The influence of the vibrational properties on charge transport in oligoacenes

Citation for published version (APA):

DOI:
10.6100/IR632791

Document status and date:
Published: 01/01/2008

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 21. Jan. 2020
The Influence of the Vibrational Properties on Charge Transport in Oligoacenes

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op maandag 18 februari om 16.00 uur

doors

Hendrik Adriaan van Laarhoven

geboren te Hulst
Dit proefschrift is goedgekeurd door de promotoren:

prof.dr.ir. R.A.J. Janssen
en
prof.dr. M. Bonn

Copromotor:
dr.ir. C.F.J. Flipse

CIP-DATA LIBRARY TECHNISCHE UNIVERSITEIT EINDHOVEN

van Laarhoven, Hendrik Adriaan

NUR 926

Trefwoorden: organische halfgeleiders / moleculaire kristallen / vibratiespectra / ladingstransport / grensvlak verschijnselen / dunne lagen / elektronenspectroscopie

Subject headings: organic semiconductors / molecular crystals / vibrational spectra / charge transport / interface effects / thin films / electron spectroscopy

This research forms part of the research programme of the Dutch Polymer Institute (DPI), project no. 429.
# Contents

## 1 General Introduction
1.1 Organic crystals ........................................ 1
1.2 General electronic features .............................. 3
   1.2.1 The band structure of solids ....................... 3
   1.2.2 Excitons ..................................... 5
   1.2.3 The generalized dielectric function and conductivity ...... 6
   1.2.4 Classical models for free and bound charges .......... 7
   1.2.5 Charge transport in soft matter ................... 8
1.3 The structural properties of pentacene ................ 9
1.4 Contents of this thesis ................................ 10
References ................................................. 13

## 2 Theoretical aspects
2.1 Introduction ............................................. 15
2.2 Band structure from ab initio methods .................. 15
2.3 The vibrational structure of pentacene, using density functional theory .... 16
   2.3.1 The vibrational structure of an isolated pentacene molecule ...... 16
   2.3.2 The coupling of the charges with the intramolecular modes ...... 18
2.4 Modulation of the transfer integral by low energetic phonon modes .......... 22
References ................................................. 26

## 3 High Resolution Electron Energy Loss Spectroscopy
3.1 Introduction ............................................. 27
3.2 The experimental technique ................................ 27
3.3 Scattering mechanisms and selection rules ............... 29
   3.3.1 Dipole scattering .............................. 29
   3.3.2 Impact scattering ............................. 33
3.4 The experimental setup .................................. 33
References ................................................. 35

## 4 The vibrational properties of thin layers of pentacene on metallic surfaces studied by HREELS
4.1 Introduction ............................................. 37
4.2 The preparation of the substrates and thin films .......... 38
4.3 The structure of thin layers of pentacene ................. 40
4.4 The intramolecular vibrations of pentacene ............... 42
   4.4.1 The intramolecular vibrations for a multi-layer of pentacene ...... 42
Chapter 1

General Introduction

1.1 Organic crystals

Since the 1940’s conduction in organic materials has been receiving attention in the physics community [1]. In the last 10 years the interest increased drastically after realising that these materials are promising for of opto-electronic applications such as field effect transistors, light-emitting diodes and solar cells. The main advantages compared to the traditional semiconducting materials such as Si, Ge and GaAs are the low costs of the material, the flexibility (particularly advantageous for displays) and the fact that their electronic, optical and mechanical properties can easily be tuned by changing the chemical structure. For an overview of the (recent) developments in the field of organic semiconductors, the reader is referred to ref. [2], [3], [4] and [5].

The organic materials that show semiconducting behaviour can be divided into two distinctly different groups: polymers and organic crystals. Both groups of materials have already been used for commercial devices: polymers for instance LEDs in Pioneer car stereos or the Philishave, and organic crystals in for instance the display of a Kodak camera. Polymer layers can be spin-coated in air on a substrate. The organic crystals in customer electronics are thin films, which are evaporated under such conditions that they are often polycrystalline or amorphous. To obtain high quality organic crystals (either thin films on a substrate or freestanding single-crystals) procedures are needed that require either ultra-high vacuum or inert gas flows, conditions that considerably increase the costs of a production process. From a scientific point of view these organic crystals are often more interesting. In contrast to the spin-coated polymers and polycrystalline films, the structure of the samples is ordered and often known. Therefore single crystals are well suitable for obtaining detailed and fundamental understanding of the charge transport mechanism, the influence of vibrational properties and electronic screening in organic materials.

In organic crystals, the building blocks of the lattice are small organic molecules, that are often (partially) conjugated, having alternating single and double bonds. This leads to a delocalization of the \( \pi \)-electrons, which enhances the intramolecular charge transport. Between the different molecules in the crystal there is a weak van der Waals bonding. Due to the \( \pi-\pi \) stacking between the neighbouring molecules in the crystal, the electronic coupling between the different molecules in the lattice is relatively high for a van der Waals bonded system, creating good charge transport. However, one has to take in mind that the influence of phonons on these soft materials is large in comparison
to classic semiconductors [6]. A special class of semiconducting organic crystals are the oligoacenes. Oligoacenes consist of multiple fused phenyl rings. When a linear molecule is formed out of these rings, their chemical formula is \( C_{4n+2}H_{2n+4} \), for instance naphthalene \((n = 2)\), tetracene \((n = 4)\) or pentacene \((n = 5)\) (see figure 1.1). The lattice structure of the latter is shown in section 1.3. Other molecules that are also mainly built by directly connecting phenyl rings, like rubrene and perylene (see figure 1.1), are also counted to this group.

Figure 1.1: The structure of various oligoacene molecules.

From this group of materials, pentacene [7–9] and rubrene [10–12] have been receiving the most interest in the last decade, mainly because they showed the highest mobilities at room temperature. For thin film pentacene transistors hole mobilities up to 40 cm\(^2\)/Vs have been reported [8] and for single crystal structures up to 35 cm\(^2\)/Vs at room temperature [7]. This is high compared to the mobility for undoped conjugated polymers [13] and comparable to the mobility of amorphous silicon. The main focus of this thesis will be on this specific material and it will be studied both as a thin film and a single crystal. Thermal motions have a large influence on the electronic properties of pentacene. As a result, various theoretical charge transport models involving vibrational aspects have been proposed for the single crystalline form of this material [14, 15]. In this work we would like to give more experimental insight in the interplay of the phonons and charge carriers, and, because of its importance for devices, describe the vibrational and electronic properties of ultra-thin films of pentacene deposited on metal surfaces.

Thin pentacene films are studied with high-resolution electron energy-loss spectroscopy (HREELS). Since this is a surface sensitive technique, vibrational and electronic properties can be studied as a function of distance to the metal-organic interface. As a result information on screening effects and the structure of interfaces can be obtained. This is valuable information for devices, where metallic contacts on pentacene may change the transport properties as a result of the specific vibrational and electronic structure at the interface.

The single crystals used in this study (grown by the group of prof. T.T.M. Palstra at the University of Groningen) are the purest organic crystals available (less than 1 out of \(10^{10}\) sites is a trap site [7]). As a result, they are highly suitable for studying the
intrinsic mechanism of charge transport in this material. In our study this has been done by THz time domain spectroscopy (in collaboration with the group of prof. M. Bonn at the AMOLF institute in Amsterdam), an optical method that provides the spectrally resolved conductivity of the material.

1.2 General electronic features

1.2.1 The band structure of solids

There are various ways to describe the behaviour of carriers in a crystalline solid and the related band structure. Here we use the tight-binding approximation [16], since it provides a simple but clear conceptual explanation for the origin of energy bands in a solid, especially in the case of an organic crystal with weak bonds between molecules. The electrons that occupy the deep-lying levels of an atom are strongly localized. When forming a solid, these orbitals remain strongly localized and hardly contribute to the electronic structure of the lattice. In the tight binding approximation the system is described by a linear combination of atomic orbitals (or molecular orbitals in the case of having a crystal built from organic molecules). The orbitals originally belonging to a single moiety remain mainly localized on this unit, except for the highest occupied orbitals, which show overlap with neighbouring moieties.

Figure 1.2: Sketch to explain the concepts of bands. The single atom/molecule has single atomic/molecular orbitals. Because of the wave function overlap and to comply with the Pauli principle they are split into two in the case of two atoms/molecules. For a large amount of atoms/molecules, each level becomes a continuum of states, the so-called bands.

Figure 1.2 shows a sketch of the split energy in a many atoms system as a result of orbital overlap. If in case of a single atom there are 3 different levels, when having 2 atoms in each others vicinity, these three different levels will each split into two because of the wave function overlap and to comply with the Pauli principle. The lower lying levels are strongly localised and have almost zero overlap with their neighbour and as a result the splitting will be small. For the higher levels, there is more overlap of the wavefunctions and as a result the splitting is bigger. In the case of having $N$ atoms, each level will split into $N$ levels, forming effectively forming a continuum.

In the case of $N$ completely free atoms, the Schrödinger equation for atom $i$ and orbital $m$ is

$$\mathcal{H}_{\text{atom}} \phi_m(r - R_i) = E_m \phi_m(r - R_i),$$

with $\phi_m(r - R_i)$ being the wavefunction for an electron at point $r$ belonging to lattice position $R_i = i_1a + i_2b + i_3c$ in the atomic energy level $E_m$. If we consider the atoms not to be completely free, the potential $V_{\text{atom}}(r - R_i)$ belonging to $\mathcal{H}_{\text{atom}}$ will deviate. This
perturbation is described by adding an extra term $v(r - R_i)$ to the potential. When only considering a single electron localized around an atom at position $R_i$, this term can be expressed as

$$v(r - R_i) = \sum_{j \neq i} V_{\text{atom}}(r - R_j). \quad (1.2)$$

The solution to the Schrödinger equation of the total system, $\mathcal{H}\psi_k(r) = E(k)\psi_k(r)$ with $\psi_k(r)$ being a wave function with wave vector $k$, is obtained by multiplying by $\psi_k^*(r)$ and integrating:

$$E(k) = \frac{\langle \psi_k | \mathcal{H} | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle} = \int \frac{d^3r \psi_k^* \mathcal{H} \psi_k}{\int d^3r \psi_k^* \psi_k}. \quad (1.3)$$

In a first order approximation to determine $E(k)$, $\psi_k$ is assumed to be a linear combination of the eigenfunctions of the single atom, $\phi_m$, for the unperturbed case of equation 1.1. Since for a material with a periodic potential any solution has to obey the Bloch theorem [16], this linear combination is of the form

$$\psi_k \approx \sum_i c_i \phi_m(r - R_i) = \sum_i e^{ik \cdot R_i} \phi_m(r - R_i), \quad (1.4)$$

with for any reciprocal lattice vector $g$, $e^{i(g \cdot R_i)} = 1$ and as a result $\psi_{k+g} = \psi_k$. When using the linear set 1.4 for strongly localized electrons the denominator of equation 1.3 is simply equal to $N$. Using the Hamiltonian for a single atom (1.1), equation 1.3 can be written as

$$E(k) \approx \frac{1}{N} \sum_{i,j} e^{i(k \cdot (R_i - R_j))} \int \phi_m^*(r - R_j)[E_m + v(r - R_i)]\phi_m(r - R_i)dr. \quad (1.5)$$

To get a feeling of the consequences for the electronic structure, consider the atomic state of interest to have a spherical wavefunction (in other words $\phi_m$ is an s-orbital). The expression above to can be simplified to:

$$E(k) \approx E_m - A - B \sum_j e^{i(k \cdot (R_i - R_j))}, \quad (1.6)$$

with

$$A = -\int \phi_m(r - R_i)v(r - R_i)\phi_m(r - R_i)dr$$

$$B = -\int \phi_m(r - R_j)v(r - R_i)\phi_m(r - R_i)dr$$

and for $j$ only the values for the nearest neighbours of $i$ are considered, so that we only describe electronic overlap between neighbouring atoms. Furthermore for simplicity reasons the crystal is considered to be cubic ($|a|, |b|, |c| = a$). As a result expression 1.6 can be simplified to

$$E(k) \approx E_m - A - 2B(cosk_xa + cosk_ya + cosk_za) \quad (1.7)$$
Since the perturbation, \( v \), of the potential, \( V \), is negative, \( A \) is positive and the center of the band lies lower than the original atomic level. Depending on \( k \) the third term of equation 1.7 can range from \(-6B\) to \(6B\). Therefore the width of the energy band is \(12B\).

For a covalent crystal, the electronic behaviour of the material is determined largely by the occupation of the shells of the single atom. If for instance the 4s level is only filled with 1 electron, as in the case of copper, the hybrid band formed out of 4s and 4p states is only partially filled (1/8). As a result electrons can move freely through the material, giving it its metallic behaviour (actually for copper the higher electronic orbitals are so delocalized that the tight binding approximation only involving the coupling between nearest neighbours is very poor). In the case of silicon the two 3s and two 3p electrons fill the lower hybrid \(sp^3\) band whereas the higher \(sp^3\) band is unoccupied. Between the energy continuums of the two subbands there is a gap with no electronic states. The size of this band gap, \(E_g\), is the energy an electron needs to go from the filled (valence) band to the unoccupied (conduction) band. Once the electron is in the conduction band it can move through the medium and it is leaving a mobile unoccupied state behind in the valence band, a so-called hole. For a material like pentacene the band gap is largely determined by the energy difference between the highest occupied molecular orbital (HOMO) and the lowest molecular orbital (LUMO). The bands in this material are rather narrow (\(\sim 0.1 \text{ eV} [15] \)) compared to covalent materials and metals, since the electronic overlap between the molecules is relatively small.

The curvature of bands \(\frac{\partial^2 E}{\partial k^2}\) is often given in terms of the effective mass, \(m^*\), since it basically represents the mass the carrier would have if it had displayed the same behaviour if it were completely free (in a free electron gas \(E = \frac{\hbar^2 k^2}{m}\)). In the case of the band described by equation 1.7, close to the \(\Gamma\)-point in the Brillouin zone \((k=0)\) the cosine functions can be written in a Taylor expansion, resulting in \(E(k) \approx E_m - A - 6B + Ba^2k^2\). For an electron at the \(\Gamma\)-point the effective mass would be

\[
\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} = \frac{2Ba^2}{\hbar^2}.
\]

(1.8)

Note that in the system described in this section vibrational aspects were not taken into account. The electronic properties can however depend significantly on the presence of thermal motions, especially in the case of a soft material like pentacene.

1.2.2 Excitons

Optical absorption spectra of oligoacenes show contributions below the band gap. These optical transitions are the result of excitons. An exciton is a bound electron-hole pair. Similar to electrons and holes it can travel through the crystal, but it does not transport net charge. Excitons do, however, transport energy in the system and can also contribute significantly to the polarizability of the medium [17]. Since the pair formation lowers the energy of the system, the energy needed to excite an exciton is equal to the energy needed to create a free electron and hole minus the exciton binding energy. Besides being created by an optical transition, excitons can also form as a result of the relaxation of electronic states with higher energy [17].

In molecular crystals various types of excitons can exist, categorised by the distance between the position of the electron and the hole in the crystal. In many solid state physics textbooks (see for instance reference [18]) excitons are divided into two groups:
strongly localised Frenkel excitons and delocalised Mott-Wannier excitons. In the case of a Frenkel exciton \cite{19}, the exciton is a neutral excited state of an isolated molecule. These excitons exist in the case that the exciton binding energy is large compared to the electron and hole band widths. The Mott-Wannier exciton is often extended over several lattice distances and can straightforwardly be represented by a hydrogen like wavefunction (with the radius being the average distance from the electron to the hole and considering the effective masses of the charges). Such excitons exist in a material with a high static dielectric constant and large band widths. As a result these types of excitons are common in semiconductors like Si and Ge, but not in organic materials.

A third intermediate type that is commonly observed in organic crystals is the charge transfer (CT) exciton \cite{20}. A CT exciton consists of an electron and hole being localized at different (often neighbouring) molecular sites (or in other words an electron has been removed from one molecule and is placed on a nearby molecule). These excitons are essentially different from the Mott-Wannier excitons, since their binding energy is large compared to the electronic band widths of the material. These CT excitons were believed to contribute little to the optical spectra of oligoacenes, since the electronic coupling between neighbouring sites was assumed to be too small to have a significant transition dipole from the ground to CT state to observe their contributions. In recent work on PTCDA, a semiconducting organic crystal, it has been shown that they do contribute significantly \cite{21,22} and also in this work it will be shown that for pentacene they give a significant contribution to the HREELS spectra.

1.2.3 The generalized dielectric function and conductivity

When discussing electronic and optical properties of solids, the generalized dielectric function is of great importance. This function describes the interaction of both the bound and free charges with an electric field over the complete frequency range. The flow of free charges (\(j\)) and the displacement of local or bound charges (\(D\)) (those valence electrons that are more strongly bound to the ion core) as the result of an applied electric field are accounted for in the Maxwell equations:

\[
\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (1.9) \\
\n\nabla \times \mathbf{H} = \mathbf{j} + \frac{\partial \mathbf{D}}{\partial t}. \quad (1.10)
\]

In the case of a plane electromagnetic wave with angular frequency \(\omega\) traveling along the z-axis through a medium and taking the magnetic permeability, \(\mu\), as unity (resulting in \(\mathbf{H} = \mathbf{B}\)), one can write the current density and dielectric displacement as a function of the electric field:

\[
j(z, \omega) = \sigma(\omega)\mathbf{E}(z, \omega) \text{ and } \mathbf{D}(z, \omega) = \epsilon_0\epsilon(\omega)\mathbf{E}(z, \omega), \quad (1.11)
\]

In the case of crystalline materials both the conductivity, \(\sigma(\omega)\), and the dielectric function, \(\epsilon(\omega)\), are scalar functions. Substituting the relations of 1.11 into the second Maxwell equation 1.10 gives the following expression:

\[
\nabla \times \mathbf{H}(z, \omega) = \sigma(\omega)\mathbf{E}(z, \omega) - i\omega\epsilon_0\epsilon(\omega)\mathbf{E}(z, \omega), \quad (1.12)
\]
which can also be expressed as:
\[ \nabla \times \mathbf{H}(z, \omega) = -i\omega \epsilon_0 \tilde{\epsilon}(\omega) \mathbf{E}(z, \omega), \] (1.13)
where \( \tilde{\epsilon}(\omega) \) is the generalized dielectric function (and the tilde indicates it is complex):
\[ \tilde{\epsilon}(\omega) = \epsilon(\omega) + \frac{i\sigma(\omega)}{\epsilon_0 \omega}. \] (1.14)

For a DC field \( (\omega = 0) \) the first term of equation 1.14 describes the response from the electrons in filled bands, whereas the second term describes the response from conduction electrons (electrons in partly filled bands). For an oscillating field \( (\omega \neq 0) \) this distinction is no longer valid, since the free charges can have a considerable out-of-phase response, whereas the bound charges can have an in-phase response, and the complex dielectric function and conductivity directly relate to one another:
\[ \tilde{\sigma}(\omega) = -i\omega \epsilon_0 \tilde{\epsilon}(\omega) \] (1.15)

Henceforth with \( \epsilon(\omega) \) and \( \sigma(\omega) \) (written without a tilde) the complex functions are meant.

When still assuming that \( \mu \) is equal to unity, which in the energy range of optical frequencies is the case for many materials, the following expression for the refractive index of a medium is valid:
\[ n = \sqrt{\mu} \sqrt{\epsilon} \approx \sqrt{\epsilon}. \] (1.16)

As a result \( \epsilon(\omega) \), \( \sigma(\omega) \) as well as \( n(\omega) \) contain equivalent information about the optical and electronic properties of a medium.

When describing the behaviour of charge carriers, as is done in chapter 6, we opt for using the complex conductivity, \( \sigma(\omega) \), since for free carriers the conductivity is predominantly real. This choice is, however, rather arbitrary.

### 1.2.4 Classical models for free and bound charges

If we only take into account the electrons in the conduction band of an isotropic crystalline material and assume the charge density is low enough for the interaction of the carriers with one another to be described by a "mean field" [23], we can treat the electrons in the conduction band as being electrons in a free electron gas with an effective mass \( m^* \) (see section 1.2.1). Now when assuming that the only interaction that these quasi-particles (moving with a drift velocity \( v_d \)) have with the solid is due to elastic scattering from e. g. defect sites, characterised by an average time between two scattering events \( \tau_s \), the motion of an electron can be expressed as follows:
\[ \frac{\partial v_d(t)}{\partial t} + \frac{v_d(t)}{\tau_s} = -\frac{e}{m^*} E(t) \] (1.17)

This simple classical description of the motion of charges through a solid is called the Drude model. In the case of an oscillating field, \( E = E_0 e^{-i\omega t} \), it leads to the following expression for the frequency dependent mobility:
\[ \mu(\omega) = \frac{v_d}{E} = \frac{e \tau_s}{m^*} \frac{1}{1 - i\omega \tau_s}. \] (1.18)
CHAPTER 1

Using expression 1.11, where \( j = -eN\mathbf{v}_d \) (\( N \) being the electron density), the conductivity in the Drude approximation is:

\[
\sigma(\omega) = Ne\mu(\omega) = \frac{\varepsilon_0 \omega_p^2 \tau_s}{1 - i\omega\tau_s} \quad \text{with} \quad \omega_p^2 = \frac{e^2 N}{\varepsilon_0 m^*}
\]

(1.19)

being the squared plasmon frequency of the medium, the frequency of the charge density waves in the case that the charges are "cold".

In the other extreme, when assuming all charges are bound, we can describe the system by a density \( N \) of independent harmonic oscillators. A displacement \( u \) from the equilibrium position will induce a dipole moment \( p = e u \). Note that for normal mode vibrations of a molecule, the dipole moment should be described with \( p = e^* u \), where \( e^* \) is the effective ionic charge, which is not equal to the elementary charge. When an external field \( E(t) \) is applied, the equation of motion is:

\[
\frac{\partial^2}{\partial t^2} u(t) + \gamma \frac{\partial}{\partial t} u(t) = -\omega_0^2 u(t) - \frac{e}{m^*} E(t),
\]

(1.20)

with \( \omega_0 \) being the eigenfrequency of the system and \( \gamma \) the damping constant. Again we consider the field to be due to a planar E-M wave with frequency \( \omega \) and we Fourier transform equation 1.20:

\[
u(\omega) = -\frac{e}{m^*} E(\omega).
\]

(1.21)

The polarization \( P = D - \varepsilon_0 E \) of a material can be written in terms of the susceptibility \( \chi(\omega) = \epsilon(\omega) \):

\[
P(\omega) = \epsilon_0 \chi(\omega) E(\omega) = (\epsilon(\omega) - \epsilon_0) E(\omega).
\]

(1.22)

For a concentration \( N \) of harmonic oscillators in an electric field \( E(\omega) \), the polarization can be written as:

\[
P(\omega) = Neu(\omega) + \epsilon_0 N\alpha E(\omega).
\]

(1.23)

When substituting equation 1.23 into equation 1.22, the following expression for the dielectric function is obtained:

\[
\epsilon(\omega) = 1 + N\alpha + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}.
\]

(1.24)

with \( \omega_p \) being the plasmon frequency introduced in equation 1.19. In this case the conductivity \( (\sigma(\omega) = -i\omega\epsilon_0 \epsilon(\omega)) \) is entirely imaginary for \( \omega \to 0 \) and \( \omega \to \infty \). The real part of the conductivity is peaked around \( \omega = \omega_0 \).

1.2.5 Charge transport in soft matter

In the previous section vibrational aspects and deformations of the lattice structure were not taken into account and charges were seen as either bound or free particles that scatter randomly. Thermal motions do play a role in describing the behaviour of free-like charges: an increase in temperature leads to a decrease in mobility of a metal due to a higher
scattering chance of the charges from phonons. However already in 1933 Landau [24]
realised that also at low temperatures in polarisable materials these deformations play
an important role in the charge transport; the creation of a charge deforms the lattice
around the charge in such a way that the electron or hole finds itself at the bottom of
a potential well which travels along with it. As a result the charge is less mobile. The
quasi-particle consisting of the charge and the cloud of phonons accompanying it is called
a polaron. For a large polaron, the deformation is extended over many lattice sites [25]
so the medium can be seen as a polarisable continuum. In the case of a small polaron,
the spatial extent of the electron or hole in the potential well is smaller than, or equal
to, a single lattice parameter [26] and the resulting potential well is deep enough for the
carrier to find itself in a “bound” state. For such a small polaron the transfer integral (the
amount of wavefunction overlap of two neighbouring electronic orbitals) to move from one
site to the other is orders of magnitude smaller than in the case of the charge being free,
since it also involves the transfer of the displacement of the nuclei.

In the previous paragraph the interplay between deformations of the lattice structure
of a crystalline material and the charge-carriers is roughly summarized. The structure of
charged organic molecules (cations or anions) differs from that of the neutral molecule [27].
For small molecules the excess charge is spread over the molecule and the structure is
deformed [28]. In the case of polymers, the charge is localized on the chain and the
resulting deformation can be local. Su, Schieffer and Heeger [29] showed that in these
polymers random distortions of the bond lengths by vibrational motions result in large
changes in the transfer integrals between sites on the chain. This is the key factor to
adequately describe the charge transport along the chain.

The vibrational structure of pentacene is more complicated than those of classic semi-
conductors, since besides the lattice vibrations, the molecules have internal vibrational
modes. Previous studies have shown that both types of vibrational modes do couple with
the charges [6, 28], which as a result makes it more difficult to adequately describe the
full interaction between the charges and the vibrations. Several models to describe charge
transport in these materials have been proposed, ranging from small polaron models [14]
to a model based on the influence of thermal motions on the size of the electronic cou-
pling between neighbouring molecules [15] (similar to the SSH model [29] for conjugated
polymers mentioned above).

1.3 The structural properties of pentacene

Pentacene (C_{22}H_{14}) (see figure 1.3) is commercially available in powder form (for instance
at Sigma Aldrich) and can be further purified by several sublimation cycles in vacuum.
Thin films of this material are obtained by organic molecular beam epitaxy (OMBE) in
UHV. Single crystals can be obtained from solution or using physical vapour transport [30].

Over the last decades several structures for single crystals of pentacene have been
reported. The first study on the structure of single crystals of pentacene dates from
1961 by Campbell, Robertson and Trotter [31]. Their crystals were grown from solution
in contrast to the more recent publications [32–34] where the pentacene crystals were
grown using physical vapour transport [30]. Campbell proposed that pentacene grows
in a triclinic layered structure with a herringbone arrangement in the layers, having two
equivalent molecules in a unit cell (which is clear from the a-b plane shown in figure 1.4).
However his choice of unit-cell differed from others by choosing the c-axis to be along the long molecular axis (the y-direction depicted in figure 1.3) instead of the c-axis shown in figure 1.5. An overview of the various structures (all obtained using X-ray diffraction) is given in table 1.3. Besides bond lengths and bond angles also the layer periodicity $d(100)$ is given, the normal distance between two rows (as depicted in 1.5). This parameter is often used (especially for thin layers) to identify the different polymorphs. Obviously the structures observed by Mattheus [32], Siegrist [33] and Holmes [34] for vapour grown crystals are almost identical, whereas the structure obtained by Campbell et al. [31] for crystals grown from solution differ. In the scope of this thesis the values determined by Mattheus et al. [32] will be used to describe the crystalline pentacene lattice.

Table 1.1: The unit cell parameters of crystalline pentacene according to [31–34].

<table>
<thead>
<tr>
<th>Author growth</th>
<th>Mattheus</th>
<th>Siegrist</th>
<th>Holmes</th>
<th>Campbell</th>
<th>Campbell$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vapour</td>
<td>vapour</td>
<td>vapour</td>
<td>solution</td>
<td>solution</td>
</tr>
<tr>
<td>a</td>
<td>6.266</td>
<td>6.253</td>
<td>6.275</td>
<td>6.06</td>
<td>7.90</td>
</tr>
<tr>
<td>b</td>
<td>7.775</td>
<td>7.786</td>
<td>7.714</td>
<td>7.90</td>
<td>6.06</td>
</tr>
<tr>
<td>c</td>
<td>14.53</td>
<td>14.51</td>
<td>14.44</td>
<td>14.88</td>
<td>16.01</td>
</tr>
<tr>
<td>α</td>
<td>76.48</td>
<td>76.65</td>
<td>76.75</td>
<td>96.74</td>
<td>101.9</td>
</tr>
<tr>
<td>β</td>
<td>87.68</td>
<td>87.50</td>
<td>88.01</td>
<td>100.54</td>
<td>112.6</td>
</tr>
<tr>
<td>γ</td>
<td>84.69</td>
<td>84.6</td>
<td>84.52</td>
<td>94.2</td>
<td>85.8</td>
</tr>
<tr>
<td>$d(100)$</td>
<td>14.12</td>
<td>14.12</td>
<td>14.06</td>
<td>14.52</td>
<td>14.52</td>
</tr>
</tbody>
</table>

The structure for the thin pentacene films varies with substrate, growth temperature and layer thickness and as a result numerous morphologies have been reported. This will not be discussed here, but will be dealt with in chapter 4.

1.4 Contents of this thesis

This thesis deals with the vibrational properties of pentacene and the influence they have on the electronic properties of the material. In chapter 2 some (previously reported) theoretical concepts are discussed that are important to this work: calculations of the band structure of crystalline pentacene by Tiago et al. [35], the vibrational structure of an isolated molecule determined by DFT methods and the coupling of these modes with a charge and the transport model for oligoacenes suggested by Troisi & Orlandi [15, 36]. Chapter 3 explains the basic principles and experimental details of high resolution electron
General Introduction

Figure 1.4: Sketch of the a-b plane of crystalline pentacene showing a single unit cell.

Figure 1.5: The structure of crystalline pentacene displayed in the [110] direction, showing a unit cell with lattice parameter c as defined by Mattheus et al. [32].
energy loss spectroscopy (HREELS). Here the concept of dipole scattering receives the most attention, since it is of relevance for the data presented in chapter 4 and 5. In chapter 4 the vibrational structure of pentacene thin films deposited on either a silver (111) or a gold (100) substrate is discussed and the effect of the layer thickness on the observed vibrational modes is studied in depth with HREELS. This technique is also used in chapter 5 to study the electronic properties. The observed electronic transitions in the HREELS spectra are modeled by taking into account the charge-vibrational coupling calculated in chapter 2. Apart from that, interface states and the presence of excitonic levels as function of layer thickness form the main interest of this chapter. Chapter 6 and 7 deal with the intrinsic charge transport in these materials, studied by terahertz time domain spectroscopy (THz-TDS). This optical technique is described in chapter 6 and chapter 7 shows how it can be used to determine the mechanism of transport in single crystals of pentacene. The results show that indeed vibrational properties have an influence on the transient conductivity. Furthermore, the dynamics of optically created carriers are studied and the effect that a higher charge density has on both the dynamics and the size of the conduction signal. These results for pentacene are compared with another oligoacene material, rubrene.
General Introduction

References


Chapter 2

Theoretical aspects

2.1 Introduction

In this chapter an overview will be given of some theoretical concepts that will be used throughout this thesis. The sections 2.2 and 2.4 presented here involve the work of others, but since their results were very valuable and essential for the interpretation of the experimental data in this thesis, we decided to instead of referring to literature, give an overview of the most relevant results. In section 2.2 the results of Tiago et al. [1] are discussed. Their GW calculations [2] give the full band structure for crystalline pentacene and by solving the Beth-Salpeter equations the energies of optical excitations, including excitons, can be determined as well. For section 2.3 density functional theory calculations for a single isolated molecule of pentacene were performed to obtain information on the intramolecular vibrations of this molecule. These results were used to calculate the contributions to the relaxation energy of each individual vibrational mode. This is of importance to be able to model the vibronic fine structure of electronic excitations in the pentacene. In the last section the charge transport model developed by Troisi and Orlandi [3,4] is introduced. This model describes the transport in oligoacene materials by the large influence low-energetic modes have on the size of the electronic coupling between neighbouring molecules.

2.2 Band structure from ab initio methods

The overview here is completely based on the work of Tiago et al. published in reference [1]. In this paper two different single crystalline structures of pentacene are discussed. The structure by Campbell grown from solution, which will be referred to as structure S, and the one of Siegrist [5] (almost equivalent to the structure reported by Mattheus et al. [6]) grown from vapour deposition, which will be called structure V. The ground state configuration has been determined by density functional theory (DFT) using the general gradient approximation (GGA) for the exchange potential. Common DFT methods hugely underestimate the values for the band gap. Hence, to obtain the band structure of pentacene the quasi-particle energies of electrons and holes were determined using a GW approximation. For both structure S and V the obtained band structure is shown in reference [1]. The quasiparticle energy gap is 2.2 eV for structure S and 1.9 eV for structure V.
To obtain the optical transitions in the material, the Bethe-Salpeter equation [7] was used, which includes the electron hole correlations. The resulting imaginary part of the dielectric function for both structures is shown in figure 2.1. Although this method does include the dynamical screening in the solid, electron-phonon interactions are not taken into account. In the a- and b-direction excitonic transitions below the quasiparticle gap are visible, which in contrast to the lowest triplet Frenkel exciton (which is not visible in an optical absorption spectrum), are transitions to charge transfer states [1]. Excitations in the c direction only significantly contribute to the spectrum at energies higher than 4.0 eV.

![Figure 2.1: The imaginary part of the dielectric function for both the S and V crystalline structure of pentacene (for the three independent polarisation directions a, b and c), calculated with ab initio methods by Tiago et al. [1] (unpublished results provided by M. L. Tiago).](image)

### 2.3 The vibrational structure of pentacene, using density functional theory

#### 2.3.1 The vibrational structure of an isolated pentacene molecule

In this work the vibrational structure of films of pentacene on metallic surfaces will be studied. To be able to judge the interaction of the surface with the pentacene or of the pentacene molecules with one another, one should know the energies of the normal modes of one isolated pentacene molecule. To obtain the vibrational modes for a single
pentacene molecule, Gaussian03 has been used, a software package that employs density functional theory (DFT) to calculate the electronic structure of molecules. In DFT, the exchange energy (the result of overlapping electron wave functions) and correlation effects (which account for the Coulomb interaction of electrons) are expressed by approximated exchange-correlation functionals. In this work a B3LYP functional is used, which is a hybrid functional, combining portions of the exact exchange interaction from the Hartree-Fock [8] method with the exchange and correlation approximations from the Becke [9] and VWN functional [10]. The basis set of wave functions has to be chosen sufficiently large for the energy and bond lengths and angles to converge. Two different basis sets were used, 6-31G(d) and 6-311+G(d,p). The 6-31G(d) exists of 15 functions for the C-atoms (including the polarized d-functions) and 2 functions for the hydrogen atoms. The 6-311+G(d,p) set is far more extended, having 19 functions for the C-atoms and 5 for the hydrogen atoms (including the p functions). When optimising the geometry of pentacene using both basis sets, the obtained bond lengths and bond angles differ by only 0.2%. As a result one would normally assume that the 6-31G(d) basis set is sufficient for calculations on this system. However, the resulting differences in the energies of the normal modes are larger and the values obtained with the 6-31G(d) can deviate up to 2% from the values obtained with 6-311+G(d,p). A lot of the reported theoretical work on pentacene has been done using the smaller basis set [11].

The pentacene molecule contains 36 atoms and therefore it has $3N - 6 = 102$ normal modes apart from the translational and rotational modes. Since it belongs to the $D_{2h}$ space group and therefore has 43 optically active (belonging to the symmetric representations $B_{1u}$, $B_{2u}$ and $B_{3u}$), 51 Raman modes ($A_g$, $B_{1g}$, $B_{2g}$ and $B_{3g}$) and 8 silent modes ($A_u$). The calculated intensities of the optically active modes calculated with the 6-31G(d) and

![Figure 2.2: IR intensities for the normal modes of an isolated molecule of pentacene calculated by Gaussian03 B3LYP using a 6-31G(d) (black line) and 6-311+G(d,p) basis set (grey line). The graph does not show the C-H stretch modes, which have an energy of \( \sim 3000 \text{ cm}^{-1} \).](image)
6-311+G(d,p) basis sets are shown in figure 2.2. The rather large differences between the two spectra do again show the importance of using the larger basis set.

2.3.2 The coupling of the charges with the intramolecular modes

Throughout this thesis the interplay between vibrational modes and charges play an important role. This paragraph shows a quantitative theoretical description of electron-phonon coupling and for the case of pentacene the coupling between intramolecular vibrational modes and holes are calculated.

For a crystalline solid the full Hamiltonian in the second quantized notation is as follows:

\[ H = H^0_{el} + H^0_{ph} + H^1 \]

\[ H^0_{el} = \sum_k \epsilon_k c^+_k c_k \]

\[ H^0_{ph} = \sum_{q,j} \hbar \omega_{qj} \left( a^+_q a_q + \frac{1}{2} \right) \]

\[ H^1 = \frac{1}{2} \sum_{k,k'} V_{k,k'} c^+_k c_{k'} \]

\( H^0_{el} \) describes the electron density of states with \( \epsilon_k \) being the energy and \( c^+_k \) and \( c_k \) the annihilation and creation operators for the electron in the state \( k \). The vibrations are described by \( H^0_{ph} \) with \( \omega_{qj} \) the frequency of a mode with wave vector transfer \( q \) and phonon branch \( j \) and \( a^+_q \) and \( a_q \) are the phonon annihilation and creation operators. \( H^1 \) represents the perturbations to the zeroth order Hamiltonian due to a (dynamic) potential \( V_{k,k'} \). This Hamiltonian is suitable for describing the electronic and vibrational properties of for instance metals and classic semiconductors, covalent crystalline materials having a basis consisting of only one or two atoms. In the case of having an organic molecular crystal, the situation is more complicated, since both intermolecular and intramolecular vibrational modes are present and the on-site (in this case at one specific molecule) Coulomb interaction is also a spatial function within the molecule itself. Therefore it is easier to write the Hamiltonian in the tight-binding approximation, taking each molecule as a separate moiety with local electronic overlaps which have a small overlap with the electronic waves from neighbouring molecules. In that case the full Hamiltonian can be written as:

\[ H = H_{el} + H_{ph} + H_{int} \]

\[ H_{el} = \sum_m \epsilon_m^0 c^+_m c_m + \sum_{mn} t^0_{mn} c^+_m c_n \]

\[ H_{ph} = \sum_{q,j} \hbar \omega_{qj} \left( a^+_q a_q + \frac{1}{2} \right) \]

\[ H_{int} = \sum_{m,n} \sum_{q,j} g_{mn}(q,j)(a^+_q + a_q)c^+_n c_m \]
where \( m \) and \( n \) are integers which refer to sites of the molecules, \( \epsilon^0_m \) is the on-site energy at site \( m \) (which includes the influence of the static Coulomb potential) and \( t^0_{mn} \) is the transfer integral, the amount of overlap between two electronic orbitals from different sites (note that as a result this also includes the Coulomb terms, but not the modulation of the transfer integral by the vibrational modes). The electron-phonon \( \mathcal{H}_{\text{int}} \) interaction changes the on-site energies for \( m = n \) and the transfer integral in the case \( m \neq n \). In this definition \( g_{mn}(q,j) \) are the electron-phonon matrix elements.

For describing the electron-phonon interaction the rigid body approximation can be used, which basically states that because of the weak van der Waals bonds between molecules, one can treat the lattice phonon modes while keeping the intramolecular geometries frozen [12]. Calculations have shown that intra- and intermolecular modes do couple among one another as well. This coupling however only involves the low energy intramolecular modes and as will be shown in chapter 7, these are not the dominating modes in the coupling with the charges.

We now return to the general Hamiltonian 2.2. Taking the lattice modes into account, assuming that the molecular moieties are rigid (and thereby basically ending up with a model system equal to those for classic semiconductors), and using the periodicity of the potential it is possible to write \( \mathcal{H}^1 \) in terms of the lattice parameters and the displacement \( \mathbf{u}_i \) of the molecule from its equilibrium position:

\[
\mathcal{H}^1 = \sum_{k,k',i} \langle k | V(\mathbf{r} - \mathbf{R}_i)| k' \rangle c_k^\dagger c_{k'}^\dagger e^{i(k-k') \cdot \mathbf{R}_i} V_{k-k'} c_{k'} c_k,
\]

(2.3)

with \( \mathbf{R}_i = \mathbf{R}_i^0 + \mathbf{u}_i \) being the location of the \( i \)th molecule. Since \( \mathbf{u}_i \ll \mathbf{R}_i^0 \) one can rewrite 2.3 using the following Taylor expansion:

\[
e^{i(k-k') \cdot \mathbf{R}_i^0} = e^{i(k-k) \mathbf{R}_i^0} [1 + i(k - k) \cdot \mathbf{u}_i],
\]

(2.4)

where \( \mathbf{u}_i \) can be written as a linear combination of the displacement vectors from the normal modes:

\[
e^{i(k-k) \cdot \mathbf{R}_i^0} = e^{i(k-k) \mathbf{R}_i^0} \left[ 1 + iN^{-1/2} (k' - k) \cdot \sum_q e^{i\mathbf{q} \cdot \mathbf{R}_i^0} \mathbf{u}_q \right]
\]

(2.5)

When substituting this last expression into equation 2.3, one can split the Hamiltonian into the static Coulomb part (for both the far field and on-site interaction) and the electron-phonon interaction:

\[
\mathcal{H}^1 = \sum_{k,k',i} e^{i(k-k) \mathbf{R}_i^0} V_{k-k'} c_{k'}^\dagger c_k^\dagger + iN^{-1/2} \sum_{k,k',i,q} e^{i(k-k+q) \mathbf{R}_i^0} (k' - k) \cdot \mathbf{u}_q c_{k'}^\dagger c_k + \sum_{k,g} V_{g} c_k^\dagger c_k,
\]

(2.6)

where \( \mathbf{g} \) is a lattice vector. Clearly the first term describes the static periodic potential in a system of size \( N \) and therefore it represents the Bloch term, which in the tight-binding
notation of equation 2.3 is embedded in the term $\mathcal{H}_{el}$. The second term represents the electron-phonon interaction:

$$\mathcal{H}^1 = \mathcal{H}_{Bloch}^1 + \mathcal{H}_{int}^1 \quad (2.7)$$

Note that expression 2.7 is written out for the case that $q$ can take on any value $k' - k + g$. When being limited to the first Brillouin zone $q = k - k'$ can be substituted into the expression. The displacements vectors $u_q$ can be written in terms of the phonon annihilation and creation operators $[13]$:  

$$u_q \cdot e_j = \sqrt{\frac{\hbar}{2M\omega_{qj}}} (a_{qj}^\dagger + a_{qj}), \quad (2.8)$$

with $e_j$ being the polarisation direction of a phonon mode from branch $j$ and $M$ the (reduced) mass of one molecular unit. In an isotropic material like for instance Si, this simply implies that only the longitudinally polarized phonons play a role, since for all transversely polarized modes $u_q \cdot s_q = 0$. As could be seen from the different $\epsilon_2$ spectra for the three polarisation directions 2.1, pentacene is far from isotropic and its phonon spectrum is not assumed to be isotropic either. Substituting this into the definition of $\mathcal{H}_{int}$ of equation 2.3 leads to the following expression for the electron-phonon matrix elements:

$$g_{qj} = \sum_q i \sqrt{\frac{\hbar N}{2M\omega_q}} V_q (\mathbf{q} \cdot \mathbf{e}_j). \quad (2.9)$$

The total dimensionless electron-phonon coupling constant for such a system is defined as

$$\lambda_{e-ph} = \sum_{q,j} \frac{2|g_{qj}|^2}{\hbar \omega_{q,j}}, \quad (2.10)$$

which by implementing equation 2.9 leads to:

$$\lambda_{e-ph} = \sum_{q,j} \frac{N}{M\omega_{q,j}^2} |\mathbf{q} \cdot \mathbf{e}_j|^2 V_q^2. \quad (2.11)$$

The next paragraph will show that in oligoacenes the coupling between these lattice vibrations and the charges indeed play a very important role in the charge transport. Although the intramolecular modes do not play the key role in the carrier transport in crystalline pentacene [3], they do contribute to the vibronic fine structure (a set of simultaneous electronic and vibrational transitions) and are actually more important than the intermolecular modes when it comes to resolving spectra of electronic transitions. The energy of intramolecular modes is in the order of 0.1 eV and of the intermolecular modes is approximately 5 meV. Typical values of the FWHM of electronic transitions in the HREELS spectra of chapter 5 are also 5 meV and as a result the relatively small vibronic contributions from intramolecular modes can be resolved whereas those of lattice phonons cannot.

As a result, in order to be able to interpret the form of electronic spectra of oligoacenes, it is important to obtain values for the coupling of these intramolecular modes with the carriers. It is extremely difficult to derive these coupling constants directly from the
system’s Hamiltonian as has just been done for the lattice phonons, since the rigid body approximation is no longer valid and one cannot use the periodicity of the vibrations itself anymore. Instead we chose to only take the local electron-phonon coupling into account and assume weak electronic coupling ($t_{mn} = 0$), resulting in being left with only the diagonal terms of equation 2.3. The Hamiltonian can as a result be diagonalised using the Lee-Low-Pines transformation and written in a more compact form [12,14]:

$$H = \sum_m \epsilon_{mm} \tilde{c}_m^\dagger \tilde{c}_m + \sum_{q,j} \hbar \omega_{q,j}(\tilde{a}_{q,j}^\dagger \tilde{a}_{q,j} + \frac{1}{2}) \quad (2.12)$$

with

$$\epsilon_{mm} = \epsilon_0^{mm} - \sum_{q,j} \hbar \omega_{q,j} g_m(q,j)^2$$

and the transformed operators $\tilde{c}_m$, $\tilde{c}_m^\dagger$, $\tilde{a}_{q,j}$ and $\tilde{a}_{q,j}^\dagger$ are defined in reference [14]. Such an approach which only involves local contributions ($m = n$) is the standard Holstein model for describing local polarons. The term $\sum_{q,j} \hbar \omega_{q,j} g_m(q,j)^2$ is in that case referred to as the polaron binding energy ($E_{pb}$), the energy resulting from the deformation of the molecule due to the presence of a charge.

The on-site energy $E_{mm}$ can be written in a Taylor expansion of the normal mode coordinates $Q(j)$, which in the harmonic approximation gives:

$$E_{mm}(Q) = \epsilon_0^{mm} + \sum_j \left( \frac{\partial \epsilon_{mm}}{\partial Q_m(j)} \right) Q_m(j) + \sum_j \frac{1}{2} M_j \omega_j^2 Q_m(j)^2 \quad (2.13)$$

with $M_j$ being the reduced mass of the system. If we now assume that the normal modes for a charged molecule differ little from those of a neutral molecule we can drop the subscript $m$. Similar to the phonon displacement vectors (see equation 2.8 and ref. [13]) the normal mode vectors can also be written in terms of phonon creation and annihilation operators ($\tilde{a}_{q,j}$ and $\tilde{a}_{q,j}^\dagger$) and when using equations 2.13 and 2.13 the polaron binding energy can be written as follows:

$$E_{pb} = \sum_j \frac{1}{2 M_j \omega_j^2} \left( \frac{\partial \epsilon_{mm}}{\partial Q_m(j)} \right)^2 \quad (2.14)$$

This quantity is similar to the relaxation energy $\lambda_{rel}$ of a molecule when it transfers from a neutral state to a charged state as is depicted in figure 2.3 [12]. For the case of pentacene the amount a specific normal mode contributes to the relaxation energy can be straightforwardly calculated using DFT methods: as shown in the previous paragraph, both the normal modes and the optimised structure of the pentacene molecule can be determined with DFT calculations using Gaussian03. By calculating the optimal structure for both neutral molecule and the anion or cation, one can determine the displacement-vector $m_i(R_i - R_i^0)$ of each nucleus (with $m_i$ being the mass of nucleus $i$) in the case of an electronic transition. By taking the scalar product of this set of vectors with the normal mode vector of the $j^{th}$ mode, $Q_j$, one can determine the relaxation energy for each normal mode:

$$\lambda_j = \frac{k_j}{2 M_j^2} \left[ \sum_i m_i(R_i - R_i^0) \cdot \dot{Q}_{i,j} \right]^2 \quad (2.15)$$
Figure 2.3: Schematic representation of a molecule going from a neutral state (energy surface 1) to a cation state (energy surface 2). This can be seen as a direct transition (i) followed by a geometric relaxation (ii) with wavevector transfer $\Delta Q$ and energy $\lambda^{(1)}_{rel}$. In the case of going from the charged state to the neutral state the relaxation energy is $\lambda^{(2)}_{rel}$. If the vibrational structure of the charged molecule is similar to that of the neutral molecule, $\lambda^{(1)}_{rel} = \lambda^{(2)}_{rel}$.

where $k_j$ is the force constant of the $j^{th}$ mode ($k_j = M_j \omega_j^2$).

The result for the case of the neutral to cation transition is shown in table 2.1. The table only shows those modes that contribute to the relaxation energy. Since both the neutral ground state and the cation and anion states belong to the same symmetry point group $D_{2h}$, in the case of pentacene the vibrational modes that contribute are $A_g$ modes, fully symmetric stretch modes. The Huang-Rhys factors that describe the strength of the charge vibrational coupling of these modes are defined as

$$S_j = \frac{\lambda_j}{\hbar \omega_j}$$

and are also displayed in table 2.1 for the case of going from a neutral to a cation state.

Obviously, as one would expect for a $\pi$-conjugated system, the contributions to the relaxation energy from C-C stretch modes (from 1000 to 1600 cm$^{-1}$) are the highest. Similar work has been done by Coropceanu et al. [15], who used a 6-31G(d,p) basis set instead of the 6-31+G(d,p) basis set in this work. There are small differences (up to 4%) in both the energies of the modes as the relaxation energy itself, but when using this data to for instance calculate the vibronic coupling of electronic transitions (as will be done in section 5.2), the differences in the resulting spectra are negligible.

2.4 Modulation of the transfer integral by low energetic phonon modes

Crystalline organic semiconductors exhibit charge mobilities that decrease with temperature [16–18]. In analogy to inorganic semiconductors, this has been interpreted as an indication of delocalized charge carriers and a 'band-like' transport mechanism [19, 20].
Table 2.1: The relaxation energies and Huang-Rhys factors for all $A_g$ modes of a single pentacene molecule transferring from a neutral to cation state, obtained by ab initio methods.

<table>
<thead>
<tr>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$\lambda_j^{(1)}$ (meV)</th>
<th>$S_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>263</td>
<td>1.0</td>
<td>0.031</td>
</tr>
<tr>
<td>616</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>646</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>741</td>
<td>0.1</td>
<td>0.001</td>
</tr>
<tr>
<td>773</td>
<td>0.2</td>
<td>0.002</td>
</tr>
<tr>
<td>990</td>
<td>0.5</td>
<td>0.004</td>
</tr>
<tr>
<td>1150</td>
<td>2.8</td>
<td>0.019</td>
</tr>
<tr>
<td>1172</td>
<td>7.4</td>
<td>0.049</td>
</tr>
<tr>
<td>1293</td>
<td>0.7</td>
<td>0.004</td>
</tr>
<tr>
<td>1370</td>
<td>0.4</td>
<td>0.002</td>
</tr>
<tr>
<td>1391</td>
<td>16.8</td>
<td>0.095</td>
</tr>
<tr>
<td>1491</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>1512</td>
<td>9.9</td>
<td>0.051</td>
</tr>
<tr>
<td>1529</td>
<td>6.7</td>
<td>0.034</td>
</tr>
<tr>
<td>3157</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>3162</td>
<td>0.1</td>
<td>0.000</td>
</tr>
<tr>
<td>3165</td>
<td>0.1</td>
<td>0.000</td>
</tr>
<tr>
<td>3189</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>$\lambda_{\text{rel}}$:</td>
<td></td>
<td>47</td>
</tr>
</tbody>
</table>

Theoretical models based on polaronic band conduction [21] indeed give a good qualitative description of the ‘band-like’ mobility of the charge carrier in oligoacenes, but the factors determining the absolute charge mobility remain unknown. However, an analysis of the high temperature mobility has indicated that the mean free path of charge carriers is of the same magnitude as the intermolecular distance [22] and it is not clear why the signature of delocalized band-like transport persists at temperatures where the mean free path is smaller than the intermolecular distances. Only recently Troisi and Orlandi [3] succeeded to overcome this discrepancy in the description of charge transfer in oligoacenes by proposing a model which stresses the influence of thermal motions on the electronic overlap.

As mentioned in the introduction of this thesis the moieties of an organic crystal are held together by weak van der Waals forces. Therefore materials like pentacene are much softer than the traditional semiconductors. Since the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of oligoacenes have rather complex shapes, the transfer integral, the electronic overlap, of these orbitals on neighbouring molecules is highly dependent on molecular displacements. Considering also the ‘softness’ of these organic crystals, it is therefore likely that the coupling of the carriers with the intermolecular vibrations plays a key role in the description of the charge carrier dynamics.

By using MD simulations for a 3x2x2 supercell in a thermal bath with classically treated phonon modes, Troisi and Orlandi evaluated the electronic coupling, $V_{ij}$ between both the HOMO and LUMO orbitals of two neighbouring molecules after every 30 fs (a procedure which they have done for all three different type of nearest neighbours in the
The described modulation of the electronic coupling of a pair of neighbouring molecules was shown to be highly uncorrelated with other pairs and therefore equivalent to the effect of disorder in the electronic structure, which leads to localization of the wave functions. This localization makes it impossible to treat the carriers in these materials with a normal band transport model. Instead Troisi and Orlandi introduced a simple one dimensional charge transport model which includes the thermal electronic disorder described in the previous paragraph. Their model system exists of a single array of planar conjugated molecules as shown in figure 2.5. Each of these molecules $j$ have only one single orbital $|j\rangle$, a mass $m$ and a displacement $u_j$ due to thermal motions. As mentioned before, this displacement modulates the transfer integral between two neighbouring orbitals $|j\rangle$ and $|j + 1\rangle$, modelled by a term $\alpha(u_{j+1} - u_j)$, with $\alpha$ being the electron-phonon coupling constant. This results, when treating the electrons quantum mechanically but the low-
energetic phonons classically, in the following Hamiltonian for this system:

\[
H = \sum_j (-V + \alpha (u_{j+1} - u_j))(|j\rangle\langle j+1| + |j+1\rangle\langle j|) + \sum_j \frac{1}{2}m u_j^2 + \sum_j \frac{1}{2}m\omega^2 u_j^2, \quad (2.17)
\]

with \(\omega\) being the frequency of the dispersionless optical phonon modes. By choosing \(L\) to be 4 Å, \(\omega = 40\) cm\(^{-1}\), \(m\) being the mass of a single pentacene molecule and using the MD calculations of reference [4] to estimate \(V\) and \(\alpha\), Troisi and Orlandi could determine the mobility as a function of temperature for their model system. Their model showed to be in close agreement with the power law dependence \(\mu(T) \sim T^{-n}\), which is usually considered to be a sign of band transport and their values for the mobility at room temperature of \(\sim 3\) cm\(^2\)s\(^{-1}\)V\(^{-1}\) are in good agreement with experimental findings [17].
References


Chapter 3

High Resolution Electron Energy Loss Spectroscopy

3.1 Introduction

Since organic materials showed promising possibilities for devices, the specific physical properties of surfaces and interfaces of these materials have gained more and more interest over the last decades. Therefore the experimental technique of electron energy loss spectroscopy, developed by J. Hillier and R.F. Baker in 1944 [1], which enables one to study both vibrational and electronic transitions in the first molecular layers of the surface, regained new interest. Advances in vacuum technology and microscopic instrumentation hugely improved its resolution and sensitivity, making it possible to resolve both inter- and intramolecular vibrations and allows for clean surfaces to be prepared in a reproducible manner. Besides its surface sensitivity (which makes it suitable for studying adsorbates on a surface [2, 3]) High Resolution Electron Energy Loss Spectroscopy (HREELS) has more advantages over the common optical methods as IR and Raman spectroscopy: It can measure energy losses as a function of parallel momentum transfer (and thereby enabling us to study the dispersion of observed modes) [4]. Its various scattering mechanisms enable observing transitions that are not allowed in optical techniques [5]. Furthermore, HREELS is capable of measuring features over a broad range (5 meV to 5 eV).

In this chapter the basic principles of HREELS will be discussed together with the underlying scattering mechanisms of the electrons and their selection rules.

3.2 The experimental technique

In HREELS an electron with a specified kinetic energy ($E_i$) and wavevector ($k_i$) is directed on the surface of interest and the kinetic energy ($E_s$) and momentum ($k_s$) of the electron after it has scattered from the surface is detected (see figure 3.1). The electron can scatter elastically from the surface and the detected momentum and energy will not change. When the electron excites a quantized elementary surface excitation (with energy $\Delta E = \hbar \omega$), the detected electron’s energy will differ as well as its wavevector. Since there is a lack of translational symmetry in the direction normal to the surface there is no conservation of wavevector in the direction perpendicular to the surface ($k_{i\perp}$). The wavevector component parallel to the surface ($k_{i\parallel}$) will be conservred within a reciprocal lattice vector, resulting in
CHAPTER 3

the following formulas expressing the conservation of both energy and parallel momentum:

\[ E_s = E_i \pm \Delta E \]  \hspace{1cm} (3.1)

\[ k_{s\parallel} = k_{i\parallel} - Q_{\parallel} - G_{\parallel} \]  \hspace{1cm} (3.2)

with \( Q_{\parallel} \) being the parallel component of the wavevector transferred from the electron to the surface.

In practice of HREELS, a monochromatic beam of electrons with energy \( (E_i) \) is formed and focussed on the sample surface under an angle \( \vartheta_i \) with the normal of the surface. By detecting the amount of scattered electrons in the incident plane as a function of their energy loss under different scattering angles \( \vartheta_s \) (see figure 3.1) information about the energy and dispersion of a certain surface mode is obtained, since the parallel wavevector transfer can simply be deduced from the the energy loss, \( \Delta E \) and the angles \( \vartheta_i \) and \( \vartheta_s \):

\[ Q_{\parallel} = \frac{\sqrt{2mE_i}}{\hbar} \left[ \sin \vartheta_i - \sqrt{\left( 1 - \frac{\Delta E}{E_i} \right) \sin \vartheta_s} \right] \]  \hspace{1cm} (3.3)

The geometry in which \( \vartheta_i = \vartheta_s \) is commonly called the specular direction and there is no parallel wavevector transfer. In the off-specular direction \( (\vartheta_i \neq \vartheta_s) \) wavevector transfer to the sample takes place.

Spectra obtained in this manner display (for a set \( \vartheta_i \) and \( \vartheta_s \)) the amount of detected electrons per second (cts) as a function of their energy-loss. As a result the spectra show peaks at those energy-losses that match a specific mode which the electrons have excited in the sample. Most of the work in this study has been done in the specular geometry. The elastic peak of zero energy loss in that case is several orders of magnitude bigger than other observed features as shown in figure 3.2. Count rates up to 500 kcts/s.
have been measured for the elastic peak, but in the scope of this thesis absolute values of the intensity are not displayed. Instead for specular spectra all data sets have been normalized in a manner that the height of the elastic peak is equal. This makes it possible to more straightforwardly compare spectra, but is not necessarily a correct comparison in all cases. Since the relative intensities of the different modes in one specific spectrum are more important to us than their absolute intensities, those effects are of minor importance. In a similar manner as the electron excites a specific mode in the surface of our sample, it can also annihilate a mode and absorb its energy. Therefore, in figure 3.2 every loss peak that is observed on the right side of the elastic peak can also be seen on the left of it. At room temperature these ”gain” peaks are less in intensity than the ”loss” peaks, but for higher temperature their relative intensities grow. In chapter 3 and 4 only the ”loss” part of the spectrum will be considered.

### 3.3 Scattering mechanisms and selection rules

If one wants to correctly address the full interaction of an electron with vibrating atoms on the surface of a substrate, one would have to use a full microscopic quantum-mechanical description. It can however be described in more simple terms by distinguishing three limiting cases (although there are no sharp well defined boundaries between them): dipole scattering, impact scattering and negative ion resonance scattering. The last regime is not relevant for the work of this thesis, where the dipole scattering mechanism is the most important.

#### 3.3.1 Dipole scattering

The dipole scattering mechanism describes the interaction of the electron with a time dependent electric dipole field above the substrate [6]. The origin of this oscillating field is changes in the charge density at the surface of the sample due to for example phonons.
In the case of dipole scattering the interaction with the surface is not very strong and the highest intensity of the scattered electrons is found near the specular direction.

An electron near the surface of a solid (at \( z = 0 \)) experiences the charge fluctuations \( \rho_1(r, t) \) in the solid in the form of a Coulombic potential

\[
\Phi(r, t) = e \int_{z<0} d^3r' \rho_1(r', t) / |r - r'|.
\]

(3.4)

The Schrödinger equation for the free electron scattering from the electric field above the surface will have the following form:

\[
\left[ -\frac{\hbar^2 \nabla^2}{2m} + V_0(r) - e\Phi(r, t) \right] \Psi(r, t) = i\hbar \frac{\partial \Psi(r, t)}{\partial t},
\]

(3.5)

where \( V_0(r) \) is the potential experienced by an electron inside the solid itself. By using the jellium model for the electrons in the solid and assuming lateral translational symmetry of the surface and therefore Fourier transforming both potentials and wavefunctions in terms of parallel wavevector and energy, one can solve the Schrödinger equation by the use of Green's functions. This is a rather complex and tedious procedure and will not be further discussed. Obviously the 0th order solution of this equation will be the elastic zero-loss scattering of the electron. The 1st order solutions will give us four possible single loss events.

Without dealing with the equation itself, one can easily understand that those four solutions must be the ones represented in the sketches of figure 3.3. From the pictures one can see that case a and d involve large transfers of momentum for the electron to scatter from the surface, whereas in b and c the change in perpendicular momentum has been provided by elastic scattering from the surface itself. As mentioned before dipole scattering commonly involves small momentum transfers, so only case b and c will be taken into account. \( R_i \) and \( R_s \) are the reflection amplitude before and after scattering. Since for dipole scattering \( \Delta E/E \ll 1 \) and the angular deflections are small, we can assume \( R_i \simeq R_s \).

\[ \begin{array}{cc}
\text{a} & \text{b} \\
\text{c} & \text{d}
\end{array} \]

Figure 3.3: The various possible single scattering processes from the dynamic dipole field above the surface. The encircled crosses indicate the moments of excitation.
We now introduce the scattering cross section, the fraction of electrons that gets scattered within a certain energy window with width \( d\hbar \omega \) and into a certain angular window with width \( d\Omega \). The derivation of the scattering cross section from the Schrödinger equation is given in reference [7] and the result is the following:

\[
\frac{d^2S}{d\Omega(k_s)d\hbar\omega} = \frac{2m^2e^2v_i^4}{\pi\hbar^3\cos \vartheta_i} \left( \frac{k_s}{k_i} \right) \frac{|R_i|^2P(Q||,\omega)}{[\epsilon_\perp^2Q_i^2 + (\omega - v_i \cdot Q||)^2]^2}.
\]  

(3.6)

with \( P(Q||,\omega) \) being the function that describes the charge density fluctuations in the medium.

Figure 3.4: Sketch of the model used in equations 3.8 and 3.9: A semi-infinite substrate with complex dielectric function \( \epsilon_b(\omega) \) on which a surface layer is deposited with dielectric function constant \( \epsilon_s(\omega) \).

In this study we look at thin organic layers deposited on a metal substrate, which can be macroscopically modeled by a semi-infinite substrate with complex dielectric function \( \epsilon_b(\omega) \) on which a surface layer is deposited with dielectric function constant \( \epsilon_s(\omega) \) as is shown in figure 3.4. For convenience, instead of expressing the scattering cross section in terms of wavevectors (as was done in equation 3.6) it is, by using the geometry described in figure 3.1, expressed in terms of two angles, namely \( \phi \) and \( \xi \). \( \phi \) is the angular deviation from the specular direction in the plane of incidence, in other words \( \phi = \vartheta_i - \vartheta_s \). \( \xi \) is the azimuthal deviation from the specular beam (out of the plane of incidence). Now we can split up the scattering cross section into a contribution from the bulk substrate and the surface layer of thickness \( d \):

\[
\frac{d^2S}{d\Omega(k_s)d\hbar\omega} = \frac{d^2S_b}{d\Omega(k_s)d\hbar\omega} + \frac{d^2S_s}{d\Omega(k_s)d\hbar\omega}
\]

(3.7)

and replace the wavevectors by a geometrical description with \( \theta_E = \hbar\omega/2E_i \), which results in the contribution from the substrate,

\[
\frac{d^2S_b}{d\Omega(k_s)d\hbar\omega} = \frac{2|R_i|^2}{\pi^2\omega_0 E_i \cos \vartheta_i} (1 - 2\theta_E)^{1/2} \cdot \left[ \frac{\theta_E \sin \vartheta_i - \phi \cos \vartheta_i \cos \xi^2 + \theta_g^2 \sin^2 \xi}{[\theta^2 + \theta^2_g]^2} \right]^{1/2} \cdot \left[ 1 + \frac{1}{\exp(\hbar\omega/k_B T) - 1} \right] \operatorname{Im} \left( \frac{1}{1 + \epsilon_s(\omega)} \right),
\]

(3.8)

and from the surface layer,

\[
\frac{d^2S_s}{d\Omega(k_s)d\hbar\omega} = \frac{2|R_i|^2d}{\pi^2\omega_0 E_i \cos \vartheta_i} (1 - 2\theta_E)^{1/2} \cdot \left[ \frac{\theta_E \sin \vartheta_i - \phi \cos \vartheta_i \cos \xi^2 + \theta_g^2 \sin^2 \xi}{[\theta^2 + \theta^2_g]^2} \right]^{1/2} \cdot \left[ 1 + \frac{1}{\exp(\hbar\omega/k_B T) - 1} \right] \operatorname{Im} \left( \frac{-1}{\epsilon_s(\omega)} \cdot \frac{\epsilon_s^2(\omega) - \epsilon_s^2(\omega)}{[\epsilon_s(\omega) + 1]^2} \right).
\]

(3.9)
with \( a_0 \) being the Bohr radius. From this set of equations it is obvious that the scattering cross section for dipole scattering is proportional to the intensity of the specular reflected beam \( |R_i|^2 \) and that the cross section is inverse proportional to the energy of the electron beam, \( E_i \).

Furthermore, in the expression for the surface layer the dielectric constant of the bulk, \( \varepsilon_b(\omega) \), is present in the last term, which expresses the field originated by charge density fluctuations. This shows that charge fluctuations in the surface layer excite the substrate, so that the field seen by the electron is that produced by both the excitations in the absorbed surface layer as well as its image in the substrate. For thin absorbed layers and a substrate with a high dielectric constant, such as metals, this results in a dynamic dipole moment parallel to the surface being completely screened by the mirror dipole in the substrate. For a dipole moment normal to the surface, the electron approaching the surface still witnesses a fluctuating dipole field. This effect is known as the dipole selection rule and it can be easily understood by the sketches in figure 3.5.

![Figure 3.5: Sketch of the dipole selection rule. In the left image the mirror dipole in the metal substrate will cancel the dipole field created by the vibrational mode of the absorbed molecule. In the image on the right an electron above the surface will still experience a dipole field, since the mirror dipole in the metal does not cancel it, but in fact enhances it.](image)

To show the key features of dipole scattering, we simplify our system and instead of writing the Coulombic potential as a function of charge density fluctuations in both substrate and surface layer, we look at one single out of plane oscillating dipole (\( P(t) = pe^{−i\omega_0 t} \)) at a metallic surface and rewrite it in terms of parallel wave vector transfer:

\[
\Phi_{\text{dyn.dipole}}(r, t) = pe^{−i\omega_0 t} \int \frac{d^2Q_∥}{\pi} e^{iQ_∥r} e^{-Q_∥z}.
\]  

(3.10)

It is obvious that the field created by the oscillating dipole extends over a distance \( Q_∥^{-1} \) into the vacuum and as a result those surface excitations with long wavelengths reach the furthest into the vacuum. In the case that an electron approaches the surface along the normal and then gets reflected under an angle \( \vartheta_s \) with the normal, the time that the electron spends in the dipole field is then \( 2 \cdot Q_∥^{-1} / v_i \), which using \( Q_∥ = m \sin(\vartheta_s)v_i/\hbar \) and \( E_i = 1/2 \cdot mv_i^2 \) results in \( \Delta t \approx \hbar/E_i \vartheta_s \). So for large scattering angles the electron passes through the field so quickly that the possibility of exciting a vibrational mode is very small. On the other hand in the adiabatic limit the electron will not excite any mode either. The scattering cross section is thus at maximum for \( \Delta t \omega_0 \approx 1 \), resulting in an optimal scattering angle of \( \hbar \omega_0 / 2E_i \). Molecular vibrations have typical loss energies of 1000 cm\(^{-1} \) and in the next chapter beam energies of around 6 eV have been used, which
results in $0.6^\circ$ being the deflection angle with the highest intensity of scattered electrons from this particular modes. The critical detection angle of the detector is about $1^\circ$, so as a result measuring in specular modes will give strong contributions from dipole scattering.

### 3.3.2 Impact scattering

From the previous section it is clear that at large deflection angles one will hardly detect any electrons that have been scattered from the dipole field above the surface. These electrons that are scattered with large wave-vector transfer interact with the surface itself ($Q^{-1}_\parallel \approx 1 \text{ Å}$) instead of exciting a vibrational mode about 50 Å above the surface. Because of the short range interaction, a macroscopic description as was done for dipole scattering will not be correct in this case. Since the regime of impact scattering is potentially very interesting (the variation in both angle and energy can give detailed information about the geometry of the system [8]) theoreticians made an effort in microscopically modeling this short range interaction. Although at first sight the selection rules for impact scattering seem very useful, since they can provide you with information on the orientation of adsorbates, in the case of our study they are of little use, since pentacene can adsorb in different directions onto the metallic substrate and the spot-size of the beam will most probably be larger than the crystalline domains. Therefore this theory will not be discussed here. An overview of some key features and selection rules can be found in reference [9]. However, we would like to make one important note regarding the cross section for impact scattering: In contrast to dipole scattering where the scattering cross section decreases for increasing energy of the incoming electron, the excitation probability for impact scattering increases for increasing beam energy. Furthermore it is not a continuous function, but a set of diffraction peaks on a monotonous background. At energies of around 5 eV the scattering cross section for near specular dipole scattering is more than 100 times larger than for impact scattering.

### 3.4 The experimental setup

All spectroscopy and preparation of the substrates has been done in an ultra-high vacuum setup with typical pressures of $5 \cdot 10^{-10}$ mbar. The preparation chambers of the setup enabled us to clean metallic surfaces by sputtering and annealing and are equipped with LEED (Low Energy Electron Diffraction) instrumentation to study the cleanliness and orientation of surfaces. Furthermore, organic layers can be evaporated onto substrates by a Knudsen cell.

The spectrometer that is used in the experimental setup is an ELS3000 from LK technologies, which is schematically drawn in figure 3.6. Electrons are created by the cathode and by sets of electronic lenses and two monochromators focussed on the sample surface. In this manner a mono-energetic beam of electrons can be created with a kinetic energy from 2 up to 200 eV. For the FWHM of the elastic peak values of less than 0.03 % of the incoming energy can be achieved, which are extraordinary low values for electron spectroscopy. By using a sufficiently large measurement time (4 x 4 seconds per channel in the case of vibrational spectra and up to 50 x 4 seconds for electronic spectra) similar values can be achieved for the FWHM of inelastic peaks.

The scattered electrons are focussed onto a channeltron by lenses and two analyzers.
By changing the voltage applied over the first analyzer, electrons with a different kinetic energy will reach the channeltron, which detects the number of electrons per unit of time. Both the superimposed starting voltage and the voltage steps (stepsize) of this analyzer can be changed, thereby enabling to measure different parts of the spectrum. The detection part of the spectrometer (the channeltron, two analyzers and one set of lenses) are fixed to the flange of the chamber. The emission part (the cathode, two monochromators and two sets of lenses) can rotate in the scattering plane, thereby enabling to change the incoming angle of the electrons.
References


Chapter 4

The vibrational properties of thin layers of pentacene on metallic surfaces studied by HREELS

4.1 Introduction

In both experimental and theoretical work on pentacene, the coupling between charge carriers and vibrational features, the intramolecular modes (vibrational modes of the molecule itself) \[1\] and the intermolecular modes (vibrational motions of the molecules in the lattice) \[2, 3\], have shown to be of great importance for the electronic transport properties of this material. Therefore it is important to have a good understanding of the vibrational properties of the material. By using Raman and IR scattering techniques \[4–6\], the bulk properties have been studied already quite intensively (although there is little or no experimental data on the optically active lattice phonons). However, these bulk techniques are not interface specific. Since pentacene is a promising material for device applications \[7–9\], knowledge of the behaviour of thin films at the interfaces with metal contacts is important. By using high-resolution electron energy loss spectroscopy (HREELS), we will show in this chapter that the vibrational structure of the material is very different from the bulk at the pentacene/metal interface. This result which has previously been reported by Eremtchenko et al. \[10\], but which is studied in more depth in this work and provides new and remarkable results. Therefore both the intramolecular (section 4.4) and intermolecular (section 4.5) modes are studied for both a layer of 6 molecular layers and a single monolayer deposited on metal surfaces. Furthermore in section 4.6 we study how the vibrational structure evolves in the intermediate range between a single monolayer and 5 layers. We also address the question whether for thin layers the vibrational structure of these thin films depends on the choice of substrate. Two different substrates were used, (111) terminated silver and (100) terminated gold. These substrates have different electronic states at the surface, notably Shockley states for Ag(111) and Tamm states for Au(100) \[11\]. Since the Shockley sp-states, in comparison to the Tamm d- an f- valence band states, lie near the Fermi-level and are highly delocalised \[11\], they are expected to interact more strongly with a material deposited onto the substrate.

In the following section the preparation of the substrates and thin films used in these experiments are discussed.
4.2 The preparation of the substrates and thin films

In order to study the interaction of pentacene with the two different metallic substrates the following experimental procedures have been used for obtaining thin films of pentacene on clean metallic surfaces.

Before evaporating the film of pentacene onto the substrate, the metallic surface has to be cleaned in UHV by at least three cycles of sputtering the surface with 3 keV argon ions followed by annealing the substrate at 750 K. LEED (low energy electron diffraction) is used to check the structure and cleanliness of the surface (see the LEED patterns in figure 4.2 and 4.3). The hexagonal pattern for Ag(111) and the square pattern for Au(100) clearly confirm the expected surface structure. The ’double points’ in the LEED pattern for Au(100) are not due to defects but are the result of a reconstruction of the surface [12]. STM (scanning tunneling microscopy) images (figures 4.4 and 4.5), which were obtained in a different UHV setup, also show the expected structure of our substrates (the honeycomb structure for Ag(111) and the expected surface reconstruction of Au(100) and show little contamination or structural defects.

![Image of a sketch of the purification process of amorphous pentacene.](image_url)

The pentacene films were prepared by depositing pentacene on the substrate surface by means of organic molecular beam epitaxy (OMBE) in UHV ($5 \times 10^{-10}$ mbar). Erude pentacene material was obtained from Sigma-Aldrich and was over 95 % pure. To obtain material that is over 99 % pure, the pentacene was placed in high vacuum at the bottom of a tube that was half inserted in an oven (see figure 4.1). By heating this oven to 510 K the pentacene evaporated. The pure material precipitates at the middle of the tube whereas the rest products would either remain at the end of the tube or be pumped off. This procedure was repeated with the obtained purified material. Before deposition the molybdenum crucible containing the amorphous pentacene was heated up to 460 K to degas the material, which is necessary since pentacene is hygroscopic. For sublimating the pentacene itself the cell was heated to 505 K. At this temperature the pentacene film on the substrate grows at a rate of one molecular layer in about 12 minutes.

To obtain well defined homogeneous monolayers of pentacene onto the substrate, we used a method similar to that of Ponjee in his work on PTCDA [13]. A film of several molecular layers was deposited onto the sample and then heated to a specified temperature (570 K) known from literature [14] which would leave only the chemisorbed molecules at the interface with the metal surface. In our case a value for the temperature was not known from literature, but we assumed, that although most probably less strong than for PTCDA (which is highly polar), the interaction between the substrate and the first absorbed layer would be stronger than the interaction between the subsequent layers. Therefore a film...
was evaporated that was thick enough to be seen by the eye. By E-beam heating the temperature of the substrate was increased with 5 K per minute, until the reflective metal surface reappeared. Using HREELS we could indeed give spectroscopic evidence that there was still a layer of pentacene present at the surface. The temperature at which this happened was 450 K, a value that matches well with the recently published work by McDonald et al. for pentacene on Au(100) [15]. Test experiments showed that although similar growth conditions and an equal distance between crucible and sample were used, layers evaporated in different setups under the same conditions do not necessarily result in equal thicknesses. Hence, it is impossible to straightforwardly compare STM data with HREELS data. Therefore STM data cannot be used to predict the thickness of layers which were made in the HREELS setup. To be able to make proper estimates of the thickness of a layer prepared in the HREELS setup, attempts were made to obtain the unique vibrational structure of the monolayer (which is described in section 3.4.2) not by evaporating the excess layers off the sample, but by evaporating a layer on the clean Ag(111) surface. Eventually by evaporating for 12 minutes at 526 K, a similar vibrational structure was obtained (see figure 4.6). It was soon discovered though that when evaporating organic materials the output of a Knudsen cell is not constant over time. Small crystals of pentacene form at the aperture of the cell and as a result the speed of growth decreases. Therefore the thickness of the layer obtained by assuming linear growth conditions is merely a rough estimation. However HREELS spectra were taken for many different samples (15 different layers on Ag(111) and 13 on Au(100)) and by comparison of both the HREELS data and the growth conditions of all these layers, we could more accurately assign a thickness to the layers (expressed in the amount of molecular layers).

Figure 4.2: LEED pattern obtained from a clean Ag(100)surface.
Figure 4.3: LEED pattern obtained from a clean Au(100)surface. The "double" points are the result of a surface reconstruction.
4.3 The structure of thin layers of pentacene

It is known from ref. [16] that the structure for a thin layer of pentacene on a a-SiO$_2$ substrate ($\leq$ 30 ML) has a herringbone structure, which is comparable to that of single crystals, although the $d$(001) spacing between molecular layers of 15.4 Å is larger than that of single crystals (14.0 to 14.5 Å). Eremtchenko et al. found a completely different structure for their thin layers of pentacene on Ag(111) surfaces. They claimed the first monolayer is disordered and the subsequent layers form ordered rows of flat-lying pentacene. Using
The vibrational properties of thin layers of pentacene on metallic surfaces studied by HREELS

Figure 4.7: STM topography image of a pentacene layer on Ag(111). The majority of the image shows the row structure, but on the left side one can see an area having the herringbone "bulk" structure. Highlighted dimensions: 0.67 nm, 2×0.75 nm. $U_T = -2$ V, $I_T = 0.1$ nA.

Figure 4.8: STM image of a pentacene layer on Ag(111). The image shows the "row" structure, that also have been observed by Eremtchenko et al. The structure can be represented by a two-dimensional unit cell with $a = 6 \pm 1$ Å, $b = 16 \pm 1$ Å and $\alpha = 79 \pm 2^\circ$.

STM data they assign a two-dimensional unit cell to the structure ($|a| = 8 \pm 1$ Å, $|b| = 18 \pm 1$ Å and $\alpha \approx 78^\circ$). However, X-ray data by Danisman et al. [17] show that the first monolayer is highly ordered and forms a (6x3) super lattice of Ag(111) with unit cell dimensions 17.28 Å x 8.64 Å. The subsequent layers show a flat-lying structure comparable to the one reported by Emertchenko et al. [10] ($|a| = 6.22$ Å and $|b| = 15.6$ Å) and have a thickness of 3.7 Å. When using Campbell’s choice of unit cell for the single-crystal [18]
as shown in table 0.1 (Campbell’s unit cell is chosen simply because in this case it is easier to interpret than the one of Mattheus et al.), the two-dimensional unit cell shows a high agreement with the bc-plane of the single crystal and the observed thickness of 3.7 Å matches well with 1/2|a|. This does suggest that the row structure observed in ref. [10] might not differ hugely from the herringbone bulk structure and it is merely the orientation that differs from the thin layers on SiO₂.

Our STM data of figure 4.7 show both structures. The herringbone structure on the left of the image has lattice vectors (|a| = 6.7 Å and |b| = 7.5 Å) which compare well with references [18] and [16]. The row structure observed in this study can be represented by a two-dimensional unit cell containing a single molecule with |a| = 6 ± 1 Å, |b| = 16 ± 1 Å and α = 78 ± 4° (as shown in figure 4.8. From the STM data it is however impossible to observe whether all molecules in this structure are orientated in a similar manner (a matter which will be discussed and investigated more extensively in chapter 5). It seems like three different structures can be identified: a first monolayer at the interface, an intermediate structure consisting of rows of pentacene and the herringbone bulk structure. It is however possible that the row structure is actually not having a distinctly different lattice structure but is rather similar to the herringbone structure, but with the c-direction almost parallel to the surface. HREELS spectra showed that for layers ≥ 5.0 ML, the vibrational structure is no longer depending on the thickness. Therefore we can safely assume that for layers of over 5.0 ML the herringbone structure is observed. In the next two sections the vibrational aspects of a multi-layer of 6.0 ML and of a monolayer will be discussed. In section 3.6, where the evolution of the vibrational structure for increasing thickness is studied, the vibrational aspects of the interlaying ”row” structure will be discussed in more detail.

4.4 The intramolecular vibrations of pentacene

In figure 4.9 one can see specular HREELS spectra (Eᵢ = 5.8 eV) for both a monolayer and a multi-layer of about 6 molecular layers (ML) deposited on a Ag(111) surface. The spectrum shows the complete range for all vibrational contributions except for the C-H stretch modes which are located at around 3100 cm⁻¹.

Since in organic molecular crystals the weak Van Der Waals forces between the adjacent molecules are orders of magnitude smaller than forces between neighboring atoms in the molecule itself, the molecule is expected to preserve its own vibrational behaviour and the vibrational modes of the pentacene crystal can be divided in intermolecular modes (or lattice phonons) and intramolecular modes. In ref. [5], however, it is shown that there is significant intermixing of the lowest-energy internal modes and the lattice phonons. The intermolecular modes (as well as the ‘mixed’ ones) will be located primarily in the range of 30 to 150 cm⁻¹ and are visible on the foot of the elastic peak. These lattice phonons will be discussed in section 3.5. In this section only the intramolecular modes are studied.

4.4.1 The intramolecular vibrations for a multi-layer of pentacene

Besides the spectra for the monolayer and multi-layer in figure 4.9 also an infrared (IR) spectrum for an isolated pentacene molecule is shown, obtained by performing DFT cal-
The vibrational properties of thin layers of pentacene on metallic surfaces studied by HREELS

Figure 4.9: Specular HREELS spectra ($\theta_i = \theta_s = 60^\circ$, $E_i = 5.8$ eV and FWHM = 14 cm$^{-1}$) for a multi-layer and a monolayer of pentacene on Ag(111). The bottom trace shows the IR spectrum for an isolated pentacene molecule obtained by DFT calculations.

Calculations using Gaussian03 with the B3LYP functional and 6-311G+(d,p) basis set as described in section 2.2. The B3LYP functional slightly underestimates the electron-electron interaction and as a result the calculated frequencies are always slightly higher in energy than those observed in experiments (also in the case when measuring in solution or in the gas phase. Therefore the calculated IR spectra is scaled with a correction factor of 0.973 (literature reports values ranging from 0.96 to 0.98). Although the calculated IR-intensities do not necessarily match with the intensity of the features in the HREELS spectrum for the multi-layer of pentacene, it is indeed clear that the optically active vibrational modes calculated for an isolated molecule, match extremely well with the contributions that are observed in the spectrum for the multi-layer and thereby corroborating that dipole scattering is the main scattering at low incoming energies. The first row of table 4.1 shows the individual peaks we could identify in the specular HREELS spectrum of a multi-layer on Ag(111) and they are compared to the optically active vibrational modes of an isolated molecule derived from the calculation.

When the calculated results are scaled with the correction factor of 0.973, every single peak in the HREELS spectra can be identified as an optically active vibrational mode (those modes having $B_{1u}$, $B_{2u}$ and $B_{3u}$ symmetry) except for small features at 1197, 1367 and 1458 cm$^{-1}$ and three peaks with energy values that do not lie in the range of the calculated vibrational modes, namely 1700, 1805 and 1930 cm$^{-1}$ (see the zoomed-in spectrum of figure 4.10). The last three specific modes have also been reported in the optical ellipsometry work of Schubert et al. [19]. Since their films were deposited onto a glass surface and similar features are observed as in our work, we can assume...
that these additional features can be attributed to the pentacene or possible oxidised pentacene, pentacenequinone [20]. DFT calculations on pentacenequinone do also not reveal any vibrational modes with an energy value in the range of 1650 cm$^{-1}$ to 2000 cm$^{-1}$. A possible explanation can be double-scattering processes. If one assumes observing a double-scattering process from the 3 modes with the highest intensity (468, 729 and 902 cm$^{-1}$), one can explain 4 out of the 6 undefined modes. Triple scattering processes could explain the two other modes (1700 and 1930 cm$^{-1}$), but statistically they have a low probability of appearing. As mentioned before, the relative intensities derived from IR calculations do not necessarily match with those of the experiment. $B_{3u}$ modes have larger intensities than $B_{1u}$ and $B_{2u}$ modes and in comparison to the IR-spectrum $B_{2u}$ modes are higher in intensity than $B_{1u}$ modes.

So far when discussing the intramolecular modes of a multi-layer, we have limited ourselves to the range of 150 to 2000 cm$^{-1}$. However, the ab initio calculations also show C-H stretch modes of pentacene in the range of 3170 to 3210 cm$^{-1}$. In this range there are 4 $B_{1u}$ and 3 $B_{2u}$ modes, which are expected to be visible in HREELS spectra for a multi-layer. Figure 4.11 shows the spectra for a mono- and multi-layer in the range of 2500 to 3500 cm$^{-1}$. Due to the fact that their energies are almost equal, it was impossible to identify these seven modes and instead a broad peak at 3050 cm$^{-1}$ is visible in the spectrum for the multi-layer. The $B_{1u}$ and $B_{2u}$ modes are not visible in the spectrum for the monolayer. The reason for the absence of these modes in the spectra for a monolayer will be explained in section 4.4.2.

![Figure 4.10: Specular HREELS spectrum for a multi-layer of pentacene on Ag(111) ($\vartheta_i = \vartheta_s = 60^\circ$, $E_i = 5.8$ eV and FWHM = 14 cm$^{-1}$) compared to an IR spectrum for an isolated pentacene molecule obtained by ab initio calculations.](image-url)

Since the interaction between neighbouring molecules is small compared to the interaction between the atoms in the molecule itself, one would not expect that the intramolecular modes display high dispersion. In figure 4.12 one can see spectra for a multi-layer for three different scattering angles and therefore three different values of wave vector trans-
Table 4.1: Vibrational features for a multi-layer of pentacene (≈ 6 ML thick) on Ag(111) compared to the result of an ab initio calculation (B3LYP 6-311+G(d,p)) calculation for a single molecule. The correction factor is 0.973. The modes indicated with (a) are the result of a double scattering process.

<table>
<thead>
<tr>
<th>ω (cm⁻¹)</th>
<th>ω(calc)(cm⁻¹)</th>
<th>ω_corr(cm⁻¹)</th>
<th>symm. mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>119</td>
<td>B₃u</td>
<td></td>
</tr>
<tr>
<td>192</td>
<td>193</td>
<td>188</td>
<td>B₃u</td>
</tr>
<tr>
<td>355</td>
<td>361</td>
<td>351</td>
<td>B₁u</td>
</tr>
<tr>
<td>454</td>
<td>469</td>
<td>456</td>
<td>B₃u</td>
</tr>
<tr>
<td>468</td>
<td>481</td>
<td>468</td>
<td>B₃u</td>
</tr>
<tr>
<td>-</td>
<td>490</td>
<td>477</td>
<td>B₂u</td>
</tr>
<tr>
<td>569</td>
<td>579</td>
<td>563</td>
<td>B₁u</td>
</tr>
<tr>
<td>620</td>
<td>639</td>
<td>622</td>
<td>B₂u</td>
</tr>
<tr>
<td>729</td>
<td>744</td>
<td>724</td>
<td>B₂u</td>
</tr>
<tr>
<td>-</td>
<td>837</td>
<td>814</td>
<td>B₁u</td>
</tr>
<tr>
<td>830</td>
<td>847</td>
<td>824</td>
<td>B₃u</td>
</tr>
<tr>
<td>860</td>
<td>889</td>
<td>865</td>
<td>B₂u</td>
</tr>
<tr>
<td>902</td>
<td>922</td>
<td>897</td>
<td>B₁u</td>
</tr>
<tr>
<td>951</td>
<td>979</td>
<td>952</td>
<td>B₃u</td>
</tr>
<tr>
<td>990</td>
<td>1016</td>
<td>988</td>
<td>B₂u</td>
</tr>
<tr>
<td>-</td>
<td>1134</td>
<td>1103</td>
<td>B₂u</td>
</tr>
<tr>
<td>1112</td>
<td>1143</td>
<td>1112</td>
<td>B₁u</td>
</tr>
<tr>
<td>1154</td>
<td>1188</td>
<td>1156</td>
<td>B₂u</td>
</tr>
<tr>
<td>1174</td>
<td>1209</td>
<td>1176</td>
<td>B₁u</td>
</tr>
<tr>
<td>1197</td>
<td>-</td>
<td>-</td>
<td>(a)</td>
</tr>
<tr>
<td>1217</td>
<td>1250</td>
<td>1216</td>
<td>B₂u</td>
</tr>
<tr>
<td>1291</td>
<td>1317</td>
<td>1281</td>
<td>B₁u</td>
</tr>
<tr>
<td></td>
<td>1358</td>
<td>1321</td>
<td>B₂u</td>
</tr>
<tr>
<td>1342</td>
<td>1375</td>
<td>1337</td>
<td>B₁u</td>
</tr>
<tr>
<td>1367</td>
<td>-</td>
<td>-</td>
<td>(a)</td>
</tr>
<tr>
<td>1383</td>
<td>1416</td>
<td>1377</td>
<td>B₂u</td>
</tr>
<tr>
<td></td>
<td>1426</td>
<td>1387</td>
<td>B₂u</td>
</tr>
<tr>
<td>1439</td>
<td>1475</td>
<td>1435</td>
<td>B₂u</td>
</tr>
<tr>
<td></td>
<td>1475</td>
<td>1435</td>
<td>B₁u</td>
</tr>
<tr>
<td>1458</td>
<td>-</td>
<td>-</td>
<td>(a)</td>
</tr>
<tr>
<td>1498</td>
<td>1540</td>
<td>1498</td>
<td>B₂u</td>
</tr>
<tr>
<td>1530</td>
<td>1576</td>
<td>1533</td>
<td>B₂u</td>
</tr>
<tr>
<td>1587</td>
<td>1639</td>
<td>1594</td>
<td>B₁u</td>
</tr>
<tr>
<td>1627</td>
<td>1670</td>
<td>1624</td>
<td>B₁u</td>
</tr>
<tr>
<td>1700</td>
<td>-</td>
<td>-</td>
<td>(a)</td>
</tr>
<tr>
<td>1805</td>
<td>-</td>
<td>-</td>
<td>(a)</td>
</tr>
<tr>
<td>1930</td>
<td>-</td>
<td>-</td>
<td>(a)</td>
</tr>
</tbody>
</table>
Figure 4.11: Specular HREELS spectra ($\theta_i = \theta_s = 60^\circ$, $E_i = 5.8$ eV) for a multi-layer and a monolayer in the range of 2500 to 3500 cm$^{-1}$.

Figure 4.12: Specular HREELS spectrum ($\theta_i = \theta_s = 60^\circ$, $E_i = 5.8$ eV) and two offspecular HREELS spectra ($\varphi = \theta_i - \theta_s = 4^\circ$ and $\varphi = 8^\circ$, $E_i = 5.8$ eV) for a multi-layer of pentacene on Ag(111).

Q$_{\parallel} = 0$ Å$^{-1}$, Q$_{\parallel} = 0.052$ Å$^{-1}$ and Q$_{\parallel} = 0.088$ Å$^{-1}$. The reciprocal lattice vectors for crystalline pentacene are $|a^*| = 0.160$ Å$^{-1}$, $|b^*| = 0.133$ Å$^{-1}$ and $|a^*| = 0.071$ Å$^{-1}$, so for wave vector transfer within the ab-plane, the reciprocal lattice vectors have not been exceeded. From the spectra it is obvious that there is no observable dispersion of the vibrational modes. The intensity for all modes decays rapidly (two orders of magnitude from 0$^\circ$ to 8$^\circ$) and therefore one can conclude that in the spectrum for Q$_{\parallel} = 0$ Å$^{-1}$...
all modes are primarily excited by dipole scattering (see section 2.3). One can however observe that in the spectrum for $Q \parallel = 0.088 \text{ Å}^{-1}$ the relative intensities of the modes are different from the spectrum for $Q \parallel = 0 \text{ Å}^{-1}$. Some of the features at higher scattering angles are apparently mainly excited by means of impact scattering.

4.4.2 The intramolecular vibrations for a monolayer of pentacene

In the case of a monolayer, when applying the selection rules as discussed in section 3.3, one would expect no modes in the spectrum with a dipole moment parallel to the surface. Comparing the spectrum for a monolayer with that of a multi-layer one can see that the modes with $B_{1u}$ and $B_{2u}$ symmetry are missing in the spectrum of the monolayer (as can be seen in both figure 4.9 and 4.11), whereas the modes with $B_{3u}$ symmetry are still present, indicating the pentacene molecules adsorbed to the Ag(111) substrate with its molecular plane parallel to the surface. Due to the chemisorption to the metallic surface the energies of these $B_{3u}$ modes are slightly shifted compared to the multi-layer and for the ab initio data to fit our results for the monolayer a correction factor of 0.955 was needed. The effect of the chemisorption on the energy of the vibrational modes is discussed in paragraph 3.6 for the two substrates, Ag(111) and Au(100). The modes at 453 and 722 cm$^{-1}$ match well with the values Emertchenko et al. [10] reported for a monolayer. Adsorption of a molecule onto a surface generally lowers the symmetry of the system. In the case of a pentacene molecule adsorbed on Ag(111) the xy-plane of the molecule is no longer a plane of symmetry and the D$_{2h}$ space group does no longer apply to the system. A specific surface point group will apply to the new system, depending on the adsorption site and the strength of the interaction. As a result of the lower symmetry, modes that in the case of a freestanding molecule or bulk were not dipole allowed can become dipole allowed. Looking at table 4.2 which shows all the contributions present in the HREELS spectrum for a monolayer on Ag(111), it is shown that all the modes can be identified as either $B_{3u}$ modes or, for several small contributions, $A_g$ modes with a high Raman scattering activity (derived from DFT calculations). Since only $B_{3u}$ and $A_g$ contributions are visible in the spectrum, the system should belong to the C$_{2v}$ surface point group. It seems a little counterintuitive that an $A_g$ mode, which is a fully symmetric stretch mode in which the nuclei move in the molecular plane, is indeed dipole allowed when being absorbed on a surface. However when the nuclei of the molecule move closer together, there can be a charge transfer between the substrate and the molecule and this charge transfer alters the electric dipole moment normal to the surface, which explains the presence of these modes. The fact that the intensity for these $A_g$ modes are orders of magnitude smaller than the intensity of the $B_{3u}$ contributions, shows that the charge transfer from the molecule to the surface is small. In fact only those $A_g$ modes that have a high Raman scattering activity are visible. Furthermore one can assume that there are no strong preferential absorption sites, because that would lead to an even lower symmetry of the system and additional vibrational modes would become dipole allowed as well. In the spectrum however, all peaks can be assigned to the $B_{3u}$ and $A_g$ modes except for a weak feature at 304 cm$^{-1}$. 
Table 4.2: Vibrational features for a monolayer of pentacene on Ag(111) compared to the result of an ab initio calculation (B3LYP 6-311+G(d,p)) calculation for a single molecule. The correction factor is 0.955. Contributions to the spectrum that are less than 1% in intensity of the largest contribution and $A_g$ modes that have a Raman scattering activity below 30 Å$^4$/amu are shown in italic.

<table>
<thead>
<tr>
<th>Monolayer DFT calc. for an isolated molecule</th>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$\omega_{calc}$ (cm$^{-1}$)</th>
<th>$\omega_{corr}$ (cm$^{-1}$)</th>
<th>symm. mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>186</td>
<td>193</td>
<td>184</td>
<td>$B_{3u}$</td>
<td></td>
</tr>
<tr>
<td>257</td>
<td>263</td>
<td>248</td>
<td>$A_g$</td>
<td></td>
</tr>
<tr>
<td>304</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>453</td>
<td>469</td>
<td>448</td>
<td>$B_{3u}$</td>
<td></td>
</tr>
<tr>
<td>590</td>
<td>616</td>
<td>588</td>
<td>$A_g$</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>646</td>
<td>618</td>
<td>$A_g$</td>
<td></td>
</tr>
<tr>
<td>722</td>
<td>746</td>
<td>712</td>
<td>$B_{3u}$</td>
<td></td>
</tr>
<tr>
<td>805</td>
<td>847</td>
<td>809</td>
<td>$B_{3u}$</td>
<td></td>
</tr>
<tr>
<td>883</td>
<td>929</td>
<td>887</td>
<td>$B_{3u}$</td>
<td></td>
</tr>
<tr>
<td>935</td>
<td>979</td>
<td>979</td>
<td>$B_{3u}$</td>
<td></td>
</tr>
<tr>
<td>958</td>
<td>1018</td>
<td>966</td>
<td>$A_g$</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>1184</td>
<td>1131</td>
<td>$A_g$</td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td>1208</td>
<td>1154</td>
<td>$A_g$</td>
<td></td>
</tr>
<tr>
<td>1356</td>
<td>1409</td>
<td>1346</td>
<td>$A_g$</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>1491</td>
<td>1424</td>
<td>$A_g$</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>1556</td>
<td>1486</td>
<td>$A_g$</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>1574</td>
<td>1503</td>
<td>$A_g$</td>
<td></td>
</tr>
</tbody>
</table>
4.5 The intermolecular vibrations of pentacene

Figure 4.13: Specular HREELS spectra for a multi-layer of pentacene on Au(100) ($E_i = 6.5$ eV) showing the contributions of the low-energetic intermolecular vibrations. The solid dashed plot is for high resolution (FWHM = 11 cm$^{-1}$) and low step size (1.6 cm$^{-1}$). The black plot for low resolution (FWHM = 14 cm$^{-1}$) high step size (3.7 cm$^{-1}$). The bars in the plot show the optical modes for the S polymorph derived from table 4.3.

Figure 4.13 shows two specular HREELS spectra in the range of 0 to 150 cm$^{-1}$ with different resolution and step size. Having a resolution lower than 15 cm$^{-1}$ was essential to be able to resolve all features on the slope of the elastic peak. The spectra show 7 peaks. The DFT calculations for an isolated molecule show only 2 optically active modes in this specific energy regime. Furthermore, as discussed in section 4.4 these low-energetic intramolecular vibrations are expected to interact with the lattice vibrations resulting in "mixed" modes.

Although the Raman active $a_g$ modes have been studied quite intensively in the past, little experimental data is known about the optically active lattice phonons since their energy is in the range of 1 to 4 THz, which is difficult to access experimentally. Della Valle et al. [4] compared Raman spectra for various temperatures with quasi harmonic lattice dynamics (QHLD) calculations of the vibrational frequencies. These calculations were done for two different morphologies of single crystalline pentacene, the morphology determined by Campbell et al. [18] (called morphology S in chapter 2) and the morphology by Holmes et al. [21] (which was called V in chapter 2). Both their experimental and theoretical work however show no results of the optical active phonon modes. Lattice dynamical calculations for S crystalline pentacene using both "rigid" and "non-rigid" molecules (in other words, not allowing or allowing interaction of low energetic intramolecular modes with the lattice phonons) were done by Filippini and Gramaccioli [5], giving results for both the $a_g$ and the $a_u$ modes. To make estimations for the position of the various phonons in the HREELS spectra, Filippini and Gramaccioli’s [5] calculations for...
Table 4.3: Comparison of Raman data at 297 K with the phonon energies derived from calculations by Della Valle et al. [4] and Filippini & Gramaccioli [5]. The last column shows the data of Filippini & Gramaccioli multiplied by a correction factor of 1.15. The modes which have an asterisk subscript are "mixed" modes.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymorph S</td>
<td>Polymorph V</td>
</tr>
<tr>
<td>calc</td>
<td>exp</td>
</tr>
<tr>
<td>----------</td>
<td>-----</td>
</tr>
<tr>
<td>43.8</td>
<td>41</td>
</tr>
<tr>
<td>53.6</td>
<td>49</td>
</tr>
<tr>
<td>59.8</td>
<td>60</td>
</tr>
<tr>
<td>104.5</td>
<td>95</td>
</tr>
<tr>
<td>151.3</td>
<td>136</td>
</tr>
<tr>
<td>163.1</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The $a_g$ modes are compared to the experimental data at room temperature of ref. [4] (see table 4.3). When using a correction factor of 1.15, the calculated modes by ref. [5] match the experimental data of ref. [4] with a maximum error of 5 %. This same factor was applied to the calculated energies of the $a_u$ modes and $a_u^*$ "mixed" modes.

In figure 4.13 the energy of these calculated modes are compared to the specular HREELS spectrum. The energies of the peaks match rather well with the calculated modes except for the last 4 $a_u^*$ modes, which according to ref. [5] result from the interaction two intramolecular modes ($A_u$ mode at 72 cm$^{-1}$ and $B_{1u}$ at 120 cm$^{-1}$). The HREELS spectrum shows a peak at 120 cm$^{-1}$, suggesting little or no interaction. Since for the evaporated thin film of our experiment a morphology is expected that matches more with structure $V$ than $S$, strong deviations from the calculations of Filippini and Gramaccioli are expected.

Off-specular spectra are shown from $Q_\parallel = 0$ Å$^{-1}$ to $Q_\parallel = 0.088$ Å$^{-1}$ in figure 4.14. It is evident that for the optically active phonon modes there is hardly any dispersion. The fact that their intensity decreases drastically for higher scattering angles indicates that they are excited by a dipole scattering process. One mode emerges at higher $Q_\parallel$, which is clearly the result of impact scattering. Comparing the peak position of this mode with the Raman data of table 4.3 suggests it is the $a_g$ mode at 90 cm$^{-1}$.

In the case of a single monolayer on Au(100) only one single phonon mode is visible (see figure 4.15). From the off-specular spectra one can conclude that this mode at
The vibrational properties of thin layers of pentacene on metallic surfaces studied by HREELS

Figure 4.14: HREELS spectra for a multi-layer of pentacene on Au(100)($E_i = 6.5$ eV) showing the contributions of the low-energetic intermolecular vibrations for different scattering angles $(\varphi = \vartheta_i - \vartheta_s)$ ranging from $0^\circ$ to $8^\circ$.

Figure 4.15: HREELS spectra for a monolayer of pentacene on Au(100)($E_i = 6.5$ eV) showing the contributions of a low-energetic vibration for different scattering angles $(\varphi = \vartheta_i - \vartheta_s = 0^\circ, 4^\circ$ and $8^\circ)$. 
65 cm$^{-1}$ is optically active and that there are no modes visible which are excited by impact scattering. Since the molecules absorb with their z-axis normal to the surface, no longitudinal modes are expected to show in the HREELS spectrum. The observed feature is the first intramolecular $B_{3u}$ mode. The Gaussian03 calculations show an energy for this mode of 38 cm$^{-1}$ (see table 4.1). The observed energy shift for this mode will be explained in section 4.6.

### 4.6 The vibrational structure of pentacene as a function of layer thickness

In the previous section we studied both a single monolayer and a multi-layer of over 5 ML, which showed the vibrational structure expected for bulk pentacene. It was shown that these two layers had different vibrational structure. Apart from a shift in energy of the vibrations, also other modes were optically active for the two different layers. Using previously reported work and STM data it was shown in section 4.3 that besides the herringbone bulk structure, a second structure occurs for coverage of less than 5 ML (see figure 4.8). By studying the evolution of the vibrational structure when increasing the thickness of the pentacene layer, we hope to obtain more insight into this intermediate region.

The HREELS spectra for layers of increasing thickness on both Ag(111) and Au(100) are shown in respectively figures 4.16 and 4.17. Instead of a smooth transition from the vibrational structure of the monolayer to the vibrational spectrum of the bulk, there are very specific additional contributions and shifts visible in the intermediate spectra. In the spectra from 1.5 to 3.0 ML two strong additional modes are visible at 536 cm$^{-1}$ and 585 cm$^{-1}$, which are obviously modes with a dipole moment normal to the surface, since they are clearly visible in the spectra for 2.0 ML whereas all $B_{1u}$ and $B_{2u}$ modes are still screened by the metallic surface. Furthermore in the spectrum of 2.0 ML the $B_{3u}$ mode visible at 830 cm$^{-1}$ for layers of more than 3.0 ML is no longer present. In section 4.4 when comparing the monolayer to the multi-layer a consistent shift to lower energy was observed for the $B_{3u}$ modes. In the spectra for 1.5 to 3.0 ML the $B_{3u}$ modes undergo strong shifts which differ from those for the monolayer. An overview of the deviant features for these intermediate layers on Ag(111) is given in table 4.4.

In this intermediate regime an additional lattice structure of pentacene is present which has a lower symmetry than the multi-layer discussed in section 4.4.1. Since the $B_{1u}$ and $B_{2u}$ modes for the 2.0 ML thick layer are largely screened, we can at least assume that the second layer is also oriented with z-axis normal to the metallic surface. The fact that the intensity of these peaks rise for the subsequent layers can either be due to the molecule tilting out of plane and rotating around the molecular axis or simply due to the fact that the metal is no longer screening the dipole moment of these modes. Therefore we can not conclude whether the 3rd layer is still flat-lying or not. A change in orientation of the molecules at a thickness of 3 ML has been observed in photo-emission experiments by McDonald et al [15], which does suggest that indeed after the 3rd molecular layer the molecular plane of the pentacene molecules is no longer parallel to the surface but the molecular axis is tilted. Since in the STM data of figure 4.7 both a flat-lying and an upstanding orientation are present, these two structures can coexist next to one another.
The vibrational properties of thin layers of pentacene on metallic surfaces studied by HREELS

Figure 4.16: Specular HREELS spectra ($\vartheta_i = \vartheta_s = 60^\circ$, $E_i = 5.8$ eV) for pentacene on Ag(111). Every trace represents a different thickness of the layer ranging from 1.0 ML (bottom trace) to 6.0 ML (top trace).

Figure 4.17: Specular HREELS spectra ($\vartheta_i = \vartheta_s = 60^\circ$, $E_i = 6.5$ eV) for pentacene on Au(100). Every trace represents a different thickness of the layer ranging from 1.0 ML (bottom trace) to 6.0 ML (top trace).
Table 4.4: Comparison of the main dipole active features in the HREELS spectrum of between the row structure (2.0 ML), the herringbone structure (6.0 ML) and the monolayer. All layers are deposited on Ag(111).

<table>
<thead>
<tr>
<th>Row structure (2 ML) cm(^{-1})</th>
<th>Herringbone (6 ML) cm(^{-1})</th>
<th>Monolayer cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>159</td>
<td>192 ((B_{3u}))</td>
<td>186</td>
</tr>
<tr>
<td>472</td>
<td>468 ((B_{3u}))</td>
<td>453</td>
</tr>
<tr>
<td>536</td>
<td>569 ((B_{1u}))</td>
<td>-</td>
</tr>
<tr>
<td>585</td>
<td></td>
<td></td>
</tr>
<tr>
<td>623</td>
<td>620 ((B_{2u}))</td>
<td></td>
</tr>
<tr>
<td>741</td>
<td>729 ((B_{3u}))</td>
<td>722</td>
</tr>
<tr>
<td>-</td>
<td>830 ((B_{3u}))</td>
<td>805</td>
</tr>
<tr>
<td>882</td>
<td>902 ((B_{3u}))</td>
<td>883</td>
</tr>
</tbody>
</table>

after evaporation. One can assume that this is a sudden transition from one orientation into the other and not a gradual process.

The vibrational spectra for the layers on Ag(111) and Au(100) look completely identical except for the monolayer spectra. In section 4.4.2 it was shown for a monolayer on Ag(111) the \(A_y\) modes of pentacene become visible in the HREELS spectrum, although the intensity was extremely low (less than 1% of the \(B_{3u}\)). In the spectrum of the monolayer on Au(100) these modes are not visible at all and the shifts in energy of the \(B_{3u}\) modes are also smaller than the ones observed for the monolayer on Ag(111), as can be seen in table 4.5. As a result we can conclude that the interaction of pentacene with the Au(100) substrate is weaker than with the Ag(111) substrate. As mentioned in section 4.1, Ag(111) and Au(100) have different surface states. Since the Shockley states in Ag(111) are close to the Fermi-level and delocalized, they are assumed to play a larger role in the chemical interaction with an adsorbed molecule, than the several eV deeper lying Tamm states. This explains why the HREELS spectra show a stronger interaction of pentacene with Ag(111) than with Au(100).

The reason why these vibrational modes (II to VII) of table 4.5 do shift to lower energies is not entirely clear. A remarkable fact is that the energy of mode I, which does not occur for the multi-layer (since it mixes with several intermolecular modes), does differ largely from the frequency value obtained by DFT calculations (38 cm\(^{-1}\)), whereas for all other modes visible in the spectrum for a monolayer (see figure 4.9), the deviations from the calculated values are less than 5% and the experimentally observed frequency is higher than the calculated value, in contrast to all other modes (as already been noted in paragraph 4.5). To understand this peculiarity, for each mode the values of \(\Delta Q_{C-H}/\Delta Q_{C-C}\) are shown in the last column table 4.5 and in figure 4.18 modes I, II and VI are sketched. \(\Delta Q_{C-H}\) is the sum of the relative displacement of the H-atom from the C-atom for each C-H bond in the molecule (obtained from the normal mode vector of the pertinent vibration) and \(\Delta Q_{C-C}\) is the same sum of displacements for all C-C bonds in the molecule. The ratio of these two numbers gives a clear indication on how much the wagging of the H-atoms contributes to the normal mode. Mode III has not been taken into account in the last column of table 4.5 because the observed peak in the monolayer
Table 4.5: The energies for the $B_{3u}$ modes for a monolayer of pentacene on Ag(111) and on Au(100) compared to the data for a multi-layer and the calculated values of the free pentacene molecules. The last column shows the ratio of $\Delta Q_{\text{C-H}}$ and $\Delta Q_{\text{C-C}}$ with $\Delta Q_{\text{C-H}}$ being the sum of the relative displacement of the H-atom from the C-atom for each C-H bond in the molecule and $\Delta Q_{\text{C-C}}$ the sum of relative displacement of the two C-atoms for each C-C bond.

<table>
<thead>
<tr>
<th></th>
<th>1.0 ML on Ag(111) cm$^{-1}$</th>
<th>1.0 ML on Au(100) cm$^{-1}$</th>
<th>multi-layer cm$^{-1}$</th>
<th>calc cm$^{-1}$</th>
<th>$\Delta Q_{\text{C-H}}/\Delta Q_{\text{C-C}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>55</td>
<td>66</td>
<td>-</td>
<td>38</td>
<td>0.29</td>
</tr>
<tr>
<td>II</td>
<td>188</td>
<td>191</td>
<td>192</td>
<td>193</td>
<td>0.31</td>
</tr>
<tr>
<td>III</td>
<td>453</td>
<td>456</td>
<td>454</td>
<td>469</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>722</td>
<td>727</td>
<td>729$^{(a)}$</td>
<td>746</td>
<td>7.0</td>
</tr>
<tr>
<td>V</td>
<td>805</td>
<td>809</td>
<td>830</td>
<td>847</td>
<td>3.1</td>
</tr>
<tr>
<td>VI</td>
<td>883</td>
<td>890</td>
<td>902$^{(b)}$</td>
<td>929</td>
<td>2.3</td>
</tr>
<tr>
<td>VII</td>
<td>935</td>
<td>939</td>
<td>951</td>
<td>979</td>
<td>3.1</td>
</tr>
</tbody>
</table>

(a) The observed peak is a combination of a $B_{3u}$ and a lower lying $B_{2u}$ mode.
(b) The observed peak is a combination of a $B_{3u}$ and a lower lying $B_{1u}$ mode.

Actually consists of contribution from two $B_{3u}$ modes.

Modes IV to VII shift to lower energy values for a monolayer (in comparison to the multi-layer) and as can be seen from the values of $\Delta Q_{\text{C-H}}/\Delta Q_{\text{C-C}}$, the modes mainly consists of the out-of-plane bending of the H-atoms (for example vibration VI depicted in figure 4.18.D). In chapter 5 will be shown that as a result of the chemisorption of the pentacene on the metal, a negative charge transfer from the metal to the molecule takes place (which also have been shown for PTCDA in ref. [22] and [23]). Apparently, as a result, the C-H bonds decrease in strength. (Although it is not entirely valid to compare it to this case, Gaussian03 calculations also show that for an anion all C-H bond lengths are 1% larger than for the neutral molecule). Mode I and II consist mainly of the bending of the C-C backbone and therefore, according to the explanation that was given above, a shift to lower energies is not expected. Instead the energy of mode I shifts to higher energies from the calculated value. The reason for this large shift is the fact that the movement of this specific mode is largely hindered when being chemisorbed on the substrate. In figure 4.18.A the structure of pentacene is shown as calculated using Gaussian03. The bonds between atoms 1 & 3, 2 & 4, 19 & 21 and 20 & 22 have more double bond character, making the terminal rings preferential sites to chemisorb the molecule to the surface. Similar behaviour has been shown for PTCDA, where the largest charge transfer from the Ag(111) substrate also occurred at the sites where there is a [C=CH-CH=C] group [22]. Figure 4.18.B shows a sketch of mode I. Compared to all other vibrations, mode I is the mode that show the largest displacements of atoms 1, 2, 21 and 22. The fact that at these atoms the molecule is most strongly bonded to the substrate, may explain the shift to higher energies for this specific mode.

In section 4.5 we identified six different optically active lattice phonons in the multi-layer of pentacene on Au(100) and one optical mode in the monolayer. In figure 4.19, HREELS spectra for these low-energetic vibrational modes are shown for various layers of pentacene on both Au(100) and Ag(111) surface. Besides the multi-layer and the
Figure 4.18: A: The structure of the pentacene obtained by DFT methods. B: Sketch of the lowest vibrational mode (with a calculated energy of 38 cm\(^{-1}\)). C: Sketch of the vibrational mode with a calculated energy at 193 cm\(^{-1}\). D: Sketch of the vibrational mode with a calculated energy at 929 cm\(^{-1}\).

Figure 4.19: Specular HREELS spectra (\(\vartheta_i = \vartheta_s = 60^\circ\)) for pentacene on Au(100) (solid lines) and Ag(111) (dashed lines). Spectra for three different structures (herringbone, row and monolayer structure) are shown.
The vibrational properties of thin layers of pentacene on metallic surfaces studied by HREELS

monolayer (which are reported in section 4.5), the low-energetic vibrations for the "row" structure are depicted. As expected the vibrational features for a thicker layer (6.0 ML) are not depending on the choice of substrate. However, for the "row" structure and the monolayer, the substrate has a rather big influence on the low-energetic modes of the layer. Since the interaction of pentacene with the Ag(111) substrate was found to be stronger than with Au(100), it is remarkable that for vibration I the deviation of the experimental from the calculated value is larger for pentacene deposited on Au(100). This peculiarity remains present when having 2.5 ML coverage. As a result we may conclude that this effect is not only caused by the chemical interaction with the surface, but is due to a different mutual interaction between neighbouring molecules. Depending on the structure in which molecules chemisorb on the surface, there can be a considerable frustration within the structure, an effect that disappears with increasing layer thickness. Apparently this frustration is larger in the case of depositing on Au(100). That only vibration I shows a really strong substrate dependence can explained by the fact that this particular mode has by far the largest effect on the electronic coupling between molecules (since it highly influences the shape of the molecular orbitals) and therefore any deviation from the bulk structure will have a high influence on the energy of this specific mode. Modes that show predominantly movement of the H-atoms are hardly effected by changes in the intermolecular coupling.

Reported STM data on the row structure on Ag(111) and Au(100) indeed showed differences in structure. As mentioned before Eremtchenko et al. [10] found a 2 dimensional unit cell with $|a| = 8 \pm 1 \, \text{Å}, |b| = 18 \pm 1 \, \text{Å}$ and $\alpha \approx 78^\circ$, whereas X-ray diffraction data by Danisman et al. [17] revealed a 6.22 Å x 15.6 Å unit cell and the STM data for pentacene on Ag(111) reported in our work showed a unit cell of $|a| = 6 \pm 1 \, \text{Å}, |b| = 16 \pm 1 \, \text{Å}$ and $\alpha = 82 \pm 4^\circ$. McDonald et al. [15] reported a unit cell with $|a| = 7.4 \, \text{Å}, |b| = 15.5 \, \text{Å}$ and $\alpha = 85.5^\circ$ for pentacene on Au(100). As a conclusion, the available STM and XRD data on the structure of pentacene deposited on both surfaces does not provide sufficient proof to explain the significant shift for this vibrational mode.

4.7 Overview

- For layers thicker than 5.0 ML, the vibrational structure does not differ anymore as a function of layer thickness and the vibrational modes which are observed are in complete agreement with the modes which were calculated by DFT methods for a single isolated molecule. These observed modes show no dispersion.

- From the HREELS data for a monolayer, which show merely the $B_{3u}$ and $A_g$ modes, it is clear that the pentacene molecule adsorbs with its molecular plane parallel to the surface. As a result of the surface interaction, the vibrational modes shift to lower energies.

- The interaction of the pentacene molecules with the Ag(111) surface is stronger than with the Au(100) surface, since for the Au(100) surface the shifts of the intramolecular modes are smaller and the $A_g$ modes are not visible in the spectrum, indicating that there is little charge transfer with the surface. This is in agreement with the difference in surface states for the two surfaces (Shockley for Ag(111) and Tamm for Au(100)).
• We were able to distinguish 5 optical lattice modes for which no dispersion was observed. Off-specular spectra show an $a_g$ phonon mode excited by impact scattering.

• For thicknesses over 1 ML and less than 4 ML, a vibrational structure is observed which is distinctly different from that of the bulk structure and the monolayer. It shows a few additional modes with an out of plane dipole moment and large shifts of the $B_{3u}$ modes. Comparing this to the observed structures of pentacene on metallic surfaces, this intermediate vibrational structure represents the ”row” structure (arrays of pentacene molecules with their long molecular axis parallel to one another).

• The energy of the low-energetic modes for layers $\leq$ 3.0 ML is substrate dependent. On Ag(111) the energies are at least 15 % lower than on Au(100). This difference in vibrational energies must be due to a difference in the way pentacene adsorbs onto the substrate. Therefore this effect is also not visible for layers of over 3.0 ML.
The vibrational properties of thin layers of pentacene on metallic surfaces studied by HREELS

References


Chapter 5

The electronic properties of thin layers of pentacene on metallic surfaces studied by HREELS

5.1 Introduction

Besides the vibrational structure which was studied in the previous chapter, HREELS also gives us the opportunity to study electronic transitions in materials. In organic materials the energy needed to excite excitonic levels or HOMO/LUMO transitions is generally in the order of an eV. In chapter 4 it was shown that for dipole scattering the cross section is a function of the ratio between the energy loss and the primary beam energy. Since the electronic excitations are in the ratio of 1 to 5 eV, a higher primary beam energy ($E_i = 25$ eV) than for the vibrational spectra is chosen to ensure the ratio $\frac{\hbar \omega}{E_i}$ (see page 31) does not vary hugely for different transitions. Experimental work has shown that using HREELS also for electronic transitions, one can observe states which are not optically allowed transitions from the ground state, but are the result of impact scattering [1]. Because of the surface sensitivity of HREELS, it provides an unique possibility to study the excitonic states and band transitions of thin layers organic materials near a metal interface and it gives valuable information on screening effects and interface states.

5.2 Electronic transitions in pentacene

In figure 5.1 a specular HREELS spectrum for 6 ML of pentacene on Ag(111) is shown for the range of 0 to 5 eV. For a thickness of 6.0 ML one can exclude contributions from the substrate itself (such as for instance surface plasmons, which are introduced in section 5.3.1) and as a result the observed features are coming from the pentacene layer. The vibrational aspects discussed in the previous chapter are still visible in the range of 0.0 to 0.4 eV. The feature visible at 0.75 eV originates from double scattering of the C-H stretch modes described in section 3.4. At 1.75 to 3.00 eV the first electronic transitions in the pentacene are visible.

Figure 5.2 shows the electronic transitions in more detail and apart from some small contributions indicated in the graph with an asterisk, five main features (indicated with capital letters) are observed in the range of 1.5 to 3.0 eV of which the energy is given in
Figure 5.1: Specular HREELS spectrum ($\theta_i = \theta_s = 60^\circ$, $E_i = 25$ eV and FWHM = 3 meV) for a 6 ML thick layer of pentacene on Ag(111) in the range of 0 to 5 eV.

Figure 5.2: Specular HREELS spectrum ($\theta_i = \theta_s = 60^\circ$, $E_i = 25$ eV and FWHM = 3 meV) for a 6 ML thick layer of pentacene on Ag(111) in the range of 1.5 to 3.0 eV showing the first optical transitions.

Figure 5.3: The imaginary part of the dielectric function of the V structure determined by GW calculations by Taigo et al. [2]. $a$, $b$ and $c$ are the three polarisation directions.
The electronic properties of thin layers of pentacene on metallic surfaces studied by HREELS

Figure 5.4: Optical absorption spectra for thin films of pentacene from the reported work of Shirotani [3] (for both crystalline and amorphous films), Vertzymacha [4] and Jentzsch [5] and ellipsometry data by Faltermeier [6] and Park [7] (showing the extinction coefficient $k$).

Table 5.1. If we now look at the imaginary part of the dielectric function of crystalline pentacene derived from the GW data by Tiago et al. [2] for structure $V$ (which was discussed in section 2.2) and average over the 3 different crystalline directions, assuming uniform excitation, the graph shown in figure 5.3 is obtained. Note that in this work the features below 1.90 eV are optical transitions involving charge transfer (CT) excitons whereas the peaks at higher energies are above gap transitions. It is obvious that the two excitonic states (A and B) differ with our experimental data by more than 0.1 eV, whereas the higher band transitions (C, D and E) match rather well (see the last column of table 5.1). However, in the HREELS spectrum a feature at 2.47 (E) eV is clearly visible, which is not visible in the data of ref. [2]. Their work however does not include the vibrational fine structure discussed in chapter 2. In their work, to account for vibronic effects, a 0.05 eV broadening was added to the electronic levels. The $A_g$ modes with the strongest contributions to the relaxation energy (as reported in section 2.3) are however around 0.15 eV.

Numerous optical spectra of electronic transitions in thin films of pentacene have been reported already [3–7] and for comparison they are shown in figure 5.4. These thin layers where nevertheless an order of magnitude thicker than the ones studied in this work and deposited on non-metallic surfaces. The observed peaks in these spectra are also shown in table 5.1. The most striking observation when comparing the literature data is that, although the energy values of the first peak (A) can differ up to 0.08 eV, the peaks at higher energies are located at similar positions in the spectra. The HREELS spectra of the 6 ML of pentacene on Ag(111) matches well with these spectra except for this first contribution, which for our 6 ML thick film is located at higher energy (1.90 eV compared to for instance 1.87 eV in ref. [5]).

In an attempt to model the spectrum of figure 5.2 with the GW data of ref. [2], we assume a shift of the excitonic modes to the energies we observe, but for the higher band transitions we use the data from figure 5.3. Furthermore the vibronic fine structure is added to the spectrum. The intensity of the vibronic levels is given by
Table 5.1: Electronic transitions observed by HREELS measurements compared to the optical absorption and photoemission spectra from literature.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>6 ML</td>
<td>120 nm</td>
<td>40 nm</td>
<td>40 nm</td>
<td>250 nm</td>
<td>unknown</td>
<td></td>
</tr>
<tr>
<td>Ag(111)</td>
<td>n-Si</td>
<td>SiO$_2$</td>
<td>sapphire</td>
<td>quartz</td>
<td>glass</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1.75)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1.90</td>
<td>1.82</td>
<td>1.86</td>
<td>1.87</td>
<td>1.84</td>
<td>1.85</td>
</tr>
<tr>
<td>B</td>
<td>1.97</td>
<td>1.94</td>
<td>1.94</td>
<td>1.96</td>
<td>1.97</td>
<td>1.97</td>
</tr>
<tr>
<td>C</td>
<td>2.14</td>
<td>2.11</td>
<td>2.12</td>
<td>2.13</td>
<td>2.13</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>(2.22)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>2.28</td>
<td>2.26</td>
<td>2.25</td>
<td>2.29</td>
<td>2.27</td>
<td>2.28</td>
</tr>
<tr>
<td></td>
<td>(2.35)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>2.47</td>
<td>-</td>
<td>-</td>
<td>2.45</td>
<td>2.47</td>
<td>2.45</td>
</tr>
</tbody>
</table>

\[ I_n \propto \frac{S^n}{n!} \exp(-S), \tag{5.1} \]

with $S$ the Huang-Rhys factor (see section 2.3) and $n$ being the final vibrational of the transition. The result of implementing the vibronic coupling is shown in figure 5.5, which shows the spectrum without vibronic components, the sum of all the vibronic components, as well as the total spectrum. For the two major contributions A and B the vibronic coupling in case of $n = 1$ and $n = 2$ were added. For the other transitions only the 1st order vibronic splitting is included. The resulting spectrum (the black solid line in figure 5.5) resembles the HREELS spectrum more and does include a feature at 2.45 eV.

Jentzsch et al. [5] observed that the position of the peak with the lowest energy is dependent on the thickness of the layer: 1.87 eV for a 40 nm thick layer, 1.85 eV for 150 nm and 1.83 eV for 280 nm. Also in the spectra of ref. [4] one can notice a minor decrease in energy of the first peak for increasing layer thickness. It is surprising that for these films of hundreds of layers thick, such shifts of the electronic states still occur since the electrical screening of the metal is not relevant anymore. Therefore the only possible scenario for understanding of this effect is that for these thick layers the morphology of the film is still changing with increasing layer thickness. This is indeed the case as it is apparent from the XRD work of Matteus et al. [8]: for their films of pentacene deposited on an a-SiO$_2$ substrate, the morphology of the top layers does still change even after growing over a thousand layers.

In ref. [3] it was shown that for an amorphous layer a single peak at 1.88 eV is visible instead of the A and B peaks. Therefore it was concluded that the two peaks are the result of a Davydov splitting (a splitting resulting from the fact that when there are two equivalent molecules present in a unit cell, the dipole transitions of the individual molecules can either be aligned or anti-parallel). The fact that the splitting in our structure is only small (0.07 eV) compared to the thicker layers is understandable, since in chapter 4 it was shown that the ”bulk structure” only starts to exist for 5 or more molecular layers.
Therefore we expect that the crystallinity of our layers is not as large as in optical spectra for thicker layers and the intermolecular \( \pi \)-electron system is less developed, resulting in a smaller splitting. In the GW-data of figure 5.3 this splitting is also visible (which automatically results from the single-crystalline structure used in the calculations).

5.3 Electronic transitions for a monolayer of pentacene

5.3.1 Surface plasmons

Before we discuss electronic transitions for ultra-thin layers of pentacene on metal substrates, it is important to realise that the metal surface itself gives rise to electronic features in the HREELS spectrum. Since for both silver and gold the real part of the dielectric function is negative and its magnitude is higher than the value of the dielectric function of vacuum or pentacene, surface plasmons can be observed in these materials: surface electromagnetic waves that propagate parallel along the metal/pentacene or metal/vacuum interface. In figure 5.6 HREELS spectra \((E_i = 25 \text{ eV})\) are shown of clean Ag(111) and Au(100) substrates and the contributions from the surface plasmons are evident. The surface plasmon for Ag(111) is located at 3.83 eV and for Au(100) at 2.61 eV. For low coverages of pentacene these features will be still present in the spectra. Ponjee [9] showed that for PTCDA on Ag(111), the actual position of the plasmon can shift to lower energy when the surface is covered.

![Figure 5.6: Specular HREELS spectra (\( \theta_i = \theta_s = 60^\circ \), \( E_i = 25 \text{ eV} \)) for clean Ag(111) and Au(100) surfaces, showing the contributions from surface plasmons.](https://example.com/figure5.6)

5.3.2 Charge neutrality levels

In chapter 4 it was already shown that, as a result of the bonding to the metallic surface as well as the electronic screening, the vibrational structure for a monolayer of pentacene on a metallic surface differs significantly from the one for thicker layers: apart from changes in
peak positions and intensities, both B_{1u} and B_{2u} modes were not present in the spectrum for the single layer and in contrast to the spectra of the multi-layer the A_g modes were visible. By comparing figure 5.2 with figure 5.7 it is clear that for the electronic structure the spectrum for a monolayer also deviates strongly from the spectrum of a multi-layer. The excitonic states described in section 5.2 are not present for the monolayer, which is expected: the molecules adsorb in a flat-lying position and therefore any charge transfer state will be entirely screened by the metallic surface. Both the spectra for Ag(111) and Au(100) of figure 5.7 actually only show two broad features: the surface plasmons described in the previous paragraph (of which the peak position has not shifted) and a contribution at 0.4 eV for Ag(111) and at 1.0 eV for Au(100).

Figure 5.7: Specular HREELS spectra (\(\vartheta_i = \vartheta_s = 60^\circ\), \(E_i = 25\) eV) for a monolayer of pentacene covering a Ag(111) and a Au(100) surface.

The energy of these transitions are far below HOMO-LUMO gap energy of the crystalline material and their origin must be found in the fact that the metal-molecule interaction introduces surface states (a so-called Induced Density of Interface States) that pin the Fermi level at the interface resulting in a so-called Charge Neutrality Level (CNL) in the gap [10]. This pinning of the Fermi level to interface states is a common finding at metal/organic interfaces which results in a dipole barrier at the surface. For multi-layers the height of this barrier can be measured using photo emission (PE) [11–13] and in figures 5.8 and 5.9 schematic energy level diagrams are shown based on those experimental data. The transport gap was chosen to be 2.1 eV, equal to the energy of the first band transition visual in the HREELS spectrum for 1.5 ML (see figure 5.10). The PE work of ref. [11] and [12] show that the position of the HOMO of pentacene shifts with less than 0.2 eV going from a layer of 2 Å to a multi-layer of 150 Å of pentacene on gold. Therefore the validity of the representations in figures 5.8 and 5.9, which are not correct for a single layer, is higher than one would expect. When assuming that the observed states in the HREELS spectra of 5.7 are the transitions from the CNL to the LUMO, which are indeed the only possible optical transitions with an energy below the gap, both the observed energy value for a ML on Ag(111) and Au(100) differ 0.4 eV from the macroscopic value for a thick layer \(E_{\text{CNL-LUMO}} = \varphi_m - \chi - \Delta_{\text{dip}}\). It is however wrong to assume that this approximation would give satisfying results for all
Figure 5.8: Band diagram for pentacene on Ag(111), showing the observed transition from the CNL to the LUMO. Values for the dipole barrier $\Delta_{\text{dip}}$, electron affinity $\chi$ and workfunction $\phi_m$ are obtained from PE and IPE data for a multi-layer [11]. The transport gap $E_{\text{gap}}$ is obtained from the first band transition visible in the HREELS spectrum for 1.5 ML of figure 5.10.

Figure 5.9: Band diagram for pentacene on Au(100), showing the observed transition from the CNL to the LUMO. Values for the dipole barrier $\Delta_{\text{dip}}$, electron affinity $\chi$ and metal workfunction $\phi_m$ are obtained from PE and IPE data for a multilayer [13]. The transport gap $E_{\text{gap}}$ is assumed equal to the one for pentacene on Ag(111) of figure 5.8.
metal/organic interfaces, since the influence of the metallic screening on the electronic levels of the organic material will differ with the choice of both adsorbance and substrate material.

A similar contribution at 0.35 eV was found in the HREELS work of Ponjee [9] for a monolayer of PTCDA on Ag(111). The intensity of this feature was however far larger (six times the intensity of the surface plasmon) than in our study of pentacene. Kraft et al. [14] observed by using scanning tunneling spectroscopy that for PTCDA on Ag(111) the CNL is pinned in the LUMO and most probably the peak observed in his spectra for a ML of PTCDA on Ag(111) show a transition within the LUMO band. Since the density of states of the LUMO is far larger than at the CNL, it is not surprising that the feature observed for PTCDA on Ag(111) is more intense than for pentacene on Ag(111).

Note that although the C-H stretch modes are not dipole active for the flat-lying pentacene on a metal substrate, in figure 5.7 these modes are clearly visible at 0.37 eV. Clearly at this low ratio of $\Delta E/E$, the relative cross section for impact scattering is larger than in the experiments of chapter 3. Furthermore, since the electronic contributions from the pentacene are rather weak in intensity (these spectra are the result of averaging over 50 scans) it does show weak contributions from vibrational modes excited by impact scattering.

5.4 The electronic transitions as a function of layer thickness

5.4.1 Excitonic features as a function of layer thickness

In paragraph 5.2 only the electronic transitions for a layer of 6 ML thick were discussed. In figure 5.2 two main features related to charge transfer excitons and three clear features related to above gap transitions were evident. In figure 5.10 HREELS spectra are shown for the electronic transitions for layers of 1.5 ML to $\sim$ 10 ML deposited on Ag(111). Note that both excitonic features A and B (which were also described in section 5.2) are present in the spectrum for 2.5 and 3.5 ML. In section 4.6 it was shown that for these thicknesses the vibrational signature of the row structure was visible in the HREELS spectra. Both features A and B are only visible in the case when a unit cell contains two equivalent molecules [2, 3]. As a result, returning to the discussion in paragraph 4.3, the 2-D description given for the unit cell of the row structure by Eremtchenko et al. [15] cannot be valid and the structure described by the Danisman et al. [16], a herringbone structure with the long axis almost parallel to the substrate’s surface, seems more correct.

As mentioned in section 5.3, for a single monolayer of pentacene on a metal surface there are no clear electronic contributions visible in the energy regime of 1.5 to 3.0 eV. For the spectra at 1.5 and 2.0 ML a main feature is shown at 2.12 eV, identical in energy to the first above gap feature observed for the multi-layer of figure 5.2. The two peaks observed in the multi-layer that were related to CT excitons (A and B) are not visible for the layers of 1.5 and 2.0 ML. Obviously, since the structure of the first monolayer deviates strongly from the herringbone structure, similar excitonic features as for the multi-layer are not expected to be observed in these spectra. It does, however, not explain the absence of any feature below the band transition at 2.12 eV in the spectra for first two molecular
The electronic properties of thin layers of pentacene on metallic surfaces studied by HREELS.

Figure 5.10: HREELS spectra ($\theta_i = \theta_s = 60^\circ$, $E_i = 25$ eV) of the electronic transitions in pentacene on Ag(111) for layers of different thickness.

Figure 5.11: Sketch of the first three layers deposited on a metal surface. 1, 2 and 3 and 4 indicate possible directions for excitonic transitions.

layers. In figure 5.11, a sketch of the structure of the first three layers (based on the XRD work of ref. [16] which has been discussed in paragraph 4.3 and 4.6) some possible orientations of the charge transfer electron-pair (numbered 1 to 4) are shown. Of those, electron-hole pairs along the orientation of 1 and 2 are possible candidates to contribute to the spectrum for 2.0 ML. The absence of any feature related to transition 1 can be easily explained by using the dipole selection rule (see section 3.3.1). In chapter 4 it was already shown that for films $\leq$ 2 ML any dipole field parallel to the interface will be completely canceled by the image dipole present in the metal. However transition 2, of which the dipole field is not parallel to the substrate, does not give rise to any clear excitonic contribution to the spectrum either. As a result one can conclude that the screening of the metal is sufficiently large to prevent an exciton formation and therefore no clear contributions from excitonic states are visible in the spectra for 1.5 and 2.0 ML coverage.

For layers $\geq$ 2.5 ML both excitonic features A and B are present. However, for the film of 2.5 ML the relative intensities of these two features differ from the intensities observed for the thicker layers: peak A is considerably lower in intensity than peak B. As shown in the sketch of figure 5.11 the 2nd and 3rd do show the herringbone structure and therefore the observed states are expected to roughly match with the ones described in the GW data for the crystalline material [2]. The first prominent singlet exciton state obtained from those calculations (agreeing with feature A in our spectra) was mainly polarised in the a-direction (transition 3). For relatively thin layers (up to 4 ML as can be seen in chapter 3), the image dipole present in the metal surface can still partly screen the dipole field induced by the electron-hole pair. Feature B is polarised in both the a- and b-direction, as can be seen from the calculated spectra of $\varepsilon_2$ of figure 2.1 (alike a electron-hole pair in the direction 4) and therefore the image dipole in the metal substrate will not cancel the dipole moment that this transition induces. As a result the difference in relative intensity as a function of layer thickness of features A and B can be explained by the screening of the dipole field by the metal substrate.
5.4.2 Higher band transitions and surface plasmon contributions as a function of layer thickness

In the previous paragraph the energy regime of 1.5 to 3.0 eV was discussed, displaying the contributions from excitons and the first above band transitions. The substrate used for those experiments was Ag(111), since the Au(100) surface plasmon is located at 2.6 eV and its contribution to the spectrum would make it difficult to resolve the features from the pentacene. In this section for layers deposited on both substrates, the higher band transitions as well as the surface plasmon of the metal surface are studied. For the first 2.0 ML on Ag(111), as can be seen in figure 5.12, the surface plasmon is still present. For the first monolayer no shift in energy from the surface plasmon for clean Ag(111) (see also figures 5.6 and 5.7) was observed. After two monolayers a shift to 3.63 ± 0.02 eV is observed. This is in contrast to Ponjéé’s observations for PTCDA on Ag(111) [9] and shows that pentacene screens the electronic contributions from the metal less strongly than the more polar PTCDA. Since the surface plasmon of Au(100) lies at an energy similar to the first band transitions of pentacene it is less easy to observe possible shift in energy. For 2.0 ML on Ag(111) the first electronic transition in the pentacene was observed at 2.12 eV, whereas on Au(100) (as seen in figure 5.13) a broad feature is observed at 2.45 ± 0.02 eV, most probably as a result of both the surface plasmon and the band transition in pentacene.

Figure 5.12: Specular HREELS spectra (θᵢ = θₛ = 60°, Eᵢ = 25 eV) of the electronic transitions in pentacene on Ag(111) as a function of layer thickness

After 1.5 ML (see figures 5.8 and 5.13) contributions for the pentacene in the region of 4 to 5 eV are visible. Although the accuracy of the calculations is less in the higher energy range [17], one can see in figure 2.1 that crystalline pentacene indeed shows optical transitions in this energy range. In a similar manner as for the excitons described in the previous section, only transitions in the b direction are expected to show in the spectrum for layers of less than 3 ML thick. Furthermore we expect not to be sensitive to transitions in the c direction. For the first layers the dipole field these transitions induce will be
Figure 5.13: HREELS spectra ($\vartheta_i = \vartheta_s = 60^\circ$, $E_i = 25$ eV) of the electronic transitions in pentacene on Au(100) as a function of layer thickness

screened by the substrate and for the thicker layers there is no real crystallinity in that direction (as explained in chapter 4 the molecules are expected to tilt slowly until they reach the orientation of the bulk structure for large thicknesses). For the layer of 2.0 ML the onset of a peak lying at an energy $> 5.0$ eV is clearly visible whereas for layers of larger thickness the peak at 4.4 eV is dominating the spectra in the higher energy range. The calculated spectrum of $\varepsilon_2$ for the V-structure shows a peak in the a-direction at 4.7 eV and in the b-direction at 5.1 eV, roughly corresponding to the scenario described above. The optical absorption spectrum of ref. [5] for a 40 nm layer on sapphire shows both peaks, at 4.5 and 5.4 eV.

In the spectra for 3.5 and 5.0 ML deposited on Ag(111) a very remarkable and surprising feature can be seen. The peak at 4.4 eV is not present in the spectra for these thicknesses, whereas in the spectra for 2.5 and 6.0 ML as well as in the spectra for pentacene on Au(100) this peak is clearly visible. Unfortunately we are incapable of giving a satisfying explanation for this.

5.5 Overview

- Specular HREELS spectra for 6.0 ML of pentacene on Ag(111) and Au(100) showed 5 clear electronic transitions in the range of 1.5 to 3.0 eV. In comparison to the computational data of Tiago et al. [2] the two CT excitons were shifted to higher energies and the observed Davydov splitting was smaller than the theoretical model for the single-crystalline structure predicts.

- By correcting for the shift in excitonic levels and adding vibronic fine structure to the theoretical data of ref. [2], a good match with the HREELS spectrum could be made.

- In HREELS spectra for a monolayer of pentacene on Ag(111) and Au(100) two
clear features were observed: a contribution from the surface plasmons of the metal substrate and a contribution originating from the transition from a charge neutrality to the LUMO (0.4 eV for Ag(111) and 1.0 eV for Au(100)). The obtained CNL levels compared well with the values obtained from PE and IPE data.

- Spectra for different layer thicknesses (1.5 to ~10 ML) showed different contributions from the excitonic levels, whereas the band transitions were present and the same for all thicknesses. The development of the excitonic features gives valuable information about the orientation of the molecules in the first three molecular layers.
The electronic properties of thin layers of pentacene on metallic surfaces studied by HREELS

References

Chapter 6

THz Time Domain Spectroscopy

6.1 Introduction

In the last two decades various techniques have been used to study the transport mechanism and mobility of the carriers in organic crystals like pentacene [1,2] and rubrene [3–5]. Most of these techniques, like for instance Time of Flight [6], Space Charge Limited Current [1] and FET measurements [7,8], need the use of contacts on the sample and thereby might introduce additional defects in the single-crystal or give rise to additional contributions to the measurement from potential barriers between sample and contact [9,10] which may complicate a proper interpretation in terms of the charge transport in the intrinsic material. Recently the technique of THz Time Domain Spectroscopy (THz-TDS) proved to be very valuable for studying the charge transport in organic materials [11–14], especially since it enables to spectrally resolve the conductivity in the THz energy regime (1 THz = 4.1 meV) in a contact-free manner. The typical timescale for electronic motions in a solid (in the case of the simple classic Drude model (see 1.2.2) this is represented by the scattering time $\tau_s$ and the plasmon frequency $\omega_p$) is in the range of femto- or picoseconds and therefore this technique provides the user with valuable information on the behaviour of the charge carriers which common dc-techniques do not provide.

Terahertz time domain spectroscopy (THz-TDS) is a so-called pump-probe method. Charges (and excitons) are optically created using laser light (of either 400 nm (3.1 eV) or 266 eV (4.7 eV) and a time $\tau$ later the response of these charges is probed using low-energetic THz pulses as is shown in figure 6.1. The detection of the E-M pulses in the time domain and to derive the complex frequency dependent conductivity from it is not a straightforward operation. In this chapter the experimental details of this technique are discussed. Section 6.2 deals with the technique to create and detect the THz pulses and the complete experimental setup. In section 6.3 it is explained how one can determine the optical conductivity of the sample in the THz frequency domain from the obtained phase and amplitude of the transmitted pulse. The last section (6.4) deals with the precautions one has to take into account when in a THz-TDS experiment the optically created free charges cool and recombine so rapidly that the probe pulse traveling through the sample does not experience a system being in one specific state.
Figure 6.1: Schematic representation of a THz-TDS experiment. The 266 or 400 nm laser pump pulses create photo-carriers in the sample and at a time \( \tau \) later the THz probe pulse \( E(t) \) travels through the sample resulting in a transmitted signal \( E_t(t, \tau) \).

Figure 6.2: Sketch of the setup used for the THz-TDS experiments.
6.2 The experimental setup

A sketch of a typical THz-TDS set-up as used in our experiments is shown in 6.2 and is described in more detail in ref. [15]. The laser system used to run the set-up is based on a Coherent Legend regenerative amplifier (Regen) seeded by a Coherent Vitesse (790 nm central wavelength, 120 fs temporal intensity FWHM, 80 MHz repetition rate, 500 mW output power) and pumped by a Coherent Evolution laser (527 nm central wavelength, 20 ns temporal FWHM, 1 kHz repetition rate, 23 W output power). This system creates 120 fs width pulses centered at 800 nm at a frequency of 1 kHz. Of its total 2.5 W power only 80 mW is used to create our THz probe pulses. This is done by focussing plane-polarized 800 nm laser pulses onto a zinc telluride (ZnTe) crystal. ZnTe is a nonlinear optical material and as a result has a large second order term for the susceptibility ($\chi^{(2)}$) [16].

Due to differential frequency mixing, a dc polarisation is induced in these materials when monochromatic light is passing through [17]. When focussing our 120 fs laser pulses with a finite bandwidth onto the ZnTe crystal instead of a dc-field, single cycle oscillations of an electric field (peak field $\sim 1$ kV/cm, $\sim 1.5$ ps duration) are created [18].

By using parabolic mirrors, these THz pulses are focussed onto a sample, which in the case of our experiments is placed in a cryostat. The THz pulses itself are traveling in an environment with a continuous dry nitrogen flow, thereby limiting the absorption of radiation by water molecules. The pump pulse, which can have an energy of 800 or by using doubling or tripling crystals 400 or 266 nm, is focussed in such a way that on the sample it has a maximum spatial overlap with the probe pulses. As will be described in the next section the refractive index of the sample material will differ slightly after generating charge carriers using the pump pulse. As a result both amplitude and phase of the THz pulse which traveled through the sample will differ slightly from the case where no carriers are created. Since these differences are rather small (the amplitudes of the transmitted pulses for the excited $E_{t}^{exc}(t)$ and non-excited case $E_{t}(t)$ only differ about 1 % in the materials used in this study), a lock-in amplifier in combination with a chopper at 0.5 kHz placed in the pump beam is used to detect the modulation, $\Delta E_{t}^{exc}(t) = E_{t}^{exc}(t) - E_{t}(t)$.

The time between the arrival of the laser pulse that excites carriers and the THz probe pulse (which in this and the following chapter will be called $\tau$) can be varied by using the first delay line depicted in figure 6.2. Since created charges cool and recombine, the refractive index of the sample is dependent on the time after excitation. As a result the obtained modulation is also a function of this delay time ($\Delta E_{t}^{exc}(t, \tau)$).

After traveling through the sample the THz probe pulses are passing through a second ZnTe crystal. Since ZnTe is electro-optically active, the THz pulse will influence the refractive index of this birefringent material [19]. The 800 nm linearly polarised laser pulses are focussed on the ZnTe crystal and on passing through its polarization will become elliptical. By using cross polarizers and balanced photo diodes, the s and p polarisation of the elliptically polarised pulses can be measured. For small modulations, the change in intensity of the s and p polarised signals is linearly proportional to the size of the applied THz field. By applying a known static field over the ZnTe crystal one can calibrate the detected signal. A second delay line (see figure 6.2) is used to vary the time between the arrival of the THz pulse and the 800 nm laser pulse at the detection crystal. In this way one can measure the size of the THz field in the time domain and record the whole pulse. This technique for detecting the transmitted THz pulses is called electro-optical sampling and is described in more detail in references [19] and [20]. Figure
Figure 6.3: The left graph shows a typical transmitted THz pulse (for pentacene at 20 K) in the time domain, $E_t(t)$. The right graph displays the magnitude of the Fourier transformed pulse, showing that the signal is most intense in the range of 0.2 to 1.2 THz.

6.3 shows such a typical THz waveform generated from the one ZnTe crystal and detected by the second ZnTe crystal using the technique described above. As can be seen from the right graph, its field is the strongest in the range of 0.2 to 1.2 THz.

6.3 The frequency dependent conductivity

$$E_t(\omega) = \frac{t_{12} t_{21} e^{i n_1 \omega d/c}}{1 + r_{12} r_{21} e^{-i n_1 \omega d/c}} E(\omega)$$

$$= \frac{t_{12} t_{21} e^{i n_1 \omega d/c}}{(n_0 + n_1)^2 e^{i n_1 \omega d/c} - (n_0 - n_1)^2 e^{-i n_1 \omega d/c}} E(\omega)$$

(6.1)

with $t_{12}, t_{21}, r_{12}$ and $r_{21}$ being the Fresnel coefficients for transmission and reflection under normal incidence (see ref. [21]).
If we now optically excite the sample, the refractive index will change by an amount $\delta n_1$, which is an additional contribution to $n_1$ from the carriers and possibly excitons) created by our pump pulse. As a result the transmitted THz field changes by $\Delta E_t(\omega) = E_t^{\text{exc}}(\omega) - E_t(\omega)$, the so-called modulation. If we now ignore reflections and thus assume that $t \approx 1$ and $r \approx 0$ (which is justifiable for a THz field propagating through our organic samples) and use first order Taylor expansions and the expressions of equations 1.15 and 1.16, we find the following expression for the ratio between modulation and transmission:

$$\frac{\Delta E_t^{\text{exc}}(\omega)}{E_t(\omega)} \approx \frac{e^{in_1(\omega)d/c} - e^{in_1(\omega)d/c}}{e^{in_1(\omega)d/c}} \approx \frac{i\delta n_1(\omega)d/c}{c} = -\frac{\sigma_1(\omega)d}{2\varepsilon_0\sqrt{\varepsilon_1}},$$

(6.2)

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_1$ the dielectric function of the sample and $\sigma_1(\omega)$ the complex conductivity of the created carriers. As a result by Fourier transforming both the measured modulation $\Delta E_t^{\text{exc}}(t, \tau)$ and transmission $E_t(t, \tau)$ one can determine the optical conductivity as a function of frequency (in the range of 0.2 to 1.2 THz). Note that to be able to determine the mobility of carriers in the material, one has to be able to determine the charge density in the material. In the case of creating charges in the sample by using laserlight, the charge density will not be uniform but a function of the direction along the path of the laser pulse, owing to the strong absorption of optical radiation in the sample.

### 6.4 Deducing the conductivity from a rapidly changing system

The method described in the previous section is only valid in the steady state when, after optically exciting carriers in the sample, the system does not change rapidly on the timescale of the propagation of the THz pulse through the sample. In such case, the optical conductivity can be seen as a property independent of time for the time of the probe pulse traveling through the sample.

![Figure 6.5: Sketch of the propagation of the THz probe pulse through a sample after optical excitation, showing the moment of excitation ($t = 0$), and at two moments in time after exciting, $t = 1$ and $t = 2$ (in arbitrary units). The darkness of the sample is a measure of the magnitude of the optical conductivity.](image)

However, when the carriers cool, recombine or get trapped so rapidly that after optically creating free charges the decay of the modulation is in the order of the THz pulse
width, expression 6.2 is no longer valid [22]: In between the time of the probe pulse reaching the sample and having completely propagated through it, the value of the optical conductivity has significantly decreased (see figure 6.5).

To obtain a correct value for the conductivity for one specific state of our sample, we should make sure that every data point is taken at a fixed time \( \tau' = \tau + t \) (see figure 6.1) after the pump pulse (its own width of 120 fs is negligible in our experiments). Therefore measuring a single modulation signal after pumping at a time \( \tau \) is not sufficient in this case and an array of measurements over a whole range of values of \( \tau \) has to be made to obtain a 2D grid of the modulation as shown in figure 6.6 [22], which shows the modulation of pentacene at 20 K (excited with 400 nm laser light) as a function of the propagation time, \( t \) (on the x-axis), and the delay time, \( \tau \) (on the y-axis). In this figure a diagonal line is shown for which \( \tau' \) is constant. Along such a diagonal line, the modulation signal \( \Delta E(t) \) is representing one specific state of the sample. By Fourier transforming this modulation trace as well as the time-dependent transmission (which is shown in figure 6.6 as a solid trace) and substituting them into 6.2, one can obtain values for \( \sigma(\omega, \tau') \). In this case \( \tau' = 0 \) is often chosen to be the time at which the spectrally integrated conductivity is at its maximum.

In the next chapter the great value of THz-TDS for understanding the charge transport in organic crystals is shown, giving information for both pentacene and rubrene about the mechanism of charge transport, the cooling of charges and the effect of the interaction of carriers with one another.

Figure 6.6: A two dimensional grid showing the modulation pulses (in the time domain \( t \)) as a function of the delay time \( \tau \) for a crystalline pentacene sample optically excited by 400nm pulses of an intensity of 20 J m\(^{-2}\) (at \( T = 20 \) K). \( \tau = 0 \) is chosen at the peak modulation signal. The solid curve shows the transmitted pulse \( E(t) \) (with the field strength \( E \) depicted on the right axis). The diagonal dashed line shows the direction in which the correct traces of \( \Delta E(t, \tau') \) should be taken to determine the conductivity \( \sigma(\omega, \tau') \) after fourier transforming the data.
References


Chapter 7

The mechanism of charge transport in oligoacenes studied by THz-time domain spectroscopy

7.1 Introduction

Recent years have seen much interest in the conductivity of pentacene, rubrene and other molecular semiconductors of the oligoacene family, fuelled by the unique properties of these materials. Oligoacenes are flexible, cheap and exhibit relatively high charge-carrier mobilities [1], allowing for novel applications in electronic devices [2–4]. Despite this interest, the nature of charge transport in the materials has remained the subject of intense debate.

Crystalline organic semiconductors exhibit charge-carrier mobilities that decrease with temperature [5–7]. In analogy to inorganic semiconductors, this has been interpreted as an indication of delocalized charge carriers and a 'band-like' transport mechanism [8, 9]. Theoretical models based on polaronic band conduction [10] indeed give a good qualitative description of the 'band-like' mobility of the charge carrier in pentacene, but the factors determining the absolute charge mobility remain unknown. However, an analysis of the high temperature mobility has indicated that the mean free path of charge carriers is of the same magnitude as the intermolecular distance [11] and it is not clear why the signature of delocalized band-like transport persists at temperatures where the mean free path is smaller than the intermolecular distances. Because of the 'softness' of these van der Waals bonded organic crystals it is possible that the coupling of the carriers with the intermolecular vibrations could play a key role in the description of the charge carrier dynamics. Troisi and Orlandi have recently formulated a model (TO model) that states that the charge-carrier mobility in oligoacenes is limited by large fluctuations of the electronic coupling between adjacent organic molecules due to thermal molecular motions [12], in particular the low energetic phonon modes with energies around 1 THz [13]. This model correctly describes the 'band-like' temperature dependence of the mobility, including its absolute value, outside the validity of delocalized transport models [12]. Direct experimental evidence has been lacking for the various proposed models. In particular, experimental insights into the role of intermolecular, low-frequency vibrational modes in determining the charge transport mechanism have been missing to date. Therefore a technique is required that allows studying the response of the charge carriers in the frequency
regime of these modes.

Terahertz (THz) spectroscopy [14] provides this opportunity and has proven useful for investigating photo-carrier dynamics in organic semiconducting materials [5,15]. By recording the modulation of the transmission of THz probe pulses after optically creating carriers in the sample, the technique allows for determination of the photoconductivity spectrum in the range 0.2-2 THz. The THz conductivity spectrum has been shown to contain detailed information on the nature of the charge transport. Band-type and disorder-induced dispersive transport, for example, have distinct spectral signatures.

In the next section it is shown that also for crystalline pentacene the THz transient conductivity spectra provide key information to understand the nature of the charge transport in the material. Section 7.3 deals with the charge dynamics of the THz modulation (which enables a better understanding of the transient conductivity spectra of section 7.2), whereas section 7.4 deals with the role of charge-charge interaction in pentacene. Finally in section 7.5 we introduce a different oligoaconene material, rubrene, study its charge transport properties and compare it with the findings for pentacene.

7.2 The mechanism of charge transport in single crystalline pentacene

We study ultra-pure, vapour-grown single-crystals of pentacene with a trap density less than $2 \cdot 10^{17}$ cm$^{-3}$ and typical dimensions of 5 mm x 5 mm x 15 µm [6]. These crystals are placed in a He cryostat at a pressure below $1 \cdot 10^{-3}$ mbar, to both control temperature and avoid effects of (photo-) oxidation [16]. Mobile charges are generated in the pentacene (absorption gap 1.85 eV) by laser excitation using 266 nm (4.7 eV) and 400 nm (3.1 eV) femtosecond laser pulses. The THz transient conductivity (THz-TC) is determined using the THz spectroscopy setup described in chapter 6. Great care is taken to exclude possible artifacts from both the pump and the probe beam: Small signals generated solely by the pump beam were subtracted from the data. Since the observed THz modulation decreases rapidly as a function of the time after excitation (as will be shown in detail in paragraph 7.3), the procedure of paragraph 6.4 is followed to obtain correct values for the conductivity. In this manner, two dimensional grids, like the one of figure 6.6, were obtained. The correct modulation traces were deducted from these images.

Figure 7.1(a) shows the conductivity plots obtained using this procedure (for 400 nm excitation at 20 K). The top trace is recorded 0.7 ps after the maximum response. In contrast to earlier THz-TC work on pentacene [17–19] in this study a marked frequency dependence of the complex conductivity is observed, most notably at early times: the traces of both the real and imaginary conductivity are indicative of a resonance at $1.1 \pm 0.1$ THz. The resonance becomes less intense at longer delay times, but is clearly visible up to 7.5 ps after excitation, and was observed in measurements on several samples (see figure 7.1(b)). The resonance is observed independent of temperature and excitation wavelength: figure 7.1(c) shows the conductivity at room temperature when exciting the sample with 266 nm laser pulses. Note that the traces in figure 7.1(c) look identical in shape to those of figure 7.1(a), exhibiting a resonance around 1.1 THz. The response in figure 7.1(c) is about 9 times lower than in figure 7.1(a) - this is partly due to a lower excitation density at 266 nm (factor of 2), but mainly because the carriers are less mobile at room temperature (the temperature dependence of the THz conductivity will
The mechanism of charge transport in oligoacenes studied by THz-time domain spectroscopy

Figure 7.1: (a) Real (solid) and imaginary (dashed) conductivity as a function of frequency at 20 K when exciting with 400 nm pulses with a laser fluence of 20 J m$^{-2}$ (all traces represent an average of 20 scans). Spectra are shown for different times after excitation, ranging from 0.7 ps to 2.1 ps (with intervals of 0.2 ps). The grey dashed-dotted line shows a fit function consisting of a frequency independent part (which represents the response from the free-carriers) [17, 18] and a Lorentzian, showing that the conductivity data for $\tau' = 0.7$ ps contain an absorption at 1.06 THz. (b) Real and imaginary conductivity at $\tau = 7.5$ ps (performed under the same conditions as figure 7.1(a) but on a different sample and averaged over 50 scans). (c) The real and imaginary conductivity at room temperature when exciting at 266 nm with a fluence of 16 J m$^{-2}$ for $\tau' = 0.7$ and $\tau' = 1.3$ ps, averaged over 30 scans.
be discussed in detail in section 6.3).

We only consider data recorded after 0.7 ps following photoexcitation, since determining the conductivity immediately following photoexcitation (when a “jump” in photoconductivity occurs), is not straightforward [20]. In ref. [21] it has been shown that for rubrene optically-active, ground-state vibrational modes in the THz region can give rise to resonances in the conductivity spectrum. This cannot explain the resonances reported here: ground state absorption spectra measured in the frequency range of 0.3 to 1.3 THz show a uniform absorption of less than 2% over the whole pentacene sample (as is evident from figure 7.2), indicating that the 1.1 THz resonance is not related to any ground state absorption of THz radiation. Modeling of our data following the method developed by Němec et al. [22] (which enables one to extract the frequency dependent chances in susceptibility resulting from a highly dynamic system), reveal that the small shifts of the resonance frequency observed in the data (fig. 7.1) can be explained by an excited state resonance at a fixed frequency of 1.1 THz.

Ai et al. [23] recently observed a THz resonance upon photoexcitation of the polymer P3HT. They showed how several classical models, like the Drude model (see 2.2.4) and the Drude-Smith model [24](an extension of the Drude model which includes scattering effects) cannot account for this observation. Attempts to fit the data of figure 7.1 with these two models were unsuccessful (one can expect though that such models cannot correctly describe charge transport in a narrow band system like pentacene). Ai et al. [23] attributed the resonance to bound polaron pairs, having observed a marked dependence of the dynamics on charge density. For pentacene, such a dependence is completely absent (as shown in section 6.4), indicating that the resonance is not due to polaron pairs.

Fratini and Cuichi [25] used dynamical mean-field theory [26] to calculate the optical conductivity for a system in which the charge transport is governed by small polarons. Their work shows that in case of strong charge-vibrational coupling (defined in reference [25] as the regime where the polaron binding energy is larger than approximately half the bandwidth) the real part of the conductivity can show a distinct resonance at an energy equalling twice the polaron binding energy. A polaron binding energy of 0.5 THz would lead to unrealistically low energy values for the lattice vibrations of pentacene. Moreover, the small polaron model proposed by Hannewald et al. [10] shows that this
The mechanism of charge transport in oligoacenes studied by THz-time domain spectroscopy

"strong" coupling regime does not apply to the case of oligoacenes. The conductivity in the "weak" coupling regime for small-polarons (at \( T \approx 0.5 \omega_{\text{phonon}} \)) does not show any pronounced features (as can be seen in figure 3(a) of reference [25]) in comparison to figure 7.1. As a result, one can not straightforwardly explain the observed resonance by using this small-polaron model.

Instead the observed absorption at 1.1 THz is attributed to nuclear modes that strongly modulate intermolecular electron transfer, i.e. the modes with the largest off-diagonal electron phonon coupling. These are the same modes that limit the charge mobility according to the TO model [12]. We justify this assignment by (i) the verification that the modes with the strongest off-resonance electron-phonon coupling are energetically in the appropriate frequency region, and (ii) proving that upon charge injection these modes become strongly coupled to the oscillating electric field.

The frequency of the modes with largest electron phonon coupling was computed following the procedure of ref. [13] using a classical molecular dynamics simulation coupled to a series of quantum chemical computations. The time dependent transfer integral \( V(t) \) between the HOMOs and the LUMOs of neighbouring molecules in the \( \mathbf{a-b} \) plane of the pentacene crystal was evaluated to identify the frequency of the modes which modulate most strongly the transfer integral. The Fourier transform of the autocorrelation function \( \langle V(t)V(0) \rangle \) was calculated and the resulting spectral density is shown in figure 7.3. The spectral density varies little within the temperature range considered experimentally and among inequivalent pairs of neighbouring molecules. Clearly, the intermolecular transfer integral is modulated more strongly for the HOMO than for the LUMO, and, more importantly, the modes that provide the strongest modulation are centered around 1 THz (33 cm\(^{-1}\)), i.e. very close to the resonance observed experimentally. This is even more clear when adding a small broadening of 10 cm\(^{-1}\) to the peaks in the spectrum to account for the temperature, possible inhomogeneities and finite spectral resolution in the experiment (figure 7.3).

It is easy to justify qualitatively the strong carrier-induced coupling of these modes to the THz radiation. Any normal mode is coupled to the electromagnetic radiation if the charge density of the system is displaced when it is deformed along that mode, i.e. when the dipole derivative \( \partial \mu / \partial q_i \neq 0 \) (\( \mu \) is the dipole moment of the system). Since a displacement along nuclear modes with strong electron-phonon coupling changes the charge carrier wavefunction dramatically, we expect these modes to be strong absorbers of radiation. For a more quantitative estimate, we consider the simple one-dimensional model Hamiltonian proposed in section 1.4 [12], describing the main physics of independent charges, whose dynamics are dominated by off-diagonal electron-phonon coupling (note that this treatment requires separation, but not thermalization of electrons and holes):

\[
H = \sum_j \left( -V + \alpha (u_{j+1} - u_j) \right) |j\rangle \langle j+1| + |j+1\rangle \langle j| \\
+ \sum_j \frac{1}{2} m \dot{u}_j^2 + \sum_j \frac{1}{2} m \omega^2 u_j^2. \tag{7.1}
\]

According to this model, localized on each molecule \( j \), there is a single electronic state \( |j\rangle \) and a harmonic nuclear mode \( u_j \) with effective mass \( m \) and frequency \( \omega \) (i.e. these optical phonons are dispersionless). The nuclear displacements of molecules \( j \) and its neighbour \( j + 1 \), \( u_j \) and \( u_{j+1} \), respectively, modulate the transfer integral between \( |j\rangle \) and \( |j+1\rangle \).
Figure 7.3: The Fourier transform of the autocorrelation function \( \langle V(0)V(t) \rangle \) for both the coupling between the HOMO levels (a, in black) and LUMO levels (b, in grey). For clarity we show an average of the spectral density obtained for all the inequivalent pairs of nearest neighbours in the \( \textbf{a-b} \) plane, since the difference between them is negligible when the broadening is introduced. The dotted traces show the original curves, whereas the solid ones represent the case of adding a broadening of 0.3 THz to the original spectra. The dotted traces c and d show the conductivity (depicted on the right axis) at \( t = 1.3 \text{ ps} \) for 20 K when optically exciting at 400 nm (c) and at room temperature when optically exciting at 266 nm (d).

with the term \( \alpha(u_{j+1} - u_j) \). The parameters of the Hamiltonian for pentacene (\( \tau, \alpha, \omega \)) have been determined in ref. [12] and they are valid at all temperatures. The radiation absorption rate at frequency \( \omega \) is proportional to \( M^2 = \sum_i |\partial\mu/\partial q_i|^2 \) (\( i \) runs over the normal modes of the system), a quantity that can be easily computed from equation 7.1 at arbitrary temperature. Calculated values of the carrier-induced absorption are very high: For example, with parameters from ref. [13] and the hole wavefunction delocalized over 10 molecules (a lower limit [13]) we find \( M^2 = 17 \text{ (\AA e)}^2 \).

The resonance at 1.1 THz is analogous to the so called soliton induced infrared (IR) absorption observed previously in conductive polymers like polycyetylene at much higher frequencies [27–29]. In pentacene, as in polycyetylene, the modes that modulate the inter-site coupling are crucial for the understanding of the charge transport mechanism. Our results demonstrate that these modes are in the THz frequency range for pentacene. There may be other coupled modes outside our frequency window, but it is apparent that the modes that modulate the charge transport most strongly, reside in the ~1 THz range. It is intuitive that the strongly coupled mode frequency is lower for crystalline organic semiconductors than for polymers. For the former, conduction requires charge delocalization amongst different molecular moieties, and low-frequency intermolecular modes will dominate, while for the latter intramolecular modes (of typically higher frequency) are...
The mechanism of charge transport in oligoacenes studied by THz-time domain spectroscopy

responsible for modulating the conduction along the polymer backbone.

The amplitude of the 1.1 THz resonance decays quickly (∼1 ps) to a lower level, which we attribute to the thermalization of the carriers. In fact, the THz complex conductivity signal has two contributions: from free carriers (mostly real and frequency-independent, observed at long delay times [18, 19]) and from carrier-activated THz (CAT) modes. At short times, the latter dominate the response; at long times free carriers dominate. Immediately after photoexcitation, carriers will be hot, and relatively delocalized. This will strengthen the CAT signal, which will diminish as carriers cool and become increasingly localized (the CAT signal is approximately proportional to the fourth power of the localization length [30]). In contrast, the free carrier signal is relatively insensitive to carrier cooling; the mobility has been shown to depend only very weakly on the precise carrier excited state [12]. As a result, the CAT signal, superimposed on the free carrier signal, loses relative strength upon carrier thermalization. This relatively fast decrease in intensity of the resonance is an observation which we could not explain using any of the other proposed charge transport model. Note that the resonant CAT signature of the charge transport behaviour is present for all delay times at both 20 K and room temperature, indicating that the conduction in the material is governed by one single mechanism at all temperatures.

In conclusion, THz transient conductivity measurements reveal that charge carriers in pentacene are strongly coupled to the low energy phonon modes that, in turn, modulate the probability of charge transfer between adjacent molecular moieties constituting the crystal. We expect such electron-phonon interactions to be a general characteristic of crystalline organic semiconductors.

7.3 The temperature dependence and the charge dynamics of the THz modulation

As mentioned in the previous paragraph, the modulation of the THz pulse consists of two contributions: the CAT signal and the contribution from free carriers. From figure 7.1 it was clear that the typical timescale on which the CAT signal decays is smaller than the timescale at which the rather frequency independent free carrier contribution decays. Figure 7.4, which is derived from figure 7.1(a), stresses this further: The conductivity at 0.9 to 1.1 THz (the range in which the contribution from the carrier induced absorption is the largest) decays very rapidly over the first 1.5 ps, compared to the baseline (0.4 THz).

In figure 7.5 charge dynamics scans (CDSs) are shown for pentacene excited at 400 nm. The modulation values (∆E/E) (taken at the time t that the transient THz pulses show a maximum) are plotted versus the delay time τ, thereby providing information on how the conductivity depends on the cooling, trapping and recombination of charges after optical excitation. It is evident from figure 7.5 that the signal increases with decreasing temperature, a behaviour which is generally interpreted as a sign of band conduction [5,17–19]. However as mentioned in the previous paragraph and section 7.2, the observed signal (∆E/E) does not consist of a contribution of free carriers only. The traces of figure 7.5 can be accurately fit with a double exponential function (A1exp(−τ/τ1) + A2exp(−τ/τ2)) as is shown by the dotted grey lines (for the same reasons as mentioned in section 7.2 the fits are performed for τ > 0.5 ps). The resulting two relaxation times are indeed of a different order of magnitude as is shown in figure 7.6. The fast component related to
Figure 7.4: The real part of the conductivity as a function of delay time $\tau$ at 0.4 THz (where the frequency independent free carrier contribution is relatively high) and at 0.9 to 1.1 THz (where the CAT signal is the strongest) for pentacene excited at 400 nm ($T = 20$ K).

Figure 7.5: THz-TDS charge dynamic traces at various temperatures for single crystals of pentacene excited at 400 nm (with a fluence of 14 J m$^{-2}$). The traces are taken at the time $t$ of the peak modulation. The choice for $\tau = 0$ ps is arbitrary and set at the peak signal. The grey dashed lines are double exponential fits of the charge dynamic traces. The fitting range is from $\tau = 0.5$ ps to 16.0 ps.
The mechanism of charge transport in oligoacenes studied by THz-time domain spectroscopy

The CAT signal is independent of temperature ($\tau_1 = 0.89 \pm 0.05$ ps) whereas the slow component is temperature dependent (as has been previously reported by Thørsmolle et al. [18]). The fact that the recombination and trapping of the carriers in pentacene is dependent on temperature can be explained by the fact that carriers are more mobile at low temperature and as a result have a higher chance of reaching a trap site or another charge. If one would like to study the temperature dependence of the free carriers, one would have to look at the size of the modulation at delay times $\tau > 4$ ps where the contribution of free carriers determines over 90% of the signal. However, since the relaxation is temperature dependent, the response at large delay times will also not give the correct relation for the conductivity as a function of temperature (since the amount of free charges is not equal at different temperatures), as is shown in figure 7.8.

![Figure 7.6](image1.png)

Figure 7.6: The relaxation times $\tau_1$ and $\tau_2$ of the peak signal of the THz modulation ($\Delta E/E$) as a function of temperature when fitting the charge dynamic traces of figure 7.5 with function of the type $A_1\exp(-\tau/\tau_1) + A_2\exp(-\tau/\tau_2)$.

![Figure 7.7](image2.png)

Figure 7.7: Fitting constants $A_1$ and $A_2$ for a double exponential fit ($\Delta E/E = A_1\exp(-\tau/\tau_1) + A_2\exp(-\tau/\tau_2)$) to the charge dynamic traces of figure 7.5 for pentacene optically excited at 400 nm (fluence of 14 J m$^{-2}$).

The correct temperature dependence for the response of the free carriers is simply given by fit parameter $A_2$, which is together with parameter $A_1$ plotted in figure 7.7. Troisi and Orlandi showed [12] that the general power law for the DC mobility in oligoacenes, $\mu \sim T^{-n}$ [7, 10] can be obtained using their model in the case of DC conduction in pentacene. However, in the AC experiments performed here, the relation of $A_2$ and $T$ cannot be modelled with a power law (and neither by the standard relations between DC mobility and temperature in the case of hopping [31] or polaronic transport [10]). As mentioned in section 1.2.1 for AC experiments the amplitude of the modulation will also contain a significant contribution from bound charges or exciton states. The presence of these quasi-particles can be the reason for not observing the behaviour that is expected in the case of a DC experiment.
7.4 Charge density effects

In many materials the charge transport properties are a function of the charge density: at high densities charge-charge interaction becomes non-negligible and give rise to higher scattering rates [32] or the formation of charge-pairs [23]. In the work of Hendry et al. [32] the effect of the charge density on the effective mass and scattering time of rutile and silicon could be successfully modelled. Thereby a straightforward relation between the charge density and the mobility could be deducted from their THz-TDS measurements. The charge transport in pentacene can not be treated with any of the standard scattering models (see section 7.2) and the signal consists of two contributions, the CAT-signal and the contribution from the carriers. As a result, possible differences in the modulation as a function of charge density can have various less conventional origins.

As we mentioned in paragraph 7.2 for pentacene excited at 400 nm, no obvious charge density effects were found. This is clear from the charge dynamics traces of figure 7.9. The peak modulation signal as a function of $\tau$ is shown for three different values of the laser fluence ($T = 20$ K), 3.7, 8.6 and 13 J m$^{-2}$. The three graphs are normalised to their respective laser fluence. Figure 7.9 shows three almost indentical curves (in both amplitude and trend). Clearly in this regime of the charge density, charge-charge interactions do not play a significant role.

When performing the experiments described in section 7.2, at low temperatures and using an excitation wavelength of 266 nm a significant decrease in the size of the THz modulation was observed compared to excitation at 400. This is apparent from the charge dynamic scans (CDSs) of figure 7.10. At room temperature the signals seem equal in size. Apart from differences in amplitude, the dynamics also differ. For both 20 K and 300 K the decay of the signal obtained when exciting at 266 nm is faster than at 400 nm.

This difference in THz modulation at different wavelengths can be explained by the optical absorption spectrum of pentacene. When traveling through a uniform medium, the intensity of the incident laser light decreases according to Lambert-Beer’s law:
The mechanism of charge transport in oligoacenes studied by THz-time domain spectroscopy

Figure 7.9: Charge dynamic traces for pentacene optically excited at 400 nm ($T = 20$ K) with a laser fluence of 13 (solid trace), 8.6 (dotted trace) or 3.7 J m$^{-2}$ (grey dashed trace). The traces are normalised by their laser fluence.

Figure 7.10: Charge dynamic traces for pentacene at both 20 K (black traces) and room temperature (grey traces) after being optically excited by 400 nm (solid traces) or 266 nm (dotted traces) laserlight. The 400 nm pulses had a fluence of 20 J m$^{-2}$ and the 266 nm of 16 J m$^{-2}$. The signals were normalised for their difference in photon density (as a result the 266 nm traces were multiplied by a factor $\frac{400}{266} \cdot \frac{20}{16}$).

\[ I(z) = I_0 (1 - R) e^{-z/\delta(\omega)}, \]  
(7.2)

where $R$ is the grade of reflection (which is close to 10%), $\delta(\omega)$ the optical penetration
depth and \( I_0 \) the laser fluence. The optical penetration depth at 400 nm is known from literature to be 14 \( \mu m \) \[18\]. From both the previously discussed experimental data from Jentzsch et al. \[33\] (see section 4.2) and theoretical data of Tiago et al. \[34\] (see section 2.2) it is evident that the absorption at 266 nm is a factor \( \sim 40 \) larger than at 400 nm. The optically created charge density in a uniform medium is:

\[
\rho(z) = Q I_0 (1 - R) \frac{E_\gamma \delta}{E_\gamma \delta} e^{-z/\delta}, \tag{7.3}
\]

where \( E_\gamma \) is the energy of one quantum of the laser light and \( Q \) the quantum efficiency, the change for an absorbed photon to create a free charge in the material. If we assume the quantum efficiency to be equal to unity and use the laser fluences of our experiments (20 J m\(^{-2}\) for 400 nm 16 J m\(^{-2}\) for 266 nm), the charge density in pentacene can be described by the profile of figure 7.11.

![Figure 7.11: Estimation of the charge density profile in a pentacene crystal when exciting the sample with either 266 nm (16 J m\(^{-2}\)) or 400 nm laser light (20 J m\(^{-2}\)).](image)

Obviously the high absorbance at 266 nm results in a relatively high carrier density near the surface where the laser light incides. The difference in THz response for 266 and 400 nm can be more clearly explained by making estimations for the carrier density in the region where a set fraction of the THz response is originated: for instance, in the case of optically exciting at 266 nm 50% of the signal comes from a region where the average charge density is \( 3.8 \cdot 10^{19} \text{ cm}^{-3} \), whereas for optical excitation at 400 nm 50% comes from a region with a charge density of \( 1.9 \cdot 10^{18} \text{ cm}^{-3} \). The fact that at 266 nm the signal comes from a region with a \( \sim 20 \) times higher carrier concentration can very well explain the observed difference in amplitude of the THz response.

In the regime where charge density effects do not play an important role, the mobility is independent of the carrier density and the conductivity depends linearly on the carrier density. In figure 7.12 the peak modulation is shown as a function of photon flux. For excitation with 400 nm pulses at low temperatures the photon flux dependence is the
The mechanism of charge transport in oligoacenes studied by THz-time domain spectroscopy

Figure 7.12: Double logarithmic plots of the maximum response as a function of fluence obtained from single crystals of pentacene at 20 K and RT, being excited with either 400 nm or 266 nm pulses. The fluence is expressed in terms of the photon flux and thereby correcting for the difference in $E_\gamma$.

closest to linear (for $\Delta E \propto \phi^\alpha$, $\alpha = 0.96 \pm 0.03$). For excitation at 266 nm at 20 K the deviation is the largest, $\alpha = 0.78 \pm 0.02$. The size of the modulation signals for pentacene in our experiments never exceeds 5% of the transmitted signal. Therefore, one can neglect the effect of changes in reflectivity of the sample as a result of a higher carrier density [35]. As a result we can conclude that the observed lower response at 266 nm to be due to charge-charge interaction as a result of a higher density. The charge-charge interaction can lead to the formation of bound charge pairs [23] and non-geminate recombination of charges and therefore could also explain the faster decay of the peak modulation. However, it still does not explain why a different dependence on charge density is obtained at low temperatures compared to room temperature (see figure 7.10). Furthermore one should not forget that the observed signal does not consist of a free carrier component only, but also the CAT contribution.

The strong temperature dependence of the charge-charge interaction can be explained by the same key features of the TO model that explained the size of the CAT signal in section 6.2. The pentacene molecules in the crystal have a density (obtained from the X-ray data of ref. [36]) of $2.92 \cdot 10^{21}$ moieties per cm$^3$, so when excited at 266 nm, 50 % of the signal comes of an area where 1 out of 77 molecules are excited. As a result charges are about 10 lattice spaces away from one another in the $a$-$b$ plane. In ref. [13] it is shown that for pentacene at room temperature the charges are delocalized over 5 sites. The delocalization of the charges is temperature dependent and at 20 K charges are expected to stretch out over more than 10 molecules. As a result it is understandable that the charge density has a larger effect on the response of the free carriers at low temperatures, since the expected delocalization of the charges is larger than the average distance between those charges and thereby limiting the charge transport in the system. On the other hand, the intensity of the carrier activated THz absorption is approximately propor-
tional to the fourth power of the size of the system, which in this case is not determined by the theoretically expected localization length but by the average distance between charges.

The differences in charge dynamics for different charge densities are less easily explained. Actually, it is mainly the ratio between the size of the CAT and free carrier contribution that differs for the various cases. In figure 7.7 one could already see that at 250 K the contribution of the free carriers (24%) is higher than at 20 K (13%). In the next set of four figures (7.13, 7.14, 7.15, 7.16), it is clear that the charge density also has a distinct influence on the ratio between CAT and carrier signal.

Figure 7.13: Charge dynamic scans for pentacene at $T = 20$ K, excited at both 266 and 400 nm with two different photon fluxes.

Figure 7.14: Similar to figure 7.13 except for the fact that the scans at 266 nm (grey traces) are rescaled in a way that their amplitude matches for the scans at 400 nm (black traces) with equal photon flux.

Figure 7.15: Charge dynamic scans for pentacene at $T = 300$ K, excited at both 266 and 400 nm with two different photon fluxes.

Figure 7.16: Similar to figure 7.15 except for the fact that the scans at 266 nm (grey traces) are rescaled in a way that their amplitude matches for the scans at 400 nm (black traces) with equal photon flux.

Figure 7.13 shows CDSs recorded at $T = 20$ K, after exciting the sample with either 266 or 400 nm laser light, both at two different values for the laser’s photon flux. When having a high photon flux ($\phi = 2.2 \cdot 10^{19}$ m$^{-2}$) the amplitude of the 266 nm scans is
considerably lower than for the 400 nm scans, completely conform our findings in the previous paragraph of this section. In figure 7.14 the CDSs obtained at 266 nm are rescaled in such a way that their peak signal is equal to those of the 400 nm scans with equal photon flux. As a result one can see that the trend of the 266 nm scans is comparable to the 400 nm scans, except that at 400 nm the relative carrier contribution is slightly higher. Similar CDSs were obtained at room temperature and displayed in figures 7.15 and 7.16. Besides the fact that even at high photon flux the peak values at 266 nm match those at 400 nm better than at low temperature (which could also be concluded from figure 7.12), there is one other remarkable difference: When comparing the 266 and 400 nm CDSs, the difference in relative contribution from free carriers is significantly larger at room temperature than at low temperature.

**Figure 7.17:** Schematic representation of the effect of charge delocalization and increasing charge density in pentacene.

This can be better understood using the sketch of figure 7.17. At low temperatures and low charge concentrations (in other words when exciting at 400 nm), charges are delocalized over more than 10 moieties and are far enough apart not to intervene with one another. As a result of the high delocalization the CAT contribution is high and as mentioned in the introductory paragraph (7.1), at low temperatures the contribution from the free charges is also high (compared to the contribution at room temperature). At low temperatures and high concentrations (when exciting at 266 nm), the charges will be so close together that their relative distance is shorter than the localization length that follows from the TO model [13]. As a result the CAT signal will be lower since the system with a net charge decreases in size. The contribution from free carriers will also be low compared to the first case since obviously the mobility of these charges will decrease as a result of the spatial overlap of the charges. At room temperature the charges are more localised. At low concentrations this leads to a decrease of both the CAT and free carrier signal compared to the signals at low temperature. Relatively the CAT signal however decreases more strongly than the free carrier contribution (since it is approximately proportional to the fourth power of the localization length). At high concentrations (exciting at 266 nm) the CAT signal will not differ from the previous case since a higher charge density will not have an effect on the already strongly localised system (the average distance between charges does in this case not exceed the theoretical localization length). The free carrier contribution does however decrease compared to the case of exciting at 400 nm, especially at high laser fluences: in graph 7.16 it is evident that the relative difference between the amplitudes of the 266 and 400 nm response at for instance $\tau = 4$ ps is larger at a photon flux of $2.2 \cdot 10^{19}$ m$^{-2}$ than at $5.3 \cdot 10^{18}$ m$^{-2}$.
Apparently although the charges are not as delocalised as they are at low temperatures and their wavefunctions do not overlap, at high densities the Coulomb interaction is still strong enough to hamper the charge transport.

### 7.5 Charge transport in rubrene

One of the most promising new oligoacene materials is 5,6,11,12-tetraphenyl tetracene, better known as rubrene [1,37], which consists of a tetracene backbone with four phenyl side-groups (two on each internal ring) as shown in figure 7.18. In a similar manner as for pentacene it can form organic single-crystals by using physical vapour transport. The main polymorph of rubrene is an orthorhombic crystal with four molecules in the unit cell [38,39]. In figure 7.19 a topview of this structure is shown. At room temperature the lattice parameters for the unit cell are $|a| = 14.43\text{Å}$, $|b| = 7.19\text{Å}$ and $|c| = 26.90\text{Å}$. The band gap at room temperature is reported to be 2.2 eV [40].

![Figure 7.18: Single rubrene molecule.](image1)

![Figure 7.19: Top view of the orthorhombic rubrene crystal showing a unit cell.](image2)

Da Silva Filho et al. [41] showed that both HOMO and LUMO of the rubrene molecule strongly resemble those of tetracene and that the phenyl side-groups of rubrene contribute little to the electronic coupling in the material. These phenyl groups do however increase the intermolecular distances in the material and as a result weaken the intermolecular electronic interactions. Therefore one would expect the carrier mobilities in this material to be less than in tetracene, but on the contrary, the room temperature hole mobility of 43 cm$^2$V$^{-1}$s$^{-1}$ reported for single crystals of rubrene [42] is higher than that of tetracene (1 cm$^2$V$^{-1}$s$^{-1}$ [43]). Since the electronic properties of the single molecules differ little, the difference in mobility has to be either due to a high trap density in tetracene [43] or a different stacking of the molecules in the lattice.

When comparing the structure of rubrene with pentacene, one can observe some remarkable differences. From figure 7.19 it is obvious that the tetracene backbones are oriented differently in the rubrene crystal compared to in tetracene and pentacene: in rubrene the tetracene backbone is oriented parallel to the $ab$-plane whereas in pentacene
The mechanism of charge transport in oligoacenes studied by THz-time domain spectroscopy

Figure 7.20: Two nearest neighbours in a pentacene crystal (type A [13]) and their displacements in the $x$-, $y$- and $z$-direction from one another.

Figure 7.21: Two nearest neighbours in a rubrene crystal and their displacements in the $x$-, $y$- and $z$-direction from one another. For simplicity reasons the rubrene molecules are represented by their tetracene backbone.

The long molecular axis is coming out of the $ab$-plane. The relative orientation of neighbouring molecules in these materials is also different as can be seen in figures 7.20 and 7.21 (for simplicity reasons only the tetracene backbone of the molecule is shown in this figure). Although the distance between molecules in the $z$-direction (using the choice of axes depicted in figure 3 of the introductory chapter) is smaller in pentacene than in rubrene (2.59 compared to 3.74 Å), the pentacene molecules are displaced from one another over a large distance in the $x$-direction (5.34 Å) whereas the rubrene molecules are not. The rubrene molecules however experience a larger displacement from one another along the long molecular axis. In ref. [41] the influence of this shift along the long molecular axis on the transfer integral was calculated and the displacement of 6.13 Å seemed to coincide with a local maximum in the hole transfer integral of $\sim$ 100 meV, a value comparable to that of pentacene (120 meV [12]).

As shown in section 7.2, the charge transport in pentacene is dominated by fluctuations in the transfer integral due to low-energetic phonon modes. For pentacene, the influence of these phonon modes on the transfer integral have been the subject of theoretical studies [13], whereas for rubrene little is known about the lattice vibrations and their influence on the electronic coupling. Raman spectra [44] show no contributions of intermolecular modes and very low interactions between the molecules are expected. Using broadband time-domain THz spectroscopy (in the range from 12 to 30 THz) Koeberg et al. [21] witnessed effects of charge-vibrational coupling for the high-energy intramolecular modes (at 15.5 THz) of rubrene. In section 2.3 vibrational spectra were shown for pentacene calculated using DFT methods. A similar calculation has been done for rubrene but with a much smaller basis set (6-31G instead of 6-311+G(d,p)). Although the resulting frequencies will have large deviations from the actual values, the results can still give a good indication of which intramolecular modes are expected to modulate the electronic coupling the most. Since the transfer integral is a rapidly changing function of the displacement along the $y$-axis (or long molecular axis) [41], vibrational modes that show large motions in that direction (like the one displayed in figure 7.22) are expected to have a high influence on
the electronic coupling. The energy of these modes range from 2 to 10 THz. Modes that displace parts of the backbone in the z-direction will most probably also slightly modulate the transfer integral and two of those are low-energetic (0.8 and 1.8 THz). In fact a recent publication by Troisi reveals that a maximum should occur at 1.6 THz [45].

In a similar manner as was done for pentacene in section 7.2, THz-TC measurements have been performed on single crystals of rubrene (grown by A. S. Molinari at the TU Delft [46] and having typical dimensions of 3 mm x 2 mm x 5 µm). In figure 7.23 the low temperature (20 K) transient conductivity is plotted for various delay-times $\tau'$ after optically creating charges with 400nm laser pulses with a fluence of 18 J m$^{-2}$. The plot differs from 7.1(a), which shows the conductivity traces for pentacene obtained at similar conditions. The conductivity for rubrene is predominantly real and rising with increasing frequency. The traces do however not show a resonance, which in the case of pentacene was attributed to a carrier induced absorption (see section 7.2). If the mechanism of transport in rubrene is alike that of pentacene, one would expect the ”y” modes described in the previous paragraph to contribute strongly to the CAT-signal. Since these modes are outside the range that is observed in the experiments of figure 7.23 and 7.24, a strong resonance can not be expected. Fitting the conductivity traces with the sum of a frequency independent part and a Lorentzian (as was done for pentacene in figure 7.1) gives a reasonable result in the case the Lorentzian has its peak position at 1.7 ± 0.2 THz (which is in fair agreement with ref. [45]).

For pentacene at $f = 0.4$ THz the free carrier component dominates the signal. At $\tau' = 1.3$ ps and $f = 0.4$ THz the conductivity of pentacene is $\sim 3.5$ times higher than rubrene. Assuming a QE of unity for both materials, for rubrene a fluence of 18 J m$^{-2}$, $\delta = 2.8$ µm [47] and $d = 5$ µm and for pentacene a fluence of 20 J m$^{-2}$, $\delta = 14$ µm [18] and $d = 15$ µm, the number of created charges in both materials are almost equal. As a result one can only conclude that the AC mobility of the charges in the single crystals of pentacene is considerably higher than in the rubrene crystals. The reported room temperature DC mobility of pentacene (35 cm$^2$/Vs [6]) is indeed higher as the one for rubrene (20 cm$^2$/Vs [48]). The conductivity at room temperature for rubrene is shown
Figure 7.23: Real (solid) and imaginary (dashed) conductivity as a function of frequency for rubrene single crystals at 20 K when exciting with 400 nm pulses with a laser fluence of 18 J m\(^{-2}\) (all traces represent an average of 10 scans). Spectra are shown for different times, \(\tau'\), after excitation, ranging from 0.5 ps to 3.7 ps (with intervals of 0.4 ps). The dotted line shows a fit function to the conductivity trace for \(\tau' = 1.3\) ps consisting of a frequency independent part and a Lorentzian with a peak position at 1.6 THz.

Figure 7.24: Real (solid) and imaginary (dashed) conductivity as a function of frequency for rubrene single crystals at room temperature when exciting with 400 nm pulses with a laser fluence of 22 J m\(^{-2}\) (all traces represent an average of 10 scans). Spectra are shown for different times, \(\tau'\), after excitation, ranging from 0.5 ps to 3.7 ps (with intervals of 0.4 ps).
in figure 7.24. The general trend is similar to the conductivity at low temperature, but the signal is a factor 3 lower, which is in agreement with the reported apparent bandlike behaviour [37]. When again comparing to the response for pentacene under similar conditions (at 298 K, excited at 400 nm with a fluence of 22 J m$^{-2}$, $\tau' = 1.3$ ps), the signal at room temperature is found to be 1.7 times higher for pentacene, compared to 3.5 times at 20 K; apparently the influence of thermal motions on the charge transport is less strong in rubrene.

Figure 7.25: Charge dynamic scans for rubrene at different temperatures. The sample was optically excited by 400 nm laser pulses with a fluence of 18 J m$^{-2}$. A diaphragm was used giving rise to a reflection, hence the second peak 0.4 ps after the peak modulation. The data were fitted with a double exponential function, which takes into account a 14 % reflection (grey dotted traces).

Figure 7.26: The constants $A_1$ and $A_2$ of the double exponential fits to the CDSs of 7.24 as a function of temperature. When assuming a similar concept as for pentacene $A_1$ as can be seen as the size of the CAT signal and $A_2$ the size of the free carrier response.

The charge dynamic scans for rubrene at various temperatures are shown in figure 7.25. Since the size of the rubrene crystals is of a similar size as the spot size of the THz probe beam, a diaphragm was used in the experiments for the THz radiation not to "leak" around the edges of the sample. As a result of using this diaphragm the charge dynamic scans for rubrene show a 14 % reflection 0.4 ps after the peak modulation.

The conductivity plots for rubrene give no clear indication of a CAT signal. If we however fit the CDSs with a double exponential function as was done in paragraph 7.3 for pentacene, it is clear for all traces of figure 7.25 the modulation signal decays with a fast ($\tau_1 = 0.7\pm0.2$ ps) and a slow component ($\tau_2 = 9\pm3$ ps). The best and most consistent fits were obtained when including the reflection in the functions and the resulting amplitudes $A_1$ and $A_2$ as a function of temperature are plotted in figure 7.26. Both components of the modulation decrease with increasing temperature. The ratio between the $A_2$ and $A_1$ is $0.23 \pm 0.03$. If one compares these CDSs to those of pentacene (fig. 7.5 and 7.7), the resemblance does suggest that the mechanism of transport in rubrene can possibly be described by the model of Troisi and Orlandi. In that case $A_2$ in figure 7.26 represents the contribution from free carriers.

Since the penetration depth of 266 nm light in pentacene was $\sim 40$ times smaller than
The mechanism of charge transport in oligoacenes studied by THz-time domain spectroscopy

Figure 7.27: Charge dynamic traces for rubrene at both $\sim 20$ K (black traces) and $\sim 200$ K (grey traces) after being optically excited by 400 nm (solid traces) or 266 nm (dotted traces) laserlight. The signals were corrected for their difference in photon density.

Figure 7.28: Double logarithmic plots of the maximum response as a function of fluence obtained from a single crystal of rubrene at 20 K, which is excited with either 400 nm or 266 nm pulses. The fluence is expressed in terms of the photon flux and thereby correcting for the difference in $E_\gamma$.

For 400 nm light, excitation at 266 nm resulted in a relatively high carrier density near the surface. As a result the CDSs showed charge density effects when exciting the crystal with 266 nm pulses with a fluence of 16 J m$^{-2}$. For crystalline rubrene no absorption data are available for photon energies exceeding 3.5 eV, but for rubrene in solution it is shown that the absorption at 266 nm is a factor 4 smaller than at 400 nm [49]. Figure 7.27 shows CDSs for rubrene excited using both 266 nm and 400 nm laser pulses. In both cases the charge densities created in the material are over 10 times smaller than the one reported for pentacene excited at 266 nm. The measured response is therefore similar in both amplitude and trend. The modulation as a function of fluence (depicted in figure 7.28) show a linear trend in the case of exciting at 400 nm as well as at 266 nm, proving that the created charge density is not sufficiently high to have strong charge-charge interaction in the material.

7.6 Overview

In this chapter THz-TDS measurements (performed at 20 K and 300 K) on ultra-pure single-crystals of pentacene and rubrene were presented. THz-TDS is a pump-probe technique that enables studying charge transport by determining the spectral optical conductivity in a contact-free manner while suppressing all forms of incoherent radiation. For the charge transport in oligoacene materials, various models have been proposed [8–10, 12] and the measurements performed in this chapter can give more insight in the validity of these models. Charge carriers were created in the ultra-pure single-crystalline samples by either 400 nm or 266 nm laser pulses. The initial decay of the THz modulation after optically creating charges was of the order of the THz pulse width. To determine correct values of the conductivity, the method described in paragraph 6.4 was used to
process the measured modulation signal. The modulation signals were also corrected for small THz signals generated by the laser pulses. Therefore, we are convinced the observed response is fully originating from the excited pentacene sample.

The spectral conductivity of pentacene at 20 K consists of two clear contributions: an almost frequency independent part and a clear resonance at $\sim 1$ THz, which was observable for all recorded times after excitation and its amplitude varied with delay time. A similar conductivity signal was obtained at room temperature, but a factor 5 lower in amplitude. Usually, the lower conductivity at higher temperature is interpreted as a clear sign of bandlike transport. Efforts to explain the observed resonance by assuming the charges form small polarons [10] were unsuccessful. Not only because the position and intensity of the resonance does not match with possible features in the conductivity traces originating from the presence of a small polaron, but also because the observed dynamics (the resonance signal decays significantly faster than the baseline signal) can also not be understood when applying this model. The formation of bound polaron pairs [23] could also not account for the observed features, since the formation of such quasi particles highly depends on the charge density in the material. For the density regime in which the measurements at 20 K were performed, no density effects were observed. Instead the resonance is attributed to the absorbance of THz radiation by those low-energetic vibrational modes that dominate the electronic coupling between neighbouring molecules [13]. This absorbance from nuclear modes is activated by the presence of delocalised charges, equivalent to the soliton induced absorption observed in polymer materials [27–29]. The presence of such a carrier activated THz absorption (CAT) gives support for the charge transport model proposed by Troisi and Orlandi [12], which states that the charge transport in oligoacenes is dominated by the large fluctuations of the transfer integral due to low-energetic phonon modes centred around 1.0 THz. The position and width of the observed feature in the conductivity traces show strong resemblance with an envelope of the “coupling intensity” of the phonon modes.

Since the intensity of the CAT signal is proportional to the fourth power of the delocalisation length of the charges, the signal will decrease rapidly as a result of “cooling” of the charges. The contribution of the free charges is relatively insensitive to cooling effects. Charge dynamical scans confirm this expected behaviour, showing a decay of the THz response that consists of two components: A fast component, which was contributed to the CAT signal and a slow component describing the dynamics of the free carriers.

The amplitude of the THz response depends on the excitation wavelength: at low temperatures excitation at 266 nm gave significantly lower modulation signals than at 400 nm (whereas similar laser fluences were used). This can be explained by the fact that the optical absorption of 266 nm light is a factor 40 larger than of 400 nm light, giving rise to substantial higher charge densities at the surface. Therefore the difference in response was claimed to be due to charge-charge interactions. However, at room temperature, a clear difference in the amplitude of the modulation for excitation at 266 nm in comparison to 400 nm excitation was not observed. The apparent charge-charge interaction seems to be dependent on temperature and therefore indirectly dependent on the mobility and/or delocalisation of the charges. Given the observed support for the validity of the model by Troisi and Orlandi, these charge density effects were explained by assuming the presence of a CAT signal and a free carrier contribution, and their estimates of the delocalisation lengths of the charges as a function of temperature.
Also for the single-crystals of rubrene the THz transient conductivity has been determined. The obtained conductivity plots for rubrene differ from those of pentacene. No clear resonance or absorption is present in the spectral domain (0.4 to 1.2 THz). The real part of the conductivity increases as a function of frequency, which might suggest that there is a maximum in response outside the domain probed by the THz beam (also because the conductivity traces can be fitted in such a way that a resonance at \( \sim 1.7 \text{ THz} \) is predicted). Although these observations do not give any straightforward support for the charge transport model which was presented for pentacene, it suggests that THz spectroscopy can possibly corroborate the validity of the charge transport model for rubrene presented in reference [45].

The charge dynamics of rubrene reveal a similar behaviour as those of pentacene: the THz response consisted of a fast (\( \sim 1 \text{ ps} \)) and a slow (\( \sim 10 \text{ ps} \)) component and the amplitude of both components decreases with increasing temperature. Although it is far from being a solid proof, the resemblance in charge dynamics does suggest that the charge transport in the materials has similarities. Considering these results, we are unable to make a substantial claim on whether the charge transport in rubrene is governed by a similar mechanism as proposed for pentacene. In order to make a more quantitative comparison of the conductivity in pentacene and rubrene, a broader THz source (enabling to measure up to 10 THz) will have to be used and more knowledge about the intermolecular vibrational modes of the material is required.
References


The mechanism of charge transport in oligoacenes studied by THz-time domain spectroscopy


Abstract

The Influence of the Vibrational Properties on Charge Transport in Oligoacenes

Over recent years there has been a growing interest in molecular semiconductors of the oligoacene family. The interest has been spurred by the unique properties of these materials for applications for electronic devices, namely being flexible, cheap and exhibiting relatively high charge-carrier mobilities. Despite this interest, the nature of charge transport in the materials has remained the subject of intense debate.

When these oligoacenes are used for device applications, they will often be evaporated as a film onto a substrate, since the fabrication process and the handling of these thin films is easier and cheaper than using single crystals. Besides the fundamental bulk properties, for the usage in devices it is also of high importance to know how the properties of these materials differ at the interface with metals, since the substrates and contacts are often metallic. Therefore in this work both the vibrational and electronic properties of thin films of pentacene have been investigated as well as the intrinsic charge transport mechanism for the single-crystalline bulk material of pentacene and rubrene.

The first main focus in this study was on the electronic and vibrational properties of thin layers of pentacene (ranging from 1 monolayer to 6 layers of pentacene molecules) evaporated on metal surfaces. These pentacene layers have been investigated using High Resolution Electron Energy Loss Spectroscopy (HREELS), which is a surface sensitive technique that probes both the vibrational and electronic states of the top layers of the sample by detecting the loss in energy of a beam of monochromatic electrons. The main advantages of this technique in comparison to techniques like IR and Raman spectroscopy are the surface sensitivity, the high spectral resolution (FWHM of 13 cm\(^{-1}\)), the broad energy range (from lattice phonons to surface plasmons and interband transitions) and the ability to measure as a function of wave vector transfer.

Pentacene was grown upon Ag(111) and Au(100) surfaces, forming thin layers of various thicknesses. The obtained vibrational spectra were compared to the vibrational modes for an isolated molecule calculated using DFT methods. The spectra of films of over 4 molecular layers showed contributions from all the optical active modes predicted by the calculation as is expected for a non-frustrated Van Der Waals bonded crystalline material. Furthermore the spectra showed low energetic features related to the lattice phonons. Both inter- and intramolecular modes showed little to no dispersion. The spectra for a monolayer deviated strongly from the vibrational structure of the multi-layers. Not only were the intermolecular modes absent, all intramolecular optical active modes with a dipole moment parallel to the interface were screened by the metal surface. In the case of a monolayer of pentacene on Ag(111) the interaction with the surface is so
strong that the symmetric $A_g$ modes became optically active as a result of charge transfer from the metallic substrate. For the intermediate regime (layers of 2 to 4 molecules) the spectra showed several contributions that cannot be explained using the calculated data on the symmetry and energy of the intramolecular modes.

With HREELS not only the vibrational aspects of the thin films were studied but also the electronic transitions. The spectra for layers of more than four molecular layers could be modeled by combining calculations on the position of both excitonic and band levels and calculations of the vibronic fine structure. For a monolayer of pentacene, states within the electronic gap were observed, the so-called Charge Neutrality Levels, which are substrate dependent. With increasing thickness the observed presence and position of the exciton states differed, thereby giving more insight in the structure of pentacene near the interface.

Terahertz Time Domain Spectroscopy (THz TDS) is a technique that allows determining the complex frequency dependent conductivity and is a powerful tool to investigate the charge transport mechanism in materials. THz TDS was used to study the charge transport as a function of temperature for single crystals of both pentacene and rubrene. For pentacene the conductivity spectra at various temperatures showed a strong absorption for the low energetic vibrational modes and thereby gave evidence for the model proposed by A. Troisi and G. Orlandi. This model describes the charge transport behaviour by one single mechanism: the large fluctuations in the intermolecular coupling of electronic states caused by thermal molecular motions. Furthermore it is shown that the charge density, and as a result the interaction between charges, plays an important role in the conductivity of these materials.

In conclusion, this work shows that vibrational aspects are a key factor in understanding the charge transport in oligoacene materials, and that good knowledge of the properties of these materials at the interface is essential, since differences in both structure and electronic interaction with the substrate give rise to different vibrational and electronic states in oligoacene materials.
Samenvatting

De aandacht voor organische halfgeleiders en vooral de oligoacenen is de laatste jaren sterk toegenomen. Dit is vooral te danken aan het feit dat deze materialen beschikken over unieke eigenschappen, die uitermate geschikt zijn voor het gebruik in elektronische componenten. Ze zijn flexibel, goedkoop en hebben een relatief hoge ladingsmobiliteit. Ondanks de grootte interesse in oligoacenen, is het onderliggende principe voor ladingstransport in deze kristallen nog steeds een punt van discussie. Voor het gebruik in elektronische componenten worden oligoacenen vaak als dunne laag opgedampt op een substraat, aangezien de fabricatie en behandeling van deze lagen eenvoudiger en goedkoper is dan het gebruik van éénkristallen. Aangezien deze substraten en de aangebrachte contacten vaak metallic zijn is het van groot belang om niet enkel meer inzicht te krijgen in het fundamentele intrinsieke geleidingsgedrag van het 'bulk' materiaal maar ook in de eigenschappen van deze materialen aan grenslagen met metalen. In dit onderzoek zijn zowel de vibrationele en elektronische eigenschappen van dunne pentaceen films als het intrinsieke gedrag van de ladingen in de bulk van pentaceen en rubreen éénkristallen onderzocht.

De vibrationele en elektronische eigenschappen voor dunne lagen pentaceen (van 1 tot 6 moleculaire lagen dik) opgedampt op een metaaloppervlak zijn bestudeerd met het gebruik van HREELS (Hoge Resolutie Electron Energie Verlies Spectroscopie). Deze techniek geeft informatie over de vibrationele en elektronische overgangen in de bovenste lagen van een oppervlak. Hiervoor wordt een monochromatische bundel elektronen gebruikt, die nadat ze aan het oppervlak zijn verstrooid, gedetecteerd worden waarbij men zowel het energieverlies als de verstrooiingsschok kan meten. De voordelen van deze techniek boven optische technieken zoals Infra-Rood en Raman spectroscopie zijn de oppervlakte gevoeligheid, de hoge spectrale resolutie, het brede energiedomein waarover gemeten kan worden (van roostertrillingen tot bandovergangen) en de mogelijkheid om de dispersie van de toestanden te meten.

Twee verschillende substraten zijn gebruikt in dit onderzoek: een zilver (111) en goud (100) oppervlak. De vibrationele spectra gemeten op de dunne lagen pentaceen aangebracht op deze oppervlakten werden vergeleken met het berekende IR spectrum voor een enkel molecuul. Voor lagen dikker dan vier moleculaire lagen, toonden de HREELS spectra alle toestanden die in het berekende spectrum voorkwamen plus een aantal laag energetische bijdragen, die konden worden toegewezen aan de roosterfononen van pentaceen. Zowel deze intermoleculaire als de intramoleculaire vibraties toonden vrijwel geen dispersie. Het spectrum voor een enkele monolaag pentaceen week sterk af van dat voor de dikkere lagen. Niet alleen waren de intermoleculaire vibraties afwezig, ook werden de modes die een dipoolmoment hebben evenwijdig aan het oppervlak volledig afgeschermd door het metaal. Voor de monolaag pentaceen op Ag(111) was de interactie op de grenslaag zodanig sterk dat, als het gevolg van ladingsoverdracht van het metaal
naar de pentaceenmoleculen, de symmetrische $A_g$ modes ook zichtbaar waren. In de spectra voor lagen in het tussenliggende regime (twee tot vier moleculaire lagen dik) waren er enkele bijdragen zichtbaar die niet toegewezen konden worden aan optisch actieve toestanden voor een enkel vrij molecuul.

Naast de vibrationele toestanden zijn ook de elektronische overgangen in deze dunne lagen onderzocht. Voor lagen dikker dan vier moleculaire lagen konden spectra goed gemodelleerd worden door zowel theoretische data over de exciton- en band-overgangen als berekeningen aan de vibrationele structuur te combineren. Voor een monolaag pentaceen, overgangen binnen de band gap waren waargenomen. De positie van deze zogenaamde Charge Neutrality Levels bleek afhankelijk van het substraat. Door het bestuderen van de positie van de exciton overgangen voor filmen van één tot vijf moleculaire lagen dik, kon er meer informatie worden gegeven over de structuur van pentaceen in dit overgangsgebied.

Terahertz tijdsdomein spectroscopie (THz TDS) is een pump-probe techniek waarmee men de complexe frequentie afhankelijke conductiviteit kan bepalen, waardoor het uitermate geschikt is voor het onderzoeken van het ladingstransport in materialen. Deze techniek is gebruikt om het geleidingsgedrag in éénkristallen van zowel pentaceen als rubreen te bestuderen als functie van de temperatuur en de ladingsdichtheid. Een sterke resonantie was zichtbaar in de conductiviteitsspectra voor pentaceen. De energie waarbij deze absorptie werd waargenomen komt overeen met de laag energetische fonontoestanden die verantwoordelijk zijn voor de sterkste modulaties van de elektronische koppelingen tussen naburige moleculen. Hiermee is een experimenteel bewijs geleverd voor het door A. Troisi en G. Orlandi opgestelde model, dat het geleidingsgedrag in oligoaceen kristallen verklaart aan de hand van de invloed die fononmodes hebben op de koppeling van energieniveaus. Verder kon met THz TDS worden aangetoond dat de ladingsdichtheid in pentaceenkristallen een grote invloed heeft op de mobiliteit van de ladingen.

Ter conclusie, dit experimentele werk toont aan dat vibrationele beweging in oligoaceen materialen bepalend is voor het ladingstransport en dat een goede kennis van de vibrationele en elektronische eigenschappen van deze materialen bij de grenslaag met een metaal noodzakelijk is omdat daar nieuwe toestanden ontstaan.
Dankwoord

Uiteindelijk na bijna vijf jaar heb ik dan toch mijn promotieonderzoek tot een einde weten te brengen, waarvan u nu het resultaat in handen heeft. Of dit einde een goed einde is, zal de tijd uitwijzen, maar het was me in ieder geval nooit gelukt zonder de hulp en steun van vele mensen. Hierbij zou ik dan ook graag mijn dank en waardering willen uitspreken voor alle mensen die me hierin hebben geholpen. Mocht het zo zijn dat ik hierbij iemand over het hoofd zie, dan zou ik me daar bij voorbaat voor willen excuseren.

Ten eerste wil ik mijn co-promotor, Kees Flipse, bedanken, die, nadat hij al bereid was geweest me te begeleiden bij mijn externe stage en afstudeerproject, mij nu wist te overtuigen om te gaan promoveren in de nanofysica. Al deze jaren heb ik met plezier samengewerkt met hem. Kees is altijd volop ideeën en enthousiasme. Zijn kijk op fundamenteel en ”spannend” onderzoek maakt hem een van de laatste romantici onder de wetenschappers (ik hoop dan ook dat hij niet teleurgesteld is in het feit dat ik die passie niet op alle momenten deelde met hem). Tijdens borrels en dienstreizen zorgde Kees ook altijd voor de nodige ambiance en onder het genot van een hapje en een drankje wist hij me altijd te entertainen met de meest uiteenlopende discussie onderwerpen.

Ook zou ik mijn eerste promotor professor René Janssen willen bedanken, die het voor mij heeft mogelijk gemaakt binnen de groep Molecular Materials and Nanostructures dit promotie onderzoek uit te voeren. Ik heb grote bewondering voor zijn tomeloze inzet voor zijn vak: ondanks zijn overvolle dagindeling wist hij toch altijd weer wat tijd vrij te maken voor mij. Zijn positivisme en enthousiasme waren altijd het juiste tegengas voor mijn pessimisme en cynisme. Zoals mijn vrouw ooit opmerkte: ik snap niet dat iemand die zo hard werkt nog altijd kan glimlachen.

Al het experimentele werk besproken in hoofdstuk 4 en 5 was nooit mogelijk geweest zonder de hulp van de technici Wijnand Dijkstra, Rein Rumphorst (die geheel onbezoldigd al een tiental jaar onze elektronica problemen oplost en verder ons van levenswijsbeden voorziet), maar vooral Gerard Wijers, de reddende engel wanneer door toedoen van mij of een andere onverlaat de HREELS opstelling defect was. Zijn uitzonderlijke expertise op het gebied van vacuumtechnieken zal nog vreselijk gemist worden wanneer hij over een paar jaar die vervelende weken tussen de vakanties in mag overslaan. Veel dank gaat ook uit naar Zdeněk Nováček, die voor mij een aantal STM experimenten heeft uitgevoerd.

Verder wil ik graag mijn kantoorgenoot, Nick Podaru, bedanken. Ten eerste omdat hij het zo lang met mij heeft weten uit te houden en ten tweede omdat hij me immer wist te amuseren met zijn Roemeense grapjes, updates over de laatste gadgets en auto’s, zijn eigen interpretatie van de Nederlandse taal en een aquarium met ofwel veel te veel of bijna geen visjes. Ook de andere collega’s (Martijn, Jean-Michel, Gheorghe, Juan, Hans, Ron, Joris, Jiri, Klára, Marta, Alex, Dimitri, Yingxin, Simon and Erik) en de studenten in onze groep (met name Friso, Erwin, Kevin, Filipé en Inge) zou ik graag bedanken voor de
goede adviezen, oeverloze discussies tijdens de koffiepauze, spannende voetbalwedstrijden
op de gang en alle andere vormen van kinderlijk amusement. Het is met pijn in mijn hart
dat ik nu besef dat ik voor het eerst in mijn leven mij eens volwassen zal moeten gaan
gedragen. Natuurlijk mag ook onze portier, Toon Wouters, niet ontbreken, die vaak “effe
kwam buurten” wanneer ik rond zeven uur nog aan het werk was.

Ik ben buitengewoon veel dank verschuldigd aan de Biosurface Spectroscopy groep
van het AMOLF instituut te Amsterdam. In de eerste plaats aan mijn tweede promotor,
professor Mischa Bonn, die mij de gelegenheid gaf in zijn groep THz-TDS experimenten
uit te voeren en vooral in het afgelopen jaar veel tijd voor mij heeft vrijgemaakt om onze
meetdata te bespreken, maar daarnaast ook in grote mate aan Mattijs Koeberg, Euan
Hendry en Joep Pijpers die mij ter plekke hielden bij de uitvoering van de experimenten
en me wegiwis maakten in de wereld van de THz spectrosopie.

Het laatste hoofdstuk van dit proefschrift was nooit tot stand gekomen zonder de
topkwaliteit organische kristallen die ik tot mijn beschikking had. Daarom wil ik dan
ook Oana Jurchescu, Anne Arkenbout en professor Thom Palstra van de Rijksuniversiteit
Groningen bedanken voor de pentaceenkristallen die zij mij gegeven hebben en Anna
Molinari, Arno Stassen en Alberto Morpurgo van de TU Delft voor de rubreenkristallen.

Zonder de theoretische data en hulp van Alessandro Troisi had de interpretatie van de
experimentele data in hoofdstuk 7 nooit tot stand kunnen komen. Verder hebben Peter
Bobbert and Krzysztof Meisel mij geholpen met goede suggesties en tips voor het doen van
DFT berekeningen aan elektron-phonon koppeling. Ik zal me Krzysztof altijd herinneren
als een sympathieke en open persoon. Graag zou ik ook Murilo Tiago willen bedanken
voor het feit dat hij mij toestond om zijn resultaten van figuur 2.1 in dit proefschrift te
plaatsen.

De laatste vijf jaar bestonden natuurlijk niet enkel uit het doen van natuurkundig
onderzoek en al de uren die ik al hardlopend doorbracht waren een welkome afwisseling.
Alhoewel ik soms hele heldere ingevingen had terwijl ik moederziel alleen over de heide
rond Eindhoven aan het struinen was, lijkt het me toch erg op zijn plaats om mijn
trainingsmaatjes (Vincent Hermes, Marco Ramaekers, Mark van den Broek, Ruben Smit
en Yassin Mahamoud) te bedanken. De trainingen samen waren altijd leuke ontspannende
momenten die de meest vervelende dagen konden breken. Aangezien ik het nu toch over
de meer relaxte tijden heb, zou ik ook graag mijn vrienden in Zuid-Afrika (Johan Jordaan,
Nakedi Maputla, Mmakoena Maremane and Piotrek Podkowa) willen bedanken voor de
schitterende vakanties die ik samen met hen gehad heb in de laatste vijf jaar.

Ik zou heel graag mijn ouders willen bedanken voor alle zorg en ondersteuning die
zij mij altijd gegeven hebben en alle kansen die ze voor mij gecreëerd hebben. Zonder
hen was het voor mij nooit mogelijk geweest dit te bereiken. Mijn zus, Annemarie, mag
natuurlijk ook niet ontbreken. Zij is er altijd voor me, of het nu is voor een gezellige
etentje of gewoon om lekker bij te kletsen (alhoewel ik natuurlijk in plaats van de uren
durende telefoongesprekken ook een paar pagina’s had kunnen typen).

Als allerlaatste zou ik de voor mij belangrijkste persoon in deze vijf jaar willen be-
danken: Eunice. Vooral in het laatste half jaar heeft haar engelengeduld en begrip ervoor
gezorgd dat ondanks de weinige vrije tijd en de grote tijdsdruk die ik had, onze relatie er
nooit onder heeft geleden. Haar liefde en zorg maakten het vijf hele mooie jaren.
Curriculum Vitae