Scattering & and absorption of light by a single molecule under a subwavelength aperture

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Scattering & Absorption of Light

by a Single Molecule

under a Subwavelength Aperture

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of

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presented by

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Summary

In this dissertation an experiment is introduced, in which a single dye molecule is excited in the optical near field of a subwavelength aperture under cryogenic conditions. The response of the molecule is observed as a fingerprint on the excitation beam and by its red-shifted fluorescence. The experiment reveals an efficient coupling between the excitation light and the molecule.

Single molecule spectroscopy was developed at the end of the 1980s. The first experiments were performed in an absorptive configuration. The detection of molecules was achieved by focusing a laser beam down to a few micrometers and cooling down the sample to liquid helium temperatures. In order to record the weak fingerprint of the molecule on the laser beam, a double lock-in detection was used. Today single molecule spectroscopy is usually performed as fluorescence excitation spectroscopy. The molecules are detected by their red-shifted fluorescence and the excitation light is blocked by an optical long-pass filter. This allows a high signal-to-noise ratio in the detection and spectroscopy of single molecules, although at the cost of sacrificing the information on the narrow-band emission of the zero-phonon line.

In many applications it is desirable to detect a quantum emitter directly in transmission. Textbook formulae suggest that in order to observe the effect of a single molecule on a laser beam, one has to focus it tightly on a region comparable to the absorption cross-section. It turns out, that in practice, this is more subtle. In this thesis the main issues are discussed and experimental results in the method of targeting the absorption cross-section of a single molecule are shown. In our configuration we use a pulled and metal coated glass fiber with a subwavelength aperture at its end to excite single DBATT (dibenzanthanthrene) molecules in the near field. By cooling the sample to below 2K, we achieve narrow zero-phonon transitions and therefore large absorption cross-sections. Our experiments show the first extinction measurements of light in the near field of a single molecule with no further noise suppressing elements. The results show an effect that is more than 3 orders of magnitude larger than in other absorption type experiments on a single molecule, demonstrating the efficient coupling of light with a single emitter in the near field. This technique might also be applied to quantum dots or systems with very small Stokes shifts.
Zusammenfassung


In vielen Anwendungen wäre es wünschenswert ein einzelnes Quantensystem direkt in Transmission zu detektieren. Um eine optimale Kopplung zu erreichen, scheint es lediglich nötig zu sein den Anregungsstrahl auf die Grössen des Absorptionsquerschnitts zu fokussieren. Leider ist die Beschreibung des Absorptionsquerschnitts jedoch nur für die Anregung mit einer ebenen Lichtwelle definiert.


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Abbreviations

\textbf{c} Sample concentration / speed of light
\textbf{d}_{21} Transition dipole moment from $|e\rangle$ to $|g\rangle$
\textbf{|e\rangle} Excited state
\textbf{|g\rangle} Ground state
\textbf{f} modal factor for the molecule
\textbf{g} modal factor for the excitation
\textbf{l} Path length in the sample
\textbf{n} Number of particles / refractive index
\textbf{p}_{1\rightarrow2} Probability to excite the molecule
\textbf{u}_{\text{det}} Unit vector at the detector
\textbf{u}_{\text{mol}} Unit vector at the molecule
\textbf{z} Tip sample distance
\textbf{A} Absorbance [1]
\textbf{A}_{\text{pl}} Area of the focussed incident beam
\textbf{E}_e Energy of the excited state
\textbf{E}_g Energy of the ground state
\textbf{E} Electric field
\textbf{E}_{\text{exc}} Electric excitation field
\textbf{E}_{\text{mol}} Electric field from the molecule
\textbf{E}_{\text{ref}} Electric reference field
\textbf{H} Magnetic field
\textbf{H}_{\text{exc}} Magnetic excitation field
\textbf{H}_{\text{mol}} Magnetic field from the molecule
\textbf{H}_{\text{ref}} Magnetic reference field
\textbf{I}_{\text{pl}} Intensity of the zero phonon line
\textbf{I}_{\text{phw}} Intensity of the phonon wing
\textbf{I}_{\text{mol}} Intensity, emitted from the molecule
\textbf{I} Intensity (on the detector)
\textbf{I}_0 Initial intensity
\textbf{I}_{\text{sat}} Saturation intensity
\textbf{L} LORENTZian line
\textbf{P} matrix, representing the polarizer
\textbf{S} POUYTING vector
\textbf{T} Temperature / Transmittance [1]
\textbf{T}_1 Lifetime of the excited state
\textbf{T}_2 Decay time of the polarization
Abbreviations

\( T_2 \)  
Dephasing time

\( U \)  
Voltage (on the tip)

\( \mathcal{V} \)  
Visibility of the extinction measurement

\( W_a \)  
Absorbed power

\( W_i \)  
Incident power

\( W_{g/e} \)  
Energy levels ground state, excited state

\( \alpha_{\text{FC}} \)  
FRANCK-CONDON factor

\( \alpha_{\text{DW}} \)  
DEBYE-WALLER factor

\( \alpha_{\lambda} \)  
NAPIERIAN absorption coefficient

\( \alpha \)  
Polarizability of the emitter

\( \beta \)  
Geometric factor

\( \delta = \omega - \omega_0 \)  
Laser detuning

\( \varepsilon_{\lambda} \)  
Linear, decadic absorption coefficient (depending on \( \lambda \))

\( \eta \)  
Modal factor (collection area)

\( \lambda \)  
Wavelength

\( \omega_0 \)  
Angular frequency between the ground and the excited state

\( \nu_0 \)  
Frequency between the ground and the excited state

\( \bar{\mu} \)  
Transition dipole moment

\( \varphi \)  
Relative phase of the incident light beam and the coherently scattered components

\( \rho_{33} \)  
Population of the vibrational state

\( \rho_{22} \)  
Population of the excited state

\( \rho_{11} \)  
Population of the ground state

\( \sigma_{\text{abs}} \)  
Absorption cross-section

\( \theta \)  
Opening angle of the microscope objective

\( \Delta \)  
Shift between zero phonon line & phonon wing

\( \Delta \nu_{\text{inh}} \)  
Inhomogeneous linewidth

\( \Delta \nu_{\text{hom}} \)  
Homogeneous linewidth

\( \Delta \nu_{\text{nat}} \)  
Natural linewidth

\( \Gamma_{\text{nat}} \)  
Natural decay rate

\( \Gamma_{\text{scat}} \)  
Scattering rate

\( \Gamma_1 \)  
Decay rate from the upper state

\( \Gamma_2 \)  
Total decay rate

\( \Gamma_2^* \)  
Total dephasing rate

\( \Omega \)  
RABI frequency

\( c = 299458792 \)  
Speed of light

\( h = 6.626068 \cdot 10^{-34} \text{m}^2\text{kg/s} \)  
PLANCK’s constant
\[ h = 1.05457148 \cdot 10^{-34} \text{m}^2\text{kg/s} \] reduced PLANCK’s constant
\[ N_A = 6.0221415 \cdot 10^{23} \text{mol}^{-1} \] AVOGADRO’s number

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>ADC</td>
<td>Analog Digital Converter</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AOM</td>
<td>Acousto Optical Modulator</td>
</tr>
<tr>
<td>APD</td>
<td>Avalanche Photodiode</td>
</tr>
<tr>
<td>CAS</td>
<td>Chemical Abstract Number</td>
</tr>
<tr>
<td>cps</td>
<td>counts per second</td>
</tr>
<tr>
<td>DAC</td>
<td>Digital Analog Converter</td>
</tr>
<tr>
<td>DBATT</td>
<td>Dibenzanthanthrene</td>
</tr>
<tr>
<td>FET</td>
<td>Field-effect Transistor</td>
</tr>
<tr>
<td>FIB</td>
<td>Focussed Ion Beam</td>
</tr>
<tr>
<td>FSR</td>
<td>Free Spectral Range</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>( \lambda / 2 )</td>
<td>Half waveplate</td>
</tr>
<tr>
<td>LSM</td>
<td>Laser Scanning Microscope</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>NA = ( n \sin \theta )</td>
<td>Numerical Aperture</td>
</tr>
<tr>
<td>Nd-YAG</td>
<td>Neodymium-doped yttrium aluminium garnet laser</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>M</td>
<td>Molecular Mass</td>
</tr>
<tr>
<td>MRI</td>
<td>Magnetic Resonance Imaging</td>
</tr>
<tr>
<td>OBE</td>
<td>Optical BLOCH equations</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PID-controller</td>
<td>Proportional-integral-differential controller</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SIL</td>
<td>Solid Immersion Lens</td>
</tr>
<tr>
<td>SNOM</td>
<td>Scanning Near-field Optical Microscopy</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal-to-noise ratio</td>
</tr>
<tr>
<td>SMS</td>
<td>Single Molecule Spectroscopy</td>
</tr>
<tr>
<td>SPCM</td>
<td>Single Photon Counting Module</td>
</tr>
<tr>
<td>TCSPC</td>
<td>Time-Correlated Single Photon Counting</td>
</tr>
<tr>
<td>TDI</td>
<td>Terrylenediimide</td>
</tr>
<tr>
<td>TMI</td>
<td>Terrylenemonoimide</td>
</tr>
<tr>
<td>VET</td>
<td>Vernier Etalon</td>
</tr>
</tbody>
</table>
1 Introduction

Although scientists like E. SCHRÖDINGER did not believe that experiments on single atoms, ions, electrons or molecules could be performed [2] – the scientific pathway in the 1970s and 1980s lead directly to the detection of single molecules. The technique of single molecule spectroscopy started with one pioneering experiment by W.E. MOERNER and L. KADOR in 1989 [3]: A single molecule was optically detected in a cryogenic experiment at $T = 1.6\text{K}$. In this, the absorption spectrum of a pentacene doped crystal was recorded. Single molecule spectroscopy would not have been so successful if the technique of fluorescence excitation spectroscopy would not have been adopted to the field by M. ORRIT in 1990 [4]. This allowed an extension of the optical detection of single molecules to room-temperature conditions by introducing the valuable tool of fluorescence detection to the field. Nowadays single molecule research is established in many areas, ranging from physics over chemistry to biology and material sciences. Single molecules became a valuable tool in monitoring movements and interactions between molecules, cells and particles, to monitor diffusion on the nanometer scale. One of the main strengths of single molecule techniques is to overcome ensemble averaging, which usually veils the individual behaviors and fluctuations at the single molecule level. Moreover, several interesting properties of single molecules allow experiments in quantum optics [5, 6, 7].

Since the early days, the focus shifted from an optimal interaction of light and matter, towards techniques using fluorescence detection. Using this technique a number of molecules can be illuminated by a wide laser beam, where the light matter interaction can be weak, but it still be possible to detect single molecules with a fairly high signal-to-noise ratio.

For applications in quantum information processing an optimal interaction between light and a single emitter is desired. An interaction will be optimal when a single photon interacts, with certainty, with a single quantum object. The quantum object may then store, change or process the information carried by the photon.

The main goal of this work is to take a single molecule and to optimize the interaction with an external light field. The experimental procedure is to perform a single molecule transmission measurement, in which the interaction is measured in a change of the incident light intensity.

The techniques which are used to establish a strong interaction are the following:

- To use the lifetime limited linewidth of a dye molecule at low temperatures, because the interaction cross-section of single molecules and light can be large.

- To confine the light to the subwavelength region, so that the interaction between light and the molecule is enhanced.

Fundamental to the experiment is a cryogenic ($T = 1.4\text{K}$) scanning near-field optical microscope, which uses aperture tips with an opening of $\approx 100\text{nm}$.
The main questions driving the research were:

- is it possible to detect a single molecule in a direct transmission measurement, without the use of noise suppressing elements, like a lock-in amplifier?
- what happens if the size of the light source is comparable to the absorption cross-section of the molecule?

The work is divided in three main chapters:

1. **Single Molecule Spectroscopy & Microscopy** sets the basics in single molecule spectroscopy, light-matter interaction, the extinction of light and near-field optical microscopy.

2. The chapter on the experimental details shows the overall experimental setup, with a special focus on laser intensity stabilization. The tip preparation process by focused ion beam milling is explained, as well as the production of a thin sample, suitable for near-field experiments.

3. The Measurement & Results are presented thereafter. The first cryogenic near-field measurements of a single molecule are presented, as well as the first transmission measurements of a single molecule without any noise suppressing elements like lock-in detection. A method how to derive different lineshapes of a single molecule by a polarizer is introduced, as well as a phase sensitive image of the transmission signal, detected on a camera. The chapter closes with a discussion and a comparison of other experiments in the field.

![Figure 1.1: The key components of the experimental apparatus (not to scale)](image_url)
2 Single Molecule Spectroscopy & Microscopy

2.1 Introduction

In the late 1950s the technique of trapping atoms was developed [8]. Experiments on single atoms opened a wide field of research.

With the development of the laser in 1960 [9] it was possible to have strong light sources with linewidths much smaller than the inhomogeneous band of dye molecules (laser-sources with a linewidth of a few hundred kHz are readily available). This led to the technique of spectral holeburning [10], which used the inhomogeneously broadened transition of dye molecules to store information by “burning” a narrow hole into the spectrum. By estimating the width of a spectral line and the distribution of molecules in an inhomogeneous line, it turned out that the spectra of certain molecules had narrow features which were detectable. These measurements of the statistical fine structure were the first steps towards single molecule detection [11].

Similar experiments allowed the first optical detection of a single molecule in 1989 by W.E. Moerner and L. Kador [3] by confining the light to a small spot of 3µm. Since then this technique has proved very important in many areas of research. Physicists, chemists and biologists use single molecule detection, ranging from fundamental research towards application oriented engineering.

The present work deals with the interaction between light and a single molecule. This chapter is dedicated outlining the theory used in this work and on this interaction – the first part explains the energy level diagram which will be used throughout the work.

To gain more insight into the field of single molecule spectroscopy the basic terminology is set and some experiments are reviewed thereafter. Experiments with electric fields, introducing a Stark shift on the molecule, allow a deeper understanding of current and upcoming experiments.

The detection of single molecules in transmission, central to this work, requires a review of transmission spectroscopy, which is still one of the main techniques used in chemistry today. Here the intuitive picture of “eating up photons” by a single molecule fails and two descriptions, one by a description of the optical theorem, the other by plotting the Poynting vector, are introduced to explain the effect of the light-matter interaction.

With the help of optical Bloch equations it is possible to estimate how an incident light beam is altered and redistributed by a single molecule. This description is not limited to molecules and can also be used to describe other systems (e.g. atoms or quantum dots), because a single molecule is approximated by a two level system.

The interaction of light and a single emitter is significantly enhanced by confining light to a small volume. The basic principles of light microscopy are explained with
a special focus on near-field optical experiments, in which light is confined to a subwavelength region.

## 2.2 Single Molecule Spectroscopy

### 2.2.1 Optical Properties of Fluorescent Molecules

A photophysical process is defined as a physical process which electronically excites a molecular system by non ionizing electromagnetic radiation, i.e. photons. For an electronic transition of a molecule a usual wavelength range is the visible spectrum of light, ranging from 300-800nm, in chemical energy of 150-400kJ/mol.

The energy levels of a molecule (and also atoms and quantum dots) can be described in terms of an energy diagram. The electronic eigenstates of a molecule are plotted where the y-axis describes an energy level. This is known as the Jablonsky diagram [12], which is plotted in figure 2.1(a).

In the following we assume that the initial state of the molecule is in the electronic, vibrational and rotational ground state. This state is usually a singlet state for organic dye molecules. An electronic transition would lead to a higher electronic (excited) state and the molecule takes up an energy which is $E = |E_e - E_g| = h\nu = h\omega$, and is therefore dependent on the energy gap between the ground and the excited state. This state also is due to the spin preserving a singlet state. Because of spin orbit-coupling, an excited molecule can also be transferred to the first triplet state. This state is long-lived (in the range of ms) and can also emit light by another spin conversion process back to the singlet ground state. The lifetime of the triplet states is usually by 3-4 orders of magnitude larger than the lifetime of the first electronically excited singlet state. Therefore the molecule is “dark” for the time it is in the triplet state. In the present work, triplet transitions are not relevant in the description of the optical properties of single molecules and are therefore neglected in all upcoming descriptions.

The assumption that the molecule is in the electronic, vibrational and rotational ground state holds at low temperature where no other states are thermally populated.

The complete energy level diagram in figure 2.1(a) shows several energy levels of a single dye molecule and can for the present work be reduced to the diagram in figure 2.1(b). This is used throughout the work and describes the electronic ground state (labeled as $|g\rangle$), the first electronic excited state (labeled as $|e\rangle$) and shows two (of several) vibrational levels of the electronic ground state. An excited molecule has two luminescent decay paths: either it immediately decays to the electronic ground state, emitting a photon of the initial excitation energy or it relaxes to a higher vibrational level and emits a red shifted photon. Further relaxation from this level to the vibrational (and electronic) ground state releases further energy from the molecule, which is usually emitted as heat or phonons.

The resulting spectral response of molecules can also be estimated from the energy level diagram: Each transition has a certain energy gap, which is defined by $E = |E_e - E_g| = h\nu = h\omega$. If an excited molecule decays back to the ground state, the emitted light has a wavelength $\lambda_j$. If the molecule decays from the excited state back to a vibrational level, the emitted energy is smaller and the emitted photon
2.2. Single Molecule Spectroscopy

![Jablonsky diagram](a) and simplified energy diagram (b).

**Figure 2.1:** The energy level diagrams used in the discussion of molecular properties in this work. The complete diagram in figure 2.1(a) shows higher electronic states, as well as the *intersystem crossing* transition to the triplet state. Although the triplet state contributes partially to the presented measurements it can be disregarded for the used recording timescales. For all further descriptions the diagram in figure 2.1(b), can be used.

is red shifted with respect to the photon, needed to excite the molecule to the first electronic excited state. The spectral asymmetry of room temperature spectra can be explained by this effect.

A room temperature absorption spectrum of a dye molecule, such as a rhodamine solution, easily detectable by the human eye (for example $10^{-5}$ mol/L), shows a broad line, with a spectral linewidth of several tens of nanometers. The main reason is that all molecules in the sample have a different surrounding (forth is referred to as *nano-environment* in the present work) and show therefore a slightly different spectrum, even if the molecules are chemically exactly the same. This effect, depending on several molecules, is called *inhomogeneous broadening*. The same phenomenon accounts for the detected fluorescence, which also shows an inhomogeneous broadening effect. Due to the collective, statistical behavior of the molecules, the resulting broadening has a *Gaussian* shape. The inhomogeneous linewidth at low temperatures $T \leq 2K$ can range from 10THz, in polymers, down to values less than 1GHz \[13\] for unstressed sublimated crystals.

When the spectrum of a *single* molecule is described, no inhomogeneous broadening occurs, only the *homogeneous broadening* is observed. All processes which lead to a broadening of a single emitter define the *homogeneous linewidth*. For a homogeneously broadened spectrum, figure 2.2 shows a homogeneously broadened spectrum as a gray background. For a further discussion, refer to \[14\]. To describe the *homogeneous broadening* in mathematical terms, we correlate the linewidth of the transition to the lifetime of the upper state:

$$\Delta \nu_{\text{hom}} = \frac{1}{\pi T_2} = \frac{1}{2\pi T_1} + \frac{1}{\pi T_2^*} \quad (2.1)$$

Here $T_1$ represents the decay time of the excited state and $T_2$ the total decay time of the polarization. The time denoted by the dephasing is $T_2^*$. 
Figure 2.2: Excitation & emission of a single molecule. When the temperature is lowered the spread of wavelengths of the emission becomes narrower. The direct transitions between the electronic states, as well as the transitions between the electronic states and the vibrational levels, are much narrower than the phonon wings, where momentum is transferred while relaxing to the ground state. In fluorescence excitation spectroscopy the excited electronic state is excited and the transitions to the vibrational levels of the ground state are probed. The conventional setup uses a filter which blocks the direct transition to the electronic ground state as well as its phonon contribution (see inserted filter curve).
If we only consider the Heisenberg principle and the fact that the energy levels of a single molecule have a finite width, the natural linewidth reads as

\[ \Delta \nu_{\text{nat}} = \frac{1}{\pi T_2} = \frac{1}{2\pi T_1} \]  

(2.2)

This is the minimal accessible value and can be observed with atoms, cold molecules or ions in a vacuum. Here \( T_2^* \) is infinite and does not contribute to the linewidth. Under ambient conditions the natural linewidth cannot be measured in solid-state systems, because the lines are broadened, but can be estimated by the radiative linewidth by a lifetime measurement e.g. with short laser pulses (see chapter 3.6.2 for such a measurement). It follows that [14]:

\[ \Delta \nu_{\text{nat}} \leq \Delta \nu_{\text{hom}} \leq \Delta \nu_{\text{inh}} \]  

(2.3)

For the case of a dye molecule in a solid state matrix, the processes which homogeneously broaden the spectral line can be suppressed at temperatures below \( T = 2K \) and for specific systems the homogeneous linewidth \( \Delta \nu_{\text{hom}} \) reaches the lifetime limited value \( \Delta \nu_{\text{nat}} \). The width of such a line can be as narrow as a few MHz. Compared to the optical frequency this would correspond to a resonator with a quality factor of \( \approx 10^8 \).

The ratio between the direct decay into the ground state and the decay into the vibrational levels is named the branching ratio. The transition from the vibrational excited levels to the vibrational ground state \( (k_{31}) \) is fast and does not show any luminescence. In the current work the energy levels of the molecules are directly transferred from the electronic ground state to the first electronic excited state, and no vibrational levels are excited. The line shape for the resulting spectrum for a single emitter has usually a Lorentzian shape, reflecting the Fourier transform of the exponential decay of the population:

\[ I(\nu - \nu_0) = \frac{1}{4\pi^2 (\nu - \nu_0)^2 + (\Delta \nu_{\text{hom}}/2)^2} \Delta \nu_{\text{hom}} \]  

(2.4)

This accounts for the direct transition from the excited state back to the ground state, as well as the direct decay into one of the vibrational levels. These transitions are the zero phonon transitions. Contributions which originate from a solid state environment where single molecules are embedded change the lineshape from a Lorentzian to a more complicated shape [15]. The factors changing the resultant spectra and the contribution to coherent and incoherent emission are discussed below.

When a molecule decays back from the excited state and a linear electron-phonon coupling is involved, the momentum conservation results in a phonon wing in the detected spectrum. The Debye-Waller factor accounts for the distribution of the phonon wing, which shows no coherent properties, in relation to the zero-phonon transition. See figure 2.3(b) for an illustrative picture on the resulting signal.

\[ \alpha_{\text{DW}} = \frac{I_{\text{zpl}}}{I_{\text{zpl}} + I_{\text{phw}}} \]  

(2.5)

The Debye-Waller factor \( \alpha_{\text{DW}} \) depends strongly on the energy landscape in the excited state and labels the relative intensity of the two components in a spectrum.
(a) Explanation of the Franck-Condon factor

(b) A single molecule decay to the ground state

Figure 2.3: The energy levels of a single molecule, plotted with a normalized molecular nuclei coordinate $q_i$. Due to the different distribution of the $\pi$-electron cloud in the ground and the excited states, the molecule has a different geometry between these two states. The Franck-Condon principle implies that any transition from the ground to the excited state undergoes no momentum transfer, i.e. the normalized molecular coordinate is not changed, and the transition proceeds vertically. Figures adapted from [16].
Figure 2.4: The HOMO and the LUMO of terylenemonoimide (TMI), shown as an isosurface on top and below the molecule. It is directly observable that the electronic distribution remains very similar and the FRANCK-CONDON-factor remains close to unity. The $\pi$-cloud does also not extend over the core of the terylene fluorophore, the imide-group blocks efficiently its extension to the attached diisopropylphenyl. For synthesis purposes this is advantageous, because no dramatic red-shift will occur. These figures are calculated as described in chapter A.1.1.

The internal phonon contribution results in a the FRANCK-CONDON factor $\alpha_{\text{FC}}$. Both factors originate in the same microscopic properties of the molecule and the environment in which it is embedded. The two factors can be separated, when we assume that the molecular-internal (accounted by $\alpha_{\text{FC}}$) and lattice vibrational modes (accounted by $\alpha_{\text{DW}}$) could be described independently.

By the description of the energy level diagram one has also to account for different distribution of possible orientations of the electronic $\pi$-cloud above a molecule (see figure 2.4). The FRANCK-CONDON principle defines that an electronic excitation always can be separated from the overall core coordinates of the molecule (assuming an agile electron and a slow movement of the atomic core in the molecule). The molecular ground state and the excited state have to have a certain overlap for the molecule to be excited. When the molecule is decaying back to the electronic ground state the integral amount of displacement is labeled as the FRANCK-CONDON factor.

For rigid molecules the DEBYE-WALLER factor and the FRANCK-CONDON factor are high, i.e. close to unity. This means that the geometry change in the molecular system is small between the ground and the excited state. Both factors reflect the direct transitions from the excited state back to the ground state of the molecule.

These factors become especially interesting if the coherent properties of a single molecule are taken into account: The coherent, elastic scattering is suppressed by smaller $\alpha_{\text{FC}}$ and $\alpha_{\text{DW}}$. For a review on the topics of different broadening mechanisms and on the specific factors contributing to the overall line shape refer to reference [16].
2.2.2 Stark-Shifts

The Stark shift represents a change in the spectrum by applying an external electric field.

The energy levels $W(E)$ which are shifted can be approached by

$$W(E) = W(0) - (\mu_e - \mu_g) \cdot E - \frac{1}{2}((E \cdot \alpha) \cdot E) + \ldots$$

(2.6)

with $\mu_e - \mu_g$ being the difference dipole moment between the dipole moment of the excited state and the dipole moment of the ground state and $\alpha$ as the polarizability [14]. This phenomenon is plotted in figure 2.5.

For a single molecule in a centrosymmetric environment where no disorder exists, the Stark effect shows only quadratic terms. In a host-matrix system in which the molecular symmetry is broken, the electric dipole moment on the molecule the effect is dominated by a linear response to the external electric field. In this work both effects were observed, depending on the crystallinity of the matrix in which the molecules were embedded. The more the system shows crystallinity, the more the effect becomes quadratical, due to the fact that the external electric field also introduces a polarization to the matrix. The first measurements of the Stark effect on a single molecule were performed by U.P. Wild and coworkers [17] and by M. Orrit [18].

The Stark shift of molecules is not limited to the case of an applied DC voltage. T. Latychevskaia performed several measurements where the external electrical field yielded to higher order effects [19]. The Stark effect also allows the detuning of one molecule with respect to another one, which can be used in quantum optical experiments [20].
2.2. Single Molecule Spectroscopy

Figure 2.6: Molecules which are used for single molecule spectroscopy [21]. From left to right: terrylene, dibenzantrene (DBATT) and pentacene. \( p \)-terphenyl is shown on the right which is often used as matrix system to embed single dye molecules. The arrow denotes the molecular transition dipole moment. In the used sample all molecules tend to stand out of the surface plane, so that the image corresponds to a realistic situation for thin \( p \)-terphenyl films.

2.2.3 Single Molecule Detection

As mentioned above, single molecules at low temperatures tend to have much narrower transitions: Different broadening processes, dynamics and changes in the solvation environment are suppressed. In certain molecule matrix systems the narrowing reduces their transition from the ground to the excited state to a lifetime limited value. Molecules can have transitions with a linewidth of a few megahertz. This is also strongly dependent on the matrix system which embeds the molecules, for a review on different linewidth in different polymer matrices see [22].

In a diluted sample it is possible to have distinct molecular transitions, spread over the spectral range of the inhomogeneous broadened band of the specific host-matrix system. For a sample spectrum, refer to figure 3.23 which is a typical cryogenic spectrum of one species in a frozen matrix. By changing the laser wavelength all molecules can be addressed individually.

Basically two options can be used to detect single molecules:

- Either the number of molecules is reduced in the observation space and the molecules can locally be addressed by light microscopy.

- Or at low temperature where the linewidth of a molecule is reduced, each molecule can be resonantly excited by a narrowband laser.

Absorption Type Experiments

The experiments on the statistical fine structures of absorption spectra observed by W.E. Moerner and coworkers [11] lead to the first optical detection of a single
molecule by W.E. Moerner and L. Kador in 1989 [3]. The authors prepared a $p$-terphenyl crystal, doped with pentacene. By illuminating the wings of the inhomogeneous line, they were able to spectrally select one molecule and to detect a fingerprint of it on the ongoing beam. To suppress the residual laser noise the transition line of this single emitter was modulated by FM STARK double modulation, applied to the sample by two indium-tin-oxide electrodes. In a follow up paper [23] the authors describe their technique in detail and how they were able to get rid of the limiting background laser fluctuations by the double modulation technique, which leads to a rather complex line shape. Summarizing the important step was the use of a lock-in-amplifier to suppress the noise of the incident laser beam. A suppression of noise by about 3-4 orders of magnitude was possible [24]. Unfortunately the absolute phase signal gets usually lost by using a lock-in amplifier\(^1\). Extended STARK shift experiments of L. KADOR and coworkers in 1999 made it possible to extend the experiment from 1989 to the radio frequency region (1 - 60MHz) [26]. Here the signal was about one order of magnitude larger than in the first experiments of W.E. Moerner and L. Kador [3].

One recent attempt to detect single molecules in transmission is described in [27] and uses a SAGNAC interferometer to detect the phase shift related to the absorption of light. Two counter propagating beams were transferred through a sample with terrylene molecules at room temperature. In their work the authors found about 19 molecules still detectable, which seems to be the lower limit before the signal is covered by noise. No further references are currently available on measuring the attenuation of a laser by a single molecule.

Fluorescence Excitation Spectroscopy

In 1990 M. Orrit and coworkers adapted the technique of fluorescence excitation spectroscopy to a single molecule [4]\(^2\). In this technique only the red-shifted luminescence of a molecule is observed. For low temperatures the frequency of a narrow band laser is scanned, and if the laser wavelength hits a molecular resonance, the red-shifted fluorescence is detected. The excitation light is efficiently blocked by a long-pass filter and the red-shifted fluorescence light is detected by a sensitive photodetector. This technique is only limited by the detector noise ($\approx$ 20-200 counts per second (cps)) and is from then on used as the standard technique for single molecule detection.

The detection of single molecule fluorescence extended the technique to ambient conditions – single molecules were detectable under conditions in which a standard microscope can be used. This step extended the field of single molecule detection further to biological applications. The detection of single molecule fluorescence is used nowadays to follow biological processes online like motor proteins, to monitor energy transfer between different molecules (FRET) and to overcome ensemble averaging in normal spectroscopy.

\(^1\)A review on the limiting factors, influencing the signal-to-noise ratio can be found in the description on a single atom absorption experiment [25].

\(^2\)Already in 1976 T. Hirschfeld was able to see an ensemble of 80-100 fluorophores, which were chemically linked together to a bigger molecule [28].
In literature almost all single molecule experiments are based on the technique of fluorescence detection. The main prerequisites on the used dye molecules are a) a high fluorescence quantum yield and b) a high photostability. Molecules with a small Stokes shift cannot be detected by fluorescence excitation spectroscopy, because of the finite width of usual filter characteristics. This would make transmission measurements favorable.

2.3 Absorption Spectroscopy

2.3.1 Beer-Lambert Law

One of the standard techniques in chemistry and biology is absorption spectroscopy. A known reference solution and an unknown sample are illuminated by a monochromatic light source. The differential signal shows that the light beam through the sample is attenuated if it contains dye molecules. The initial intensity of light is usually written as $I_0$ and the transmitted intensity is $I$. The derived results in absorption spectroscopy are usually plotted in units of transmittance $T$ or absorbance $A$. The transmittance $T$ is simply the ratio between the resulting intensity $I$ and the initial light intensity $I_0$. $T = \frac{I}{I_0}$. The absorbance $A$ is defined as the logarithmic function: $A = -\log \left( \frac{I}{I_0} \right)$. The findings of Bouger, Lambert and Beer result in a) the linear proportionality between the absorbance and the optical path length $l$), the logarithmic behavior of the transmission vs. the optical path length and c) the linear proportionality of the absorbance to the concentration of an absorbing compound.

All together this melts down to the Beer-Lambert(-Bouguer) law:

$$A_\lambda = -\log \left( \frac{I}{I_0} \right) = c \varepsilon_\lambda l$$

(2.7)

where $c$ represents the concentration of the sample, $\varepsilon_\lambda$ the linear, decadic absorption coefficient and $l$ the path length through the medium. Usually this law is rewritten in optics as

$$I = I_0 e^{(-\alpha_\lambda c l)}$$

(2.8)

with $\alpha_\lambda$ as the Napierian absorption coefficient ($\alpha = (\ln10) \varepsilon_\lambda$).

Now, since we know the concentration and by this also the number of molecules ($N$) in a sample, we can associate an absorption cross-section $\sigma_{\text{abs}}$ to each molecule. The Beer-Lambert(-Bouguer) law becomes:

$$I = I_0 e^{(-\sigma_{\text{abs}} Nl)}$$

(2.9)

The absorption cross-section represents the area in which a single molecule behaves as a black disk. It follows, that the relation between the Napierian absorption coefficient and the absorption cross-sections is as follows:

$$\sigma_{\text{abs}} = \alpha_\lambda / N_A$$

(2.10)
All of the key quantities, such as the absorption coefficient and also the absorption cross-section are wavelength dependent. Hitting a molecular resonance the molecule shows a strong response to the optical field. When no transitions of a molecule are driven, the molecule is transparent and shows only a small response to the incident light. Non resonant Rayleigh scattering becomes important, which is proportional to the 4th power of the frequency of the incident light. This process leads to the blue sky with the air scattering stronger in the blue wavelength region. Calculations of the absorption cross-section of a molecule by measuring the room-temperature absorption coefficient, results in values for $\sigma_{\text{abs}}$ which is in the same magnitude as the physical extension of the molecule. By comparing the coefficients it can be shown that

$$\sigma_{\text{abs}} = 1000 (\ln 10) \varepsilon_\lambda / N_A \quad (2.11)$$

By reducing the temperature and thus reducing the linewidth of the electronic transition by freezing out several decay channels, the value $\sigma_{\text{abs}}$ becomes larger. The area below the absorption spectrum remains roughly the same, but the resonant interaction of the molecule to the external lightfield enhance. At low temperatures the absorption cross-section increases tremendously \cite{14}.\footnote{Furthermore the survival time (time until a bleaching event occurs) of a single molecule is significantly enhanced. Thereby it is possible to get more and more photons in total of a single molecule. In the current work the molecules usually survived for an arbitrary time, until an external invasive event occurred (e.g. mechanical interaction with the cryostat). For a further discussion of the emissivity see \cite{29}.}

### 2.3.2 Calculating the Scattering Cross-section

Not only molecules change the intensity of an ongoing light beam, also pure two level systems can scatter light out of an ongoing beam.

The complete term for the scattering cross-section for a resonantly driven two level system can be estimated if we calculate the differential attenuation of an incident light beam which is transmitted through a resonant optical medium. The resonant, elastic scattering of atoms in a light field is simply proportional to the population of the atom in the excited state and its decay rate $\Gamma_{\text{nat}}$. This is the maximum rate with which a two-level system could emit single photons.

With a population of the excited state noted as $\rho_{22}$ and a decay rate of $\Gamma_{\text{nat}}$, the scattering rate reads

$$\Gamma_{\text{scat}} = \Gamma_{\text{nat}} \rho_{22} \quad (2.12)$$

For the population of the upper state $\rho_{22}$ we can write \cite{30}:

$$\rho_{22} = \frac{S_0/2}{1 + S_0 + 4\delta^2 / \Gamma_{\text{nat}}} \quad (2.13)$$

with $S_0 = \frac{\Omega^2}{\Gamma_{\text{nat}}^2}$ and $\delta = (\omega - \omega_0)$ as the detuning from resonance. So

$$\Gamma_{\text{scat}} = \frac{\Gamma_{\text{nat}} S_0}{2} \frac{2}{1 + S_0 + 4\delta^2 / \Gamma_{\text{nat}}^2} \quad (2.14)$$
In an optical medium with \( n \) scatterers the differential dependence of the intensity on the optical axes reads as

\[
\frac{dI}{dz} = -\hbar \omega n \Gamma_{\text{scat}}
\]  

(2.15)

assuming the system to be on resonance \((\omega - \omega_0 = \delta = 0)\), as well as the low excitation limit \((S_0 \ll 1)\) and defining \( I_{\text{sat}} = I/S_0 = \frac{\pi \hbar c \Gamma_{\text{nat}}}{3\lambda^3} \) we can associate to the differential change of intensity

\[
\frac{dI}{dz} = -\hbar \omega n \frac{I}{I_{\text{sat}}} \frac{\Gamma_{\text{nat}}}{2} = -\sigma_{\text{scat}} n I
\]  

(2.16)

solving this differential equation, it can be shown that it derives to

\[
I(z) = I_0 e^{-\sigma_{\text{scat}}nz}
\]  

(2.17)

for a calculation of \( \sigma_{\text{scat}} \) for one scatterer this can be reformulated to

\[
\sigma_{\text{scat}} = \frac{\hbar \omega \Gamma_{\text{nat}}}{2I_{\text{sat}}} = \frac{\hbar \omega \Gamma_{\text{nat}} 3\lambda^3}{2\pi \hbar c \Gamma_{\text{nat}}} = \frac{3}{2\pi} \lambda^2
\]  

(2.18)

Interestingly the scattering cross-section on resonance is only dependent on the transition frequency and independent of all other atomic or molecular properties. This equation can also be derived in similar ways, see e.g. [31].

This is the maximal achievable scattering cross-section for a single quantum system. This entity is strictly defined only valid under the condition of plane wave illumination and for a pure two level system, which is resonantly driven. Under ambient conditions usually the transitions are broadened and not lifetime limited – then the scattering cross-section reduces to much smaller values. The linebroadening of the resonance can be expressed as a reduced lifetime of the excited state. This is the main diminishing factor of \( \sigma_{\text{scat}} \).

The scattering cross-section becomes:

\[
\sigma_{\text{scat}} = \frac{3\lambda^2 \Gamma_{\text{nat}}}{2\pi \Gamma_{\text{hom}}}
\]  

(2.19)

These equations are only valid for a two level system which is perfectly oriented with its transition dipole moment along the incident polarization of the incoming light. Adding the geometrical factor \( \beta \), which accounts for the orientation of the transition dipole moment, relative to the incident laser field. This geometrical factor \( \beta = 3 \cos^2 \theta \) is 3 at maximum.

\[
\sigma_{\text{scat}} = 3 \cos^2 \theta \frac{\lambda^2 \Gamma_{\text{nat}}}{2\pi \Gamma_{\text{hom}}}
\]  

(2.20)
As explained in chapter 2.2.1 for a molecule that is resonantly driven, only a part of the light is emitted on the 0-0 transition. The branching ratio expresses what amount of light is emitted on the incident wavelength of light in relation to the distribution to vibrational levels. Here the differential overlap between the energy levels of the excited state to the ground state becomes important. To account for the overlap between the excited level and the different states of the ground state the FRANCK-CONDON-factor $\alpha_{FC}$ is introduced. However, even if the light is emitted by a decay of the excited molecule into the electronic ground state, a certain amount of light is not coherent with the incident light field. This leads to a further diminishing factor $\alpha_{DW}$, which accounts for the phonon wing of the transition. The scattering cross-section for a molecule reads

$$\sigma_{\text{scat}} = 3 \cos^2 \theta \alpha_{DW} \alpha_{FC} \frac{\lambda^2}{2\pi} \frac{\Gamma_{\text{nat}}}{\Gamma_{\text{hom}}}$$ (2.21)

This description is fully equivalent to the description in [32]. Now it is possible to calculate the scattering cross-section of a single molecule since we know its microscopic properties under plane wave illumination. By defining the scattering cross-section one major problem remains: One might think that the absorption of light by a single emitter has no relation to its scattering properties. To get more insight into the topic of light-matter interaction, it is important to understand the process in the terms absorption and scattering discussed below.

### 2.3.3 Extinction

#### Absorption

Although the above terms associate the term absorption to the phenomena of an attenuated light beam behind the sample, the term is usually defined as the amount of energy which is transferred to other forms of energy. When a black object is exposed to light, the usual interaction of light with this object results into a heating of the object. The amount of absorbed light is equivalent to the thermal change of the system. In this respect we can associate for the single molecule the energy dissipation over the fast decay over channel $3 \rightarrow 1$ as the transfer to heat. If we would monitor the emission from the electronic excited state to the vibrational levels of the electronic ground state, we would indirectly record the amount of energy which is transferred to heat, since we know that for every emitted red-shifted photon a certain ratio is also transferred to warm up the system. The obtained fluorescence excitation spectra show accordingly an absorption line.

On the other hand a single atom, if it is treated as a pure two level system, does not contribute to the absorption process at all, if we define it as the transfer to heat. A resonantly driven atom, that is weakly excited on resonance with a continuous wave laser would cycle from the ground to the excited state by absorbing a photon and then by emitting a photon on the driving optical frequency from the excited state back to the ground state. In the terminology of the the EINSTEIN coefficients the term $B_{12}$ is also defined as absorption and is describing the amount of light

---

4 Unfortunately the notation in [32] differs slightly from ours, and also in literature several sources define the reducing factor as $\frac{\Gamma_{\text{nat}}}{\Gamma_{\text{crit}}}$ and not $\frac{\Gamma_{\text{nat}}}{\Gamma_{\text{hom}}}$. The introduced description is equivalent.
which is “eaten” up by a single two-level system. This definition will not be used. The definition of absorption to be the amount of light which is transferred to other forms of energy (heat) is from now on the terminology which is used in the present work.

**Scattering**

Nevertheless if we take a pure two level system, the intensity of a transferred, directed light beam is attenuated. This effect is only due to scattering light out of the ongoing beam. If the single two-level system is excited, it releases a photon by a different polar pattern than the initial mode of the incident light beam. Scattering assumes that the system is something like a small “shiny” particle. Scattering can happen basically in two different ways: The scattering can be *elastic*. Then the phase relation between the incident light beam and the scattered photon is preserved, but the directionality is not preserved. A process of elastic scattering is RAYLEIGH-scattering.

If the scattering event happens in an *inelastic* manner, the phase relation between the incident light and the scattered photon is lost and the emission is incoherent. The whole system shows in scattering the response as a driven classical harmonic oscillator with a phase shift of \( \frac{\pi}{2} \) on resonance. Sweeping the laser frequency over the complete resonance, the driven emitter shows a phase change of \( \pi \).

**Extinction**

If we monitor the amount of light on a detector behind the sample, we have to take into account both components, absorption and scattering. The recorded signal is the *extinction*, that is defined as sum of scattering and absorption. This is the signal which is detected in a transmission experiment,

\[
\text{Extinction} = \text{Scattering} + \text{Absorption} \quad (2.22)
\]

An elegant treatment of this description can be described in terms of the optical theorem.

**2.3.4 Optical Theorem**

If we assume a single emitter to be placed in the middle of our observation space and a virtual sphere \( \Sigma \) centered at the origin (as shown in 2.7(a)), all energy which is flowing into the sphere also has to leave the sphere\(^5\). This can be written as follows:

\[
W_{\text{in}} = W_{\text{out}} \quad \text{or} \quad W_{\text{tot}} = W_{\text{in}} - W_{\text{out}} = 0 \quad (2.23)
\]

The incident power \( W_{\text{in}} \) which is flowing into the system results from the excitation fields, \( \mathbf{E}_{\text{exc}} \) and \( \mathbf{H}_{\text{exc}} \). The component \( W_{\text{out}} \) consists of two components: The coherent components \( W_{\text{coh}} \) and the incoherent emission from the single emitter \( W_{\text{abs}} \) (e.g. heat). By introducing the Poynting vector \( \mathbf{S} = \mathbf{E} \times \mathbf{H} \), representing the energy flow through the system, we can derive:

\(^5\)steady state assumption
Figure 2.7: Different situations to detect the response of a molecule on a far-field detector. Figure 2.7(a) shows the case where a molecule is excited in a plane wave and the detector in the far field is exactly on axis. The detected signal is a dispersive curve, similar to the phase shift of a driven classical harmonic oscillator.

\[
W_{\text{tot}} = \int_\Sigma S \, d\mathbf{A} + \left( \int_{\text{coherent}} W_{\text{abs}} - \int_{\text{incoherent}} W_{\text{abs}} \right) = 0 \quad \Rightarrow \quad - \int_\Sigma S \, d\mathbf{A} = W_{\text{abs}} \quad (2.24)
\]

and by decomposing the coherent electric and magnetic field into exciting and molecular components

\[
E = E_{\text{exc}} + E_{\text{mol}} \quad \text{and} \quad H = H_{\text{exc}} + H_{\text{mol}} \quad (2.25)
\]

the absorbed power is [33]:

\[
W_{\text{abs}} = - \int_\Sigma S \, d\mathbf{A} \quad (2.26)
\]

\[
= - \int_\Sigma \left\{ E_{\text{exc}} \times H_{\text{exc}} - W_{\text{scat}} + E_{\text{mol}} \times H_{\text{mol}} - W_{\text{scat}} - E_{\text{mol}} \times H_{\text{exc}} - E_{\text{exc}} \times H_{\text{mol}} - W_{\text{ext}} \right\} \, d\mathbf{A}
\]

This proves that the total absorbed power is assembled by the scattered components \( W_{\text{scat}} \) and the extinction \( W_{\text{ext}} \). For a transmission measurement the detector covers usually not a hole sphere around the emitter. If only a small fraction of the sphere is covered by a detector the directly scattered component \( W_{\text{scat}} \) becomes negligible small, \( W_{\text{scat}} \approx 0 \), so that \( W_{\text{abs}} \approx - W_{\text{ext}} \).

In the forward direction on axis the spherical scattered components \( E_{\text{mol}} \) and \( H_{\text{mol}} \) behave like a plane wave. In all other angles the integrand \( S_{\text{ext}} \, d\mathbf{A} \) oscillates rapidly [34, 35], so it does not contribute significantly to the extinguished power \( W_{\text{ext}} \). With an integration over the area \( D \) of a detector which is placed in the forward direction it can be shown that [34]:

\[
-W_{\text{abs}} = \int_\Sigma S_{\text{ext}} \, d\mathbf{A} \approx \int_D S_{\text{ext}} \, d\mathbf{A} \quad (2.27)
\]

the detected power \( W_{\text{det}} \) is
2.3. Absorption Spectroscopy

\[ W_{\text{det}} = \int_D \{E_{\text{exc}} \times H_{\text{exc}}\} \, dA - W_{\text{ext}} \quad (2.28) \]

So the drop of intensity on the detector reflects the measured extinction. The optical theorem summarizes the effect which is detected on a far-field detector by pointing out that a detector directly on axis with a physical extension which covers more than the first FRESNEL zone\(^6\) detects directly the extinction signal \(-W_{\text{ext}}\). If the detector covers more than the FRESNEL zone the signal oscillates quickly and levels out.

In figure 2.7 all important cases for a transmission experiment are illustrated: in 2.7(a) the detector is placed in the far field, directly on axis and is infinitesimally small. The resulting signal shows the extinction of light by an emitter which behaves like a driven classical harmonic oscillator and shows a dispersive curve. If the first FRESNEL zone is covered, the detector detects a signal which only shows a drop in the intensity (see equation 2.27).

In the case that the single emitter is located in a GAUSSIAN focus, the resulting signal on the detector can be described by a \(\frac{\pi}{2}\) phase shift by the emitter and a \(\frac{\pi}{2}\) GOUY phase shift [36]. The same holds for the description for an aperture. Figure 2.7(c) shows the case for an emitter in the center of an aperture. Both phaseshifts together result in a drop of intensity detected on the detector. This effect is independent of the detector dimension.

2.3.5 An Intuitive Picture

The optical theorem describes the signal which is detected by a far-field detector and relates this to the incident light field and the POYNTING vector \(\mathbf{S}\), which describes the flow of energy for optical fields.

The authors H. PAUL & R. FISCHER introduce an intuitive view on the extinction of light in their paper “Light Absorption by a Dipole” [37], which describes a single dipole which is placed in space and excited by a plane wave. The basic idea is to plot the POYNTING vector for the situation as in figure 2.8. The plane wave excites the dipole system, that is located in the origin of the plot from the left. The plotted streamlines of the POYNTING vector “flow” into the excited dipole.

The basic steps in deriving the picture of the POYNTING vector are to set up the formulae for the initial exciting plane wave and also the dipolar radiation. The initial intensity was assumed to be as large that the effect of a spontaneous emission from the upper level can be neglected. The probability to find the system in the excited state would be 1/2. At this point the effect of a single emitter is the largest. For a probability to find the dipole in the excited state of 0, the system cannot emit any photon and no effect occurs. When the probability to find the molecule in the excited state is unity, also no effect is expected: The system shows transparency and is “charged” with a photon. In the classical picture the system can be treated like an antenna.

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\(^6\)This happens quasi automatically: The lateral extension of the FRESNEL zone can be calculated as \(0.5\sqrt{\lambda z}\), with \(z\) being the distance to the detector. So a detector which has an extension of 500\(\mu\)m covers the first FRESNEL zone, if the detector is as far away as our detector (2m). If the detector is only 1mm away from the sample under study, the size of the detector had to be smaller than 10\(\mu\)m to include only the first FRESNEL zone.
Figure 2.8: Visualizing the Poynting vector with streamlines for a dipole extinction experiment. The dipole is placed in the middle at point (0,0). The description is a purely classical picture where the exciting plane wave is coming from the left. The virtual absorption cross-section is sketched on the left side. All streamlines within this area travel into the middle of the picture. All units are in $k = \omega/c$.

If the dipole is strongly driven, the process of stimulated emission can occur. Then the figures in 2.8 changes as if the illumination would come from the right side and the propagating wave would take out energy from the system.

The picture can be derived relatively simple: The electric and magnetic field are defined for the light source and for the dipole and then the Poynting vector is visualized (see chapter A.3.1 for the equations). One of the main steps was a convenient visualization. The shown streamline plot could be obtained by making the coordinates $xy$, respectively $xz$ from the Poynting vector dependent from another variable $t$. The final plots look like 2.8. The code to derive the plot is given in the appendix A.3.1.

This picture is defined for a single emitter in a plane wave excitation. By changing the incident field from a plane wave to e.g. a focussed spot, the properties of the picture change also. The above derived picture of an absorption cross section is strictly only defined for a plane wave excitation.

Parallel to this publication also C. Bohren shows in [38] a single metal particle which extincts light from an area which is larger than its physical extension. A following paper by E. Shamonina and coworkers [39] shows calculations to the effective aperture of a receiving dipole in a plain wave. Here the calculations of H. Paul & R. Fischer are reproduced and the effective shape of the aperture is shown, especially under conditions where a detuning $\delta = (\omega - \omega_0)$ and a linewidth $\Gamma$ are introduced.

### 2.3.6 Coherent and Incoherent Photons

The fact that the attenuation of the transmitted light through a sample is described as the extinction in an interferometric manner, needs a closer look on the different components on the detector. Only components which show a fixed phase relation between the incident light and the light emitted from the molecule contribute to the effect of extinction, that is associated to the cross-terms in equation 2.35. Further-
more the scattered components of the molecular field $\langle \hat{\mathbf{E}}_{\text{mol}}^- \cdot \hat{\mathbf{E}}_{\text{mol}}^+ \rangle$ also take into account the incoherent emissions by the molecule. First of all all the branching ratio, splitting the emission into the incident wavelength and the red-shifted fluorescence diminishes the effect, because these photons cannot destructively interfere with the incident field.

The transition dipole moment for the transition from the excited state to the electronic and vibrational ground state is labeled as $d_{21}$.

If the illumination is not uniform and we want to account for different field components in different directions, we introduce a modal factor $f$, which describes the angular dependence of the emission as $f = |f|e^{i\phi}$ we can write the intensity (coherent and incoherent line like in figure 2.3(b)) to the ground state to be proportional to the population in the excited state $\rho_{22}$ as

$$I_{21} = |f|^2 |d_{21}|^2 \rho_{22} \quad (2.29)$$

which represents the scattered emission, with coherent and incoherent components. It is equivalent to:

$$I_{21} = I_{21}^{\text{coh}} + I_{21}^{\text{incoh}} = \langle (\hat{\mathbf{E}}_{\text{mol}}^{-\text{coh}} + \hat{\mathbf{E}}_{\text{mol}}^{-\text{incoh}}) \cdot (\hat{\mathbf{E}}_{\text{mol}}^{\text{coh}} + \hat{\mathbf{E}}_{\text{mol}}^{\text{incoh}}) \rangle$$

$$= \langle \hat{\mathbf{E}}_{\text{mol}}^- \cdot \hat{\mathbf{E}}_{\text{mol}}^+ \rangle \quad (2.30)$$

The important component in the extinction measurement is indeed the term $2\mathcal{R}(\langle \hat{\mathbf{E}}_{\text{exc}}^- \cdot \hat{\mathbf{E}}_{\text{mol}}^+ \rangle)$. The 0-0 transition to the electronic and vibrational ground state is split into a direct transition and also the phonon wing, with an intensity ratio, described by the Debye-Waller factor (see chapter 2.2.1). The coherent component of the 0-0 transition is described by:

$$\langle \hat{\mathbf{E}}_{\text{mol}}^{\text{coh}}(r) \rangle = \sqrt{\alpha_{\text{DW}}} d_{21} \rho_{22} u_{\text{det}} \quad (2.31)$$

here $u_{\text{det}}$ is the unit vector from the excitation field on the detector at the position $r$. For the extinction also the excitation field $\langle \hat{\mathbf{E}}_{\text{exc}} \rangle$ has to be described. For this we also introduce a modal factor $g = |g|e^{i\phi}$ describing (similar to the factor $f$) the mode from excitation laser onto the detector. The component of the excitation field can be written as:

$$\langle \hat{\mathbf{E}}_{\text{exc}}^+(r) \rangle = [\langle \hat{\mathbf{E}}_{\text{exc}}^+(r_m) \rangle \cdot u_{\text{mol}}] g u_{\text{det}} \quad (2.32)$$

The intensity of the excitation field on the detector reads as

$$I_{\text{exc}} = \langle \hat{\mathbf{E}}_{\text{exc}}^- \cdot \hat{\mathbf{E}}_{\text{exc}}^+ \rangle = |g|^2 [\langle \hat{\mathbf{E}}_{\text{exc}}^+ \rangle \cdot u_{\text{mol}}]^2 \quad (2.33)$$

The extinction component of equation 2.35 reads as follows:

$$2\mathcal{R}(\langle \hat{\mathbf{E}}_{\text{exc}}^- \cdot \hat{\mathbf{E}}_{\text{mol}}^+ \rangle) = 2\mathcal{R}(\langle \hat{\mathbf{E}}_{\text{exc}}^- \rangle \cdot u_{\text{mol}}) g u_{\text{det}} \cdot \langle \hat{\mathbf{E}}_{\text{mol}}^{\text{coh}^+} \rangle$$

$$= \sqrt{\alpha_{\text{DW}}} d_{21} g f [\langle \hat{\mathbf{E}}_{\text{exc}}^- \rangle \cdot u_{\text{mol}}] \rho_{21} \quad (2.34)$$

To account for the amount of light on a far-field detector, it can be calculated as:
\[ I_{\text{det}} = \langle \hat{E}_{\text{exc}}^- \cdot \hat{E}_{\text{exc}}^+ \rangle + 2\Re(\langle \hat{E}_{\text{exc}}^- \cdot \hat{E}_{\text{mol}}^+ \rangle + \langle \hat{E}_{\text{mol}}^- \cdot \hat{E}_{\text{mol}}^+ \rangle) \]  

(2.35)

This description of the intensities can be used for all further descriptions. To achieve the values of \( \rho_{22} \) and \( \rho_{21} \) we use the optical BLOCH equations, that will be described in the next section.

### 2.3.7 Optical Bloch Equations

The formalism of optical BLOCH equations represents the state of a three level system. This approach adopts a semiclassical description: The levels of the molecule under study are quantized but the light field is not.

In this chapter the three level case is introduced. If the fact is considered that the lifetime of the vibrational level is short with respect to the lifetime for the excited state, the two level case \([40]\) can be used with modified values for the lifetime of the excited state.

#### Three-level Systems

For a three level system one can describe the complete state of the system in terms of a density matrix like

\[
\rho = \begin{pmatrix}
\rho_{11} & \rho_{12} & \rho_{13} \\
\rho_{21} & \rho_{22} & \rho_{23} \\
\rho_{31} & \rho_{32} & \rho_{33}
\end{pmatrix}
\]  

(2.36)

The populations read as follows, where the levels are \( \rho_{11} \) for the population in \( |g\rangle \), \( \rho_{22} \) for the population in \( |e\rangle \) and \( \rho_{33} \) for the population in the vibronic state.

\[
\rho_{11} + \rho_{22} + \rho_{33} = 1
\]  

(2.37)

Due to the fact that the emitted photons when the system drops to the vibrational level are not coherent with the incident laser field, one can write for the coherences:

\[
\rho_{13} = \rho_{31} = \rho_{23} = \rho_{32} = 0
\]  

(2.38)

To find the equations of motion we can write for the density matrix in the rotating wave approximation

\[
\dot{\rho}_{11} = -\frac{1}{2}i\Omega(\rho_{12} - \rho_{21}) + k_{21}\rho_{22} + k_{31}\rho_{33}
\]  

(2.39)

\[
\dot{\rho}_{22} = \frac{1}{2}i\Omega(\rho_{12} - \rho_{21}) - (k_{21} + k_{23})\rho_{22}
\]  

(2.40)

\[
\dot{\rho}_{33} = k_{23}\rho_{22} - k_{31}\rho_{33}
\]  

(2.41)

\[
\dot{\rho}_{12} = \frac{1}{2}i\Omega(\rho_{22} - \rho_{11}) - (i\delta + \Gamma_2/2)\rho_{12}
\]  

(2.42)

The whole description for a three level system reduces back to a two level system, if we take into account
2.3. Absorption Spectroscopy

\[ k_{31} \gg k_{23} \]  

This implicates that the system has its population basically never in the excited vibrational states of the electronic ground state. The lifetime of a single molecule is in the nanosecond timescale for the first electronic excited state ($\approx$ MHz linewidth) and about three orders of magnitude smaller for the vibrational states. These states will only be weakly populated and we introduce a correction factor

\[ K = 1 + \frac{k_{23}}{2k_{31}} \]  

The steady state Bloch vector \( \begin{pmatrix} u \\ v \\ w \end{pmatrix} \), which is a geometrical description for a two-level quantum mechanical system, can be described by the following components:

\[
u = -\frac{\Omega}{2} \frac{\delta}{\left(\delta^2 + \Gamma_2^2/4 + \Omega^2 K \Gamma_2/\Gamma_1\right)} \tag{2.45}
\]

\[
v = -\frac{\Omega}{2} \frac{\Gamma_2}{\left(\delta^2 + \Gamma_2^2/4 + \Omega^2 K \Gamma_2/\Gamma_1\right)} \tag{2.46}
\]

\[
w = \frac{\Omega^2}{2} \frac{\Gamma_2}{\Gamma_1 \left(\delta^2 + \Gamma_2^2/4 + \Omega^2 K \Gamma_2/\Gamma_1\right)} - \frac{1}{2} \tag{2.47}
\]

here $\Gamma_2 = \frac{1}{T_2}$ represents the overall decay rate, $\Gamma_1$ is the decay rate of the upper state and $\Gamma_2^*$ the dephasing rate. These findings are completely equivalent to the described steady state Bloch vectors in [40], where the assumption $\Gamma_2 = \frac{1}{2} \Gamma_1$ accounts for the situation of a pure two level system with no dephasing and the correction factor $K$ to be unity.

For the steady state population $\rho_{22}$ and for the coherence $\rho_{21}$ we can write:

\[
\rho_{22} = \frac{\Omega^2 \Gamma_2}{2 \Gamma_1 \left(\delta^2 + \Gamma_2^2/4 + \Omega^2 K \Gamma_2/\Gamma_1\right)} \tag{2.48}
\]

\[
\rho_{21} = -\frac{\Omega (\delta - i \Gamma_2/2)}{2 \left(\delta^2 + \Gamma_2^2/4 + \Omega^2 K \Gamma_2/\Gamma_1\right)} \tag{2.49}
\]

With the assumption of low excitation ($\Omega^2 \ll (\Gamma_2/\Gamma_1)$), and a Lorentzian line-shape of

\[
\mathcal{L}(\nu) = \frac{1}{\delta^2 + \Gamma_2^2/4 + \Omega^2 (\Gamma_2/\Gamma_1) K} \simeq \frac{1}{\delta^2 + \Gamma_2^2/4} \tag{2.50}
\]

these equations reduce to:

\[
\rho_{22} = \frac{\Omega^2 \Gamma_2}{2 \Gamma_1} \mathcal{L}(\nu) \quad \rho_{21} = -\frac{1}{2} \Omega (\delta - i \Gamma_2/2) \mathcal{L}(\nu) \tag{2.51}
\]

To describe the physical origin of the terms which are used to describe the altered transmission of light, we can rewrite the Rabi frequency as $\Omega = \sqrt{\alpha_{\text{PDW}} d_{21} \langle |\hat{E}_{\text{exc}}(r_m)| \cdot u_{\text{mol}}|/h}$ and $\varphi$ being the relative phase-shift. The cross terms like in 2.35 can be described as:
The formula which can be used to derive the intensity on a detector reads as [41]:

\[ I_{\text{det}} = I_{\text{exc}} \left[ 1 + \alpha \frac{\Gamma_2}{2\Gamma_1} \frac{|g|^2}{|f|^2} L(\nu) \right] \]

\[ - \alpha \frac{\Gamma_2}{2} \frac{|g|^2}{|f|^2} L(\nu) \left( \delta \cos \varphi + \frac{\Gamma_2}{2} \sin \varphi \right) \]

For further calculations and to determine the coherently and incoherently scattered photons, one can write:

\[ R_{\text{coh}} = |u - iv|^2 \quad R_{\text{incoh}} = \rho_{22} - R_{\text{coh}} = w + \frac{1}{2} - (u - iv)^2 \]

The components of emission on the wavelength of the incident light and the red shifted component can simply be calculated by the different rates with which the system decays, either directly to the electronic ground state or to the vibrational levels.

\[ I_{23} = k_{23}\rho_{22} \quad I_{21} = k_{21}\rho_{22} \]

With the assumed values, which are estimated from experiments of \( k_{23} = 7\text{MHz}, \) \( k_{21} = 3\text{MHz} \) and \( k_{31} = 10\text{GHz} \) and a dipole moment of \( 10^{-32}\text{Vm} \) and a dephasing rate of \( \Gamma_2^* = 5\text{MHz} \) and assuming an excitation intensity of \( I_0 = 1\text{GHz} \) everything roughly corresponds to the experimental conditions from this work. The plotted examples are using the above equations and parameters.

In figure 2.10 the amount of coherent and incoherent photons is plotted, as well as the ratio between these two components. The figure 2.10(a) describes a system where the dephasing rate \( \Gamma_2^* \) is zero and is described by the pure two level system equations as follows:

**Figure 2.9:** Different simulated extinction lineshapes for frequency scans (\( \delta \)) with different values for \( \varphi \). For these calculations equation 2.54 was used.
2.3. Absorption Spectroscopy

Figure 2.10: Left: Coherent and incoherent photons emitted by a pure two level system. No further broadening mechanisms are taken into account. The upper, grayish curve shows the ratio of coherent to incoherent photons. In the right figure a dephasing rate of $\Gamma_2^* = 5$MHz is introduced. The ratio from coherent to incoherent photons is smaller as in the case of no dephasing.

\[
\frac{1}{\eta^2} \langle I_{\text{coh}} \rangle = |u + iv|^2 = \frac{s}{2(1 + s)^2}
\]  \hspace{1cm} (2.57)

with $s$ being the saturation parameter, defined as $s = \frac{\Omega^2/2}{\delta^2 + (\Gamma/4)^2}$ and $\eta$, representing a modal factor, which represents the collection area. For small excitation energies the behavior is a linear increase of the coherent emission. After a maximum value at $s = 1$ the amount of coherent photons decreases.

To describe the incoherently emitted photons one can write:

\[
\frac{1}{\eta^2} \langle I_{\text{incoh}} \rangle = \rho_{22} - |u + iv|^2 = \frac{s^2}{2(1 + s)^2}
\]  \hspace{1cm} (2.58)

Here the quadratic dependence on the excitation intensity can be seen.

The relation between coherent and incoherent photons of a single quantum system without dephasing is inversely dependent on the excitation intensity. This is plotted in figure 2.10 as a gray line.

\[
\frac{\langle I_{\text{coh}} \rangle}{\langle I_{\text{incoh}} \rangle} = \frac{1}{s}
\]  \hspace{1cm} (2.59)

If dephasing is introduced with a rate of $\Gamma_2^* = 5$MHz the picture changes to figure 2.10(b). Still the behavior of the coherent photons starts linearly, whereas the incoherent photons do not show a quadratic behavior in the first part anymore. Nevertheless the ratio of coherent to incoherent photons changes similar as in the plot without dephasing. The values are smaller for the case with dephasing.

The ratio of coherent and incoherently emitted photons becomes important, when the extinction of light is described in terms of an interference phenomenon. When the initial light intensity starts linear as the incident light intensity, the extinction
Figure 2.11: Ratio of coherent to incoherent photons, plotted as function of the dephasing rate and the excitation power. It can derived that a change in the rate of $\Gamma_2^*$ results in the same change as a saturation of the molecule.

effect starts as a constant (see also figure 4.35). For low excitation powers the signals behave as follows:

$$I_{\text{scat}}, I_{\text{fluor}} \propto I_{\text{exc}}$$  \hspace{1cm} (2.60)

When the single molecule is excited with more power, the line in the fluorescence excitation spectrum broadens as it would be the case for a pure two level system. The optical BLOCH equations can be used to plot the behavior of a single molecule as well for fluorescence excitation spectra, as for measurements on the initial wavelength which resonantly excite the molecule and its resulting measurements. The amount of coherent and incoherent photons can be estimated and the overall extinction of light can be described.

The summarized results in this section are:

- changing the excitation intensity has the same effect on the ratio of coherent to incoherent photons as introducing a dephasing rate $\Gamma_2^*$, the ratio becomes proportional to $\frac{1}{\Gamma_2^*}$ (see figure 2.11)

- The amount of coherent light shows a deviation from the behavior of LORENTZian line shapes. This effect could not be measured directly, because both components on the incident wavelength appear the same time with a LORENTZian lineshape.

2.4 Microscopy & Near-field Optics

The interaction between a single molecule and an external light field is strongly dependent on the interaction area of both components. The probability $p_{1\rightarrow2}$ of light interacting with the molecule increases as
where $A$ represents the area on which the incident light field is focussed. By further and further confining the light the interaction becomes larger and the effect is getting bigger. Usually the confinement of light is done by focussing the amount of light to a small area. The maximum achievable confinement is then limited by the wave nature of light and is called the *diffraction limit*. In this chapter the diffraction limit is reviewed and specific cases of light microscopy are explained. To confine light in a microscopic setup further than this classical limit, near-field optical methods are introduced. The chapter closes with a review on experiments with highly confined light and a single emitter.

### 2.4.1 The Diffraction Limit

When light propagates through an optical focussing system the focal spot size is limited by diffraction. The resulting pattern of the focussed light is not an infinite small point and the overall distribution is given by an *Airy* function. The focal pattern and a cross-section through the intensity distribution can be seen in figure 2.12. In principle the lateral extension of this function goes up to infinity and depends on the wavelength and the parameters of focussing.

The equation to derive such a distribution with the first order *Bessel* function ($J_1$) reads as follows:

$$I = I_0 \left( \frac{2J_1(\lambda\pi)}{\lambda\pi} \right)^2$$  

and follows basically the concept of *Huygens* principle and the *Fraunhofer* diffraction on a circular aperture. Also in microscopy the size of the aperture matters: The bigger the incident angle onto the sample, the higher the resolution can be. The different components result in a smaller spotsize through interference. This quantity as *numerical aperture* is defined as $NA = n \sin \theta$ with $n$ as the refractive index and $\theta$ as the incident angle of the light from the microscope objective towards the sample. With microscope objectives the limiting factor is the refractive index ($n$) of the medium towards the sample. With usual *air-objectives* (refractive index $= 1$) the numerical aperture cannot exceed the value 1. Only objectives with a higher index medium between the actual objective and the sample can exceed this value. Modern microscope objectives for ambient temperatures can have numerical apertures up to 1.6 by using an immersion liquid (usual an oil with a high index of refraction) between the sample and the objective.

For low temperatures such objectives are not available due to the lack of immersion liquids. The only option to exceed this value is the use of an objective which has an immersion medium “built in” – for cryogenic conditions only solid immersion lenses (SILs) [42] would allow to achieve numerical apertures larger than 1.

E. Abbe formulated the diffraction limit and the *Rayleigh* criterium defines two different points as resolved, if their center is more far away than the first minimum of the resulting function, that is located at $\approx 1.22\lambda$. Then the depth of the dip between the structures is 26.5 % (see figure 2.13).

The diffraction limit is defined by the radius of the first minimum of the resulting *Airy* function. It can be formulated as
Figure 2.12: Cut through a diffraction limited spot on the image plane. The first minimum of the resulting AIRY function is at 1.22 \( \lambda \). The gray curve shows the original AIRY function fitted with a GAUSSian curve.

\[
r = 0.61 \frac{\lambda}{n \sin \theta} = \frac{1.22 \lambda}{2 \text{ NA}}
\]

Which assumes a circular symmetry of the focal spot (strictly not given, see \([43]\)) and incoherent illumination. A plot for two spots which are just resolved by the RAYLEIGH criterium is shown in figure 2.13.

In practice the focus of an optical system is often fitted by a GAUSSian distribution. The error of this fit is small, which can be seen in detail in the enlarged region in figure 2.12(b).

2.4.2 Confocal Microscopy

The description above accounts for a usual optical microscope and describes either an image derived by a complete illuminated sample or the minimum size of a focussed spot. The confocal microscope enhances the optical properties of usual microscopy by introducing a pinhole in the detection path and also by a confined illumination of the sample. The key components of a confocal microscope are shown in figure 2.14.

Usually a confocal microscope illuminates and detects the sample through the same microscope objective. The resolution increases, because the illumination volume and also the detection volume overlap and result in a slightly steeper function to form an image.

The resolution limit of a confocal microscope is smaller than the value, introduced in equation 2.63. Both, the illumination volume and the detection volume contribute to yield the resolution given by

\[
r = 0.44 \frac{\lambda}{n \sin \theta} = \frac{0.88 \lambda}{2 \text{ NA}}
\]

For a confocal microscope one also has to take into account the polarization of light which is focussed on the sample. Usually the laser source is highly polarized and the focal spot is slightly laterally elongated perpendicular to the polarization axis. Recently different illumination polarizations have been taken into account, see e.g.
Figure 2.13: Two spots in the image plane at the resolution limit of an optical microscope. Two spots can be classified as resolved, if their centers are further apart than the first minimum of the AIRY function (see figure 2.12, the minimum is at 1.22 $\lambda$). Following this definition, the resolution can be defined as in equation 2.63. The height of the intensity dip in the middle of the structure amounts to 26.5%.

Figure 2.14: In this figure the principle setup of a confocal microscope is shown. One major component is the pinhole in the detection arm, which allows a higher resolution in the depth of the sample. Objects which are not in the image plane are virtually cut out by the pinhole and do not contribute to the detected signal. In our experiments the small (125$\mu$m diameter) detector area of an APD was used as a pinhole in the detection arm. The beam quality of the excitation beam is optimized by the excitation pinhole, in our experiments usually an optical single mode fiber.
[44], which would account especially for our situation of well aligned molecules (see chapter 3.6.2). Although the resolution of a typical confocal microscope could not be smaller than the diffraction limit, it is still possible to locate a single emitter with a much higher accuracy. In a paper BLOESS and coworkers were able to show a localizing accuracy of 3.4nm [45] which is basically a single molecule experiment where the signal-to-noise ratio of a single molecule signal allows to find the center of the emission with a high accuracy.

2.4.3 Scanning Near-field Optical Microscopy (SNOM)

The diffraction limit is a fundamental limit of optical microscopy. A few methods would allow to confine light too much a smaller volume than discussed above. The microscopy with two photon excitation [46] or methods like the the “Stimulated Emission Depletion” [47] allow resolutions which are better than the diffraction limit.

Further methods allow a much higher resolution when field gradients are used to locate objects much smaller than the optical wavelength. For optical frequencies the technique of STARK microscopy allows the localization of single molecules to an accuracy of ±2nm [48]. These methods compare to MRI (Magnetic resonance imaging), by using a field gradient to detect certain shifts in narrow band transitions.

Another way to beat the diffraction limit is to use confining geometries to have a smaller excitation or detection volume. This idea, brought up by E.H. SYNGE in 1928 [49] was to take a pinhole in a metal plate or a quartz cone to get a subwavelength source of light. The same idea was independently suggested by J. O’KEEFE in [50]. These ideas were not limited to the optical domain and inspired researchers to perform the first measurements in the microwave domain [51] – the wavelength was about 30mm and the used pinhole was 500µm, which results in a resolution of λ/60.

After some decades D. POHL and coworkers realized the first near-field optical microscope [52] in 1984. In their article the authors compare the idea to an acoustic stethoscope. An opening, much smaller than the wavelength of light, is scanned laterally in the close proximity to the sample. The distance from the source to the sample should not be much larger than the lateral extension of the aperture. This technique is called either “Scanning Near-field Optical Microscopy” (SNOM) or “Near-field Scanning Optical Microscopy” (NSOM).

Near-field optical experiments can be performed in several different modes. The basic setups are shown in figure 2.15 and explained in detail in [53]. The standard method is to use an optical fiber tip, which is coated by an opaque layer of metal (preferably Aluminum, because of the small skin depth, see page 48) and couple light into the optical fiber. The resulting light source, which can be much smaller than the optical wavelength of light is then used to illuminate the system under study (figure 2.15(a)). This method named transmission mode SNOM is probably the most often used method, and is used in the current work. It is also possible to detect in the other direction and have a photodiode on the other side of the fiber (figure 2.15(b)). By applying a scatterer at the end of a near-field tip the resolution of such a nanoscopic light source can be good as below 10nm [54].
Figure 2.15: Three different SNOM configurations: The aperture SNOM uses the near-field tip as a small light source to illuminate a small part of the sample. The detector is placed in the far field and detects usually the component which is propagated through the sample. In collection mode SNOM the sample is illuminated and the detector is placed at the end of the fiber leading to the near-field tip. For optimal lateral resolution the SNOM with an active probe – scattering SNOM – is preferable, which is independent of an optically opaque coating of a fiber tip. In this work the first two measurement types were used. Usually normal transmission mode SNOM was used to excite the molecules under study. For optimized tip placement the laser beam was also scanned confocally (as in figure 2.15(b)) over the sample.
2.4.4 Radiation of a Near-field Tip

In the method of *transmission mode* scanning optical microscopy the light is coupled into the optical glass fiber and at the opening the light leaves the near-field tip. The evanescent near-field component of this light shows an exponential decay in the intensity and also specific properties which are important to excite a single molecule.

For a theoretical description of the radiation pattern of a near-field tip, the theory of BETHE [55] and BOUWKAMP [56] is used in the current work to estimate how the radiation pattern looks and to account for the impact on a single emitter. In the original work by BETHE and the corrections by BOUWKAMP the light transmission through a subwavelength hole in an infinite conducting metal sheet is calculated. The overall description shows qualitatively and quantitatively good agreement with the measured results, which is shown e.g. in [57].

More recent calculations [58, 59] make use of numerical solutions and do not only take into account the transmission properties, but also further imaging and polarization properties of objects. One drawback on the theory of BETHE and BOUWKAMP is that the finite conductance of the opaque metal coating of the tips is not considered. Numerical methods can also account for different shaped holes [60].

The transmission of the holes is proportional to the 6th power of the aperture radius [55]. The calculations of the intensity distribution ($|E|^2$) are shown in figures 2.16 and 2.17. Figure 2.16 shows the calculation of the intensity distribution in front of the tip (color scale) and also the field lines, which shows the flow of energy from one side of the tip to the other half side. The different E-field components are used and followed in a streamline plot. The red bar in figure 2.16(a) shows the line which is followed in figure 2.16(b). Here the exponential decay [61] of intensity from the tip aperture can be seen. Therefore all distance dependent measurement of molecular STOKES shifted fluorescence are fitted with an exponential curve.

The field plots in figure 2.17 show the emission pattern as it would be seen by a single molecule. Depending on the orientation of the transition dipole moment the specific field components would excite the molecule differently. All patterns are plotted with a floating scale. The y-component of the field (orthogonal to the incident polarization) is very weak and would not been visible if the scale would be equal in all plots.

The thermal heating of the end of the fiber was expected to be a source of fluctuations in the spectral position and linewidth of single molecule resonances. With an input power of $1 \cdot 10^{-3}$W the resulting output power is $\approx 1 \cdot 10^{-8}$W, the rest is transferred to heat. For a further discussion on the thermal effects of near-field aperture tips, refer to [62, 63].

In the literature only a few experiments are described in which a single emitter is excited with a near-field tip. In this chapter the main references are reviewed which are important in the field. This is not necessary limited to single molecules, also quantum dots and single gold particles are investigated by transmission mode SNOM.

For molecules a pioneering work by E. BETZIG can be found [57], who performs for the first time a measurement on single molecules with a near-field tip at room temperature. The different orientations of DIi molecules embedded in PMMA is
Figure 2.16: BETHE-BOUWKAMP simulation for a tip field. The color plot in the back shows the field strength of the excitation, whereas the yellow lines are field lines how the field evolves from one part of the tip to the other side. The red bar in figure 2.16(a) shows the cut used in figure 2.16(b). This plot shows the dramatic decrease in the intensity with respect to the distance from the tip. In this plot only the sum of the x- and z-component is plotted. The y-component is much smaller and is negligible compared to the other components.

Figure 2.17: Visualizing the intensity (|E|^2) for a BETHE-BOUWKAMP calculation. This shows the field components for the field vectors, if the input polarization is oriented along the x-axis. The plots are calculated for a distance of 50nm above the tip aperture, which has a size of 100nm.
investigated and compared to theoretical descriptions of the radiation field of a near-field tip. This work was improved by the use of well defined tips by J.M. Veerman \[64\]. In reference \[65\] H. Gersen and coworkers introduce another single molecule experiment which is performed at room temperature with an aperture SNOM.

For gold particles a recent article reviews the use of a SNOM \[66\].

For a single quantum dot a similar measurement was performed by \[67, 68\]. Also \[69\] describes an experiment at $T = 4.2$K. A newer experiment \[70\] maps the exciton wave function of a quantum dot.

The vision to perform SNOM on single molecules at low temperatures dates far back. Already W.E. Moerner and coworkers attempted to perform a cryogenic SNOM measurement \[71\]. Unfortunately the authors were limited by their experimental setup which lead to a situation where the tip was not laterally scannable with respect to the molecule. Another early theoretical description of single molecule SNOM in transmission is introduced in \[72\].
3 Experiment

3.1 Introduction

The experimental setup consists of a cryogenic confocal microscope and an extension with a scanning near-field optical microscope. Everything can be operated at low temperatures \((T = 1.4K)\). The sample chamber is usually evacuated or filled with a low pressure of gaseous helium for thermal exchange.

This chapter covers the main parts of the experimental setup. First the cryogenic system is introduced. Afterwards the optical system is explained in detail, with a special focus put on the intensity stabilization of the laser. As a prerequisite of all measurements optical near-field tips are needed. A detailed overview of the near-field tip preparation and characterization is given.

The tips have to be in the close proximity to the sample (0 - 1000nm), so the cryogenic near-field setup and the shear-force detection is explained. At the end of this chapter the specific samples and molecules used for single molecule spectroscopy are reviewed.

The sample preparation process as well as the characterization is published in the frame of this work [73].

![Diagram of setup](image)

**Figure 3.1:** A schematic view of the setup that was used for the experiments. For a more detailed view refer to the other figures or see the references in the text.

3.2 Cryostat

The cryostat system (Cryovac, Troisdorf) consists of a helium bath-cryostat with two He-reservoirs: an upper and a lower reservoir, with 8 liters, respectively 6 liters (see figure 3.2). Both reservoirs are connected by a transfer tube which can be
opened or closed by a needle valve, the cold valve. The sample chamber is attached below the lower reservoir and is usually evacuated or filled with a low pressure ($\approx 1$ mbar) of He. By evaporative cooling the lower reservoir and the sample chamber can be cooled down to $T = 1.4$K.

The system is surrounded by a high-vacuum insulation (which is pumped by a Pfeiffer turbo-molecular pump) and two copper shields which are wrapped in super-insulation-foil. The windows of the system are tilted by 5° with respect to the optical axis to prevent back reflections. In figure 3.2 only the vacuum sealing windows are shown although also the inner copper shields have windows with no further sealing. All windows are made of quartz (Heraeus Quarzglas, Material: SUP1) and are antireflection coated.

For electrical contact of several components, a mounting ring with 40 contacts was mounted around the upper opening of the sample chamber. For all electrical contacts manganin wires were used because of their small heat conductivity. For the high voltage piezo actuators, a special teflon insulated cryocable was used (Lakeshore, Cryocable, type: CYRC). The electrical contacts were accessible on top of the cryostat by a multi-core plug (Fischer-connector, type: 107A052) which had a connector to an external connection box, where all channels were accessible over BNC-jacks. No common ground was used. The temperature in the sample chamber was measured with two calibrated Germanium diodes (Lakeshore) and for the higher temperature regime two Pt-100 sensors (Telemeter Electronics) which were mounted in small copper blocks and thermally connected with epoxy-glue (Deltabond 152, Wakefield engineering) on the ground plate. The temperature sensors were sampled by a $100\mu$A constant current source. The signal was monitored by a millivoltmeter and also recorded before and after each measurement.

The cryostat could be opened at the bottom to have free access to the sample chamber, which is about 140mm in diameter and has a height of 90mm. Before opening the cryostat had to be at ambient temperature and the insulating vacuum had to be flushed. To minimize the formation of water films on the inner cryostat surface, the vacuum chamber was usually flooded only with dry nitrogen and closed as fast as possible, i.e. within a few hours. All handling steps were performed with latex gloves. For cooling the cryostat from ambient conditions, the turbo molecular pump had to evacuate the insulating vacuum for about a day, to reach a pressure of $\leq 10^{-5}$ mbar. No further pre-cooling was performed and the reservoirs were directly filled with liquid helium. The typical procedure to fill and cool down the cryostat took about 3-4 hours, when the system was initially at ambient temperatures.

For single molecule experiments the temperature of the lower reservoir was reduced to $T = 1.4$K by evaporative cooling. The procedure to cool down to $T = 1.4$K from $T = 4.2$K takes about 15-20 minutes and the cryostat maintains the temperature for about 14 hours. Usually the cryostat was kept over months at $T = 4.2$K and was only cooled down to $T = 1.4$K before the experiment. Experiments on the very same molecule could be performed over weeks, due to the fact that no change occurs to the system.

\footnote{In figure 3.2 also other parts, namely electrical throughputs, and the exhaust from the upper reservoir, are not shown to simplify the figure.}
Figure 3.2: The $^4$He-bath-cryostat consists of a vacuum-system with 3 chambers: The innermost sample chamber is filled with exchange gas (usually $^4$He with $\approx 1$ mbar) so the experiment runs in a gaseous phase and not in superfluid helium (below the $\lambda$-point a thin film of superfluid helium covers the whole insert). To cool the sample chamber it is attached to a 6L helium reservoir, which can be evacuated to reach temperatures below the boiling point of liquid helium ($T=4.2K$). The upper helium reservoir holds 8L of helium, and a cold valve connects both reservoirs. Two copper shields block thermal radiation from the inner chamber and are not sealed with respect to each other.
3.2.1 Transfer System

A transfer system was designed for an easy access of the near-field setup (see figure 3.13). The stability was secured by a three-point support. It contains the SNOM-head with electronics and coarse positioning mechanics constructed of piezo sliders. For a tip exchange the transfer-system had to be warmed up to ambient conditions at the top of the cryostat. This has to be done carefully to minimize the stress on the piezo and glue points on the system, due to different expansion coefficients.

The electrical contacts for the near-field setup were put into the cryogenic system by a multicore plug (Fischer-connektor, type: 105A058) and were contacted by manganin wires to a contact ring at the bottom of the transfer system. To allow high voltage throughput, a special insulated cryocable was used for the piezo-sliders (Lakeshore, Cryocable, Type: CYRC). In the same way the optical fiber, leading to the SNOM head, was fed through the transfer system.

3.2.2 Sliders

A slider system was used for coarse positioning of the microscope objective (one axis, z) and for tip-positioning (three axes, xyz). These sliders are based on the slip-stick principle: an electrical signal, driven in a sawtooth like shape, shifts the slider slowly in one direction. Afterwards the voltage is quickly reduced to zero and by inertia the piezos slips back. The voltage supplied to the sliders controls the step-size. The step-size is not the same in both directions, especially for the slider which works up- and downwards.

Usually the slip-stick-sliders work quite well, however sometimes the sliders jammed or had a reduced travel due to dirt on the bearing points. Due to the fact that the sliders are driven at 400V and that the sample chamber is filled with He-gas during the experiment, discharges took place between the slider contact and the ground. Usually the exchange gas was evacuated to guarantee a proper movement and to protect the shear-force electronics (see chapter 3.5.1), which were easily destroyed by discharges in the He-atmosphere. For a detailed description of the used slider system see [74].

3.3 Optical Setup

3.3.1 Laser System

The laser used in the experiment was a Coherent 899-21 autoscan dye ring laser. It was pumped by an Coherent Verdi 8 frequency doubled Nd-YAG-Laser at $\lambda = 532$nm. The laser dye was either rhodamine 6G [75] with a wavelength range $\lambda = 560 - 600$nm or sulforhodamine B [75] for $\lambda = 595 - 630$nm. The dye was dissolved in methanol and the solvent was ethyleneglycole (Radient Dyes, Fluka) to give the correct viscosity for the dye-jet. To span a wider wavelength range, both dyes were mixed and the wavelength range of the laser was extended. For further red tuning to $\lambda = 620 - 680$nm 4-Dicyanomethylene-2-methyl-6-p-diethylaminostyryl-4-H-pyran (DCM) [75] was used as a laser dye.
3.3. Optical Setup

Figure 3.3: The optical setup on the experiment table. The light was directed either via a confocal way or into a fiber which leads into the cryostat. Both arms can be blocked independently by shutters. For the detection on the excitation and the fluorescence wavelength, a tilted notch filter divides the two spectral components. For details on the setup see the text.

For the laser frequency to be scanned continuously, the laser remains locked to its internal, thermalized reference cavity, and a glass plate is tilted in the cavity to change the frequency. After some alignment, a scan over 30GHz could be done without a mode hop. For longer, extended scans, several parts of 10GHz were stacked. The computer control of the laser allowed to drive the laser to an arbitrary laser frequency within the range of the laser dye. As an absolute frequency measure, an acusto-optical modulator (AOM, a piezo-mechanically moved quartz crystal) and two reference cavities (VET) were attached behind the laser. This assembly is called the autoscan unit.

The laser was either controlled by a computer via the autoscan-box or remotely by an ethernet to RS232 converter (Lantronix UDS-10) via a Labview-Software (see chapter 3.3.6). A primitive control language allows to change the laser frequency, but does not allow fine laser scans. For the scans of 30GHz an internal ramp ranging from -5 to 5V was generated by a computer controlled DAC-Card which controls directly the tilt of the glass plate in the reference cavity. This ramp signal was not continuous, but a stair-case signal, moving from one frequency to the next over several steps.

The laser light was attenuated by a gray filter wheel and after an intensity stabilization by an AOM (see chapter 3.3.3) transferred to a second laser table containing the experiment through an optical single mode fiber (Nufern, HP-460) with FC-APC plugs and two Martok fiber couplers with 10× microscope objectives.
Figure 3.4: On the experimental table the light is controlled by a half waveplate to turn to a needed polarization and the intensity is monitored and fed back by a PID-controller to the AOM (see figure 3.9). The fabry perot is online monitored with each measurement and has a free spectral range of 378MHz.

3.3.2 Confocal Setup

The laser light on the optical table was further characterized (intensity, wavelength) in a closed box² (see figure 3.4) and then reflected over a beam-splitter to the telecentric system and through optical quartz windows (20mm diameter) into the cryostat.

For the detection of single molecules, a standard confocal microscope was constructed, similar to figure 2.14. The light was focussed onto the sample and the light from the molecules was detected via the same optical path, but in the opposite direction.

For the terrylene samples the setup was built such that the excitation light is reflected over a tilted 595nm notch-filter and the detected red-shifted light passed through this notch-filter (Super notch, Kaiser Optical). After the notch-filter a long-pass filter (Omega optical, AELP-585) was used to block the excitation light further. The setup was extended to be suitable also for other wavelength, and the excitation reflected over a pellicle (96% transmission Thorlabs). Behind the pellicle a photo-detector was used for online monitoring of the excitation power. To cover several orders of magnitude, a logarithmic photodiode transimpedance amplifier was constructed (for a circuit diagram see chapter A.4.3). To split the light emitted by a single DBATT molecule into the 0-0 transition and the Stokes shifted fluorescence, a tilted 632.8nm notch filter was used (Semrock, Rochester). A further long-pass filter (Omega Optical, 621AELP) was used to block residual components of the excitation light. To detect the excitation light and block the

²to reduce stray light coming from the laboratory
3.3. Optical Setup

Figure 3.5: A telecentric system, for scanning the laser focus across the sample. Two galvanelectric mirrors are used to scan the beam. If the beam is scanned, lens 1 and lens 2 are hit on different positions and on the exit the beam turns around the back focal plane focus of the microscope objective in the cryostat. If a plane wave is entering the objective in the back focal plane, the beam is focussed on different points on the sample. For wide-field illumination a flipable lens (labeled as red) focuses the light onto the galvonic mirrors and is focussed in the back focal plane and illuminates a large area on the sample.

red-shifted fluorescence, a 620nm short pass filter (Omega Optical) was mounted in front of the APD.

Telecentric Scanning

For the confocal microscope the laser focus had to be scanned laterally to address different regions on the sample area and to allow a change of the focus position if the sample was mounted off-center to the optical light path.

The beam scanning was realized by a telecentric system, consisting of two 2” lenses with a focal length of 250mm. The overall length of the telecentric optic was about 1m and the light path was built in a straight way right behind the cryostat. The overall scanning range of the telecentric on the sample was more than 200µm, i.e. it covered the observed sample area on the camera images.

A positive side-effect of the telecentric was the virtual image plane in the telecentric optic, which was often used to align the optical setup. A fluorescing cardboard sheet placed in the virtual image plane, could be used to align the APDs.

To align the telecentric optic the cryostat had to be at ambient conditions and a collimated laser beam (e.g. from a HeNe-laser) was sent onto the microscope objective from the sample side and is thereby focussed in the back focal plane. The first telecentric lens behind the cryostat images this focus and collimates the beam. Removing the microscope objective (just by taking it out from the opened cryostat), the second lens (more far away from the cryostat) could be aligned with respect to the first lens and then the scanning mirrors could be aligned to the focus, if just the second telecentric lens was in the setup. One critical point was the centering of the telecentric lenses. To overcome this issue, the lenses were mounted in a special
holder, which allowed an easy exchange of the lenses with a disk containing a 2mm hole in the center. By exchanging both lenses with such disks, the lens mounts were aligned to the optical axis.

The mirror for beam scanning was either a usual dielectric mirror, held in a motor controlled gimbal mount and later changed to a system of two galvanic mirrors (Typ 6220H, Cambridge Research), because of the backlash in the mirror mount and the motor gear. The galvanic mirrors were first aligned mechanically and fixed with a mounting plate directly onto the optical table. For later experiments the galvanic mirrors were held by a 3 axes translation stage (Thorlabs, PT3/H) to easily compensate for a changed microscope objective position in the chilled cryostat. The scan range of the galvanic mirrors was reduced by a voltage divider to optimize the 16bit resolution of the DAC-PCI-card in the computer for a scan range, slightly larger than $200 \times 200 \mu m^2$. The pixel spacing was about 3 - 5nm on the sample. In the small scan range of the telecentric system no distortions were observed. For an extended scan range and for higher accuracy the system of a gimbal mount should be preferred, because the center of rotation is for the galvanic mirrors not at the same position. For a detailed review of distortions by a telecentric system, refer to [76] or [77].

For wide-field imaging, a lens with 100mm focal length was mounted directly in front of the galvanic mirrors to focus approximately in the back focal plane of the microscope objective, and to illuminate a larger region on the sample. The red-shifted fluorescence was usually detected on a camera, as shown in figure 3.4.

Two main measurement modes were used in this dissertation:

1. The confocal illumination and detection mode – the light is transferred onto the sample with a microscope objective and the signal is detected on the same way back on single photon detectors.

2. The near-field illumination and far-field detection mode – the light is transferred to the sample with a near-field aperture tip and detected by the confocal setup, which is described above.

**Microscope Objective**

The imaging setup in the cryostat consists of a sample scanner (Piezosysteme Jena, Tritor) which has a range of $100 \times 100 \times 100 \mu m^3$ at room temperature. At low temperatures ($T = 1.4K$) this range reduces to $7 \times 7 \times 7 \mu m^3$. The whole sample scanner frame has an extension of $30 \times 70 \times 70 mm^3$ and a hole in the middle allows the mounting of a microscope objective, which is located on a piezo slider system for focussing.

The microscope objective is a standard, commercially available objective (Olympus ACH60X). This objective is not corrected or optimized for low-temperature experiments and was taken out of the outer housing to fit into restricted geometry of the cryostat. The microscope objective has a numerical aperture of 0.8, a focal length of 3mm. The diameter of the back aperture is 4.8mm, and was matched by the width of the laser beam. The position of the back aperture is 21mm from the thread into the inside of the objective. The microscope objective was able to stand a large
Figure 3.6: An early measurement with light stabilized in front of the fiber. The intensity fluctuations are measured on an APD behind the cryostat on the excitation wavelength. The light in front of the fiber coupler was stabilized to about 1%. The integration time per pixel was 100 ms.

number cooling and warming cycles, no further image distortions or cracks in the objective were observed.

3.3.3 Laser Stabilization

Intensity stabilization was a major issue in this work. The main feedback loop was built with a detector (see circuit diagram in chapter A.4.3) close to the experiment (OPT101, Burr-Brown, see figure 3.4) and an acusto-optical modulator (AOM, Panasonic EFLM 200 with a Brimrose Driver for 200MHz) close to the output of the laser (see figure 3.9). The zero order deflection is cut by a small iris diaphragm (Thorlabs), whereas the first order is taken as a source of laser light for the experiment. Nominally all frequencies in the experiment are 200MHz shifted to the original laser frequency. To optimize the coupling efficiency through the AOM, the light was focussed by a 200mm lens and the AOM was mounted on a rotation stage. A throughput efficiency of 35% into the first diffracted order could be reached by a careful adjustment.

The electronic feedback loop was a PID-controller, where a set-point was held and the output signal was fed back to the AOM-controller.

Especially for the tip experiments the light coming out of the fiber had to be very stable. Jitter, thermal and other mechanical fluctuations changed the amount of light coming out of the fiber because of two reasons: a) the transmission was changed due to bends in the fiber and b) the polarization of the light in the fiber was fluctuating and the preferred output polarization of the tip was not matched. The first approach was to have a stable light source in front of the fiber coupler to the SNOM-tip and to shield the fiber coupler from mechanical jitter like from air.
Figure 3.7: To control the intensity which comes out of the aperture tip, a fiber feedback system was built. The optical single mode fiber leading into the cryostat was bend in a small undulator such that a small amount of light is scattered out and detected by a photodiode, amplified by a programmable instrumentation amplifier. The light scattered out of the bend is specific to the intensity of light in the fiber and its polarization state due to the birefringence of the fiber. The signal of the amplified photodiode is fed back into a PID controller which changes the signal for the AOM.

Figure 3.8: Recorded light of an aperture tip, recorded behind the cryostat. Figure 3.8(a) shows the ALLAN deviation of the measurement with an integration time of 5ms and the resulting percentage of noise on the binned and integrated measurement times. The upper curve shows an ALLAN deviation of an actual measurement, whereas the lower curve shows the simulated shot noise for the same experimental conditions. Figure 3.8(b) shows a typical noise level at an integration time of 10ms after implementation of the feedback control (figure 3.7).
Figure 3.9: A dye laser (Coherent 899) supplies the light for the experiment and is sent into an AOM which is controlled by an PID-controller to stabilize the intensity. To optimize the throughput intensity the light is focussed into the AOM (200mm focal length) and the polarization is optimized. The light is transferred to the experimental table with a single mode fiber (Nufern, 460-HP). To optimize the coupling efficiency to the fiber a negative lens on a xy-translation stage is placed in front of the fiber coupler.

Unfortunately this did not allow to have a more stable signal at all. The fluctuations which were measured right behind the cryostat output were large, as in figure 3.6.

For further intensity stabilization of the light exiting of the SNOM-tip, the light inside the optical fiber was directly used for an intensity feedback. It was detected by a photodiode, located at the input of the fiber into the transfer system. At this point the fiber was bent several times and the light scattered out of the core was detected on a photodiode (OPT101, Burr-Brown). This signal was amplified by a programmable instrumentation amplifier (PGA204, Burr-Brown, the gain could be set to 1, 10, 100 and 1000) and was fed over a voltage divider to the PID-controller, which controlled the AOM (see above).

To characterize the intensity fluctuations, the light was detected with the standard detection scheme (APDs in the far field). The resulting noise level was interpreted as a deviation from the mean value. At low count rates the signal is dominated by shot noise, at higher count rates systematic effects occur. To monitor this behavior the Allan deviation was plotted (see figure 3.8(a)). In this graph the standard deviation is plotted as a function of the binning width. The measurements were recorded with an integration time of 5ms and the noise was plotted for all possible time bins of this measurement. The shot noise, the square root of the measured counts, gives a lower bound to this value.

The linewidth was estimated to be below 1MHz (the laser specifications estimate a line width better than 500kHz). Nevertheless, during all experiments the transmission of the laser light through a reference cavity was monitored and drifts and mode hops during a laser scan could be observed. The free spectral range of the confocal
reference cavity was 378MHz\textsuperscript{3}. One mirror of the reference cavity was controllable
by an piezo-electric actuator and was locked to a fringe of a frequency stabilized
HeNe-laser, which counter propagates in an orthogonal polarization through the
reference cavity.

\subsection*{3.3.4 Detection}

The single molecule fluorescence was detected on avalanche photodiodes (APDs)
\cite{SPCM-AQR-14, Perkin Elmer}. For counting the clicks coming out of these single
photon counting modules (SPCMs) a counter was built. The TTL peaks of the APD
are counted and binned for a defined time (1-1000ms). Depending on the counts
a certain voltage is generated (2mV per count), which can be recorded online with
the ADC-input of the measurement program.

To protect the APDs from room light and to have a security control, a shutter
was built with a small electro-magnet and mounted directly onto the APD. This
also helped to reduce the amount of stray light on the APD significantly.

The dark count rates of the 4 APDs were spanning a range from 40 to 80cps. These
values were measured under realistic conditions with a 100ms integration time after
thermalization of the APD for 15 minutes. For the transmission measurements the
APDs usually were thermalized for some minutes before use to account for count rate
shifts in the first minutes. In between the measurements the APDs were protected
from light simply by closing the shutter.

The APDs were mounted on a three-axes translation stage to allow fine alignment
of the detector with respect to the beam. For focussing usually a 50mm lens was
used, which was also held in a xy-translational mount. To align the APDs, a fluo-
rescent cardboard was placed into the virtual focus plane in the telecentric optic.
Illuminating this card with an attenuated laser beam, all APDs could be aligned.

\subsection*{3.3.5 Imaging Setup}

Two cameras were used to record images from the sample. A \textbf{PCO Sensicam}
(1024×768 pixels) and an \textbf{Andor Ixon DV860 ECS} camera (128×128 pixels). The
PCO camera had a higher pixel resolution, but the dynamic range was limited to
12bit. The \textbf{Andor Ixon} camera had a 16bit dynamic range and was used to record
the transmission measurements on the camera.

The optical signal was sampled between the galvanic mirrors and the first lens of
the telecentric optic by a pellicle beam-splitter (see figure \ref{fig:33}). To acquire images
in fluorescence excitation mode, a long-pass filter (\textbf{Omega Optical}) was mounted
in the optical pathway to the camera. The focussing optics of the camera was a
commercial 300mm zoom objective (\textbf{Sigma}) with a \textbf{Nikon} bayonet mount.

\textbf{White Light Imaging}

To acquire images of the sample under study and also to have a better control on
the current properties of the sample, usually white light images were taken. The
sample was illuminated by a cold light lamp through the cryostat windows from

\footnote{The cavity had a length of \( \approx 198\text{mm} \) \( (FSR = \frac{\lambda}{4\pi}) \)}
behind. Usually the images had a better quality when the transfer system was placed between the light source and the sample.

### 3.3.6 Data Acquisition

Data acquisition was performed with two PCI data acquisition cards from Data Translation. The cards were two DT3016 and a DT334 card. One DT3016 card was used to

1. give out two analog signals: laser ramp and the trigger signal.
2. to read synchronized 16 channels (e.g. the photon counters)
3. to control 12 digital output ports (shutters, mirrors, stepper motors)

The second DT3016 card was used to read specific values before and after each measurement and to control the x- and y-position of the sample scanner. The DT334 has 8 analog outputs and was used to control devices which were not necessarily synchronized to other output signals. Such signals as galvo- and STARK-voltage and also the z-position of the sample scanner were used asynchronously controlled by this card.

For a better control the second output channel of the first DT3016 card was used to put out an alternating 5V signal – here remotely other devices could be controlled and synchronized. A pulse-shaper, as described in section A.4.2 was used to modify this signal to better control the measurements on each pixel.

The program to control the measurements was written in LabView from National Instruments. Other programs were used to acquire images from the used cameras (Camware and Ixion), to acquire data and control the dye-laser (Autoscan 2.06, Coherent) and to control the autocorrelation cards (SPCM, ver. 8.5, Becker & Hickl).

### Measurement Modes

The innermost measurement loop in the Labview program consists of a laser frequency scan. The other scan parameters are set (position, STARK voltage, etc.) and then a laser scan is initiated and synchronously all 16 channels from the first measurement card are read in. To realize this, the scan parameters are loaded into the data acquisition card and then the scan is launched and runs automatically, controlled only by the card. After finishing the laser scan the buffered data are read by the computer, the data is stored and the scan-parameters are changed. For a faster recording of shear-force signals, a measurement option without laser scanning was implemented.

### 3.4 Near-field Aperture Tips

In near-field optical measurements several approaches can be used, e.g. aperture less, pulled fiber with aperture, etc. For our experiments almost all tips were produced with an aperture at the end.
To prepare the tips a commercial single mode fiber (Nufern, 460-HP) was used and pulled with a commercial pipette puller (Sutter Instruments P-2000). The pulling parameters were taken previous experiments, but later refined by a detailed study of the pulling parameters. The switchable parameter set consists of a) heating b) delay c) pulling strength. The length of the fiber was in the order of 500 - 1000mm, to allow splicing to the fiber inside the cryostat. The length of the tapered region was 10 − 50μm, depending on the parameters of pulling.

In addition to the pulling technique, etching was used to produce tips with a less steep angle, to obtain a better transmission through the fiber. When the tip angle is less steep the cut-off at the fiber end happens at a later time in the fiber and the transmission can be higher. Usually the tips were etched with an aqueous 40% HF solution, which was over-coated with iso-octane. The etching was performed in a teflon-beaker and took about 30min at room temperature. To have reproducible results the etching setup was shielded from air fluctuations by a plastic cover.

Later investigation under the electron microscope showed, that this technique was resulted in fluctuating results, different tip geometries and a higher surface roughness. A preferable solution would be tube-etching [78], which results in a little more effort, because the residual fiber-cladding has to be removed by boiling sulfuric acid.

### 3.4.1 Coating the Tips

The tips were coated with an aluminum-layer in an evaporation chamber (Baltec BAE), evaporated from a tungsten-boat (Balzers). The tips were held in a special, centrosymmetric holder, which was rotated by a motor with approximately 2 Hz during the coating process. All evaporations were done after a pressure below 1 · 10−6mbar in the evaporation chamber by pumping for about one day. The motor was turned on and below the closed shutter the aluminum was heated to melt, to coat the whole tungsten boat and then heated further to get rid of dirt. After reducing the heat and opening the shutter the aluminum layer was coated with a rate around 10nm/s onto the rotating tips. First tips were produced with a coating thickness of 100nm, which resulted in a coating of 15nm, not sufficient for complete opaqueness of the tip (the skin depth of Aluminum of about 6.5nm for $\lambda = 615nm$). Afterwards the coating thickness was increased to ca. 300nm, resulting in a layer of 250nm around the tip. The quality of the evaporated films was high, as it could be seen from the SEM-images.

### 3.4.2 Tuning Forks

For the purpose of approaching the tip to the sample, a shear-force feedback mechanism [81, 82, 83] was realized by gluing the coated tip onto a quartz tuning fork. The tuning-forks were either Farnell, 221-533 or Golledge MS05203, Batch 045313, GDX-1C/A, 6pF, resonance at 32.7680kHz = 215Hz. The first step was to solder the tuning fork into a small IC-socket for later mounting. After this the tuning fork was aligned properly with respect to the holder and the small ceramic

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4The optimal parameter were: Heat = 300, Fil = 0, Vel = 18, Del = 126, Pul = 150.
5The skin-depth can be calculated as $d = \frac{\lambda}{4\pi\sqrt{\varepsilon}}$ where $\varepsilon = n^2 - k^2 + 2ink$ [79, 80].
3.4. Near-field Aperture Tips

Figure 3.10: The tip preparation as a step-by-step process: The single mode optical fiber is melted by an CO$_2$-laser and pulled to obtain two sharp needles. The tips are mounted into a holder and placed in an evaporation chamber and turned through the evaporation process. To prepare the tuning forks the first step is to solder them into an IC-plug and to open the protective can. An electrical insulation on the upper side of the tuning fork is necessary to prevent an electrical contact between the tip-coating and the excitation voltage of the fork. Under an optical microscope the tip is glued onto the tuning fork. All steps are controlled by an xyz-translator with micrometer accuracy. After hardening of the glue the fiber-tip is electrically contacted with a 0.1mm copper wire and conductive silver (Fluka). After gluing a strain relief the tips are mounted into another holder and transferred into the focussed ion beam machine.
sealing was squeezed with pliers to crack the mounting cement from the tuning fork to the can, which usually protects it from air and other mechanical influences. The tuning fork was afterwards insulated on the upper side to glue the metal-coated tip onto the device. Usually this was done under a microscope with an epoxy-glue\(^6\) (UHU Sofortfest), applying a small droplet of the glue with a sharp needle. For an electrical contact of the outer metal coating the tip was contacted with a 0.1mm copper wire, bent into a coil, fitting around the fiber and was electrical contacted with conductive silver (Fluka). After this gluing and contacting process a strain relief was constructed with epoxy glue.

The fiber scanning near-field optical microscope tip (SNOM-tip, see chapter 2.4.3) sticks out for about 50 - 100µm over the edge of the tuning fork. The tuning fork is held in the shear force electronics by an IC-socket holder, which has a little degree of freedom of tilt. The tuning-fork assembly is put into place by pliers and bend slightly upwards, so that the lower end is slightly more in front as the upper end. It was crucial to ensure that when approaching the tip to the sample the tip itself touches the sample and not a part of the tuning fork itself.

After the gluing process, the tuning forks usually show a smaller resonance signal, shifted to higher frequencies (33-36kHz). The quality factors were low at room-temperature due to the mechanical damping by the epoxy-glue. Under vacuum conditions or at a low helium pressure the quality-factors were significantly higher. After cooling down the tuning fork the quality factors were in the range of 5000-10000 $\equiv$ a linewidth of 3 - 6Hz.

### 3.4.3 FIB Milling

After complete coating of the tips, the end had to be cut off. This was either done by controlled manipulation of the tip or later done by focussed ion beam milling. The controlled manipulation of the tip was performed either by coating the tip from below, so that a certain aperture remains open during the coating process or by touching the end of the tip with a piezo controlled approach mechanism towards a solid surface. The results were not sufficient and the tips were later prepared only by focussed ion beam milling.

Modifying the end of the tip in the focussed ion beam machine was done in a specialized holder. The tip was held such, so that no quartz or other parts of the tuning fork were in the way for taking an image. Quartz or other materials charge up and deform the electron micrograph images dramatically or result in a drift of the tip itself.

The cutting process was done at EMPA Dübendorf in a dual beam focussed ion beam apparatus, combined with an electron microscope FAI Strata DB 235. The electron gun was placed on top of the machine and the Ga-Ion-Beam milling source was tilted by 52°. Normally the tips had to be driven in the crossing points of the two beams, tilted by 52° and then cut by the ion beam. The alignment to this isocentric point was crucial and performed in several steps by tilting the sample back and forth. Before each cut the electron beam was optimized to record an image right after the cutting process. The spot size for the electron micrograph images was set

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\(^6\)epoxy glue is one of the few glues which can be used at cryogenic temperatures, glues like cyanacrylate simply get stiff and break.
3.4 Near-field Aperture Tips

![Near-field Aperture Tips Image](image)

(a) Before FIB-milling  
(b) After FIB-milling  
(c) After FIB-milling

**Figure 3.11:** A focused ion beam image right before the cut and right after the cut, note the very end is sliced off from the first to the second image. The tip was milled with the same current as the picture were taken. So every taken microscopy image ablates the tip coating a little bit. The acquisition time for an image was \( \approx 0.5 \text{ sec} \), the time to cut the end of the tip \( \approx 30 \text{ sec} \). In figure 3.11(c) an electron micrograph image of a tip with an aperture of \( \approx 100 \text{nm} \) is shown.

to the value 3 and the acceleration voltage was usually 5kV. Due to the tilt of the stage, the electron micrograph images focus onto the end of the tip in an angle of 52°.

The cuts were usually done with a current of 10pA. This current was low enough to take images before the cutting process and right after the cutting process. For cutting a program for silicon was taken, resulting in cutting times from 10 to 120 seconds. The image acquisition by the ion beam took about 1-5 seconds and had only a weak influence on the tip-structure. The resulting opening diameter of the tips which were used in our experiments ranged from 80 to 200nm. After the focused ion beam milling, the tips were optically characterized (see chapter 4.4.5) and sealed in a small container in pure, dry nitrogen to avoid oxidation of the aluminum coating. To use the tips in the experiment they were spliced to the fiber, going down within the transfer system of the cryostat.

A similar tip preparation process is also used in other groups [84].

### 3.4.4 Electron Microscopy

The used tips were controlled before and after the experiments. Normally electron microscopy images were taken directly in the FIB at EMPA.

After the experiments the tips were investigated under a Zeiss Leo 1530 at ETH Hönggerberg at low voltages of about 3kV. Usually the tips showed no severe modifications, only tips which were used to perform shear-force measurements showed sometimes a squeezed metal coating.
3.5 Near-field Setup

The near-field setup was constructed completely on the baseplate of the transfer system (see figure 3.14), so it was possible to take the whole system out of the cryostat. On this platform the three coarse sliders were mounted and the fast piezo to control the tip directly and a shear force electronics holding the SNOM-tip were mounted.

In the literature some cryogenic SNOM setups are described [85, 86, 87]. One approach is described with a cold finger [88], in which only the sample is cooled.

3.5.1 Shear Force Control

The distance from the tip to the sample was controlled by a shear force mechanism [81, 82, 83]. The tuning fork excitation was always driven on its resonance and the amplitude and its phase were detected on an oscilloscope. Basically the phase component\(^7\) was used to be fed back to an PID-controller, which was carefully aligned not to oscillate but to have a fast response. The feedback is directly fed into a high voltage amplifier (1:15) to control the fast piezo stack, which had a travel of \(\approx 600\text{nm}\). One major problem was the time constant of the feedback control due to different throughput capacitances to the outside of the cryostat.

While approaching the sample towards the tip the shear force phase remains the same over the time no interaction exists between the sample surface and the tip. From a certain point on the interaction between the tip and the sample increases and the phase changes dramatically. Usually the contact point was measured only once before all other measurements.

To determine the height of specific samples the shear force mode of the scanning program was used. For a sample image see figure 3.12(b), which had a recording time of ca. 7 hours, due to the slow feedback and large feed-through capacitances from the inner part of the cryostat to the outside.

To excite the tuning fork an external oscillator (HP33120) was used, which was electrically decoupled by a transducer and the signal was divided by a resistor voltage divider (1:1000). This signal of about 1mV was directly fed into the cryostat onto the tuning fork. The oscillator had to be accurate and had to be able to control also the millihertz regime, because of the quality factor of the resonance was in the range of 5000-10000.

The tuning fork signal in the cryostat gave a weak signal and was optimized by a self built electronics. This consists of a transimpedance amplifier, with a feedback resistance of 10M\(\Omega\). For earlier amplification on the signal path the first transistor in the operational amplifier was complemented by an GaAs-MESFET (CF 739, Siemens), located close to the tuning fork (about 4mm distance) in the cryostat. The signal was conditioned by subtracting an offset voltage with another operational amplifier.

The output of the electronics was directly attached to a lock-in amplifier (Stanford Research, SR830) and the x- and y-component were given out to an oscilloscope and were also fed back to the shearforce feedback loop.

\(^7\)usually the x- and y-component are monitored on the oscilloscope. By driving the system on its resonance the phase change is equivalent to the x-component, which is used for the feedback.
Figure 3.12: The shear force electronics consists basically of a transimpedance amplifier. The input transistor of the operational amplifier is supported by an external GaAs-MESFET which is located in the cryostat. Si devices would not work, because no more carriers are available at $T=1.4\text{K}$. The second operational amplifier subtracts a potential offset voltage. The excitation of the tuning fork is realized with an external oscillator (HP 33120), which is attached with a galvanic decoupled transducer.

A shear force image of $7\times7\mu\text{m}^2$, recorded at $T=4.2\text{K}$. The height of the structure is $\approx 150\text{nm}$. The recording time was $\approx 420\text{min}$. 
Figure 3.13: Schematic figure of the cryogenic SNOM. On the figure the main parts are highlighted: a) the coarse approach slip-stick sliders (range ≈ 10mm, only one is shown in the figure) b) the sample-scanner, consisting of a frame with a size of about with a range of 7µm in all directions and c) a fast piezo to control the tip-sample distance with a much higher speed than the inert sample scanner. The microscope objective is located inside the sample scanner. The sample is held on the scanner by small magnets.

Unfortunately the electronics tend to break after a few handling steps, just because the sensitivity of the thin insulating layer in the transistor. Gas discharges were often a point of failure which were breaking the shear force electronics. The handling issue was solved by protecting the transistor electrically, either by 100kΩ resistors where the signal was able to overcome this resistance, or (on the gate side of the transistor) with a crossed pair of silicon 1N4148 diodes, which was conducting at room temperature and due to the frozen carriers an infinite resistor at T=4.2K and below. For detailed circuit diagram see chapter A.4.1. After building the electronics we became aware of an article, describing a similar concept by Yang and coworkers [89]. An alternative design without the use of a lock-in is described in [90].

For all electronic components in the setup a common ground point was used. Here all devices were plugged in, in a star like configuration to reduce the amount of noise by potential ground-loops.

3.5.2 Tip Approach

For a coarse tip approach to the sample the distance was monitored by a camera outside of the cryostat from the side. Here the approach was done until the tip-sample distance was small, but still recognizable. The distance was monitored by observing the image and the mirror image on a camera, the light scattered out
3.5 Near-field Setup

Figure 3.14: Photograph of the SNOM head, which can be put into the cryostat without opening the whole system through the transfer tube with a diameter of 50mm. The lower copper platform can be set onto a three point mount at the bottom of the cryostat. The piezo sliders for approach and horizontal movement are mounted on the base plate, whereas the height control is mounted on the left-hand side, holding the fast piezo which holds the shear-force electronics and the tuning fork.

of the tip and its reflection on the sample surface could be observed. The lateral displacement was usually monitored by a confocal illumination of the sample and the scattered light was monitored by a camera from the side. This coarse approach was stopped at ≈ 0.1-0.3mm in front of the sample surface, not to endanger the tip.

Further tip approach was done by an iterative procedure: The fast piezo, which is controlled by the shear-force electronics is driven to its maximal voltage (approaching the sample surface) and the sample scanner is slowly moved towards the tip, while monitoring 4 signals: the x- and y-signal of the tuning fork resonance, its amplitude and also the voltage on the fast piezo. The tip approach was performed in steps of ≈ 7nm in 200ms. When the sample scanner was almost extended to its maximal range (≈ 6µm) the sample scanner was retracted and the coarse approach mechanism with the slip-stick slider was moved a few steps (≈ 20) towards the sample and the procedure started over again. The tip-sample approach in the cryostat took usually a few hours for spanning the range of 0.1-0.3mm. When the tip was approached one time, it was only retracted by a few hundred steps (≈ 100µm) during the night or experimental breaks. The approach on the next morning was realized in less than a hour. For refilling during the experiment a gentle technique was developed, so that only the sample scanner had to be retracted ≈ 6µm, and nevertheless the cryostat could be refilled.
Figure 3.15: A sample image at room temperature ($\approx 150 \times 250 \mu m^2$). One sees the usual distribution after the spin coating process. The lower left corner is located closer to the rotation center of the spin-coater. Usually close to the center the crystals are laterally larger. From the center outwards the crystals get smaller and are distributed in lines pointing outwards.

### 3.6 Sample

#### 3.6.1 Spin Casted Samples

The basic requirements for a sample for an single molecule optical near-field experiment (SIMONE) are a) the sample must be thin, so that the near-field tip gets closer than the optical wavelength to the molecules and b) the molecules have to be rigidly embedded, so that their spectral properties do not change too much if the tip touches the sample. To prepare the samples a precursor solution of $p$-terphenyl in toluene was doped with a small amount of a toluene-dye solution and spincasted onto coverslips. The coverslips were first cleaned by a detergent and after this cleaned step by step in an ultrasonic bath in acetone, ethanol and methanol. After this the coverslips were put into a cleaning solution called “piraña”, consisting of a 1:1 mixture of concentrated sulfuric acid and 30% aqueous solution of $H_2O_2$. In this solution the coverslips were stored under the hood. To use a coverslip one was taken out, rinsed with deionized water and afterwards dried under a high pressure nitrogen flow. After drying the coverslips were put directly onto the spincoater. The precursor solution was prepared by dissolving 0.3g $p$-terphenyl (Acros Lasergrade) in 100mL toluene (Sigma-Aldrich, spectrophotometric grade). The solution was doped with a few percent of a saturated dye solution, either terrylene solution in toluene or DBATT...
3.6. Sample

Figure 3.16: The spincasted sample is produced on a “piraña” cleaned coverslip where 25μL of the precursor solution is applied on. A slow spincasting process allows the formation of extended thin crystalline areas of p-terphenyl. The orientation of the embedded molecules is dominated by the counter polarity of the cover-slip surface and the sample system. All organic molecules tend to stick upwards that the touching area to the strong polar cover slip is reduced. The arrows, pointing upwards, show the typical orientation of the transition dipole moment of the embedded molecules which are equally oriented.

solution in toluene. The dyes were purchased from PAH-Institute, Greifenberg. For the later DBATT samples the doping concentration of the precursor solution was 2%.

To prepare the samples a spin-coater PWM32, Headway Research, Inc. was used. The following procedure was taken: First a little droplet (25μL) is put onto a clean coverslip. The spin-coater turns initially with 1000rpm and after 30 sec the speed is increased to 3000rpm for 2 seconds. Afterwards the sample is ready and characterized further under an optical microscope. For a detailed review on the sample preparation process, refer to [73], or to the original work [91, 92].

The usual sample thickness was checked by means of AFM to be in the order of 20nm. The molecules under study were often weakly embedded, especially for the near-field experiments. To enhance the stability a further annealing step was taken and the sample was put into a preheated oven at 150°C and annealed for 150min. The annealing process resulted in islands with heights larger than the average sample. The average thickness in the performed measurements was ≈ 50nm. For a height profile of a sample, characterized at low temperatures see figure 3.17.

3.6.2 Room Temperature Characterization

After the sample preparation process the sample was characterized by optical microscopy. The distribution of crystal areas showed large, extended areas in the center of the coverslip and smaller crystals at the edges (see figure 3.15). To determine the film regions and their crystallinity two crossed polarizers were introduced
Figure 3.17: Cryogenic shear force image of an annealed spincoated sample, measured in the cryogenic setup at T=4.2K. The sample shows a height of ≈ 50nm. In the middle of the observation area a warp can be seen. Here the tip “crashed” several times into the sample.

into the microscope and turned to maximal extinction. Due to the trirefrингence of \( p \)-terphenyl (\( n_1=1.6, n_2=1.7, n_3=2.0, [93] \)) the crystal areas could be observed.

Right after this characterization steps the sample was usually mounted directly into the opened cryostat and held by two small magnets (SmCo, DE32, IBS-Magnete, Berlin) on the sample scanner.

To optimize the annealing parameters, also AFM-measurements were performed. Unfortunately the distribution of sample heights was not homogeneous over the whole area of the cover-slip.

**Molecular Orientation**

The embedding of the dopant dye in the crystalline film was characterized by room-temperature single molecule spectroscopy in another setup. Surprisingly all dopant molecules showed similar emission pattern, because they were embedded with the long molecular axis perpendicular to the surface. This is plausible, when the polarity of the molecules is taken into account: The highly unpolar organic molecules from the precursor solution tend to reduce their touching area with the highly polar glass surface, which is especially polar after the aqueous cleaning process (see chapter 3.6.1). The dopant molecules tend to point upwards in the same way. For a discussion of the structure of terrylene in \( p \)-terphenyl see e.g. [94]. The doughnut-like pattern for molecules with a perpendicular oriented transition dipole moment is described already in the literature [95] and is illustrated in figure 3.19(a).

In the first cryogenic SNOM-measurements the molecules showed also a significant sensitivity to the \( z \)-component of the tip-field. See chapter 2.4.4 for a discussion and the corresponding measurement in chapter 4.3.

For a further determination of the orientation from different molecules in the sample, back focal plane images were taken at room temperature with a high numerical aperture objective. For the current sample system B. BUCHLER and coworkers per-
Figure 3.18: A terrylene doped p-terphenyl sample at room temperature, which shows the typical doughnut shaped pattern for all embedded molecules. All molecules are oriented perpendicular to the surface. This is also a sign for the crystallinity of the sample.

Figure 3.19: The emission of an oriented molecule results in a doughnut like pattern. The resulting output polarization shows usually a “doughnut mode”, which is shown in figure 3.19(b).
formed this measurement for a terrylene doped sample and found out orientations around $15^\circ \pm 5^\circ$ tilted to the surface normal [96].

The sample doped with DBATT molecules was examined in a room-temperature setup with a microscope objective with a numerical aperture of 1.4 (Zeiss Apochromat, not polarization preserving). To determine the out-of-plane orientation of the molecules in the sample we took images with a setup, which was focussed in the back focal plane of the microscope objective. By this the emission, dependent on the embeddence angle of the single molecule, can be recorded. To image the back focal plane a BERTRAND lens was introduced, consisting of a two lens system to reduce the size of the pattern on the used camera (PCO Sensicam) to fit onto an area of $\approx 60 \times 60$ pixel. After an integration time of 1-5 sec the recorded pattern looked like figure 3.20(a) and could be fitted, resulting in a determined orientation of $25^\circ \pm 5^\circ$.

The method to determine the molecular embedding is explained in detail in [97]. The method to fit the resulting emission pattern is adapted from [98]. This orientation holds also for low temperature experiments, assuming that the orientation does not change during the cooling process in the cryostat.

**Lifetime Measurements**

To determine the lifetime of the excited state of DBATT molecules embedded in the $p$-terphenyl film, the sample was also examined in a room-temperature experiment and excited with pulsed excitation by a frequency doubled Nd-YAG laser with a pulse-length of less than 30 psec\(^8\) and a repetition rate of 75MHz (Time-Bandwidth).

\(^8\)the nominal pulse-length was 13psec, but the laser was transferred through a long optical fiber ($\approx 30m$), which increased the pulse-length. In an optical oscilloscope (Hamamatsu) the pulse length was measured to be below 30psec.
3.6. Sample

![DBATT lifetime histogram](image)

**Figure 3.21:** DBATT lifetime histogram for a single molecule, embedded in a thin, spincoated $p$-terphenyl crystal. The excitation is realized with a pulsed frequency doubled Nd-YAG laser. The measurement is performed at room temperature.

To have a smaller repetition rate a pulse picker (APE GmbH, Berlin) was used with a division factor of 15, to have a 200nsec time-window for the fluorescence decay. The fitted natural lifetime of the excited state was $20 \pm 3$ns, which corresponds to a full-width half maximum linewidth of $8 \pm 1$MHz. For a typical measurement on a single molecule see figure 3.21.

### 3.6.3 Linewidth Distribution in Different Samples

The described sample was extensively characterized in room temperature experiments and showed an excellent photostability. Nevertheless the behavior at cryogenic conditions was not guaranteed to be optimal. Here the first characterizations at cryogenic conditions are presented (T=1.4K).

Usually the samples were built into the cryostat and after one day of evacuation when the cryostat was cooled down to liquid helium temperatures. After a first optical characterization of the sample on the camera (white light images) large film regions were selected and a spectral characterization was performed in confocal mode. If the sample was not located well, several approaches were taken to change the sample position in the chilled cryostat, like a modified transfer system with a knife to shift the sample position from above.

For a further ongoing spectral characterization of the sample the laser was controlled by the provided scan software and the different APDs were read in by the ADC in the control unit of the laser itself.

Figure 3.22 shows an image of the sample at cryogenic temperatures, acquired by the camera, while the sample was illuminated by white light from the opposite side.
Figure 3.22: The sample at cryogenic temperatures, illuminated by widefield illumination and scanned over 30GHz (white spots). The image is afterwards illuminated with white light and superimposed to the recorded frequency scan. The area is $\approx 200 \times 200\mu m^2$. 
3.6. Sample

Figure 3.23: A fluorescence excitation spectrum from 484GHz to 491GHz (ca. 610 - 619nm) of the sample shown in figure 3.22. The in labeled region figure 3.22 is excited confocally.

of the cryostat (from where the SNOM-tip approaches the sample). The image is superimposed with a sequence of images, acquired by wide-field illumination with a narrow-band laser and a detection of the red-shifted fluorescence. The single bright spots can be associated to single molecules which light up when their specific transition is driven. The figure shows large extended film regions and the tendency of self-cleaning by the crystal structures: The dopant molecules tend to move to the crystal edges. On the labeled region a confocal scan was performed over a few terahertz. The inhomogeneous distribution of the molecular fluorescence excitation spectrum could be seen in figure 3.23.

A histogram of the measured linewidths is plotted in figure 3.24, showing a maximum below 100MHz. Much narrower molecules could also be found. See e.g. figure 4.11(a).

3.6.4 Molecule-Matrix Systems

In this section some typical molecules used for cryogenic single molecule studies are introduced, for chemical structure denote figure 2.6.

Terrylene

Tribenzo[de,kl,rst]pentaphene
CAS: 188-72-7
C_{30}H_{16} - M=376.45g/mol

In the current work several experiments were performed on the system of terrylene molecules embedded in p-terphenyl. The system is easy to excite and both cryogenic setups were tested and aligned with a terrylene doped sample.
Terrylene is a molecule, first synthesized by E. Clar [99]. Its use in single molecule experiments was shown first by M. Orrit and coworkers [18] and later further researched by S. Kummer.

Terrylene has been the workhorse under the molecules for cryogenic single molecule studies. It has a high fluorescent quantum yield (estimated by W.E. Moerner to be around 0.7 [100]) and is excitable by a R6G dye laser. The transition is around 578nm for a doped p-terphenyl crystal. The reported linewidth is in this matrix system between 30 and 55MHz. For a review see [101, 102, 103]. The Franck-Condon factor is estimated by W.E. Moerner [100] to be 0.4. Recent experiments describe also spectroscopy on terrylene in a supersonic expansion [104, 105].

The geometry of the system is $9.203\,\text{Å} \times 16.125\,\text{Å} \times 4.439\,\text{Å}$ [106].

**DBATT**

Naphthaceno[2,1,12,11-opqra]naphthacene

CAS: 188-42-1

$C_{30}H_{16}$ - $M=376.46\,\text{g/mol}$

The system of dibenzanthanthrene (DBATT) was first described in single molecule experiments by A. Boiron in [107] for embedded molecules in a Shpols’kii matrix of hexadecane. F. Jelezko and coworkers describe a system of DBATT molecules in naphthalene crystals [108]. A more detailed review on this system can be found in [109].

The system of DBATT molecules, embedded in the crystalline p-terphenyl sample was used to provide an alternative to the orientation of the molecules in the terrylene-p-terphenyl system. The system DBATT in p-terphenyl was not described in the literature so far and the 0-0 transition was determined by R. Pfab to be around 611nm. In the annealed samples the transition was slightly red-shifted and was
found to be around 615nm. All experiments in this work on DBATT molecules were performed at a wavelength of $\approx 615$nm.

DBATT shows a low contribution of the triplet state. In [110] saturation measurements are performed and the contribution of the triplet state in the saturation is calculated to be only 13%.

We estimated Debye-Waller factor ($\alpha_{DW}$) of the system to be around $0.25 \pm 0.05$, which is slightly larger than the estimated values for the system in naphthalene [109].

The geometry of the system is $9.640 \text{Å} \times 17.931 \text{Å} \times 3.922 \text{Å}$ [106].

**p-terphenyl**

**CAS:** 26140–60–3

$\text{C}_{18}\text{H}_{14} - M=230.30\text{g/mol}$

For several samples the matrix system of $p$-terphenyl was used. $p$-terphenyl is an aromatic system which is also used as a laser dye for short wavelength ($\lambda \leq 350$nm). No transitions are available above $\lambda = 400$nm, so the crystal is transparent in the spectral region of our studies.

The crystal structure of $p$-terphenyl has been extensively studied and forms a monoclinic unit cell of $a=8.1\text{Å}, b=5.6\text{Å}$and $c=13.6\text{Å}$. The long molecular axis lie in a slight (15°) angle with respect to the other axis.

Below $T=193K$ $p$-terphenyl undergoes a phase transition and the rotation of the inner phenyl ring is frozen out. For a detailed review on the mechanical properties of $p$-terphenyl, see [111].
4 Measurements & Results

4.1 Introduction

The fundamentals of single molecule spectroscopy and of near-field optics were introduced in chapter 2. Combining these two methods we get to the interesting situation where the absorption cross-section of a single molecule at low temperatures $\sigma_{\text{abs}}$ is larger than the size of the light source used in the experiment.

To achieve an optimal interaction between a single molecule and the near-field tip, we performed scanning near-field optical microscopy (SNOM) on a single molecule at $T=1.4K$. Simultaneously we recorded the red-shifted fluorescence of the molecule and in extended studies also the transmitted light on the incident wavelength. Throughout all measurements frequency dependent spectra were recorded.

Depending on the local position of the molecules in the sample, different shapes could be observed in a frequency scan. This data, showing the spatial dependence, is presented, as well as the different approaches used to maximize the visibility of the signal.

After introducing polarization optics to the setup, the polarization dependence was studied. The signal can be perfectly fitted with minimal input parameters. These experiments are published in the frame of this dissertation [41].

For an analysis of the mode overlap, the plain beam was monitored and the unfocussed beam emerging from the microscope objective was recorded on a sensitive camera. These measurement research the angular dependence.

At the end of this chapter a summary of the findings is presented which is emphasized by actual measured data.

4.2 Stark Measurements

The optical transitions of a single molecule are changed by an external electrical field. This effect is introduced and explained in chapter 2.2.2. This phenomenon was used to localize single molecules in real space by scanning a small electrode with a size of $3\mu m$ scanned roughly 400nm above the sample. Here, at each point 10 different tip voltages were applied and for each molecule-tip position the behavior of a single molecule was monitored. The resulting signal at each pixel could be fitted with a quadratic curve. By now plotting the overall Stark shift in relation to the tip position, it is possible to determine the molecules position to an accuracy of $\pm 2nm$. This method was applied to terrylene molecules and was published in [48]. A detailed review of this experiment can be found in the dissertation of C. Hettich [6].

For the experiments with a sharp near-field aperture tip the overall Stark shift was expected to be much larger with sharp tips, because the field gradients are much
Figure 4.1: With a fixed tip position the molecular resonance is shifted and the linewidth is changed. In this figure the perturbing field by the tip is compensated by a voltage of about 5V. The tip-sample distance was in this experiment 200nm. The same experiment was repeated several times with different tips and also with and without shear-force feedback, where the tip is excited with a frequency of $\approx 34\text{kHz}$ – the type of the spectral response is always the same.

The first measurements were performed without any light sent into the optical fiber tip. The setup was used in a confocal mode, so that a diffraction limited spot could be used to illuminate the sample with the incident laser and the fluorescence excitation spectrum was recorded.

4.2.1 Voltage Dependent Spectra

To monitor the spectral linewidth of the molecule with respect to the external field, an external voltage source was used to change the tip voltage. The counter electrode was the cryostat, which was grounded on the central ground point. With a fixed position of the tip above a molecule and changing the external tip voltage, the spectral transition and the linewidth were observed to change. The sampled molecules show a linear STARK effect. These early measurements were performed on unannealed samples with terrylene. Whereas all measurements on annealed films showed a quadratic STARK effect.

Interestingly the minimum linewidth was found at a certain voltage (see figure 4.1). This was most probably an effect of ion implantation of the focused ion beam.
4.2. Stark Measurements

milling which had a certain charge impact on the tip, and could be compensated
with an external voltage. By optimizing the applied voltage on the tip so that the
influence on the molecule was small, no further change of the voltage was needed to
detect optimally other molecules.

4.2.2 Coarse Positioning on the Axis

The positioning of the tip with respect with the molecule was of critical importance: In the actual
experiment the near-field tip, the molecule and the confocal detection spot had to be on the optical axis.
Usually the molecules were easily found in a confocal configuration. If a single molecule was spectrally se-
lected, then the confocal signal was optimized by scanning the galvanic mirrors until the maximum signal
was obtained. This procedure was usually performed in a few minutes, resulting in a laser scanned image of
the molecules fluorescence.

In later measurements the tip had to be placed on
the optical axis as well. This was a critical issue be-
cause initially the excitation of the molecule by the tip
was not realized, and it was imperative that the tip
should not touch the sample. This would endanger the
chosen molecule by shifting its resonance by pressure
effects. To reach the optimal position of the fiber tip,
the tip was brought into close proximity of the sam-
ple and the excitation power was increased. While
detecting the light through the fiber tip (with a pho-
tomultiplier placed right behind the fiber coupler) the
laser focus was again scanned by the galvanic mirrors.
Afterwards the resulting, almost GAUSSian, image was
processed. By controlling the sample scanner together
with the relative calibrated galvanic mirrors, the tip
could be driven on axis with the detection focus and
the molecule.

4.2.3 Position Dependent Stark Shift

After coarse positioning of the tip, a chosen molecule
was monitored by its confocally detected fluorescence excitation signal. The tip was
then laterally scanned over the molecule. While performing a frequency scan on
each tip position, the molecular resonance frequency was monitored. Due to the
perturbing field of the tip, the molecule showed a large frequency shift. Usually the
tip was grounded, but nevertheless the resulting STARK shift of the molecule was
spread over tens of GHz. A typical measurement can be seen in figure 4.3. Here
two molecules are observed in a fluorescence excitation scheme in a focussed spot
(∅ ≈ 1µm). Only one molecule is strongly influenced spectrally by the tip position,
Figure 4.3: Monitoring the molecular response while scanning a FIB-milled near-field tip over the molecule. The molecular response shows the shape of the tip. This method is a combination of the single molecule light-source [112] and the STARK-microscopy [48].

whereas the other (lines at 2.7GHz and 4.5GHz respectively) shows spectral jumps, but no further shift by an external field. The strongly influenced molecule monitors the field from the tip and resembles the tip shape, also the small plateau of the tip can be seen. The tip was scanned in constant height mode with a distance of ≈ 100nm.

The STARK shift measurement of a single molecule, which is changed by a perturbing macroscopic object, is a new kind of microscopy, where the STARK shift is used to image an object relative to the molecules position. This method is a combination of the single molecule light source, which was used to image a microscopic sample [112] and the method of STARK microscopy [48, 113].

A more accurate processing of the data shows a change in the linewidth of the molecule which is changed by the presence of the tip. The maximum linewidth is at the position of the maximum STARK shift (at about 10.5GHz). Early assumptions that this effect could be related to the dithering of the tip due to the shear force detection scheme, could be disregarded by turning off the tuning fork excitation and also by scanning the tip in different directions. Furthermore, the signal would be
Figure 4.4: Near-field tip, positioned laterally above the molecule, approached with 5 alternating voltages (-15V, -7.5V, 0V, 7.5V, 15V) towards the molecule. The graph shows that depending on the tip-voltage the molecule is shifted in different directions, as well as the line broadens with a higher field seen by the molecule. This experiment shows the ability to apply a tip-voltage that the molecule is only weakly influenced by approaching the tip towards the molecule. The linewidth is also the smallest if this voltage is applied.

broadened most where the biggest slope from the tip field occurs. Other broadening mechanisms must be responsible for this broadening effect. This effect was used, but not further researched.

4.2.4 Voltage & Distance Dependent Spectra

In another experiment not only the voltage applied to the tip was changed, but also the tip-sample distance. Before the measurement the tip was parked laterally above the molecule. Then the tip was approached and different voltages were applied. In the observation space one molecule showed a strong response to the external applied field. The measurement and a fit is shown in figure 4.4.

For the fit of the experimental signal all fluorescence frequency scans were fitted with a Lorentzian first and afterwards the linewidth, the intensity and the spectral shift were independently fitted. The fit function used to describe the change in the linewidth and the spectral position was

\[
\text{position, linewidth} = a \text{ voltage} \frac{1}{(\text{distance} - b)^2 + c}
\]  

(4.1)

where \(a\) represents the amplitude, \(b\) a relative shift and \(c\) the background level of the fit. This function assumes a distance dependence of \(\frac{1}{r^2}\), but is not based on further theoretical assumptions. Interestingly the result of the independent fits of the spectral position and the linewidth agree well: The overall change in the
Figure 4.5: Analyzing the distance and voltage dependence of the molecular response two fits were produced: All line positions were analyzed and their specific line position were fitted. In the right graph the same procedure was applied to the linewidth. Both fits were performed independently and the ideal tip-voltage is for figure 4.5(a) -2.18V and for figure 4.5(b) -2.29V.

linewidth seems to be strongly related to the spectral position. If the tip voltage is applied that the overall frequency shift is minimized, also the linewidth has its minimum extension. The levels on which this occurs are fitted to be -2.18V for an unaltered spectral position and -2.29V for the narrowest linewidth of the data presented in figure 4.5.

For all further measurements the tip-voltage was such applied such, that a minimum spectral shift occurs when the tip-sample position was changed. This was applicable for all experiments, molecules and matrices. For an example see figure 4.6.

4.3 Single Molecule SNOM at 1.4K

To reach the goal of measuring the extinction of light by a single molecule, first the molecules had to be excited by the light coming out of a near-field tip. This was not a trivial issue, because any input of light into the fiber tip heats up the very end [62, 63]. Any heat transferred to the molecule would broaden the line that it is not observable anymore. The first experimental approaches were gently increasing the amount of light, but not resulting in an excitation of the molecule. After increasing the incident light intensity by some orders of magnitude at a certain point the molecules were observable in fluorescence excitation mode.

At constant distances several linescans and also images of single molecules were recorded. The Stark shift was such aligned that the minimal linewidth was reached and to obtain an image, all lines were fitted with a Lorentzian line. For the presented images the intensity of the Lorentzian fit is presented. The linescans were
also performed in shear-force mode, i.e. when the tip was under constant feedback of the electronics, for the images the tip was held at a constant distance.

The first SNOM measurements were performed on terrylene molecules. The linescan in figure 4.7 shows a typical behavior of a molecule responding to the $z$-component of the tip field (for an instructive picture see figure 4.8(a)). This measurement was recorded with the tip approached to the sample and the distance was only controlled by the feedback loop.

For all further measurements the overall tip-molecule alignment by SNOM was the basic prerequisite which had to be guaranteed to perform any further measurements. No detailed studies of near-field imaging were performed. In the mean time a similar result was published by J. Butter and coworkers [114]. As one important basis the sample thickness has to allow near-field studies, i.e. an approach to the molecule which is closer than the optical wavelength. If the tip would be more far away, two things happen: a) The excitation from the tip drops, as expected, exponentially with the distance and b) due to the fact that the tip acts as a small, point like light source, the resolution is usually in the same range as the distance from the aperture to the molecule. The sample also has to guarantee the mechanical and spectral stability of the molecules. As mentioned above, also possible effects of heating the molecule have to be taken into account. Lateral images were also recorded (see figure 4.8(b)).

Due to the overall orientation of the transition dipole moment the molecule was changed from terrylene to DBATT. The molecule does not show two lobes which show the sensitivity to the $z$-component of the in the measurement anymore, but
Figure 4.7: One of the first SNOM measurements on a single molecule at 1.4K. After positioning a single molecule under the near-field tip, linescans were performed to find the center. The molecule under study on this picture is terrylene which has a transition dipole moment along its long axis (see also chapter 3.6.4) and which is embedded with an angle of about 15° to the surface normal. The resulting excitation is strongly limited to the z-component of the near-field of the tip (see chapter 2.4.4).

Figure 4.8: An illustrative picture how terrylene molecules react on the light field of a near-field tip. In 4.8(b) one of the first SNOM images can be seen.
4.4 Extinction Measurements

The main goal of this work was to achieve optimal interaction between light, emerging from a near-field tip and a single molecule at low temperatures. All measurements which were described so far used fluorescence excitation spectroscopy, and an optimal interaction was not needed. In this chapter the detection is extended to the incident wavelength, whereas the detection of the red-shifted fluorescence is performed simultaneously.

4.4.1 Measuring the Attenuation of a Laser Beam by a Single Molecule

By performing a SNOM measurement on a single molecule, the detected light coming from the optical fiber tip is altered. A theoretical description of this effect is presented in chapter 4.5.2. The transmitted light of the optical fiber tip through the sample shows an imprint of the single molecule on the detector.

To perform an extinction measurement of light by a single molecule no complete SNOM images had to be taken. The usual way to perform the measurements was to “park” the tip a few ten nanometers in front of the sample and try to excite single molecules through the tip. This was detected by the method of fluorescence excitation spectroscopy. The signal was then maximized by lateral movement of the

Figure 4.9: Two tip-linescans over a single DBATT molecule at T=1.4K. In the later stage of the experiments these linescans were performed routinely to position the tip carefully above the molecule. The molecular response is different to the results in figure 4.7, because the transition dipole moment is oriented at ≈ 25° to the surface normal of the sample.

one intensity maximum on which the tip was aligned, showing the further tilted transition dipole moment of the molecules.

A SNOM linescan of a DBATT molecule can be seen in figure 4.9 with a FWHM of 200nm, respectively 190nm. This was performed for all further measurements and the tip was aligned to the maximum of the intensity.
sample and monitoring the red shifted fluorescence. For an example see figure 4.9. On the maximum position of the fluorescence excitation signal, all following steps were performed. With the tip in position, several STARK measurements were also performed. Here the maximum of the STARK parabola (in the annealed crystals usually a quadratic STARK effect was observed) and the minimum linewidth was chosen to get the narrowest line, which was also not changed dramatically by the presence of the tip (for a further discussion see chapter 4.5.3).

To measure the extinction, the light in the fiber was attenuated, until the detected intensity on the excitation wavelength was close to the maximal count rate \( \approx 4.2 \cdot 10^6 \text{cps} \) of the home built counter. The count rate used for the measurement was measured to be about \( 1 \cdot 10^6 - 3 \cdot 10^6 \) counts per second. The used counter had a maximal output of \( 2^{12} \) counts, so the integration time had to be reduced to a few milliseconds (1-5ms from 30ms, which was the usual value for the fluorescence excitation spectra). To get the signal on an appropriate signal-to-noise ratio, an integration of 50-200 frequency scans was performed for the same tip-sample position. An overall transmission measurement had to be recorded about 10-100 times longer than for the pure fluorescence excitation signal. For a processing of the data the simultaneously recorded fluorescence excitation data was fitted with a Lorentzian and frequency jumps or jitter of the molecular transition were compensated by shifting the frequency scans by a few MHz to allow further averaging. Depending on the strength of the fluorescence excitation signal, also this reference had to be averaged before (taking a bin of several lines which were recorded in fluorescence excitation mode).

The feedback loop, controlling the light intensity was locked on the in-fiber detector, see chapter 3.3.3. This was necessary because the fluorescence excitation spectra were insensitive to small fluctuations on the excitation intensity while the detection on the incident wavelength was not. In this configuration (tip on fixed position, STARK voltage optimized), several measurement were performed. The signal on the detector in the far field was showing dispersive line shapes, as described in chapter 2.3.7.

When several molecules were located in the observation area, and excited by the near-field tip, different line-shapes could be observed in a single scan. One example is given in figure 4.10. Here both molecules have a different phase relation to the incident field and show therefore a different lineshape in their extinction signal. This feature is caused by different modes traveling from the molecule towards the detector, in the theoretical framework of this work these parameters were denoted as \( f \) and \( g \), representing the components from the molecule and from the tip. If in one scan two different lineshapes were detected, the overall tip position remained the same, consequently the modal parameter \( g \) was the same for both molecules. All data which were recorded in the transmission configuration, were fitted with equation 2.54. As a measure of the linewidth the fluorescence excitation signal was taken. The excitation intensity was fitted to the outer rims of the spectrum. The unknown absolute values for the parameters like the modal factors \( f \) and \( g \), the dipolemoment \( d_{21} \) and the Debye-Waller \( \alpha_{DW} \) factor, were assumed to be one summarized constant, entering into the visibility and the lineshape. Due to the fact that the excitation was weak, it was assumed that the scattering term could be neglected. The remaining fit parameters were the visibility, defined as
4.4. Extinction Measurements

\[ V = \left| \frac{I_{\text{det}} - I_{\text{exc}}}{I_{\text{exc}}} \right| \] and the relative phase between the incident light and coherently scattered components \( \varphi \).

The maximum effect in a transmission measurement showed a visibility of 6% in a direct measurement of the extinction signal. Here no further noise suppression like lock-in techniques were used. By shifting the resonance of the raw data (see figure 4.11) to account for spectral diffusion of the molecule, the resulting signal can be seen in figure 4.12.

### 4.4.2 Distance Dependence

After observing a dispersive shape in some of the measurements, it was assumed that the line shape can be controlled by changing the tip position with respect to the molecule. For a distance dependent measurement the sample approached slowly towards the molecule.

The background intensity, monitored on the transmission signal far off resonance showed a behavior as in figure 4.13. The signal shows a strong drop of the intensity when the tip is very close to the sample (0-250nm), and it shows a sinusoidal behavior with a period corresponding to the incident wavelength.

Such a signal is also observed in the dissertation of B. Hecht and was used in some SNOM measurements as a measure for the tip-sample distance [71].

This approach curve was fitted with the following equation and a distance calibration was performed.

\[ I = a \cos (kz + \psi)e^{-z/z_0} + o \quad (4.2) \]

Here \( a \) represents the amplitude, \( o \) the offset, \( k \) a wavevector, \( \psi \) a phaseshift and \( z_0 \) a characteristic decay length.

In a distance dependent scan the fluorescence intensity was observed to drop exponentially with distance. This behavior was also observed in the near-field experi-
Figure 4.11: Transmission measurement with simultaneously recorded. Tip sample distance: $\approx 60\text{nm}$. Compensating STARK Voltage: -4.52V

Figure 4.12: The averaged data from figure 4.11: All lines with respect to the fitted fluorescence shifted and all lines averaged. Total recording time: $\approx 44\text{sec}$. The right axis denotes the recorded counts on the detector. Noise floor about 0.3%.
4.4. Extinction Measurements

Figure 4.13: The light intensity of a near-field tip which is detected on a detector in the far field. The curve is fitted by equation 4.2. The rapid drop of the intensity was used in other experiments as a way to monitor the tip-sample distance [71].

Figure 4.14: Processed data from the figures 4.16 and 4.17 for z-dependent measurement 1. The fluorescence intensity (max. of a LORENTZ fit) is plotted.

ments which were used to prepare the measurements. One z-dependent measurement of the fluorescence can be seen in figure 4.14(a).

The scan shown in the figures 4.14 and 4.15 was recorded as 20 distances, for each distance the spectrum was recorded 100 times. The applied tip voltage was -27.3V. The resulting linewidth is $\approx 70$MHz and does not change over the whole distant dependent scan of about 400nm, which is a sign that no further line broadening mechanisms came into play. The integrated lines for the fluorescence data are shown in the figures 4.16. The overall transmission signal is presented in 4.17. For the fit of the overall transmission signal the equation 2.54 was used.

The z-dependent scans have been processed and the overall geometry was used as a base for FDTD calculations. The resulting numerical simulations were showing qualitatively the same behavior than the experimental findings. The findings are presented in figure 4.18.

Z-dependent measurements have been performed many times. The overall change
Figure 4.15: Processed data as in figure 4.14 (z-dependent measurement 1) with the background and the phase information relative to the tip-sample distance. The background shows the same behavior as in figure 4.2 the phase undergoes a complete phase change from a dispersive shape to a peak to another dispersive shape and a dip.

Figure 4.16: The fluorescence observed for the z-dependent measurement 1 on the far-field detector of a single molecule under the aperture of a near-field tip. No specific broadening is observed in these experiments.
Figure 4.17: The evaluation of the transmission signal, simultaneously recorded as figure 4.16, dependent on the tip-sample distance. All different line shapes can be observed – in the close proximity a dispersive line shape can be seen.
Figure 4.18: Finite difference time domain (FDTD) calculation for the specific geometry as used in figure 4.19 and 4.20.

Figure 4.19: z dependent scan of the fluorescence intensity and plotted visibility in a distance dependent scan for a second molecule and a different aperture diameter (measurement 2). The tip-aperture diameter was 200nm.
in the transmission signal differed within samples. Obviously the influence of the position of the molecule within the sample was important. The behavior, observed in the z-dependent measurements remains the same: An exponential increase of the fluorescence intensity, the background signal which is similar to the described approach curve and a change in the phase. The visibility behaved similar to the background signal (always a minimum at 200-300nm).

The phase behavior of the transmission signal seems to be dependent on the lateral alignment of the tip and the overall integrated signal on the detector. By the use of a pinhole in front of the detector the set of modes emerging from the tip-molecule configuration towards the detector is reduced. If the two mode components \( f \) and \( g \) remain the same and therefore the relative phase behavior of \( \varphi_f \) and \( \varphi_g \) remains unchanged the observed change in the phase could be suppressed. In the presented distant dependent scans no pinhole was introduced and the relative phase change was large.

### 4.4.3 xy-Scan

Furthermore lateral scans were performed on a single molecule, on which the signal was recorded on both channels, the fluorescence and the transmission. The scans were lengthy because of the long integration time to detect the transmission signal.

The presented xy-scan is recorded at a constant height of the tip to the sample surface of \( z = 93 \text{nm} \), with a compensating tip voltage of \( U = -6.3 \text{V} \), the total recording time was 195min. The each of the 6×15 pixels was recorded 20 times to get an average signal. Unfortunately the mechanical influence of the tip shifted the spectral position of the molecule and the measurement stopped when the tip was in the next line, which is not presented.

Figure 4.21(a) shows an SNOM image in fluorescence excitation mode. This is completely equivalent to the SNOM measurements presented above. It was also possible to detect the transmission signal which was simultaneously recorded. The fitted visibility is plotted in figure 4.21(b)
When we laterally scanned the tip position with respect to the molecule, we also changed the line shape of the transmission signal. This phase behavior is shown in figure 4.22.

4.4.4 Polarization

To optimize the excitation of the molecule in front of the tip the polarization of the tip and the molecule was studied. These properties were usually monitored by a sheet polarizer (New Focus, 5511), turned in the detection path. Depending on the orientation of the molecules transition dipole moment the signal in the fluorescence excitation changed while turning the polarizer. The preferred polarization direction could be determined by such a measurement. The slightly out of plane oriented molecules showed a behavior as in figure 4.23(b). The extinction ratio ($\approx 1 : 2$) of the signal represents the $z$-orientation, determined to be around $25^\circ$ out of plane (see chapter 3.6.2).

The overall background signal showed a much higher extinction ratio ($\approx 1 : 17$, see figure 4.23(a)). This is in agreement with the fact that specific tips had a good polarization preserving and showed a preferred output polarization. The output was ranging from 15000 cps up to 250000 cps. In this experiment the tip-sample distance was $z = 57$nm. The compensating tip-voltage was set to $U = -6.3V$. Interestingly the main axis of the polarization of the fiber in relation to the molecule were shifted by $\kappa \approx 21^\circ$ (this angle can be found by comparing the minima in figure 4.23(a) and 4.23(b)). By turning the polarizer by an angle $\vartheta$ and adapting the integration time to keep the same signal to noise ratio for all lines we detected a full polarizer turn ($180^\circ$). As the analyzer angle $\vartheta$ changes, also the relative phase between the incident light and the molecular emission changes. This resulted in different lineshapes as it can be seen in the background normalized figure 4.25.

By changing the polarizer angle $\vartheta$ the mode parameters (described as $f$ and $g$ in chapter 2.3.7) change and the relative contributions of the incident light and the elastically scattered contributions of the molecule change. By adding the lines for the angles $\vartheta$ and $\vartheta + \pi/2$ the signal shows an all absorptive shape for all $\vartheta$. The

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**Figure 4.21:** Two dimensional plot of the fluorescence intensity of a single molecule under a near-field tip. Figure 4.21(b) shows the visibility of the transmission signal with respect to the tip position.
4.4. Extinction Measurements

Figure 4.22: The inner most line (line 6) of the shown lateral scan. The two inserts show the phase and the visibility, fitted to each pixel. Denote that the spectral position slightly shifts due to the Stark effect.

Figure 4.23: Fitted background and fluorescence intensity to the raw data of 4.25(a). Here the relative tilt between the preferred polarization of the tip and the molecular transition dipole moment becomes obvious.
surplus signal in the situation of maximal suppressed incident laser intensity reaches 10%.

The polarizer scan assumes that the background signal which is recorded far from resonance, can be described by a projection of the incident polarization \( \mathbf{E}_{\text{exc}} \) onto the orientation of the polarizer \( \mathbf{P} \)

\[
I_{\text{exc}} = C_{\text{exc}}|\mathbf{P} \cdot \mathbf{E}_{\text{exc}}|^2
\]

(4.3)

where \( C_{\text{exc}} \) is the amplitude of the background, \( \mathbf{P} \) describes the analyzer and \( \mathbf{E}_{\text{exc}} \) represents the incident wave from the tip.

The polarizer can be described by

\[
\mathbf{P} = \begin{pmatrix}
\cos \vartheta \\
\sin \vartheta
\end{pmatrix}
\]

(4.4)

here \( \vartheta \) is the polarizer angle. The incident light field can be described as

\[
\mathbf{E}_{\text{inc}} = \cos (\phi_{\text{inc}}) \mathbf{e}_x + i \sin (\phi_{\text{inc}}) \mathbf{e}_y
\]

(4.5)

where \( \phi_{\text{inc}} \) represents the elipticity of the incident light and \( \mathbf{e}_x \) and \( \mathbf{e}_y \) are unit vectors along the x- and y-axes (\( \hat{x} \)) and (\( \hat{y} \)).

With these equations the excitation intensity can be fitted, as shown in figure 4.23(a).

Similarly the field of the red shifted photons can be described by a certain elipticity \( \phi_{\text{mol}} \) which is introduced by the molecule and a relative angle \( \kappa \) between the two components (about 21° shift between the two components, see 4.23(a) and 4.23(b)):

\[
\mathbf{E}_{\text{mol}} = (\cos \kappa \cos \phi_{\text{mol}} + i \sin \kappa \sin \phi_{\text{mol}}) \mathbf{e}_x + (\sin \kappa \cos \phi_{\text{mol}} + i \cos \kappa \sin \phi_{\text{mol}}) \mathbf{e}_y
\]

(4.6)

The overall intensity for this amount reads:

\[
I_{\text{mol}} = (C_{\text{mol},\perp}|\mathbf{P} \cdot \mathbf{E}_{\text{mol}}|^2 + C_{\text{mol},\parallel})L(\delta)
\]

(4.7)
4.4. Extinction Measurements

Figure 4.25:

Polarizer scan in the detector arm – basically the raw data, normalized to a standard background. The features are directly observable. In respect to the polarizer rotation different line shapes can be observed.
Fitted phase behavior.

with $\mathcal{L} = \frac{T_{\text{hom}}^2}{\pi^2 T_{\text{hom}}^2}$. Furthermore the components of the molecular contribution are disassembled into two components: $C_{\text{mol},\perp}$, describing the component of the molecule which is oriented along the film surface and can be extincted by using the polarizer; $C_{\text{mol},z}$ is the component of the light which is out of plane and cannot be extincted, because the emission is mostly polarized along the z-axis. The fitted data of the red shifted fluorescence can be seen in figure 4.23(b).

To calculate the visibility $V$ the following equation can be used:

$$V = |C_{\text{yel},\perp}|^2 P \cdot E_{\text{mol}}|^2 + 2 C_{\text{if}} (P \cdot E_{\text{inc}})^* (P \cdot E_{\text{mol}}) e^{i \phi_0}|$$ (4.8)

here $C_{\text{if}}$ represents the interference component and $\phi_0$ the phase at a polarizer angle at $0^\circ$. Similar as before $C_{\text{yel},\perp}$ represents the component of the incident light which can be extincted by the polarizer. The visibility of the polarizer scan was fitted by this equation. The number of photons which contributes to the visibility is calculated and presented in figure 4.24(b).

The phase can be calculated with the fitted values as

$$\Phi = \text{Arg}(C_{\text{yel},\perp}|P \cdot E_{\text{mol}}|^2 + 2 C_{\text{if}} (P \cdot E_{\text{inc}})^* (P \cdot E_{\text{mol}}) e^{i \phi_0})$$ (4.9)

By these assumptions the phase behavior can be simulated. In figure 4.26 the calculated and measured phase can be seen.

With these assumptions and the overall fitted linewidth of 35MHz, the spectra can be fitted. The fitted lines and the overall simulated scan can be seen in figure 4.27 and in figure 4.28.

The optical fiber (with bends and the pulled, coated tip) acts like a waveplate, which transform the linear input polarization into an arbitrary output polarization state. According to some experimental work [115, 116] this change of polarization
4.4. Extinction Measurements

Figure 4.27:
All measured lines fitted. For details see text.

Figure 4.28:
Simultaneous fit to all recorded lines of the polarizer scan. All data from the previous fits (see figure 4.27) are used to simulate this figure.
remains constant over time (under laboratory conditions), and can be compensated by optical elements in front of the fiber coupler. To characterize the output polarization state of our fiber probe, we performed the following measurements to determine the STOKES-parameters, which give values for the total intensity, degree of linear polarization, degree and direction of circular polarization, and amount of unpolarized light (in the far field).

We assign $z$ to the optical axis, and $x$ to be the direction perpendicular to the laser table. To measure the STOKES-parameters, first a calcite polarizer (analyzer) is aligned in $x$-direction, which is $0^\circ$, and the power of transmitted light determined. Then the polarizer is rotated to $45^\circ$, then along the $y$-axis, and to $135^\circ$. This gives the first three STOKES parameters:

\[
S_0 = I(0) + I(90) \quad S_1 = I(0) - I(90) \quad S_2 = I(45) - I(135) \quad (4.10)
\]

To determine the degree of circular polarization, a quarter wave plate is inserted in front of the analyzer with its fast axis along $x$. The analyzer is then rotated to $45^\circ$ and $135^\circ$. This gives

\[
S_3 = I(45, \frac{\pi}{2}) - I(135, \frac{\pi}{2}) \quad (4.11)
\]

For the setup the determined the STOKES-parameters of the far field of the tip as $S_0 = 1$, $S_1 = 0.66$, $S_2 = -0.13$, and $S_3 = 0.48$. According to [115], the amount and angle of retardation given by the fiber can be calculated and compensated with a BEREK variable waveplate. Such a waveplate (NEW FOCUS, 5540) was used to optimize the output polarization state of the tip. The procedure was to measure the extinction ratio with a sheet polarizer in the far field: The polarizer was rotated while monitoring the resulting far-field intensity of the tip. At the same time the variable waveplate was aligned such that the extinction ratio was optimized.

### 4.4.5 Imaging the Extinction on a Camera

To image the overlap the excitation and molecular emission modes, the propagating beam was monitored. For this purpose the focusing optics in front of the camera was removed and the beam was sent directly on the camera. The ideal measurement would have been to monitor the image in the back focal plane, but unfortunately this procedure is tedious, because everything is located in the cryostat and proper alignment cannot be done with a cooled and closed cryostat.

The focussed image of a tip looked like small, diffraction limited spot if the objective in front of the camera was in place. The method to align the focus of the microscope objective on the tip was always optimized to the highest peak on the camera image. By this method also the overall quality of the tips was checked – if the tip had small pinholes due to insufficient or inhomogeneous coating with aluminum, this could be easily monitored, by slight defocussing the microscope objective with respect to the end of the tip.

After removing the focusing optics of the camera (basically to unscrew the camera objective, see figure 4.29 for the setup), a superposition of two components becomes visible: The back focal plane image (as in [97]) and the FRAUNHOFER diffraction
Figure 4.29: The setup used to determine the mode-overlap between the tip emission and the molecule. The current setup was modified by removing the focussing lens in front of the camera. This is not a real back focal plane imaging, which would have been hard to align by with the cryostat in place.

Figure 4.30: The mode structures, observed with the setup, shown in 4.29. The arrow denotes the orientation of the transition dipole moment, as monitored by a polarizer in the far field.
from the output aperture, leading to several rings in the rim of the propagating beam. The later effect is unwanted and should be avoided in further setup configurations. Nevertheless, the smoothness and the symmetry of the free propagating beam could be judged, as well as the polarization properties, putting a polarizer between the tip and the camera. A sample image is shown 4.30(a).

Usually the tips were judged by looking on the

- symmetry of the pattern
- extinction ratio of light in the polarizer configuration

Tips that showed an asymmetric pattern and a strongly preferred polarization direction were sorted out. Also directly after fabricating the tips in the focussed ion beam machine the tips (3.4.3), their properties were controlled in an equivalent room-temperature setup. Basically the same properties (for the focussed image and plain beam) were observed in these experiments. To get more insight the mode-overlap of the tip and the molecule several measurements were performed to map the emission pattern of a molecule directly in the same manner as described for the tip.

For these measurements the setup in figure 4.29 was used with a long pass filter and the molecular fluorescence was monitored with a camera. The excitation was performed in confocal mode. Two sample images, with the determined orientation of the transition dipole moment are presented in figure 4.30(b) and 4.30(c). Note that the other single molecule transmission experiment this light was focussed onto one pixel, the APD.

The qualitative agreement between the images taken from the tip and the molecular image suggested that in this configuration the mode overlap can be high. The pattern showed a high similarity in the far field and for the transmission measurements. Due to the interferometric behavior of the transmission we expected that this overlap had an important impact on the overall effect. These assumptions do not account for the actual near-field components.

The overall effect on the transmission signal was expected to be strongly angle dependent. This assumption was made due to several experiments when a pinhole in the detection path caused a different phase behavior and is also described in literature [117]. With the camera in place and by monitoring the raw beam on the camera a frequency and angle dependent image was recorded: The scan was recorded with a tip-sample distance of \( z = 212 \text{nm} \). The compensating tip-voltage was \( U = 4.51 \text{V} \). The frequency was scanned over \( \Delta \nu = 1.8 \text{GHz} \) and was divided into 30 pixel (60MHz/pixel).

Simultaneously the signal was recorded on the APDs, which were recording on the incident wavelength as well as the red-shifted fluorescence. The signal on the APDs and the integrated camera image are plotted in figure 4.31.

The recorded image (out of resonance) is shown in figure 4.32. It shows the emission and the preferred output polarization of the tip. Each pixel for the resulting image was assembled by a floating average over three pixels in the camera image to remove noise. Afterwards the different frequency scans were independently fitted with a linear curve. Afterwards all frequency scans on each pixel were fitted and the resulting visibility is plotted in figure 4.33.
4.4. Extinction Measurements

Figure 4.31: Measuring the extinction signal on a camera and simultaneously detecting with two APDs in the far field. Figure 4.31(c) is the overall integrated signal of the camera.

Figure 4.32: Plain image of the tip emission. The main polarization axis of the excitation light is labeled.
Figure 4.33: Visibility of the transmission signal. On different pixels a different visibility of the extinction signal was observed. The preferred output polarization of the tip is labeled and also the main axis of the transition dipole moment of the molecule was labeled. For the two pixels with the highest observed visibility two different lines are shown explicitly.

On different pixels a different phase behavior of the transmission signal was observed. Figure 4.34 shows an image of the different phase.

The idea to record a phase sensitive picture of a single molecule was performed by imaging the extinction directly on a camera.

This corresponds to a “single molecule hologram”. Similar experiments were suggested by B.W. Peuse and coworkers in 1982 [117] and its extension to single molecules imaging was proposed by T. Plakhotnik [118].

4.5 Discussion

The experimental findings show that a transmission experiment on a single molecule with a subwavelength aperture is possible. The experimental results show a maximal change in the transmission of 10%. A detailed discussion what main parameters influence the transmission effect is presented hereafter.

4.5.1 The Visibility of the Measured Signal

By performing fluorescence excitation spectroscopy, the red-shifted light emitted from the molecule could be described simply by fitting the resulting spectra with a Lorentzian line. This results in values for the intensity, the linewidth and the spectral position. Simultaneously the transmission signal was recorded. In chapter 2.3.7 a theoretical framework was introduced, which was used to describe the ex-
4.5. Discussion

experimental findings. All resulting transmission measurements could be fitted and the theoretical description included the linewidth, the visibility (as percentage deviation from the unaltered transmission) and the phase, describing the relative phase behavior of the incident light and the coherent emission from the molecule.

The experiments show that the visibility and the phase behavior is depending on the tip-molecule position. It can be theoretically described, but how the influencing parameters change the phase of the dispersive lineshape is determined by the modal parameters $f$ and $g$. In this chapter a picture is introduced, showing the influencing parameters in the experiment, reflected by the theoretical description in equation 2.54.

The phase behavior between the two fields is summarized with a relative phase of $\varphi$. This phase is a measure, depending on the modal parameters $f$ and $g$. The corresponding phases can be represented by $\varphi_t$ and $\varphi_g$. The fact that on the camera images (see chapter 4.4.5) different phases were observed, suggests that all measurements which are recorded on a single pixel detector show a sum of several phases, focussed onto the detector area. The phase depends strongly on the different components which are summed on the detector. The optical path is not equal for all angle components of the detected beam. Numerical simulations by M. AGIO allow to describe all parameters of the measured distance dependent scans. The phase, the visibility and the change in the background intensity are reproduced by the numerical simulations (see figure 4.18).

The visibility is proportional to $\frac{f_{\text{nat}}}{f_{\text{hom}}}$ and to the DEBYE-WALLER factor. Furthermore the modal parameters $f$ and $g$ also have an important influence on the detected visibility. Similar as in the absorption cross-section the visibility changes proportional to $\cos^2 \theta$. 

**Figure 4.34:** Phase behavior on different camera pixels. Over the image the overall phase change is $2\pi$.

**Figure 4.36:** The situation of near-field excitation results in an optimal mode overlap. Measured from the far-field detector the excitation dipole and the tip emission are on the same position. This optimizes the interaction between the near-field tip and the molecule.
Taking into account the measured values for the radiative lifetime $\Gamma_{\text{nat}}$ of $8 \pm 2$ MHz, a measured linewidth of 35 MHz and an estimated Debye-Waller factor of 0.25 (estimated from bulk measurements, see figure 3.25 and from reference [109]), the visibility could be $\alpha_{\text{DW}} \Gamma_{\text{hom}} / \Gamma_{\text{nat}} \approx 16$ times larger than measured. For the direct measurement, shown in figure 4.12(b), the value would approach a visibility of 100%. Indeed, for far-field excitation the maximum visibility imprinted on the excitation beam, could reach values of up to 50% [119]. The maximum achievable effect with near-field excitation exceeds the value for far-field excitation due to the geometrical overlap of the excitation field and the molecular dipole. The tip emission in the far field resembles a microscopic emitting dipole as the molecule. These findings can be deduced from the camera images like figure 4.30 and is illustrated in figure 4.36.

4.5.2 Comparison with other Measurements

Since the first measurements made on single molecules [3] were also performed in a transmission measurement configuration, a comparison of the obtained results with the findings of this work might be interesting.

One of the major breakthroughs made in this work is the fact that the resulting imprint on the ongoing laser beam can detected without any further noise suppression, like lock-in detection, for example.

In the pioneering experiments [3, 23], a slightly different phase behavior by multiple reflections could also have happened, imprinting not only a drop of intensity on the ongoing beam. This effect would have been relatively small, due to the fact that the beam was only slightly focussed and the situation shows equivalent behavior to the plane wave excitation as discussed in chapter 2.3.4. Also the extended measurements by L. Kador [26] in 1999, described as “The line shape represents the derivative of a Lorentz profile with equal amplitude above and below the baseline” show different lineshapes for different molecules embedded in the sample. The authors attribute this with molecules showing an opposite Stark effect. This explanation may will be correct, but in this measurement, the resulting signals could also have been obscured by the detection scheme.

If the molecule resonates well with the external field and the field of the emitter increases with respect to the excitation field, the direct scattering terms becomes more significant. A complete drop of intensity down to zero (= 0% transmission) is not possible, because the scattered field will always contribute to the detected signal.

In a paper by T. Plakhotnik and V. Palm [120] the effect of extinction is measured by performing an experiment in the backward direction: The authors study the interference between the light coherently emitted by a molecule and a certain component of the initial light field. The phase relation is fixed by using the back reflection of light by the crystal surface in which the system is embedded (see figure 4.37). Depending on the thickness of the crystal, and therefore the phase difference between the initial light with respect to the molecular emission, the shapes of the resulting signal changes.

The overall intensity of light on the detector $I_{\text{det}}$ simply is defined to be additive for both components:
The authors rewrite the equation (with $\delta = (\omega - \omega_0)$), to be

$$I_{\text{det}} = |\sqrt{I_{\text{ref}}} e^{i\varphi} + \sqrt{I_{\text{mol}}} \frac{\Gamma_{\text{hom}}}{\delta + i\Gamma_{\text{hom}}}|^2 \quad (4.13)$$

where $\varphi$ is the relative phase between the incident field and the molecular contribution. This phase difference is associated with the depth of the molecule in the crystal $\varphi = 4\pi nd/\lambda$. By further simplification the equation

$$I_{\text{det}} = I_{\text{ref}}[1 - 2A_0 \Gamma_{\text{hom}} \times \frac{\Gamma_{\text{hom}} \sin \varphi + \delta \cos \varphi}{\Gamma_{\text{hom}}^2 + \delta^2}] \quad (4.14)$$

can be derived. Here $A_0$ defines $\sqrt{I_{\text{mol}}/I_{\text{ref}}}$ and represents the visibility of the resulting signal.

Using this formulae the global results of [120] can be fitted (being dispersive line shapes and drops in the intensity). To account for higher excitation energies the equation is slightly changed and accounts for saturation broadening of the single molecule. In principle the same equations can be used to derive different line shapes in different directions. Only the relative phase between the incident light and the component of light scattered by the emitter is changing the overall line shape.

By showing that this effect is an interference effect the absolute numbers of photons are small. E.g. having an initial amount of $10^6$ photons per second ($I_{\text{exc}}$) and an overall effect of 10% by the single emitter (corresponding to a change in the count rate to $10^4$ photons per second), the count rate which is emitted by the molecule ($I_{\text{mol}}$) for this effect is only $10^4$ photons per second. This “self-homodyning” effect [121] allows the detection of few coherently scattered photons.

From the experimental point of view the main “trick” the authors were using was that the general amount of back reflected light is much smaller than for a transmission experiment, which would detect the same interference in the forward direction. By using a sub diffraction aperture in front of the detector, and subsequently modifying the modal structure of the backreflected components in respect with the coherently scattered components of the molecule, the amount was decreased further, so that the intensities were getting into a comparable amount and the effect was increased to a visibility of $\approx 2\%$. This modification of the modal parameters can be described in our theoretical framework as different parameters for $f$ and for $g$.

The description of the extinction as an interference effect is not new. Similarly the effect was observed on an atomic beam [117]. Also on small particles the technique was described by [122].

Recent measurements on quantum dots [123] also show slightly dispersive curves, which are not interpreted correctly in the cited reference. In a follow up paper [124]...
the authors extend their findings and compare forward and backward scattered components of the quantum dot and describe their findings in the context of interference phenomena.

4.5.3 Possible Effects Changing the Molecular Properties

Approaching the molecule with a near-field tip, several effects could influence not only the described properties like phase, visibility and background intensity. Further effects, like line-broadening or quenching of the fluorescence could principally appear. Changes in the lifetime of the excited state and a subsequent broadening of the line like observed in [96] or originally in [125] could also appear. In the described measurements of this work the above effects are not observed or obscured by spectral diffusion. Interpreting the raw data, regarding linebroadening and spectral shifts, suggest that these effects do not extend the picture, suggested by equation 2.54. The broadening and spectral shifts by the STARK effects dominate the spectral position and the linewidth.
Figure 4.35: Although the ratio of coherent to incoherent photons changes with an inversely proportional relationship to the excitation power, the visibility of the detectable extinction signal decreases not as fast and starts off at a certain, constant value. This is obvious, because not only the excitation power but also the amount of coherent photons start at low excitation powers linearly.
5 Conclusion & Outlook

In this work the first cryogenic near-field optical spectroscopy on a single molecule was performed, where the tip could be scanned in all three dimensions. Single molecules were excited by near-field tips, which had openings between 80 and 200nm. The resulting signal was directly observed using a detector in the far field, without the use of any noise-suppressing elements. Simply by recording the red-shifted fluorescence from the molecule, the first cryogenic single molecule SNOM images were recorded. In the detection setup not only the fluorescence excitation signal was measured, but also the strong interaction of the subwavelength light source, allowed the separate analysis of the transmitted light at the incident wavelength. The maximum observed drop in intensity by a direct detection was 6%. By introducing a polarizer in the detection arm, it was possible to determine the orientation of the molecule and to alter the ratio between the excitation light and the scattered light of the molecule. As the angle of the polarizer changed, the resultant spectrum changed from an absorptive to a dispersive shape. At polarizer angles perpendicular to that of the incident light polarization, the spectrum consisted of a peak, showing a surplus signal of 10%. Further experiments using a camera to observe the unfocussed beam emerging from the tip, showed a different phase behavior at different observation angles. The introduced theoretical framework describes the experimental findings well by pointing out that a change in the transmission can be described by the interference of the incident and the elastic scattered light. At different angles the modal overlap changes and the detected signal shows a different visibility.

The challenge to perform a single molecule experiment in transmission with a scannable near-field tip has been present in the single molecule community for a long time. One of the main visions was to detect a single molecule, even if its properties do not allow the use of fluorescence excitation techniques. Indeed, with the introduced experiment it would be possible to detect emitters with a very small Stokes shift. Such emitters would be detectable with the introduced method. Since we do not rely on the fluorescence, one might think that non-fluorescing, purely absorbing molecules could be detected by the introduced method. However it should be borne in mind, that the strength of the interference signal is proportional to the ratio of $\Gamma_{\text{nat}}/\Gamma_{\text{hom}}$ – so that emitters with broad transitions will also show only a weak signal in the extinction measurement.

The introduced theoretical description shows that the amount of coherently scattered light by a single emitter starts linearly for small excitation intensities $4.35$. By describing the resultant change in intensity on a far-field detector as an interference effect, it becomes clear that the visibility starts at a certain level for low excitation intensities. For a low excitation power this method would only be limited by the dark count rate of the detector and would not depend on its quantum efficiency. Experiments like the excitation of one molecule by another [126] would benefit from this idea of requesting a high signal to noise ratio with very low count rates. This
would be one way to perform such a measurement, where fluorescence excitation spectroscopy would fail. Other estimates of the signal-to-noise ratio do take this effect into account enough [127].

The ability to scan the near-field tip with respect to the molecule, allowed extended studies, in which the key parameters could be changed to achieve an optimal interaction between the light and the dye molecule. Depending on the lateral position and the distance of the tip to the molecule, the lineshape changed and the coupling strength was tunable.

For applications, one major drawback of the configuration with the near-field tip is the poor transmission of light though the optical fiber system. The measured transmission of the used fiber tips is in the range of $1 \times 10^5 - 1 \times 10^6$ – the enormous light-matter interaction, proven by a 10% altered transmission signal, accounts only for the photons which are emitted by the near-field tip. This issue may be overcome by introducing pinholes immediately in front of the single molecule emitter, however, the ability to have a scannable configuration would then be sacrificed. Another possibility would be to focus the incident light to a small spot using, for example, a solid immersion lens. In this way an efficient coupling between the incident light and the molecule should be achievable.

By introducing a polarizer in the detection arm it was possible to observe a 10% peak in intensity of the transmitted light at the incident wavelength, when the polarizer was at an angle perpendicular to that of the incident light polarization. If the extinction ratio of the incident laser light emerging from the tip would be higher, this experimental configuration could be used to detect only the direct emission by a single molecule. By this method it would be possible to produce single photon sources which work at the incident laser wavelength. In this configuration the antibunched emission of a single molecule could be used e.g. for single photon sources.

Another interesting path for upcoming experiments would be to follow the temporal evolution of the measured extinction signal. In such an experiment a red-shifted photon is detected. Then the molecule is known to be in the ground state and will therefore have no influence on the ongoing laser beam. When this signal is temporally correlated to an detected photon at the incident wavelength, this would be a measure of the time evolution of the extinction signal. Similar measurements are performed by L.A. Orozco and coworkers [128], as well as in [129], where the authors implement different monochromators before the photodetector in order to perform photon-photon correlations at differing wavelengths.
A Appendix

A.1 Calculations on Molecules

A.1.1 Semiempirical Methods

The current host/matrix systems in single molecule spectroscopy have several distinct features, which allow an ideal research on these model systems. For an overview of used dyes, at low temperatures, see e.g. \[21\]. An extension to real-life samples like cells or distinct matrix systems which show other advantages, would be desirable. Especially for microscopy purposes the solubility of molecules which is currently low, because all systems are highly apolar should be dramatically enhanced. Here the main points of optimization are a) line broadening mechanisms in a defined matrix should be as small as possible b) the fluorescence quantum yield should be unity c) the triplet states should deplete fast or should not be populated at all. Chemical properties should include good solubility, no strong permanent dipole-moment in the ground state and chemically good modifiable\(^1\).

To reach this goal a few synthesis directions were estimated. The established dyes like terrylene, TDI, pentacene and DBATT have transition wavelength in the red part of the visible spectrum, but all of these dyes have a rigid fluorophoric core and are only weakly soluble in organic solvents – so a chemical modification is a quite demanding task. Perylene based synthesis would be the chemists choice: Due to good solubility it is possible to perform perylene chemistry with a small amount of solvents and it is relatively easy, also because of the potential symmetry of the resulting product. Unfortunately pure perylene has an zero phonon transition around \(\lambda = 443.8\)\(\text{nm}\) \[131\], which is significantly in the blueish region of the spectrum. The disadvantages are an increased fluorescence background and a higher request to the laser system. In this region only stilbene dye lasers and a frequency doubled TiSa-lasers can be used. By chemical modification, especially on the rim of the fluorophoric region, the extension of the delocalized \(\pi\)-electrons is increased, leading to a red shift in the zero-phonon band transition. Unfortunately a shift towards \(\lambda = 500\)\(\text{nm}\) makes it difficult and other stilbene or coumarin dye-lasers have to be used. The frequency doubled TiSa lasersystem is not available any more in this region.

To reach the red visible and the near infrared region chemical modifications of terrylene dyes seem to be advantageous. An important drawback is the bad solubility of these dyes. This makes the dyes on the one hand stable, but especially a modification towards solubility seems to be hard. One approach would be to attach dendrimeric structures which are rigid and shape persistent, not quenching the flu-\(^1\)During the time of this dissertation several strides were made to get to water soluble rylene dyes \[130\].
orescence of the inner core. Especially the group of K. MÜLLEN contributes to this field of chemical synthesis [132].

To determine new pathways to get to a better sample, a computational chemistry approach was taken into account. To estimate the extension of the electronic orbital distribution ($\pi$-cloud), the transition wavelength for an electronic transition, the transition dipole moment and the exact geometry. Furthermore possible synthesis pathways and possible products were evaluated. Here the main directions were possible line broadening factors (enhanced quenching by permanent dipole moments, or by extended freely moving alkyl chains), the strength of the transition dipole moment and the transition frequency.

The molecules were usually designed into a z-matrix using first Chemdraw and then Hyperchem. Afterwards an geometry optimization was performed, using an MM+ force field and an iterative approach by POLAK RIBIERE to a step-to-step threshold of smaller than 0.001kcal/Åmol. Already the geometry optimization allowed to study possible quenching mechanisms. Long alkyl chains take a long time to reach the minimum in excitation energy and also cause quenching by opening further quenching pathways to the fluorophore body.

For a calculation of the orbital distribution of the $\pi$-cloud a PM3 single step semi-empirical approach was taken with Hyperchem. An example could be seen in figure 2.4. The estimated electronic spectrum showed a significant systematic error shifted to the blueish region. This is usual for an estimation for molecules calculated without a matrix system. By using the ZINDO/S method for calculations and adopting the $f_{\pi\pi}$ value to 0.444, one can estimate the electronic spectrum of several components with an error of $\pm 10$nm. Although it is hard to account from a semi-empiric calculation to a low temperature spectrum, the estimation of a transition wavelength is possible. Especially possible pathways with perylene synthesis were discarded after realizing that the transition wavelength was about $\lambda = 500$nm.

Further calculation on molecules was performed with Gaussian 98. A sample Gaussian input file is given in the appendix A.1.2.

To calculate the direction and intensity of the transition dipole moments the program Gaussian’98 was used. The constructed z-matrix, after the first geometry optimization (see above), was used to perform another two step geometry optimization. Later on the semi-empirical method ZINDO (ZERNER’S Intermediate Neglect of Differential Overlap by MICHAEL ZERNER) was used. This semi-empiric method allows to calculate electronic spectra. The transition dipole moment can be easily read out of the Gaussian output file. Furthermore the dipole strength of all electronic transitions. A sample Gaussian input file is given in the chapter A.1.2.

A.1.2 Gaussian Input File

%mem=784MB
%chk=terrylene.chk
#PM3 Opt
geometry optimization
0 1
C 0 x1 y1 z1
[...]
A.2 Tip Design

A novel tip design was developed, in which a small metallized sphere made of silica is the local probe which has a defined, focused ion beam milled hole in it. The tips can be produced either by melting the fiber-end to a small sphere or by gluing a glass bead onto a fiber-end, which is sliced and shows a plateau.

Figure A.1: The figure A.1(a) shows the proposal of a new tip design. The figure A.1(b) shows an actual fiber with a spherical tip of 3µm diameter, produced by melting of the fiber end.
Some of the problems of sharp aperture-tips are overcome by this new design. The fiber diameter does not thin below cutoff, which will substantially increase light transmission, and in addition reduce the heating of the tip. The well defined, rounded geometry will also permit an easier treatment of the measured data, especially concerning electrical stray fields, emitted from the aperture probe.

To optimize the polarization maintaining properties of a near-field aperture tip, one development was to engineer a hole into the tip, which enhances one polarization more than the other. The milling procedure was as follows: normal slicing the aperture end, observing the aperture, cutting a slit into the aperture. See figure A.2. In a room-temperature characterization the polarization maintaining properties were proven to be significantly better than for other tips. The results are not yet completely processed.

### A.3 Mathematics

#### A.3.1 Poynting vector

In the frame of this work the paper [37] of H. Paul and R. Fischer was followed to get to the Poynting vector. Here the used equations are presented.

The Poynting vector reads

\[
S = E \times H = E_{\text{exc}} \times H_{\text{exc}} + E_{\text{mol}} \times H_{\text{exc}} + E_{\text{mol}} \times H_{\text{mol}} + E_{\text{mol}} \times H_{\text{mol}} \tag{A.1}
\]

which is the same description as for the optical theorem. The components to this equations is a description for the initial wave:
\[ E_0 = \frac{100}{4\pi\varepsilon_0} \left( \frac{\omega}{c} \right)^3 d_{12} \]  
(A.2)

\[ E_{\text{exc}} = (0, 0, E_0 \cos(\omega t - kx)) \]  
(A.3)

\[ H_{\text{exc}} = (0, -\sqrt{\varepsilon_0 \mu} E_0 \cos[\omega t - kx], 0) \]  
(A.4)

And the according expressions for a single dipole (as in the original paper in cartesian coordinates):

\[ E_{rD} = \frac{\cos \theta d_{12} k^2}{2\pi\varepsilon_0 r} \left[ \frac{1}{kr} \cos(\omega t - kr) + \frac{1}{(kr)^2} \sin(\omega t - kr) \right] \]  
(A.6)

\[ E_{\theta D} = -\frac{\sin \theta d_{12} k^2}{4\pi r} \left[ (1 - \frac{1}{(kr)^2}) \sin(\omega t - kr) - \frac{1}{kr} \cos(\omega t - kr) \right] \]  
(A.7)

\[ E_{\phi D} = 0 \]  
(A.8)

\[ H_{r D} = H_{\theta D} = 0 \]  
(A.9)

\[ H_{\phi D} = -\frac{\sin \theta d_{12} c k^2}{4\pi r} \left[ \sin(\omega t - kr) - \frac{1}{kr} \cos(\omega t - kr) \right] \]  
(A.10)

\[ \mathbf{E}_D = \{ E_{rD}, E_{\theta D}, E_{\phi D} \} \]  
(A.11)

\[ \mathbf{H}_D = \{ H_{r D}, H_{\theta D}, H_{\phi D} \} \]  
(A.12)

\[ \text{Streamline Plot} \]

Mathematica source to get a streamline plot for the Poynting vector:

\[
n1[t] := \text{poynt}[[1]]/.x \to f[t]/.z \to g[t];
\]

\[
n2[t] := \text{poynt}[[2]]/.x \to f[t]/.z \to g[t];
\]

\[
sol1 := \text{NDSolve}[
\{f'[t] == n1[t],
g'[t] == n2[t],
f[0] == -2 \text{xstart},
g[0] == \text{zstart}
\},
\{f, g\}, \{t, 0, 0.2\}, \text{MaxSteps} \to \text{Infinity}, \text{MaxStepSize} \to .01 \};
solut := \text{Evaluate}[\{f[t], g[t]\}/.\text{sol1}];
\]

\[
\text{stop = solut}[[1, 1, 0, 1, 1, 2]];
\]

\[
\text{ParametricPlot}[\text{solut}, \{t, 0, \text{stop}\}];
\]

\textbf{A.3.2 Bethe-Bouwkamp calculations}

To calculate the emission pattern of a near-field tip the theoretical descriptions of a subwavelength hole in an infinite conducting screen from \textsc{Bethe} [55] and
Bouwkamp [56] were used. The incident light field is x-polarized and reads as follows:

\[ \mathbf{E}_0 = \{2i \sin k_z, 0, 0\} \quad \mathbf{H}_0 = \{0, 2 \cos k_z, 0\} \]  

To calculate the different field components the following equations are used. Here \( a \) represents the radius of the opening in the aperture tip.

\[
\begin{align*}
\mathbf{E}_x &= ikz - \frac{2i}{\pi} \cdot ikau \left[ 1 + v \arctan v + \frac{1}{3} \cdot \frac{1}{u^2 + v^2} + \frac{x^2 - y^2}{3a^2(u^2 + v^2)(1 + v^2)^2} \right] \quad (A.15) \\
\mathbf{E}_y &= -\frac{4ikxyu}{3\pi a(u^2 + v^2)(1 + v^2)^2} \quad (A.16) \\
\mathbf{E}_z &= \frac{4ikxv}{3\pi(u^2 + v^2)(1 + v^2)} \quad (A.17) \\
\mathbf{H}_x &= \frac{4kyv}{\pi a^2(u^2 + v^2)(1 + v^2)^2} \quad (A.18) \\
\mathbf{H}_y &= 1 - \frac{2}{\pi} \cdot \left\{ \arctan v + \frac{v}{u^2 + v^2} \right\} + \frac{2v(x^2 - y^2)}{\pi a^2(u^2 + v^2)(1 + v^2)^2} \quad (A.19) \\
\mathbf{H}_z &= -\frac{4ayu}{\pi a^2(u^2 + v^2)(1 + v^2)} \quad (A.20)
\end{align*}
\]

with

\[
\begin{align*}
\phi &= \arctan \frac{x}{y} \quad (A.22) \\
x &= a\sqrt{(1 - u^2)(1 + v^2)} \cdot \cos \phi \quad (A.23) \\
y &= a\sqrt{(1 - u^2)(1 + v^2)} \cdot \sin \phi \quad (A.24)
\end{align*}
\]

A.4 Electronics

A.4.1 Transimpedance Amplifier

The transimpedance amplifier was used to amplify the signal of the tuning fork of the shear-force detection scheme. The diode-pair as well as the 100 kΩ resistors in the cryogenic side are not necessary for the operation of the electronics, they only protect the very sensitive GaAs-transistor. The electronic is further described in chapter 3.5.1.

A.4.2 Pulse Shaper

A pulse shaper was constructed to convert an alternating input signal to a train of single pulses. For every change a single pulse is generated. The design allows to select either only rising or only falling slopes, as well as both.
Figure A.3: Schematic of the shear force electronics.

Figure A.4: Schematic of the pulsshaper.
Figure A.5: The linear photodiode. The right hand side shows a programmable instrumentation amplifier.

A.4.3 Photodiodes

Normal Photodiode

For measurements of usual light intensities on the table, ranging from 100nW - 10mW a standard photodiode was used. The device OPT101, Burr-Brown is ideal, because it includes the transimpedance amplifier directly on the chip. A circuit diagram can be seen in figure A.5.

Logarithmic Photodiode

To monitor the overall power in a wide range a logarithmic photodiode was used. The device consists of a photodiode (FDS100, purchased from Thorlabs) and a commercial logarithmic amplifier (LOG 112, Burr-Brown). Alternatively the same device was also designed with a photodiode from Hamamatsu, S6786.

The device works well in a power range from 2nW to 1mW. Below 1nW the signal is limited by the performance of the photodiode and the noise exceeded the reference current of the amplifier. Then the signal dropped to the negative supply voltage.
Figure A.6: The logarithmic photodiode.
B Bibliography


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