6,14}. The probability for two photons to interact with each other¹⁵ within the same molecule is also

increased in this experiment, which could be the basics for all-optical transistor-like operations.

1.2. Single molecule spectroscopy at low temperature

The systems studied in this thesis are fluorescent molecules (guest) surrounded by condensed matter. In particular, we look at polycyclic-aromatic hydrocarbons (PAH's), which are organic molecules composed mainly of carbon and hydrogen. Owing to the sp^2 hybridization of the carbon atoms, those molecules are commonly planar and one pure *p-orbital* lies perpendicular to the plane of the molecule. These free orbitals favor the delocalization of the electrons which confers the aromatic character to these molecules.

The observation of single molecules is achieved when the fluorescent dye is highly diluted into a solvent, which in our single molecule (SM) systems is called the host. The optical properties of the guest are determined by the electrostatic solvent-guest interactions. These interactions depend on the solid-state structure and chemical properties of the host. In this thesis we report systematic studies of different single molecules (perylene, terrylene and dibenzoterrylene) embedded in different hosts (single molecular crystals with and without substituents methyl groups, poly-crystals, alkanes and polymers).

An insight into the theoretical foundations needed to describe our systems and to understand and interpret our observations is introduced now. The molecular spectra in cold matrixes can be described on the basis of the Born-Oppenheimer adiabatic approximation, which allows for the separability of degrees of freedom with different characteristic frequencies. In the adiabatic approximation the total Schrödinger equation is solved sequentially for electrons and nuclei.

First, the electronic distribution can be determined for a fixed configuration of the nuclear coordinates (on a single point). A complete electronic energy landscape can be obtained by slightly changing the nuclear coordinates. The shape of such a landscape for small amplitudes around a minimum can be described with an harmonic oscillator potential. Because the dependence of the electronic properties on the nuclear coordinates is negligible under this approximation, the electronic wavefunction can be calculated at the corresponding minimum of the harmonic potential.

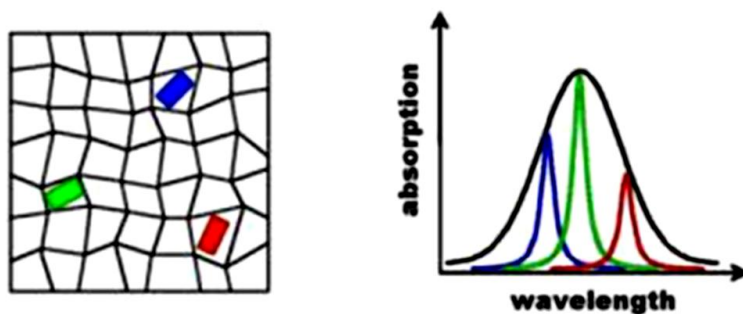
For the experimental conditions of our experiments at low temperature and inside condense matter, the nuclear contribution into the total Schrödinger equation, can be again separated into different degrees of freedom if they present clearly distinguishable frequencies. One contribution corresponds to intramolecular degrees of freedom of the guest molecule, like molecular twisting, stretching, bond deformation or any other vibrational mode (optical phonon). The other contribution comes from intermolecular electrostatic interactions between the guest molecule and its surroundings (acoustic phonon).

The interactions between the guest molecule and the host are described in terms of an electron-phonon coupling. When the frequencies of the molecular vibrations of the guest are comparable to the frequencies of acoustic phonons of the host, a strong coupling between the guest and host can exist, and therefore the adiabatic approximation (separation of variables with different frequencies) does not hold anymore. In the case of some of our studied molecular crystals, the phonon frequencies are clearly different from the molecular vibration frequencies. This frequency miss-match, responsible for weak electron-phonon coupling, is the experimental condition that allows for the observation of zero-phonon lines (ZPL's) of a guest inside of a host.

Because of the optical excitation, the interactions between the host molecules and the embedded guest are different when the guest is in the ground state than when it is in the excited state. The stabilization energy of the electronic configuration of any of these

two states comes mainly from Van der Waals interactions. The guest molecule on its excited state has a stronger polarization coefficient than in the ground state, and therefore the stabilization energy for the excited state is higher. As a result, the potential energy curve for each state at thermodynamic equilibrium has slightly different nuclear coordinates. The slight change of the nuclear coordinates has implications on the curvatures of the potentials, leading to different frequencies of the normal modes.

When many impurities are embedded in a solid (Scheme 1.4) the local environments for each guest molecule are different. As a result, the stabilization energy expected for each molecule will also depend on the insertion geometry (relative orientation) of a single guest respect to the hosts surrounding it. This randomness leads to a broad distribution of resonant frequencies for innumerable guests in the spectrum of bulk solid solutions.



Scheme 1.4: (Left) Representation of three molecules embedded in a solid giving rise to inhomogeneous distribution. Due to the different orientation and local surroundings of each molecule, their absorption lines are slightly shifted with respect to the others (Right).

In principle, the probable number of insertion geometries of guest molecules within the host is extremely big (all possible combinations). This is known as the “*inhomogeneous distribution*” of the system, which is close related to the degree of crystallinity of the host. As an example of this, is that when the host is a crystalline

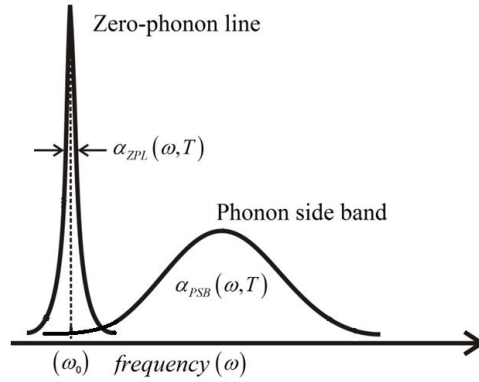
structure with long order range, the potential energy landscape could show well defined minima. As a result, a major number of guest molecules can occupy these potential minima, and give rise to spectroscopic insertion sites that appear in the bulk absorption or fluorescence spectra.

1.3. Zero-phonon line of a single molecule

For one single impurity, the spectral response of the electronic transition to light is expressed as the Fourier-transform of its temporal response. However, the interaction with the phonon bath at thermal equilibrium induces a modulation of the resonance frequency. In a simplified manner, the nuclear displacement can be expressed as a stochastic function that depends on thermal fluctuations giving rise to the quantized nature of phonons. The absorption spectrum, α , of a single molecule (Scheme 1.5) is defined in Eq. 1 by two contributions that depend on (ω, T) , frequency and temperature:

$$\alpha(\omega, T) = \alpha_{ZPL}(\omega, T) + \alpha_{PSB}(\omega, T) \quad \text{Eq.1}$$

The zero-phonon line (α_{ZPL} , ZPL) corresponds to a quasi-elastic scattering of the electronic excitation between states with the same vibrational modes, without any creation or annihilation of phonons in the bath. The “phonon side band” (α_{PSB} , PSB) corresponds to an inelastic scattering of the electronic transition with creation or annihilation of one or more quanta of vibrational energy. The PSB is formed by transitions that occur between two vibrational states with different quantum numbers.



Scheme 1.5: Absorption spectrum of a single molecule showing the ZPL and the corresponding PSB, The shape is defined by the frequency (ω) and the temperature (T). The axis shows increasing frequency towards the right side (High energy).

The ZPL of a single molecule has a finite width (γ_0) defined by (Eq.2) the inverse of the total decay time of the coherence (T_2). This optical dephasing is governed by two terms: T_1 is the non-adiabatic process that induces decay of the population of the excited state, which determines its lifetime; and T_2^* is the pure dephasing time or “decoherence” which describes the time it takes for the electronic coherence to be dissipated by fluctuations of the phonon bath.

$$\gamma_0 = \frac{1}{\pi T_2} = \frac{1}{2\pi T_1} + \frac{1}{T_2^*} \quad \text{Eq.2}$$

1.4.Sensitivity of single molecules

The high sensitivity of the narrow $\alpha_{ZPL}(\omega, T)$ of a SM to any chemical or physical perturbation on its local environment is the reason why the use of single fluorescent probes has become a used technique in the field of optical sensing at nanometer scale. The optical linewidth (γ) in fluorescence excitation spectra as a function of temperature (T) shown in Eq.3, is a phenomenological expression.

$$\gamma(T) = \gamma_0 + bT^\delta + \Delta\gamma_{LFM} \exp(-E_{act} / k_B T) \quad \text{Eq.3}$$

Here, γ_0 is the natural lifetime-limited linewidth, bT^δ describes the interactions with tunneling two-level systems (TLS's) with ($\delta \approx 1$), and $\Delta\gamma_{LFM} \exp(-E_{act} / k_B T)$ is a broadening due to dephasing by phonons and quasi-localized low-frequency vibrational modes with activation energy (E_{act}), and temperature T . The different contributions of the TLS's and the low-frequency modes can be determined from the line broadening of a single-molecule, which allow identifying the nature of the active phonons in the host²¹. On the one hand, a TLS jumps at comparatively low rates between two configurations. The jumping times are broadly distributed. Therefore, the effect of a TLS on the line shape of a molecular absorption are small shifts of the transition energy leading to a line broadening when many TLS's are present in the local environment. Such a broadening is called "spectral diffusion" (SD) in analogy to a diffusion of a particle in one dimension. Low frequency modes (LFM's), on the other hand, have frequencies much higher than TLS, ranging from GHz to THz. Therefore, the fluctuations induced by the LFM's in the electronic transition are averaged in the slow evolution of the optical coherence, and as a result only contribute to the pure dephasing process (T_2^*). In chapter 2 we use the ZPL to probe the activation energies of localized modes in the surrounding of an impurity.

Even when the host is selected to avoid the presence of low-frequency vibrations that interact with the optical transition of the single molecule, they are always present to

some extent, and therefore they have to be considered when studying single impurities. The use of external fields to control and produce a response of the spectral properties of the ZPL has been used to tune the resonance of the molecule to any other desired frequency²². The perturbation of a single molecule by the presence of an optical or an electric field will be presented to contribute to the discussion of this thesis.

When any guest molecule is embedded in a transparent solid matrix (host), chemical and physical interactions with the neighbor molecules influence the observed optical properties. Matrices lacking long-range order will generally give rise to broad distributions of electronic transition energies, and therefore to broad featureless inhomogeneous bands. Crystalline matrices, in contrast, often give rise to well-defined insertion sites where the guest molecule and its first solvent shell are matched with the rest of the crystal. This situation gives rise to narrow spectroscopic bands, as for many molecular crystals and Shpol'skii matrices of *n*-alkanes. The residual disorder of the crystalline lattices (impurities, dislocations, grain boundaries, surfaces, etc.) is responsible for the observed inhomogeneous distribution.

Electrostatic interactions between two molecules follow from the static charge distributions of these molecules. For large intermolecular distances, they vary as a power law of distance, for example as $1/r^3$ for a dipole-dipole interaction. The Van der Waals interaction results from interaction between induced dipole moments and presents a $1/r^6$ dependence. All of these forces determine the stabilization energies of the ground and excited states and therefore the energy of electronic and vibronic transitions.

In the experiments, the temperature and pressure are changed from room temperature and atmospheric pressure to 1.5 K and pressure $< 10^{-5}$ mbar. These changes have an effect on the distances and the relative orientation of the molecules, which determines their electronic transitions. The way to describe this effect is with an electrostatic description that relates the thermodynamic properties and the polarizabilities of the host and the guest, depending on the distance²³. The change of frequency ($d\tilde{\nu}$)

corresponding to a temperature decrease (dT) can be thought of as resulting from a volume reduction, bringing the host and guest molecules in closer proximity. The total frequency shift as a function of temperature is then related to the hydrostatic compressibility (κ) and to the thermal expansion (ϕ_{term}) of the material by²⁴:

$$\frac{d\tilde{\nu}}{dT} = -\frac{3\phi_{term}}{\kappa} \left(\frac{\delta\tilde{\nu}}{\delta P} \right)_T \quad \text{Eq.4}$$

with

$$\phi_{term} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

The temperature dependence of the compressibility factor (κ) varies less than 5 % within our experimental conditions (1.5 – 20 K)²³.

When the sample is irradiated with a laser beam, the optical linewidth can present broadening, frequency jumps or spectral shifts^{25,26}. The most important parameters that determine whether or not a single-molecule system can be used as a single quantum emitter are the efficiency of the emitted photons from the single molecule within its ZPL, the stability of the resonant linewidth and the photo stability of the dye before it bleaching²⁷.

The increasing excitation intensity (I) induces a broadening of the homogeneous linewidth (γ_0) due to increasing thermal fluctuations on the bath. Such a relation is shown in Eq. 5, can in principle increase with no limit. We use this equation to determine at which excitation intensity the molecule starts to be saturated (I_s).

$$\gamma = \gamma_0 \sqrt{1 + \frac{I}{I_s}} \quad \text{Eq.5}$$

$$R(I) = R_{\infty} \frac{I}{I + I_s} \quad \text{Eq.6}$$

At the same time that the line becomes broader the number of emitted photons R also depends on the excitation intensity. At low intensity $I < I_s$ the rate of emitted photons increases linearly with the higher excitation intensity. However, a single two-level system has a natural lifetime of the excited state that determines a maximum emission rate. Optical saturation occurs when the rate of excitation equals the emission rate of the two-level system. Considering a three-level quantum system, three different rate constants are present, and one has the lower rate constant. This steady-state condition determines the maximum emission rate that can be obtained from the other processes. In poly-aromatic hydrocarbons (PAH's) this is the long-lived triplet state (T_1) which is populated via intersystem crossing (ISC) after optical excitation to the S_1 state with a very low probability.

The maximum number of detected photons R_{∞} measured at saturation, are well below the expected maximum emission rate ($\approx 10^9$ $h\nu/s$). This is mainly due to low collection efficiency of the experiment, which depends on the orientation of the excitation dipole, the orientation of the emissive dipole, total internal reflection, the numerical aperture of the collecting optics, the quantum efficiency of the detectors, all transmission of optics and electronic noise sources.

The transition energy of a single two-level system (TLS) can be tuned when applying an external voltage^{28,29}. For centrosymmetric molecules like terrylene, perylene or dibenzoterrylene (Tr, Pr and DBT) the static transition dipole moment in gas phase is zero and should give rise to a quadratic dependence of the electronic transition frequency on the applied field. However, the experiments that have been performed on single molecules showed linear Stark-effect with a broad distribution of frequency shifts and broadenings^{22,28,29}. The reason seems to be that when these molecules are embedded in

the solids, the presence of microscopic forces breaks their symmetry, so the static transition dipole moment is not zero. The excitation frequency change ($\Delta\nu$) of a single molecule in an electric field (\vec{E}) follows the phenomenological expression:

$$h\Delta\nu = -\Delta\vec{\mu}_E \cdot f_e \vec{E} \quad \text{Eq.7}$$

Where $\Delta\vec{\mu}_E$, is the difference between excited and ground state dipole moments. At the single molecule level the homogeneous electric field (\vec{E}) has to be corrected with a local field factor f_e .

1.5. Outline of the thesis

This section is organized in a way that you can connect between the main goals of the project with the main milestones founded during the development of the thesis, which gave us the reasons to perform each experiment. At the very beginning, terrylene was the selected molecule to try to develop the optical transistor because is a dye with very low intersystem crossing rate and high fluorescence quantum yield. With this, the molecule does not blink during the intensity traces, which is a requirement for our controlled “switching” experiment. Terrylene has been measured by single molecule spectroscopy (SMS)³⁰⁻³² in different matrices, and the absorption lie around 570 ± 10 nm for the singlet state, and lifetime limited lines are also reported. However, the energy at which the lowest triplet state lies above the ground state has never been measured due to the same low intersystem crossing rate. Quantum chemical calculations predict approximately a 1 ± 0.1 eV transition energy. The other candidate was perylene, a smaller but similar dye with singlet absorption in the blue, at 445 nm. Compared to other polyaromatic molecules, perylene has been much less studied^{33,34}. No lifetime-limited lines have ever been reported. However, the phosphorescent emission is known to appear at 778 nm when embedded in an anthracene crystal³⁵. The need of a near infrared laser for the triplet of terrylene or in the blue for the study of the perylene singlet was a crucial element in the choice of the system and in the development of the project.

As a first action to determine the triplet energy of terylene, we went to the Institute of Physics in Warsaw, with Prof. Kozankiewicz who is an expert in triplet state spectroscopy of PAH's. There we tried to measure the direct absorption from the ground state to the triplet state from a pure single crystal of terylene, but without success. At the same time, the group in Warsaw was working in the preparation of crystals of 2, 3-dimethylantracene (2, 3-DMA) co-sublimated with dibenzoterylene (DBT). The experiments in Warsaw are a bit different from what we do in Leiden, because of different laboratory facilities. So, we proposed to take a sample of the doped crystals and perform the experiments at 1.5 K that were complementary to the experiments at 5 K that they have reported³⁶. **Chapter 2** demonstrates the application of single-molecule confocal fluorescence spectroscopy and correlation spectroscopy (FCS) to study the physical origin of spectral diffusion in solids^{37,38}. We report the spectroscopic properties of single (DBT) molecules embedded in a single crystal of 2,3-DMA. Also, we look at fluorescence correlation traces as a function of temperature and laser intensity³⁹. The physical origin of the spectral diffusion and instabilities appear to be directly connected with librational degrees of freedom of the methyl groups in the host molecules together with the dipolar disorder in the crystalline structure.

Not knowing the energy of triplet terylene, we started thinking of possible hosts in which perylene could be isolated showing narrow and stable lines (but we had no blue laser). At a conference in Hole-Burning and Single Molecule, in Tübingen (HBSM 12) I had a discussion with Prof. Naumov from Russia. He had studied terylene in a polycrystal of *ortho*-dichlorobenzene⁴⁰. I found this host very interesting first because of the very high energy of the triplet (357 nm) and singlet (256 nm) which allowed for look at perylene at 447 nm, without intermolecular quenching processes. I started studying the bulk fluorescence of perylene as a function of temperature for 10 different hosts using a 405 nm diode laser. I found that in fluorene, alkane (C₁₂), *o*-DCB and also the isomer *para*-DCB, perylene showed narrow fluorescent peaks when the temperature was decreased to 5K. However, at this point we had no single frequency and tunable blue laser to perform SMS of perylene. So, we decided to look for stable terylene in *p*-DCB

which as a solid has some advantages from its isomer *o*-DCB reported by Naumov. **Chapter 3** presents the complete single molecule characterization of a new system of terrylene in *p*-DCB at 1.5 K. The sample preparation is much simpler than the co-sublimation method. It was possible to put the mixture inside glass capillaries. We found in the capillaries the formation of a very strong site at 597 nm which cannot be distinguished when we studied films in coverslips. The main result is the observation of lifetime-limited lines all over the 25 nm of the inhomogeneous distribution from 575 nm to 597 nm.

The observation of stable terrylene molecules proved that *p*-DCB is a convenient host to stabilize lifetime-limited lines, as well as *o*-DCB reported by Naumov et al. At the same time, these positive results pushed our research again towards the triplet of terrylene. So we came with a new idea “if the transition to the triplet is so forbidden is due to optical selection rules...why not use electrons instead of photons?”. So we contacted Prof. Stefan Tautz, in the Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, in Germany which perform electron energy-loss spectroscopy in some organic materials. It was a collaboration of more than one year. **Chapter 4** presents a complete study of the vibrational and electronic spectroscopy of terrylene made by EELS. In order to do these experiments terrylene was sublimated at $198 \pm 5^\circ\text{C}$, and thin films were grown on top of a gold Au (111) surface. The energy loss spectrum was recorded for the vibrational range of the spectrum ($0\text{--}4000\text{ cm}^{-1}$) and compared to the Infrared spectrum (FTIR) of Tr in a KBr pellet. The complete fluorescence from a single terrylene in *p*-DCB (CHAPTER 3) was useful to distinguish the non-IR active modes that could appear in HREELS. We look for the electronic excitation of those films using an incident beam of 12 eV. The energy for the singlet-singlet transition was found at 17200 cm^{-1} in good agreement with the optical absorption 17482 cm^{-1} . However, the determination of the energy for the singlet \rightarrow triplet transition was unsuccessful. After this negative result and other non-reported attempts to determine the triplet energy of terrylene, we made the decision to go for single perylene molecules. This implied to buy a single-frequency tunable laser in the blue.

While looking for the available lasers, we started with an experiment in which the acoustic vibrations of a quartz tuning fork were coupled to the ZPL of one of our best systems: DBT in anthracene. **Chapter 5** shows a clear step towards the coupling between a nanomechanical resonator and a quantum emitter as proposed lately by Puller et.al⁴¹. First, single crystals of anthracene were doped with DBT and studied at 1.5 K. Fluorescence excitation linewidths of 32 ± 5 MHz were observed at 785 nm wavelength as reported by Nicolet et.al¹³. Second, a commercial quartz tuning fork was studied as a function of temperature and one single mode at 32 kHz was observed with Q factor ≈ 40000 . When the doped crystal was brought to optical contact with the tuning fork, the frequency of the fork was changed to 20 kHz and its Q factor strongly reduced. However, the linewidth of the DBT molecule remained unchanged. The tuning fork was then driven at different voltages at their main resonances (kHz). The fluorescence time traces of single DBT's were used to extract indirectly, the frequency of the fork. We found that the maximum sensitivity, which is the minimum displacement required to still has a detectable change in the signal, was about 0.14×10^{-7} nm Hz^{-1/2}.

The blue lasers with the spectral requirements for single molecule spectroscopy were not available from the shelf of any of the main laser suppliers in Europe. We started collaborating with Toptica to develop a tunable single-frequency laser in the blue in order to record the fluorescence excitation lines of perylene. It took few months for Toptica to develop and implement the technology on their blue pro-series. The laser diodes are made of Aluminum Nitride, and due to the external cavity had a coarse tunability of 3 nm, therefore the determination of the zero-phonon line from any of the chosen systems required a spectral accuracy in the order of ± 1 nm. We looked for perylene at 1.5 K in *p*-DCB but no lasers were available for the strange 437 nm maximum. Fluorene on the other hand showed the narrower bulk emission peak, but the maximum appeared at 457 nm. Finally, *o*-DCB showed a nice narrow peak at 447 nm were diodes were available, and also at the same wavelength as reported before. **Chapter 6** presents for the first time the observation of lifetime-limited lines from perylene at low temperature.

► 1 Introduction

Fluorescence excitation spectroscopy showed lifetime limited ZPL's of 23 ± 5 MHz, which correspond to the expected lifetime-limited value considering a lifetime $T_1 = 9 \text{ ns}^{42}$. We report the saturation profile and line broadening as a function of excitation intensity.

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