Doctoral Thesis

Single-molecule spectroscopy at subkelvin temperatures

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Single-Molecule Spectroscopy at Subkelvin Temperatures

A dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZÜRICH

For the degree of
Doctor of Natural Sciences

presented by
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2000
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Abstract

The work presented in this thesis has involved the measurement of fluorescence-excitation spectra of single-molecules doped in crystalline and disordered host matrices down to a temperature of 30 mK. By measuring the linewidths as a function of temperature, one obtains information about the broadening mechanisms at hand. In addition, at very low temperature one can directly measure the lifetime-limited linewidth, which until now has usually been assumed to be equal for all molecules. In this thesis, it is shown that this is not the case, and that the width of the lifetime-limited linewidth distribution depends on the level of disorder in the host.

The first half of this thesis provides background for understanding the second half, in which the experimental results are presented. The background is presented in four chapters covering the areas of the fundamentals of single-molecule spectroscopy, transition dipole moments and the local field factor, the tunneling two-level system model, and single-molecule lineshape theory.

The presentation of the measurements begins with a single-molecule microscopy study of the linewidth distributions for single terrylene and ditertbutylterrylene molecules in polyvinylbutyral at 1.8 K, which motivated the measurements that were performed at lower temperature. It is shown that the results are in disagreement with the standard tunneling two-level system model, but that the incorporation of a distribution of molecule–polymer coupling strengths removes this disagreement. Additionally, the experimental observation of a correlation between the single-molecule line areas and the matrix–molecule interaction strength is presented. Both the necessity for a distribution of coupling strengths and the existence of the correlation
are thought to arise from a distribution of transition dipole moments for the chromophores.

Measurements at lower temperature were performed using a custom-built \(^3\)He/\(^4\)He dilution refrigerator. With this instrument, linewidth distributions have been measured as a function of temperature down to 30 mK for single terrylene molecules in naphthalene (a crystalline sample) and polyethylene (a semi-crystalline polymer), thereby obtaining information about the broadening mechanisms at hand in the two hosts. For naphthalene, an activated temperature dependence is observed, and for polyethylene the temperature dependence of the average linewidth is best described by a linear relationship over the full temperature range. In the low-temperature limit, a distribution of linewidths remains in both hosts indicating the presence of a lifetime distribution, and there is a positive correlation between the linewidths and the line areas. For naphthalene, the ratio of the standard deviation of the distribution to its mean measured at low temperature is \(\sim4\%\). For polyethylene, where there was more disorder, the relative standard deviation is \(\sim18\%\).

From simulations of the linewidth–line area correlation for terrylene in polyethylene, it is shown that the distribution of lifetimes is caused both by variations of the radiative and the non-radiative transition rates. The ratio of the radiative and nonradiative contributions to the linewidth varies from molecule to molecule, but on average \(\sim70\%\) of the linewidth originates from the radiative contribution and the rest arises from additional dephasing caused by nonradiative transitions. The standard deviations of the radiative and nonradiative transition rate distributions are about equal. It is ultimately shown that a radiative lifetime distribution generally arises from the same interactions responsible for inhomogeneous broadening.

In addition, linewidth distributions are simulated and the standard TLS model (with a few slight modifications) is used to extract the TLS–single molecule coupling strength distribution and the distribution of lifetime-limited linewidths for single terrylene molecules in polyethylene. Gaussian distributions of lifetime-limited linewidths with relative standard deviations of \(\sim20\%\) are seen to fit the data well.
Zusammenfassung


Messungen bei tieferen Temperaturen wurden mit einem speziellen $^3\text{He}/^4\text{He}$ Mischkryostaten durchgeführt. Mit diesem Kryostaten und einem Mikroskopie-Aufbau wurden die Linienbreiteverteilungen ab 30 mK als Funktion der Temperatur für einzelne Terrylen-Moleküle in Naphthalin (Kristall) und Polyethylen (semikristallines Polymer) durchgeführt. Mit diesen Messungen wurden Informationen über die Verbreiterungsmechanismen für die beiden Wirtsstrukturen gewonnen. Für die Naphthalin-Matrix wurde eine aktivierte Temperaturabhängigkeit beobachtet, während für Polyethylen die Temperaturabhängigkeit über den ganzen Temperaturbereich linear ist. Bei Temperaturen nahe dem absoluten Nullpunkt zeigen die Linienbreiten in beiden Umgebungen eine Variation, die auf eine Verteilung der Lebenszeiten schließen lässt. Zusätzlich existiert eine positive Korrelation zwischen Linienbreite und -Fläche. Für Naphthalin beträgt die Standardabweichung der Verteilung 4% der mittleren Linienbreite. Für Polyethylen ist die relative Breite der Verteilung größer, nämlich 18% der Linienbreite, was durch die im semikristallinen Polymer größere Unordnung zu erklären ist.


Symbols

Abbreviations and Acronyms

ACF Autocorrelation function
ADC Analog to digital converter
DAC Digital to analog converter
DTBT Ditertbutylterrylene
ISC Inter-system crossing
ITFC Intensity–time–frequency correlation
LISD Light-induced spectral diffusion
PE Polyethylene
PMT Photo-multiplier tube
PVB Polyvinylbutyral
SMS Single-molecule spectroscopy
SNR Signal-to-noise ratio
TLS Tunneling two-level system

Mathematical and Physical Symbols

a Linear Stark shift coefficient
$A_{pw}$ The integrated intensity of the phonon wing
$A_{zpl}$ The integrated intensity of the zero-phonon line
b Quadratic Stark shift coefficient
$C_b$ The background count rate per Watt of excitation power
c$_{ep}$ The electron–phonon coupling constant
\( \langle C_{ij} \rangle \) The ensemble average of the TLS–SM coupling strength

\( C_V \) The specific heat at constant volume

\( D \) The detection efficiency, \( D = \eta_{\text{det}} F_{\text{opt}} \), were \( \eta_{\text{det}} \) is the quantum efficiency of the detector and \( F_{\text{opt}} \) is the collection efficiency of the optical system

\( D(\omega - \omega_0, t) \) The spectral diffusion kernel

\( d \) The distance between TLS potential minima

\( E \) The energy splitting of a TLS, expressible in terms of the asymmetry and coupling energy as \( E = \left[ \Delta^2 + J^2 \right]^{1/2} \)

\( E_{dc} \) dc Electric field applied in a Stark shift experiment

\( E_{ex} \) The excitation energy of a chromophore

\( E_{ext} \) External electric field

\( E_{int} \) Internal electric field

\( E_{loc} \) Local electric field

\( \mathcal{E} \) The zero-point energies of the isolated wells in a TLS

\( f_j \) Frequency excursion caused by a jump of the \( j^{th} \) TLS

\( g(E) \) The density of phonon states per unit volume and unit energy with energy difference \( E \)

\( \hbar \) \( \hbar/2\pi \). \( \hbar \) is Planck's constant, \( \hbar = 6.6262 \cdot 10^{-34} \) J s

\( \mathcal{H} \) The tunneling two-level system Hamiltonian

\( \mathcal{H}_{1,\psi} \) The TLS interaction Hamiltonian in the diagonal representation

\( \mathcal{H}_{1,\varphi} \) The TLS interaction Hamiltonian in the localized representation

\( I(\omega) \) The frequency spectrum of a single molecule

\( I_{\text{sat}} \) The saturation intensity

\( I_{\text{sat}}^{\text{sat}} \) The saturation intensity in the absence of spectral diffusion

\( I_{\text{sat}}^{\text{eff}} \) The effective saturation intensity measured for an ensemble

\( J \) The TLS coupling energy

\( K \) Effective rate factor, \( K = 1 + 0.5 \sum m \frac{k_{m}^{n}}{k_{m}^{n}} / k_{31}^{n} \). Related to the maximum emission rate \( R_{\text{max}} \) by \( R_{\text{max}} = (2KTR_{\text{rad}})^{-1} \)

\( \bar{k} \) The phonon wavevector
Symbols

\(k_B\) Boltzmann constant, \(1.38 \times 10^{-23} \text{ J K}^{-1}\)

\(k_{ij}\) Transition rate from state \(i\) to state \(j\)

\(\mathcal{L}\) Local field factor

\(m\) The effective mass of a TLS tunneling particle

\(N_d\) The dark count rate of the detector

\(N_{\text{TLS}}\) The total number of TLSs

\(n(0)\) The distribution of TLS energy splittings

\(n_B(E)\) The thermal occupation factor obtained for Bose-Einstein statistics. \(n_B(E) = \frac{\exp(E/k_B T) - 1}{\exp(E/k_B T)}\)

\(n(t, T)\) The number density of TLSs that change state during a time \(t\) at a temperature \(T\)

\(P_0\) The laser power

\(p_i\) The occupation probability for state \(i\) of a TLS

\(\bar{R}\) The average distance between a chromophore and the solvent molecules responsible for the solvent shift

\(R(E)\) The TLS relaxation rate

\(R_\infty\) The maximum emission rate for a SM. \(R_\infty = (2KT_{rad})^{-1}\)

\(r_j\) TLS–chromophore distance for the \(j^{th}\) TLS

\(S\) The beam area on the sample

\(s_{\text{int}}\) The internal error

\(T_1\) Lifetime of the excited state

\(T_2\) Dephasing time

\(T\) The temperature

\(T_{rad}\) Radiative lifetime of the excited state

\(t_s\) The measurement time per scan

\(V_0\) The height of the potential barrier between the two TLS potential wells

\(v_\kappa\) The velocity of sound for phonons with polarization \(\kappa\)

\(W_{ij}\) The transition rate from state \(i\) to state \(j\) of a TLS

\(x\) The mole fraction of \(^3\text{He}\) in a \(^3\text{He}/^4\text{He}\) mixture
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<th>Definition</th>
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<tr>
<td>$z$</td>
<td>The number of solvent molecules interacting with a chromophore to cause the solvent shift</td>
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<tr>
<td>$\alpha_B$</td>
<td>The molecular polarizability of a solvent molecule</td>
</tr>
<tr>
<td>$\alpha_c$</td>
<td>TLS-chromophore coupling constant</td>
</tr>
<tr>
<td>$\alpha_{DW}$</td>
<td>The Debye–Waller factor</td>
</tr>
<tr>
<td>$\alpha_{FC}$</td>
<td>The Frank Condon factor</td>
</tr>
<tr>
<td>$\beta$</td>
<td>The prefactor for the activated broadening term in the linewidth</td>
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<tr>
<td>$\Gamma_m(I, T)$</td>
<td>The measured power-broadened linewidth</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>The lifetime-limited linewidth</td>
</tr>
<tr>
<td>$\Gamma_{tot}$</td>
<td>The total linewidth</td>
</tr>
<tr>
<td>$\Gamma_0$</td>
<td>The homogeneous linewidth</td>
</tr>
<tr>
<td>$\gamma_{\kappa}$</td>
<td>The TLS deformation parameter</td>
</tr>
<tr>
<td>$\gamma_{rad}$</td>
<td>The radiative linewidth</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>The TLS asymmetry parameter</td>
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<tr>
<td>$\Delta \alpha$</td>
<td>The molecular polarizability for a chromophore</td>
</tr>
<tr>
<td>$\Delta E_a$</td>
<td>The activation energy</td>
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<tr>
<td>$\Delta \mu_{SM}$</td>
<td>The induced dipole moment change for a single molecule</td>
</tr>
<tr>
<td>$\Delta \mu_{TLS}$</td>
<td>The dipole moment difference between the two TLS states</td>
</tr>
<tr>
<td>$\Delta \nu_{sol}$</td>
<td>The solvent shift</td>
</tr>
<tr>
<td>$\Delta \omega(t, T)$</td>
<td>The width of the spectral diffusion kernel</td>
</tr>
<tr>
<td>$\delta \epsilon$</td>
<td>The TLS asymmetry shift caused by an applied strain field</td>
</tr>
<tr>
<td>$\delta \nu_0$</td>
<td>The Stark shift</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>The dielectric constant</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>The permittivity of free space. $\epsilon_0 = 8.854 \cdot 10^{-12}$ F M$^{-1}$</td>
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<td>$\eta_j$</td>
<td>Relative TLS–chromophore orientation parameter</td>
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<tr>
<td>$\kappa$</td>
<td>The phonon polarization</td>
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<tr>
<td>$\Lambda$</td>
<td>The combined TLS parameter, $\Lambda = \Delta \mu_{SM} \Delta \mu_{TLS} \mathcal{C} \eta / r^3$</td>
</tr>
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<td>$\lambda$</td>
<td>The TLS tunneling parameter. $\lambda = d(2mV_0 / \hbar^2)^{1/2}$</td>
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Symbols

$\lambda_{\text{max}}$ The maximum tunneling parameter that is active given the measurement time

$\lambda_{\text{min}}$ The minimum tunneling parameter that is active given the measurement temperature

$\mu_{\text{vac}}$ The free-space transition dipole moment

$\mu_0$ The permeability of free space. $\mu_0 = 4 \pi \cdot 10^{-7} \text{ N A}^{-2}$

$\xi_j$ TLS occupation parameter. $\xi_j = 0$ ($\xi_j = 1$) indicates that the $j$'th TLS is in its ground (excited) state

$\hat{\rho}$ Density operator

$\rho_{ij}$ Density matrix element

$\rho_{\text{TLS}}$ The TLS density

$\sigma_{\text{laser}}$ The contribution from laser calibration errors to $\sigma_{\text{meas}}$

$\sigma_{\text{meas}}$ The standard deviation of the measured linewidth distribution

$\sigma_{\text{random}}$ The contribution from random measurement errors to $\sigma_{\text{meas}}$

$\sigma_{\text{sat}}$ The contribution from random saturation intensity inhomogeneities to $\sigma_{\text{meas}}$

$\sigma_{\tau}$ The contribution from a distribution of lifetimes to $\sigma_{\text{meas}}$

$\sigma_{\text{tot}}$ The total cross section

$\sigma_z$ The Pauli spin matrix

$\tau$ The TLS relaxation time

$\tau_m$ The measurement time per single-molecule linewidth

$\Phi_{\text{SM}}(t)$ The part of the single-molecule dipole autocorrelation function arising from TLSs

$\phi_f$ The fluorescence quantum yield

$\varphi_i$ The Eigenstates of the TLS potential in the localized representation

$\phi_j(t)$ The part of the single-molecule dipole autocorrelation function arising from the $j$'th TLS

$\chi_{\nu}^2$ The reduced chi-squared value

$\psi_i$ The Eigenfunctions of the TLS potential in the diagonal representation

$\Omega$ The average zero-point frequency for the TLS potential wells. The average of the zero-point energies for the two TLS potential wells is $\hbar \Omega$.

$\Omega_R$ The Rabi frequency. $\Omega_R = \bar{\mu}_{\text{vac}} \cdot \vec{E}_{\text{loc}} / \hbar$
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_0$</td>
<td>Resonance frequency</td>
</tr>
<tr>
<td>$\omega_x$</td>
<td>The phonon frequency</td>
</tr>
</tbody>
</table>
When I heard the learn'd astronomer,
When the proofs, the figures, were ranged in columns before me,
When I was shown the charts, the diagrams, to add, divide, and measure
them,
When I sitting heard the learned astronomer where he lectured with much
applause in the lecture room,
How soon unaccountable I became tired and sick,
Till rising and gliding out I wander'd off by myself,
In the mystical moist night-air, and from time to time,
Look'd up in perfect silence at the stars.

- Walt Whitman
1. General Introduction
1.1 Motivation

The bulk of the work presented in this thesis has entailed the measurement of the of single-molecule spectra in crystalline and disordered host matrices down to a temperature of 30 mK. These low temperatures were reached by using a custom-built $^3$He/$^4$He dilution refrigerator.

The significance of the low temperature becomes clear when the linewidth is separated into two parts as follows,

$$\Gamma(T) = \Gamma_r + \Gamma_d(T),$$

(1.1)

where $\Gamma_r$ is the lifetime-limited contribution, which includes contributions from radiative and non-radiative transitions from the excited to the ground state, and $T$ is the temperature. The physical origin of the dephasing contribution $\Gamma_d(T)$ depends on the host and the temperature. In amorphous hosts at low temperature, the dominant source is broadening from tunneling two-level systems (TLSs) [1,2]. In crystals, there is usually no dephasing from TLSs, however there can be dephasing from local vibrations. For both types of hosts, the dephasing contribution is a function of the temperature and $\lim_{T\to0} \Gamma_d = 0$ [3]. (The differences between dephasing in crystalline and amorphous hosts are explained in detail in Chapter 5.)

By measuring the temperature dependence of $\Gamma(T)$, one obtains information about the broadening mechanism at hand. For example, one can deduce the distribution of TLS energy splittings in an amorphous host, or the energy splitting of the local vibration in a crystalline host. By measuring $\Gamma(T)$ at the very low temperatures accessible with the $^3$He/$^4$He dilution refrigerator, one can also measure the value of $\Gamma_r$.

A preview of some experimental results that illustrate the difference between disordered and crystalline hosts is shown in Figure 1.1, where the average linewidth vs the temperature for single terylene molecules in naphthalene and polyethylene are plotted together in the same graph. One sees an activated temperature dependence for the naphthalene host and a linear temperature dependence for polyethylene.
Both of these observations are consistent with the theoretical models for dephasing in these systems. This will be discussed at greater depth in the following chapters. Something else to notice is that the curves intersect at $T = 0$ and the values for the intercepts are both in good agreement with the lifetime-limited values for the linewidth of terrylene in polyethylene that have been deduced from measurements of the lifetime [4,5]. The temperature dependence for terrylene in naphthalene was measured by three generations of Ph.D. students in three different laboratories. The hollow circles are data points that were measured by Hermann Bach and Thomas Nonn (as indicated). The agreement of the data is an illustration of the reliability of single-molecule spectroscopy techniques.

As mentioned above, at very low temperatures one can directly measure $\Gamma_T$. Until now, $\Gamma_T$ has usually been assumed to be equal for all molecules. In this thesis,
it is shown that this is not the case, and in fact the width of the distribution depends on the level of disorder of the host. In fact, a distribution of radiative lifetimes should be present in any sample exhibiting inhomogeneous broadening. This is an interesting and important result which had not been realized using ensemble spectroscopy techniques like hole burning and photon echoes.

Another important aspect to notice in Figure 1.1 is that the line broadening in naphthalene freezes out at \( \sim1.2\) K. Such behavior is typical for crystals, and for many systems the broadening freezes out at an even higher temperature. Such dephasing from local vibrations also occurs in disordered systems like polyethylene, but it is not as well-defined since the energy splitting depends on the geometry of the site of the impurity molecule, and in an amorphous system each impurity molecule has a unique local environment. For that reason, one needs to work below temperatures of \( \sim1\) K to be sure that one can isolate dephasing from TLSs in amorphous systems. This is another motivation for doing measurements at the temperatures accessible with the \(^3\text{He}/^4\text{He}\) dilution refrigerator.

### 1.2 Preview

In Chapter 2, the fundamental concepts needed to understand the technique of single-molecule spectroscopy are introduced. The measurements described in this thesis were all performed using fluorescence-excitation spectroscopy, which is explained in detail. Following that, the requirements necessary for isolating the fluorescence from a single molecule using fluorescence-excitation spectroscopy are presented.

The concepts of the local field factor and the transition dipole moment are very important for the interpretation of experimental results in general, and play a central role in the results presented in this thesis. In Chapter 3, the local field factor is discussed and its relationship to the transition dipole moment is pointed out. In addition, experiments are reviewed for which the effect of the local field factor was neglected and the conclusions were misleading.
Chapters 4 and 5 present theoretical background necessary for understanding the conclusions of this thesis. In Chapter 4, the tunneling two-level system (TLS) model is presented from a general point of view. In Chapter 5 lineshape theory is discussed. The TLS–single molecule coupling mechanism is examined in detail, and the application of TLS theory to modeling distributions of single-molecule linewidths is presented. The time and temperature dependence of the linewidth is also discussed. Finally, the intensity-time frequency correlation spectroscopy technique is reviewed. This technique enables measurements on a faster time scale than is accessible with conventional spectroscopic techniques.

Details on the experimental apparatus are presented in Chapter 6. The Dilution refrigerator and the laser system, as well as the apparatuses that were used for single-molecule microscopy and time-resolved studies are presented in detail.

In Chapter 7, results are summarized that were collected at 1.8 K for the single terrylene molecules in polyvinylbutyral, which is an amorphous polymer. These measurements gave the first clues that one should expect to observe a distribution of transition dipole moments and hence a distribution of lifetimes and lifetime-limited linewidths, and served to motivate the measurements that were performed at lower temperature. The reader may find the measurements presented in Chapter 7 less convincing than those presented in the following two chapters. This is because the measurements were performed at 1.8 K, where a considerable amount of line broadening is still present. In fact, the average linewidth for the single molecules presented in Chapter 7 was an order of magnitude larger than the lifetime-limited linewidth, so the interpretation of the data is more involved than for the measurements performed at lower temperature. But the data analysis shows that the presence of a transition dipole moment distribution reflects itself in a distribution of coupling strengths between the probe molecules and tunneling two-level systems.

In Chapters 8 and 9, measurements that were done at temperatures down to ~30 mK are presented for single terrylene molecules in naphthalene and polyethylene hosts, respectively. Naphthalene served as a good test sample for the low-temperature apparatus since it is a crystalline host and hence the single-molecule resonance frequencies are very stable. Polyethylene is a semi-crystalline polymer,
and hence the lines exhibit more broadening and jumping behavior. In the low-
temperature limit, a distribution of linewidths remains in both hosts indicating the
presence of a distribution of lifetimes. For naphthalene, the ratio of the standard
deviation of the distribution to its mean is \( \sim 4\% \). For polyethylene, where there is
more disorder, the relative standard deviation is \( \sim 18\% \).

In Chapter 9, the time and temperature dependence for single-molecule line
broadening in polyethylene is investigated in detail. Linewidth distributions are
simulated and the standard TLS model (with a few slight modifications) is used
to extract the TLS–single molecule coupling strength distribution and the distri-
bution of excited-state lifetimes from experimental data. Gaussian lifetime-limited
linewidth distributions with relative standard deviations of \( \sim 20\% \) are seen to fit the
data well, but variations in the average lifetime of \( \sim 10\% \) are observed for samples
with different densities.

In addition, simulations of the linewidth–line area correlation are used to ex-
tract the radiative and nonradiative contributions to the linewidth distribution. In
Appendix B, a simple quantum mechanical model is presented and compared to ex-
perimental data to show that the distribution of the radiative lifetimes in disordered
media is a general effect caused by the same interactions responsible for inhomoge-
neous broadening. At higher temperature, the distribution of lifetimes would narrow
depending on the mobility of the host molecules. Whether or not a distribution of
lifetimes is observable would depend on the ratio of the time scale of the molecular
motion to that of the measurement time. Measurements of the lifetime variations on
fast time scales might shed additional light onto local structures and dynamics with
potential applications even to the study of single biomolecules under physiological
conditions.
2. Fundamentals of low-temperature single-molecule spectroscopy

In this chapter, the fundamentals of the technique of fluorescence-excitation spectroscopy are explained. This involves discussing the general experimental technique and presenting a mathematical model for the interaction between single molecules and light. The main requirements for performing single-molecule spectroscopy (SMS) are then explained, and types of studies for which SMS is particularly well-suited are discussed.
2. Fundamentals of low-temperature single-molecule spectroscopy
2.1 Specifics on fluorescence-excitation spectroscopy

The first single-molecule spectroscopy (SMS) experiments were performed using absorption spectroscopy and a sophisticated modulation technique, which was necessary to overcome the shot noise from the relatively strong excitation laser light [6]. A much better signal-to-noise ratio can be achieved using fluorescence-excitation spectroscopy, and since the first application of the technique on SMS [7], the vast majority of experiments have been done using fluorescence excitation, including all of the experiments presented in this thesis.

2.1.1 Conventional experimental details

To understand the fundamentals of SMS, first one should know how the experiments are performed. Here the simplified experimental apparatus shown schematically in Figure 2.1 is discussed to draw attention to the most important concepts. The sample is a thin, transparent solid, doped with the probe molecules to be studied. These dopant molecules, which are also sometimes called impurity or guest molecules, are the molecules whose spectra are studied. The sample is held in a cryostat which provides the low temperature. It is necessary to perform SMS experiments at low temperature since the SM absorption lines are temperature dependent and increase exponentially with increasing temperature. In order to have the frequency resolu-
tion necessary to resolve the spectra of single molecules, one needs to work at low
temperature. At higher temperature, single molecules can be detected if the probe
centration is low enough, but spectroscopic resolution is lost.

The probe molecules are excited through windows in the cryostat with a laser
light having a bandwidth of approximately $\Delta \nu = 1$ MHz. The narrow-band light
source is required for resolving the SM absorption lines since they can be rather
narrow at low temperature. For example, the lifetime-limited linewidth for terrylene
molecules in the matrices studied for this thesis is $\sim 42$ MHz.

Figure 2.2 shows the complex energy-level structure of a single impurity
molecule embedded in a solid host. (This type of representation is commonly re¬
ferred to as a Jablonski diagram.) The singlet-state manifold is on the left, and the
triplet state manifold is on the right. Solid arrows represent radiative transitions and
radiationless transitions are shown as broken arrows. In radiationless transitions,
the excess electronic excitation is converted directly into heat ultimately through
the creation of phonons. This process is generally referred to as internal conversion
(IC) when it occurs between states in the same manifold, and inter-system crossing
(ISC) when it occurs between different manifolds. The physics behind these various
transitions has been reviewed in the literature [8]. Fluorescence is only observed
to originate from the $S_1$ state owing to the rapid internal conversion between the
closely spaced excited states (Kasha's rule).

An excitation with absorption frequency $\omega$ can in general involve electronic,
vibrational, and phonon states. An excitation not involving phonons is generally
called a zero-phonon line, an example of which is marked $\omega_00$ in Figure 2.2. There
are zero-phonon absorption lines to all of the vibrational sublevels, but the $\omega_00$
absorption marked in Figure 2.2 is the purely-electronic zero-phonon line. Absorp¬
tions involving the creation of phonons are blue shifted from the zero-phonon line
and make up the broad phonon wing of the line.

At liquid helium temperatures, the impurity can simply be thought of as a three-
level system, consisting of the $S_0$, $S_1$, and $T_0$ states. Only the ground vibrational
level in any of these three levels is thermally populated. Any excitation to an
excited vibrational sublevel quickly decays to the ground vibrational state, since the
Figure 2.2: A Jablonski diagram. The SM vibrational levels are the thin lines that are enumerated in the ground state. The host’s phonon energy levels are the lighter, nearly continuous levels. The relevant decay rates $k_{21}$, $k_{23}$, and $k_{31}$ are also indicated. The transitions are classified as radiative (solid lines) or radiationless (broken lines). ISC: inter-system crossing; $\omega$: absorption of a photon with frequency $\omega$; $\omega_0$: the resonance frequency for zero-phonon line of the purely electronic transition; $F$: fluorescence; IC: internal conversion.
excited vibrational lifetimes (picoseconds) are much shorter than the electronic state lifetimes (nanoseconds).

The $S_0 \rightarrow S_1$ transition is the transition that is most often probed in single-molecule spectroscopy at low temperature. The short lifetimes of the vibrational sublevels make the transitions involving excitation to vibrational sublevels much broader and therefore difficult to resolve. When the molecule is excited to the $S_1$ state, fluorescence can occur to any number of vibrational sublevels of the ground state. In order to distinguish the SM fluorescence from scattered laser light, one uses filters to remove the scattered laser light, as indicated in Figure 2.1. In the process, one discards the strong 0–0 fluorescence and collects only the Stokes-shifted component of the fluorescence.

2.1.2 Radiation rates

In order to quantitatively describe and analyze SM spectra, one usually starts with the optical Bloch Equations. The interaction strength between the electric field and the molecule in the dipole approximation is determined by the Rabi frequency

$$\Omega_R = \frac{\mu_{\text{vac}} \cdot \vec{E}_{\text{loc}}}{\hbar}, \quad (2.1)$$

where $\mu_{\text{vac}}$ is the transition dipole moment, $\vec{E}_{\text{loc}}$ is the local electric field amplitude of the laser light, and $\hbar$ is Planck's constant. The local field is the major topic of discussion in Chapter 3. In the rotating wave approximation the Bloch Equations for a molecule with typical energy-level structure (Figure 2.2) are [9]:

$$\dot{\rho}_{11} = k_{21} \rho_{22} + \sum k_{31}^m \rho_{33}^m + i \Omega_R (\rho_{21} - \rho_{12}) , \quad (2.2)$$

$$\dot{\rho}_{22} = -\left(k_{21} + \sum k_{23}^m\right) \rho_{22} - i \Omega_R (\rho_{21} - \rho_{12}) , \quad (2.3)$$

$$\dot{\rho}_{12} = \left(i (\omega - \omega_0) - T_2^{-1}\right) \rho_{12} + i \Omega_R (\rho_{22} - \rho_{11}) , \quad (2.4)$$
Radiation rates

and

\[ \dot{\rho}_{33} = k_{23}^{m} \rho_{22} - k_{31}^{m} \rho_{33}, \quad (2.5) \]

where \( \omega \) is the laser frequency, \( \omega_0 \) is the resonance frequency of the molecule, \( k_{21} \) is the decay rate from the excited to ground state, \( T_2 \) is the dephasing time, and \( k_{23}^{m} \) and \( k_{31}^{m} \) are the inter-system crossing (ISC) rates. The \( m \) superscripts on the triplet-level rates indicate the triplet nature of the triplet state. Usually the triplet levels can be treated as a single state and then the sums and the \( m \) superscripts in Equations 2.3 and 2.4 can be ignored.

The spontaneous emission rate \( R \) is equal to \( \rho_{22}/T_{rad} \), where \( T_{rad} \) is the radiation lifetime of the excited state. The steady-state solution of these equations for \( R \) is

\[ R = \frac{2\Omega_R^2 T_1 T_2 / T_{rad}}{1 + [(\omega - \omega_0) T_2]^2 + 4 K \Omega_R^2 T_1 T_2}, \quad (2.6) \]

where \( K = 1 + 0.5 \sum k_{23}^{m} / k_{31}^{m} \) and \( T_1 = (k_{21} + \sum k_{23}^{m})^{-1} \). From Equation 2.6 it follows that the emission rate cannot exceed \( R_{\infty} = (2K T_{rad})^{-1} \).

A two-level SM (\( K = 1 \)) with the typical lifetime \( T_{rad} \) on the order of 10 ns has a maximum emission rate on the order of \( 5 \times 10^7 \) Hz. In experiments, such large values can be observed very rarely. The main problem is related to the triplet state. The radiative transition from the triplet state to the ground state is forbidden and, as a consequence, the triplet state is very long-lived. Due to ISC, a molecule may be transferred from the excited singlet state to the triplet state. Such a molecule will not emit any photons and will not return to the ground singlet state until time \( 1/k_{31} \) passes. This changes the maximum count rate and the saturation conditions dramatically. Usually \( k_{23} \approx (10^6 - 10^8) \) Hz, but very often \( k_{31} \) at low temperature is on the order of \( 1 \times 10^4 \) Hz and hence the coefficient \( K \approx 10^2 - 10^5 \). Molecules with \( K < 10 \) are considered to be good candidates for SMS, for which \( R_{\infty} \approx 5 \times 10^6 \) Hz is a realistic estimate. A photomultiplier count rate of \( 10^4 \) Hz is expected, taking into account the total photon detection efficiency which is typically \( \sim 2 \times 10^{-3} \).

At low intensities such that \( \Omega_R^2 \ll T_1 T_2 K \) and \( \Omega_R^2 \ll T_1 T_2 / T_{rad} \), the radiation rate is unsaturated and the linewidth is \( \Gamma_0 = 1/\pi T_2 \). When \( 4\Omega_R^2 T_1 T_2 K = 1 \), the
emission rate on resonance ($\omega = \omega_0$) equals $R_\infty/2$ and the linewidth is $\sqrt{2}\Gamma_0$. This is the so-called saturation regime. The corresponding electric field amplitude is

$$E_{sat} = \frac{\hbar}{\mu_{vac}\sqrt{KT_1T_2}}. \quad (2.7)$$

Usually the average energy flux $I = 0.5E^2(\varepsilon_0/\mu_0)^{1/2}$ is measured in an experiment, where $\varepsilon_0$ and $\mu_0$ are the permittivity and permeability of free space [10]. With this, one finds the corresponding saturation intensity

$$I_{sat} = \frac{\varepsilon_0c\hbar^2}{2\mu_{vac}^2T_1T_2K}, \quad (2.8)$$

where $c$ is the speed of light in vacuum. So far in this discussion, the influence of the polarizability of the matrix on the saturation intensity has been neglected. This comes in through the local field factor. This is a main topic of discussion in Chapter 3, where a more precise expression for the saturation intensity is given and a few examples of experimental results are discussed for which the effect of the local field factor was neglected, which lead to misleading conclusions.

2.2 The main requirements for performing single-molecule spectroscopy

The number of impurity-host systems in which SMS has be performed is quite small. Though the number of solvent-solute systems where SM spectral lines have been observed has been growing, this number is still only about 20 [11]. Very careful choice of the chromophore and the host matrix based on the requirements explained in this section is required.

There are two main requirements that a single molecule-host pair has to fulfill in order to be a candidate for single-molecule spectroscopy. Only one molecule can be in the observation volume under study, and the fluorescence from that single molecule has to be distinguishable from the background fluorescence. Here these requirements are described in detail.
2.2.1 Having one molecule in the observation volume

This is done by taking advantage of spatial and spectral selectivity — concepts that are visualized in Figure 2.3. Spectrally, selectivity can be achieved by taking advantage of inhomogeneous broadening. At low temperature, the homogeneous linewidth becomes very narrow and approaches the lifetime-limited linewidth. In a disordered system, the width of the distribution of resonance frequencies can be much broader than the homogeneous linewidth. Even when doped in a crystalline matrix, single molecules have slightly different resonance frequencies. A crystal is never ideal and every molecule has different surroundings and hence a different solvent shift of the resonance frequency [12]. Figure 2.3a is a simulation of an inhomogeneous band consisting of the sum of 100 normally-distributed Lorentzian lines. The width of the Lorentzian lines is 10% of the standard deviation of the Gaussian distribution of resonance frequencies. For simplicity, all homogeneously-broadened lines have the same amplitude. With such an inhomogeneously-broadened
distribution it is possible to resolve single-molecule resonances on the wings of the distribution.

Spatial selectivity is achieved by geometric means, namely, by focusing the excitation light down to a small spot, by using a thin sample with a thickness of about a micron, and by using a low concentration of impurity molecules. These concepts are illustrated in Figure 2.3b. At low temperature, impurity-molecule concentrations between $10^{-6}$ and $10^{-8}$ mol $\cdot$ l$^{-1}$ are typically used.  

### 2.2.2 Distinguishing single-molecule fluorescence from the background

In the end, this requirement all boils down to the signal-to-noise ratio (SNR). The SNR depends on the photo-physical properties of the probe molecules and the host material, as well as on the collection efficiency of the detection system. On the side of the photophysical properties of the probe molecules, the total cross section has to be large and the fluorescence quantum yield has to be high. The host material, on the other hand, has to interact as little as possible with the laser and the probe molecule. In this section the factors influencing the SNR are discussed in detail, and ultimately the SNR is expressed in terms of these factors.

#### The total cross section $\sigma_{\text{tot}}$

For a probe molecule to have a chance at being a candidate for single-molecule spectroscopy, first of all it has to have a large total cross section. The total cross section $\sigma_{\text{tot}}$ defines the number of pure absorptions per second, $\sigma_{\text{tot}} I$ caused by light of intensity $I$. It is well known that at low laser intensity the resonance total cross

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1 At room temperature, single-molecule lines are very broad and hence spectral selectivity is lost. Under such circumstances, one can still detect single molecules using spatial selectivity but with even thinner samples ($\sim 50$ nm) and with much lower concentrations ($\sim 10^{-9}$ mol $\cdot$ l$^{-1}$).

2 The notation followed by J.D. Jackson [10] is also being followed here, where the total cross section $\sigma_{\text{tot}}$ is the sum of the scattering cross section $\sigma_{\text{sc}}$ and the absorption (or reaction) cross section $\sigma_{\text{r}}$. The total cross section then represents the sum of the scattering and nonradiative dissipation terms.
Distinguishing single-molecule fluorescence from the background

section for a two-level atom including radiationless energy losses is given by

\[ \sigma_{\text{tot}} = \frac{3\lambda^2 \gamma_{\text{rad}}}{2\pi \Gamma_{\text{tot}}} \]  

(2.9)

where \( \lambda \) is the wavelength, \( \gamma_{\text{rad}} \) is the radiative linewidth, and \( \Gamma_{\text{tot}} \) is the total linewidth [10]. Neglecting nonradiative broadening, \( \sigma_{\text{tot}} \) is on the order of \( 10^{-9} \) cm\(^2\) for visible light, or \( 10^5 \) times larger than geometrical cross-section of a molecule.

For multi-atom molecules doped into solid matrices \( \sigma_{\text{tot}} \) is reduced from what one would expect for a simple atom in a vacuum by two additional factors, namely, the Debye–Waller factor \( \alpha_{\text{DW}} \) and the Frank Condon factor \( \alpha_{\text{FC}} \). Both of these factors arise from the complex energy-level structure that was shown in Figure 2.2.

The Frank–Condon factor takes into account a reduction of the total cross section due to the vibrational sublevels of the molecule. This factor is determined by the spatial overlap of the vibrational wavefunctions for the ground and the excited states. Naturally, \( \alpha_{\text{FC}} \) depends on the geometry of the probe molecules. The requirements to be placed on \( \alpha_{\text{FC}} \) are actually not that strict, because there is a trade-off between having a stronger absorption of the 0–0 line and having more Stokes-shifted fluorescence. The ability of a molecule to emit Stokes-shifted fluorescence is also a factor affecting the suitability of a molecule for SMS. As was shown in Figure 2.1, filters are normally used to block the excitation laser light. These filters also block the 0–0 fluorescence.

The Debye–Waller factor is a measure of the relative strength of the zero-phonon absorption line compared to the phonon wing, and is strongly dependent on the temperature. \( \alpha_{\text{DW}} \) is normally written as

\[ \alpha_{\text{DW}}(T) = \frac{A_{\text{zpl}}(T)}{A_{\text{zpl}}(T) + A_{\text{pw}}(T)} \]  

(2.10)

where \( A_{\text{zpl}}(T) \) and \( A_{\text{pw}}(T) \) are the integrated intensities of the zero-phonon line and the phonon wing, respectively. Each vibrational line has a phonon wing arising from absorptions to excited phonon states where the absorption is accompanied by the creation of phonons [3].
Putting in these extra factors that reduce the total cross section and also including a term which takes into account the geometrical orientation of the transition dipole moment with respect to the polarization of the excitation light, one gets

\[
\sigma_{\text{tot}} = \alpha_{DW}^2 \alpha_{PC} \frac{\gamma_{\text{rad}}}{I_{\text{tot}}} \cos^2 \theta \frac{3 \lambda^2}{2\pi}.
\]  

(2.11)

The fluorescence quantum yield \( \phi_f \)

For a molecule to be a successful candidate for single-molecule spectroscopy, not only does it have to be a strong absorber — it also has to have a large fluorescence quantum yield \( \phi_f \), which depends on the inter-system crossing rates. Inter-system crossing can have a dramatic effect on the overall number of fluorescence photons measured, since the triplet state lifetime can be as long as several seconds. The triplet state is a dark state, since while the molecule is in the triplet state it is no longer available for excitation. Molecules that are good for SMS have inter-system crossing quantum yields as low as \( \sim 10^{-6} \).

Host requirements

In addition to having a low radiationless transition probability for the SM, the emission from the host molecules must be very low. In the excitation volume there may be \( \sim 10^{11} \) solvent molecules, and it is necessary to distinguish the impurity molecule’s fluorescence from the fluorescence coming from all of these host molecules. Therefore, the interaction between the impurity molecule and the laser has to be \( \sim 11 \) orders of magnitude stronger than the interaction between the laser and the host molecules. In practice, when one chooses a transparent host medium, a major part of the background comes from out-of-focus molecules rather than directly from the host material.

Also needing consideration are the low-temperature elastic properties of the host material, which are represented by the electron–phonon coupling constant \( c_{\text{ep}} \).
The tunneling two-level system relaxation rate is proportional to $c_{ep}$, therefore $c_{ep}$ determines the amount of line broadening at hand, which in turn affects the total cross section $\sigma_{tot}$ through $\Gamma_{tot}$. For a given dopant chromophore, it has been shown that the amount of spectral-hole broadening in polymer hosts can vary by more than an order of magnitude depending on the host material [13]. The same study has also pointed out that the matrix effects are general, and the relative amount of broadening that one observes in different hosts is independent of the type of chromophore used.

The signal-to-noise ratio (SNR)

The factors discussed in this section can be summarized by a quantitative estimate for the SNR. Based on the properties of the sample and the apparatus the SNR can be expressed as [14]

$$SNR = \frac{D\phi_f\sigma_{tot}P_0\tau_m/S\nu}{[(D\phi_f\sigma_{tot}P_0\tau_m/S\nu) + C_bP_0\tau_m + N_d\tau_m]^{1/2}}.$$  \hspace{1cm} (2.12)

where $D$ is the detection quantum efficiency, $P_0$ is the laser power, $\tau_m$ is the measurement time, $S$ is the beam area on the sample, $\nu$ is the photon energy, $C_b$ is the background count rate per watt of excitation power, and $N_d$ is the dark count rate. The detection quantum efficiency $D = \eta_{det}F_{opt}$ is equal to the fraction of the photons that the SM emits which are actually counted at the detector. It is proportional to the quantum efficiency of the detector itself, $\eta_{det}$ and the collection efficiency of the optical system $F_{opt}$.

The three noise terms in the denominator of Equation 2.12 are from shot noise from the single-molecule, shot noise from the background luminescence, and dark counts. With a good detector, for example a cooled photo-multiplier tube, the dark counts are low (~5 Hz), and the third term in the denominator is negligible. The term arising from background shot noise often produces the main component of the noise. This background can arise from cutoff filter luminescence and out-of-focus molecules, for example.
2. Fundamentals of low-temperature single-molecule spectroscopy

### 2.3 What are the uses of single-molecule spectroscopy?

When the requirements explained in the previous section are met, one can measure single-molecule spectra like that shown in Figure 2.4. This spectrum was measured for a single terrylene molecule in a naphthalene crystal at a temperature of 1.2 K and with an intensity slightly higher than the saturation intensity (the chemical structure of terrylene is shown in the inset). The solid line is a Lorentzian fit to the data, which has a linewidth of ~70 MHz. The difference between the measured linewidth and the lifetime-limited linewidth of ~42 MHz is due to power broadening. The signal-to-noise ratio (SNR) in this spectrum is ~50, and the time required to scan the full spectrum was ~100 s. The excitation intensity was 400 mW/cm$^2$ and the laser wavelength was 574.385 nm.

![Figure 2.4: An example of a fluorescence-excitation spectrum of a single terrylene molecule in a naphthalene crystal.](image)

The SNR is quite high, considering the signal arises from a single-quantum system. Spectra with an even higher SNR can be produced by reducing the excitation volume with a confocal detection scheme and measuring the spectrum repeatedly. The spectrum shown in Figure 2.4 was acquired using single-molecule microscopy and the number of molecules per scan was the optimized quantity, rather than the SNR.
2.3.1 Quantum optics studies

With the high signal-to-noise ratios achievable, single-molecule spectroscopy lends itself to quantum optics studies, where the light–matter interaction can be tested on a single-quantum system. Single molecules doped in solids have an advantage over single ions and atoms for such studies because the molecules are confined inside a solid host and therefore the trapping is not an issue.

One example of a quantum optics study that has been performed is the observation of the purely quantum mechanical effect of photon antibunching in the fluorescence collected from single pentacene molecules in $p$-terphenyl [15]. This experiment was actually one of the more convincing proofs that the fluorescence from a single quantum system can be measured. Another quantum optics study that has been performed was the use of single dibenzanthanthrene molecules in an $n$-hexadecane matrix as triggered single-photon sources [16].

2.3.2 Analytical chemistry and biology studies

Another important use of single-molecule spectroscopy that is not pursued in this thesis is its application to analytical chemistry and biology. In fact, this use of single-molecule spectroscopy is growing rapidly and might even overtake the other two applications.

To name a few of the studies of this type that have been performed, the fluorescence spectra and lifetimes have been used in single-molecule identification experiments [17]. Different approaches of illumination and detection have also been used for determining the orientation of the transition dipoles of the probe molecules [18,19]. Techniques like these will be useful in fluorescence resonance energy transfer studies, which are important in many biomolecular systems.
2.3.3 Studying disorder in solids

The other main direction of study for single-molecule spectroscopy is the use of single molecules as probes for studying their local environment. This is a strategy that is particularly popular in the study of disordered systems, where theories describing the linewidths of impurity molecules can be tested with a higher level of sensitivity than is accessible with ensemble measurement techniques. This is because one has access to the distributions of molecular properties rather than just the mean values that one normally finds in an ensemble measurement.

As was shown in Figure 2.3, the spectra of impurity molecules in solids is inhomogeneously broadened at low temperature. This is because each impurity molecule has a unique local environment and hence a slightly different value for the solvent shift of the resonance frequency. In disordered systems, the resonance frequencies of impurity molecules can also be seen to fluctuate in time. These fluctuations take place on time scales ranging from nanoseconds to years, and are thought to arise from tunneling of the host molecules between different spatial configurations. In a disordered system, the host molecules are not constrained by symmetry to occupy a single potential minimum and can tunnel between different local minima even at very low temperatures, thereby perturbing the resonance frequency. It can be thought of as a perturbation to the solvent shift. This phenomenon is commonly referred to as spectral diffusion. By measuring the linewidth of single molecules as a function of time and temperature, one can investigate the mechanisms behind spectral diffusion.

Gaining insight into both static and dynamical disorder in solids through their effects on single-molecule spectra has been the primary goal of this thesis. The main model describing the tunneling of host molecules is described in Chapter 4, but first, the concepts of the transition dipole moment and local fields are introduced, which are important for the understanding of both static and dynamical disorder.
3. The transition dipole moment and local fields

The local field factor is important to consider when interpreting experimental data, as the main conclusions of this thesis demonstrate. This will hopefully become clear to the reader in future chapters. For now, a review of the importance of the local-field factor and an explanation of the theory behind it are presented. In addition, the relationship between the local-field factor and the transition dipole moment is discussed, and several molecular properties that depend on the transition dipole moment are pointed out.
3. The transition dipole moment and local fields
3.1 Local Fields

In the traditional picture of the local-field factor, the electric field in Equation 2.1 is the local electric field $E_{\text{loc}}$ that would be observed in a cavity containing a SM if the SM were removed and the site were left empty. This electric field differs from the laser electric field $E_{\text{ext}}$ outside of the sample and from the internal macroscopic electric field $E_{\text{int}}$. The geometry of the model is shown in Figure 3.1a. $E_{\text{int}}$ is reduced from $E_{\text{ext}}$ by the buildup of charge on the outer surfaces of the sample. According to the Fresnel formulae for normal incidence [10], $E_{\text{int}}$ can be written

$$E_{\text{int}} = \frac{2E_{\text{ext}}}{\varepsilon^{1/2} + 1}$$

(3.1)

when one assumes the sample is isotropic and continuous with a dielectric constant $\varepsilon$.

The local field is related to $E_{\text{int}}$ by the local field tensor $\hat{\mathcal{L}}$, where $E_{\text{loc}} = \hat{\mathcal{L}} E_{\text{int}}$. In the Lorentz approximation, one considers a continuous, homogeneous, isotropic medium [20] and $\hat{\mathcal{L}}$ can be written

$$\hat{\mathcal{L}} = \mathcal{L} = \frac{\varepsilon + 2}{3} \hat{I},$$

(3.2)

where $\hat{I}$ is the unit matrix. Here the $c$ subscript is meant to indicate that the matrix has been approximated as homogeneous, isotropic, and continuous.

In the Lorentz approximation, all three electric field quantities point in the same direction and the vector nature of the field can even be neglected. Combining everything together, the local field can be expressed as

$$E_{\text{loc}} = \frac{2\mathcal{L}}{\varepsilon^{1/2} + 1} E_{\text{ext}} = \frac{2}{3} \frac{\varepsilon + 2}{\varepsilon^{1/2} + 1} E_{\text{ext}}.$$  

(3.3)
Figure 3.1: a) The electric fields inside and outside of the sample in the Lorentz approximation. b) In a disordered sample, the local environment varies wildly from point to point in the sample.
3.2 The transition dipole moment–local field factor equivalence

The relationship between the local field factor and the transition dipole moment becomes clear when one examines the Rabi frequency of the probe molecule, which can be written as

$$\Omega_R = \frac{\vec{\mu}_{\text{vac}} \cdot \vec{E}_{\text{loc}}}{\hbar} = \frac{\vec{\mu}_{\text{vac}} \mathcal{L} \langle \vec{E}_{\text{int}} \rangle}{\hbar}. \quad (3.4)$$

$\langle \vec{E}_{\text{int}} \rangle$ is the macroscopic field in the medium, as discussed in Section 3.1 of this chapter. $\vec{\mu}_{\text{vac}}$ is the transition dipole moment of the chromophore in free space. Rather than being viewed as affecting the internal field $\vec{E}_{\text{int}}$ (as it is conventionally viewed [20]), the local field factor can be viewed as changing the transition dipole moment of the guest molecule into the effective transition dipole moment $\vec{\mu}_{\text{eff}} = \vec{\mu}_{\text{vac}} \mathcal{L}$. Viewing the effect of the polarizability of the medium on the probe molecule in terms of the transition dipole moment is a more fundamental way of looking at the problem because the transition dipole moment is affected even when no electric field is applied.

So far, the local field has been discussed under the assumption that the microscopic structure can be ignored and the sample can be treated as a continuous medium with dielectric constant $\epsilon$. This is only an approximation. Figure 3.1b illustrates a model of the microscopic host geometry surrounding a chromophore. The polymer chains are represented by curved lines. Far from the chromophore, the sample appears continuous from the point of view of the probe molecule, because the number of chains per unit radius becomes large. The influence of this part of the sample can be well described by Eq. 3.2. However, on a nanometer scale the concept of $\epsilon$ does not hold, and the contribution from the nearby chains must be treated differently. On the size scale of a single molecule ($\sim 1 \, \text{nm}$), the dielectric is neither isotropic nor homogeneous, therefore a distribution of local-field factors is expected.

Strictly speaking, $\mathcal{L}$ is an average over the spatial volume occupied by an optical electron, but the effective dipole moment of a chromophore with a free-space tran-
sition dipole moment $\tilde{\mu}_{\text{vac}}$ in the presence of a polarizable object with polarizability $\hat{\alpha}$ can be approximated by [21]

$$\tilde{\mu}_{\text{eff}} = \tilde{\mu}_{\text{vac}} - \hat{\alpha} \frac{3 (\tilde{\mu}_{\text{vac}} \cdot \hat{n}) \hat{n} - \tilde{\mu}_{\text{vac}}}{R^3}. \quad (3.5)$$

$R$ is the distance between the chromophore and the polarizable object, and $\hat{n}$ is the unit vector pointing from the chromophore to the polarizable object. The second term originates from the induced dipole in the polarizable object resulting from the dipole field of the chromophore. Equation 3.5 holds for both transition dipole moments (ac fields) and permanent dipole moments (dc fields), but $\hat{\alpha}$ depends on the frequency.

One interesting consequence of Eq. 3.5 is that there should be a distribution of natural lifetimes $T_1$ among the molecules, since $T_1 \propto 1/|\tilde{\mu}_{\text{eff}}|^2$ [22]. Perturbations to the natural lifetime as large as 10% for 9,10-dichloroanthracene–inert gas heteroclusters have been observed in experiments and examined theoretically [23]. The polarizabilities of inert gas atoms are roughly an order of magnitude smaller than the polarizabilities for molecules typically used as hosts for single-molecule spectroscopy. Knowing this, one might expect to observe a distribution of lifetime-limited linewidths, which is exactly what was observed and is presented in Chapters 8 and 9.

In the next section, examples of experimental results are discussed for which the effect of the local field factor was neglected, which lead to misleading conclusions.

### 3.3 Review of relevant experiments

Next a few examples of the importance of considering the local field factor for the interpretation of experimental data are presented. The first example has to do with measurements of the saturation intensity.

In the first SMS paper where saturation effects were observed [24], the authors pointed out a discrepancy of an order of magnitude between the measured saturation intensity and that calculated according to Equation 2.8, using the values $k_{23}$,
3.3. Review of relevant experiments

$k_{31}$, $\mu_{\text{vac}}$, and $T_1$ measured for a bulk sample. Later Basché et al. [25] performed more careful measurements. For every molecule $k_{31}$, $k_{31}$, and $I_{\text{sat}}$ were precisely determined, the polarization of the laser light was adjusted for maximum emission signal, and the position of the Gaussian laser beam was adjusted to center the beam on the molecule. Finally, the width of the beam was measured using the SM as a probe. In spite of these extra measurements, the disagreement between measured and calculated saturation intensities remained. One sees this discrepancy in the data in Table 3.1, where the first four columns are taken from [25].

Table 3.1: Saturation intensity and triplet bottleneck factors for seven single pentacene molecules in p-terphenyl.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$K$ (exp.)</th>
<th>$I_{\text{sat}}$ (exp.)$^a$</th>
<th>$I_{\text{sat}}$ (calc.)$^a$</th>
<th>$I_{\text{sat}}$ (calc.)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.1</td>
<td>7.6</td>
<td>32.6</td>
<td>10.2</td>
</tr>
<tr>
<td>2</td>
<td>8.6</td>
<td>3.7</td>
<td>30.7</td>
<td>9.7</td>
</tr>
<tr>
<td>3</td>
<td>8.0</td>
<td>21.0</td>
<td>32.9</td>
<td>10.4</td>
</tr>
<tr>
<td>4</td>
<td>8.2</td>
<td>11.0</td>
<td>32.0</td>
<td>10.1</td>
</tr>
<tr>
<td>5</td>
<td>8.5</td>
<td>5.4</td>
<td>30.7</td>
<td>9.7</td>
</tr>
<tr>
<td>6</td>
<td>7.9</td>
<td>4.7</td>
<td>33.1</td>
<td>10.4</td>
</tr>
<tr>
<td>7</td>
<td>8.3</td>
<td>11.9</td>
<td>31.7</td>
<td>10.4</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>9.5</td>
<td>31.7</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$Data and estimate from Reference [25].

$^b$Estimated when the local field factor of 1.78 is taken into account.

To resolve this discrepancy, first it should be mentioned that Ambrose et al. [24] and Basché et al. [25] ignored the local field factor, which can actually have a dramatic effect on the calculated saturation intensity. From Equations 2.7 and 3.3, one finds

$$I_{\text{sat}} = \frac{(\varepsilon^{1/2} + 1)^2}{4C^2} \times \frac{\varepsilon_0 c \hbar^2}{2\mu_{\text{vac}}^2 T_1 T_2 T K},$$

which is inversely proportional to $L^2$. 

\[3.6\]
Finding the local-field factor for this system is not so straightforward since $p$-terphenyl is birefringent, and the transition dipole moments for the pentacene molecules are oriented out-of-plane with the polarization of the laser light. de Vries and Wiersma reported the relationship $E_{loc} = 1.78 \, E_{ext}$ between the external and local fields for this system [26]. Ignoring the out-of-plane orientation of the molecules, the values of $I_{sat}$ corrected using this factor are presented in the fifth column of Table 3.1.

With this correction, the agreement between the average calculated and measured values of $I_{sat}$ is reasonable, but significant deviations between the $I_{sat}$ values for the individual molecules remain. The measured values of $I_{sat}$ for molecules 2 and 3 differ by nearly a factor of six.

$p$-terphenyl is a birefringent crystal, so one would expect to see some variation in the measured values of $I_{sat}$ due to that. But the linear input polarization was rotated to maximize the count rate for each molecule. If the polarization were transformed to circular polarization, this would cause at the most a difference of a factor of two in the measurements. The value of $I_{sat}$ for molecule two could really be smaller than average if the molecule has a large local field factor. The influence of $\mathcal{L}$ on $I_{sat}$ is actually slightly more complicated than it looks in Equation 3.6 because $T_1$ and $T_2$ should also depend on $\mathcal{L}$, as was explained in the previous section. So, to estimate the values of $\mathcal{L}$ that would cause the distribution of $I_{sat}$ in Table 3.1 is not very straightforward.

An experiment for which the influence of the local-field factor is simpler to deduce is a Stark effect experiment for the same system that was performed by Wild et al. [27]. The resonance frequency shift caused by an applied dc electric field was measured as a function of field amplitude. The observed frequency shifts were seen to obey the polynomial function

$$\delta \nu_0 = aE_{dc} + bE_{dc}^2,$$  \hspace{1cm} (3.7)

where $E_{dc}$ is the amplitude of applied dc electric field. The measured Stark data are presented in Table 3.2 (Table 1 in [27] with an additional row for $\mathcal{L}$). Using the parameter $b$, Wild et al. calculated the polarizability differences between the ground
and the excited states of the pentacene molecules using the relation \( \Delta \alpha = -2\hbar b / L^2 \). For all molecules the same local field factor of 1.95 was used. Wild et al. concluded that there were differences in polarizability from molecule to molecule of about 25%.

Table 3.2: Solvent shifts, Stark coefficients, and local-field factors for single pentacene molecules in p-terphenyl.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta \nu_{sol} )^a</td>
<td>1746.5</td>
<td>1746.5</td>
<td>1746.4</td>
<td>1746.0</td>
<td>1746.0</td>
<td>1745.8</td>
<td>1745.8</td>
<td>1745.4</td>
</tr>
<tr>
<td>( a )^b</td>
<td>0.71</td>
<td>0.37</td>
<td>3.9</td>
<td>5.6</td>
<td>0.05</td>
<td>0.02</td>
<td>1.0</td>
<td>0.59</td>
</tr>
<tr>
<td>( b )^c</td>
<td>-2.8</td>
<td>-2.2</td>
<td>-4.9</td>
<td>-3.3</td>
<td>-2.4</td>
<td>-3.6</td>
<td>-3.0</td>
<td>-4.5</td>
</tr>
<tr>
<td>( \mathcal{L} )</td>
<td>1.8</td>
<td>1.6</td>
<td>2.3</td>
<td>1.9</td>
<td>1.6</td>
<td>2.0</td>
<td>1.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

^a\ cm^{-1}  
^b\ Hz \ m \ V^{-1}  
^c\ \mu \text{Hz m}^2 \ V^{-2}

These variations would contradict the solvent shift theory [12, 28]. For non-polar solutes in non-polar solvents the first term contributing to the solvent shift arises from the dispersion interaction. For long polyenes the dispersion interaction is strong and the solvent shift can be estimated by considering it alone. Assuming all solvent molecules to have the same distance \( R \), the shift can be expressed as

\[
\Delta \nu_{sol} = \frac{\alpha_B z}{6R^6} \left( \frac{1}{4} E_{ex} \Delta \alpha + \mu^2_{vac} \right),
\]

where \( \alpha_B \) and \( \Delta \alpha \) are the the molecular polarizabilities for the solvent and chromophore molecules, respectively. \( E_{ex} \) is the chromophore excitation energy, and \( z \) is the number of solvent molecules interacting with the chromophore.\(^1\) The first term in Equation 3.8 is a universal shift for all transitions, and the second term

\(^1\)The chromophore–solvent molecule distance dependence for the solvent shift is very sensitive to how one integrates over the spatial distribution of solvent molecules. For a spatially uniform distribution of particles, the spatial dependence is \( R_c^{-3} \), where \( R_c \) is the "radius" of the solute molecule.
predicts an extra shift for strongly-allowed transitions. For pentacene, $\mu_{\text{vac}} = 0.71 \pm 0.24$ D [26], and $E_{ex} \Delta \alpha / 4 \geq 30$ D$^2$. Hence, the chromophore polarizability term gives the main contribution to the solvent shift, which has the absolute value of 1745 cm$^{-1}$ for pentacene in p-terphenyl [29]. Equation 3.8 is rough, but it is clear that if the difference of $\Delta \alpha$ were about 25%, the variation of the solvent shifts for the SMs would have the same order of magnitude, whereas the standard deviation of the solvent shift was only about 0.02% of the magnitude of $\Delta \nu_{\text{solv}}$. Equation 3.8 was derived for nonpolar solvents and chromophores, but it is seen to hold well for polar molecules as well.

Again, this contradiction can be resolved by assuming different local field factors for different molecules. The local-field factors necessary to produce the variations that were observed in the quadratic Stark shifts are provided in the fifth row of Table 3.2. The variation of the local-field factor would be $\sim 13\%$.

In fact, the transition dipole moment affects many properties of a single molecule. In addition to the saturation intensity, Stark shifts, and the lifetime of the excited state, the coupling strength between single-molecule probes and environmental perturbers is also affected. This is examined in detail in Chapter 7. But first, the main model for the perturbers that are thought to dominate at low temperature is presented.
4. The tunneling two-level system model

In this chapter, the tunneling two-level system (TLS) model is presented from a general point of view. As an example, the model is used to calculate the anomalous low-temperature specific heat, which is one of the first problems to which the model was applied. In addition, a simple quantum mechanical picture is presented, TLS dynamics are discussed, and the arguments for having a constant density of tunneling states are presented.
4. The tunneling two-level system model
‘Well, there you are,’ said Mr Tompkins, ‘your “zero-motion” has run away. Is that according to the rules?’

‘Of course it is,’ said the professor, ‘in fact this is one of the most interesting consequences of quantum theory. It is impossible to hold anything inside an enclosure provided there is enough energy for running away after crossing the wall. Sooner or later the object will just “leak through” and get away.’ ‘Then I will never go to the Zoo again,’ said Mr Tompkins decisively, and his vivid imagination immediately drew a frightful picture of lions and tigers ‘leaking through’ the walls of their cages. Then his thoughts took a somewhat different direction: he thought about a car locked safely in a garage leaking out, just like a good old ghost of the middle ages, through the wall of the garage.

George Gamow, "Mr Tompkins in Paperback"

4.1 Fundamentals

In a perfect crystal, the atoms are constrained by symmetry to occupy a single potential minimum. In contrast, some atoms in a disordered system are thought to move in multi-dimensional potentials provided by neighboring atoms. Atoms or groups of atoms can be arranged in different spatial configurations. Even at very low temperatures, rather than the arrangements being frozen in, transitions between configurations occur by phonon-assisted tunneling. The two-level system (TLS) model fairly accurately describes many low-temperature properties of glasses that arise from these configurational changes [30]. The model was first proposed to explain anomalous thermal and acoustic properties of amorphous solids at low temperatures [31, 32], and was later applied to dephasing of optical transitions, as it is done in following chapters.

TLSs are the simplest reduction of the complex multi-dimensional potential energy surface. At any point in a glass, certain atoms or groups of atoms have access to two (or more) potential energy minima, because nearly degenerate configurations
of matrix atoms may exist, and the system may switch between these configurations by tunneling through the potential energy barrier.¹ This leads to a splitting of the ground state as in the ammonia molecule. A conceptual picture of a TLS is shown in Figure 4.1. Since the two equilibrium positions of a TLS correspond to different

![Figure 4.1: Conceptual picture of a TLS. The TLS (black) is shown in different positions in the left and right illustrations. Since there is a void in the vicinity of the TLS, it can switch between the two spatial configurations by phonon-assisted tunneling.](image)

atomic positions, tunneling transitions can be thought of as a type of structural relaxation.

A TLS can be mathematically modeled as a particle in a nearly symmetric double well potential, like that shown in Figure 4.2a. The potential curve is a section of the 3N-dimensional configuration space along the coordinate connecting two local minima. At low enough temperature, only the ground state in either of the potential wells is thermally populated and the problem can be treated as a two-level system. Transitions between these two states (linear combinations of the two localized states) occur by tunneling through the barrier, where the energy difference between the two states is compensated by the creation or annihilation of phonons.

To understand the properties of tunneling two-level systems in general, it is instructive to discuss their effect on a simple quantity like the specific heat, the low-

¹This is a simplified picture. In the basis set that diagonalizes the Hamiltonian the TLS is delocalized and is present in both wells simultaneously. One should always look at a problem in the basis set that diagonalizes the Hamiltonian.
Figure 4.2: Mathematical picture of a tunneling two-level system. 
a) The potential. The two localized states are separated by a barrier of height $V_0$ and have an asymmetry $\Delta$. b) The wavefunctions in the localized representation. c) The wavefunctions in the energy representation, for which the Hamiltonian is diagonalized.
temperature properties of which were one of the first things successfully reproduced using the TLS model.

In 1907 Einstein published a microscopic model for the specific heat in one of the first papers on quantum effects in solids. Einstein showed that when one assumes that Planck's quantization rule also holds for the elastic vibrations in solids, the specific heat arising from lattice vibrations could be expressed as

\[
C_V = \int_0^\infty \left( \frac{E^2}{k_B T^2} \right) \frac{\exp \left( \frac{-E}{k_B T} \right)}{[1 + \exp \left( \frac{-E}{k_B T} \right)]^2} g(E) \, dE 
\]

(4.1)

\[
= \int_0^\infty \left( \frac{E^2}{k_B T^2} \right) \text{sech}^2 \left( \frac{E}{k_B T} \right) g(E) \, dE ,
\]

(4.2)

where \(g(E)\) is the density of phonon states per unit volume and per unit energy with energy difference \(E\) [33]. The hyperbolic secant form is often used for compactness. For simplicity, Einstein assumed all of the modes to have the same frequency of oscillation. Even with this simplification, the model predicts the low temperature behavior of the specific heat in crystals qualitatively. Quantitative agreement can be found by using the density of states derived by Debye, who assumed the crystal to be an elastic solid with modes quantized according to the boundary conditions imposed by the size of the crystal. Debye found the density of states to be proportional to \(\omega_k^2\) and \(V\), where \(\omega_k\) is the phonon frequency and \(V\) is the volume of the crystal. One nice thing about the Debye theory is that there is a perfect analogy between the density of states in an elastic, isotropic crystal and the density of states in a cavity relevant for blackbody radiation [34].

In addition to the heat capacity arising from energy stored in lattice vibrations, amorphous solids have a contribution from TLSs. It is relatively straightforward to show that the heat capacity of a single two-level system with energy splitting \(E\) is [33]

\[
C_V = N k_B \left( \frac{E}{k_B T} \right)^2 \frac{\exp \left( \frac{E}{k_B T} \right)}{[1 + \exp \left( \frac{E}{k_B T} \right)]^2} .
\]

(4.3)

To find the total specific heat for an ensemble of TLSs, this has to be integrated over the distribution of TLS energy splittings \(n(E)\).
Both of the original papers on tunneling two-level systems provide several arguments why the density of states for the TLS energy splittings is constant over the relevant range of energies. With \( n(E) \) constant, integrating Equation 4.3 over the density of states yields

\[
C_V \simeq \frac{\pi^2}{6} k_B T n(0),
\tag{4.4}
\]

for the heat capacity, with \( n(0) \) being the constant density of states [31]. Using Equation 4.4 and data measured for the specific heat in amorphous silicon, Jäckle was able to derive a value of \( 4.35 \times 10^{31} \) erg\(^{-1}\) cm\(^{-3}\) for \( n(0) \) [35]. In Section 4.4 the arguments that the density of states is constant are summarized. But first a simple quantum mechanical picture is formalized.

### 4.2 Simple quantum mechanical treatment

Each TLS potential can be represented as in Figure 4.2 as two overlapping harmonic potentials. One can calculate the Eigenvalues for the TLS starting with the localized Eigenfunctions \( \phi_1 \) and \( \phi_2 \) as a basis set. The complete Hamiltonian can be conveniently written as

\[
\mathcal{H} = \mathcal{H}_1 + (V - V_1) = \mathcal{H}_2 + (V - V_2). \tag{4.5}
\]

\( \mathcal{H}_1 \) and \( \mathcal{H}_2 \) are the Hamiltonians for the particle in the localized potentials \( V_1 \) and \( V_2 \), and \( V \) is the double-well potential [30]. In the localized representation, the Hamiltonian in matrix form can be written

\[
\hat{\mathcal{H}} = \begin{bmatrix}
\varepsilon_1 + \langle \phi_1 | V - V_1 | \phi_1 \rangle & \langle \phi_1 | \mathcal{H} | \phi_2 \rangle \\
\langle \phi_2 | \mathcal{H} | \phi_1 \rangle & \varepsilon_2 + \langle \phi_2 | V - V_1 | \phi_2 \rangle
\end{bmatrix}. \tag{4.6}
\]

If the extension of each localized wavefunction into the barrier is small, then the terms \( \langle \phi_1 | V - V_1 | \phi_1 \rangle \) are negligible compared to the zero-point energies \( \varepsilon_i \) and
they can be neglected. Choosing the zero for the energy scale to be the average of the ground state energies in the two wells, one can write

\[
\hat{\mathcal{H}} = \frac{1}{2} \begin{bmatrix} -\Delta & J \\ J & +\Delta \end{bmatrix}.
\]  

(4.7)

\(\Delta\) is the TLS asymmetry parameter and \(J\) is the coupling energy, expressible in terms of the geometry of the double-well potential as

\[
J = \hbar\omega e^{-\lambda} = \hbar\Omega \exp \left[ -d \left( \frac{2mV_0}{\hbar^2} \right)^{1/2} \right].
\]

(4.8)

\(m\) is the mass of the tunneling particle, \(d\) is the distance between the two potential wells, and \(\hbar\Omega\) is approximately equal to the average of the zero-point energies in the two wells. If the potentials for the two wells are identical apart from being shifted in energy, then the zero in the energy scale will be half way between the two wells.

Typical values for the tunneling parameter \(\lambda\) for active TLSs can be calculated by requiring the coupling energy \(J\) to be less than the thermal energy. A temperature of 1 K corresponds to an energy of \(\sim 10^{-4}\) eV, therefore only splittings of \(\leq 10^{-4}\) eV can contribute to the thermal properties below 1 K. By assuming \(\hbar\Omega = 10^{-2}\) eV, one finds that this corresponds to a value \(\lambda \approx 5\) from Equation 4.8. This is equivalent to a proton tunneling through a barrier of 0.1 eV with \(d = 0.7\) Å [30].

The matrix 4.7 can be diagonalized to yield the Eigenstates in the diagonal representation. These states can be written as

\[
\psi_1 = \varphi_1 \cos \theta + \varphi_2 \sin \theta
\]

(4.9)

and

\[
\psi_2 = \varphi_1 \sin \theta - \varphi_2 \cos \theta.
\]

(4.10)
The Eigenfunctions have Eigenvalues of $\pm E/2$, where

$$E = \left[ \Delta^2 + J^2 \right]^{1/2},$$

(4.11)

and $\tan 2\theta = J/\Delta$. Introducing the $\sin \theta$ and $\cos \theta$ factors is a trick to simplify the notation. When $\Delta = 0$, these equations give the expected symmetric and antisymmetric solutions.

In the diagonal representation, the Hamiltonian takes the form

$$\hat{\mathcal{H}} = \frac{1}{2} E \sigma_z,$$

(4.12)

where $\sigma_z$ is the Pauli spin matrix. Formally, this problem is perfectly analogous to a spin-1/2 particle in a magnetic field, which is one aspect that makes the model attractive to theoreticians.

4.3 Tunneling two-level system dynamics

At this point, it is useful to introduce a few simplifications. Firstly, the dipole approximation is assumed to be valid. The acoustic and/or optical fields that could cause a TLS transition have wavelengths much longer than the physical size of a TLS. In addition, one can normally assume that external fields primarily affect the asymmetry energy $\Delta$ and changes in the barrier height can be ignored [36]. This implies that external fields do not affect the coupling energy $J$. These arguments are based on measurements of the volume thermal expansion and acoustic attenuation as a function of pressure, which indicate that the number of tunneling states per volume is not a function of pressure.

Assuming that external fields primarily affect the asymmetry energy $\Delta$, the interaction Hamiltonian is diagonal in the localized representation $(\varphi_1, \varphi_2)$ and can
be written

\[ \hat{H}_{1,\psi} = \frac{1}{2} \begin{bmatrix} \delta \epsilon & 0 \\ 0 & -\delta \epsilon \end{bmatrix} \]  

(4.13)

When transformed to the diagonal representation \((\psi_1, \psi_2)\), the interaction Hamiltonian takes the form

\[ \hat{H}_{1,\psi} = \frac{\delta \epsilon}{2} \begin{bmatrix} \Delta/E & J/E \\ J/E & -\Delta/E \end{bmatrix} \]  

(4.14)

Transitions between the diagonalized states can take place through the interaction of the system with electric and strain fields.

One can probe the TLS properties by applying strong external fields and taking coherence into account [37]. For thermal properties, coherence can be neglected. For example, any TLS in a solid is subjected to randomly varying strain fields which can be treated as the superposition of independent phonon modes. The strain field of each phonon is weak, and the TLS–phonon interaction can be treated using perturbation theory and ignoring phase coherence, which is equivalent to the interaction of an atom with electromagnetic radiation in a black-body cavity. The coupling arises from deformations of the TLS potentials caused by elastic waves.

The shift of the asymmetry energy \(\delta \epsilon\) is proportional to the deformation parameter \(\gamma_\kappa\), which is defined as \(\gamma_\kappa = \partial \Delta / \partial e\), where \(e\) is the amplitude of the elastic field. Expressing \(\delta \epsilon\) as the product of the deformation potential and the elastic field amplitude, one finds the matrix element for the absorption or emission of a phonon of momentum \(\hbar \vec{k}\) and polarization \(\kappa\) [35]

\[ \langle \vec{k}, \kappa; 2 | \hat{H}_{1,\psi} | 1 \rangle = \gamma_\kappa \left( \frac{k}{2 \rho \nu_\kappa} \right)^{1/2} \frac{J}{E} \]  

(4.15)
4.3. Tunneling two-level system dynamics

The square root factor is the strain field amplitude that one finds by setting the time-averaged classical energy per unit volume equal to the energy of a phonon. $\rho$ is the density and $v_\kappa$ is the speed of sound for phonons with polarization $\kappa$.

An active TLS is continuously absorbing and emitting thermal phonons. Ignoring phase information, the only important parameters are the TLS occupation probabilities, the rate equations for which can be written as

$$\dot{p}_1 = -p_1 W_{12} + p_2 W_{21}$$

and

$$\dot{p}_2 = p_1 W_{12} - p_2 W_{21}.$$  \hspace{1cm} (4.16)  \hspace{1cm} (4.17)

$W_{12}$ ($W_{21}$) is the transition rate from state 1 to 2 (2 to 1) when no external acoustic field is applied.

In thermal equilibrium, the time-independent equilibrium populations $p_1^0$ and $p_2^0$ are related by

$$\frac{p_2^0}{p_1^0} = \exp \left( -\frac{E}{k_B T} \right) = \frac{W_{12}}{W_{21}}.$$  \hspace{1cm} (4.18)

One can then define a TLS relaxation time $\tau$ such that

$$\tau^{-1} = W_{12} + W_{21} = W_{12} [1 + \exp (E/kT)].$$  \hspace{1cm} (4.19)

The transition rates $W_{12}$ and $W_{21}$ can be found using time-dependent perturbation theory, which yields

$$W_{12} = \sum_\kappa \frac{2\pi}{\hbar} \left| \langle \psi_1 | \hat{H}_{\text{int}} | \psi_2 \rangle \right|^2 g(E) n_B(E),$$  \hspace{1cm} (4.20)

where the sum is over phonon polarizations $\kappa$, $g(E)$ is the phonon density of states, and $n_B(E) = [\exp (E/k_B T) - 1]^{-1}$ is the thermal occupation factor obtained for
Bose-Einstein statistics. With this and the Debye density of phonons

\[ g(E) = \frac{E^2}{2\pi^2 \hbar^3 v^3} , \]  

(4.21)

the TLS relaxation rate \( R \)

\[ R(E) = \tau^{-1}(E) = \sum_k \frac{\gamma_k^2 E^2}{v_k^5 2\pi \rho \hbar^4} \coth (E/2k_BT) = c_{ep} E J^2 \coth (E/2k_BT) \]  

(4.22)

can finally be written, where \( c_{ep} \) is the electron-phonon coupling constant.

### 4.4 The density of states

It is usually argued that the density of TLS states is constant. The arguments behind this assumption are summarized below. The density of states can be expressed as

\[ n(E)dE = \left\{ \left( \frac{\partial}{\partial E} \right) \int_0^E \int_{J_{\text{min}}}^{J_{\text{max}}} P(\Delta)P(J)d\Delta dJ \right\} dE , \]  

(4.23)

where \( P(\Delta) \) and \( P(J) \) are the probability densities for wells with asymmetry \( \Delta \) and coupling energy \( J \), respectively. To find \( n(E) \), first \( P(\Delta) \) and \( P(J) \) have to be found. The distribution for the coupling energy \( P(J) \) can be found from the distribution for the tunneling parameter \( \lambda \), which depends on the geometry of the well according to Equation 4.8.

It is simple to argue that the distribution of asymmetry parameters \( P(\Delta) \) is constant over the relevant energy scale. The maximum asymmetry corresponds to the glass transition temperature. This is \( \sim 0.1 \text{eV} \) for \( \text{SiO}_2 \). For polymers it is about an order of magnitude smaller. Since \( P(\Delta) \) has to be symmetric in \( \Delta \), one can reasonably assume that \( P(\Delta) \) is a Gaussian with a width of \( \sim 10^{-2} \text{eV} \), centered at \( \Delta = 0 \). Since the asymmetry of the contributing states at low temperature is \( \sim 10^{-4} \text{eV} \), only the center 1% of the distribution contributes, which is essentially flat.

Slightly more intricate arguments are necessary to argue that the distribution of \( \lambda \) values must also be flat. First, the region of relevant values for \( \lambda \) can be
4.4. The density of states

estimated. A lower bound for \( \lambda \) is found from the requirement that the two levels have to be degenerate to within an amount of approximately \( k_B T \). The minimum energy splitting \( E \) is found when the asymmetry \( \Delta \) is zero, or when \( E = J \). With Equation 4.8, one finds

\[
\lambda_{\text{min}} = \ln \left[ \frac{\hbar \Omega}{E} \right].
\]  

(4.24)

Here \( \hbar \Omega \) is the zero-point energy for the oscillation in one of the wells, which is usually taken as about \( 10^{-2} \) eV. With \( T = 1 \) K and \( k_B T \sim 10^{-4} \) eV, an acceptable value for \( \lambda_{\text{min}} \) is \( \sim 5 \).

There is also an upper bound on \( \lambda \). The density of states with tunneling rates on the time scale of the measurements is much smaller than the total density of modes with asymmetries of less than \( k_B T \). Since glasses are in a metastable state, there are large numbers of states with arbitrary asymmetries. Accidentally degenerate states can be inaccessible to tunneling if they are separated from the occupied states by large energy barriers. To impose a reasonable limit on the maximum value of \( \lambda \), a rough estimate of the tunneling rate can be written as \( w \simeq w_0 \exp [-\lambda] \). The condition \( \tau_m > 1/w \) imposes the condition

\[
\lambda_{\text{max}} = \ln \left[ w_0 \tau_m \right],
\]  

(4.25)

where \( \tau_m \) is the measurement time.

The important parameter for finding the density of states in Equation 4.23 is \( J \). Since \( \lambda \) depends on \( J \) only very weakly (logarithmically), a strongly varying distribution of \( \lambda \) produces only a weakly varying distribution for \( J \). If one assumes that the distribution for \( \lambda \) is constant, then

\[
P_J(J) = \frac{P_0}{J} \quad [J_{\text{min}} < J < J_{\text{max}}],
\]  

(4.26)

where \( P_0 \) is a constant. Assuming an exponential distribution for \( \lambda \) only changes the dependence on \( J \) to \( P(J) \propto 1/J^2 \). Because of this weak dependence, the distribution for \( \lambda \) is normally assumed to be constant. The limits \( J_{\text{min}} \) and \( J_{\text{max}} \) can be found
from the limits found for $\lambda$ in Equations 4.24 and 4.25. Without these limits the
distribution would not be normalizable.

With the above distributions for $P(J)$ and $P(\Delta)$, it can be easily shown that
$n(E)$ is constant using Equation 4.23. The precise value of $n(0)$ can then be found
by comparing the model to experimental data.

Now that the nuts and bolts of the TLS theory have been introduced, the model
can be applied to single-molecule spectroscopy.
5. Lineshape theory applied to single-molecule spectroscopy

This chapter begins with a discussion that highlights the differences between SM spectra in glasses and crystals. This is followed by an examination of the TLS–SM coupling mechanism. Then lineshape theory is presented in the context of single-molecule spectroscopy, and an expression is found for the linewidth as a function of time and temperature. Finally, a method for studying the linewidth as a function of time called intensity-time-frequency correlation spectroscopy is reviewed, which provides a means for measuring spectra with higher time resolution than is normally achievable with traditional methods.
5. Lineshape theory applied to single-molecule spectroscopy
5.1 Single-molecule line broadening — glasses versus crystals

The line broadening of impurity molecules in crystals is known to be an activated process. This was first confirmed on the SM level by Ambrose et al. [24] for pentacene molecules in $p$-terphenyl (p-TP). The spectra for nearly all of the molecules were stable and could thus be measured as a function of temperature and compared to the activation law:

$$\Gamma = \Gamma_T + \beta \exp\left[-\frac{\Delta E_a}{k_B T}\right], \quad (5.1)$$

where the $\Gamma_T$ term is the lifetime-limited contribution. The model assumes that the molecule can be excited to a local vibrational (librational) sublevel with an energy $\Delta E_a$ by absorbing a phonon [38]. This changes the electronic transition frequency since in general the librational energy is different in the excited and ground electronic states. Since population/depopulation of the librational sublevel is a stochastic process, the electronic transition frequency is a temperature-dependent, stochastic function of time. This leads to temperature-dependent broadening and line shifts. The latter is determined from the time-averaged transition frequency. For $\Delta E_a/(k_B T) \gg 1$, the temperature shift is proportional to the broadening. The pre-exponential factor depends on parameters of the librational mode. For pentacene in $p$-TP Ambrose et al. showed that the broadening followed Equation 5.1 and was insignificant below a temperature of about 4 K. In addition, the values found for $\Delta E_a$ and $\beta$ were in agreement with values previously reported for bulk samples.

In amorphous hosts the behavior is more complicated than in crystalline systems because of tunneling two-level systems (TLSs). TLSs cause additional spectral
dynamical effects to arise that can occur on time intervals much longer than the
time scale of phonon excitation of librational sublevels. The dynamics have been
shown to last as long as days [39].

In an amorphous system, the local environment at each point in the glass is
unique. When a glass is doped with a chromophore like terrylene, each dopant
molecule has a unique environment and hence properties like the linewidth are dis¬
tributed. The time and temperature dependence of the linewidth is also distributed.

In spite of the success of the TLS model for explaining macroscopic properties,
not much has been learned about the microscopic nature of spectral diffusion in
glasses. One reason for this is that conventional measurement techniques like hole
burning measure averages from a large numbers of TLSs and are not sensitive to the
details of the model. SMS can be useful for investigating the model details, because
the truly microscopic dynamics that occur in the neighborhood of the molecules can
be probed. By comparing lineshape theories to measured linewidth distributions,
one can gain insight into the TLS–SM interaction mechanism and the properties of
the host as well.

5.2 SM–TLS coupling

TLS transitions (flips) cause the transition frequencies of probe molecules doped
into a glass to undergo spectral diffusion. At any point in a glass, the total electric
and strain fields are influenced by many TLSs, and the time-dependent transition
frequency of a guest SM can be written as

\[ \omega(t) = \omega_0 + \sum_j \xi_j(t) f_j, \]  

(5.2)

where \( \xi_j = 0 (\xi_j = 1) \) indicates that the \( j'th \) TLS is in its ground (excited) state,
and

\[ f_j = 2\pi c \frac{n_j}{\tau_j^3} \]  

(5.3)
is the frequency shift induced by excitation of the \( j' \)th TLS. \( \alpha_c, \eta_j, \) and \( r_j \) are the TLS–chromophore coupling constant, the relative orientation parameter, and the TLS–chromophore distance for the \( j' \)th TLS, respectively. In the standard model, \( \alpha_c \) is assumed to be the same for all TLS–SM pairs.

The theory is largely phenomenological because very little is known about the microscopic nature of TLSs, however there is reasoning behind Equations 5.2 and 5.3. The TLS–SM interaction is assumed to be dipolar, having a \( 1/r^3 \) distance dependence. Usually, the interaction is said to arise from “elastic” dipole TLSs, whose flips cause mechanical strain fluctuations. This was already discussed in Chapter 4. The effect of TLS flips on the chromophore resonance is like a pressure effect, which has been studied extensively with hole-burning techniques [40]. The mechanical displacements are thought to cause density fluctuations in the vicinity of the chromophores, affecting the size of the \( \Delta \nu_{\text{sol}} \) in Equation 3.8 through the dependence on the average distance between the chromophore and the solute molecules, \( \bar{R} \).

If the matrix is polar, elastic dipole flips may also cause a shift of charges and permanent dipoles in the matrix, which can also cause energy shifts. The TLS–SM interaction could also originate from “electric” dipoles if the two states of the TLSs have different electric dipole moments. Then a TLS state flip itself can cause Stark shifts of the chromophore without displacement of the matrix. The TLS–SM coupling is actually a sum of electric and elastic dipole contributions. Very often the problem is treated purely in terms of the elastic dipole interaction, but it is important to realize that the effect of elastic dipoles takes place through electrodynamical interactions. The electric dipole interaction is important for the conclusions that are presented in Chapter 7, so before going on, the importance of electric dipole coupling is highlighted.

It has been shown that the electrostatic contribution to the static guest–host interaction is roughly 2–3 orders of magnitude smaller than the dispersive contribution for octaethylporphin in polystyrene [41]. Unpublished measurements of the absorption spectra of terrylene in different polymer matrices (polyethylene (PE), polymethylmethacrylate (PMMA), polyisobutylene, polyvinylbutyral (PVB), and polystyrene) show that the solvent shifts for terrylene in polar and non-polar ma-
traces are similar in size. In fact, the deviations in the absolute wavelength of the shifted lines from host to host are much smaller than the inhomogeneous bandwidths. Therefore the dispersion interaction contribution to the solvent shift is much larger than the electrostatic contribution even for polar hosts. In spite of this, the electric dipole contribution to the dynamical coupling constant can be significant.

It has been shown that the Stark effect for single terrylene molecules in PE is linear because the molecular symmetry is broken by the matrix [42]. Therefore the magnitude of the frequency shifts caused by electrostatic interactions between a SM and a fluctuating TLS is directly proportional to the local electric field. The electric dipole contribution to the coupling constant from Equation 5.3 can then be estimated as

\[
\alpha_c = \frac{1}{4\pi\epsilon\epsilon_0} \mathcal{L} \Delta \mu_{SM} \Delta \mu_{TLS},
\]

where \( \Delta \mu_{TLS} \) is the dipole moment difference between the two TLS states, \( \Delta \mu_{SM} \) is the induced permanent dipole moment change of the chromophore in the host, \( \epsilon \) is the dielectric constant, and \( \mathcal{L} \) is the local field factor (as discussed in Chapter 3). According to recent hole-burning measurements [43], the TLSs in PMMA have an average dipole moment difference between the two TLS states of 0.4 D. The average induced permanent dipole moment change for terrylene in PE has also been measured and is \( \sim 2 \) D [42] (a factor of two higher than the average modulus of the projection along the electric field.) Using these values and \( \epsilon = 2.84 \) for PMMA [44] gives \( \alpha_c \approx 70 \text{ GHz nm}^3 \) as a rough estimate for the electric dipole contribution to the coupling constant. \( \Delta \mu_{SM} \) strongly depends on the host [45] and is probably larger in PMMA than in PE since PMMA is polar. Anyhow, the above estimate for \( \alpha_c \) is between the values estimated by Geva and Skinner for terrylene in PE (12 GHz nm\(^3\)) and in PMMA (190 GHz nm\(^3\)) [2], which are also only rough estimates because they depend on the values for the TLS densities which are only approximately known. Phonon echo measurements have also shown that there is an intrinsic electric dipole moment of tunneling systems even in undoped silicon of about 0.6 D [46].

Normally, the coupling parameter \( \alpha_c \) is treated as a constant in the simulations, but as is written in Equation 5.4, it is a product of several parameters. There are
two distinct types of parameters affecting the TLS–SM interaction: those explicitly connected to the probe molecules, which may be referred to as inhomogeneous parameters, and those associated with the bath of TLSs, which can be called homogeneous. Each SM has a unique value for each inhomogeneous parameter that affects the interaction strength of the SM with the entire bath of TLSs. Each SM interacts with many TLSs which are randomly distributed in space, whose homogeneous parameters all come from the same distributions.

Each SM has unique values for $\Delta \mu_{SM}$ and $\mathcal{L}$, but each TLS has different values for $\Delta \mu_{TLS}$, $\eta$, and $\tau$. A molecule that has a large value for $\Delta \mu_{SM}$ or $\mathcal{L}$ has a larger interaction strength with the whole bath of TLSs. To illustrate this mathematically, one can group all parameters into the single parameter $\Lambda = \mathcal{L} \Delta \mu_{SM} \Delta \mu_{TLS} \eta / \tau^3$, which describes the TLS–SM interaction for a single molecule. The probability distribution for $\Lambda$ turns out to be

$$P(\Lambda) = \frac{4\pi}{3} \frac{\Delta \mu_{SM} \mathcal{L} \rho_{TLS} \langle |\eta \Delta \mu_{TLS}| \rangle}{\Lambda^2 N_{TLS}},$$  \hspace{1cm} (5.5)$$

which is shown mathematically in Appendix A. $\rho_{TLS}$ is the TLS density and $N_{TLS}$ is the number of TLSs considered. This depends on the upper distance cut-off $r_{\text{max}}$, which must be large enough for the SM line shapes to reach asymptotic values. Equation 5.5 shows that the distributions of the homogeneous parameters $\eta$, $\Delta \mu_{TLS}$, and $\tau$ can be replaced by average values in the simulations without changing the resulting distribution of SM line shapes, whereas the specific values of $\Delta \mu_{SM}$ and $\mathcal{L}$ for the SM enter the distribution explicitly.

### 5.3 Simulations of linewidth distributions

In this section, a method for simulating linewidth distributions that was published by Geva and Skinner is reviewed [2]. This method, with a few small exceptions, is followed for comparing the TLS model and the measured distributions that are presented in Chapters 7 and 9.
Given a time-dependent SM resonance frequency as described by Equations 5.2 and 5.3, one can ultimately find the spectrum of a SM in a bath of TLSs by taking the Fourier transform of the dipole autocorrelation function, which can be expressed as

$$I(\omega) = \text{Re} \left( \frac{1}{\pi} \int_0^\infty dt e^{i\omega t} e^{-t/T_1} \Phi_{SM}(t) \right). \quad (5.6)$$

There are two factors contributing to the dipole autocorrelation function. The decay term, $e^{-t/T_1}$, is the part that would normally produce the Lorentzian line shape for an unperturbed transition. The second factor, $\Phi_{SM}(t)$, provides the broadening contribution from TLS dynamics, which can be written as

$$\Phi_{SM}(t) = \prod_j \phi_j(t) \quad (5.7)$$

assuming that the TLSs do not interact with each other. $\phi_j(t)$ is the part of the dipole autocorrelation function arising from the $j^{th}$ TLS, which can be expressed as

$$\phi_j(t) = \exp \left[ -2\pi i f_j \int_0^t d\tau \xi_j(t) \Theta(R_j - 1/\tau_m) \right]. \quad (5.8)$$

Here $\xi_j(t)$ is a stochastic function of time which indicates whether TLS $j$ is in its ground ($\xi_j = 0$) or excited ($\xi_j = 1$) state. The time average in Equation 5.8 is performed over all possible realizations of $\xi(t)$. $R_j$ is the sum of upward and downward tunneling rates (Section 4.3). $\Theta(R_j - 1/\tau_m)$ is a step function which serves the purpose of cutting off TLSs that flip at a slower rate than the inverse of the measurement time. $\phi_j(t) = 1$ for TLSs with $R_j - 1/\tau_m < 0$. For TLSs with flip rates faster than $1/\tau_m$, it can be shown that Equation 5.8 reduces to

$$\phi_j(t) = \left[ \cosh \Omega_j t + \frac{\theta_j}{\Omega_j} \sinh \Omega_j t \right] \exp \left[ -\frac{1}{2} (R_j + 2\pi i f_j) t \right]. \quad (5.9)$$

Here

$$\Omega_j = \sqrt{\frac{R_j^2}{4} - \frac{f_j^2}{4} - i \left( p_j - \frac{1}{2} \right) f_j R_j} \quad (5.10)$$
5.3. Simulations of linewidth distributions

and

\[ \theta_j = \frac{\theta_j}{2} - i (p_j - 1/2) f_j. \] (5.11)

\( p_j \) is the time-averaged occupation probability of the excited state for TLS \( j \).

Simulating the linewidth of a SM in practice consists of the following main steps:

1. Specifying the measurement time \( \tau_m \), the temperature \( T \), the electron–phonon coupling constant \( c_{ep} \), and the TLS–SM coupling strength \( \alpha_c \). \( \tau_m \) and \( T \) are determined by the experimental conditions, and \( c_{ep} \) can be taken from the results of acoustic experiments. Usually \( \alpha_c \) is used as a free parameter.

2. Determining the TLS parameters \( \Delta, J, r, \) and \( \eta \) for each TLS using a Monte Carlo method.

3. Calculating \( R, \phi(t), \Omega, \) and \( \vartheta \) for each TLS.

4. Taking the fast Fourier transform of the product \( \Phi_{SM}(t)e^{-t/2T} \) (Equation 5.6).

Until now, this model had been tested on data for which the number of molecules measured per distribution varied between 68 and 211. Often the details of a theoretical model strongly depend on the wings of the distribution, and so to perform a sensitive comparison between an experiment and simulations, the measurement must involve enough molecules so that the wings can be characterized. For Poissonian statistics, to know the height of a column in a histogram to 10% accuracy, one must acquire 100 events for that column. The distribution must be at least 10 columns wide, and so one needs to measure about 1000 molecules. In Chapter 7, the model described above is compared to distributions for which the spectra of as many as 919 molecules were measured. The measurements were enabled using single-molecule microscopy, which is presented in Chapter 6.
5.4 Linewidth as a function of time and temperature

To approach the calculation of the width of a SM line undergoing spectral diffusion as a function of time and temperature, it is instructive to refer back to work that was done to treat the problem of spectral diffusion for ensembles [47].

If one begins with a SM having a resonance frequency $\omega_0$ at $t = 0$, the normalized probability that at time $t$ the transition frequency will be $\omega$ is

$$D(\omega - \omega_0, t) = \frac{\Delta \omega(t, T)/\pi}{(\omega - \omega_0)^2 + [\Delta \omega(t, T)]^2},$$

where

$$\Delta \omega(t, T) = \frac{2\pi^2}{3\hbar} \langle C_{ij} \rangle \left\langle \frac{\Delta E}{E} n(t, T) \right\rangle_{j, E}.$$  

$D(\omega - \omega_0, t)$ is the so-called spectral diffusion kernel, and $\Delta \omega(t, T)$ is its width. $\Delta$ and $E$ are the TLS asymmetry and total energy splitting, respectively, and $\langle C_{ij} \rangle$ is the ensemble average of the TLS-SM coupling strength, which has the dimensions of Energy x Volume. $n(t, T)$ is the number density of TLSs that change state during a time $t$ at a temperature $T$. For a single TLS, it is the probability that the TLS will switch state after a time $t$ at a temperature $T$.

The occupation probability for the excited state of a TLS is

$$p = 1/ (1 + \exp(E/k_BT)).$$

The probability that the TLS can be found in the ground state is simply $1 - p$. The TLSs that contribute to broadening and hence $n(t, T)$ are those TLSs that switch state during the measurement time. The probability for a TLS that was originally in its excited state to be later found in the ground state is $p(1 - p)$. Likewise the probability that a TLS switches from ground to excited state is $(1 - p)p$. To find $n(t, T)$, one needs to add these two probabilities and multiply them by the time-
dependent transition probability for the TLS to get [48]

\[ n(t, T) = \frac{1}{2} \text{sech}^2 \left( \frac{E}{2k_BT} \right) [1 - \exp(-Rt)] . \quad (5.15) \]

\( R \) is the TLS tunneling rate given by Equation 4.22, which depends on the total energy splitting \( E \), the coupling energy \( J \), and the temperature.

Explicitly writing out the ensemble average in Equation 5.13 one finds

\[ \Delta \omega(t, T) = \frac{2\pi^2}{3\hbar} \langle C_{ij} \rangle \int_0^{E_{\text{max}}} dE \text{sech}^2 \left( \frac{E}{2k_BT} \right) \int_{R_{\text{min}}}^{R_{\text{max}}} dR P(R, E) [1 - e^{-Rt}] . \]

(5.16)

For tunneling rates slow enough such that \( Rt \) is small, the term in square brackets is small. Thus the integral is dominated by TLSs with rates much faster than the measurement time. Because of this, one can do a trick to simplify the integral by changing the lower limit in the integral over \( R \) to \( t^{-1} \) and neglecting the exponential term [49]. This results in

\[ \Delta \omega(t, T) \sim \int_0^{E_{\text{max}}} dE \text{sech}^2 \left( \frac{E}{2k_BT} \right) \int_{t^{-1}}^{R_{\text{max}}} dR P(R, E) . \quad (5.17) \]

What remains is to find the distribution function \( P(R, E) \), and then Equation 5.17 can be integrated. One can write

\[ P(R, E) = \int d\Delta \int dJ \delta \left\{ R - cJ^2E\coth \left[ E/2k_BT \right] \right\} \delta \left\{ E - \sqrt{\Delta^2 + J^2} \right\} P(\Delta, J) \]

(5.18)

\[ \sim \frac{1}{R \{1 - R/R_{\text{max}}(E)\}^{1/2}} , \quad (5.19) \]

where \( R_{\text{max}} = cE^3\coth \left[ E/2kT \right] \) is the maximum tunneling rate for a TLS with energy splitting \( E \). With this, Equation 5.17 can be integrated (with the approximation that only fast TLSs are included) to find

\[ \Delta \omega(t, T) \sim \langle C_{ij} \rangle T \ln (t) . \]

(5.20)
Several temperature dependence studies that have been performed at temperatures above 1 K have shown that the hole width in hole-burning experiments typically varies as $T^{1.3}$ rather than as $T$ as predicted by Equation 5.20 [49]. To patch up the TLS model so that it agrees with these measurements, a phenomenological modification was made to the asymmetry parameter distribution so that rather than being constant, it is proportional to $\Delta^\mu$, where $\mu$ is 0.3. This produces a $T^{1.3}$ temperature dependence, and the normalized distribution for $\Delta$ becomes

\[ P(\Delta) = \frac{1 + \mu}{\Delta_{max}^{1+\mu}} \cdot \Delta^\mu \quad 0 \leq \Delta \leq \Delta_{max}. \]  

(5.21)

The distribution is zero at energies above the limit $\Delta_{max}$, which should be set such that $\Delta_{max} \gg k_B T$ [2].

However, the measurements presented in Chapter 9 for terylene in polyethylene show that the temperature dependence at temperatures below 1 K varies linearly rather than as $T^{1.3}$. The $T^{1.3}$ dependence might in fact be an artifact that arises at higher temperature that has nothing to do with TLSs. As evidence for this, Zilker and Haarer showed that their photon echo data measured in the range between 0.4 and 2.4 K could be fit as a sum of a linear and an activated term. They also fit the data to a $T^{1.3}$ dependence, which fit well above 1.2 K, but deviated strongly from the data below 1 K [50].

In Chapter 7, simulations of linewidth distributions for terylene molecules in polyvinylbutyral are presented for which $\mu$ was set to 0.3. These measurements were performed at 1.8 K. In Chapter 9, measurements are presented for the linewidths of single-terrylene molecules in polyethylene for which a linear temperature dependence of the average linewidth was observed to hold in the the range of temperatures from 30 mK to 1.83 K. To perform simulations and compare the standard tunneling model to the experimental data, $\mu$ was set equal to zero.
5.5 Intensity-time-frequency correlation spectroscopy

Some of the experiments presented in Chapter 9 were done on a faster time scale using the intensity-time-frequency correlation technique [51], which is a trick for obtaining better time resolution than one can obtain with conventional spectroscopy.

Rather than scan a SM spectrum slowly enough to collect enough photons to achieve the desired signal-to-noise ratio (SNR), one scans the spectrum many times quickly with a poor SNR, finds the autocorrelation function (ACF) for each scan, and then adds the autocorrelation functions. The time resolution is determined by the time that it takes to scan the SM spectrum per scan.

Taking the ACF effectively shifts the line center to the origin. Hence, when the ACFs for all the scans are added, they overlap. Frequency jumps that occur on time scales slower than a scan may cause the center frequency of the line to appear at different positions in each scan, but do not affect the width of the ACFs.

The ITFC is defined as [51]

\[
\text{ITFC}(\omega') \equiv \left( \frac{1}{N} \sum_{k=1}^{N} I_k(\omega') \star I_k(\omega') \right) = \frac{1}{N} \sum_{k=1}^{N} \int_{-\omega_r/2}^{+\omega_r/2} I_k(\omega') I_k(\omega + \omega') d\omega ,
\]

which is just the average of the ACFs. \(I_k(\omega')\) is the \(k'\)th single-scan spectrum. \(\omega_r\) is the frequency interval of the scans, which has to be chosen so that the intensity of the SM is negligible at the edges of the scan. The ACF of a Lorentzian with width \(\Gamma\) is a Lorentzian centered at the origin with a half-width of \(\Gamma\).

For a single scan and for the ITFC, the time resolution is determined by the time that it takes to scan the line per scan. This is shorter than the time that it takes to perform the full scan, and is determined by the ratio of the linewidth \(\Gamma\) to the scan range \(\omega_r\). If the measurement time per scan is \(t_s\), then the time to measure the SM per scan is \(\tau_m = \frac{\Gamma}{\omega_r} t_s\). When one adds all of the fast scans together, one has a spectrum with low noise and a measurement time determined by the total
measurement time for all $N$ scans, namely, $Nt_s$. One can determine the linewidth as a function of measurement time for intermediate times by adding adjacent fast scans and then taking the ITFC. For example, if two adjacent fast scans are added and $\omega_r \gg \Gamma$, the measurement time is equal to $t_s$. Adding three adjacent fast scans yields a time resolution of $2t_s$. With this data analysis technique, one obtains the linewidth as a function of measurement time, which can be compared to Equation 5.20.

The ITFC method has the advantage that the ITFC spectrum is defined without having to specify the time scale of the experiment. The dependence of $\phi_j(t)$ on $\tau_m$ in Equation 5.8 is a weakness of the lineshape theory presented in Section 5.3, because the TLS flips are random, and there is no sharp cut-off tunneling rate.

The ITFC method is applied to acquire data with high time resolution in Chapter 9. For more mathematical details on the ITFC technique, the reader is referred to reference [52].
6. Experiment

In this chapter, details on how the experiments were carried out are presented. First, the dilution refrigerator is presented, which is the instrument that allowed for the measurements at such low temperatures. The final two sections explain the optical apparatuses and the data-handling equipment that were used to collect the data. One apparatus was based on single-molecule microscopy, which enabled the measurement of many SM spectra in parallel. The second apparatus was based on a photo-multiplier tube detector, so higher time resolution could be achieved.
6. Experimental apparatus
6.1 Dilution Refrigerator

The measurements described in this thesis were performed both with ordinary bath cryostats and with a dilution refrigerator custom built by Oxford Instruments. The bath cryostats were used only for the results presented in Chapter 7, which were performed at a temperature of ~1.8 K. Since bath cryostats are standard equipment they are not discussed here.

The most significant and impressive part of the experimental apparatus is probably the dilution refrigerator that was used to do the measurements below one Kelvin. The principles of operation and the performance of the system are discussed below.

6.1.1 Low-temperature properties of $^3\text{He}/^4\text{He}$ mixtures

The function of a dilution refrigerator is based on the special properties of $^3\text{He}/^4\text{He}$ mixtures at low temperature. Figure 6.1 shows the phase diagram for such a mixture [53]. $x$ is the mole fraction $^3\text{He}$ in the mixture, and $T$ is the temperature. At temperatures below 0.86 K (the tri-critical point), the mixture separates into two phases. One of these phases is rich in $^3\text{He}$ (the concentrated phase), and the other phase is mostly $^4\text{He}$ (the dilute phase). Above the coexistence curve, the mixture is either superfluid or normal, depending on whether the point $(T, x)$ is to the left or to the right of the Lambda curve. At the coexistence curve, the mixture separates into the concentrated and dilute phases. Because of its lower density, the $^3\text{He}$ rich phase floats on top of the dilute phase. If one begins at the point $(T, x)$ in the phase diagram shown in Figure 6.1 and lowers the temperature keeping $x$ constant, the two phases begin to form at the temperature $T'$ when the coexistence curve is reached. As the temperature is further lowered, the $^3\text{He}$ concentration in the dilute phase is determined by the left branch of the coexistence curve, and the $^3\text{He}$ concentration in the concentrated phase is determined by the right branch of the coexistence curve.

Since the enthalpy of the $^3\text{He}$ in the dilute phase is higher than in the condensed phase, it is possible to obtain cooling by "evaporating" the $^3\text{He}$ from the concentrated
Figure 6.1: A phase diagram for a $^3$He/$^4$He mixture. $T$ is the temperature and $x$ is the mole fraction of $^3$He in the mixture.
phase into the dilute phase. The key to the function of a dilution refrigerator is the fact that even at $T = 0\,\text{K}$, the concentration of $^3\text{He}$ in the dilute phase is nonzero, so this evaporative cooling effect works all the way down to temperatures of a few mK.

Figure 6.2 illustrates the main cooling mechanism in a dilution refrigerator. It is conceptually helpful to imagine the concentrated phase of the mixture as pure liquid $^3\text{He}$, and the dilute phase as $^3\text{He}$ gas. The $^4\text{He}$ (which makes up the majority of the dilute phase) is inert, and the $^3\text{He}$ "gas" moves through the liquid $^4\text{He}$ with little interaction. The $^4\text{He}$ in fact acts like a "heavy vacuum", in which the $^3\text{He}$ atoms have an increased effective mass. When the top surface of the dilute phase is kept above a temperature of $\sim 0.6\,\text{K}$, the vapor pressure for $^3\text{He}$ gas above the surface of the dilute phase is approximately three orders of magnitude larger than the vapor pressure for $^4\text{He}$, even though the dilute phase may only consist of $\sim 10\%\,^3\text{He}$. Hence $^3\text{He}$ evaporates preferentially from this surface. This destroys the equilibrium in the mixture and causes $^3\text{He}$ to evaporate across the phase boundary. This process continues to work even at the lowest temperatures because the equilibrium concentration of $^3\text{He}$ in the dilute phase is still finite, even as the temperature approaches absolute zero.
6.2 Principles of operation

How the system works in practice is illustrated in Figure 6.3. The system consists of two separate circuits, one containing the mixture and one containing pure $^4$He. The system has a 50 liter reservoir of $^4$He (not shown) from which $^4$He is drawn through a needle valve into a smaller reservoir (the 1K pot). The 1K pot is pumped to reduce the temperature and contains superfluid $^4$He. Like with an ordinary bath cryostat, the temperature of the 1K pot is determined by the vapor pressure of $^4$He above the liquid helium and varies between 1.5 and 2.2 K.

Before an experiment, the 1 K pot cools the dilution unit enough to condense the mixture into the system and to cool it to approximately 1.5 K. In order to reach
phase separation, the temperature has to be reduced to below 0.86 K. To reach this point, the system is cooled by evaporation and condensation cycles of $^3$He, hence the system acts like an ordinary refrigerator with $^3$He for the refrigerant. With this process alone, one can reach a temperature of about 0.3 K. The still is the first part of the system to cool below 1.5 K, since this is where the $^3$He evaporates from. The incoming $^3$He is then cooled through the heat exchangers, and gradually the rest of the dilution unit is cooled to the point where phase separation occurs. At this point, the evaporative cooling effect arising from the $^3$He crossing the phase boundary kicks in.

For continuous operation of the system, $^3$He is extracted from the dilute phase and returned to the concentrated phase keeping the system in a dynamic equilibrium. The $^3$He is pumped away from the liquid surface in the still, which is typically maintained at a temperature of 0.6 to 0.7 K. At this temperature, the vapor pressure of the $^3$He is about 1000 times higher than that of $^4$He, so $^3$He evaporates preferentially. About 20 mW of heat is provided to the still to promote the evaporation of $^3$He. Evaporation of $^3$He from the still causes the concentration of $^3$He in the still to be lower than in the dilute phase of the mixing chamber, and a flow of $^3$He is promoted from the mixing chamber to the still by an osmotic pressure difference. The $^3$He leaving the mixing chamber is used to cool the returning flow of concentrated $^3$He through the heat exchangers.

The mixture pumps are used to remove the $^3$He from the still, and compress it to a pressure of a few hundred mBar. The gas then passes through a liquid nitrogen cooled cold trap and a liquid $^4$He cooled cold trap to remove impurities before returning to the cryostat, where it is pre-cooled in the main helium bath and condensed in the 1K pot. The condenser itself is simply a narrow piece of copper tubing with an additional impedance provided by blocking the tube with a short length of wire. This maintains a high enough pressure in the 1 K pot region for the gas to condense.

The sample to be studied is mounted onto a microscope objective and submersed directly into the mixing chamber, ensuring good thermal contact with the dilute...
For the measurements presented in Chapters 8 and 9, the temperature of the sample was measured with a RuO$_2$ resistance thermometer, which was calibrated at the factory using nuclear orientation thermometry [54,55] with a sample of $^{60}$Co mounted directly on axis with the windows. Measurements were performed down to temperatures of 30 mK.

6.3 Single-molecule microscopy

These days, single-molecule microscopy can mean several things, because single-molecule studies have been performed using several different types of microscopy. All of the work described in this thesis has been done with conventional wide-field microscopy, as opposed to near-field scanning optical microscopy [56] or scanning confocal optical microscopy [57]. All of these forms of microscopy have advantages and disadvantages when compared to the other two forms. For the experiments described here where statistical distributions are measured, the wide-field version is the microscope of choice, since an entire image is acquired in parallel with a wide-field microscope, as opposed to having a small excitation volume which is then scanned. To compare an experiment with theoretical models, it is useful to know the statistical distribution of molecular parameters. SM microscopy has been demonstrated as a powerful tool for analyzing statistical distributions by providing observation of a large number of molecules in parallel. From here on, the term "microscopy" is meant to refer to wide-field microscopy.

The single-molecule microscopy apparatus that was used to collect most of the data in this thesis is drawn schematically in Figure 6.4. Fundamentally, the system is simply a high-tech microscope that is able to image the fluorescence light emitted from single molecules at very low temperatures. The different parts of the apparatus that enable this microscope to function are described below.
In order to describe the function of the SM microscopy apparatus used for the measurements, the system can be conveniently broken down into two main parts, namely, the optical system and the computer-control system. These two elements are discussed separately in the following sections, starting with the optics.

### 6.3.1 Optics

The first instrument in the string of optics shown in Figure 6.4 is the light source, which consisted of a single-mode dye laser (Coherent 899) pumped with an argon ion laser (Coherent I-200). The argon laser was used in multi-line mode with a output power of \(~5 W\) to pump the ring dye laser, which was filled with Rhodamine 6G dye.

The dye laser contains a birefringent filter, a thick etalon, and a thin etalon which allow for single-mode laser oscillation. Bidirectional lasing is suppressed using a Faraday rotator. To suppress frequency fluctuations, fringe-locking is performed.
by monitoring the transmitted intensity through a low finesse temperature-stabilized cavity. The error signal is applied to a piezo transducer onto which one of the laser cavity mirrors is mounted. In this way a frequency stability in the order of 1 MHz (rms) on the time scale of about one second can be obtained. The laser frequency is tuned with a scanning Brewster plate which has a maximum scan range of 30 GHz. A wave meter reads the absolute laser frequency with a precision of 200 MHz and a reproducibility of 50 MHz. Single-mode operation was verified by monitoring the transmission of the Fabry-Perot Etalon (Coherent 240) which had a free spectral range of 1.5 GHz. Fluctuations in the laser output power were reduced using the power stabilizer (EOD LA310).

The quarter-wave plate was used to produce circularly polarized laser light for exciting the molecules, which lessened the preference for measuring molecules with dipole moments parallel to any given direction, and hence homogenized the excitation polarization to some extent. The circularly-polarized light was then focused with a 25 cm focal length lens through the cryostat windows to a spot approximately 100 μm in diameter on the sample. The sample was mounted on a microscope objective that produced an image of the sample outside of the cryostat. The microscope objective was a solid mirror objective formed from two homocentric suprasil components [58]. The optical properties of this objective are nice for working in superfluid helium, because the full light path in the objective is in the suprasil. The performance and characteristics of the spherical mirror objective have been reviewed in the literature [58].

To block the background from scattered laser light, the fluorescence light from the sample passed through holographic notch (Kaiser HSPF-572.0-1.5) and cut-off filters (Schott 610) before it was imaged onto an image-intensified CCD camera (Hamamatsu C2400-80). (For the polyvinylbutyral experiments, Schott 590 colored glass filters worked better than Schott 610 filters and were used instead.)

The laser frequency was scanned with an external ramp voltage that was produced by the computer control system and was synchronized with the acquisition of images. The computer-control system is described next.
6.3.2 Computer-control system

Two different computer-control systems were used for the acquisition of microscopy data, which were developed for two different laboratories. Both systems were developed by Markus Traber. The first system was based on an Sun/Sparc-5 workstation, and the video images were stored on an external video disk. This system was described in Hermann Bach’s PhD thesis [59], and will not be further described here. This system was used to acquire the data presented in Chapter 7. The second system was used to collect the data presented in Chapters 8 and 9. The main features of this system are described here. The development of the system required several months of computer programming and testing, and a great deal of technical expertise. For this reason, the following description is only a general overview.

The necessary hardware components for running the system are listed in Table 6.1, and the configuration of the instruments and the paths of communication are illustrated in Figure 6.5.

The digital to analog converter (DAC) is used to produce the laser scan over the GPIB bus. The laser frequency is controlled with analog voltages between the values of -5 and +5 Volts by applying an external ramp voltage to the laser. Before an experiment, a voltage ramp with ≤ 2000 points is stored in the buffer of the DAC. A trigger pulse sent from the MaxPCI causes the next programmed ramp voltage value to activate and hence the frequency is scanned in sync with the acquisition of images. The shutter is controlled with TTL I/O pulses so that it is open only during the data acquisition time.

Table 6.1: Hardware.

<table>
<thead>
<tr>
<th>Bus System</th>
<th>Type</th>
<th>Function</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCI</td>
<td>MaxPCI</td>
<td>Image Processing</td>
<td>Datacube Inc.</td>
</tr>
<tr>
<td>GPIB</td>
<td>DAC488</td>
<td>Digital to Analog Converter, TTL I/O</td>
<td>IOtech</td>
</tr>
<tr>
<td>Analog</td>
<td>C2400-80</td>
<td>Camera</td>
<td>Hamamatsu</td>
</tr>
<tr>
<td>TTL</td>
<td>Mechanical</td>
<td>Shutter</td>
<td>Home Built</td>
</tr>
</tbody>
</table>
The tasks of acquiring, processing, and storing video frames were performed using a MaxPCI image processor from Datacube. The MaxPCI receives camera images at video rate (25 Hz) and transforms each image with a programmable analog to digital converter into a digital data stream consisting of 512 x 512 pixels with 8 Bit depth. These digital images are then processed according to the mode of operation that has been selected by the user. There are four operating modes of the MaxPCI:

- **Live Mode**: Live display of the camera images on the monitor.
- **Record Mode**: Like live mode, but with the storage of the images on the hard disks.
- **Play Mode**: Video sequences are recalled from the hard disks and displayed on the monitor.
- **Average Mode**: Camera images are added, displayed on the monitor, and saved on the hard disks.
6.4. Time-Resolved Studies

The heart of the computer-control system is the application program IPSTOOL (short for "Image Processing for Spectroscopy Tool"), which runs under Windows NT 4.0 and with PC/Intel Hardware. The program, written in C++, makes function calls to three different libraries. For controlling the MaxPCI, IPSTOOL uses calls from the software library ImageFlow, a library specifically designed for use with the MaxPCI. For the control of external instruments over the GPIB Bus, the GPIB library from National Instruments was used. The graphical user interface was developed with the class library MFC from Microsoft. MFC simplifies the creation of the user interface since it is programmed completely in C++.

The minimum acquisition time per image was ~170ms, which is much longer than the 40 ms that one would have if the images were stored at video rate. Each of the images consisted of ~260 kBytes, so most of the time delay arises from the time it takes to store the images on the hard disk. It was possible to reduce the amount of dead time by averaging images. Although it took ~170ms to store a single image, it took only ~240ms to store the average of 4 images. To scan a single-molecule fluorescence-excitation spectrum with 20 points per linewidth required about 5 seconds with this apparatus.

After an experiment, the images were transferred to a Sparc 5 workstation and analyzed using the software PV-Wave. Since the data files were often very large (~1 GByte), analyzing the data was the rate-limiting step for data acquisition. During the course of the work described in this thesis, approximately 600 GBytes of data were collected.

6.4 Time-Resolved Studies

With single-molecule microscopy, one has the ability to measure the spectra of many molecules in parallel with the added drawback that the time resolution is rather poor.

To have better time resolution, one can work with a single-channel detector like a photo-multiplier tube (PMT). Time-resolved measurements done with a PMT are complementary to the distributions of parameters that are possible to measure with
a microscopy apparatus. As mentioned above, the camera system could scan single-molecule spectra on a time scale of about 5 seconds. SM lines could be scanned with the same frequency resolution using the PMT-based apparatus described below on a time scale as fast as 60 ms. The SNR of SM spectra scanned this quickly was quite poor, but the spectra could be scanned repeatedly and then the ITFC method described in Section 5.5 could be applied to analyze the data. Thus an acceptable SNR could be achieved while preserving the time resolution. Doing experiments on a faster time-scale involved developing the apparatus and the software for controlling the data acquisition. Both of these tasks are described below.

6.4.1 Fast scan apparatus

The apparatus used to perform fast scans is shown in Figure 6.6. The part of
the system leading up to the dilution refrigerator was identical to the microscopy apparatus described previously, except that the voltage ramp for scanning the laser frequency was produced by the SR400 photon counter rather than the datacube that was used with the camera system. Downstream from the dilution refrigerator, an adjustable pinhole was situated in an image plane of the sample. This provided spatial selectivity by restricting the sample volume observable with the PMT. The pinhole was actually mounted on an $xyz$ stage, so it could be easily moved for aligning the optics. The light passing through the pinhole could be imaged onto the camera for adjustment purposes by inserting a flipable mirror into the light path. After the optics were aligned, the flipable mirror was removed and the light from the pinhole was imaged onto the PMT. When the pinhole was fully closed, fluorescence emitted from a spot with a diameter of $\sim 5\mu$m passed through to the detectors.

The signal from the PMT passed through a preamplifier and was sent to photon counter (Stanford Research SR400). The SR400 was computer controlled with GPIB calls from the PC. An external port of the SR400 was also used to produce the laser ramp for controlling the laser scan.

6.4.2 Computer control

The computer control for the SR400 was developed using the software LabWindows/CVI from National Instruments. This software simplifies the development of programs for controlling the instruments while at the same time it is very transparent, since the software is developed in the C program language. The main advantage of LabWindows/CVI is that one can download instrument drivers from National Instruments which consist of GPIB function calls for controlling the instruments. There are also libraries of function calls for displaying, analyzing, and storing data that simplify the development of the C programs.

LabWindows/CVI was used to develop a program to control the SR400 over a GPIB bus. The user would enter the discriminator level, the number of frequency steps, the step period, and the number of scan repetitions on a graphical user interface and then start the data acquisition. The computer program would then
configure the SR400 with GPIB calls and start the data acquisition. The external ports of the SR400 were used to control a shutter and to produce the voltage ramp for scanning the laser frequency.

The data collected during a scan was stored in the internal buffer of the SR400. Between scans, the data was sent to the PC and plotted on the screen. The highest time resolution was achieved when the SR400 communicated with the computer as little as possible, which is why the buffer of the SR400 was used to store the scan data. At the end of the final scan, the data could then be saved to a file.

The time resolution of the system was limited by the speed with which the SR400 could collect data. Between each acquisition period, there are an unavoidable 2 ms of dead time, which is intrinsic in the SR400 and limited the time scale of the measurements. If one acquires scans with a 2 ms integration time for each count period, the counter has 50% dead time since the SR400 needs 2 ms to re-initialize the counter between periods. Because of this 2 ms dead time, the improvement in time resolution over the camera system described previously was limited to two orders of magnitude.

With this apparatus, the linewidths of single terylene molecules in polyethylene were measured as a function of measurement time, and the results were compared with the distributions of linewidths measured with the camera system. These results are presented in Chapter 9.
In this chapter, discrepancies between measured single-molecule linewidth distributions and distributions simulated with the standard tunneling model are studied for terylene and di-tert-butylterrylene dopant molecules in polyvinylbutyral. The experimental data has been carefully checked for systematic errors. It is shown that the results are in disagreement with the standard model, but that the incorporation of a distribution of molecule-polymer coupling strengths would remove this disagreement. Additionally, the experimental observation of a surprising correlation between the single-molecule line areas and the matrix–molecule interaction strength is presented, and a hypothesis is put forward for its physical origin.
7. Polyvinylbutyral
And over the grass at the roadside a land turtle crawled, turning aside for nothing, dragging his high-domed shell over the grass. His hard legs and yellow-nailed feet threshed slowly through the grass, not really walking, but boosting and dragging his shell along. The barley beards slid off his shell, and the clover burrs fell on him and rolled to the ground. His horny beak was partly open, and his fierce, humorous eyes, under brows like fingernails, stared straight ahead.

John Steinbeck, “The Grapes of Wrath”

7.1 Background

In this chapter, simulated and measured linewidth distributions are compared for terrylene and di-tertbutylterrylene (DTBT) molecules in polyvinylbutyral (PVB), thus testing the adequacy of the TLS model for simulating linewidth distributions. The measurements were performed in a $^4$He bath cryostat at 1.8 K.

In many previous papers on TLS dephasing of optical transitions, in order to improve agreement between the TLS model and experimental results, attention has been focused on the effect of adjusting TLS parameter distributions (see for example [1, 49, 60]), and less emphasis has been placed directly on the TLS–chromophore interaction mechanism. Here the emphasis is placed on the interaction mechanism.

The agreement between measured linewidth distributions and theoretical distributions predicted with the standard tunneling model has so far been marginal [2], with a few recurring discrepancies: experimental distributions are generally broader than those predicted by theory, and there are usually more narrow-linewidth molecules measured than predicted.

7.2 Experimental details and data analysis

Either terrylene or DTBT molecules were co-dissolved with PVB in dichloromethane. The solutions were filtered with solvent resistant filters (Gelman Sciences, 0.45 μm pore size, Acrodisc PTFE filters) and either spin-coated
or cast onto microscope cover slips. The samples were then baked under vacuum for several hours at ~80°C, which is slightly above the glass transition temperature for PVB. The samples had final chromophore concentrations of ~10^{-6} M and thicknesses of ~1 μm. The thicknesses were determined using an atomic force microscope to measure the depth of a scratch made through the sample. SMs could not be observed in samples thinner than ~200 nm, presumably because of surface broadening effects [61]. All of the measurements were performed with a sample temperature of 1.8 K.

The data were collected using the single-molecule microscopy apparatus that was explained in Chapter 6. The laser wavelength was in the range from 571 to 575 nm, which is on the red edge of the inhomogeneous band for both terrylene and DTBT in PVB, whose inhomogeneous absorption bands were observed to be centered 565 nm. All molecules (except for the intensity-ramped terrylene measurements presented in Section 7.3) were measured with intensities below 50 mW/cm². 100 mW/cm² is the saturation intensity for terrylene in PE [62]. The saturation intensities for terrylene and DTBT in PVB should be much higher since the typical linewidths are about four times broader in PVB than in PE [63]. Digitized fluorescence images of the sample were collected at a series of excitation frequencies, resulting in three-dimensional data cubes having one frequency and two position coordinates [64], from which fluorescence-excitation spectra for single molecules (SMs) were extracted. Since the data was usually quite noisy, the SM search procedure is a critical step in the data analysis so it is described in detail below.

Each data cube contained from six to eight 500-image scans of the same 10 GHz frequency range so that the reproducibility of SM features could be assessed. To search the huge data files (~1 GByte) for SMs, the six to eight scans were first summed up into a single scan. Then a 1 GHz running average in the frequency dimension was performed. This procedure roughly equalizes peak intensity values to the integrated line intensities, which in principle should be the same for broad- and narrow-linewidth molecules. Searching for peaks in the integrated intensity is therefore less biased than searching for absolute maxima, which favors narrow linewidth molecules since they are on average brighter. This point is further discussed in Section 7.3. A compressed sample image was then formed by taking
the difference between the maximum and minimum intensities for each \( x, y \) point in the averaged data. Peaks were then found in the compressed image.

Frequency trajectories for each of the frequency scans were then extracted from the data at the \( x, y \) coordinates of the peaks in the compressed image. The features having amplitudes of at least double the standard deviation of the noise that were also observed repeatedly were counted as single molecules. For a simple characterization, the SM line shapes were fit with Lorentzians, which gave good estimates for the full width at half maximum even though the individual line shapes were not Lorentzians. The whole data handling and analysis procedure took several hours on a SPARC 5 workstation for each 10 GHz scan.

### 7.3 Linewidth distributions

Shown in Figure 7.1 are six measured (a-f) and six simulated (g-l) fluorescence-excitation spectra of DTBT molecules in PVB. The Lorentzian fits are also shown. The measured spectra are averages of 8 consecutive 20 second scans, and have been selected at random from the list of DTBT molecules. Simulations are performed following the procedure described in Chapter 5, with the exception that noise was also added to the spectra. To reduce the time of the calculations, simplifications can also be implemented. To a very high degree of accuracy, linewidth distributions calculated at different values of \( \alpha_c \) were identical to within a scaling factor. This follows from the simplified expression for the dipole autocorrelation function presented by Pfluegl et al. [65]. The noise level on the SM spectra was characterized for all 919 of the molecules by taking the difference between the raw spectra and the Lorentzian fits and dividing the noise into two components. The peak contribution scaled by the signal intensity has an average value of 37% of the peak height at the maximum, and the background noise level is roughly constant for all molecules and equals 20% of the average peak height. The noise on the simulated spectra has two components which were chosen to match the measured noise levels.

Adding noise broadens the simulated linewidth distribution, which is illustrated in Figure 7.2. Three simulated linewidth distributions having different noise
Figure 7.1: Measured (a-f) and simulated (g-l) fluorescence-excitation spectra of single DTBT molecules in PVB, shown with Lorentzian fits. The horizontal axes are the frequency in GHz and the vertical axes are intensity in arbitrary units. Random noise was added to the simulated spectra (see text).
levels are shown. The narrowest distribution has no added noise. The other two distributions were simulated with peak (background) noise contributions of 37% (20%) and 55% (30%). The distributions with added noise are 10% and 15% broader than the noiseless histogram for the peak noise levels of 37% and 55%, respectively. (The peak (background) noise level of 37% (20%) matches the level on the experimental data.)

Figure 7.2: Examples of simulated linewidth distributions. The narrowest distribution (shaded) was simulated without adding noise to the spectra. The thin-lined distribution had an added peak noise level of 37% of the peak height (to match the noise level on the measured spectra), and was about 10% broader than the noiseless distribution. The broadest distribution had a noise level of 55% of the peak height and was 15% broader and more symmetric than the noiseless distribution.

Figure 7.3a is a histogram of measured linewidths for 919 DTBT molecules in PVB. The statistics are improved over the previously measured histogram of terylene in PVB [66], with more than four times as many molecules measured. A simulated fit to the data is shown, produced by finding the best fit using the TLS-chromophore coupling strength (\(\alpha_c\) in Equation 5.3) as an adjustable fit parameter in the simulations, which gives a value of \(\alpha_c = 121\,\text{GHz nm}^3\). A fit to a coupling constant distribution is also shown, which is discussed in Section 7.4. The distributions
containing 1600 molecules were normalized to the number of measured molecules for the fitting procedure.

The agreement between the two distributions may not look so bad, but in fact it is highly unlikely that the two distributions were sampled from the same parent distribution considering the number of molecules measured in the experiment. To obtain a quantitative measure for the dissimilarity between the two distributions, one can analyze the disagreement statistically by calculating $\chi^2$ for a goodness-of-fit estimation [67], where

$$\chi^2 = \frac{1}{\nu} \sum_{i=1}^{N} \left( \frac{1}{\sigma^2_i} (y_i - y(x_i))^2 \right). \quad (7.1)$$

The $y_i$ are the bin heights for the measurements and the $y(x_i)$ are the heights of the simulated bins. $\nu$ is the number of degrees of freedom. For comparing the distributions in Figure 7.3, $\nu = N - 2$ where $N$ is the number of bins, owing to the fact that there is one adjustable fit parameter ($\alpha_e$) and a constraint for the normalization. Assuming that the molecular counting procedure obeys Poissonian statistics, the uncertainty for each point is the square root of the number of molecules in the bin. $\sigma_i$ in Equation 7.1 includes the uncertainties of both distributions added in quadrature. This gives $\chi^2 \simeq 3.6$ ($\nu = 22$). According to the probability distribution for $\chi^2$, the probability that the two distributions were sampled from the same parent distribution (the confidence interval) is approximately $10^{-7}$ [67]. The confidence intervals are very sensitive to the noise level. When noise was not added to the simulated spectra, the probability was only $10^{-12}$. The best agreement was found when the noise level was increased to 55% on the peak and 30% on the background (50% more noise than on the experimental spectra), where the probability increased to 0.2%. As the noise was further increased, the confidence interval decreased because the simulated distributions became more symmetric and could no longer reproduce the sharp experimental linewidth cut-off at the natural linewidth.

Since the theory and experiment were in such poor agreement, the probe molecule was switched to terrylene, for which there was already a published linewidth distribution [66], and a more thorough investigation into possible systematic errors was performed, beginning by considering the emission rates. Well below saturation,
7.3. Linewidth distributions

Figure 7.3: a.) DTBT data with a fit to a single coupling constant. Also shown is a fit to an $\alpha_c$ distribution. The confidence intervals for the fits to a single $\alpha_c$ and a smooth $\alpha_c$ distribution are $10^{-7}$ and 50%, respectively. b.) The $\alpha_c$ distribution found from fitting the data in a.) The hollow vertical bar shows the value for the best fit of a single $\alpha_c$ (121 GHz nm$^3$). The two filled vertical bars show a bi-modal distribution (92 GHz nm$^3$ and 168 GHz nm$^3$) that fits the experimental distribution with a confidence interval of $\sim$30%.
since the saturation intensity for a single molecule is proportional to the linewidth \( \Gamma \) [11], the emission rate is

\[
R(I) = R_\infty \frac{I}{I_s} \propto R_\infty \frac{I}{\Gamma}.
\]

(7.2)

Since the rate is inversely proportional to \( \Gamma \), the single-molecule line amplitudes and hence the signal-to-noise ratios should be smaller for broad-linewidth molecules.

This could create a bias towards measuring narrow lines if the line amplitudes for the broad molecules are insufficient to distinguish them from the noise. To reduce this possible bias, the broader linewidth molecules can be measured at higher intensity since the photo count rate goes up linearly with intensity while the shot noise is proportional to the square root of the rate. Since their saturation intensity is larger, there should be no saturation broadening as long as \( I/\Gamma \) is below \( I_{\text{sat}}/\Gamma_0 \), where \( \Gamma_0 \) is the lifetime limited linewidth and \( I_{\text{sat}} \) is the saturation intensity for molecules with lifetime limited linewidths.

The total integrated emission from a SM should be independent of the linewidth. Below saturation, the total number of photons emitted by a single molecule during a scan is proportional to the area under the SM line profile. Ignoring the phonon wing, the area is

\[
A_{\text{spl}} = R\Gamma \propto R_\infty I \propto \Omega_R^2,
\]

which follows from Equation 7.2. \( \Omega_R \) is the Rabi frequency, which specifies the strength of the coupling between the SM and the electric field. This relation is further discussed at length in Sections 7.5 and 7.6.

To test if the measured linewidth distributions are intensity dependent, the distribution of linewidths was measured at three linearly increasing intensities: 50 mW/cm\(^2\), 100 mW/cm\(^2\), and 150 mW/cm\(^2\). The molecule search was based on the line area discrimination procedure described in Section 7.2. The confidence intervals for the agreement between the three resulting linewidth distributions are: 95%, 75% and 75% for the low and medium intensity, the medium and high intensity, and the low and high intensity measurements, respectively. Since these three
distributions are statistically indistinguishable, they can be combined into the single distribution with 486 molecules that is shown in Figure 7.4. The confidence interval for the agreement between the distribution and a fit to a single $\alpha_c (\alpha_c = 154 \text{ GHz nm}^3)$ is $\sim 0.2\%$. Interestingly, there is less line broadening for DTBT than there is for normal terrylene.

We have statistically compared the combined distribution with the distribution measured by Kozankiewicz et al. [66], and we get $\chi^2 \simeq 3.9 (\nu = 10)$, which has a confidence interval of approximately $0.01\%$. The peak in Kozankiewicz' distribution is shifted to larger linewidths. The distribution could depend on the sample preparation technique. Kozankiewicz et al. used acetone as a solvent for sample preparation, and they did not bake the samples to remove the excess solvent, which may cause additional line broadening.

### 7.4 Fitting the data to a coupling constant distribution

Owing to the fact that the TLS–SM coupling parameter $\alpha_c$ includes factors for the induced SM dipole moment $\Delta \mu_{SM}$ and the local field factor $L$, both of which are non-renormalizable inhomogeneous parameters, it may be necessary to include a distribution for $\alpha_c$ in the simulations (see Section 5.2 for a discussion on inhomogeneous parameters). This is a main topic of discussion in Section 7.6. Rather than fitting the experimental distributions to single $\alpha_c$, as was done in Section 7.3, the distributions have been fit using a model modified to include an $\alpha_c$ distribution. For the fit, a series of $M$ distributions was calculated for $M$ different TLS–SM coupling constants $\alpha_c$. Distributions calculated with larger $\alpha_c$ are broader and the peak positions are shifted to larger linewidths. A linear combination of these distributions was fit to the experimental distribution.

The $M$ calculated distributions were broken into $N$ bins and expressed vectorially as $\tilde{D}_m = [D_{m1}, D_{m2}, \ldots, D_{mN}]$, the index $m$ running from 1 to $M$. The experimental distribution was broken into the same bins and expressed as
Figure 7.4: a.) Terpylene data with a fit to a single coupling constant \( \alpha_c \). Also shown is a fit to an \( \alpha_c \) distribution. The confidence intervals for the fits to a single \( \alpha_c \) and a smooth \( \alpha_c \) distribution are 0.2\% and 65\%, respectively. b.) The \( \alpha_c \) distribution found from fitting the data in a.) The hollow vertical bar shows the value for the best fit of a single \( \alpha_c \) (154 GHz nm\(^3\)). The two filled vertical bars show a bi-modal distribution (90 GHz nm\(^3\) and 177 GHz nm\(^3\)) that fits the experimental distribution with a confidence interval of \( \sim 30\% \).
7.4. Fitting the data to a coupling constant distribution

\[ \tilde{Y} = [Y_1, Y_2, \ldots, Y_N]. \]

A vector of probabilities for the \( M \) coupling constants \( \tilde{P} = [P_1, P_2, \ldots, P_M] \) was found such that the function

\[ \chi^2_{\nu} = \frac{1}{\nu} \sum_{n=1}^{N} \left( \frac{Y_n - \sum_{m=1}^{M} D_{mn} P_m}{\sigma_n^2} \right)^2 \]

was minimized. \( \chi^2_{\nu} \) is the same function that discussed previously when comparing linewidth distributions. There were two restrictions applied to the probability vector \( \tilde{P} \): all of the entries had to be nonnegative and the vector had to be smooth. To fulfill the non-negativity requirement, the minimum was found within the volume of the vector space with nonnegative probabilities. To fulfill the smoothness requirement, the \( \alpha_c \) distribution was smoothed as much as possible while still being within the range of the statistical uncertainty of the experimental distribution. It was assumed that the distribution is perfectly smooth when each point in the curve is the average of its two neighboring points. (A perfectly smooth distribution would not be realistic because only a straight line is perfectly smooth by the above definition for smoothness.)

The histograms simulated with \( \alpha_c \) distributions are shown with the experimental data in Figures 7.3a and 7.4a. The \( \alpha_c \) distributions themselves are shown in Figures 7.3b and 7.4b. For the calculation of \( \chi^2_{\nu} \), again one needs to know the number of degrees of freedom. In this case \( \nu \) is not as well defined, since there is not a clear number of parameters in the fitting procedure. However, using an \( \alpha_c \) distribution is like generating an additional parameter for the width of the distribution, and perhaps another for the asymmetry. We therefore have 3 parameters — the mean, the width, and the asymmetry. The normalization is an additional constraint. One can therefore assume that \( \nu = N - 4 \). With this, the \( \alpha_c \) distribution fits have confidence intervals of 55% \( (\chi^2_{\nu} = 0.92, \nu = 21) \) for DTBT and 65% for terrylene \( (\chi^2_{\nu} = 0.85, \nu = 21) \).

Both linewidth distributions can also be reasonably fit with a simple sum of the two coupling constants that are shown as filled vertical bars in the \( \alpha_c \) distributions with confidence intervals of \( \sim 30\% \) in both cases. The best fits for a single coupling constant \( \alpha_c \) are also shown as hollow vertical bars. The \( \alpha_c \) distribution for the best
fit to the data always has a complex structure, but there is no reason to believe that
the structure is real given the statistical uncertainty of the data. The smoothness
requirement eliminates this structure without significantly altering the mean and
width of the distribution.

The linewidth distribution depends on the product of the coupling constant
and the TLS density, thus the distributions in Figures 7.3b and 7.4b could also be
caused by a fluctuation of the TLS number interacting with the probe molecules,
which follows directly from Equation 5.5. However, these fluctuations would have
to be much larger than Poissonian fluctuations, which are already included in the
theory containing a single coupling constant since the TLSs are randomly distributed
in space.

Actually, a distribution of coupling strengths should not come as a surprise,
knowing that the chromophore transition frequency is inhomogeneously broadened.
The inhomogeneous broadening indicates that there is a distribution of static cou-
pling constants. The results presented here seem to indicate that there is a distri-
bution of dynamic coupling as well.

### 7.5 Linewidth–line area correlation

The relationship in Equation 7.3 predicting that the line areas should be independent
of the linewidths was checked by making a scatter plot of the linewidths vs the areas
under the SM curves. Figure 7.5 is such a plot for the DTBT molecules in PVB
from the histogram in Figure 7.3. The line area $A_{zpi}$ was normalized to the average
area for each data set independently, since the detected emission varies from day
to day due to power changes, detection efficiency fluctuations, etc. There is a clear
correlation between the linewidths and the line areas. This correlation is also present
in most other systems checked, including terrylene in PE, n-alkanes, and PVB.

The correlation coefficient for a simple linear regression to the data is 0.67. The
cone shape is caused by two factors: a distribution of the relative orientation of the
SMs with respect to the laser polarization causing an area distribution for a given
7.5. Linewidth–line area correlation

Figure 7.5: The linewidth vs the normalized line area for the DTBT data from Figure 7.3.

linewidth, and spectral diffusion, which causes a linewidth distribution for a given area. For example, assuming no spectral diffusion and perfect intrinsic correlation \( A_{zpl} = k \Gamma \sin^2 \theta \), where \( k \) is the slope of the correlation. For a random distribution of orientations, the correlation coefficient would be 0.75.

A linear regression does not appear to fit the data well though, because too much weight is given to the points for large \( \Gamma \) where the scatter is large. To do a weighted fit, the average values for the points within the \( A_{zpl} / \langle A_{zpl} \rangle \) ranges given by the shaded areas in Figure 7.5 were calculated, which contain an approximately equal number of data points. The solid line is a weighted linear fit to the averaged points, found using the uncertainties in the linewidths as weighting factors. The slope of the fit is 430 MHz and the \( y \) intercept is 70 MHz. The magnitudes of these values and their significance are discussed in the next section. The slope is observed to decrease due to saturation as the power is further increased, but no saturation is seen up to an intensity of 150 mW/cm².
7.6 The role of a distribution of transition dipole moments

The correlation shown in Figure 7.5 is an experimental fact, the cause of which is most likely related to the disagreement between measured linewidth distributions and simulations in which a single coupling constant is used.

One can dismiss photo-induced spectral diffusion as the cause of the correlation in Figure 7.5. Note that the areas and not the emission rates are represented on the x-axis. The correlation therefore has the effect of somewhat evening out the emission rates for broad and narrow lines, but on average the narrow lines still have higher amplitudes (molecules with equal amplitudes lie on a straight line through the origin.) Therefore the power dissipated to the matrix upon excitation is on average greater for the narrow lines, which undergo less spectral diffusion.

The correlation is probably also unrelated to the phonon wing. In Equation 7.3, the contribution from the phonon wing to the line area was neglected. The relative area of the zero phonon line to the phonon wing is characterized by the Debye–Waller factor $\alpha_{DW}$, which depends on the electron–phonon coupling and the temperature. The phonon wing is usually $10^3 - 10^4$ times broader than the zero phonon line [68] and cannot be observed in SM spectra. At liquid $^4$He temperatures, $\alpha_{DW}$ is $\sim 0.5$ or higher for systems that are good for SMS. If $\alpha_{DW}$ varies and increases with the linewidth, this could conceivably cause the correlation seen in Figure 7.5, but there is no clear reason why $\alpha_{DW}$ should be larger for broad lines. If anything, it should be larger for the narrow lines, since it increases in more-ordered systems where there is less spectral diffusion [13].

The most likely cause for the correlation is the effective transition dipole moment, or equivalently, the local field factor, which was a topic of discussion in Chapter 3. As illustrated in Figure 3.1, the local environment for each probe molecule is different, and hence, according to Equation 3.5, the transition dipole moments for each probe molecule are different. This is equivalent to the existence of a local field factor distribution.
Assuming that the correlation is caused by a local-field factor distribution, the distribution can be roughly estimated from the data by taking the square root of the line areas and normalizing the mean value to $\mathcal{L}_c$. Doing this, one gets a relative width of the $\mathcal{L}$-factor distribution of $\Delta \mathcal{L}_{FWHM}/\langle \mathcal{L} \rangle \approx 50\%$, which is only an upper bound since the relative angular orientation between the laser polarization and $\mu_{eff}$ also causes a distribution of line areas, but one can then estimate the lower bound for the average distance between the SM and the polarizable object perturbing it’s transition dipole moment.

It has been found from *ab initio* calculations that a PVB monomer unit has a dc polarizability of $\sim 15 \, \text{Å}^3$.\(^1\) When $\mu_{vac}$ is collinear with $\hat{n}$, the effective dipole is reduced by the factor $2\alpha \mu_{vac}/R^3$. When $\mu_{vac}$ is perpendicular to $\hat{n}$, $\mu_{eff}$ is increased by $\alpha \mu_{vac}/R^3$. Therefore the effective local field factor should be $\mathcal{L}_c \left( 1 - 2\alpha/R^3 \right)$ when $\mathcal{B}$ is at the poles of $\mu_{vac}$ and $\mathcal{L}_c \left( 1 + \alpha/R^3 \right)$ when $\mathcal{B}$ is at the equator of $\mu_{vac}$. $\mathcal{L}_c$ takes into account the contribution from the continuum-like part of the sample far from the chromophore and can be found from Equation 3.2. With these limits, one must assume $R \sim 5 \, \text{Å}$ if $\Delta \mathcal{L}_{FWHM}/\langle \mathcal{L} \rangle = 0.5$. The length and width of terrylene molecules are roughly 13.5 and 6.7 Å, respectively [69]. The thickness estimated from the inter-molecule spacing for crystallized perylene molecules is approximately 3.5 Å [70]. The necessary distances are therefore about the size of the molecular dimensions. A larger $\mathcal{L}$-factor strengthens both the SM–laser field coupling and the SM–TLS coupling, causing both a higher emission rate and stronger diffusional broadening. This can explain the correlation seen in Figure 7.5.

Now the slope of the correlation curve in Figure 7.5 can be analyzed. The abscissa represents the normalized area of the SM lines, which according to Equations 7.3 and 3.4 is equal to the normalized square of $\mathcal{L}$, $X = \mathcal{L}^2/\langle \mathcal{L}^2 \rangle$. If one assumes that $\Gamma = f(\zeta)\mathcal{L} + \Gamma_0$, where $f(\zeta)$ is independent of $\mathcal{L}$ but depends on a large number of other variables like the TLS parameters, then the linewidth should roughly go as the square root of the normalized area, and this is not what is observed. The linewidth could be proportional to $\mathcal{L}^2$ if $\Delta \mu_{SM}$ is also proportional to $\mathcal{L}$. In this

\(^1\)The isotropic *ab initio* (CPHF RHF/6-31G*) polarizability of 4,6-Dimethyl-2-propyl-1,3-dioxane is 14.4 Å\(^3\). The Eigenvector with the largest Eigenvalue (16.4 Å\(^3\)) is roughly parallel to a line through the C(1)-C(4) atoms of the dioxane moiety. Calculations performed by Ernst-Udo Wallenborn.
case, $\Gamma = f(\zeta)C^2 + \Gamma_0$, and for the averaged points in Figure 7.5

$$Y_i = \langle \Gamma \rangle_b X_i + \Gamma_0,$$

where $\langle \Gamma \rangle_b$ is the average broadening contribution to the linewidth. This predicts a linear correlation with a slope of $\langle \Gamma \rangle_b = 499$ MHz for the molecules in Figure 7.5, in fair agreement with the experiment, where the slope is 430 MHz and the intercept is 70 MHz.

The microscopic origin of $\Delta \mu_{SM}$ is the local symmetry breaking around the probe molecule. $\Delta \mu_{SM}$ is proportional to the strength of the internal fields arising from the charge distribution in the matrix [71]. A possible origin of a linear correlation between $C$ and $\Delta \mu_{SM}$ could be that these fields are also enhanced by the local-field factor.

In Chapter 3, the concept of a distribution of local-field factors was used to explain a discrepancy between measured and calculated saturation intensities for pentacene in p-terphenyl as well as the distribution of quadratic Stark shift coefficients in the same system. For that system, the projection of local field tensor onto the polarization of the laser light was estimated to be 2.1, with a relative width of the distribution $\Delta C_{\text{FWHM}}/\langle C \rangle = 13\%$. Since p-terphenyl is a crystalline host, the molecular orientations are not random and hence this value is not averaged over orientations.

### 7.7 Concluding remarks on polyvinylbutyral

Distributions of linewidths for terrylene and di-tertbutylterrylene molecules in polyvinylbutyral have been carefully measured with special attention paid to checking possible systematic errors. DTBT molecules undergo less spectral diffusion than do normal terrylene molecules, which may be a result of shielding from the matrix by the bulky tert-butyl groups, reducing either the induced dipole moment or the local field factor. Experimental results and simulations compared using the standard model were in disagreement with each other. The agreement could be greatly im-
proved by adding noise to the simulated spectra, but the best agreement was found when the experimental distributions were fit to a modified version of the standard model that allowed for a distribution of TLS–SM coupling constants.

A correlation between the SM areas and linewidths has also been observed, which is an interesting result that has not been recognized with ensemble measurements like hole-burning and photon echoes. With photon echo decays, for example, it may be difficult to observe the non-exponentiality that would result from a distribution of lifetimes, particularly if the measurements do not span a large dynamic range [72].

This correlation has also been observed for the two systems presented in the following chapters, namely, naphthalene and polyethylene, and also for n-alkanes, which is not discussed here. This leads one to believe that the correlation is a universal property arising from disorder. One possible explanation for the correlation is that there is a distribution of effective transition dipole moments (or equivalently local field factors) caused by environmental inhomogeneities — a hypothesis which is also consistent with the shape of the linewidth distributions.

This hypothesis can be checked by working at lower temperature, which is the topic of discussion of the following two chapters. Since the lifetime also depends on the transition dipole moment, the distribution can be measured more directly by measuring the linewidth distribution at very low temperatures, at which the dynamical contribution to the linewidth is frozen out.
8. Naphthalene

The linewidth distributions for single terrylene molecules in a naphthalene crystal have been measured at temperatures down to 30 mK. The linewidth distribution becomes narrower with decreasing temperature, and has a full width at half maximum of approximately 4.3(13) MHz at 30 mK and an average linewidth of 42.7(3) MHz.
8. Naphthalene
8.1 Motivation

In this chapter, spectroscopic measurements for single terrylene molecules in a naphthalene crystal are presented. The SM spectra were measured down to a temperature of 30 mK using the $^3$He/$^4$He dilution refrigerator that was presented in Section 6.1.

The motivation for these experiments was to measure the linewidth distribution in a near-perfect crystal to see if there is a distribution of lifetime-limited linewidths, which might indicate a distribution of transition dipole moments or of non-radiative relaxation rates. A distribution of transition dipole moments was deduced from a correlation between the linewidth and the line areas presented in the previous chapter, and would also be consistent with the inferred distribution of TLS-SM coupling strengths.

The spectra of single terrylene molecules in naphthalene crystals are known to be very stable [59]. For this reason, naphthalene was a good host system with which to begin the low-temperature measurements since it is a rather simple host to study, especially when compared to an amorphous system like polyvinylbutyral (Chapter 7). Naturally, one would like to utilize the low temperature range accessible with the dilution refrigerator to study line broadening in more disordered systems as well. Such experiments were performed on polyethylene and are described in Chapter 9.

8.2 Experimental details

Mixed crystals of terrylene in naphthalene were prepared by co-sublimation under a nitrogen atmosphere [59], which produced thin crystals with excellent optical quality. A single crystal was used as a sample, which had a thickness of $\sim 10 \mu m$ and a diameter of approximately 1 mm. The concentration of terrylene molecules was $\sim 10^{-8}$ molar. The sample was mounted on a spherical mirror microscope objective [58] and immersed in the mixing chamber of the $^3$He/$^4$He dilution refrigerator described in Chapter 6. The data were collected using the single-molecule microscopy apparatus described in Chapter 6. Since the terrylene concentration was quite low ($\sim 10^{-8}$ molar), this facilitated the measurement of the distribution of linewidths. The laser
The wavelength was \(~574.3\) nm. The inhomogeneous linewidth was on the order of a few hundred GHz. For each data set, 1000 digitized fluorescence images of the sample were collected at sequential excitation frequencies covering a 2 GHz range, from which fluorescence-excitation spectra for terrylene molecules were extracted. The time required for a 1000 image scan was \(~3\) minutes. The time over which an SM line was measured per scan was \(~5\) seconds. The measurements were repeated several times, and Lorentzian functions were fit to each SM line in each scan. 10 scans of a typical SM are shown in Figure 8.1. An error estimate was assigned to the linewidth for each SM by calculating the standard deviation of the mean from the set of measurements.

Figure 8.1: Ten scans of a typical terrylene molecule in a naphthalene crystal. The excitation power was kept very low to avoid power broadening. The SNR of the spectrum is \(~10\). The data cube from which these scans were extracted was measured in 40 minutes. The linewidth found for this molecule was 49.6(12) MHz.
8.3 Results

8.3.1 Saturation intensity

To enable a power-broadening correction, the linewidths for 15 single molecules were measured with intensities of 200 and 800 mW/cm² at 1.2 K. The two linewidth distributions are shown in Figure 8.2. With the relation $\Gamma = \Gamma_r \sqrt{1 + I/I_s}$, the average saturation intensity $I_s$ found from the broadening of the average linewidth for the 15 molecules is $\sim 950$ mW/cm². This value is used to correct other data presented below for power broadening. From the broadening observed for the measurements at higher intensity, the power broadening contribution to the width of the distribution of linewidths measured at 30 mK can be estimated (Section 8.4).
8.3.2 Temperature dependence

In addition, the linewidth distribution has been measured at three different temperatures. The average linewidths, which have been corrected for power broadening, are plotted against the temperature in Figure 8.3. The measurement at 1.8 K was performed by Hermann Bach [59] and the measurements at 1.65 and 2.1 K were performed by Thomas Nonn. At the lowest three temperatures, the average linewidths are equal considering the size of the error bars. This indicates that the mechanism causing the broadening at higher temperature is inactive at temperatures below \( \sim 1.2 \) K. The low-temperature limit for the linewidth found from the weighted average of the two points at lowest temperature is 43.7(3) MHz.

![Figure 8.3](image-url)
8.3.3 Linewidth–line area correlation

Figure 8.4 is a scatter plot of the linewidths vs the line areas for 54 molecules measured at 30 mK. About half of the molecules were measured with a laser intensity of 100 mW/cm² and half were measured with an intensity of 50 mW/cm². For consistency, the linewidths for the lower intensity measurements were scaled up to the linewidths that would be expected at 100 mW/cm² using a saturation intensity of 950 mW/cm². The solid line is a linear least-squares fit to the data, showing a positive correlation as was observed for terrylene and di-tert-butylterrylene in PVB (see Chapter 7). The slope and intercept for the weighted fit are 1.7(3) MHz and 43.7(4) MHz, respectively.
8.3.4 Linewidth distribution

The normalized distribution of linewidths for the 54 molecules is shown in 8.5, which fits well to a Gaussian function with a standard deviation $\sigma$ of $2.7(4)$ MHz and a full width at half maximum (FWHM) of $\sim 6.4(9)$ MHz. The narrower distribution shown in the inset of Figure 8.5 is the distribution of error bars, fit to a Gaussian with a mean of 1.5 MHz.

![Figure 8.5: A histogram showing the linewidth distribution with a Gaussian fit. The narrower curve in the inset is the error bar distribution.](image)

The mean of the distribution of errors is approximately two times smaller than the standard deviation of the linewidth distribution, indicating an underlying distribution of linewidths that is not accounted for by the random errors in the data points. This is a major topic of discussion in Section 8.4.

All of the data for the 54 molecules shown in Figures 8.4 and 8.5 were collected after the sample had been at 30 mK for at least two weeks, which is $\sim 4$ orders of magnitude longer than the measurement time for a single molecule. Non-equilibrium broadening effects [39] are therefore not expected to arise.
8.4 Analysis of the width of the linewidth distribution

One can assume that there are four contributions to the width of the distribution shown in Figure 8.5. One contribution, $\sigma_{\text{random}}$, is from the random errors in the measurements. $\sigma_{\text{sat}}$ is from inhomogeneities in the ratio of the laser intensity to the saturation intensity. Another contribution, $\sigma_{\text{laser}}$, is from errors in the laser scan range. A final contribution, $\sigma_T$, would arise from a distribution of natural lifetimes at 30 mK. One can assume that the width of the distribution in Figure 8.5 results from adding these four contributions in quadrature, namely,

$$\sigma_{\text{meas}}^2 = \sigma_{\text{random}}^2 + \sigma_{\text{sat}}^2 + \sigma_{\text{laser}}^2 + \sigma_T^2.$$  

One can estimate $\sigma_{\text{random}}$ by calculating the size of the error that one would expect based on the size of the error bars, which is sometimes referred to as the internal error [73]. The internal error $s_{\text{int}}$ is related to the errors of the individual points $s_{\text{2,j}}$ by the relation

$$\frac{1}{s_{\text{int}}^2} = \sum_{j=1}^{N} \frac{1}{s_{\text{2,j}}^2},$$

where $N$ is the number of molecules. $s_{\text{int}}$ is the standard deviation of the mean. To find the standard deviation of the distribution, it is necessary to multiply $s_{\text{int}}$ by $\sqrt{N}$. Using the errors of the 54 measurements from Figure 8.4 gives an estimate for $\sigma_{\text{random}} = s_{\text{int}}N^{1/2} = 1.5(2)$ MHz, which is consistent with the most probable error in the distribution shown in the inset of Figure 8.5.

Next $\sigma_{\text{sat}}$ needs to be estimated, which is the fraction of the width caused by the inhomogeneities in $I/I_s$. These inhomogeneities can arise even in a near-perfect crystalline sample because of birefringence, inhomogeneities in the laser intensity, a distribution of terylene orientations within the sample, or a distribution of inter-system crossing rates or triplet lifetimes.
From the broadening of the distribution at higher intensity shown in Figure 8.2, the power broadening contribution to the width of the distribution at 30 mK can be estimated at the intensity that was used to perform the measurements ($I < 100 \text{ mW/cm}^2$). Given the function $\Gamma = \Gamma_r (1 + I/I_s)^{1/2}$ and setting $I/I_s = x$, the variance of the linewidth distribution may be written as

$$\sigma_{\text{meas}}^2 = \frac{\Gamma^2 x^2}{4(1 + x)} \sigma_x^2 + S^2 = \sigma_{\text{sat}}^2 + S^2,$$  
(8.3)

where $S$ is the part of the width that is caused by everything besides power broadening, which should be equal for the two distributions measured at different intensities. $\sigma_{\text{sat}}$ is larger for the distribution measured at higher power. $\sigma_x/x$ is simply a scaled measure of the intensity inhomogeneities, which one can assume is equal for measurements at different intensities.

$\sigma_x/x$ can be found from measurements of $\sigma_{\text{meas}}$ for the same molecules at two intensities. $\sigma_{\text{meas}}$ for the distributions in Figure 8.2 are 4.8(1) and 7.5(2) MHz for the measurements at 200 and 800 mW/cm$^2$, respectively. The average saturation intensity found from the shift of the average linewidth for the two distributions is $\sim 950$ mW/cm$^2$. With all of this information, one finds $\sigma_x/x = 0.47(12)$ and power broadening contributions to $\sigma_{\text{meas}}$ of $\sim 1.9$ and $\sim 6.0$ MHz for the distributions in Figure 8.2.

An independent estimate of $\sigma_x/x$ can be found from the distributions of single-molecule line intensities by dividing the standard deviation by the mean intensity. This gives $\sigma_x/x = 0.60(8)$ for the data in Figure 8.5. This should give a slight overestimate for $\sigma_x/x$ because it also includes detection inhomogeneities, which have nothing to do with power broadening, but it does not include inhomogeneities of the inter-system crossing rates. Taking the weighted average of the two values results in $\sigma_x/x = 0.56(6)$. Using this value to calculate $\sigma_{\text{sat}}$ from Equation 8.3 gives 1.2(1) MHz.

One additional source of broadening, $\sigma_{\text{laser}}$, is caused by errors in the laser scan range. The precision of the laser has been checked using a homemade cavity constructed from a zerodur tube by measuring the reproducibility of the free spectral range of the cavity while scanning 2 GHz intervals with the same scan rate, frequency
step size, and frequency offsets as were used for the linewidth measurements. ~1% errors were found. This gives \( \sigma_{\text{laser}} \approx 0.5 \) MHz, which is small compared to the other sources of broadening.

Finally, using Equation 8.1 and the values calculated above for \( \sigma_{\text{meas}}, \sigma_{\text{laser}}, \sigma_{\text{rand}}, \) and \( \sigma_{\text{sat}} \), one finds \( \sigma_{r} = 1.8(6) \) MHz, meaning the width of the remaining lifetime-limited distribution is 4.3(13) MHz (FWHM).

8.5 Concluding remarks on naphthalene

The estimate found in the previous section for the width of the distribution of linewidths after having accounted for the sources of broadening at hand is the real width of the distribution. A distribution of linewidths at 30 mK could be caused by either a distribution of radiative or non-radiative lifetimes. If the distribution were caused by the non-radiative lifetime, the broader molecules would be lower in intensity. If, on the other hand, the broader molecules have a shorter radiative lifetime, this indicates that they have a larger transition dipole moment, which would also cause a stronger interaction with the laser light making the molecules brighter. The positive slope of the correlation in Figure 8.4 suggests that there is a significant distribution of radiative lifetimes. A scatter plot like that shown in Figure 8.4 has also been measured for terrylene in polyethylene, where the distribution of linewidths is broader. In the next chapter, the correlation is analyzed in detail and Monte Carlo simulations are performed in order to extract the radiative and nonradiative lifetime contributions.

The data measured at 30 mK shows that there could be about a 10% variation in the natural lifetimes for terrylene molecules in naphthalene. The microscopic origin of this variation can be a distribution of effective transition dipole moments, which would be consistent with the conclusions presented in Chapter 7 for the studies on polyvinylbutyral at 1.8 K.

The investigation of a distribution of lifetime-limited linewidths and hence transition dipole moments continues in the next chapter, in which studies that have been
performed on polyethylene are presented. Polyethylene is a semi-crystalline polymer, and hence its properties are somewhat between those of polyvinylbutyral and naphthalene.
9. Polyethylene

Linewidth distributions for single terrylene molecules in polyethylene have been measured in the temperature range from 30 mK to 1.83 K and on time scales between 60 ms and 100 s. The temperature dependence of the average linewidth is best described as linear over the full temperature range. At 30 mK, the linewidth distribution has a standard deviation of \( \sim 7.9 \text{ MHz} \) and an average linewidth of \( 42.8(6) \text{ MHz} \), which indicates that there is about a 20% variation in the natural lifetimes. From simulations of the linewidth–line area correlation, it is shown that the distribution is caused both by variations of the radiative and the nonradiative transition rates. The ratio of the radiative and nonradiative contributions to the linewidth varies from molecule to molecule, but on average \( \sim 70\% \) of the linewidth originates from the radiative contribution. In order to extract the the distribution of lifetime-limited linewidths and the coupling constant distribution from the data, the linewidth distributions were simulated as a function of temperature using the TLS model.
9. Polyethylene
9.1 Introduction

The spectra of single terrylene molecules in polyethylene (PE) have been measured with a $^3$He/$^4$He dilution refrigerator between temperatures of 30 mK and 1.83 K, and the data has been used to extract the temperature dependence of the average linewidth, the lifetime-limited linewidth distribution, the distribution of excited-state lifetimes, and the tunneling two-level system-probe molecule coupling constant distribution. A distribution of lifetime-limited linewidths indicates the presence of a distribution of effective transition dipole moments, $\mu_{\text{eff}}$, or of non-radiative relaxation rates. A distribution for $\mu_{\text{eff}}$ was put forward as the cause of the correlation between the linewidth and the line areas that was observed for terrylene in PVB (Chapter 7) and the Gaussian distribution of lifetime-limited linewidths that was observed for terrylene in naphthalene (Chapter 8). Since PE is more disordered than naphthalene, one would expect to observe a broader distribution of lifetime-limited linewidths in PE.

As with Naphthalene (and all other hosts), the average linewidth of the terrylene molecules in PE depends on the temperature and can be written as $\Gamma_0(T) = \Gamma_\tau + \Gamma_d(T)$, where $\Gamma_\tau$ is the lifetime-limited contribution, and $T$ is the temperature. The form taken by $\Gamma_d(T)$ depends on the broadening mechanism. For amorphous systems, $\Gamma_d(T)$ is usually assumed to be linear, as was explained in Section 5.4.

9.2 Single-molecule microscopy experiments

Two different samples were used to perform the measurements. One of the samples consisted of a thin PE film uniformly doped with terrylene molecules. The thickness of this film was $\sim 1 \mu$m. The second sample was a sandwiched sample, in which a piece of the thin doped PE film was sandwiched between two undoped layers of PE. This was done to insure that none of the terrylene molecules were within several microns of the surface. Complicated broadening effects assumed to arise from surface phonons [61], as well as lifetime changes arising from changes in the vacuum mode.
structure [74] can complicate interpretation of the linewidth distributions in thin samples. The sandwich sample was used to check the results against such effects.

To prepare the thin doped layer, a bulk sample was prepared by means of diffusion, by heating a small amount of terrylene together with some PE at 180°C under vacuum for several hours. A small amount of the hot mixture was then pressed under high pressure between two polished stainless steel flats (also heated to 180°C) to produce a ~1μm thick film, and then cooled by dropping the film together with the stainless steel flats into a bath of liquid nitrogen. For the sandwich sample, a piece of the doped film was then melted between two undoped PE films, so that no SM was within ~10μm from the sample surface. The films were pressed together by applying a slight pressure and then cooled by dropping them together with the stainless steel flats into a bath of liquid nitrogen. Judging from the number of SMs observed, the terrylene concentration in the doped film was ~10⁻⁶ molar.

The experiments to measure the linewidth distribution as a function of temperature were performed using the single-molecule microscopy apparatus described in Chapter 6, so that the spectra from as many molecules as possible could be measured in parallel. The laser wavelength was set between 572 and 574 nm. Fluorescence-excitation spectra were extracted from digitized fluorescence images of the sample that were collected at sequential excitation frequencies covering a range from 1 – 4 GHz. The time required for a 1000 image scan was ~4 minutes. The time during which a SM line was measured in a scan was ~5 seconds. The measurements were usually repeated three times for each scan range.

9.2.1 Minimizing the effect of light-induced spectral diffusion

Light-induced spectral diffusion (LISD) influences the SM spectra at all temperatures, but especially at low temperature since the lines are narrower and small spectral jumps are more significant. Figure 9.1 illustrates the problem of LISD. Three scans of a SM spectrum are shown at increasing excitation intensity. As the intensity goes up, the SNR improves, while at the same time the probability for the molecule to undergo a photo-transformation increases. In the spectrum measured
Figure 9.1: An example of a molecule undergoing light-induced spectral diffusion. The SM undergoes a \(~100\text{MHz}\) spectral jump in the spectrum acquired at 40 mW/cm\(^2\).
at 40 mW/cm², the molecule undergoes a light-induced spectral jump of ~100 MHz and appears at a new center frequency later in the scan. 100 MHz is a large spectral jump. The distribution of spectral jumps has a width of ~18 MHz for this system (unpublished data). If a jump is small, then depending on whether the jump is in the same or the opposite direction as the laser scan, the line will appear to be broader or narrower than it really is.

To reduce the effect of LISD on the 30 mK linewidth distribution, the measurements were performed with 20 mW/cm² excitation intensity or lower, and the following four criteria had to be met for a SM to be included in the distribution:

1. The relative error in the measured linewidth Γₘ defined by the relation

\[
\frac{\sigma_\Gamma}{\Gamma_m} = \frac{1}{\text{SNR} \sqrt{N_p}} \times 2.5
\]  

had to be less than 12%. SNR is the signal to noise ratio, N_p is the number of points per linewidth, and 2.5 is a coefficient determined from numerical simulations, which in the limit of low noise, small frequency step size, and a large scan range is 2.3. Equation 9.1 can be derived analytically from the equations for a nonlinear least-squares fit of a Lorentzian to noisy data. For a typical linewidth of 50 MHz, N_p = 25 and a 12% error in the linewidth corresponds to a SNR of 4.

2. The standard deviation of the SM spectrum from a Lorentzian fit (σₘ|ₜ|) within 200 MHz of the molecule’s center frequency should not be more than ~14% larger than the average value of σₘ|ₜ| calculated from fits to all of the molecules in the scan. Per 40 MHz there are 200 data points, hence \(2 \left(1/\sqrt{200}\right) = 0.14\) and 14% corresponds to a deviation of 2σ.

3. The magnitude of the residuals at the line center should not be more than ~10% larger than the background residuals. This rejects molecules close to each other in frequency (Δν < 50 MHz) and blinking molecules, since there are large deviations from the fit in such cases.

4. The residuals for a Lorentzian fit to the SM spectrum must follow the Gaussian distribution for the residuals determined from all of the SM spectra in the
scan. To check this, all of the molecules were fit to Lorentzians, and the average standard deviation for all of the fits together was calculated ($\sigma_{\text{tot}}$). The distribution of deviations between the fit and the data points for each SM was then compared to $\sigma_{\text{tot}}$. Molecules with more than 7% of the deviations larger than $2\sigma_{\text{tot}}$ were rejected. According to the Gaussian probability distribution, only 4.6% of the data points should lie more than $2\sigma_{\text{tot}}$ from the fit.

Typically about 20 molecules out of 150 in each scan met all four requirements. At high excitation intensity, many molecules were rejected because of LISD. At low intensity the noise increased, making $\sigma_T/\Gamma_m$ larger than the upper limit of 12%.

For the higher temperature measurements, these restrictive criteria were not followed. For a molecule to be counted, it had to be observed repeatedly, and show no clear distortions or splittings from spectral jumps. At higher temperature, there is no physical reason for a SM spectrum to be described by a Lorentzian function anyway because of spectral diffusion.

### 9.2.2 Correcting the data for power broadening

An additional source of broadening of single-molecule spectra is power broadening, a consideration of which is important for the interpretation of the data presented below. Solving Equation 2.6 (the equation for the SM emission rate) for the linewidth (the FWHM of the excitation line) gives

$$
\Gamma_m (I, T) = \Gamma_0 (T) \sqrt{1 + 4\Omega_H^2 T_1 T_2 K} \simeq \Gamma_0 (T) \left(1 + \frac{I}{2I_{\text{sat}}}\right) . \quad (9.2)
$$

$I$, $I_{\text{sat}}$, and $\Gamma_0 (T)$ are the intensity, the saturation intensity, and the zero intensity linewidth, respectively. $\Gamma_m (I, T)$ is the measured power-broadened linewidth. The approximation arising from expanding the square root holds to within ~0.1% for the data presented below.

In the presence of spectral diffusion, the power-broadened linewidth is [75]

$$
\Gamma_m (I, T) = \Gamma_d (T) + \Gamma_r \sqrt{1 + I/I_{\text{sat}}} \simeq \Gamma_d (T) + \Gamma_r (1 + I/2I_{\text{sat}}) . \quad (9.3)
$$
$I_{sat}$ is the saturation intensity in the absence of spectral diffusion. The last approximation can be made at low laser power and thus Equation 9.3 can be written like Equation 9.2 with $\Gamma_0(T) = \Gamma_d(T) + \Gamma_r$ and $I_{sat} = I_{sat}(T_0(T)/\Gamma_r)$.

The average linewidths presented below are corrected for power broadening in terms of ensembles. Expanding the square root and taking the ensemble average of Equation 9.2 gives

$$\langle \Gamma_m(I, T) \rangle \simeq \langle \Gamma_0(T) \rangle + \left< 4 \left[ \frac{\mu_{eff} \cdot \bar{E}_{int}}{2\hbar} \right]^2 T_1 K \right> = \langle \Gamma_0(T) \rangle \left( 1 + \frac{\langle I \rangle}{2I_{sat}} \right). \quad (9.4)$$

$$I_{sat} = \frac{\hbar^2 \epsilon_0 c}{2} \frac{\langle \Gamma_0(T) \rangle}{\langle |\mu_{eff}|^2 T_1 K \rangle} \quad (9.5)$$

is an effective saturation intensity for the ensemble. $\langle I_{sat} \rangle$ is similar to $I_{sat}$, but the second fraction on the right-hand side is replaced by $\langle \Gamma_0(T)/|\mu_{eff}|^2 T_1 K \rangle$. Equation 9.4 can be used to correct for power broadening at all temperatures by knowing $I_{sat}$ and $\langle \Gamma_0(T) \rangle$ from measurements at at least one temperature. $\langle \Gamma_0(T) \rangle$ is the only temperature-dependent quantity in Equation 9.5.

$I_{sat}$ was measured at 50 mK and 1.8 K. At 1.8 K, $I_{sat} = 600(240)$ mW/cm$^2$, and at 50 mK, $I_{sat} = 300(40)$ mW/cm$^2$. These values for $I_{sat}$ are within the range of values for $I_{sat}$ measured by Tchenio et al. for this system [62]. $I_{sat}$ is broadly distributed owing to the random orientation of the molecules. $I_{sat}$ for the other temperatures was found approximately from a fit of the data to Equation 9.5.

The laser focusing and the intensity varied during the ~1 year data collection period. The absolute intensity is difficult to estimate, so to correct for power broadening as accurately as possible, the relative average laser intensity was inferred from the average SM intensities at 50 mK and 1.83 K using the approximation

$$\langle I_2 \rangle \simeq \left( \frac{\langle R_2 \rangle \langle \Gamma_m(I_1, T_1)^{-1} \rangle}{\langle R_1 \rangle \langle \Gamma_m(I_2, T_2)^{-1} \rangle} \right), \quad (9.6)$$

which follows from Equation 2.6. $\langle I_i \rangle$ and $\langle R_i \rangle$ are the average laser intensity and SM emission rate. Equation 9.6 is approximate, since it was assumed that $T_1$ and
9.3. Temperature dependence

Temperature dependent. For the $T < 1$ K and the $T > 1$ K data, $\langle I_i \rangle$ values were found relative to measurements performed at at 50 mK and at 1.83 K, respectively. All data collected at 1 K or below were power broadened by $\leq 4\%$.

9.3 Temperature dependence

The linewidth distribution was measured at 13 different temperatures. The data is summarized in Table 9.1. Some of the measurements were performed in the thin-film sample and some were performed in the sandwich sample, as indicated (the sample preparation was described in Section 9.2.) The temperature, the number of molecules measured, the average linewidth, and the standard deviation of the distribution are included in the table for each of the measurements.

$\langle \Gamma_0(T) \rangle$ is plotted vs the temperature in Figure 9.2. The solid lines are linear least-squares fits to the data collected with the thin-film sample (circles) and the sandwich sample (diamonds). Fits to $T^{1.3}$ curves are also shown for comparison. A $T^{1.3}$ dependence has been observed for many disordered systems at higher temperatures with hole-burning and photon echoes [49, 76]. The power law that fits the data gives information about the distribution of TLS energy splittings [77] (see the discussion at the end of Section 5.4).

The fit parameters, $\chi^2$, and the confidence intervals $\mathcal{P}$ for least-squares fits to the data are presented in Table 9.2 for both a linear and a $T^{1.3}$ temperature dependence. The slope is slightly smaller and the intercept is larger for the data collected with the thin-film sample. Although the differences in slope and intercept are not very large, they are nevertheless statistically significant. The differences in the two data sets are examined further in Section 9.7 where the linewidth distributions are fit to the TLS model.

The intercepts for the linear least-squares fits are close to values recently found by Harms et al. using time-resolved techniques to determine the bulk lifetimes for terrylene in PE at 4.2 K [4]. An emission wavelength dependence for the lifetime was observed, with corresponding $\Gamma_r$ values between $\sim 35(1)$ and $\sim 40(1)$ MHz. In
Table 9.1: Temperature dependence data. All of the \( \langle \Gamma_0 \rangle \) values have been corrected for power broadening. The final column contains the standard deviations for the distributions.

<table>
<thead>
<tr>
<th>T [mK]</th>
<th>N</th>
<th>( \langle \Gamma_0 \rangle ) [MHz] ( ^a )</th>
<th>( \sigma ) [MHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sandwich sample</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>380</td>
<td>42.8(6)</td>
<td>12(1)</td>
</tr>
<tr>
<td>43</td>
<td>32</td>
<td>42.6(23)</td>
<td>13(2)</td>
</tr>
<tr>
<td>50</td>
<td>407</td>
<td>43.5(5)</td>
<td>10(1)</td>
</tr>
<tr>
<td>950</td>
<td>65</td>
<td>73.4(41)</td>
<td>32(4)</td>
</tr>
<tr>
<td>1200</td>
<td>157</td>
<td>87.3(20)</td>
<td>36(3)</td>
</tr>
<tr>
<td>1480</td>
<td>584</td>
<td>92.5(13)</td>
<td>34(1)</td>
</tr>
<tr>
<td>1640</td>
<td>93</td>
<td>102.5(39)</td>
<td>39(4)</td>
</tr>
<tr>
<td>1830</td>
<td>75</td>
<td>101.6(32)</td>
<td>33(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thin-film sample</td>
<td></td>
</tr>
<tr>
<td>247</td>
<td>421</td>
<td>51.0(5)</td>
<td>12(1)</td>
</tr>
<tr>
<td>490</td>
<td>300</td>
<td>58.4(11)</td>
<td>17(1)</td>
</tr>
<tr>
<td>710</td>
<td>359</td>
<td>63.7(12)</td>
<td>21(1)</td>
</tr>
<tr>
<td>1060</td>
<td>123</td>
<td>76.5(22)</td>
<td>30(2)</td>
</tr>
<tr>
<td>1800</td>
<td>436</td>
<td>96.4(28)</td>
<td>57(3)</td>
</tr>
</tbody>
</table>

\( ^a \) The numbers in parenthesis are the standard deviations of the mean, in the units of the last decimal place.
Figure 9.2: The average linewidth as a function of temperature. The diamonds and the circles were measured with the sandwich and the thin-film sample, respectively. The solid lines are linear least-squares fits to the data, and the dashed lines are fits to a $T^{1.3}$ dependence.

Table 9.2: Fit data and $\chi^2_v$ values for fits to the temperature dependence data for the thin-film and sandwich polyethylene samples.

<table>
<thead>
<tr>
<th></th>
<th>$\langle \Gamma_0 \rangle = a + bT$</th>
<th></th>
<th>$\langle \Gamma_0 \rangle = \tilde{a} + \tilde{b}T^{1.3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$ MHz</td>
<td>$b$ MHz/K</td>
<td>$\chi^2_v$</td>
</tr>
<tr>
<td>Thin Sample</td>
<td>44.0(10)</td>
<td>30.0(22)</td>
<td>0.39</td>
</tr>
<tr>
<td>Sandwich Sample</td>
<td>41.7(3)</td>
<td>35.2(8)</td>
<td>1.08</td>
</tr>
</tbody>
</table>
an earlier study, a lifetime of 3.78 ns was reported for terrylene in PE by Moerner et al. [5], corresponding to $\Gamma_r = 42$ MHz. The linewidths in Figure 9.2 may be slightly affected by the linewidth of the laser, which might increase them by up to 1 MHz.

Judging by the confidence intervals, the linear relationship fits the data better than the $T^{1.3}$ temperature dependence for both samples. If all of the data is combined into one data set and fit simultaneously, the linear fit still fits reasonably well ($P = 25\%$), while the $T^{1.3}$ dependence fits very badly with an infinitesimal confidence interval. This is because the three lowest-temperature data points fall several standard deviations away from the $T^{1.3}$ fit.

Looking at the data, one might be tempted to say that there is not a difference between the two samples. But when one carefully analyzes the linewidth distributions and compares them to simulated distributions a clear difference in the lifetimes becomes evident, which is shown in the next section.

### 9.4 Linewidth distributions

So far in this chapter, the data has been presented in terms of ensemble averages, which could have been measured with an ensemble technique like hole burning, for example. In this section, the power of single-molecule spectroscopy for measuring the distributions of parameters is revealed.

The linewidth distributions for two temperatures spanning the temperature range under study are shown in Figure 9.3. The distribution is narrowest at the lowest temperature, but it does not collapse to a single value, as one would expect to observe if all of the molecules making up the distribution had the same lifetime-limited linewidth.

Figure 9.4 is a plot of the 30 mK linewidth distribution for 380 SMs shown with a weighted Gaussian fit. The standard deviation of the distribution is 8.7 MHz.\(^1\) The

---

1As seen in Table 9.1, the standard deviation of the distribution found from the data directly is 12 MHz. This is larger because the tail of the distribution extending to broad linewidths has a stronger influence on the standard deviation of the distribution than on the weighted fit. In the following discussion Gaussian distributions and errors are assumed for simplicity.
Figure 9.3: The distributions of linewidths for $T = 30$ and $1480 \text{ mK}$ shown with distributions simulated following the procedure explained in Section 9.7.
molecules were scanned several times, so the distribution of errors for the linewidths could also be determined. The most probable error is $\sim 3.4$ MHz.

Figure 9.4: The linewidth distribution for 380 SMs measured at 30 mK with transition frequencies between 17446 cm$^{-1}$ and 17455 cm$^{-1}$, which is on the red side of the inhomogeneous band. The solid line is a weighted Gaussian fit. The events marked by vertical lines are 15 linewidths measured using the ITFC technique. The insets show the spectra of four typical single molecules.

As explained in Chapter 8, assuming there are several contributions to the width of the linewidth distribution at 30 mK, the measured width can be expressed as

$$\sigma_{\text{meas}}^2 = \sigma_{\text{random}}^2 + \sigma_{\text{sat}}^2 + \sigma_{\text{laser}}^2 + \sigma_{\text{LISD}}^2 + \sigma_{\text{SSD}}^2 + \sigma_{\tau}^2. \quad (9.7)$$

$\sigma_{\text{LISD}}$ and $\sigma_{\text{SSD}}$ are the contributions from light-induced and spontaneous spectral diffusion, respectively. The SM lines in naphthalene did not undergo either effects, so
it was not necessary to include these terms previously. $\sigma_{LISD}$ is tricky to estimate. The four restrictive criteria described in Section 9.2 were intended to minimize $\sigma_{LISD}$, but it can not be completely eliminated. Further along in Section 9.5 it is shown to be insignificant by measuring the SM spectra with higher time resolution. $\sigma_{SSD}$ estimated below with the help of simulations is 0.2 MHz.

The other terms in Equation 9.7 can be found as was done in Chapter 8. A reasonable estimate for $\sigma_{\text{random}}$ is the most probable error in the error distribution, namely, $\sim 3.4$ MHz. For $\sigma_{\text{sat}}$ one finds $\sigma_z/x = 0.37$, which gives $\sigma_{\text{sat}} = 0.64$ MHz. As found in Chapter 8, $\sigma_{\text{laser}} \approx 0.5$ MHz, which, like $\sigma_{\text{sat}}$, is also very small compared to $\sigma_{\text{random}}$. Finally, using Equation 9.7 and the values found above for $\sigma_{\text{meas}}$, $\sigma_{\text{laser}}$, $\sigma_{\text{random}}$, and $\sigma_{\text{sat}}$, one finds $\sigma_T = 7.9$ MHz.

### 9.5 Fast Scan experiments

In the previous section, it was shown that the standard deviation of the linewidth distribution is 7.9 MHz. In this section, it is proven that this width does not arise from light-induced spectral diffusion (LISD). Clearly the SM spectra are influenced by LISD, which is only more apparent at lower temperature where $\Gamma_0(T)$ is narrower and small jumps are more visible. The laser intensity can be decreased to reduce LISD, but eventually one has an insufficient signal to noise ratio for the measurements. If a spectral jump occurs and if the jump distance is small in comparison to the SM linewidth ($<1/3$ of $\Gamma$), such lines can pass the four tests discussed in Section 9.2. For this reason a contribution from LISD can affect the linewidth distribution. Such a contribution could also contribute to the correlation between the linewidth and the line area shown in the inset of Figure 9.4.

To be sure that the linewidth distribution was not caused by LISD, further studies have been performed using the intensity-time-frequency correlation technique that was briefly explained in Section 5.5. Implementing this method increased the time resolution by a factor of 40. If the probability for a molecule to undergo a spectral jump is directly proportional to the excitation rate, then reducing the scan
time by a factor of 40 while keeping the excitation intensity constant also decreases the probability for the molecule to undergo LISD during a scan by a factor of 40.

9.5.1 Linewidth distribution

Using the fast scan apparatus explained in Chapter 6, the linewidths were carefully measured both as a function of measurement time and of excitation intensity for 15 single molecules at 30 mK. Several more molecules were observed, but only molecules for which both the intensity and measurement time dependence on the linewidth were measured were counted. The measurement at two different intensities was used to correct the data for power broadening. Since an influence of LISD on the measured linewidth would depend critically on the total number of excitations, the linewidths were measured with at least two different measurements times as well. These two measurement times were usually 140 ms and 250 ms. No difference in the linewidths was observed for molecules measured with different minimum measurement times.

The linewidth distribution for these 15 single molecules is shown in Figure 9.4 with the distribution of linewidths measured for 380 molecules with the camera system. The characteristics of the fast scan distribution are compared to the characteristics of the distribution measured with the camera system in Table 9.3.

Table 9.3: Comparison of single-molecule microscopy and fast scan linewidth distribution measurements. The number of molecules measured, the average linewidths, the standard deviations of the distributions, as well as the measurement times per linewidth are presented.

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>N</th>
<th>$\langle \Gamma \rangle$/MHz</th>
<th>$\sigma$/MHz</th>
<th>$\tau_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-molecule Microscopy</td>
<td>380</td>
<td>42.8(6)</td>
<td>7.9(6)</td>
<td>5 s</td>
</tr>
<tr>
<td>Fast Scans</td>
<td>15</td>
<td>40.6(20)</td>
<td>7.6(20)</td>
<td>140 ms</td>
</tr>
</tbody>
</table>

One should bear in mind that the reason why only 15 SMs were included in the fast-scans distribution is that the technique for measuring fast scans is a single-channel technique, and only one molecule can be measured at a time. What should
also be noticed is that the measurement time per linewidth, $\tau_m$, is smaller by a factor of 40 for the fast scans apparatus. This illustrates the trade-off between multi-channel camera detection and single-channel PMT detection.

Since the mean and width of the distribution are the same when one measures the lines with a factor of 40 increase in the speed, the width of the distribution is intrinsic and does not arise from LISD.

9.5.2 ITFC for single molecules at higher temperature

Actually, the main power of the ITFC technique is to measure the time scales on which spectral diffusion occurs. For the molecules presented in Section 9.5.1, there was practically no spectral diffusion taking place because the measurements were performed at 30 mK. To illustrate the power of the technique, a few molecules were also measured at 1.42 K and the linewidth was calculated as a function of the measurement time. Figure 9.5 is a plot of the linewidth vs the natural logarithm of the measurement time for two single molecules. As predicted by Equation 5.20, the linewidth is proportional to the natural logarithm of $\tau_m$.

![Figure 9.5: ITFC for two single molecules measured at 1.42 K. It is within the errors of the measurements for the two curves to intersect with an ITFC half-width of 40 MHz on the time scale of 4 ns, which would correspond to the lifetime of the excited state.](image)
Clearly the time-dependence of the linewidth is different for the two single molecules. This is because the slope is proportional to the coupling constant, and the coupling constant is proportional to the effective transition dipole moment of the molecule, $\mu_{\text{eff}}$. Therefore the $\mu_{\text{eff}}$ values for these two molecules must differ by about a factor of two.

### 9.6 Analysis of the linewidth–line area correlation

Figure 9.6a is a scatter plot of the normalized linewidths vs the normalized line areas for 380 SMs measured at 30 mK. The data shows a positive correlation as was observed for terrylene and DTBT in PVB (Chapter 7), and for terrylene in naphthalene (Chapter 8). Interestingly, the linewidth–line area correlation is already visible in the fluorescence-excitation spectra shown in Figure 9.4, where the broader molecules have larger areas.

To extract the radiative and nonradiative contributions from the measured linewidths, the scatter plot in Figure 9.6a was analyzed. The line area can be written as $A \propto (\vec{\mu}_c \cdot \vec{\xi})^2 \gamma / \Gamma \propto \cos^2 \theta \gamma^2 / \Gamma$, where $\vec{\xi}$ is the macroscopic electric field vector, $\theta$ is the angle between $\vec{\xi}$ and $\vec{\mu}_c$, and $\gamma$ and $\Gamma$ are the radiative and total linewidths, respectively. For a radiative lifetime distribution, the broad molecules have larger areas and a positive correlation would arise. A non-radiative lifetime distribution would cause a negative correlation.

The equation $A = \cos^2 \theta \gamma^2 / \Gamma$ has been used for the Monte Carlo simulation shown in Figure 9.6b. Gaussian radiative and nonradiative linewidth distributions were assumed with the constraints $\sigma_\gamma^2 + \sigma_k^2 = \sigma_r^2$ and $\langle \gamma \rangle + \langle k \rangle = \langle \Gamma \rangle$, where $k$ is the nonradiative linewidth. The fluorescence quantum yield $\phi_f$ was fixed at 0.7, consistent with experimental data [42]. Molecules with $A / \langle A \rangle < 0.5$ do not appear Figure 9.6a because their spectra are too noisy to be fit reliably. To reproduce this in the simulation, the condition $A / \sqrt{\Gamma} > 2$ was used as a criterion for a molecule to be included, which is consistent with the upper bound of 7% for the error in the linewidth that was used for screening the data for Figure 9.6a. $\sigma_\gamma / \sigma_k$ was varied until the correlation coefficient, the slope, and the intercept for a linear regression
matched the features of the measured scatter plot. This yielded a value of \( \sigma_\gamma/\sigma_k \approx 1 \). There are comparable contributions from both radiative and nonradiative decay.

![Figure 9.6: Scatter plots of the normalized linewidth vs the normalized line area. a) Data measured at \( T = 30 \text{ mK} \). The slope, the intercept, and the correlation coefficient are 0.28(4), 0.72(4) and 0.33(3), respectively. b) Points simulated using a Monte Carlo method. The values for all of the above parameters are within the error bars of the parameters for the measured scatter plot.](image)

The reason why a lifetime distribution has not been observed previously is because its effect is difficult to observe with ensemble techniques. Monte Carlo simulations of the decay of an ensemble of molecules with \( \phi_f = 0.7 \) and the value of \( \sigma_\gamma/\sigma_k \) found above show that the ratio of the deviations from a single-exponential fit to the peak signal is only about 1% at the peak of the exponential decay and about 0.2% at the baseline when the measurements are performed over a time scale of three lifetimes, as was done for terrylene in PE at 4.2 K [4].

### 9.7 Simulating linewidth distributions

In contrast to other hosts like PVB for which the average SM linewidth is an order of magnitude larger than \( \Gamma_\tau \), for terrylene molecules in PE the average linewidth at 1.8 K is only about a factor of two larger than \( \Gamma_\tau \). For this reason, lifetime variations
play a significant role in the linewidth distribution and have to be included in the model — especially at lowest temperature.

For the simulations, it has been assumed that $\alpha_c$ and $\Gamma_r$ both have Gaussian distributions. Since broadening from spectral diffusion is strongest at the higher temperatures, the 1.48 K data was used to find the $\alpha$ distribution. The 30 mK data was used to find the $\Gamma_r$ distribution, since at such low temperatures the broadening of the linewidth distribution from spectral diffusion is negligible (~0.2 MHz). This can be shown by simulating a linewidth distribution with constant $\Gamma_r$ while using the $\alpha$ distribution found from the data at 1.48 K.

The parameters were found by guessing initial values, simulating distributions, and then minimizing $\chi^2$ in a goodness-of-fit comparison. After the suitable parameters had been found, the distributions of linewidths were simulated for the intermediate temperatures and $\chi^2$ was calculated with no fit parameters. The parameters that were found to best fit the data are shown in Table 9.4. The confidence intervals for the agreement between the data and the simulations produced by fitting the sandwich-sample data are shown in the third column of Table 9.5. Since the temperature dependence of the average linewidth was linear, the phenomenological constant $\mu$ was set equal to zero (Section 5.4).

Table 9.4: The mean and standard deviation for the coupling constant and lifetime-limited linewidth distributions found by comparing the data to simulated linewidth distributions for the sandwich and the thin-film samples.

<table>
<thead>
<tr>
<th></th>
<th>sandwich sample</th>
<th>thin-film</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle \alpha_c \rangle$ [GHz nm$^3$]</td>
<td>11</td>
<td>8.5</td>
</tr>
<tr>
<td>$\sigma_{\alpha_c}$ [GHz nm$^3$]</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\langle \Gamma_r \rangle$ [MHz]</td>
<td>39.1 ± 2.6</td>
<td>42.4 ± 2.7</td>
</tr>
<tr>
<td>$\sigma_{\Gamma_r}$ [MHz]</td>
<td>8.5 ± 2.25</td>
<td>6.7 ± 2.5</td>
</tr>
</tbody>
</table>

The simulated linewidth distributions for $T = 30$ and 1480 mK are shown in Figure 9.3 together with the measurements. The simulated linewidth distribution for 30 mK is very close to the Gaussian $\Gamma_r$ distribution used as input to the sim-
Table 9.5: The number of measured molecules $N$ and the confidence intervals $P_{\text{sand}}$ and $P_{t-f}$ for fitting the distributions with the parameters given in Table 9.4 for the sandwich and thin-film samples, respectively.

<table>
<thead>
<tr>
<th>$T$ [mK]</th>
<th>$N$</th>
<th>$P_{\text{sand}}$ [%]</th>
<th>$P_{t-f}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sandhill sample</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>380</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>407</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>1480</td>
<td>584</td>
<td>45$^a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thin-film sample</td>
<td></td>
</tr>
<tr>
<td>247</td>
<td>421</td>
<td>0.1</td>
<td>66</td>
</tr>
<tr>
<td>490</td>
<td>300</td>
<td>4</td>
<td>65</td>
</tr>
<tr>
<td>710</td>
<td>359</td>
<td>50</td>
<td>75</td>
</tr>
<tr>
<td>1800</td>
<td>205$^b$</td>
<td>1</td>
<td>55</td>
</tr>
</tbody>
</table>

$^a$For comparison, the confidence interval found with a constant $\alpha_c$ value is 5%, and when constant $\alpha_c$ and $\Gamma_r$ values are assumed $P = 1%$.

$^b$This number is smaller than the total number of molecules measured at this temperature because about half of the data was collected at rather high intensity and it is difficult to correct the width of the distribution for power broadening.
ulation. The low-temperature data can actually be fit better when one assumes a Gaussian distribution of lifetimes rather than a Gaussian $\Gamma_T$ distribution, but the $\Gamma_T$ distribution found from the $T_1$ distribution for such a fit does not have a first moment and it is problematic to compare the average linewidths.

The data from the thin-film sample cannot be fit with the same $\Gamma_T$ and $\alpha_c$ distributions as the measurements performed in the sandwich sample. The disagreement is most pronounced at 250 mK and is no longer strongly visible at 710 mK. The simulated distributions and distributions measured in the thin-film sample for temperatures of 250 mK and 710 mK are presented in Figure 9.7. The shaded distributions are the experimental data, and the dashed lines are distributions simulated using the parameters found to fit the data measured in the sandwich sample.

![Figure 9.7: Comparison of simulated and measured linewidth distributions at 250 mK (part a) and 710 mK (part b). The shaded distributions are the measured data. The dashed and solid lines are simulated distributions for average lifetime-limited linewidths of 39.1 and 42.4 MHz, respectively.](image)

The peak linewidth for the 250 mK data is broader for the measured distribution than for the simulations, and a significant difference is visible in the linewidth distributions. This could either be caused by a larger coupling strength or a shorter lifetime. Since the slope of the temperature dependence is proportional to the average coupling strength, the disagreement must be caused by a shorter lifetime in the thin-film sample, because the slope is smaller for the thin-film sample than for the sandwich sample (see Figure 9.2). The mean and standard deviations of the $\Gamma_T$
distributions found by fitting the data are presented in Table 9.4. The error bars correspond to approximately two standard deviations, and were found by varying the given parameter until the confidence interval for the agreement between the simulation and the data dropped below 5%. The $\Gamma_r$ distribution that best fits the linewidth distribution at 250 mK (the dashed curve shown in Figure 9.7a) had a 10% larger mean value than the best fit to the 30 mK distribution, which was statistically significant (~2σ).

The data measured at 710 mK is shown in Figure 9.7b with distributions simulated using the $\Gamma_r$ distributions found from fitting the sandwich and thin-film data at 30 mK and 250 mK, respectively. Both simulations fit the data well. The good agreement at 700 mK is partially accidental, since the linear temperature dependences cross for the two samples at $T \sim 0.5$ K. Hence, the narrower lifetime-limited linewidth in the sandwich sample partially compensates for the reduced spectral diffusion in the thin-film sample. At 1.8 K the disagreement becomes pronounced again because the curves begin to diverge and the precise form of the $\alpha$ distribution becomes important. The thin-film sample has less spectral diffusion arising from TLSs, judging from the slope of the temperature dependence and the best-fit value for $\alpha$ in Table 9.4.

Neither of the surface effects once feared are present in the thin-film sample. The average coupling constant for the thin-film sample is slightly smaller than the coupling constant in the sandwich sample as indicated by the slope of the temperature dependence. So extra broadening from surface phonons does not appear to arise [61]. There also does not seem to be a perturbation of the lifetime from the interface between the polyethylene and the liquid helium. This effect would produce a lengthening rather than a shortening of the lifetime [78].

Perhaps the shorter lifetime in the thin-film sample simply results from a higher refractive index since the thin film was produced by squeezing the sample under high pressure. The same thin film was used to make the sandwich sample, but it was effectively annealed when the layers were melted together. This is another way of saying that the variations in lifetime arise from a local-field effect.
The lifetime of a probe molecule should be inversely proportional to $\mu^2_{\text{eff}}$ and hence inversely proportional to the square of the local-field factor. Expressing the dielectric constant in terms of the refractive index $n$, the radiative lifetime of a probe molecule relative to its free-space lifetime is

$$\frac{T_{\text{rad}}(n)}{T_{\text{rad}}^\text{vac}} = \left(\frac{n^2 + 2}{3}\right)^{-2} \frac{1}{n}.$$

(9.8)

The extra factor of $1/n$ arises from a change in the speed of light in the medium. By linearizing this equation around $n = 1.5$ one can show that a reduction of the lifetime of 10% corresponds to an increase of the refractive index by $\sim 3\%$. This is not such a large increase when one considers that the density of crystalline polyethylene is 15% higher than for amorphous PE at room temperature [79].

It might at first seem counterintuitive that for a sample in which the probe molecules have a larger local-field factor, the coupling constant does not increase as well. The coupling constant actually goes down, judging from the slope of the temperature dependence. This may not be contradictory. If the higher local field is caused from a higher host density, then there would presumably be fewer voids in the sample. If the picture of a tunneling two-level system shown in Figure 4.1 is correct, then a denser sample having fewer voids would also have fewer tunneling two-level systems per unit volume.

### 9.8 Concluding remarks on polyethylene

The linewidth distribution measured for single terrylene molecules in polyethylene at a temperature of 30 mK shows that there is about a 20% variation in the natural lifetimes. From the simulations of the scatter plots shown in Figure 9.6, one finds that this distribution of lifetimes has both radiative or non-radiative contributions. The simulations reveal that the fluorescence quantum yield is approximately 0.7, and the standard deviations of the radiative and nonradiative lifetime distributions are about equal.
In addition, the temperature dependence of the average linewidth is indistinguishable from a linear dependence over the range of temperature studied, in agreement with the photon echo studies of Zilker et al. conducted below 1 K [80]. This indicates that local heating from the interaction of the SMs with the laser light is insignificant, even at 30 mK.

Linewidth distributions were simulated and compared to the distributions of measured linewidths and the data at all temperatures were consistent with the same coupling constant distributions. Interestingly, the simulations revealed that the lifetimes of the probe molecules in different samples depend on the sample preparation technique and can vary by at least as much as 10%.

In Appendix B, a simple quantum mechanical model is presented and compared to experimental data to show that the distribution of the radiative lifetimes in disordered media is a general effect caused by the same interactions responsible for inhomogeneous broadening. At higher temperature, the distribution of lifetimes would narrow depending on the mobility of the host molecules. Whether or not a distribution of lifetimes is observable would depend on the ratio of the time scale of the molecular motion to that of the measurement time.
9. Polyethylene
Appendices
A. Renormalization of homogeneous parameters

With $\Lambda = D \mu r^{-3}$ where $\mu = \Delta \mu_{\text{TLS}}$ and $D = \mathcal{L} \Delta \mu_{\text{SM}}$ and assuming $\mu \eta > 0$, the probability distribution for $\Lambda$ can be found given the probability distributions for $r$, $\eta$, and $\mu$ by summing all parameters that are consistent with a given value of $\Lambda$:

$$P(\Lambda) = \int_{\eta \mu > 0} P(\eta, \mu) d\eta d\mu \int_0^{r_{\text{max}}} \delta(D \mu \eta r^{-3} - \Lambda) P(r) dr ,$$  \hspace{1cm} (A.1)

where $P(\eta, \mu)$ is the probability distribution for $\eta$ and $\mu$, and $P(r)$ is the probability distribution for $r$. The integral is nonzero only for $r_{\text{max}} > (D \eta \mu_{\text{max}} / \Lambda)^{1/3}$, which always holds if $r_{\text{max}} > (D \eta_{\text{max}} \mu_{\text{max}} / \Lambda)^{1/3}$. Substituting $P(r) = 3r^2 / r_{\text{max}}^3$ and integrating over $r$ one finds

$$P(\Lambda) = \frac{D}{r_{\text{max}}^3 \Lambda^2} \int_{\eta \mu > 0} \eta \mu P(\eta, \mu) d\mu d\eta ,$$  \hspace{1cm} (A.2)

and finally

$$P(\Lambda) = \frac{D \langle |\eta \mu| \rangle}{r_{\text{max}}^3 \Lambda^2} = \frac{4\pi}{3} \frac{D \rho_{\text{TLS}} \langle |\eta \mu| \rangle}{\Lambda^2 N_{\text{TLS}}} .$$  \hspace{1cm} (A.3)
B. Luminescence lifetimes of single molecules in disordered media

In what follows, a simple microscopic model which is a development of ideas presented in [21,28] is presented, which shows that for nonpolar chromophore molecules in nonpolar hosts the distribution of lifetimes, the inhomogeneous broadening, and also the solvent shift of the transition frequency can largely be accounted for by the same mechanism – the dispersion interaction. In fact, a lifetime distribution should be present in any sample where the resonances are inhomogeneously broadened.

A chromophore molecule (an impurity) is described by a series of electronic states with state vectors $|\varphi_k\rangle$ ($k = 0, 1, 2...$) and energies $E_k$ where $E_0$ is set to zero. The transition dipole moments are $-e\langle\varphi_j|\vec{r}|\varphi_k\rangle = \vec{\mu}_{jk}$, where $\vec{r}$ is the electron radius vector. The impurity’s volume, defined by a radius $R_{\text{min}}$, is not available for host molecules. We take the host to consist of non-interacting molecules with one ground $|\psi_g\rangle$ and three excited states $|\psi_m\rangle (m = 1,2,3)$ with energy $F$ and dipole moments $\vec{d}_m = -e\langle\psi_g|\vec{r}|\psi_m\rangle$, where $\vec{r}$ is the electron radius-vector of the molecules. The three moments are orthogonal to each other and thus the polarizability tensor is diagonal with equal Eigenvalues. When densely packed, the host molecules have a density $n_s$. The interaction between the impurity and host molecules is taken to have the form of a dipole-dipole interaction

$$\tilde{w} = e^2 \sum_i \frac{3(\vec{r} \cdot \vec{n}_i)(\vec{n}_i \cdot \vec{\rho}_i) - (\vec{r} \cdot \vec{\rho}_i)}{|\vec{R}_i|^3},$$  \hspace{1cm} (B.1)
where the sum is performed over all host molecules, $\vec{R}_i$ is the vector drawn from the impurity to molecule $i$, and $\vec{n}_i = \vec{R}_i/|\vec{R}_i|$. The host structure is modeled by randomly distributed voids – regions where a host molecule is missing. The concentration of voids $n_v \ll n_s$. The perturbed state vectors of the combined system for the ground $|\varphi_0\psi_g\rangle'$ and first excited state $|\varphi_1\psi_g\rangle'$ are

$$
|\varphi_0\psi_g\rangle' = |\varphi_0\psi_g\rangle - \sum_{k,m} |\varphi_k\psi_m\rangle \frac{\langle \varphi_k\psi_m | \hat{\omega} | \varphi_0\psi_g \rangle}{F + E_k - E_{0,1}}. 
$$

This combined system can be thought of as a “supermolecule,” whose wavefunction representing both the impurity and its local environment is localized mostly in the core region. The part of the host further away is nearly continuous from the point of view of the core region and can be treated using the Lorentz approximation.

The transition dipole moment $\mu_c$ from state $|\varphi_0\psi_g\rangle'$ to state $|\varphi_1\psi_g\rangle'$ of the combined system is

$$
\mu_c^2 = \mu^2 - 2\mu^2 \alpha \sum_{i=1}^{N} \frac{3\cos^2 \theta_i - 1}{R_i^3}, 
$$

where $\bar{\mu} = \bar{\mu}_{01}$ and $\theta_i$ is the angle between $\vec{R}_i$ and $\vec{\mu}$. $\alpha = 2d^2F/(F^2 - E_1^2)$ is the polarizability tensor Eigenvalue for the host molecules at the transition frequency of the impurity. Calculating the frequency shifts is a more complicated matter and in order to keep the physical picture simple, only the ground and first-excited electronic states for the impurity are considered and the transition frequency shift $\delta\nu$ is

$$
\delta\nu = -\alpha \left\{ \frac{\mu^2 E_1}{\hbar F} \right\} \sum_{i=1}^{N} \frac{3\cos^2 \theta_i + 1}{R_i^6}. 
$$

Though the spatial distribution of host molecules is correlated because of their finite size, it is taken as homogeneous and uncorrelated. With this approximation,

$$
\nu_{vac} - \langle \nu \rangle \approx \alpha \left\{ \frac{\mu^2 E_1}{\hbar F} \right\} \frac{8\pi(n_s - n_v)}{3R_{min}^3}. 
$$

The factor in curly brackets is the part mainly depending on higher electronic states. When they are included this factor is a sum of terms containing the impurity po-
larizability and $\mu^2$ [28]. This factor is treated as a parameter below and eventually cancels.

To analyze the inhomogeneities it is convenient to consider an effective interaction between voids and the impurity molecules, which can be described by Eq. B.1 with opposite sign and $R_i$ understood as the distance to the $i$'th void. If the spatial void distribution is homogeneous, $\langle \mu_i^2 \rangle = \mu^2$. The variance of the distributions for $\delta \nu$ and $\mu_i^2$ can be estimated using the central limit theorem, and the radiative linewidth distribution can be found from the $\mu_i^2$ distribution since $\gamma \propto \mu_i^2 \cdot [9/(\epsilon + 2)^2]$, where the Lorentz correction is included in square brackets for completeness. The variances of the radiative linewidth and the transition frequency (the inhomogeneous linewidth) are equal to the number of voids multiplied by the variances calculated with the single void distribution function. Corresponding standard deviations are

$$\sigma_\gamma = 8\langle \gamma \rangle \alpha \sqrt{\pi n_v/(15R_{\min}^3)} \quad \text{(B.6)}$$

and

$$\sigma_\nu = 4\alpha \left\{ \frac{\mu_i^2 E_i}{hF} \right\} \sqrt{2\pi n_v/(15R_{\min}^2)} \quad \text{(B.7)}$$

Though $\langle \nu \rangle$, $\sigma_\gamma$, and $\sigma_\nu$ depend on many parameters, with Eqs. B.5, B.6, and B.7 and the classical Clausius-Mossotti equation [10], which reads $\alpha(n_s - n_v) = 3(\epsilon - 1)(\epsilon + 2)^{-1}/4\pi$, one can derive the simple relation insensitive to those parameters

$$R \equiv \frac{\sigma_\nu/\langle \nu \rangle}{\sigma_\gamma/\langle \gamma \rangle} = \frac{\epsilon + 2}{2^{3/2}(\epsilon - 1)} \quad \text{(B.8)}$$

where $\epsilon$ is the dielectric constant of the medium. This shows the fundamental connection between the distribution of linewidths and inhomogeneous broadening caused by the dispersion interaction.

Using the measurement of $\sigma_\gamma/\langle \gamma \rangle = 0.2$ and estimates based on available data [42,81] of $(\langle \nu \rangle - \nu_{\text{vac}})/\langle \nu \rangle = 0.09$ and $\sigma_\nu/\langle \nu \rangle = 0.01$, one gets $R = 0.6$. With $\epsilon = 2.3$ Eq. B.8 predicts $R = 1.2$. When the electronic states with $k \geq 2$ are also included in the equation for $\sigma_\nu$, the estimate for $R$ can be slightly smaller because a sum over a large set of states having different values and orientations for $\mu_{jk}$ weakens the
dependence on $\theta_i$ [82]. States with $k \geq 2$ also change the factor $E_1/F$ to $\overline{E}/F$ [28]. The estimate for $R$ may also be decreased by van der Walls attraction forces, which reduce the void concentration in the immediate vicinity of the chromophore, thus increasing $\nu_{\text{vac}} - \langle \nu \rangle$ while decreasing $\sigma_\nu$.

An inspection of Eqs. B.3 and B.4 may give the impression that $\gamma$ and $\delta \nu$ should be strongly correlated. Though there is partial correlation, $\gamma$ is not a simple function of $\nu$. This is shown in Fig. B.1 where a Monte Carlo simulation of a scatter plot for $\gamma/\langle \gamma \rangle$ vs $\delta \nu/\langle \nu \rangle$ is shown. Thus, though all 380 molecules had almost equal transition frequencies, they could nevertheless have a distribution of lifetimes. In Fig. B.1 the well-known $\nu^3$ dependence [22] on $\gamma$ has not been accounted for, which would cause a stronger positive correlation [83].

![Figure B.1: A Monte Carlo simulation of a scatter plot for $\gamma/\langle \gamma \rangle$ vs $\delta \nu/\langle \nu \rangle$. The solid line is the inhomogeneous band. With the radiative lifetime found from the data ($T_1/\phi_f \approx 5.5$ ns) the value $\mu^2/h\nu = 30\text{Å}^3$. $\alpha = 10\text{Å}^3$ (reasonable for a medium-sized $n$-alkane), $\overline{E}/F = 1$, and $R_{\text{min}} = 6\text{Å}$ were also assumed. Since crystalline PE is $\sim 20\%$ denser than amorphous PE, $n_v = 0.2n_s$. From the Clausius-Mossotti equation the densities $n_v = 0.0018/\text{Å}^3$ and $n_s = 0.009/\text{Å}^3$ were found (assuming $\epsilon = 2.3$).]
Bibliography


[54] R. Richardson and E. Smith, Experimental techniques in condensed matter physics at low temperatures (Addison-Wesley, Redwood City, California, 1988).


[81] I. Renge, $\nu_{\text{vac}} = 19230(50) \ \text{cm}^{-1}$ for terrylene (unpublished).


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