Theoretical studies towards a ferroelectric organic field-effect transistor based on functional thiophene molecules

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1 Introduction

1.1 Motivation

Electronic devices based on organic semiconducting materials, e.g. thin-film organic field-effect transistors (OFETs) or organic light-emitting diodes (OLEDs), have attracted growing interest in recent years due to their promising electrical, optical and mechanical properties. The conventional set-up of an OFET device is shown in Figure 1.1 (a). It consists of the dielectric gate, the source and drain contacts and the organic semiconductor. The latter operates as the conducting channel for the charge carriers that move from the source to the drain electrode. The gate electrode controls the charge induced into the channel.

In particular, functional thiophene-based molecules are candidates with good prospects for application as the organic semiconducting material in the OFET device, see e.g. Refs. [1–7]. They possess an extended, polarisable aromatic \( \pi \)-electron system that promotes the self-assembly, i.e. the high structural ordering, of the molecules in the organic film. The charge transport in the organic film is realised in the direction perpendicular to the plane of the thiophene rings via a hopping transport mechanism, i.e. the mobile charges (electrons or holes) jump along the HOMO or LUMO states of the stacked molecules [1, 5, 8–10]. Thus, a good \( \pi-\pi \)-overlap and a consequent stacking of the thiophene molecules in the film perpendicular to the substrate is essential to achieve excellent electric properties such as high charge carrier mobilities and low resistive losses [2–4].

Among various approaches to obtain thiophene-based molecules with the desired molecular orientation, the two very promising molecules \( \alpha,\omega\)-dicyano-\( \beta\beta' \)-dibutyl-quarterthiophene (DCNDBQT) and 5-cyano-2-(butyl-4-phosphonic acid)-3-butylthiophene (CNBTPA) were designed and synthesised by Haubner et al. [11], see Figure 1.1 (c). The high-order lamellar stacking arrangement of the cyano-substituted thiophene molecules is promoted by the formation of intermolecular CN···HC hydrogen bonds and dispersive \( \pi-\pi \)-interactions [11–13]. The phosphonic acid group of the CNBTPA molecule acts as the anchoring group to the substrate and well-anchored, robust self-assembled monolayers are formed, as it has been shown by non-contact atomic force microscopy and X-ray diffraction [11]. In general, the phosphonic acid headgroup has become an attractive coupling group due to its high affinity towards various metal oxide surfaces [11, 14–18]. However, in many cases the exact binding state of the phosphonic acid anchoring group to the adsorbate surface is still much debated.
The highly polarisable thiophene-based molecules are also very attractive materials that are potentially applicable as the field-sensitive organic semiconducting component of a so-called ferroelectric OFET device, cf. Figure 1.1 (b) [19, 20]. In such device, an electric field is induced by the polarisation of the ferroelectric substrate that serves as gate field in the device. Thus, it is essential to establish the influence of the electric field on the organic material.

The object of this thesis is to investigate the structural and electronic properties of the thiophene-based molecules with respect to their application as the (field-sensitive) organic semiconducting material in (ferroelectric) OFET devices. Moreover, we study in detail the applicability of the phosphonic acid headgroup as the anchoring group to bind the functional thiophene molecules to the dielectric or ferroelectric support. All investigations are performed employing quantum-chemical ab initio and density-functional theory based calculations. (We will give more detailed introductions to the studied topics separately in the respective chapters.)

1.2 Outline

This thesis is organised as follows: In Chapter 2, we give a short overview on the fundamentals of quantum-mechanics and introduce the most important quantum-chemical methods used throughout this work with a special focus on the density-functional based tight-binding method (DFTB), which has been mostly applied. Furthermore, we introduce
the dispersion-corrected DFT-functionals, which are employed to study the intermolecular
\( \pi-\pi \)-stacking interactions and give the basics of the perturbation theory for the consider-
ation of an external electric field. We conclude this chapter with the quantum-chemical
description of periodic structures and a short introduction to the geometry optimisation
methods employed in this thesis.

In Chapter 3, we study in detail the adsorption of (alkyl) phosphonic acids on alu-
minium oxide and titanium oxide surfaces by means of density-functional based calculations. We evaluate the stability and ordering of the adsorbed phosphonic acids with respect
to their binding mode and to the surface structure of the adsorbate. Moreover, the structural
and electronic properties of the adsorption complexes are examined, which are important
for their application in organic-based electronic devices.

In Chapter 4, we focus on the CN···HC hydrogen bond and the \( \pi-\pi \)-stacking interaction
between functional thiophene-based molecules that are supposed to promote the formation
of well-ordered self-assembled layers in the semiconducting organic film. Hence, this in-
vestigation is mainly dedicated to study the influence of the intermolecular interactions on
the geometry and technologically relevant electronic properties of the molecules.

In order to assess their potential as field-sensitive organic semiconducting component
in a ferroelectric OFET device, we establish the influence of an external electric field on
a set of phosphonic acid and thiophene-based molecules in Chapter 5. In particular, we
calculate the polarisabilities of the molecules to get a first qualitative estimation of their
field-sensitivity in general. Furthermore, the HOMO-LUMO gap energy as well as the en-
ergies of the frontier molecular orbitals of quarterthiophene and their derivates are studied
as a function of the electric field strength and the molecular orientation. We summarise and
conclude this work in Chapter 6.
2 Computational methods

2.1 Fundamentals of quantum-mechanics

2.1.1 The Schrödinger equation

In quantum-mechanics, the wavefunction $\Phi$ fully characterises the state of a molecular system consisting of $N$ electrons and $M$ nuclei \[21\]. In general, $\Phi$ is a complex function and depends on the coordinates and spins of all electrons \[\vec{x}_i=(\vec{r}_i; \sigma_i)\] and nuclei \[\vec{X}_k=(\vec{R}_k; \Sigma_k)\], and on the time ($t$):

$$\Phi = \Phi(\vec{x}_i, \vec{X}_k, t). \quad (2.1)$$

The Schrödinger equation \[22–24\] is the main equation to determine the wavefunction $\Phi$ within a non-relativistic quantum-mechanical theory:

$$\hat{H} \Phi = i\hbar \frac{\partial}{\partial t} \Phi. \quad (2.2)$$

In the special case that the Hamiltonian $\hat{H}$ does not depend on the time explicitly and no external time-dependent fields are present, the wavefunction can be factorised into two terms:

$$\Phi(\vec{x}_i, \vec{X}_k, t) = \Psi(\vec{x}_i, \vec{X}_k) \cdot \varphi(t). \quad (2.3)$$

The first term depends on the positions and spins, and the second one only on the time. This factorisation leads us to the stationary (time-independent) Schrödinger equation:

$$\hat{H} \Psi = E \Psi. \quad (2.4)$$

Therein, the Hamiltonian consists of the kinetic energy operator $\hat{T}$ of the particles and the potential $V$ of the Coulomb interactions within the molecule $^1$:

$$\hat{H} = \hat{T} + V \quad (2.5)$$

$$\hat{T} = - \sum_{k=1}^{M} \frac{\nabla_k^2}{2M_k} - \sum_{i=1}^{N} \frac{\nabla_i^2}{2} \quad (2.6)$$

$$V = - \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{Z_k}{|\vec{r}_i - \vec{R}_k|} + \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_{k=1}^{M} \sum_{l=1}^{M} \frac{Z_k Z_l}{|\vec{R}_k - \vec{R}_l|}. \quad (2.7)$$

$^1$In the following, the equations are written in atomic units, i.e. we set $\epsilon^2 \equiv e^2/4\pi\varepsilon_0 = \hbar = m_e = 1$. 
The three terms of the potential, $V_{eK}$, $V_{ee}$, and $V_{KK}$, describe the attraction between the electrons and the nuclei, the repulsion between the electrons and the repulsion between the nuclei, respectively. $Z_k$ and $M_k$ (in units of the electron mass) denote the nuclear charges and masses, respectively.

The Schrödinger equation [Eq. (2.4)] results in the total energy of the system. Moreover, by applying a suitable ansatz for $\Psi$, its solution yields the eigen functions and the eigen values of the energy of the particles in the system. However, in most cases the Schrödinger equation can not be solved analytically and, hence, approximations are necessary in practice.

### 2.1.2 The Born-Oppenheimer approximation

One main approximation, which is generally applied in quantum-chemical methods, was introduced by Born and Oppenheimer [25]. It takes into account that the masses of the nuclei are significantly larger than the mass of the electron ($M_k \gg m_e$). Thus, the nuclei are hypothetically in rest on the time scale of electronic motion, i.e. the nuclei are fixed in a certain configuration. Then, the wavefunctions of the nuclei and the electrons can be separated according to:

$$\Psi = \Psi_{el}(\vec{x}_i) \cdot \chi_K(\vec{X}_k).$$ \hspace{1cm} (2.8)

As a result, we obtain the electronic Schrödinger equation:

$$\sum_{i=1}^{N} \frac{\nabla^2_i}{2} \Psi_{el} + (E_{el} - V_{eK} - V_{ee}) \Psi_{el} = 0,$$

and the Schrödinger equation for the movement of the nuclei:

$$\sum_{k=1}^{M} \frac{\nabla^2_k}{2M_k} \chi_K + (E_{tot} - E_{el} - V_{KK}) \chi_K = 0.$$ \hspace{1cm} (2.10)

The electronic wavefunction $\Psi_{el}$ depends only on the position and the spin of the electrons, whereas the coordinates of the nuclei are included in the electronic energy $E_{el} = E_{el}(\vec{R}_k)$. The total energy $E_{tot}$ results from the sum of the electronic energy $E_{el}$ and the repulsive potential $V_{KK}$, which is a constant for a chosen set of nuclear coordinates:

$$E_{tot}(\vec{R}_k) = E_{el}(\vec{R}_k) + V_{KK}.$$ \hspace{1cm} (2.11)

The functions $E_{el}(\vec{R}_k)$ set up the so-called potential energy surfaces.

### 2.2 Quantum-chemical methods

The main scope of quantum-chemical methods is to determine the electronic energy $E_{el}$ and the electronic wavefunction $\Psi_{el}$ of a molecular system by solving the many-particle electronic Schrödinger equation [Eq. (2.9)]. In particular, $\Psi_{el}$ can be used to calculate further
(electronic) properties of the molecule. Among the large number of different quantum-chemical methods, we will focus in this section on the so-called \textit{ab initio} and density-functional theory based methods. Moreover, we will present just their basic ideas. For a detailed description of the methods, we refer the interested reader to general textbooks and the references mentioned in the text.

\subsection{Ab initio methods}

In general, methods that do not include any empirical or semi-empirical parameters in their equations are called \textit{ab initio} methods. They are derived directly from first principles of quantum-mechanics, i.e. they are wavefunction-based, and they do not include any experimental data. One type of the \textit{ab initio} quantum-chemical methods to solve the electronic Schrödinger equation is the Hartree-Fock method \cite{21, 26, 28}. In a first step, Hartree wrote the many-particle electronic wavefunction as a product of \(N\) single-particle wavefunctions, where \(N\) is the number of electrons in the system:

\[
\Psi_{el} = \prod_{i=1}^{N} \psi_i(\vec{x}_i). \tag{2.12}
\]

However, electrons are indistinguishable particles, and they are fermions. Therefore, the many-particle wavefunction must be antisymmetric with respect to the exchange of the particles. This condition is not covered by Hartree’s product [Eq. (2.12)] and, hence, an antisymmetrised product wavefunction was introduced as a suitable ansatz, which is called Slater determinant (SD) \cite{29}:

\[
\Psi_{SD}^{el} = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \cdots & \psi_N(\vec{x}_1)
\psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \cdots & \psi_N(\vec{x}_2)
\vdots & \vdots & \ddots & \vdots \\
\psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \cdots & \psi_N(\vec{x}_N)
\end{vmatrix}. \tag{2.13}
\]

Therein, each \(\psi_i\) is a product of two functions:

\[
\psi_i(\vec{x}_i) = \psi_i(\vec{r}_i) \cdot \eta_i(\sigma_i). \tag{2.14}
\]

The first one depends on the position and the second one depends on the spin (\(\uparrow\) or \(\downarrow\)) of the respective electron. The Slater determinant satisfies the Pauli-principle: if two one-particle wavefunctions (or spin orbitals) are equal, two rows of the determinant are equal and the whole determinant becomes zero.

By applying the variational principle, this approach converts the many-particle electronic Schrödinger equation [Eq. (2.9)] into a set of effective one-particle equations:

\[
\hat{h}_i \psi_i = \varepsilon_i \psi_i. \tag{2.15}
\]

Therein, the effective one-particle Hamiltonian, \(\hat{h}_i\), is written as:

\[
\hat{h}_i = \frac{1}{2} \nabla_i^2 - \sum_{k=1}^{M} \frac{Z_k}{|\vec{r}_i - \vec{R}_k|} + \sum_{j}^{N}(\hat{J}_{ij} - \hat{K}_{ij}). \tag{2.16}
\]
The Coulomb operator, $\hat{J}_{ij}$, describes the interaction of the electron $i$ with the averaged charge distribution of another electron $j$ in the spin orbital $\psi_j$:

$$\hat{J}_{ij} = \int |\psi_j(\vec{r}_j)|^2 \frac{1}{|\vec{r}_i - \vec{r}_j|} d^3r_j. \quad (2.17)$$

$\hat{K}_{ij}$ is the exchange operator that leads to the exchange of the variables in the two spin orbitals:

$$\hat{K}_{ij} \psi_i(\vec{r}_i) = \psi_j(\vec{r}_i) \int \psi_j^*(\vec{r}_j) \frac{1}{|\vec{r}_i - \vec{r}_j|} \psi_i(\vec{r}_j) d^3r_j. \quad (2.18)$$

The $\hat{h}_i$ depend through these two operators on the spin orbitals. Hence, the one-particle equations [Eq. (2.15)] have to be solved iteratively by applying the so-called self-consistent field (SCF) method: Initially, a suitable set of spin orbitals is chosen to solve the Hartree-Fock equations. The resultant new set of orbitals is employed in the iteration and so forth. The iteration process is stopped when the orbitals have converged.

The solutions of the so-called Hartree-Fock equations [Eq. (2.15)] are the one-particle wavefunctions $\psi_i$. Their respective eigen values are the energies $\varepsilon_i$, for which the total energy $E_{\text{HF}}$ is minimal:

$$E_{\text{HF}} = 2 \sum_{i=1}^{N/2} \varepsilon_i + 2 \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (J_{ij} - \frac{1}{2}K_{ij}). \quad (2.19)$$

The Hartree-Fock method approximates the wavefunction of the ground state by a single Slater determinant that does not correspond to the exact wavefunction. The resulting difference between the energy $E_{\text{HF}}$ and the exact energy of the ground state $E_0$ is the so-called correlation energy $E_{\text{C}}^{\text{HF}}$:

$$E_{\text{C}}^{\text{HF}} = E_0 - E_{\text{HF}}. \quad (2.20)$$

All ab initio methods that are developed based on the Hartree-Fock method later on, the so-called post-Hartree-Fock methods, correct the Hartree-Fock energy by taking the electron correlation into account, i.e. they include the electron-electron interaction in a more accurate way than does the Hartree-Fock method, in which the electron interaction is only averaged. In particular, the inclusion of the electron correlation is essential for the description of intermolecular interactions like hydrogen bonds or dispersion interactions that are in the focus of Sections 4.3 and 4.4, respectively.

One type of post-Hartree-Fock methods are, e.g., the configuration interaction (CI) or coupled-cluster (CC) methods [30, 31] that take into account excited state configurations of the electrons, i.e. they include a finite number of Slater determinates in which occupied orbitals are replaced by unoccupied ones. Another type of methods is the Møller-Plesset perturbation theory of second or fourth order (MP2 and MP4, respectively) [30, 32] that adds electron-correlation effects by means of Rayleigh-Schrödinger perturbation theory. Although the energy of the ground state can be calculated very precisely by these post-Hartree-Fock methods, the computational effort increases dramatically with increasing number of electrons. Therefore, the ab initio methods are applicable only for rather small
systems. In practice, the MP2 method is usually applied to investigate the intermolecular interactions in organic molecules. Moreover, it gives good results on the geometries and energies of hydrogen bonds and dispersion interaction. Therefore, we use this method as a benchmark later in this work to study the intermolecular interactions among functional thiophene based molecules (see Sections 4.3 and 4.4).

### 2.2.2 The density-functional theory

The density-functional theory (DFT) \[33–35\] has become a very popular alternative to the wavefunction-based \textit{ab initio} methods, since it allows the calculation of larger molecular systems or even periodic structures at much lower computational costs. The DFT method is based on the electron density that is defined for a system containing \(N\) electrons as:

\[\rho(\vec{r}) = N \int d^3r_2 d^3r_3 \ldots d^3r_N |\psi(\vec{x}, \vec{x}_2, \vec{x}_3, \ldots, \vec{x}_N)|^2.\]  \hspace{1cm} (2.21)

Hence, the many-electron system is described by the probability density of all electrons. A detailed knowledge of the many-particle wavefunction is not necessary. Moreover, the \(N\)-electron problem is reduced to 3 instead of \(3N\) variables.

The fundamentals of the DFT are the two so-called Hohenberg-Kohn theorems that were published by Hohenberg and Kohn in 1964 \[36\].

**The Hohenberg-Kohn theorems**

The first Hohenberg-Kohn theorem states that the energy of the ground state, \(E_0\), can be written as a unique functional of the electron density \(\rho(\vec{r}, s)\):

\[E_0[\rho(\vec{r})] = F[\rho(\vec{r})] + \int V_{\text{ext}}(\vec{r})\rho(\vec{r}) d^3r.\]  \hspace{1cm} (2.22)

The external potential, \(V_{\text{ext}}(\vec{r})\), corresponds to the potential of the electron-nucleus interaction (\(V_{eK}\) [Eq. (2.7)]). The functional \(F[\rho(\vec{r})]\) in Eq. (2.22) is a universal functional. It contains the kinetic energy, \(T[\rho(\vec{r})]\), the meanfield interaction of the electrons, \(E_H[\rho(\vec{r})]\), and a part \(E_{\text{XC}}[\rho(\vec{r})]\), that is the so-called exchange-correlation energy and that accounts for the self-interaction, the exchange and the correlation effects of the electrons:

\[F[\rho(\vec{r})] = T[\rho(\vec{r})] + E_H[\rho(\vec{r})] + E_{\text{XC}}[\rho(\vec{r})].\]  \hspace{1cm} (2.23)

The second Hohenberg-Kohn theorem is a variational principle for the energy. Thereby, the energy \(E_0[\tilde{\rho}]\), which is calculated employing Eq. (2.22), is an upper limit for the exact energy \(E_0\) of the non-degenerate ground state for every chosen density \(\tilde{\rho} = \rho + \delta \rho\):

\[E_0 \leq E_0[\tilde{\rho}]\]  \hspace{1cm} (2.24)

Moreover, the density \(\tilde{\rho}\) has to be chosen in such a way that there exists a local external potential that yields a Hamiltonian, for which \(\tilde{\rho}\) is the density of the ground state.
The Kohn-Sham equations

Although the functional $F[\rho(\vec{r})]$ appears in the first Hohenberg-Kohn theorem [Eq. (2.22)], there is no statement about its explicit form or how to derive it. The mean-field interaction energy of an electronic charge distribution, the so-called Hartree-part, is the only known part:

$$E_{\text{H}}[\rho(\vec{r})] = \frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r'. \quad (2.25)$$

In 1965, Kohn and Sham developed a scheme that approximates the functional $F[\rho(\vec{r})]$ [37]. They made the following variational ansatz for the electron density:

$$\rho(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2. \quad (2.26)$$

The $\psi_i$ are arbitrary variational functions or so-called Kohn-Sham orbitals of a non-interacting system that possesses the same electron density as the real interacting system. The kinetic energy of the interacting system can then be approximated by an expression that yields the exact kinetic energy of the non-interacting reference system:

$$T = -\frac{1}{2} \sum_{i=1}^{N} \langle \psi_i \mid \nabla^2 \mid \psi_i \rangle. \quad (2.27)$$

Those parts of the “real” kinetic energy, that are not taken into account by this approach, are added to the exchange-correlation energy. The exchange-correlation energy can be defined as:

$$E_{\text{XC}} = \int \rho(\vec{r})\varepsilon_{\text{xc}}[\rho(\vec{r})] d^3r, \quad (2.28)$$

where $\varepsilon_{\text{xc}}$ is the exchange-correlation energy per particle.

By inserting Eq. (2.26) into Eqs. (2.22), (2.23) and (2.25), and subsequently employing the variational principle on the energy with respect to the $\psi_i$, a set of one-particle equations is obtained, the so-called Kohn-Sham equations:

$$\hat{h}_{\text{KS}}\psi_i = \varepsilon_i \psi_i, \quad (2.29)$$

where

$$\hat{h}_{\text{KS}} = -\frac{1}{2} \nabla^2 + V_{\text{KS}} \quad (2.30)$$

and

$$V_{\text{KS}} = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' + V_{\text{XC}}[\rho(\vec{r})] - \sum_{k=1}^{M} \frac{Z_k}{|\vec{r} - \vec{R}_k|}. \quad (2.31)$$

The exchange-correlation potential, $V_{\text{XC}}[\rho(\vec{r})]$, is defined as the functional derivative of the exchange-correlation energy with respect to the density $\rho$:

$$V_{\text{XC}}[\rho(\vec{r})] = \frac{\delta E_{\text{XC}}[\rho(\vec{r})]}{\delta \rho(\vec{r})}. \quad (2.32)$$
The connection to the “real” system is made by choosing the Kohn-Sham potential ($V_{KS}$) such that the obtained Kohn-Sham orbitals yield the ground state electron density of the real system of interacting electrons by employing Eq. (2.26). In practice, the Kohn-Sham equations are solved iteratively by applying the SCF scheme (Section 2.2.1), since $V_{KS}$ depends on the electron density: At first, a suitable starting density is chosen for which the Kohn-Sham potential is calculated. This potential determines a new density that is employed in the Kohn-Sham equations, and so forth.

Finally, the total energy of a system consisting of $N$ electrons and $M$ nuclei can be written as a functional of the density:

$$E_{tot}^{DFT} = \sum_{i=1}^{occ} \varepsilon_i - \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' d^3r + E_{XC} - \int \rho(\vec{r})V_{xc}[\rho(\vec{r})]d^3r. \quad (2.33)$$

### The exchange-correlation energy

In principle, the Kohn-Sham formalism is exact and leads to the exact total energy of the ground state. However, the explicit and exact forms of $E_{XC}$ or $V_{XC}$ are unknown and approximations have to be introduced. Nowadays, the aim of modern DFT is to improve the approximations of these quantities more and more.

The most traditional approach is the local-density approximation (LDA) that is based on the model of the homogeneous electron gas:

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r})\varepsilon_{X}^{\text{unif}}[\rho(\vec{r})]d^3r. \quad (2.34)$$

In this model, the electrons are distributed in front of a homogeneous positive background charge such that the total system is neutral. $\varepsilon_{X}^{\text{unif}}$ is the exchange-correlation energy per particle of a homogeneous electron gas with the density $\rho(\vec{r})$, that, in principle, can be calculated exactly. It can be separated into two parts:

$$\varepsilon_{XC}[\rho(\vec{r})] = \varepsilon_{X}[\rho(\vec{r})] + \varepsilon_{C}[\rho(\vec{r})]. \quad (2.35)$$

The first term ($\varepsilon_{X}$) is the exchange energy of an electron in a homogeneous electron gas of a specific density, for which, Bloch and Dirac found the following expression in 1929\cite{38, 39}:

$$\varepsilon_{X}[\rho(\vec{r})] = -\frac{3}{4} \sqrt{3\rho(\vec{r})} \frac{1}{\pi}. \quad (2.36)$$

For the correlation energy $\varepsilon_{C}$ an equivalently exact form does not exist, but, in 1980, Ceperly and Alder performed very accurate numerical Monte-Carlo simulations \cite{40}. Based on those, various authors derived analytical expressions for $\varepsilon_{C}$. The most popular functional is that of Vosko, Wilk and Nusair (VWN) \cite{41}. The LDA is also employed in the DFTB method, which will be described in Subsection 2.2.3.

The LSDA is the extension of the LDA for spin-polarised systems, especially, for molecules with an odd number of electrons. For those systems, the density $\rho$ consists of
the two non-equivalent densities $\rho_\uparrow$ and $\rho_\downarrow$ of all “spin up” and “spin down” electrons, respectively [42]:

$$E_{\text{XC}}^{\text{LSD}}[\rho_\uparrow, \rho_\downarrow] = \int \rho(\vec{r}) e_{\text{XC}}^{\text{unif}}[\rho_\uparrow(\vec{r}), \rho_\downarrow(\vec{r})] d^3 r,$$

(2.37)

$$\rho(\vec{r}) = \rho_\uparrow(\vec{r}) + \rho_\downarrow(\vec{r}).$$

(2.38)

A very popular correction functional to the L(S)DA is the generalised gradient approximation (GGA). In general, it is given by:

$$E_{\text{XC}}^{\text{GGA}}[\rho_\uparrow, \rho_\downarrow] = \int f(\rho_\uparrow, \rho_\downarrow, \nabla \rho_\uparrow, \nabla \rho_\downarrow) d^3 r.$$  

(2.39)

In particular, the GGA by Perdew et al. [43] attempts to improve the calculation of molecular properties like total energies, atomisation energies, energetic barriers or binding energies with respect to the LDA and LSDA. The main idea is to account for the inhomogenities in the slowly varying density by a Taylor expansion. There are various proposals for the explicit dependency of the integrand $f$ on the densities $\rho_\uparrow$ respective $\rho_\downarrow$ and their gradients $\nabla \rho_\uparrow$ respective $\nabla \rho_\downarrow$ including also semi-empirical functionals, e.g. PW86 [43], BLYP [44, 45], PW91 [46, 47]. A very common, parameter-free functional is that of Perdew, Burke and Ernzerdorf (PBE) [48] that we will employ later in this work in Section 4.3 and Chapter 5.

The LCAO scheme

In general, the Kohn-Sham orbitals ($\psi_i$) are represented by a linear combination of a finite set of appropriate basis functions to solve the Kohn-Sham equations [Eq. (2.30)] [21, 33]. Within the ansatz of the linear combination of atomic orbitals (LCAO), the $\psi_i$ are expressed by a set of atomic orbitals:

$$\psi_i = \sum_\mu c_{\mu i} \varphi_\mu(\vec{r} - \vec{R}_\alpha),$$

(2.40)

with the nuclei $\alpha$ centered at $\vec{R}_\alpha$. Therein, either so-called Gaussian-type orbitals (GTOs):

$$\varphi_\mu(x, y, z) \propto x^i y^j z^k e^{-\alpha r^2} \quad i, j, k = 0, 1, 2..., $$

(2.41)

or Slater-type orbitals (STOs):

$$\varphi_\mu(\vec{r}) \propto r^{n-1} e^{-\xi r} Y_{lm} \left( \frac{\vec{r}}{r} \right),$$

(2.42)

are used as basis functions, wherein, $n$, $l$ and $m$ are the principal, azimuthal and magnetic quantum numbers of the respective orbitals $\mu$; and $i, j, k, \alpha$ and $\xi$ are the orbital exponents.

By employing the LCAO-Ansatz together with the variational principle we obtain a set of secular equations:

$$\sum_\mu c_{\mu i} (H_{\mu \nu}^{\text{KS}} - \varepsilon_i S_{\mu \nu}) = 0, \quad \forall \ \mu, i,$$

(2.43)
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where $H_{\mu\nu}^{KS}$ and $S_{\mu\nu}$ are the Hamilton and overlap matrices, respectively:

$$H_{\mu\nu}^{KS} = \langle \varphi_{\mu} | \hat{H} | \varphi_{\nu} \rangle,$$

(2.44)

$$S_{\mu\nu} = \langle \varphi_{\mu} | \varphi_{\nu} \rangle.$$  

(2.45)

These equations have to be solved self-consistently by applying the SCF scheme (cf. Subsection 2.2.1) with respect to the coefficients $c_{\mu i}$. The LCAO method is also employed in the DFTB method that will be described in the following subsection.

2.2.3 The density-functional tight-binding method

The so-called density-functional based tight-binding method (DFTB) [49–58] is the most prevalently applied method in this work. It has been developed for the efficient calculation of large molecules. Over the years the standard DFTB method has been systematically improved including, just to mention, a self-consistent charge extension (SCC-DFTB) [54], a spin-dependent formulation [59] and a time-dependent description of excited states (TD-DFTB) [60]. Nowadays, it is well qualified for the efficient calculation of geometries and electronic properties of numerous systems including large molecules, clusters and even solids.

The standard DFTB method [49–53] is based on the density-functional theory of Hohenberg and Kohn [36] in the formulation of Kohn and Sham [37] (cf. Section 2.2.2). The single-particle eigenfunctions ($\psi_i$) are expanded in a minimal basis of optimised localised pseudo-atomic orbitals [Eq. (2.40)]. The basis functions $\varphi_\mu$ are determined by SCF-DFT-LDA calculations on the isolated neutral atoms employing a large set of Slater-type orbitals [Eq. (2.42)]. Thereby, an additional harmonic potential $(r/r_0)^n$ is taken into account that weakens the long-range parts of the wavefunction. In particular, it keeps the electron density unchanged in the bonding-relevant region. The exponent $n$ has only little effect on the results. It is usually kept to $n = 2$ for all atoms [52]. The cut-off radius $r_0$ is set to $r_0 = 2r_{\text{cov}}$. The parameter $r_{\text{cov}}$ is the covalent radius of the atom [52]. As a result, we obtain optimised basis sets $\{\varphi_\mu\}$ and atomic densities $\rho_\alpha^0$ for each atom type.

With these, the Hamilton [Eq. (2.44)] and overlap [Eq. (2.45)] matrix elements are calculated for various interatomic distances. The diagonal elements of the Hamilton matrix ($H_{\mu\mu}^0$) are replaced by the atomic eigen values of the free, neutral and spherical atoms. The non-diagonal elements ($H_{\mu\nu}^0$) are calculated within a two-center approximation:

$$H_{\mu\nu}^0 = \langle \varphi_{\mu} | \hat{T} + V_{\text{eff}}[\rho_\alpha^0] + V_{\text{eff}}[\rho_\beta^0] | \varphi_{\nu} \rangle \quad \mu \in \alpha, \nu \in \beta, \alpha \neq \beta.$$

(2.46)

Hence, the effective potential results from a simple superposition of the potentials of the neutral pseudo-atoms. Analogously, the electron density is written approximately as superposition of atomic contributions:

$$\rho(\vec{r}) = \sum_\alpha \rho_\alpha(\vec{r}).$$

(2.47)
It is important to stress at this point that the mathematical approach to solve the Kohn-Sham equations corresponds to that of the non-orthogonal tight-binding (TB) methods. However, in contrast to the empirical TB methods, all matrix elements in DFTB are obtained from DFT-LDA calculations and none is determined through fitting to experimental data. Moreover, the scheme to determine the matrix elements is generally valid and, hence, the method is transferable for all elements of the periodic table.

Using the Kohn-Sham eigenvalues ($\varepsilon_i$) and the density calculated with DFTB as well as the atomic effective potential, the total energy within DFTB is written as:

$$E_{\text{tot}}[\rho] = \sum_i \varepsilon_i n_i - \frac{1}{2} \sum_{\alpha,\beta} \int V_{\text{eff}}(\vec{r}) \rho_{\alpha}(\vec{r}) d^3r - \frac{1}{2} \sum_{\alpha,\beta} \int \frac{Z_{\alpha} \rho_{\beta}(\vec{r})}{r_{\alpha}} d^3r + \frac{1}{2} \sum_{\alpha \geq \beta} U_{\text{rep}}(|\vec{R}_{\alpha} - \vec{R}_{\beta}|).$$

Within a further approximation, all terms except the sum of the eigenvalues are merged into a short-range repulsive energy, $E_{\text{rep}}$, and we obtain:

$$E_{\text{tot}} = \sum_i \varepsilon_i n_i + E_{\text{rep}} = \sum_i \varepsilon_i n_i + \sum_{\alpha \geq \beta} U_{\text{rep}}(|\vec{R}_{\alpha} - \vec{R}_{\beta}|).$$

The atom-specific and pair-wise potentials $U_{\text{rep}}(|\vec{R}_{\alpha} - \vec{R}_{\beta}|) = U_{\text{rep}}(R_{\alpha\beta})$ are determined from the calculation of suitably chosen reference systems, i.e. from the difference between the total energy of a parameter-free DFT calculation and the respective electronic energy obtained by DFTB.

Hence, the main advantage of the standard DFTB method is that numerical integration and iterative solving algorithms are avoided. Therefore, this method is highly efficient. Moreover, it gives reasonable results for a large number of various systems. Especially, those systems are excellently described, where the population of electrons of the atoms in the system does not change much like, e.g., in homonuclear or in strong covalent organic compounds. However, it is also applicable to calculate the properties of strongly ionised systems, where the electrons are shifted almost completely to the more electronegative atom like in salts or Zintl alloys. In polar heteroatomic systems, the redistribution of partial charges has to be considered. Therefore, the standard DFTB was extended by a self-consistent charge correction scheme (SCC-DFTB) that allows for a more accurate description of, e.g., large biomolecules [54, 59].

In the SCC-DFTB method, a second-order Coulomb correction term is introduced into the total energy expression [Eq. (2.50)]. It is derived from a second-order expansion of the Kohn-Sham energy with respect to atomic charge fluctuations, see Ref. [54] for a detailed derivation. The total energy is then given by:

$$E_{\text{tot}} = \sum_i \varepsilon_i n_i - \frac{1}{2} \sum_{\alpha,\beta} \gamma_{\alpha\beta}(R_{\alpha\beta}) \Delta q_{\alpha} \Delta q_{\beta} + \sum_{\alpha \geq \beta} U_{\text{rep}}(|\vec{R}_{\alpha} - \vec{R}_{\beta}|).$$

The $q_{\alpha}$ denotes the charge that is centered at atom $\alpha$ and that is obtained from a population analysis (usually Mulliken). The parameter $\gamma_{\alpha\beta}(R_{\alpha\beta})$ is related to the chemical hardness
2.2 Quantum-chemical methods

\( \eta_\alpha \) or the Hubbard parameter \( U_\alpha \). For short distances, i.e. both charges are with formal exactness localised at the same atom, the \( \gamma_{\alpha\alpha} \) are approximated by the difference between the ionisation potential and the electron affinity of the atom:

\[
\gamma_{\alpha\alpha} \approx I_\alpha^\alpha - E_a^\alpha \approx 2\eta_\alpha \approx U_\alpha.
\]  

(2.52)

Then, a suitable expression for the \( \gamma_{\alpha\beta} \) can be derived, too, that depends only on the distances between the atoms \( \alpha \) and \( \beta \), and on the Hubbard parameters \( U_\alpha \) and \( U_\beta \), see Refs. \[54, 59\]. The Hubbard parameters can be obtained for each atom type by calculating the second derivative of the total atomic energy with respect to the occupation number of the highest occupied atomic orbital (HOMO) using DFT-LDA:

\[
U_\alpha = \frac{\partial^2 E_{\text{DFT}}}{\partial n_{\text{HOMO}}} = \frac{\partial E_{\text{HOMO}}}{\partial n_{\text{HOMO}}}. 
\]  

(2.53)

By variation of the energy expression [Eq. (2.51)] with respect to the minimal basis, we obtain a set of secular equations [Eq. (2.43)]. Therein, the Hamilton matrix elements are given by:

\[
H_{\mu\nu} = H_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_\xi (\gamma_{\alpha\xi} + \gamma_{\beta\xi}) \Delta q_\xi = H_{\mu\nu}^0 + H_{\mu\nu}^1.
\]  

(2.54)

These equations have to be solved iteratively to determine the coefficients \( c_{\mu\nu} \), because the Hamiltonian depends on the \( c_{\mu\nu} \) by the Mulliken charges and by \( \gamma_{\alpha\beta} = \gamma_{\alpha\beta}(c_{\mu\nu}) \). (This is the reason for the notation “self-consistent-charge”.) Hence, one disadvantage of this correction is that the self-consistency cycle increases the computation time considerably and several new parameters have to be introduced.

However, in conclusion, the (SCC)-DFTB method described here is highly efficient in comparison to standard DFT or \textit{ab initio} methods. Therefore, this method is very suitable to investigate the adsorption of phosphonic acid on metaloxides as well as the structural and electronic properties of the (large) functional thiophene-based molecules in this work.

2.2.4 Inclusion of dispersion interactions within DFT

Dispersion interactions, although weak compared to covalent bonds, play a crucial role in a wide range of fields including, e.g., the \( \pi-\pi \)-stacking interactions in self-assembly monolayers of thiophene-based molecules investigated in this work (Section 4.4).

In principle, wavefunction-based post-Hartree-Fock methods account for these van-der-Waals interaction by including the electron-electron correlation, cf. Section 2.2.1. Moreover, highly-sophisticated coupled-cluster calculation with single, double, and perturbative triple excitations, CCSD(T), \[61\] employing very large basis sets are reported as the most accurate method to describe the \( \pi-\pi \)-stacking interactions in aromatic \( \pi \)-electron systems, see Ref. \[62\] and references therein. However, this method is computationally very demanding and its applicability is, thus, restricted to molecular systems containing just a
small number of atoms. In practice, MP2 calculations [32] are widely used to study the intermolecular interactions in organic molecules, although it is well known that this method tends to overestimate the strength of the \(\pi-\pi\)-interaction in comparison to CCSD(T) [62].

For the investigation of larger systems, density-functional theory methods have become an attractive alternative due to their much lower computational cost. However, one of the major deficiencies of standard DFT functionals is their inability to describe dispersion interactions correctly [63]. Although the exact \(E_{XC}\) must also include dispersion, currently available LDA and GGA functionals do not cover the correlation between distant dipolar density fluctuations. Hence, they do not reproduce the well-known \(R^{-6}\) dependence of the dispersion interaction energy on the distances \(R\) between two separate neutral (non-overlapping) fragments.

To address this deficiency, various solutions have been proposed, see e.g. Refs. [63, 64]. In particular, novel density functionals are being developed that tend to incorporate dispersion. These are either non-local van-der-Waals density functionals or pure [semi-local (hybrid)] density functionals. Other correction schemes include pseudo-potential based approaches and symmetry adapted perturbation theory. An alternative and one of the most popular approaches is adding an empirical long-range dispersion correction term to the standard DFT [65–70]. These are so-called DFT-DC (or DFT + disp) methods. In general, the correction \(E_{\text{disp}}\) is of the form:

\[
E_{\text{disp}} = -s_6 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{C_{ij}^6}{R_{ij}^6} f_d (R_{ij}), \tag{2.55}
\]

where \(N\) is the number of atoms, \(R_{ij}\) is the interatomic distance and \(C_{ij}^6\) are averaged pairwise dispersion coefficients. The quotient \(C_6/R^6\) is a classical London-like term and \(f_d(R)\) is an appropriate step function needed to damp the \(R^{-6}\) at short distances. The global scaling factor \((s_6)\) adjusts the correction to the repulsive behaviour of the chosen density functional. The two main advantages of the empirical correction are first, the negligible computational time to calculate the \(E_{\text{disp}}\) and second, the minimal effort to interface these methods with existing DFT codes, since only atomic coordinates are required. However, the overall-accuracy of the results strongly depends on the atomic coefficients, \(C_{ij}^6\), that are usually computed using averaged atomic polarisabilities. In general, these polarisabilities are obtained empirically through fitting.

Two widely-used DFT-DC implementations are applied later in this work (Section 4.4). These are the functions of Grimme [69] and of Head-Gordon et al. [70] that we will denote B97D and wB97xD, respectively:

\[
f_{\text{d}}^{\text{B97D}} (R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_0-1)}}, \tag{2.56}
\]

\[
f_{\text{d}}^{\text{wB97xD}} (R_{ij}) = \frac{1}{1 + a(R_{ij}/R_0-12)}. \tag{2.57}
\]
Here $R_t$ denotes the sum of atomic van-der-Waals radii. The coefficients are calculated according to the following equation:

$$C_{ij}^6 = \sqrt{C_i^6 C_j^6} \quad \text{with} \quad C_i^6 = 0.05NI_i^p \alpha_i.$$  \hfill (2.58)

Therein, $I_i^p$ and $\alpha_i$ are the atomic ionisation potential and the static dipole polarisability for atom $i$, respectively.

We also employ the SCC-DFTB-DC method where the dispersion is included via a Lennard-Jones potential [66]:

$$U(R_{ij}) = d_{ij} \left[ -2 \left( \frac{R_t}{R_{ij}} \right)^6 + \left( \frac{R_t}{R_{ij}} \right)^{12} \right] \quad \text{for} \quad R_{ij} \geq R_0,$$  \hfill (2.59)

$$U(R_{ij})^{\text{short-range}} = U_0 + U_1 R_{ij}^5 + U_2 R_{ij}^{10} \quad \text{for} \quad R_{ij} < R_0.$$  \hfill (2.60)

$R_0 = R_t / \sqrt{2}$ is the distance at which the potential turns from repulsive to attractive. The well depth $d_{ij}$ and the van-der-Waals distance $R_t$ are built via the geometrical mean $d_{ij} = \sqrt{d_i d_j}$ respective $R_t = \sqrt{R_t^i R_t^j}$ of the atomic parameters $d_i, d_j, R_t^i$ and $R_t^j$, which are taken from the Universal Force Field (UFF) [71]. The parameters $U_0, U_1$ and $U_2$ ensure a smooth functional behaviour at $R_0$. They are calculated according to:

$$U_0 = \frac{396}{25} d_{ij}, \quad U_1 = \frac{25}{672} \frac{d_{ij}}{R_t^5}, \quad U_2 = -2^{2/3} \frac{552}{25} \frac{d_{ij}}{R_t^{10}}.$$  \hfill (2.61)

The dispersion energy is then obtained from the sum over all pair-wise contributions $U$:

$$E_{\text{disp}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N U(R_{ij}).$$  \hfill (2.62)

As it was already found in Refs. [54, 65, 66] and as we will also show later in Section 4.4, the dispersion corrected SCC-DFTB-DC method gives reasonable results for the intermolecular interactions in large molecular systems in comparison with \textit{ab initio} and other dispersion corrected DFT methods at much lower computational effort.

### 2.2.5 Perturbation theory for external electric fields

In quantum-chemical methods, an external electric field is often considered by “Rayleigh-Schrödinger perturbation theory”. Within this theory, the Hamiltonian $\hat{h}$, which describes the perturbed system, can be expanded in a Taylor series starting from the unperturbed quantity $\hat{h}^{(0)}$ in terms of a parameter $\lambda$:

$$\hat{h} = \hat{h}^{(0)} + \lambda \hat{h}^{(1)} + \lambda^2 \hat{h}^{(2)} + \cdots.$$  \hfill (2.63)

Analogously, we obtain for the energy:

$$\hat{E}_n = \hat{E}_n^{(0)} + \lambda \hat{E}_n^{(1)} + \lambda^2 \hat{E}_n^{(2)} + \cdots.$$  \hfill (2.64)
For many physical problems it is sufficient to terminate the Hamiltonian after the first order term, i.e. \( \hat{h} = \hat{h}^{(0)} + \lambda \hat{h}^{(1)} \). In case of a uniform external electric field, the perturbation corresponds to a potential \( V' \) that is added to the Hamiltonian \( \hat{h}^{(0)} \) of the unperturbed system [cf. Eq. (2.30)]:

\[
\hat{h} = \hat{h}^{(0)} + \lambda \hat{h}^{(1)} = \hat{h}^{(0)} + V' = \hat{h}^{(0)} - \hat{\mu} \cdot \vec{F}.
\]  (2.65)

It describes the interaction of the molecule with the electric field using the dipole moment operator, which is defined as:

\[
\hat{\mu} = \sum_i q_i \vec{r}_i.
\]  (2.66)

Then, we obtain the more simplified expression for an electric field that is applied, e.g., along the z-axis:

\[
\lambda \hat{h}^{(1)} = -\hat{\mu}_z F_z = -F_z \sum_i q_i \hat{z}_i.
\]  (2.67)

Here, the strength of the field \( F_z \) plays the role of the parameter \( \lambda \).

In the SCC-DFTB method, the interaction of the molecule with an external electric field is considered within the Mulliken approximation \([72]\). The interaction energy of the electric field with the partial charges \( q_\alpha \) of the atoms are given by:

\[
E_{\text{Field}} = - \sum_\alpha \Delta q_\alpha \sum_{j=x,y,z} F(j)x_\alpha(j),
\]  (2.68)

where \( F(j) \) and \( x_\alpha(j) \) are the Cartesian components of the electric field and the atoms, respectively. Then, the following basic expression for the perturbated Hamilton matrix is obtained:

\[
H_{\mu\nu} = H_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_{\xi} (\gamma_{\alpha\xi} + \gamma_{\beta\xi}) \Delta q_\xi - \frac{1}{2} S_{\mu\nu} \sum_{j=x,y,z} F(j) [x_\alpha(j) + x_\beta(j)].
\]  (2.69)

For planar molecules, the coordinates of the atoms perpendicular to the molecular plane are zero and the last term of Eq. (2.69) vanishes. Hence, the influence of the electric field in this direction can not be calculated within the approximations of SCC-DFTB.

The calculation of the polarisability of a molecular system is a first qualitative estimate to evaluate its sensitivity towards an applied electric field. The static response properties of a molecule can be derived by a Taylor expansion of the field-dependent energy \( E(\vec{F}) \). That means for an electric field in, e.g., z-direction that we expand the energy with respect to \( F_z \) at the point \( F_z = 0 \):

\[
E(F_z) = E^{(0)} + \left( \frac{dE}{dF_z} \right)_{F_z=0} F_z + \frac{1}{2!} \left( \frac{d^2E}{dF_z^2} \right)_{F_z=0} F_z^2 + \frac{1}{3!} \left( \frac{d^3E}{dF_z^3} \right)_{F_z=0} F_z^3 + \cdots.
\]  (2.70)

The zeroth order term \( E^{(0)} \) is the value of the total energy in the absence of the electric field. Usually the above expression [Eq. (2.70)] is written as:

\[
E(F_z) = E^{(0)} - \mu_z F_z - \frac{1}{2!} \alpha_{zz} F_z^2 - \frac{1}{3!} \beta_{zzz} F_z^3 - \cdots.
\]  (2.71)
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Therein, $\mu_z$, $\alpha_{zz}$ and $\beta_{zzz}$ are the z-components of the static dipole moment, polarisability and first hyperpolarisability tensors, respectively. Moreover, we obtain for an electric field $\vec{F}$ in general:

$$E(\vec{F}) = E(0) - \sum_i \mu_i F_i - \frac{1}{2!} \sum_{i,j} \alpha_{ij} F_i F_j - \frac{1}{3!} \sum_{i,j,k} \beta_{ijk} F_i F_j F_k - \cdots. \quad (2.72)$$

In this work, we use the finite-field method [73, 74] to calculate the polarisabilities of the molecules (Section 5).

2.2.6 Description of periodic structures

The introduction of periodic boundary conditions [75, 76] is an efficient method to describe condensed matter like solid, liquid or amorphous phases. In general, such systems are described by a unit cell that is periodically repeated ad infinitum. The shape of the unit cell is defined by the three primitive vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$. The cell in reciprocal space, the reciprocal cell or so-called first Brioullin zone, is defined by the three reciprocal lattice vectors $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$ that can be derived from the primitive vectors of the unit cell in real space according to:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\Omega}, \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\Omega}, \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\Omega}, \quad (2.73)$$

where $\Omega = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ is the volume of the unit cell.

Within the concept of periodic boundary conditions, the wavefunction $\psi_k$ of an electron in an external periodic potential $V(\vec{r}) = V(\vec{r} + \vec{R}_p)$ can be written as (Bloch’s theorem [77]):

$$\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r}) \quad (2.74)$$

with the Bloch functions:

$$u_k(\vec{r}) = u_k(\vec{r} + \vec{R}_p). \quad (2.75)$$

The $u_k(\vec{r})$ can be expanded into a basis set of nuclear-centered atomic orbitals as it is realized e.g. within the DFTB method. The wavefunction then depends on the reciprocal space vectors $\vec{k}$. In general, only a finite set of $\vec{k}$-points is necessary to sample the first Brioullin zone. The number of required points depends on the size of the box and on the specific features of the system (e.g. symmetry, metallic or semiconducting material). Monkhorst and Pack [78, 79] proposed a quite general $\vec{k}$-point sampling for all symmetries. Therein, a set of $q$ vectors is written in terms of the primitive reciprocal lattice vectors as

$$\vec{k} = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3, \quad (2.76)$$

where the integers $n_i$ are given by $n_i = (2r - q - 1)/2q$ and $r = 1, 2, ..., q$.

In this work, we used quite large supercells containing several unit cells and more than 100 atoms to study the adsorption of phosphonic acid on aluminum and titanium oxide in Chapter 3. I.e. the reciprocal cells were very small and, thus, a small number of $\vec{k}$-points was
required for the Brioullin zone sampling. Moreover, in most cases, we considered just one \( \vec{k} \)-point, the \( \Gamma \)-point (\( k = 0 \)) for the geometry optimisation and the calculation of the electronic structure and the energy. Furthermore, we employed the repeated slab method for the description of the surface structures and adsorption models. I.e. the supercell contained a twodimensional slab in \( (x,y) \)-direction. In \( z \)-direction, we introduced a vacuum region, which was large enough to ensure that the periodic images of the slab in adjacent supercells do not interact. Also, the slab thickness was chosen large enough that the two surfaces of the slab do not interact with each other.

2.2.7 Optimisation methods

Within the Born-Oppenheimer approximation (cf. Section 2.1.2), the electronic Schrödinger equation is solved for a fixed configuration of the nuclei. Thus, the forces acting on the atoms are given by the first derivative of the total energy with respect to the nuclei coordinates. The forces can be used to optimise the geometry of a system. The system is in a minimum of the potential energy surface, if the forces on all nuclei vanish and all the second derivatives of the total energy with respect to the nuclei coordinates are positive.

The most common optimisation technique to find a minimum is the steepest-descent method \([76]\): A series of function evaluations are performed in the negative gradient direction, i.e. along a search direction defined as \( \vec{d} = -\vec{g} \). The gradient \( \vec{g} \) is the first derivative of the function with respect to all variables. Once the function starts to increase, an approximate minimum is determined by interpolation between the calculated points. At this interpolated point, a new gradient is calculated and used for the next line search. This algorithm always lowers the function value for sufficiently accurate line minimisations and, thus, assures the approach to the minimum. However, the rate of convergence slows down close to the minimum.

The conjugate-gradient algorithm, that has been applied throughout this work for the optimisation of the periodic and molecular structures, is a prevalently used alternative optimisation method \([76]\). The first step is equivalent to a steepest descent step, but subsequent searches are performed along a line formed as a mixture of the current negative gradient and the previous search direction according to:

\[
d_i = -\vec{g}_i + \beta_i \vec{d}_{i-1}.
\]  
(2.77)

I.e. the line search is performed along a line that is “conjugate” to the previous search direction(s). There are several ways of choosing the parameter \( \beta \), but the formula of Polak-Ribiere is usually preferred in practice:

\[
\beta_i = \frac{\vec{g}_i (\vec{g}_i - \vec{g}_{i-1})}{\vec{g}_{i-1}^2 \vec{g}_{i-1}}.
\]  
(2.78)

The conjugate gradient algorithm requires only slightly more storage, but has much better convergence characteristics than the steepest descent method. Also, the inclusion of sym-
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Symmetry constraints reduces the number of variables that have to be optimised and, hence, accelerates further the geometry optimisation.

The simulated annealing technique is another optimisation technique to find and characterise the minima on the potential energy surface. In particular, it is applied for systems that possess multiple conformations (local minima) to identify the most preferred one (global minimum). It belongs to the molecular dynamics methods that iteratively solve Newton’s equation of motion for the atoms on the energy surface and, thus, calculate the trajectories of the particles in the system:

\[ M_k \ddot{R}_k(t) = F_k[R(t)]. \] (2.79)

\( M_k \) and \( R_k \) are the mass and the position vector of every nucleus. \( F_k \) is the force on the nucleus in dependence on the position of all nuclei \( R(t) \) at time \( t \). The available energy for the system is distributed between the potential and the kinetic energy and is related to the simulation temperature. Hence, the system can overcome barriers separating minima. For a high enough energy and a very long (impracticable) simulation time, the whole potential energy surface can be sampled. In practice, however, the time step \( \Delta t \) has to be chosen quite small (\( \sim 10^{-15} \) s) for integrating Newton’s equation and, thus, the accessible simulation time is usually short (pico- or nanoseconds). [76]

In the simulated annealing method, the system is heated to a very high temperature, that makes bond-breaking and thus conformational interconversions possible. After a certain amount of time, the system is cooled again to the temperature of interest. The resulting minimum is compared to the initial one with respect to energy. In this work, we used the simulated annealing method to evaluate the stability of the adsorption complexes of phosphonic acid on TiO\(_2\) surfaces in Section 3.4.
3 Adsorption of phosphonic acid on metal oxide surfaces

3.1 Introduction

The structure, formation and properties of self-assembled monolayers (SAMs) [80–82] of organic molecules on metal and metaloxide surfaces have been intensively studied in recent years due to their potential applications in many different fields including corrosion protection, sensors, organic electronic devices and adhesion promotion, see e.g. [11, 83–88]. In order to create a SAM, it is necessary to find a molecule capable of self-assembly that can bind covalently to a specific surface. In general, this molecule consists of three parts: an anchor group, a spacer group and a terminal functional group [80].

The terminal functional group (tail group) determines the properties of the SAM surface. Nonpolar groups such as methyl (–CH₃) groups result in highly hydrophobic surfaces being thus applicable in the field of corrosion protection [81, 85]. Polar groups such as hydroxyl (–OH), carboxyl (–COOH) or amino (–NH₂) groups are able to react with an over-layer. Therefore, they are good candidates to act as adhesion promoters on reactive metal (oxide) surfaces or organic coatings [81, 83]. Also, thiophene-based functional molecules were designed and characterized [11, 86, 87]. Their structure allows surface polymerisation as well as formation of polymers using additional monomers, resulting in densely packed films with long conjugated units [86, 87]. Moreover, they can promote the essential highly-ordered lamellar stacking of functional thiophene-based molecules in the next layer perpendicular to the surface of the oxidic substrate [11], see Figure 1.1 (c). Thus, they are potentially applicable in the field of organic-based electronics.

The spacer group between the anchor and terminal group usually consists of a long alkyl chain with 10 to 18 methylene groups (–CH₂–). It influences the intermolecular interactions and promotes the ordering and orientation of the molecules within the monolayer [80, 81]. It might also influence the film formation and growth process [82, 89].

The anchor group (headgroup) is responsible for the adsorption of the molecule by forming chemical bonds to the substrate surface. Thus, the choice of this group strongly depends on the nature of the adsorbent material. The thiol group (–SH) is applicable to metals, especially gold surfaces, whereas phosphonic acids (–PO(OH)₂), carboxylic acids (–COOH), sulfonic acids (–SO₂(OH)), silanols (–Si(OR)₃) and silyl (–SiR₃) groups are more
suitable for adsorption on oxide materials such as Al/Al$_2$O$_3$, Ti/TiO$_2$ and mica minerals [14, 80, 81, 89, 90]. Especially, the phosphonic acid headgroup has attracted growing interest as anchoring group in recent years. Robust, well-anchored monolayers of organophosphonic acids are obtained on, e.g., aluminium and titanium oxide surfaces due to the formation of strong covalent bonds between the phosphonic acid group and the substrate surfaces [17, 83, 84, 86, 89, 91–104].

SAMs consisting of long-chain alkyl phosphonic acids (APAs) adsorbed on aluminium oxide surfaces were studied extensively experimentally [17, 83, 84, 89, 91–96]. Highly hydrophobic monolayers were obtained and characterized by contact angle measurements [83, 89, 92–94, 96]. It was also shown by Fourier transform infrared (FTIR) spectroscopy that the CH$_2$ vibrational energy decreases with the adsorption time, indicating that the formed film is initially disordered, becoming gradually oriented as the adsorption takes place [83, 84, 89, 94, 95]. In addition, P=O and P–OH stretch bands are absent from the FTIR spectra of the adsorbed APAs. Instead, there are bands attributed to the symmetric and asymmetric stretches of the RPO$_2^-$ group. This indicates that APAs bind to the aluminium surface via three symmetric P–O–Al bonds [83, 93]. The same result was found by inelastic tunneling spectroscopy (IETS) on adsorbed phosphonic and vinylphosphonic acids [105, 106].

In contrast, the exact binding state of the phosphonic acid coupling group to the TiO$_2$ surface is not easy to access experimentally and is still much debated [17, 86, 97–103]. The phosphonic acid can bind to the surface via one, two or three symmetric P–O–Ti bonds, i.e. monodentate, bidentate and tridentate binding of the acidic group, respectively. On the basis of FTIR spectroscopy, the tridentate binding is proposed to be the most likely adsorption structure of organo phosphonic acids on TiO$_2$ due to the absence of the P–OH and P=O absorption bands [98]. However, this result is still open to question, since the absorption band of TiO$_2$ occurs in the same region [17, 99, 103]. Also, the absorption bands of the different P–O stretching modes greatly overlap and depend on the degree of hydrogen bonding or metal binding [17]. Indeed, it was found experimentally that hydrogen bond interactions are involved in the assembly and surface attachment of phosphonic acids on TiO$_2$ [102, 103]. On the basis of NMR spectroscopy, a mixture of bi- and tridentate bound phosphonic acids is proposed to be present on TiO$_2$. Besides signals ascribed to tridentate bound phospionate species, some spectroscopic evidence was obtained for incomplete deprotonation of the phosphonic acid pointing towards a bidentate configuration [17, 98, 100, 101, 103]. The presence of bi- and tridentate linked phosphonic acids on TiO$_2$ was also found recently by X-ray diffraction characterisation [104].

On an atomistic scale, only a few theoretical studies exist beside this work that focus on the bonding between the phosphonic acid molecules and the aluminium or titanium oxide surface. Hector et al. [107] calculated the reaction energetics of the adsorption of vinyl phosphonic acid on the OH-terminated (0001) surface of corundum (α-Al$_2$O$_3$). The authors propose that the adsorption of vinyl phosphonic acid depends on the geometry of the adsorption site. Moreover, they show evidence that adsorption favors tridentate complexes,
in which the phosphonic acid headgroup is bound to the aluminium oxide surface via three P–O–Al bonds. Nilsing et al. studied the adsorption of phosphonic acid on the surface of anatase (101) and rutile (110) using periodic boundary conditions within hybrid \textit{ab initio} Hartree Fock density functional theory calculations [108, 109]. They considered adsorption models including non-dissociated and single dissociated phosphonic acid groups. According to their results, the phosphonic acid binds to the anatase (101) and rutile (110) surface in foremost a monodentate binding mode.

In the current chapter, we investigate the adsorption of the phosphonic acid molecule on aluminium and titanium oxide surfaces by means of efficient SCC-DFTB calculations, see Sections 3.3 and 3.4, respectively. Our main objective is to get a more basic understanding of the phosphonic acid adsorption with respect to the binding mode of the acid and to the geometric considerations of the surface structures. In Section 3.3, we also studied in more detail the structural ordering of long-chain APAs adsorbed on the aluminium oxide surfaces. Furthermore, in Section 3.4, we compare the phosphonic acid as an adsorbate to formic acid, which is also a common anchoring molecule, with respect to its structural and electronic properties in the adsorption complexes on titanium oxide surfaces.

### 3.2 Computational details

We used the SCC-DFTB method (cf. Section 2.2.3) with periodic boundary conditions (cf. Section 2.2.6) as implemented in the DFTB+ program [110] throughout this study. The geometry optimisations of the periodic structures (bulk, surface slabs and adsorption model structures) were performed using the \( \Gamma \)-point approximation (cf. Section 2.2.6) and the conjugate-gradient algorithm (cf. Section 2.2.7) until the root-mean-square of the residual force is below \( 10^{-4} \) Hartree/Bohr.

We optimized the lattice parameters and the atomic positions of the bulk unit cells and created the symmetric and periodic surface slabs as supercells of the optimized bulk structures (cf. Section 2.2.6). A minimum vacuum distance of 40 Å was added in the direction perpendicular to the surface to avoid self-interaction of the slabs. In order to avoid artificial dipoles, the adsorbates were added on both sides of the slabs.

Furthermore, the simulated annealing technique (cf. Section 2.2.7) was used to identify the stability of the local minima of the adsorption complex structures on the TiO\(_2\) surfaces. Each of the corresponding molecular dynamics simulation used a velocity Verlet algorithm to integrate Newton’s equation of motion with a total of 3000 time steps at an increment of 0.25 fs. The NVT ensemble was used, wherein moles, volume and temperature are conserved, applying the Anderson thermostat [111] to exchange energy with the MD system. The temperature profile included a linear heating from 0 K to 600 K within 500 time steps, a 2000 time step sampling at 600 K and a final exponential cooling to 10 K.
3.3 Adsorption of phosphonic acid on aluminium oxide surfaces

3.3.1 Description of the bulk and surface structures

The native aluminium surface, which is used experimentally to grow SAMs of organic molecules, is usually covered with an oxide layer that consists mostly of non-crystalline alumina [112, 113]. In ambient humidity this oxide film reacts with water producing a hydroxylated film. The major part of this film is pseudoboehmite that is the layered structure of the aluminium oxyhydroxides modification boehmite (γ-AlOOH) intercalated with water between its layers. However, loosely bound crystals of the aluminium hydroxide modification bayerite (β-Al(OH)₃) as well as single hydroxyl groups in the alumina matrix were also found [114]. Since the structural elements of bayerite and boehmite can be found (in short-range order) in the amorphous oxide film, and corundum (α-Al₂O₃), the stable phase of crystalline alumina, is one of the most important ceramic materials, we used crystalline OH-terminated surface models based on these three structures in our investigation. Moreover, from the large number of possible surface structures we chose the simplest surfaces of each mineral, namely α-Al₂O₃ (0001), β-Al(OH)₃ (001) and γ-AlOOH (010), because the first one is the most common corundum surface and the latter ones are terminated by hydroxyl groups. These are supposed to react with the phosphonic acid via an acid-base condensation mechanism to form P–O–Al bonds [107]. By investigating the three models separately, a more basic understanding of the phosphonic acid adsorption is accessible, especially with respect to geometric considerations. In the following some details regarding the bulk and surface structure of each model are presented with a focus on α-Al₂O₃ (0001), which is the most extensively studied aluminium oxide surface due to its technological applications. The possible adsorption sites of each surface model for mono-, bi- and tridentate binding of the phosphonic acid and their geometric considerations will be discussed later in Section 3.3.4.

Corundum

The crystal structure of α-Al₂O₃ (Figure 3.1) consists of a hexagonal close-packed array of oxygen atoms, in which aluminium atoms occupy two thirds of the octahedral vacancies in the oxygen sublattice at alternating positions above and below the center of these sites. The structure can be viewed either in its primitive rhombohedral cell containing two molecular units (10 atoms, $D_3^h$ ($R3c$) symmetry) or in its conventional hexagonal unit cell containing six molecular units (30 atoms) [115, 116]. The clean (0001) surface of α-Al₂O₃ is terminated by a single layer of aluminium atoms under ultra-high vacuum conditions, but the surface is terminated by OH groups in presence of water [117]. For this reason, we optimised the geometries of α-Al₂O₃ (0001) surface models terminated with Al and OH.

Initially, the lattice constants of the hexagonal unit cell and the Al–O bond lengths of the bulk structure were optimised and are found in good agreement with experimental
3.3 Adsorption of phosphonic acid on aluminium oxide surfaces

Figure 3.1: The hexagonal crystal structure of corundum ($\alpha$-Al$_2$O$_3$): view of plane (01\bar{1}0) on the left and (0001) on the right side. Large spheres represent Al atoms and small spheres represent O atoms.

[115, 118, 119] and theoretical data [120] (cf. Table 3.1). SCC-DFTB slightly underestimates one of the Al–O bond length by 1.5% in comparison with the experimental and DFT-GGA results. It overestimates the lattice constants by 1.4% in comparison with the LDA results of Siegel et al. [120]. In all other cases, the deviation between our SCC-DFTB calculations and the results reported in the literature is less than 1%.

Furthermore, we optimised periodic structures containing 18 and 36 stacked atomic layers corresponding to the thickness of one and two bulk unit cells in $c$ direction to determine the minimum slab thickness of the surface models. These models will further be denoted as models Al$_{18}$ and Al$_{36}$, respectively. We obtained the related OH-terminated surface models, OH$_{18}$ and OH$_{36}$, by removing the top aluminium layer from the models Al$_{18}$ and Al$_{36}$ and saturating the remaining oxygens with hydrogen atoms. The Al$_{36}$ and and OH$_{36}$ surface models are shown in Figure 3.2.

In Table 3.2, we present the distances between the atomic layers calculated for the four surface models. The atomic layers are labeled according to Figure 3.2. We found that the interlayer distances do not differ very much for the 18 and 36 layer models. For the Al-terminated surface, a remarkable characteristic is the strong contraction of the first (Al1–O1) and the third (Al2–Al3) atomic interlayer distances by 33% and 37%, respectively, compared with the bulk values. We also observed a strong contraction by 27% for the first Al2–Al3 interlayer distance of the OH-terminated surface. This is similar to other theoretical [120, 127, 128] and experimental [117, 129–131] studies, in which the respective contractions range from 30% to 86%.
Table 3.1: Optimised bulk lattice constants of corundum ($\alpha$-Al$_2$O$_3$, I), bayerite ($\beta$-Al(OH)$_3$, II) and boehmite ($\gamma$-AlOOH, III) as well as Al–O bond lengths in comparison with other experimental and theoretical results. The latter are obtained with either $^a$ the generalised gradient approximation or $^b$ the local density approximation. Lengths are given in Ångström, angles are given in degree.

<table>
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<tr>
<th></th>
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<th>Exp.</th>
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</tr>
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<td>1.86 [120]$^a$</td>
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<tr>
<td></td>
<td>1.94</td>
<td>1.97 [118]</td>
<td>–</td>
<td>1.97 [120]$^a$</td>
<td>–</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$\beta$</td>
<td>90.27</td>
<td>90.27 [121]</td>
<td>90.26 [122]</td>
<td>90.07 [123]$^a$</td>
<td>90.47 [124]$^a$</td>
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</tr>
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<td>OH···O</td>
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<td>2.24 [121]</td>
<td>–</td>
<td>2.27 [123]$^a$</td>
<td>–</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>2.888</td>
<td>2.876 [125]</td>
<td>2.868 [126]</td>
<td>2.904 [123]$^a$</td>
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<td>1.90 [125]</td>
<td>1.90 [126]</td>
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<td>–</td>
</tr>
<tr>
<td>Al–O</td>
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<td>1.86 [125]</td>
<td>1.88 [126]</td>
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<td>–</td>
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<td></td>
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<td>1.94 [125]</td>
<td>1.95 [126]</td>
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<td>–</td>
</tr>
<tr>
<td>OH···O</td>
<td>2.07</td>
<td>1.81 [125]</td>
<td>–</td>
<td>1.61 [123]$^a$</td>
<td>–</td>
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Table 3.2: Calculated distances between the atomic layers [Å] in the surface models $Al_{18}$, $Al_{36}$, $OH_{18}$, $OH_{36}$ of $\alpha$-Al$_2$O$_3$ (0001) and percent relaxation (in parenthesis) with respect to the bulk. The atomic layers are in an Al–O–Al series and are labeled by their atom type and their layer numbers counted from the top of the surface according to Figure 3.2. The bulk interlayer distances are: Al–O = 0.818 Å and Al–Al = 0.530 Å.

<table>
<thead>
<tr>
<th>Labels</th>
<th>$Al_{18}$</th>
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<th>$OH_{18}$</th>
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<tr>
<td>A11–O1</td>
<td>0.546 (−33.3)</td>
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<tr>
<td>O1–Al2</td>
<td>0.914 (11.7)</td>
<td>0.913</td>
<td>0.889 (8.7)</td>
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<tr>
<td>Al2–Al3</td>
<td>0.334 (−37.1)</td>
<td>0.334</td>
<td>0.388 (−26.9)</td>
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<tr>
<td>Al3–O2</td>
<td>0.981 (20.0)</td>
<td>0.981</td>
<td>0.936 (14.5)</td>
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</tr>
<tr>
<td>O2–Al4</td>
<td>0.842 (3.0)</td>
<td>0.842</td>
<td>0.853 (4.3)</td>
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</tr>
<tr>
<td>Al4–Al5</td>
<td>0.501 (−5.5)</td>
<td>0.501</td>
<td>0.497 (−6.3)</td>
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<tr>
<td>Al5–O3</td>
<td>0.858 (4.9)</td>
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<td>0.860 (5.1)</td>
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<tr>
<td>O3–Al6</td>
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<td>0.857 (4.8)</td>
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<td>Al6–Al7</td>
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<td>Al8–Al9</td>
<td>—</td>
<td>0.496</td>
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</table>
3.3 Adsorption of phosphonic acid on aluminium oxide surfaces

Figure 3.2: Al-terminated (left) and OH-terminated (right) $\alpha$-$\text{Al}_2\text{O}_3$ (0001) surface models containing 36 stacking layers ($\approx26$ Å). Each layer is labeled from the top of the surface. Large spheres represent Al atoms, small spheres represent O atoms and light blue spheres represent H atoms.
The Al–O bond lengths are less affected by this surface reconstruction. The (shorter) Al–O bond lengths in the first three Al layers are 1.74 Å (–8%), 1.87 Å (–0.5%) and 1.92 Å (+2%) for the Al-terminated models and 1.87 Å (–0.5%), 1.91 Å (+2%) and 1.90 Å (+1%) for the OH-terminated models. The respective deviations from the bulk value (1.88 Å) are given in parenthesis. Also, the bond lengths and interlayer distances starting from the seventh atomic layer on are converged, i.e. Al5–O3, 4.1 and 3.6 Å below the surface for the Al- and the OH-terminated model, respectively. They are close to those values of the bulk. Hence, we conclude that a slab thickness of 18 atomic layers is sufficient to represent the α-Al₂O₃ (0001) surface.

Bayerite

Bayerite, β-Al(OH)₃ (Figure 3.3), is a natural solid and a precursor of α-Al₂O₃[112, 121–124]. It consists of a pseudo-trigonal layer structure, in which the basic structural unit is formed by double-layers of OH ions with aluminium ions occupying two thirds of the octahedral interstices within the layers. The layers of octahedral Al–OH are arranged in an AB sequence and are oriented nearly perpendicular to the c direction. Therefore, the OH ions in one unit are positioned between the OH ions of the adjacent unit. Our SCC-DFTB calculation of the bulk lattice constants overestimates the cell size in each direction by 3.2% compared with the experiment. This trend is also present in the GGA calculations (Table 3.1), where the deviation is about 1–2%. The overestimation of the lattice constants is rather more reflected in the interlayer distances than in the Al–O bond length. The calculated OH⋯O hydrogen bonds are longer by 0.4 Å than those determined by experiment [121, 122] and GGA calculations [123, 124], see Table 3.1. Thus, SCC-DFTB tends to overestimate hydrogen bond lengths that determine the interlayer spacing.

Boehmite

Boehmite [112, 123, 125, 126], γ-AlOOH (Figure 3.4), exhibits a layered structure with an orthorhombic symmetry. The layers are composed of chains formed by dimers of AlOOH that extend along the a axis. The OH ions of one layer are localised between the OH ions of the adjacent layers. Optimisation of their bulk lattice constants with SCC-DFTB gives values that are again slightly larger than those reported in the literature (cf. Table 3.1). We obtain the largest deviation with respect to experimental results for the b axis, which is the direction of the stacking layers. This is again mainly reflected in an overestimation of the interlayer spacing. In particular, our calculated OH⋯H hydrogen bonds are longer by 0.2 Å compared with the experimental value.

The structures of bayerite and boehmite, both consist of hydroxyl terminated layers that are linked by hydrogen bonds. Thus, we created the (001) surface model of bayerite by repeating the bulk unit cell twice and adding a vacuum region along the c direction. We built the (010) surface model of boehmite by simply adding a vacuum region along the b direction of the bulk unit cell. Both surface models were optimised afterwards.
3.3 Adsorption of phosphonic acid on aluminium oxide surfaces

Figure 3.3: Views of planes (100) (left) and (001) (right) of bayerite \((\beta-\text{Al(OH)}_3)\) bulk structure. Colors of the atoms are as in Figure 3.2.

Figure 3.4: Bulk boehmite \((\gamma-\text{AlOOH})\): planes (100), (001) and (010), from left to right. Colors of the atoms are as in Figure 3.2.
3.3.2 Alkyl phosphonic acids

The geometries of the free phosphonic acid (PA, HPO(OH)$_2$) and the alkyl phosphonic acid molecules (APA, general formula: $C_nH_{2n+1}PO(OH)_2$) were also optimised with SCC-DFTB. In this work, we investigated APAs with different lengths of the alkyl chain, i.e. $n=2$ (EPA), 5 (PPA), 10 (DPA) and 18 (ODPA). The structures of the investigated molecules are illustrated in Figure 3.5. The calculated bond lengths and angles of the PA and APA molecules are presented in Table 3.3. We include a comparison of the values of the PA molecule with the parameters obtained by full DFT calculations [132]. Averaged values of the P–OH bond lengths and H–P–OH angles are given in some cases because of the C$_s$ symmetry of the PA molecule. Moreover, we also list only averaged bond lengths, valence and dihedral angles of the alkyl chains, since their values differ by a maximum of 0.01 Å, 3° and 0°, respectively.

We note from Table 3.3 that the calculated bond lengths and angles in the phosphonic acid headgroup of the APAs are very similar to those of the simple PA molecule. Small deviations can be explained by the two different substituents, which is an H atom in the PA and an alkyl chain in the APAs. Moreover, the geometric parameters of the APAs have constant values nearly independent on the length of the alkyl chain. The methylene units in the alkyl chains keep their initial staggered (all-trans) zig-zag conformation corresponding to (C–C–C–C) dihedral angles of 180°.

Furthermore, we found a quite good agreement between our SCC-DFTB calculations and the DFT results of Joswig et al. [132] for the PA molecule, see Table 3.3. The largest deviations between SCC-DFTB and DFT are obtained for the H/C–P=O valence angle (−4.4%).
3.3 Adsorption of phosphonic acid on aluminium oxide surfaces

Table 3.3: Bond lengths, valence and dihedral angles of PA and APAs calculated with SCC-DFTB. The parameters of the PA molecule are compared with the DFT results of Joswig et al. [132]. Lengths are given in Ångström, angles are given in degree.

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<th>PPA</th>
<th>DPA</th>
<th>ODPA</th>
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<td></td>
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</tr>
</tbody>
</table>

and the P–OH bond lengths (+3.0%). The calculated P–OH bond using SCC-DFTB is also overestimated in comparison with the experimental result of 1.54 Å [133] by +8%. However, the calculated P=O bond length is in very good agreement with the experiment (1.47 Å) [133].

We conclude, that the SCC-DFTB method describes also the structure of the PA and APA molecules reasonable well. This further demonstrates the applicability of this method to investigate the adsorption as well as the orientation and ordering of the molecules on the aluminium oxide surfaces.

3.3.3 Adsorption reaction

The adsorption of the PA and APAs on the surface of alumina is proposed to proceed via an acid-base condensation mechanism in three steps [107], which is shown in Figure 3.6 (d). Initially, the P–OH groups react stepwise with two hydroxyl groups of the surface forming two symmetric P–O–Al bonds. I.e., first a monodentate and then a bidentate adsorption complex is build, see Figures 3.6 (a) and (b), respectively. To explain the formation of the third P–O–Al bond, i.e. the tridentate adsorption complex, cf. Figure 3.6 (c), D’Andrea et al. [16] proposed the formation of a hydrogen bond between the phosphoryl oxygen and a surface hydroxyl group (P=O ⋯ H–O). The absence of the P=O bands in the FTIR spectra [83, 93] would then be explained by a decrease in the extinction coefficient, that is in their opinion not uncommon in the spectroscopy of adsorbed species. However, to explain the
Figure 3.6: (a) Monodentate, (b) bidentate and (c) tridentate binding modes of EPA on the surface of α-Al₂O₃ (0001). O atoms are red, Al atoms are violet, H atoms are light grey, C atoms are dark grey and P atoms are yellow. (d) Stepwise condensation reaction between the phosphonic acid headgroup and the aluminium oxide surface.

The presence of vibrations corresponding to a resonance stabilised R–PO₂⁻³ moiety in the spectra and thus, the presence of three symmetric P–O–Al bonds, a chemical reaction between the P=O and the surface is required.

One possibility for this reaction is that the P=O group reacts with an unsaturated Al atom on the surface [91, 134], but in this case the surface coverage would strongly depend on the number of unsaturated Al atoms on the surface. A second hypothesis is that in an acidic medium one of the OH groups on the surface could be protonated and released as water, permitting that the third P–O–Al bond is formed resulting in the tridentate adsorption complex. SAMs are usually prepared in aqueous acidic media. Under these conditions, unsaturated Al atoms present at the surface would be expected to be oxidised immediately. For this reason, we chose the second mechanism to be the most likely reaction path.

In both mechanisms the resulting tridentate complex has a positive charge caused either by an unsaturated aluminium or by the insertion of a proton from the medium, as it will be the case in the current models. In actual systems, many negatively charged ions are present in the amorphous aluminium oxide matrix as well as in the aqueous acidic medium around the surfaces to balance the positive adsorbate. To avoid the very complex problem of simulating such an environment, we removed a single proton of a neighboring surface hydroxyl group for each tridentate adsorbed phosphonic acid molecule to balance the charge of our models.
3.3 Adsorption of phosphonic acid on aluminium oxide surfaces

3.3.4 Description of the possible adsorption sites

Corundum (0001)

The possible adsorption sites on the $\alpha$-$\text{Al}_2\text{O}_3$ (0001) surface model are shown in Figure 3.7. According to Ref. [107], there are three different sites in total, that we label $s1$, $s2$ and $s3$. Each of them consists of three hydroxyl groups forming a triangle. The triangular geometry of the adsorption sites is very suitable for binding the phosphonic acids especially in a tridentate binding mode due to the tripodal arrangement of the anchor group. The sites differ by the dimensions of the OH triangles and by the distance to the Al atom below the center of the triangle. The O–O distances within the sites are 2.80, 2.49 and 3.00 Å, and the Al atoms are 0.89, 1.28 and 3.07 Å below the centers of the triangles, respectively. For each adsorption site there is only one possible bidentate complex, because the three oxygen atoms of one triangular site are equivalent. Also, there is only one monodentate adsorption site, because the single OH groups on the surface have the same structural environment.

Bayerite (001)

The (001) surface of $\beta$-$\text{Al(OH)}_3$ is more complex, and we define the adsorption sites according to the binding mode, as shown in Figure 3.8. For the tridentate binding, four adsorption sites can be identified, namely $ts1$, $ts2$, $ts3$ and $ts4$. The average O–O distances in each tridentate site are 2.78, 3.04, 2.98 and 3.51 Å for $ts1$, $ts2$, $ts3$ and $ts4$, respectively. The center of site $ts1$ is characterised by an Al atom at a distance of 1.02 Å below the plane of the
oxygen triangle, whereas the centers of \( \text{ts2}, \text{ts3} \) and \( \text{ts4} \) are characterised by OH groups, which O atoms lie 2.00, 2.04 and 4.49 Å below the triangular planes, respectively. For the bidentate binding, we distinguish the sites \( \text{bs1}, \text{bs2}, \text{bs3} \) and \( \text{bs4} \). The O–O distances of the bidentate adsorption sites are 2.80, 3.54, 2.74 and 3.46 Å, respectively. Finally, there are two monodentate sites, \( \text{ms1} \) and \( \text{ms2} \).

**Boehmite (010)**

On the (010) surface of \( \gamma \)-AlOOH, there are no different sites for mono- and tridentate adsorption, see Figure 3.9. Due to their symmetry, all hydroxyl groups on this surface are equally accessible to bind the PA molecules. However, we identify three different bidentate sites \( \text{bs1}, \text{bs2}, \text{bs3} \) with O–O distances of 2.89, 3.72 and 4.71 Å respectively. The subsurface atoms below the centers of the O–O connection lines consist of Al atoms in case of \( \text{bs1} \) and \( \text{bs2} \), and an O atom in case of \( \text{bs3} \). The subsurface Al atoms are at distances of 1.23 Å and 2.95 Å below the centers of the O–O connection lines of \( \text{bs1} \) and \( \text{bs2} \), respectively, whereas the subsurface O atom of site \( \text{bs3} \) is localised at a distance of 1.66 Å.

### 3.3.5 Surface coverage

In the present investigation, we considered two different surface coverage rates. On the one hand, the adsorption of a single molecule on each surface in the simulation cell is studied. For this, we enlarged the supercells, so that the interaction between a phosphonic acid molecule and its periodic image is negligible. On the other hand, we considered a maximum “geometrical” coverage, i.e. a maximum occupation of the adsorption sites on the surfaces for each binding mode. The construction of the adsorption models with this maximum surface coverage is attached to some certain conditions:

(i) Every threefold site next to a bound acid is not accessible for binding another phosphonic acid in a tridentate binding mode, because a proton is removed to balance the charge. In this way, only half of the reactive sites on the surface of \( \alpha \)-Al\(_2\)O\(_3\) and \( \beta \)-Al(OH)\(_3\) can be used to bind the acids. In case of \( \gamma \)-AlOOH, where all hydroxyl groups are equivalent, no hydroxyl groups are left on the surface in the tridentate adsorption complexes, because either they are bonded to a phosphonic acid or their H atom is removed for charge balance.

(ii) For the mono- and bidentate binding no charge has to be neutralised and, in principle, all OH groups are accessible for binding. However, the packing density of the (alkyl) phosphonic acids is not only limited by the number of available binding sites on the surface, but also by the cross sectional area of the PA headgroup \( (\sigma = 0.23 \text{ nm}^2, \text{estimated from the molar volume of HPO(OH)}_2) [135] \). Thus, only every second diagonally situated OH group on the surface of \( \gamma \)-AlOOH, only every second OH group of site \( \text{ms2} \) on the surface of \( \beta \)-Al(OH)\(_3\) and only every third OH group on the surface of \( \alpha \)-Al\(_2\)O\(_3\) is used for the monodentate complexes, since the distance between adjacent OH groups is too small and
3.3 Adsorption of phosphonic acid on aluminium oxide surfaces

Figure 3.8: Adsorption sites on the $\beta$-Al(OH)$_3$ (001) surface model. From top to bottom: tridentate, bidentate and monodentate sites. Colors of the atoms are as in Figure 3.2.
neighboring phosphonic acid headgroups would hinder each other due to sterical interactions. Furthermore, two arrangements are possible to cover the surface of $\gamma$-AlOOH with the maximum number of bidentate bound phosphonic acid molecules. The molecules can be placed either in rows or in a staggered arrangement, see Figure 3.10.

The sizes of the periodic simulation cells, the number of bound (alkyl) phosphonic acid molecules per cell and the resulting surface coverages are summarised in Table 3.4. The maximum adsorbate densities calculated for mono- and bidentate phosphonic acids on the different surfaces range from 4.3 to 4.7 nm$^{-2}$. These values are in good agreement with the maximum packing density of $\sigma^{-1} = 4.35$ nm$^{-2}$ for close packed monolayers of APAs, that is estimated by the cross-sectional area of the phosphonic acid headgroup [16]. Also, this result is comparable with experimental determined surface coverages reported for ODPA on mica [14], TiO$_2$ [90, 136], ZrO$_2$ [136] and Si/SiO$_2$ [18] that range from 3.5 to 4.9 nm$^{-2}$. Furthermore, it can be seen from Table 3.4 that the different surface models exhibit similar coverages. This is important to note, since all three surface types are studied separately in order to draw conclusions for the amorphous aluminium oxide surface.

### 3.3.6 Determination of the most favored adsorption sites

Adsorption complexes of phosphonic and ethyl phosphonic acid with the three different surface models were constructed and optimised using all possible mono-, bi- and tridentate adsorption sites defined in Subsection 3.3.4. Due to the different stoichiometry of the adsorption reaction for the tridentate binding, a direct comparison with the two other modes is not possible. (In particular, we had to balance the positive charge in the tridentate complexes by removing a proton of a surface hydroxyl group.) Hence, we cannot determine the most favored binding mode by this approach. Indeed, we determine the most favored adsorption site for a specific binding mode, a specific surface structure and surface coverage.
3.3 Adsorption of phosphonic acid on aluminium oxide surfaces

Figure 3.10: Staggered (left) and row (right) bidentate adsorption of ethyl phosphonic acid on site bs1 of boehmite (010). Colors of the atoms are as in Figure 3.6.

Table 3.4: Number of bound molecules per simulation cell and surface coverages for the different binding modes and surface structures. The size of the periodic surface cells are given in unit cells of the corresponding bulk structure. I: corundum, α-Al₂O₃ (0001), II: bayerite, β-Al(OH)₃ (001), III: boehmite, γ-AlOOH (010).

<table>
<thead>
<tr>
<th>Model</th>
<th>Acid</th>
<th>Cell size</th>
<th>No. of molecules</th>
<th>Surf. cov. / nm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>axbxc</td>
<td>mono</td>
<td>bi</td>
</tr>
<tr>
<td>I</td>
<td>PA,</td>
<td>2x2x1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>EPA</td>
<td>2x2x2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>4x1x4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>I</td>
<td>PPA,</td>
<td>3x3x1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>DPA</td>
<td>3x2x1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>5x1x4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>I</td>
<td>ODPA</td>
<td>5x5x1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>5x3x1</td>
<td>1</td>
<td>1</td>
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<td></td>
<td>8x1x7</td>
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<td>1</td>
</tr>
<tr>
<td>I</td>
<td>PA, EPA,</td>
<td>2x2x1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>II</td>
<td>PPA, DPA,</td>
<td>1x1x1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>III</td>
<td>ODPA</td>
<td>2x1x2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>
Table 3.5: Relative energies [kJ·mol⁻¹] of the adsorption complexes of phosphonic (PA) and ethyl phosphonic (EPA) acids on the various adsorption sites of α-Al₂O₃ (0001) (I), β-Al(OH)₃ (001) (II) and γ-AlOOH (010) (III). The labels m, b and t refer to mono-, bi- and tridentate binding of the acids, respectively.

<table>
<thead>
<tr>
<th>Model</th>
<th>Ads. site</th>
<th>Single molecule</th>
<th>Max. Surf. coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PA</td>
<td>EPA</td>
</tr>
<tr>
<td>I</td>
<td>bs2</td>
<td>81.52</td>
<td>63.04</td>
</tr>
<tr>
<td></td>
<td>bs3</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>ts2</td>
<td>221.91</td>
<td>234.24</td>
</tr>
<tr>
<td></td>
<td>ts3</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>II</td>
<td>ms1</td>
<td>11.35</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>ms2</td>
<td>0.00</td>
<td>20.04</td>
</tr>
<tr>
<td></td>
<td>bs1</td>
<td>85.38</td>
<td>87.01</td>
</tr>
<tr>
<td></td>
<td>bs2</td>
<td>16.81</td>
<td>50.54</td>
</tr>
<tr>
<td></td>
<td>bs3</td>
<td>73.16</td>
<td>57.11</td>
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<td></td>
<td>bs4</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>ts2</td>
<td>181.62</td>
<td>174.06</td>
</tr>
<tr>
<td></td>
<td>ts3</td>
<td>104.31</td>
<td>102.74</td>
</tr>
<tr>
<td></td>
<td>ts4</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>III</td>
<td>bs1</td>
<td>118.32</td>
<td>36.16</td>
</tr>
<tr>
<td></td>
<td>bs2</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>bs3</td>
<td>322.68</td>
<td>244.21</td>
</tr>
</tbody>
</table>

<sup>a</sup> Staggered coverage; <sup>b</sup> Row coverage.

by comparing the total energies of the respective adsorption complexes. ¹

**Corundum (0001)**

The relative energies of the adsorption complexes between a single PA or EPA molecule in the various adsorption sites and in different binding modes on the α-Al₂O₃ (0001) surface are summarised in Table 3.5 (I). The respective values obtained for the maximum (geometrical) surface coverage are also included. We found that monodentate adsorption on this surface is unselective, but site s3 is favored for bi- and tridentate adsorption complexes at both low and high coverages. The PO–Al bonds of the tridentate complex on site s2 are not symmetric, because one of the bonds is approximately 0.15 Å longer than the other two. Moreover, bi- and tridentate complexes are not stable in site s1. Instead, they react back to a monodentate complex. Similar trends were observed by Hector et al. [107], who calculated adsorption enthalpies for vinyl phosphonic acid on this surface. We assume that the instability at sites s1 and s2 is due to the fact that each O atom at these sites is bonded to

¹The total energies were calculated by single-point-energy calculations of the optimized adsorption complexes using suitable sets of k-points obtained with the Monkhorst-Pack procedure [78, 79] (cf. Section 2.2.6).
the central Al atom and adsorption of the phosphonic acid would result in strained and unstable, bipyramidal cages with smaller Al–P distances and, thus, a larger atomic repulsion. In contrast, the Al atom below the center of s3 is localised in the third Al layer and has no bonds to the O atoms of the site. Thus, no bipyramidal cages are present and the repulsive effect acting on the adsorbate is much lower.

**Bayerite (001)**

In case of β-Al(OH)$_3$ (001), we found that site ts4 is the most favored site for a tridentate adsorption, see Table 3.5 (II). Similar to s3 of α-Al$_2$O$_3$ (0001), the subsurface atom of this site is localised at the largest distance below the triangular plane, so that the repulsive effects are lowest. In contrast to ts4, the repulsion and strain effects acting on ts1 are strong enough to destabilise all tridentate models due to the possible formation of unstable bipyramidal cages. In fact, ts1 is very similar to the site s1 of α-Al$_2$O$_3$ (0001). The sites ts2 and ts3 are more unfavorable than ts4, not only due to the shorter distances to the subsurface OH groups, but also due to the asymmetry of the O–O distances in the adsorption site. In the monodentate complexes, the PA molecule favors adsorption on site ms2 while the EPA molecule prefers site ms1. For PA bidentate complexes, the most favored site is bs4, but the energy difference compared with complexes at bs2 is rather small. For EPA bidentate complexes, bs4 is favored only at low coverage. For the highest coverage, the least favored site is bs1, but concluding from the energies none of the other sites is particularly preferred.

**Boehmite (010)**

The γ-AlOOH (010) surface is unselective with respect to mono- and tridentate complexes. The first are stable, whereas adsorption at the latter is not, because the asymmetry of the adsorption site makes this binding mode energetically unfavorable. Bidentate adsorption, in contrast, is shown to be site selective and adsorption of a single molecule at bs1, bs2 and bs3 results in stable complexes. In any case, the energetically preferred adsorption site is bs2, see Table 3.5 (III). For this site, the distance to the subsurface aluminium atom is larger than for bs1 and the distance between neighboring O atoms is smaller than for bs3. Indeed, the large O–O distance of 4.71 Å in site bs3 leads to a diagonal displacement of an O atom towards a second one in the bidentate adsorption complexes. This results in an O–O distance of 2.82 Å, which is similar to that in the free phosphonic acid molecule (2.7 Å).

On the highly covered γ-AlOOH (010) surface, the PA alignment in rows is only stable on site bs1. However, it is energetically much more unfavorable than the staggered configuration, probably due to lateral interactions between neighboring PA molecules. Staggered adsorption on site bs3 is not stable; optimisation of this complex results in the staggered adsorption structure on bs2. This is energetically the most favored site and arrangement for bidentate adsorption of phosphonic acids on γ-AlOOH (010).
Further conclusions

The selection of a specific adsorption site is more pronounced as the number of phosphonic acid bonds to the surface increases, as we note from Table 3.5. In a tridentate configuration the phosphonic group is closer to the surface than in a monodentate arrangement, thus the repulsion interaction and strain effects between the phosphonic acid and subsurface atoms below the center of the sites are stronger, destabilising the adsorbate structure and increasing the regioselectivity. The alkyl chain has obviously only small influence on the selection of the adsorption site. The preferred sites for adsorption of PA and EPA are the same for all surfaces, coverages and binding modes except for monodentate adsorption on $\beta$-Al(OH)$_3$ (001). Moreover, we state that the energetically favored sites allow a chemically logical adsorption sequence, i.e. on all surfaces the favored monodentate site is localised within the most favored bidentate site, that itself is localised within the favored tridentate site. This strongly supports our assumed adsorption mechanism, i.e. the above mentioned step by step condensation reaction (cf. Subsection 3.3.3).

In Table 3.6, we present the bond lengths involving the phosphorous atom in the most favorable adsorption complexes on each surface. Neither the P=O nor the P–OH bond lengths are significantly affected by the binding of the molecule to the surface. They are also similar to the respective bond lengths calculated for the free phosphonic acid molecules, cf. Table 3.3. However, the P–OAl bonds increase slightly when going from monodentate to bidentate complexes, probably as a manner to balance a higher strain arising from the more rigid arrangement of the bidentate adsorption. The tridentate complexes have the shortest P–OAl bonds and the three P–OAl bonds have approximately the same values. This agrees well with the picture of the resonance stabilised $\text{PO}_2^3^-$ group, where the P–O bonds are symmetric. The value of the P–OAl bond length in the tridentate models is also very similar to that calculated in the $\text{PO}_3^2^-$ group (1.57 Å). Furthermore, we found that the bond lengths of the same adsorption mode for different surfaces have the same values.

3.3.7 Structural ordering of the adsorbed long-chain alkyl phosphonic acids

We used the most favored adsorption sites of each surface structure summarised in Figure 3.11 to investigate the adsorption of APAs with longer carbon chains (PPA, DPA and ODPA, cf. Figure 3.5). In particular, we focus on the structure of the adsorbed APA molecules in the SAM in dependence on the surface structure, the surface coverage, the binding mode and the length of the alkyl chain. Thereby, mono-, bi- and tridentate adsorption complexes and the two surface coverage rates defined in subsection 3.3.5 are considered.

SAM height

The thickness of the SAMs is calculated as the height of the adsorbed APA molecules above the surface. We define the SAM height as the distance between the average plane of su-
Table 3.6: Lengths [Å] of phosphorus bonds in the adsorption complexes of the most energetically favored sites on \( \alpha\text{-Al}_2\text{O}_3\) (0001) (I), \( \beta\text{-Al(OH)}_3\) (001) (II) and \( \gamma\text{-AlOOH}\) (010) (III). First numbers refer to adsorption of a single molecule, second numbers to the maximum covered surface. The labels m, b and t refer to mono-, bi- and tridentate binding of the acids, respectively.

<table>
<thead>
<tr>
<th>Model</th>
<th>Acid</th>
<th>Ads. site</th>
<th>P–OAl</th>
<th>P=O</th>
<th>P–OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>PA</td>
<td>( m )</td>
<td>1.62 / 1.69</td>
<td>1.48 / 1.48</td>
<td>1.77 / 1.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( bs3 )</td>
<td>1.71 / 1.76</td>
<td>1.48 / 1.48</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ts3 )</td>
<td>1.59 / 1.59</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>EPA</td>
<td>( m )</td>
<td>1.68 / 1.67</td>
<td>1.48 / 1.49</td>
<td>1.70 / 1.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( bs3 )</td>
<td>1.73 / 1.79</td>
<td>1.48 / 1.48</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ts3 )</td>
<td>1.59 / 1.60</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>II</td>
<td>PA</td>
<td>( ms1 )</td>
<td>1.66 / 1.68</td>
<td>1.47 / 1.48</td>
<td>1.70 / 1.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( bs4 )</td>
<td>1.72 / 1.82</td>
<td>1.48 / 1.47</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ts4 )</td>
<td>1.60 / 1.60</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>EPA</td>
<td>( ms2 )</td>
<td>1.67 / 1.70</td>
<td>1.48 / 1.48</td>
<td>1.71 / 1.73</td>
</tr>
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<td></td>
<td></td>
<td>( bs4 )</td>
<td>1.73 / 1.86</td>
<td>1.48 / 1.48</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ts4 )</td>
<td>1.63 / 1.64</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>III</td>
<td>PA</td>
<td>( m )</td>
<td>1.62 / 1.67</td>
<td>1.48 / 1.48</td>
<td>1.71 / 1.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( bs2 )</td>
<td>1.70 / 1.75</td>
<td>1.48 / 1.49</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>EPA</td>
<td>( m )</td>
<td>1.63 / 1.71</td>
<td>1.48 / 1.47</td>
<td>1.74 / 1.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( bs2 )</td>
<td>1.71 / 1.78</td>
<td>1.49 / 1.47</td>
<td>—</td>
</tr>
</tbody>
</table>

Figure 3.11: Surface structures and preferred adsorption sites for mono- (M), bi- (B) and tridentate (T) binding of the APAs: a) \( \alpha\text{-Al}_2\text{O}_3\) (0001), b) \( \beta\text{-Al(OH)}_3\) (001), c) \( \gamma\text{-AlOOH}\) (010). O atoms are red, Al atoms are blue and H atoms are white.
Figure 3.12: a) SAM height and chain tilting, b) chain distortion and c) (from top to bottom) staggered ($\varphi = 180^\circ$), eclipsed ($\varphi = 120^\circ$) and gauche ($\varphi = 60^\circ$) conformations of the methylene units. O atoms are red, Al atoms are blue, H atoms are white, C atoms are brown and P atoms are yellow.

The primary factor defining the SAM height is the tilting of the alkyl chains with respect to the surface normal, although variations in the length of the APAs after adsorption are observed. Therefore, we calculate the tilt angles of the APAs as:

$$\theta_{\text{tilt}} = \cos^{-1}\left(\frac{h_{\text{SAM}}}{l_{\text{alkyl}}}\right),$$

where $h_{\text{SAM}}$ is the SAM height and $l_{\text{alkyl}}$ is the length of the adsorbed alkyl chain, see Figure 3.12 (a). We define $l_{\text{alkyl}}$ as the distance between the average of the O atoms of the anchoring phosphonic acid group and the farthest carbon atom of the alkyl chain. Experimentally, tilt angles – as listed in Table 3.8 – are estimated from the measured height of the SAMs supposing that the length of the fully extended, optimised, free molecules, that are approximately 7.5, 13.5 and 23.5 Å for PPA, DPA and ODPA, respectively.

**Tilt angles**

The primary factor defining the SAM height is the tilting of the alkyl chains with respect to the surface normal, although variations in the length of the APAs after adsorption are observed. Therefore, we calculate the tilt angles of the APAs as:

$$\theta_{\text{tilt}} = \cos^{-1}\left(\frac{h_{\text{SAM}}}{l_{\text{alkyl}}}\right),$$

where $h_{\text{SAM}}$ is the SAM height and $l_{\text{alkyl}}$ is the length of the adsorbed alkyl chain, see Figure 3.12 (a). We define $l_{\text{alkyl}}$ as the distance between the average of the O atoms of the anchoring phosphonic acid group and the farthest carbon atom of the alkyl chain. Experimentally, tilt angles – as listed in Table 3.8 – are estimated from the measured height of the SAMs supposing that the length of the adsorbed APA is the same as in the all-trans configuration of the free acid molecule. However, it is reasonable to assume that the self-assembly process results in some conformational change of the adsorbed molecules. On the
### Table 3.7: Average height [Å] of APA monolayers on each surface at different coverages and binding modes. I: corundum, α-Al₂O₃ (0001), II: bayerite, β-Al(OH)₃ (001), III: boehmite, γ-AlOOH (010).

<table>
<thead>
<tr>
<th>Acid</th>
<th>Mode</th>
<th>Single Molec.</th>
<th>Max. Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>PPA</td>
<td>mono</td>
<td>6.3</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>bi</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>tri</td>
<td>6.7</td>
<td>6.2</td>
</tr>
<tr>
<td>DPA</td>
<td>mono</td>
<td>12.0</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>bi</td>
<td>12.7</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>tri</td>
<td>11.5</td>
<td>11.4</td>
</tr>
<tr>
<td>ODPA</td>
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<td>20.6</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>bi</td>
<td>23.6</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td>tri</td>
<td>19.7</td>
<td>21.0</td>
</tr>
</tbody>
</table>

### Table 3.8: Experimental SAM heights [Å] and tilt angles [deg.] of ODPA on different substrate surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Height</th>
<th>Tilt angle</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>mica</td>
<td>18</td>
<td>40</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>16.5</td>
<td>46</td>
<td>[137]</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>45</td>
<td>[138]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>22</td>
<td>33</td>
<td>[102]</td>
</tr>
<tr>
<td>Si/SiO₂</td>
<td>18</td>
<td>40</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>-</td>
<td>[139]</td>
</tr>
<tr>
<td>Au/Cu(upd)</td>
<td>20</td>
<td>30</td>
<td>[140]</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>31</td>
<td>[84]</td>
</tr>
</tbody>
</table>
Adsorption of phosphonic acid on metal oxide surfaces

Table 3.9: Average tilt angles [deg.] of the phosphonic acids with respect to the surface normal for different coverages and binding modes. The values between parenthesis were estimated considering the length of the free acid with fully extended carboxylic chain. I: corundum, α-Al$_2$O$_3$ (0001), II: bayerite, β-Al(OH)$_3$ (001), III: boehmite, γ-AlOOH (010).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Acid</th>
<th>Single Molec.</th>
<th>Max. Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>mono</td>
<td>PPA</td>
<td>38</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>(33)</td>
<td></td>
<td>(39)</td>
</tr>
<tr>
<td></td>
<td>DPA</td>
<td>33</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>(27)</td>
<td></td>
<td>(35)</td>
</tr>
<tr>
<td></td>
<td>ODPA</td>
<td>33</td>
<td>35</td>
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<tr>
<td></td>
<td>(29)</td>
<td></td>
<td>(30)</td>
</tr>
<tr>
<td>bi</td>
<td>PPA</td>
<td>31</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>(25)</td>
<td></td>
<td>(26)</td>
</tr>
<tr>
<td></td>
<td>DPA</td>
<td>27</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>(19)</td>
<td></td>
<td>(13)</td>
</tr>
<tr>
<td></td>
<td>ODPA</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>(0)</td>
<td></td>
<td>(15)</td>
</tr>
<tr>
<td>tri</td>
<td>PPA</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>(27)</td>
<td></td>
<td>(34)</td>
</tr>
<tr>
<td></td>
<td>DPA</td>
<td>31</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>(31)</td>
<td></td>
<td>(33)</td>
</tr>
<tr>
<td></td>
<td>ODPA</td>
<td>33</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>(33)</td>
<td></td>
<td>(25)</td>
</tr>
</tbody>
</table>

one hand, we think this to be due to the chemical modification of the head group during the adsorption reaction. On the other hand, it might be induced by the dispersion interactions between the alkyl chains, which attempt to minimise the repulsive forces.

Our calculated tilt angles are listed in Table 3.9. For comparison, the tilt angles calculated using the length of the free all-trans APAs are given in parenthesis. In some cases, the difference between the two calculated tilt angles is large, indicating that the APA molecule is shortened or stretched during adsorption. However, we note, that large differences between the two $\theta_{\text{tilt}}$ may be caused by relatively small changes in $l_{\text{alkyl}}$. In average, the length of the adsorbed APAs is changed by less than 0.5 Å.

The alkyl chains of the APAs in the three binding modes are tilted by angles in very similar ranges: from $10^\circ$ to $52^\circ$ for the monodentate, from $0^\circ$ to $46^\circ$ for the bidentate, and from $0^\circ$ to $43^\circ$ for the tridentate adsorption complexes. Hence, we conclude, that the tilt angle cannot be used to determine whether the APA forms one, two or three bonds with the surface. Moreover, the tilt angles and SAM heights obtained in the case of single molecule adsorption are very similar to the case of full coverage, indicating that these properties are not significantly affected by the SAM density on the surfaces studied in this section.
If the head groups of the APAs are as closely packed as the lateral dimensions of the alkyl chains allow, the tilt angles should be close to zero according to Liakos et al. [94]; however, as the SAM density decreases, the APAs should tilt to maximise the dispersion forces. Liakos et al. reported that, despite of reaching the full coverage of aluminium surfaces with APAs, the alkyl chains were still tilted. They attribute this to the density of adsorption sites on the surface, that would limit the number of adsorbed molecules to an amount, at which the alkyl chains are not maximally packed.

On the one hand, our present results for the full coverage models are in agreement with this hypothesis. In our case, the maximum coverage ranges from 4.3 to 4.7 molecules per nm$^2$ for mono- and bidentate adsorption, which is in agreement with the maximum packing density of the bulky phosphonic acid headgroup, cf. Section 3.3.5. However, it is lower than the packing of alkyl chains would allow. Moreover, the maximum surface coverage for the tridentate models is even half of those of mono- and bidentate adsorption complexes. Hence, it is even lower than the coverage that the bulky phosphonic acid head group would allow.

On the other hand, the present calculations result in very similar tilt angles for both the minimum and maximum covered surfaces, in average 29° and 30°, respectively. This might be an indication that dispersion forces are important only at higher coverages (very short inter-chain distances). If we assume that the tilt angle of a single molecule corresponds to the maximum tilting and if dispersions forces were significant in the current models, the tilting observed in the case of full coverage should be lower, since the SCC-DFTB method employed in this study does not account for dispersion forces. Thus, we conclude, that conformational organisation in SAMs might result from minimisation of repulsive forces, rather than by maximisation of dispersion interactions. In addition, as pointed out by Zhechkov et al. [66], the cohesive energy between graphite sheets (determined by dispersion interactions) is about 40 meV per carbon atom, which corresponds to less than 1 kcal per mol of carbon atoms. Moreover, the APAs in the present investigation only have sp$^3$ carbons, that present even weaker dispersion forces than the sp$^2$ carbons in graphite.

**Distortion**

To analyse the structure of the SAMs in more detail, we also calculated the dihedral angles of the methylene groups in the alkyl chains of the adsorbates, which quantify the degree of distortion in the carbon chain, see Figure 3.12 (b). A staggered (all-trans) conformation of the methylene units results in a dihedral angle of 180°, whereas a dihedral of 120° refers to the eclipsed configuration, as depicted in Figure 3.12 (c). The calculated, average dihedral angles are shown in Table 3.10. On the one hand the average dihedral angle for the singly adsorbed APA molecules differs from 180° by less than 5° in almost all cases. On the other hand, we observe larger deviations for the fully covered surfaces. We assume that these conformational changes result from the rotation of the chains minimising the repulsive forces between hydrogen atoms of neighboring alkyl chains. It might also be due to the
Table 3.10: Average dihedral angles [deg.] between the methylene groups of the phosphonic acids adsorbed with different surface coverages and binding modes: I: corundum, α-Al₂O₃ (001), II: bayerite, β-Al(OH)₃ (001), III: boehmite, γ-AlOOH (010).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Acid</th>
<th>Single Molec.</th>
<th>Max. Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>mono</td>
<td>PPA</td>
<td>179</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>DPA</td>
<td>177</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>ODPA</td>
<td>179</td>
<td>179</td>
</tr>
<tr>
<td>bi</td>
<td>PPA</td>
<td>178</td>
<td>179</td>
</tr>
<tr>
<td></td>
<td>DPA</td>
<td>177</td>
<td>179</td>
</tr>
<tr>
<td></td>
<td>ODPA</td>
<td>170</td>
<td>177</td>
</tr>
<tr>
<td>tri</td>
<td>PPA</td>
<td>180</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>DPA</td>
<td>180</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>ODPA</td>
<td>179</td>
<td>179</td>
</tr>
</tbody>
</table>

In fact, that dispersion forces are not included in the standard SCC-DFTB method. However, we expect that these contributions not surpass the repulsive forces between the chains.

We also noted that the distortion of the alkyl chains in the fully covered surfaces is influenced by the binding mode of the phosphonic acids. The average dihedral angles tend to be closer to 180° (all-trans) as the number of formed Al–O–P bonds increases. This disorganisation can be caused by the PA head group, that is freely rotating in the monodentate complexes and that is totally rigid in the tridentate ones, while assuming an intermediate rigidity in the bidentate adsorbates. The rotation of the phosphonic group can cause the alkyl chains to bounce off each other, thus causing higher disorder. Another possibility is that order in the tridentate complexes is higher due to the lower coverage used in the models, as explained in Section 3.3.5, that leaves more space for the APA molecules.

Nevertheless, we can see in Table 3.10 that the most distorted chains in the full coverage regime have average dihedral angle at minimum of 132° (monodentate PPA on bayerite). Although this is still a configuration between the fully staggered (all-trans) and the eclipsed conformations shown in Figure 3.12 (c), we note that single dihedral angles of the methylene groups in the alkyl chains can have smaller values, cf. Figure 3.12 (b). Altogether, the rotation-energy barriers are known to be quite small for alkyl chains. As a consequence, the methylene units are supposed to be capable of rotating at room temperature. Within SAMs, these rotations are likely inhibited by the lateral interactions, but we expect that the alkyl chains still have some mobility as it was also pointed by Love et al. [141].
3.4 Adsorption of phosphonic acid on titanium oxide surfaces

3.4.1 Description of the bulk structures

Rutile and anatase are the most important crystallographic structures of TiO$_2$ under ambient conditions [142]. In the bulk structures, each Ti atom is coordinated to six neighboring O atoms that are located at the vertices of an octahedron. The two axial Ti–O bonds of the octahedron are slightly longer than the four equatorial Ti–O bonds. Each O atom is surrounded by three Ti atoms lying in a plane at the corners of an isosceles triangle. The two phases, anatase and rutile, differ in the connection pattern of the Ti–O octahedra. Also, the octahedra in anatase are significantly more distorted than in rutile.

The two tetragonal unit cells of bulk anatase and rutile are illustrated in Figure 3.13. They are determined by the two lattice parameters $a$ and $c$ and by the internal parameters $d^\text{ax}$ and $d^\text{eq}$, which correspond to the axial and equatorial Ti–O bond lengths within the octahedron, respectively. The unit cell of rutile contains two TiO$_2$ units, whereas the unit cell of anatase contains four TiO$_2$ units. We found that the deviations in the final atomic positions and lattice parameters of the optimised bulk structures are all within 1.5 % for rutile and 2.5 % for anatase compared with experimental values, cf. Table 3.11. Moreover, our results are in good agreement with those results obtained by other investigations using full ab initio Hartree-Fock or DFT methods [143, 144].
Table 3.11: Structural parameters [Å] of bulk rutile and anatase: Comparison of SCC-DFTB (this work) with other experimental and theoretical results. The latter are obtained by *ab initio* Hartree Fock calculations (HF) and by density-functional theory calculations (DFT). Within DFT the different exchange-correlation functionals LDA, PBE and BLYP are used. The results of two hybrid HF-DFT functionals, B3LYP and PBE0, are also included. The difference between calculated and experimental determined values are given as a percentage in parentheses.

<table>
<thead>
<tr>
<th>Method</th>
<th>Method</th>
<th>a</th>
<th>c</th>
<th>(d^{\text{ax}})</th>
<th>(d^{\text{eq}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. [145]</td>
<td>Exp. [145]</td>
<td>4.587</td>
<td>2.954</td>
<td>1.976</td>
<td>1.946</td>
</tr>
<tr>
<td>This work</td>
<td>This work</td>
<td>4.611 (+0.5%)</td>
<td>2.970 (+0.5%)</td>
<td>1.967 (-0.5%)</td>
<td>1.969 (+1.2%)</td>
</tr>
<tr>
<td>LDA [143]</td>
<td>LDA [143]</td>
<td>4.546 (-0.9%)</td>
<td>2.925 (-1.0%)</td>
<td>1.952 (-1.2%)</td>
<td>-</td>
</tr>
<tr>
<td>PBE [143]</td>
<td>PBE [143]</td>
<td>4.634 (+1.0%)</td>
<td>2.963 (+0.3%)</td>
<td>1.999 (+1.2%)</td>
<td>-</td>
</tr>
<tr>
<td>BLYP [143]</td>
<td>BLYP [143]</td>
<td>4.679 (+2.0%)</td>
<td>2.985 (+1.0%)</td>
<td>2.021 (+2.3%)</td>
<td>-</td>
</tr>
<tr>
<td>HF [144]</td>
<td>HF [144]</td>
<td>4.575 (-0.3%)</td>
<td>2.987 (+1.1%)</td>
<td>1.985 (+0.5%)</td>
<td>1.947 (+0.1%)</td>
</tr>
<tr>
<td>B3LYP [144]</td>
<td>B3LYP [144]</td>
<td>4.639 (+1.1%)</td>
<td>2.974 (+0.7%)</td>
<td>2.013 (+1.9%)</td>
<td>1.954 (+0.4%)</td>
</tr>
<tr>
<td>PBE0 [144]</td>
<td>PBE0 [144]</td>
<td>4.591 (+0.1%)</td>
<td>2.955 (+0.0%)</td>
<td>1.989 (+0.7%)</td>
<td>1.940 (-0.3%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rutile</th>
<th>Anatase</th>
<th>3.782</th>
<th>9.502</th>
<th>1.979</th>
<th>1.932</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. [145]</td>
<td>Exp. [145]</td>
<td>3.809 (+0.7%)</td>
<td>9.735 (+2.5%)</td>
<td>1.995 (+0.8%)</td>
<td>1.955 (+1.2%)</td>
</tr>
<tr>
<td>This work</td>
<td>This work</td>
<td>3.735 (-1.2%)</td>
<td>9.534 (+0.3%)</td>
<td>1.973 (-0.3%)</td>
<td>-</td>
</tr>
<tr>
<td>LDA [143]</td>
<td>LDA [143]</td>
<td>3.786 (+1.0%)</td>
<td>9.737 (+2.5%)</td>
<td>2.002 (+1.2%)</td>
<td>-</td>
</tr>
<tr>
<td>PBE [143]</td>
<td>PBE [143]</td>
<td>3.828 (+1.2%)</td>
<td>9.781 (+2.9%)</td>
<td>2.014 (+1.8%)</td>
<td>-</td>
</tr>
<tr>
<td>BLYP [143]</td>
<td>BLYP [143]</td>
<td>3.771 (-0.3%)</td>
<td>9.688 (+2.0%)</td>
<td>1.976 (-0.2%)</td>
<td>1.937 (+0.3%)</td>
</tr>
<tr>
<td>HF [144]</td>
<td>HF [144]</td>
<td>3.783 (+0.0%)</td>
<td>9.805 (+3.2%)</td>
<td>2.000 (+1.1%)</td>
<td>1.945 (+0.7%)</td>
</tr>
<tr>
<td>B3LYP [144]</td>
<td>B3LYP [144]</td>
<td>3.758 (-0.6%)</td>
<td>9.704 (+2.1%)</td>
<td>1.980 (+0.1%)</td>
<td>1.931 (-0.1%)</td>
</tr>
<tr>
<td>PBE0 [144]</td>
<td>PBE0 [144]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
3.4 Adsorption of phosphonic acid on titanium oxide surfaces

3.4.2 Description of the surface structures

Rutile (110)

Rutile is the thermodynamically most stable TiO$_2$ phase. Its (110) surface has the lowest surface energy [142, 146], and it is the most studied single crystal TiO$_2$ surface [147]. The unit cell of the TiO$_2$ rutile (110) surface model used in the present work is shown in Figure 3.14 (a). It is constructed from a 2 x 2 orthogonal surface slab with dimensions $a = 5.939$ Å and $b = 13.042$ Å in the [001] (x-axis) and [1T0] (y-axis) directions, respectively. The slab thickness is about 16 Å, corresponding to five layers of Ti$_2$O$_4$ units along the direction perpendicular to the surface (z-axis). The surface unit cell contains 40 TiO$_2$ units and is periodically repeated in x- and y-directions.

The rutile (110) surface remained stable during the geometry optimisation. Our relaxed (110) surface [Figure 3.14 (a)], contains two different kinds of Ti atoms. There are rows of six-fold-coordinated Ti atoms, Ti-6c(1), and five-fold-coordinated Ti atoms, Ti-5c(2), along the [001] direction, whereby the latter have one dangling bond perpendicular to the surface. Two kinds of O atoms are present as well. Rows of three-fold-coordinated O atoms, O-3c(4), connect the chains of Ti-6c(1) and Ti-5c(2) atoms. The two-fold-coordinated, bridging O atoms, O-2c(3), connect surface Ti-6c(1) atoms above the surface plane.

In Table 3.12, we list our calculated displacements of the atomic positions in the first two Ti$_2$O$_4$ layers with respect to the bulk system and compare them with other experimental [148] and theoretical [146, 149, 150] results. The labelling of the atoms follows that in Figure 3.14 (a). We note that the main displacements occur in the first Ti$_2$O$_4$ layer perpendicular to the surface, while those in the second Ti$_2$O$_4$ layer are much smaller. In agreement with the experiment, we found that the Ti-6c(1) atoms and the neighboring O-3c(4) atoms move outwards, whereas the Ti-5c(2) atoms move inwards. Bridging O-2c(3) atoms are found to contract in experiment, while they move outwards in our calculation. However, also other theoretical studies found a too small contraction of these O atoms [146, 149, 150].

Anatase (101)

The (101) face is the thermodynamically most stable surface of anatase [142, 151]. The optimised orthogonal 2 x 1 (101) surface unit cell is shown in Figure 3.14 (b). It contains 24 TiO$_2$ formula units, and its dimensions are $a = 7.619$ Å and $b = 10.453$ Å in [010] (x-axis) and [101] (y-axis) direction, respectively. The slab thickness is about 9 Å, corresponding to 18 atomic layers with different coordinate values in the direction perpendicular to the surface (z-axis). The surface unit cell contains 24 TiO$_2$ units and is periodically repeated in x- and y-directions.

The anatase (101) surface is very corrugated with a characteristic sawtooth profile perpendicular to the [010] direction, see Figure 3.14 (b). O–Ti–O double chains are connected by rows of two-fold-coordinated bridging O atoms, O-2c(1), along the [010] direction. Half
Figure 3.14: TiO$_2$ surface models: a) Rutile (110) b) Anatase (101). Adsorbates: c) Phosphonic acid, HPO(OH)$_2$, PA d) Formic acid, HCOOH, FA. Grey, red, white, yellow and green spheres are Ti, O, H, P and C atoms, respectively.

Table 3.12: TiO$_2$ rutile (110) surface model: Calculated displacements [Å], normal to the surface, using SCC-DFTB (this work) in comparison with experiment (Exp.) and other theoretical models including the different exchange-correlation functionals LDA, PBE and GGA-II. T-I: FP-LAPW-PBE (full-potential linear augmented plane-wave), T-II: LCAO-PBE (linear combination of atomic orbitals), T-III: PW-PP-LDA (plane-wave pseudo-potential) and T-IV: PW-PP-GGA-II. The atoms are labelled according to Figure 3.14 (a).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6c(1)</td>
<td>0.27</td>
<td>0.12 ± 0.05</td>
<td>0.08</td>
<td>0.23</td>
<td>0.13</td>
<td>0.23</td>
</tr>
<tr>
<td>Ti-5c(2)</td>
<td>−0.11</td>
<td>−0.16 ± 0.05</td>
<td>−0.23</td>
<td>−0.17</td>
<td>−0.17</td>
<td>−0.11</td>
</tr>
<tr>
<td>O-2c(3)</td>
<td>0.10</td>
<td>−0.27 ± 0.08</td>
<td>−0.16</td>
<td>−0.02</td>
<td>−0.06</td>
<td>−0.02</td>
</tr>
<tr>
<td>O-3c(4)</td>
<td>0.22</td>
<td>0.05 ± 0.05</td>
<td>0.09</td>
<td>0.03</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td>O-3c(5)</td>
<td>0.07</td>
<td>0.03 ± 0.05</td>
<td>−0.09</td>
<td>0.02</td>
<td>−0.07</td>
<td>0.03</td>
</tr>
<tr>
<td>Ti-6c(6)</td>
<td>0.12</td>
<td>0.07 ± 0.04</td>
<td>0.07</td>
<td>0.14</td>
<td>0.06</td>
<td>0.12</td>
</tr>
<tr>
<td>Ti-6c(7)</td>
<td>−0.05</td>
<td>−0.09 ± 0.04</td>
<td>−0.13</td>
<td>−0.10</td>
<td>−0.08</td>
<td>−0.06</td>
</tr>
<tr>
<td>O-3c(8)</td>
<td>0.01</td>
<td>0.00 ± 0.08</td>
<td>−0.05</td>
<td>0.00</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>O-3c(9)</td>
<td>0.04</td>
<td>0.02 ± 0.06</td>
<td>−0.04</td>
<td>0.03</td>
<td>−0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>O-3c(10)</td>
<td>0.01</td>
<td>−0.09 ± 0.08</td>
<td>−0.04</td>
<td>−0.01</td>
<td>−0.01</td>
<td>0.03</td>
</tr>
</tbody>
</table>
3.4 Adsorption of phosphonic acid on titanium oxide surfaces

Table 3.13: TiO$_2$ anatase (101) surface model: Calculated displacements [Å], normal to the surface, using SCC-DFTB (this work) and other theoretical models like empirical inter atomic potentials (EIP) or plane-wave pseudo potentials together with the local density approximation (LDA) or the generalised gradient approximation (GGA). The atoms are labelled according to Figure 3.14 (b).

<table>
<thead>
<tr>
<th>Labels</th>
<th>This work</th>
<th>LDA [143]</th>
<th>GGA [151]</th>
<th>EIP [152]</th>
<th>GGA [153]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-2c(1)</td>
<td>−0.04</td>
<td>−0.02</td>
<td>−0.06</td>
<td>−0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>Ti-5c(2)</td>
<td>−0.17</td>
<td>−0.18</td>
<td>−0.17</td>
<td>−0.02</td>
<td>−0.12</td>
</tr>
<tr>
<td>O-3c(3)</td>
<td>0.20</td>
<td>0.15</td>
<td>0.21</td>
<td>0.15</td>
<td>0.28</td>
</tr>
<tr>
<td>O-3c(4)</td>
<td>0.03</td>
<td>0.06</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Ti-6c(5)</td>
<td>0.13</td>
<td>0.20</td>
<td>0.11</td>
<td>0.03</td>
<td>−</td>
</tr>
<tr>
<td>O-3c(6)</td>
<td>−0.15</td>
<td>−0.07</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>O-3c(7)</td>
<td>0.07</td>
<td>0.04</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Ti-6c(8)</td>
<td>−0.10</td>
<td>−0.14</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>O-3c(9)</td>
<td>−0.06</td>
<td>−0.04</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
</tbody>
</table>

five-fold- and half six-fold-coordinated Ti atoms are present, Ti-5c(2) and Ti-6c(5), respectively, as well as three-fold-coordinated O atoms, O-3c(3,4).

In Table 3.13, we summarise our calculated atomic displacements of the anatase (101) surface model and compare them with other theoretical investigations. The labelling of the atoms follows that in Figure 3.14 (b). We found that upon relaxation the O-3c(3,4) and Ti-6c(5) atoms move outwards, whereas the O-2c(1) atoms and the Ti-5c(2) atoms move inwards. Thus, the surface exhibits a slightly buckled geometry and reproduces previous calculations using other theoretical methods [143, 151–153].

3.4.3 Adsorption reaction

The chemically active sites on the surfaces of anatase (101) and rutile (110) are the unsaturated acidic cations, Ti-5c atoms, and the basic anions, O-2c atoms, see Figure 3.14 (a) and (b) [154, 155]. The bonding of acidic molecules to these active sites can be classified in two ways. The first one counts the number of covalent bonds between the adsorbate and the active Ti-5c atoms of the substrate. The binding can be either monodentate, bidentate or tridentate. The second possibility focusses on the chemistry of the adsorbate in the adsorption process. The adsorption can be molecular (non-dissociative) and/or dissociative. The acid is adsorbed on the surface as a complete, i.e. non-dissociated molecule, in the molecular process. This is only possible for the monodentate adsorption, where in the present case the O atom of the water molecule or the double-bound phosphoryl respective carbonyl oxygen is coordinated to a surface Ti-5c atom. In the dissociative adsorption process, the water molecule or the formic respective phosphonic acid dissociates into acidic anions (OH$^-$, HCOO$^-$, H$_2$PO$_5^-$, HPO$_4^{2-}$) and one or two surface-bound protons. The acidic anions are adsorbed on the surface by bonding of the one, two or three available adsorbate
O atoms to surface Ti-5c atoms. Thus, in the dissociative process all three binding states – mono-, bi-, and tridentate – are possible.

The adsorption energies, which are reported in the following for the various adsorption models, were calculated from the difference in total energy of the adsorption complex (M@TiO$_2$) and the clean surface slabs and the respective adsorbate molecule in the gas phase (M):

$$E_{\text{ads}} = E_{\text{tot}} [\text{TiO}_2] + n * E_{\text{tot}} [\text{M}] - E_{\text{tot}} [\text{M@TiO}_2]$$ (3.2)

Therein, $n$ is the number of adsorbed molecules on the slab. Hence, according to this definition, a positive value of $E_{\text{ads}}$ indicates stable adsorption.

### 3.4.4 Surface coverage

In our adsorption models, there are two adsorbate molecules on the surfaces corresponding to a 0.5 monolayer coverage in terms of the number of adsorbates per surface Ti-5c atom. The maximum coverage for the monodendate complex is twice that of the bidendate complexes, i.e. a 1 monolayer coverage. However, Ojamäe et al. [156] and Bates et al. [157] found that also for the monodentate binding of formic acid on rutile (110) a coverage of 0.5 is the most favorable with respect to the adsorption energy per adsorbate. Moreover, the 0.5 monolayer coverage corresponds to grafting densities of 2.51 molecules/nm$^2$ and 2.58 molecules/nm$^2$ for anatase (101) and rutile (110), respectively, that are in agreement with those determined experimentally for PA on TiO$_2$ (2.5-4.8 molecules/nm$^2$) [90, 97, 98, 101, 136]. Thus, we chose a 0.5 monolayer coverage for the monodentate as well as for the bidendate complexes.

### 3.4.5 Adsorption of water

To test further the reliability of the surface models and the employed SCC-DFTB method, we investigated the molecular and the dissociative adsorption of water and also formic acid on the surfaces of rutile (110) and anatase (101). These systems are already extensively studied experimentally as well as theoretically.

In case of molecular adsorption of water, the oxygen of the non-dissociated H$_2$O molecule is attached to a Ti-5c surface atom. In case of dissociative adsorption, the OH$^-$ anion remaining from the dissociated H$_2$O is bonded to a Ti-5c atom by its O atom and the proton is covalently bonded to a bridging O-2c atom on the surface. The optimised structures of the molecular and dissociative adsorption complexes of water on the surfaces of rutile (110) and anatase (101) are shown in Figure 3.15. The respective calculated adsorption energies are summarised in Table 3.14. Our results are in good agreement with the experimental ranges and with those results obtained by other theoretical investigations using DFT-based methods. Moreover, we found that molecular adsorption of water on both surfaces is clearly favored in comparison with dissociative adsorption. This was also established by experiment [142, 158–163] and other theoretical studies [151, 164–168].
3.4 Adsorption of phosphonic acid on titanium oxide surfaces

Figure 3.15: Optimised structures of molecular (a-b) and dissociative (c-d) adsorbed water on rutile (110). Optimised structures of molecular (e-f) and dissociative (g-h) adsorbed water on anatase (101). The bond lengths are given in Ångstrom. Dotted lines indicate hydrogen bonds. Colors of the atoms are as in Figure 3.14.

Table 3.14: Calculated adsorption energies [kJ/mol] for molecular (Mol) and dissociative (Diss) adsorption of water on the surface of anatase (101) and rutile (110) in comparison with experiment and other theoretical results using DFT based methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Rutile (110)</th>
<th>Anatase (101)</th>
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<td></td>
<td>Mol</td>
<td>Diss</td>
</tr>
<tr>
<td>This work</td>
<td>83.4</td>
<td>48.5</td>
</tr>
<tr>
<td>Theor.</td>
<td>95.5</td>
<td>87.8</td>
</tr>
<tr>
<td>Theor.</td>
<td>82.1</td>
<td>58.9</td>
</tr>
<tr>
<td>Theor.</td>
<td>77.1</td>
<td>–</td>
</tr>
<tr>
<td>Exp.</td>
<td>59-101</td>
<td>–</td>
</tr>
</tbody>
</table>
3.4.6 Adsorption of formic acid

The most common anchoring molecules in the coupling of functional organic components to TiO₂ surfaces are carboxylic acids. They are especially applied in dye-sensitized solar cells to bind the dyes on nanocrystalline TiO₂ electrodes [170–173], because they are highly efficient in terms of good interfacial electronic coupling [174]. However, they slowly desorb from the semiconductor surface in the presence of water [172, 175, 176]. The problem of the long-term stability might be also ascribed to the photocatalytic activity of anatase to oxidise carboxylic acids in the presence of water and ultraviolet rays [177]. Furthermore, bifunctional long-chain carboxylic acids tend to form undesirable looping structures [81, 178, 179]. To model the adsorption of carboxylic acids on TiO₂ surfaces, we studied the bonding of formic acid on both rutile (110) and anatase (101) surfaces. Moreover, we compare our results to the adsorption of phosphonic acid later in this work, which is the most promising alternative anchoring group that might overcome the problem of the long-term stability.

In case of molecular monodentate adsorption of formic acid on anatase (101) and rutile (110) [Figure 3.16 (a-d,g,h)], the carbonyl oxygen of the formic acid molecule is attached to a surface Ti-5c atom. The OH group is free to form a hydrogen bond to an O-2c surface atom. As the Ti-5c and O-2c atoms are arranged in pairs on the surface of anatase (101), there are two configurations for hydrogen bonding in the monodentate complex possible referring to [180]. We will call the first one “intra-pair”, where the involved cation and anion belong to the same pair, see the adsorption complex $M1-fa-A$ in Figures 3.16 (a) and (b). The second configuration, we will call “inter-pair” one, where the involved ions belong to different pairs, see the adsorption complex $M2-fa-A$ in Figures 3.16 (c) and (d). In the dissociative bridging bidentate adsorption complexes both oxygens of the FA molecule link the adsorbate to the surface [Figure 3.16 (e,f,i,j)]. The FA hydroxyl group is dissociated. The two O atoms bind to two different Ti-5c atoms, while the proton binds covalently to a surface O-2c atom.

Table 3.15: Calculated bond distances [\(\text{Å}\)] of the free HCOOH molecule and of different optimised adsorption complexes of HCOOH at the surface of anatase (101) and rutile (110). The notation of the atoms follows that in Figures 3.14 (d) and 3.16.

<table>
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<th>Rultile (110)</th>
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</thead>
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<td></td>
<td></td>
<td>M1-fa-A</td>
<td>M2-fa-A</td>
</tr>
<tr>
<td>C–H1</td>
<td>1.13</td>
<td>1.14</td>
<td>1.14</td>
</tr>
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<td>C–O1</td>
<td>1.21</td>
<td>1.26</td>
<td>1.26</td>
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<tr>
<td>C–O2</td>
<td>1.43</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>O2–H2</td>
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<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>O1–Ti</td>
<td>–</td>
<td>2.24</td>
<td>2.24</td>
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<tr>
<td>O2–Ti</td>
<td>–</td>
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<tr>
<td>H2–O</td>
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<td>1.29</td>
<td>1.29</td>
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</tbody>
</table>
3.4 Adsorption of phosphonic acid on titanium oxide surfaces

Figure 3.16: Optimised structures of molecular monodentate (a-d) and dissociative bidentate (e-f) adsorbed HCOOH on anatase (101). Optimised structures of molecular monodentate (g-h) and dissociative bidentate (i-j) adsorbed HCOOH on rutile (110). Colors of the atoms are as in Figure 3.14.

Table 3.16: Adsorption energies [kJ/mol] of the optimised different adsorption complexes of HCOOH at the surface of anatase (101) and rutile (110) in comparison with other theoretical results using Hartree-Fock (HF), DFT or HF-DFT Hybrid (B3LYP) methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Anatase (101)</th>
<th>Rutile (110)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M1-fa-A</td>
<td>M2-fa-A</td>
</tr>
<tr>
<td>This work</td>
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<td>118.5</td>
</tr>
<tr>
<td>B3LYP</td>
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<tr>
<td>DFT-GGA</td>
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<td>88.8</td>
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<tr>
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<td>91.8</td>
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<td>DFT-GGA</td>
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<td>87.8</td>
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<tr>
<td>DFT-GGA</td>
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<td>96.5</td>
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<tr>
<td>HF</td>
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</table>
The geometric details and calculated adsorption energies of the optimised adsorption complexes are summarised in Tables 3.15 and 3.16. All adsorption complexes remained stable during simulated annealing. In agreement with other experimental [156, 186–190] and theoretical results [156, 157, 181, 184, 185, 190], we found that FA prefers to bind in a bidentate fashion on the surface of rutile (110). The dissociative bidentate adsorption complex is more stable than the molecular monodentate one by 78.3 kJ/mol. Moreover, our adsorption energies are in good agreement with adsorption energies calculated by other theoretical investigations using DFT-based methods, cf. Table 3.16. However, Nilsing et al. [109] found that the monodentate adsorption is the preferred binding state on rutile (110). They assume that this is due to their choice of a too small slab size. Indeed, it was stated in Refs. [109, 156, 157] that the slab thickness influences the adsorption energies significantly and, hence, the finding of the preferred binding mode. Ojamäe et al. [156] found that the binding state depends on the slab thickness. According to their results, the bidentate binding mode is the most stable one on a six-layer slab, whereas the monodentate binding is preferred on a two-layer slab of rutile (110). Our model corresponds to a five-layer slab [cf. Figure 3.14 (a)] and is, thus, sufficient to determine the most favored binding mode correctly.

For the adsorption of FA on anatase (101), we found that the “intra-pair” arrangement (M1-fa-A) is only slightly more stable than the “inter-pair” arrangement (M2-fa-A) by 6.2 kJ/mol, but the bridging bidentate adsorption complex is the preferred adsorption mode. Comparing the adsorption energies it is more stable than the monodentate complex M1-fa-A by 57.8 kJ/mol. This is contrary to the results of Nilsing et al. [108] and Vittadini et al. [180]. They have calculated the molecular monodentate adsorption complex to be the most favored one, cf. Table 3.16. However, in agreement with our results, Raghu- nath et al. [182] found that the dissociative bidentate adsorption is the most favored binding mode of FA on anatase (101). Recently, Szieberth et al. [191] found either the monodentate or the bidentate complex to be the most stable depending on the choice of the basis set and the DFT functionals. Experimentally, both molecular and dissociated configurations of FA were observed on TiO$_2$ samples exposing mostly anatase (101) surfaces [192–194]. Moreover, the bridging bidentate coordination of the carboxylic group on nanostructured TiO$_2$ was found for several photosensitizing ruthenium dyes [195–197]. As outlined, the exact binding state of FA on anatase (101) is still debated.

As we note from Table 3.15, the Ti–O bond lengths of all complexes are very similar. The final structure of the FA molecule in the bidentate and to some extend even in the monodentate complexes is similar to that of the resonance stabilised HCOO$^-$ moiety, that has C–O bond lengths of 1.28 Å. Moreover, in the optimised structure of the monodentate complexes, the H atom of the FA is localised between two O atoms, belonging to the surface and to the acid. Thus, the O–H bond lengths are very similar in the three monodentate complexes, but they are significantly prolonged by about 25% compared with the O–H bonds of the free acid or surface OH groups. These similarities in the stable mono- and bidentate adsorption complexes might lead to the assumption that both binding modes are equally likely to be present on the TiO$_2$ surfaces. Also, they might to some extend
explain the experimental finding of both mono- and bidentate binding on anatase (101) [192–194]. However, with respect to the calculated adsorption energies, we conclude that the dissociated bidentate adsorption complex is the most stable one on both anatase (101) and rutile (110) surfaces. Moreover, we will analyse in more detail the electronic properties of the adsorption complexes in subsection 3.4.8. These results will further support our finding of the preference of the bidentate complexes.

3.4.7 Adsorption of phosphonic acid

Monodentate adsorption

Three respective two different complexes can be built as starting structures for molecular monodentate adsorption of phosphonic acid on anatase (101) [Figures 3.17 (a-f)] and rutile (110) [Figures 3.18 (a-d)]. In all cases the phosphoryl oxygen is coordinated to a surface Ti-5c atom. The OH groups of the PA are free to form hydrogen bonds to two surface O-2c surface atoms. The respective optimised monodentate adsorption complexes are illustrated in Figures 3.17 (g-l) and 3.18 (e-h). Their geometrical details and calculated adsorption energies are summarised in Tables 3.17, 3.18 and 3.19.

Only the complex M1-pa-A remained its initial geometry during the optimisation and simulated annealing. This is in contrast to the results of Nilsing et al. [108, 109], in which all complexes are found to be stable. The P–O bond lengths in this complex are comparable with those of a resonance stabilised HPO\textsuperscript{2−} anion, which has P–O bond lengths of 1.57 Å. Similar to the monodentate adsorption complexes of formic acid, the two H atoms of the adsorbate are each located between two O atoms, one belonging to the surface and one to the acid. Also, the O–H bond distances to the surface and to the acid are similar, but are significantly longer by about 25% than in the free PA molecule.

All other monodentate adsorption complexes are not stable and strongly tend to form bidentate configurations during optimisation and simulated annealing. Moreover, we found that their structures are more stable by up to 100 kJ/mol due to the formation of a second P–O–Ti bond. Thus, we conclude that bidentate adsorption on the surface of TiO\textsubscript{2} is more stable than the simple monodentate adsorption.

Bidentate adsorption

In the dissociative bidentate adsorption complexes, two adsorbate oxygens link the adsorbate to the surface. In total four chemically equivalent bidentate structures can be constructed for the anatase (101) surface, cf. Figures 3.19 (a-h). In Figures 3.20 (a-d), we illustrate the two possible dissociative bidentate complexes of PA on rutile (110). It is characteristic for all these bidentate structures that one or both PA hydroxyl groups are dissociated. While two O atoms of the PA bind to two different Ti-5c atoms, the protons covalently bind to surface O-2c atoms. The residual third oxygen or undissociated hydroxyl group forms a hydrogen bond to a surface OH group or a surface O-2c atom, respectively.
Figure 3.17: Monodentate adsorption of HPO(OH)$_2$ on the anatase (101) surface: Starting structures (a-f) and geometry-optimised structures (g-l). In the starting geometry of the adsorption complexes $M1$-pa-$A$ and $M2$-pa-$A$, the PA molecule is bonded to three and in case of $M3$-pa-$A$ to two different pairs of Ti-5c and O-2c. Dotted lines indicate hydrogen bonds. Colors of the atoms are as in Figure 3.14.
Figure 3.18: Monodentate adsorption of HPO(OH)$_2$ on the rutile (110) surface: Starting structures (a-d) and geometry-optimised structures (e-h). The two OH groups of the PA bind to two surface O-2c atoms from the same row and from different rows in case of the starting structures $M1$-$pa$-$R$ and $M2$-$pa$-$R$, respectively. Dotted lines indicate hydrogen bonds. Colors of the atoms are as in Figure 3.14.

Table 3.17: Calculated bond distances [Å] of the free HPO(OH)$_2$ molecule (cf. Section 3.3) and of different optimised adsorption complexes of HPO(OH)$_2$ at the surface of anatase (101). The notation of the atoms follows that in Figures 3.14 (c), 3.17 and 3.19.

<table>
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<td>1.42</td>
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<td>1.51</td>
<td>1.47</td>
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<td>–</td>
</tr>
<tr>
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<td>–</td>
<td>1.27</td>
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<td>–</td>
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<td>1.89</td>
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<tr>
<td>O2–Ti</td>
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<td>–</td>
<td>1.98</td>
<td>–</td>
<td>1.97</td>
<td>1.98</td>
<td>1.89</td>
<td>1.89</td>
</tr>
<tr>
<td>O1–Ti</td>
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<td>1.94</td>
<td>–</td>
<td>2.22</td>
<td>2.23</td>
<td>2.24</td>
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<td>–</td>
</tr>
<tr>
<td>H3–O</td>
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<td>1.30</td>
<td>–</td>
<td>–</td>
<td>1.99</td>
<td>–</td>
<td>0.99</td>
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<tr>
<td>H2–O</td>
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<td>1.29</td>
<td>0.99</td>
<td>1.27</td>
<td>0.99</td>
<td>0.99</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Table 3.18: Calculated bond distances [Å] of the free HPO(OH)$_2$ molecule (cf. Section 3.3) and of different adsorption complexes of HPO(OH)$_2$ at the surface of rutile (110). The notation of the atoms follows that in Figures 3.14 (c), 3.18 and 3.20.

<table>
<thead>
<tr>
<th>Labels</th>
<th>PA</th>
<th>Rutile (110)</th>
</tr>
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<td></td>
<td></td>
<td>M1-pa-R</td>
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<td>P-H1</td>
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<td>1.42</td>
</tr>
<tr>
<td>P-O3</td>
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<td>1.86</td>
</tr>
<tr>
<td>P-O2</td>
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<td>P-O1</td>
<td>1.47</td>
<td>1.47</td>
</tr>
<tr>
<td>O3–H3</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>O2–H2</td>
<td>0.98</td>
<td>–</td>
</tr>
<tr>
<td>O1–H3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>O1–H2</td>
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<tr>
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<td>–</td>
</tr>
<tr>
<td>H3–O</td>
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</tr>
<tr>
<td>H2–O</td>
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</tr>
</tbody>
</table>

Table 3.19: Adsorption energies [kJ/mol] of the optimised different adsorption complexes of HPO(OH)$_2$ at the surface of anatase (101) and rutile (110).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Anatase (101)</th>
<th>Rutile (110)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Labels</td>
<td>$E_{\text{ads}}$</td>
</tr>
<tr>
<td>monodentate</td>
<td>M1-pa-A</td>
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<tr>
<td></td>
<td>M2-pa-A</td>
<td>257.1</td>
</tr>
<tr>
<td></td>
<td>M3-pa-A</td>
<td>127.7</td>
</tr>
<tr>
<td>bidentate</td>
<td>B1-pa-A</td>
<td>260.5</td>
</tr>
<tr>
<td></td>
<td>B2-pa-A</td>
<td>260.0</td>
</tr>
<tr>
<td></td>
<td>B3-pa-A</td>
<td>273.0</td>
</tr>
<tr>
<td></td>
<td>B4-pa-A</td>
<td>276.8</td>
</tr>
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</table>
The bidentate complexes retained their initial adsorption features during optimisation and also simulated annealing. (Only the initial hydrogen bonds of the structures B2-pa-A and B3-pa-A were not stable). The final optimised structures are shown in Figures 3.19 (i-p) and 3.20 (e-h). Our calculated bond lengths and adsorption energies are summarised in Tables 3.17, 3.18 and 3.19. By comparing the adsorption energies, we found that the structures B4-pa-A and B2-pa-R are the preferred bidentate adsorption complexes. The adsorbed PA molecule is fully dissociated in both optimised structures. The phosphoryl oxygen is not involved in the surface bonding, but forms hydrogen bonds to surface hydroxyl groups. Indeed, the complex B4-pa-A is more stable than the adsorption complex B3-pa-A by 4 kJ/mol due to this hydrogen bonding. However, the gain in energy due to the dissociation of the second P–OH groups is four times larger compared with model B1-pa-A. The stabilisation due to dissociation in case of rutile is 26 kJ/mol, if one compares the adsorption energy of B1-pa-R and B2-pa-R. Therefore, we conclude that the complete dissociation of the PA and the resultant formation of two surface OH groups is energetically more important for the surface bonding than the (additional) formation of hydrogen bonds.

One might argue that we do not account for the energetic barrier of the OH dissociation and the proton transfer to the surface O-2c atoms in this investigation. However, the formation of dissociative bidentate structures, i.e. the dissociation of the first P–OH group as well as the formation of the P–O–Ti bond and the surface hydroxyl group, happened spontaneously during optimisation of the monodentate adsorption complexes. The dissociation of the second P–OH group is not barrier-free, since it did not take place spontaneously during optimisation of, e.g., B1-pa-A and B1-pa-R on anatase (101) respective rutile (110), but the total gain in energy is less than 30 kJ/mol compared with the most stable structures, as discussed above.

Furthermore, we found that all bidentate adsorption complexes, in which at least one P–OH group is dissociated, have quite similar adsorption energies. Also, the geometries of the bidentate structures present on the surface of rutile (110) are comparable with the corresponding adsorption structures on anatase (101), e.g. B1-pa-A and B1-pa-R, B4-pa-A and B2-pa-R. Hence, we conclude that the different bidentate adsorption complexes are equally likely to be present on the TiO$_2$ surfaces.

**Tridentate adsorption**

A tridentate adsorption on clean TiO$_2$ can be realised only via a fully deprotonated PA anion binding to three different surface Ti-5c atoms. However, we found no stable product structure of this adsorption type for the clean anatase (101) surface and the clean rutile (110) surface. On both surfaces, the rows of Ti-5c atoms are separated by rows of protruding O-2c atoms. Thus, the distance to the third coordinatively unsaturated Ti is too large and the formation of a third Ti–O–P bond is sterically hindered. The same result was reported by Nilsing et al. [108, 109], recently.
3 Adsorption of phosphonic acid on metal oxide surfaces

Figure 3.19: Bidentate adsorption of HPO(OH)$_2$ on the anatase (101) surface: Starting structures (a-h) and geometry-optimised structures (i-p). In the starting structures of B1-pa-A and B2-pa-A, the phosphoryl O atom and one O atom of the dissociated OH groups of the phosphonic acid bind to two Ti-5c atoms. The non-dissociated OH group of the acid forms a hydrogen bond to a O-2c atom that belongs to a different or to the same pair of Ti-5c and O-2c in case of B1-pa-A and B2-pa-A, respectively. In the starting geometries of B3-pa-A and B4-pa-A, the two OH groups of the PA molecule are dissociated and the two dissociated O atoms bind to two surface Ti-5c atoms. The double-bound oxygen of the adsorbate is linked by hydrogen bonds to one or two surface OH groups that belong to the same or to a different pair of Ti-5c and O-2c in case of B4-pa-A and B3-pa-A, respectively. Dotted lines indicate hydrogen bonds. Colors of the atoms are as in Figure 3.14.
3.4 Adsorption of phosphonic acid on titanium oxide surfaces

Figure 3.20: Bidentate adsorption of HPO(OH)$_2$ on the rutile (110) surface: Starting structures (a-d) and geometry-optimised structures (e-h). In the starting structures of B1-pa-R, the phosphoryl O atom and one O atom of the dissociated OH groups of the PA bind to two Ti-5c atoms. The non-dissociated OH group of the acid forms a hydrogen bond to a O-2c atom. In the starting geometry of B2-pa-R, the two OH groups of the PA molecule are dissociated and the two dissociated O atoms bind to two surface Ti-5c atoms. The double-bound oxygen of the adsorbate is linked by hydrogen bonds to two surface OH groups. Dotted lines indicate hydrogen bonds. Colors of the atoms are as in Figure 3.14.
Comparison to other theoretical and experimental results

According to our SCC-DFTB calculations, the over-all most stable adsorption complexes are the bidentate structures $B4$-$pa$-$A$ and $B2$-$pa$-$R$ on the surface of anatase (101) and rutile (110), respectively. This is contrary to results of Nilssing et al. [108, 109], who calculated a molecular monodentate adsorption of PA to be the most stable structure on anatase (101) and rutile (110). However, in the present work we also investigate adsorption complexes involving fully deprotonated PA molecules, which have not been considered in their study [108, 109] or in many other theoretical works [108, 109, 198, 199], yet. In fact, we found that these are the most stable ones. Furthermore, we use larger surface models and add the adsorbate on both side of the slabs to minimise artificial dipoles. Another difference is the surface coverage that was 0.25 in the study of Nilssing et al. [108, 109] and that is 0.5 in the present work. Despite the theoretical method and applied basis set, the surface coverage and especially the slab thickness has influence on the preference of either monodentate (molecular) or bidentate (dissociative) adsorption, as we already discussed in Sections 3.4.5 and 3.4.6. Recently, Raghunath et al. [199] intensively studied the adsorption and decomposition pathways of PA on TiO$_2$ anatase (101) and rutile (110) surfaces. They found the preference of a monodentate adsorption mode for the anatase surface and a bidentate adsorption mode for the rutile surface. Furthermore, the adsorption of nucleotide cytidine monophosphonate on rutile (110) was investigated using the SCC-DFTB method [198]. Again, in agreement with our results, the bidentate binding state is clearly favored having an adsorption energy of 550 kJ/mol.

Our results agree with the experimental finding of the presence of bidentate linked PA on TiO$_2$ [17, 98, 101, 103] and the importance of hydrogen bond interactions for the surface attachment [102, 103]. On the basis of NMR spectroscopy, tridentate bound phosphonic acids are proposed to be present on TiO$_2$ surfaces, too [17, 98, 100, 101, 103]. In contrast to this, we found in agreement with hybrid HF-DFT calculations [108, 109] that the tridentate adsorption complexes are not stable on both clean anatase (101) and rutile (110) surfaces due to the geometrical mismatch of the surface structures to form a third Ti–O–P bond. However, most of the investigated stable mono- and bidentate adsorption complexes show three bonds in the sense that the remaining P=O or P–OH group forms a hydrogen bond to the surface. In addition, there is a stable monodentate adsorption complex $MI$-$pa$-$A$ [Figures 3.17 (g-h)], in which the PA is adsorbed corresponding to a symmetric HPO$_3$$^2$ group, as it is usually proposed for the tridentate bonding. Furthermore, on natural TiO$_2$ surfaces there are always O-vacancy defects present in the rows of bridging twofold coordinated oxygen atoms [142]. Under ambient conditions, water molecules dissociate at these sites into an OH group, which fills the vacancy, and a proton, which binds to another bridging O-2c site [147, 163]. These surface OH groups might react with the P–OH groups via an acid-basic condensation mechanism similar to those reported for PA on hydroxylated Al$_2$O$_3$ surfaces, cf. Section 3.3. This extends the possibilities for mono-, bi- and tridentate adsorption structures enormously, and thus, even tridentate adsorption might be stable.
From the present results, we conclude that the discrepancy in the experimental finding of the preferred binding state of PA on TiO\textsubscript{2} can be attributed to the fact that there are several bidentate adsorption complexes, which have different chemical and structural properties, but similar adsorption energies, and which are, thus, equally likely to be found on TiO\textsubscript{2} surfaces.

**Comparison with the adsorption of formic acid**

The preferred adsorption modes of both formic and phosphonic acid on rutile (110) and anatase (101) are dissociative bridging bidentate complexes. A comparison between the calculated adsorption energies (cf. Tables 3.16 and 3.19) reveals that the binding of phosphonic acid to TiO\textsubscript{2} is stronger than that of formic acid. This is in good agreement with other experimental [99, 103, 200, 201] and theoretical [108, 109] results. Particularly, we found that the adsorption of phosphonic acid is by 94 kJ/mol and 61 kJ/mol more stable than the adsorption of formic acid on the surface of anatase (101) and rutile (110), respectively.

The Ti–O bond lengths of the the most stable bidentate complexes of phosphonic acid are about 0.3 Å shorter than in the most stable formic acid adsorption complexes. This is an additional indication for the formation of stronger and more stable bonds in case of phosphonic acid. Also, we found that the O–O distance in the adsorbed phosphonic acid group matches better to the distance between the fivefold coordinated Ti atoms on the surface (rutile: 2.98 Å, anatase: 3.76 Å) than that in the adsorbed formic acid. However, the adsorbate O–O and surface Ti–Ti distances in all bidentate complexes coincide well with the O–O distances in the free resonance stabilised anions (HCOO\textsuperscript{−}, HPO\textsubscript{2}\textsuperscript{3−}) and with the Ti–Ti distance in the clean anatase (3.81 Å) and rutile (2.97 Å) surfaces, respectively, cf. Tables 3.18, 3.17 and 3.15. This gives further reason that bidentate adsorption is favored over monodentate adsorption for both adsorbate acids on both surfaces.

**3.4.8 Electronic properties of the most stable adsorption complexes**

In the following, we discuss the electronic properties of the most stable adsorption complexes of formic acid and phosphonic acid on the TiO\textsubscript{2} surfaces. At first, we focus on the Mulliken charge distribution in the adsorption complexes in order to access the electronic origin of the stability trends and the related geometry features. The net charges of selected atoms in the adsorption complexes are listed in Table 3.20. They are compared with the charges of the corresponding atoms in the clean surfaces and free acids.

From this comparison, we can draw a series of conclusions: (i) The Ti-5c atoms of the surface, that are bonded to the adsorbates, are more positively charged than those of the clean surface. (ii) This trend is more pronounced for the anatase surface than for the rutile surface, indicating that the higher adsorbate binding strength of anatase is of electronic origin. In more detail, the Ti-5c atoms get six-fold coordinated upon adsorbate bonding and, thus, saturated. They approach the charges of the other Ti-6c atoms in the slab. Likewise,
the O-2c atoms get three-fold coordinated upon bonding of the protons of the acids. They are more negatively charged due to this saturation than the O-2c atoms of the free surfaces. However, they do not resemble the charges of the O-3c atoms in the slab, since the O-2c atoms are three-fold coordinated not only to Ti atoms but also to an H atom. The charges of the O-3c atoms in the slab approach those of the respective bulk O atoms. This indicates that the organic layer effectively causes the abrupt coordination change at the top of the clean surface. Hence, the O-3c atoms experience a chemical environment upon adsorption of the acids, which is similar to the bulk situation. (iii) The described effects are more developed in the bidentate complexes, where all surface Ti-5c atoms become six-fold coordinated and equally charged due to adsorbate bonding. (iv) The changes with respect to the pristine surface are more pronounced in the adsorption complexes involving phosphonic acid, in which additionally all O-2c atoms are saturated and equally charged by bonding of adsorbate H atoms. Altogether, we conclude that the analysis of the Mulliken charges corroborates the preference of the bidentate complexes on the investigated surfaces and the formation of more stable complexes in case of phosphonic acid adsorption.

Next, we analyse the electronic structure of the most stable adsorption complexes to evaluate the influence of the anchoring group on the electronic properties of the system. The calculated densities of states (DOS) for the adsorption complexes on anatase (101) and rutile (110) are depicted in Figures 3.21 and 3.22, respectively. The DOS curves contain a wide valence band region from $-6$ eV to $-1.3$ eV for anatase and from $-7$ eV to $-1$ eV for rutile. They are primarily built up by the O\textit{2}p states from both the O atoms of the surfaces and the adsorbates. The edges of the conduction bands are localised at about $1.3$ eV and $1$ eV above the Fermi level in case of anatase and rutile, respectively. They are mainly composed of the Ti\textit{3}d states of the surface.

In principle, the DOS curves can be seen as a superposition of the DOS of the respective clean surfaces and the molecular orbitals of the free acids. The adsorbates contribute more strongly to the DOS in the valence band region than in the conduction band region. This we further confirm by a visualisation of the highest occupied and lowest unoccupied molecular orbitals of the adsorption complexes, i.e. the HOMO and the LUMO, respectively, see Figure 3.23. Except for complex B-fa-R, there is a strong coupling between the HOMO of the adsorbate and that of the surface. Hence, the HOMO of the adsorption complexes are delocalised over the adsorbate and the substrate slab. In case of B-fa-R, the HOMO is exclusively localised on the rutile slab. We found no orbital coupling of the adsorbate and the surface slab for the LUMO of B-fa-R and B2-pa-R. The LUMO is localised only on the Ti\textit{3}d orbitals of the rutile surface slab. There is a weak coupling between the O\textit{2}p states of the bonding O adsorbate atoms and the Ti\textit{3}d states of the anatase surface for B-fa-A and B4-pa-A. Hence, the LUMO is delocalised to some extent on the adsorbate and the anatase surface.

The calculated band gaps of B-fa-A and B4-pa-A are 3.24 eV and 3.35 eV, respectively. They are slightly smaller than the calculated band gap of clean anatase (101) (3.44 eV). In case of rutile (110), the band gaps of B-fa-R and B2-pa-R are calculated to 3.08 eV and 2.98 eV, respectively. They are larger than the band gap obtained for the clean surface (2.64 eV).
3.4 Adsorption of phosphonic acid on titanium oxide surfaces

Table 3.20: Mulliken net charges of selected atoms in the adsorption complexes as well as in the respective free surfaces and adsorbates. The Mulliken charges of the Ti and O atoms in the bulk structures are 0.899 and \(-0.450\) in case of anatase and 0.928 and \(-0.464\) in case of rutile, respectively. The notation of the atoms follows that in Figures 3.14, 3.16, 3.17, 3.19 and 3.20.

<table>
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<td>0.501</td>
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<td>(-0.078)</td>
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<tr>
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<td>–</td>
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<tr>
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<td>(-0.330)</td>
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<tr>
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<td>(-0.451)</td>
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<td>–</td>
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<tr>
<td>O3</td>
<td>–</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(-0.433)</td>
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<td>–</td>
<td>–</td>
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<tr>
<td>Ti-5c(-O)</td>
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<td>–</td>
<td>–</td>
<td>0.895</td>
<td>0.924</td>
<td>0.917</td>
<td>0.933</td>
<td>0.945</td>
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<td>0.979</td>
<td>0.980</td>
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<tr>
<td>Ti-5c</td>
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<td>–</td>
<td>–</td>
<td>0.806</td>
<td>0.786</td>
<td>0.820</td>
<td>0.868</td>
<td>–</td>
<td>0.950</td>
<td>0.893</td>
<td>–</td>
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<tr>
<td>O-2c(-H)</td>
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<td>–</td>
<td>(-0.473)</td>
<td>(-0.506)</td>
<td>(-0.511)</td>
<td>(-0.490)</td>
<td>(-0.504)</td>
<td>(-0.510)</td>
<td>(-0.460)</td>
<td>(-0.497)</td>
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</tr>
<tr>
<td>O-2c</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(-0.474)</td>
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<td>(-0.465)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(-0.453)</td>
<td>(-0.483)</td>
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<tr>
<td>Ti-6c(5,1)</td>
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<td>–</td>
<td>–</td>
<td>0.904</td>
<td>0.917</td>
<td>0.918</td>
<td>0.911</td>
<td>0.942</td>
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<tr>
<td>O-3c(3,4)</td>
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<td>–</td>
<td>–</td>
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<td>(-0.412)</td>
<td>(-0.426)</td>
<td>(-0.441)</td>
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<td>(-0.429)</td>
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<tr>
<td>O-3c(4,4)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(-0.419)</td>
<td>(-0.423)</td>
<td>(-0.440)</td>
<td>(-0.439)</td>
<td>(-0.449)</td>
<td>(-0.431)</td>
<td>(-0.429)</td>
<td>(-0.427)</td>
<td>(-0.445)</td>
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<tr>
<td>O-3c(6,5)</td>
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<td>–</td>
<td>–</td>
<td>(-0.405)</td>
<td>(-0.422)</td>
<td>(-0.420)</td>
<td>(-0.426)</td>
<td>(-0.431)</td>
<td>(-0.442)</td>
<td>(-0.513)</td>
<td>(-0.486)</td>
<td>(-0.467)</td>
</tr>
</tbody>
</table>
We conclude that the strong orbital coupling at the edges of the valence and the conduction band in case of anatase leads to a decrease in the band gap energy. Also, the band gap energy is slightly smaller for formic acid than for phosphonic acid. This indicates that the orbital coupling is somewhat stronger in case of formic acid. On the other hand, the weak or lacking coupling of the molecular orbitals of the adsorbate and the surface states at the band edges on rutile (110) results in an increase of the band gap energy. The change in the gap energy is somewhat larger in case of formic acid, since there are no contributions of the adsorbate to the HOMO and LUMO levels of the adsorption complex.

However, the electronic properties of a system are not only dependent on the anchoring group. The functional molecule, which is supposed to be bonded via the investigated acidic groups on TiO\textsubscript{2} surfaces, might be designed such that additional occupied molecular bands are introduced in the band gap. On the one hand, those bands can be localised on the functional molecule. On the other hand, they can be delocalised over the entire interface. Therefore, they bear the potential to change the electronic properties at the band edges. For instance, Gemming et al. \cite{198} reported negligible coupling between the \textit{p} states of the aromatic part of a cytidine monophosphate and the Ti\textit{3d} states of the rutile surface. There, the HOMO and LUMO are localised exclusively within the aromatic system of cytosine and the Ti atoms of the rutile slab, respectively. Similar findings were reported for pyridine-4-phosphonic and pyridine-4-carboxylic acid adsorbed on anatase (101) \cite{202}.

\section{3.5 Final conclusions}

In this chapter, we investigated in detail the adsorption of phosphonic acid on aluminium oxide and titanium oxide surfaces using the SCC-DFTB method. We extensively demonstrated the reliability of the SCC-DFTB method for the bulk and surface structures as well as for the adsorption model structures. Thereby, we found a good agreement in many points with experimental and theoretical results.

In case of aluminium oxide, we studied OH-terminated surface models based on \textit{α}-Al\textsubscript{2}O\textsubscript{3} (0001), \textit{β}-Al(OH)\textsubscript{3} (001) and \textit{γ}-AlOOH (010) and examined all possible adsorption sites for binding the phosphonic acid via one, two or three symmetric P–O–Al bonds, i.e. for monodentate, bidentate and tridentate binding of the acidic group, respectively. As the complexes with different binding modes have different stoichiometries in their adsorption reaction, we could not establish the most favorable adsorption mode. However, we determined the preferred adsorption site for each binding mode in all three surface models by comparing the total energies of the complexes.

In general, we found that the preference of an adsorption site is influenced by three factors. (i) For the favored sites the distances to the central subsurface atoms is the largest to keep the repulsive interaction low. (ii) The O atoms of the favored sites are bonded to different Al atoms and are not bonded to the atom below the centers of the sites to reduce strain effects in the adsorption complex. (iii) The O–O distance in the preferred adsorption
Figure 3.21: Density of states (DOS) for the most stable adsorption complex of formic acid (B-fa-A, left) and phosphonic acid (B4-pa-A, right) on anatase (101). The black line denotes the total density of states. The filled areas correspond from top to bottom to the partial DOS curves of surface Ti and O(s) atoms, and adsorbate O(a) and P atoms, respectively. In the first row the density of states for the clean anatase (101) surface and the energies of the molecular orbitals for the free HCOOH (left) and HPO(OH)$_2$ (right) are given for comparison. The Fermi level is shifted to zero.
Figure 3.22: Density of states (DOS) for the most stable adsorption complex of formic acid (B-fa-R, left) and phosphonic acid (B2-pa-R, right) on rutile (110). The black line denotes the total density of states. The filled areas correspond from top to bottom to the partial DOS curves of surface Ti and O(s) atoms, and adsorbate O(a) and P atoms, respectively. In the first row the total density of states (black line) for the clean rutile (110) surface and the energies of the molecular orbitals for the free HCOOH (left) and HPO(OH)$_2$ (right) are given for comparison. The Fermi level is shifted to zero.
3.5 Final conclusions

Figure 3.23: Γ-point orbital-isosurfaces of the HOMO and LUMO of the most stable adsorption complexes of HPO(OH)$_2$ and HCOOH on the surface of anatase (101) and rutile (110). The HOMO and the LUMO of the clean surfaces and the free molecules are given for comparison. The colors of the atoms are as in Figure 3.14.
sites are similar to that of the free PA molecule.

We also showed evidence that regioselectivity increases when going from mono- to tridentate adsorption complexes. On all surfaces, the energetically favored sites for mono-, bi- and tridentate binding of the acids allow a logical adsorption sequence. This strongly supports our assumed step-by-step condensation reaction. The P–O bond lengths are little or not affected by the surface coverage in any binding mode. However, we obtained a contraction of the P–OAl bonds that result from a resonance stabilisation of the phosphonic acid group in the tridentate models. Also, the bond lengths of the same binding mode were identical on different surfaces. This points towards the tendency of the phosphonic acids to adsorb at similar sites. Moreover, the attachment of an alkyl chain has no influence on the selection of the preferred adsorption sites.

Furthermore, we focussed on the structure of long-chain alkyl phosphonic acids adsorbed on the aluminum oxide surfaces. We found that the thickness of the SAMs, i.e. the height of the adsorbed APA is always shorter than the length of the fully extended, all-trans APA molecules due to the tilting of the alkyl chains. Moreover, mono-, bi- and tridentate adsorption models showed very similar tilt angles. We conclude that the tilting of the APA molecules does not reflect their binding modes on the surface. The tilt angles obtained for the single adsorbed APA molecules do not significantly differ from the angles observed in the fully covered surfaces. The tilt angle is expected to be reduced as the alkyl chains approach the maximum packing. Therefore, we infer that the density of adsorption sites (that is similar in all three surface models) limits the concentration of phosphonic acids in the SAMs to a situation in which the maximum packing of the alkyl chains is not reached. In addition, we found that the alkyl chains are more distorted in the full-coverage situation than in case of adsorption of just a single PA molecule on the surfaces. This we attribute to the tendency of minimising the repulsive forces between hydrogen atoms of neighboring alkyl chains. We also noted that the distortion of the alkyl chains decreases with increasing number of formed Al–P–O bonds due to the different rigidity of the PA head group or due to the lower coverage used in the tridentate models. Although we think that dispersion forces are expected to be too weak to significantly influence SAM properties such as tilt angles, their influence cannot be totally discarded and further investigations, e.g. the dynamic aspects, might account for these contributions.

In case of titanium oxide, we studied a large set of adsorption complexes for phosphonic acid on clean anatase (101) and rutile (110) surfaces. Furthermore, we compare these results with those of the adsorption of formic acid. Topics of specific interest were the binding strength and the structural and electronic changes in the underlying substrate at the two prototype TiO$_2$ interfaces between an inorganic, ionic substrate and a chemically anchored acidic molecule.

The tridentate adsorption complexes of phosphonic acid are not stable on both surfaces. Mono- and bidentate complexes resulted in stable configurations with adsorption energies exceeding 125 kJ/mol. However, we found a strong trend of the monodentate adsorption geometries relaxing towards the bidentate configuration. According to our calculations, the
3.5 Final conclusions

The strongest adsorption complexes on both clean surfaces have bidentate configurations, but there are several further bidentate adsorption complexes having similar adsorption energies but different geometries. Hence, they are equally likely to be present on the TiO$_2$ surfaces. We also determined that the preferred adsorption mode of the formic acid on both surface structures is a dissociative bridging bidentate complex. The bidentate adsorption geometry is more rigid and the degrees of freedom for movement are reduced compared with monodentate adsorption. This might promote the ordering of the anchored functional molecules on the substrate, which is desired for their application in most (opto-)electronic devices. We found a similar result for self-assembled monolayers of long-chain alkyl phosphonic acids on aluminum oxide surfaces.

The binding of phosphonic acid to TiO$_2$ is significantly stronger than that of formic acid indicated by a larger adsorption energy and shorter Ti–O bond lengths. The preference of the bidentate complexes and the more stable adsorption complexes in case of phosphonic acid was further supported by a detailed analysis of the Mulliken charge distribution in the adsorption complexes. As a first conclusion, we state that for the design of robust and well-anchored organic films on TiO$_2$ substrates phosphonic acids are the preferable choice as coupling agent in comparison with carboxylic acids.

Concerning the electronic properties, we found a strong interfacial electronic coupling between the molecular orbitals of the adsorbates and the electronic states of the surface slab in case of anatase (101) resulting in a small decrease of the band gap energy compared with the clean surface. In contrast, we found no or only a weak such coupling on rutile (110) leading to an increase of the band gap energy. In both cases, the anchor groups bind to the surface via oxygen atoms, so that the metal atoms of the free slab surface experience a rather bulk-like situation. Thus, as a second conclusion, we state that proper anchoring of the organic film can help to re-establish bulk electronic properties at the substrate side of the interface. Moreover, our results demonstrate that the electronic properties of an organic-inorganic system can be modified by the inclusion of a suitable spacer group and the design of the functional molecule.
4 Intermolecular interactions between thiophene-based molecules

4.1 Introduction

α-Oligothiophenes usually form a herringbone structure in the crystals, i.e. the thiophene rings of two neighboring oligothiophenes take nearly perpendicular, T-shaped orientations, see e.g. [203–206]. However, some α,ω-dicyano-oligothiophenes were shown to adopt parallel, π-stacked rather than herringbone structures. This makes the molecules to be highly attractive for application as organic semiconducting materials in OFET devices [11, 12, 207]. The high-order lamellar stacking of the molecules within the organic film perpendicular to the dielectric substrate is promoted by the formation of intermolecular CH···NC hydrogen bonds and dispersive π–π-stacking interactions [11–13], cf. Figure 1.1 (c).

The CH···NC hydrogen bonds are supposed to be insulating, since no charge carriers are exchanged between the organic film and the dielectric gate substrate. Moreover, no strong dipoles are induced in the molecules by the hydrogen bond and the electronic structure of the organic semiconducting layer is not changed. Also, the film of the cyano-substituted oligothiophenes is usually built up by vapour deposition [11] and, thus, (chemically) clean, since no byproducts are produced during the formation and growth of the self-assembly organic layer.

In general, the presence and importance of CH···X hydrogen bonds for the structure formation and crystal packing was postulated in many other organic, molecular crystals, see e.g. [208–210]. X here denotes a hydrogen bond acceptor, i.e. O, N, Cl or S. However, hydrogen bonds including C–H groups as proton donors are very weak and their strength may be comparable with the van-der-Waals interaction. In more detail, the C–H donor strength depends on the carbon hybridisation: C(sp)–H > C(sp²)–H > C(sp³)–H, and increases with the number of adjacent electron-withdrawing groups [211]. It was shown for CH···O contacts [212, 213] that mean C···O distances correlate with the conventional C–H acidities, if there is little or no steric hindrance to the approach of an O atom to a C–H group. The CH···O bond becomes shorter and stronger with increasing acidity of the C–H group. It is well accepted that the CH···O contact, which is also the most studied interaction among these CH···X contacts, is a “real” hydrogen bond, see e.g. [208, 213–215]. Since the electronegativities of O and N are comparable, and since the majority of short CH···O
contacts is attractive, it is concluded that at least some of the short CH···N contacts might also be attractive \[208\].

In this chapter, we investigate in detail the intermolecular interactions between thiophene-based molecules by means of quantum-mechanical \textit{ab initio} and DFT-based calculations. In particular, the CH···NC hydrogen bond interaction and the $\pi$-$\pi$-stacking interaction are studied in Section 4.3 and 4.4, respectively. We evaluate the influence of the computational method, of the chosen basis set and of substitution on the intermolecular interactions employing dimers of (1-cyano-)thiophene. Furthermore, we investigate the hydrogen bond and the $\pi$-$\pi$-stacking interactions in a chain respective in a stack of DC-NDBQT molecules [Figure 1.1 (c)] applying the SCC-DFTB(-DC) method. The focus of this study is to examine the influence of the intermolecular interactions and of the number of molecules in the chain/stack on the geometry and electronic properties, which are relevant for the application in technological devices. Moreover, the present investigation on the intermolecular interactions are the basis for the study of the hopping transport in stacks of thiophene-based molecules. In particular, the stacking parameters were included in the determination of the hopping transport parameters and the calculation of the conductivity employing the Green function method \[8–10\].

4.2 Computational details

Highly-sophisticated quantum-mechanical methods are needed for a good and accurate description of hydrogen bonds and $\pi$-$\pi$-stacking interactions, as we discussed in Sections 2.2.1 and 2.2.4. In particular, those methods should include electron-electron correlation, cf. Refs. \[62, 216\] and references therein. Møller-Plesset methods such as MP2 perturbation theory \[32\] are widely used in practice to study the intermolecular interactions in organic molecules. In addition, large basis sets including polarisation and diffuse functions are necessary to obtain reasonable results \[216\]. Thus, 6-31G* is the minimum basis set needed to study hydrogen bonded or $\pi$-stacked systems. Furthermore, the basis set superposition error (BSSE) has to be considered that introduces a nonphysical attraction between the two monomers due to the different size of basis functions employed for the dimer and the isolated monomers \[216\]. To correct this BSSE, we used the counterpoise method developed by Boys and Bernardi \[217\] throughout this work.

Our general procedure for the present investigation of the intermolecular interactions was the following: We performed single-point-energy (SPE) calculations of the dimers in dependence on the hydrogen bond and stacking parameters (cf. Sections 4.3.1 and 4.4.1) and calculated the interaction energy according to:

$$E_{\text{int}} = E_{\text{tot}}(\text{Oligomer}) - n \ast E_{\text{tot}}(\text{Monomer}).$$ (4.1)

Therein, $n$ is the number of molecules in the oligomer, e.g. $n=2$ in case of the dimer. The monomers were optimised in advance at the respective level of computation, except in case
of MP2, for which the B3LYP/6-31G* geometries were used. Afterwards, we optimised the structures of the dimers with the minimum interaction energy at the respective levels of theory.

We carried out MP2 calculations of (1-cyano-)thiophene dimers using the following basis sets: 6-31G*, 6-311G*, 6-31+G*, 6-311++G**, cc-pvdz, cc-pvtz and aug-cc-pvdz, to determine the optimum basis set required for the study of the intermolecular interactions in thiophene-based molecules. MP2 calculations of very large systems are computationally demanding. For these systems density-functional theory based methods provide an attractive alternative. Thus, we evaluated the applicability of various DFT-based methods to investigate the intermolecular interactions in the present system. In case of the hydrogen bond interaction in 1-cyano-thiophene dimers, we employed the SCC-DFTB method [49–58] and the two DFT-functionals B3LYP [218, 219] and PBE [48]. In case of the \( \pi-\pi \) stacking interaction between thiophene dimers, DFT-functionals have to be used that account for dispersion interactions. Therefore, we investigated thiophene dimers considering the dispersion-corrected DFT-functionals B97D [69] and wb97xD [70], as well as the SCC-DFTB-DC method, where the dispersion is included similar to Grimme’s scheme [52–54, 66], cf. Section 2.2.4. For the DFT-SPE calculations and the subsequent optimisation, we used the cc-pvdz and the 6-311++G** basis set in case of the hydrogen bond and \( \pi-\pi \)-stacking interaction, respectively.

We investigated the CH\( \cdot \cdot \cdot \)NC hydrogen bond in dimers of substituted 1-cyano-thiophene at the MP2/cc-pvdz level of computation. MP2, B97D and SCC-DFTB-DC calculations along with the 6-311++G** basis set were employed to study the \( \pi-\pi \)-stacking interaction in 1-cyano-thiophene dimers. The efficient SCC-DFTB(-DC) method were applied to establish the intermolecular interactions in chains respective stacks of DCNDBQT molecules. All MP2 and DFT calculations are performed by the Gaussian09 program suite [220]. The DFTB+ code [110] is used for the SCC-DFTB(-DC) calculations.

### 4.3 CH\( \cdot \cdot \cdot \)NC Hydrogen bond interaction

#### 4.3.1 Hydrogen bond parameters

There are essentially two main parameters to study the nature of a hydrogen bond: the interaction energy and the intermolecular structure [216]. The interaction energy gives an indication of the strength of the hydrogen bond. The structure, i.e. the distance and angle of the hydrogen bond, gives an indication of the directionality of the interaction, which is essential for a hydrogen bond. In the present investigation, we performed SPE calculations on each dimer and calculated the interaction energy in dependence on the N\( \cdot \cdot \cdot \)H distance \( (d) \) and the CH\( \cdot \cdot \cdot \)N angle \( (\beta) \), see Figure 4.1, employing Eq. (4.1). The distance \( d \) was varied from 2.0 Å to 3.5 Å in increments of 0.1 Å. The angle \( \beta \) ranged from 120° to 180° in steps of 10°. In each case, the structures of the dimers with the minimum interaction energy were optimised afterwards at the respective level of theory.
4.3.2 Hydrogen bond interaction between 1-cyano-thiophene molecules

Influence of the the basis set

We performed MP2 calculations of 1-cyano-thiophene dimers (R=H, cf. Figure 4.1) using different basis sets to evaluate the influence of the chosen basis set on the structure and stability of the CH⋯NC hydrogen bond. In Table 4.1, the calculated minimum interaction energies and the respective optimum hydrogen bond parameters \(d\) and \(\beta\) are summarised. We found that the CH⋯NC hydrogen bond parameters are not very sensitive to the basis set. Especially, the deviations in the intermolecular structure are merely 4%, i.e. 0.1 Å in case of the distances and 6° in case of the angles. The interaction energy varies by only 6.4 kJ/mol. We chose the cc-pvdz basis set to study further the CH⋯NC hydrogen bond in the present system.

In this case, the distance \(d\) and angle \(\beta\) are 2.43 Å and 150°, respectively. This is similar to intermolecular CH⋯N distances and angles determined experimentally in various organic, molecular crystals, which range from 2.44 Å to 2.83 Å and from 125° to 177°, respectively [12, 208, 221, 222]. The CH⋯N distance in dimers of \(\alpha,\omega\)-dicyano-terthiophenes
Figure 4.2: Interaction energy $E_{\text{int}}$ of the hydrogen bond in dimers of 1-cyano-thiophene in dependence on the N···H distance ($d$) and the CH···N angle ($\beta$) calculated by SPE calculations using MP2/cc-pvdz + BSSE counterpoise correction.

was calculated to 2.2 Å using B3LYP/3-21G* [13].

The calculated interaction energy amounts to $-21.73$ kJ/mol. According to the hydrogen bond classification of Rozas [216] and Desiraju [223] weak hydrogen bonds have interaction energies smaller than $-20.92$ kJ/mol, respectively $-16.74$ kJ/mol, and H···X distances between 2.0 and 3.0 Å. Hence, we state that the CH···NC hydrogen bond interaction in the dimers of 1-cyano-thiophene molecules is weak but distinguishable from a pure van-der-Waals interaction. Moreover, a fundamental difference between hydrogen bonds and the van-der-Waals interaction lies in their different directionality characteristics. Hydrogen bonds are inherently directional with linear or close to linear geometries favored energetically over bent ones. In contrast, van-der-Waals contacts are isotropic, with interaction energies independent of the contact angle [224]. In Figure 4.2, we plot the interaction energy $E_{\text{int}}$ as a function of the N···H distance ($d$) and the CH···N angle ($\beta$), which we determined by SPE calculations using MP2/cc-pvdz. We note that $E_{\text{int}}$ depends on both parameters $d$ and $\beta$. With increasing angle $\beta$, $E_{\text{int}}$ decreases – i.e. the strength of the hydrogen bond increases – until its minimum at $\beta=150^\circ$ and $d=2.5$ Å. Thus, the CH···NC contact in dimers of 1-cyano-thiophene shows directionality, which is characteristic for the presence of a hydrogen bond. Furthermore, the H···N distance found (2.43 Å) is significantly shorter than the sum of the van-der-Waals radii of H and N (1.2+1.5=2.7 Å) and the C-H···N unit shows quite good linearity (150°). These are further indicative characteristics of the formation of a hydrogen bond like interaction [216].
Influence of the computational method

To evaluate the influence of the computational method on the hydrogen bond parameters, we compare in Table 4.1 the MP2/cc-pvdz results of the 1-cyano-thiophene dimer with results calculated using DFT-based methods along with the cc-pvdz basis set. The best agreement with MP2 is obtained by the DFT method using the generalised gradient approximation of Perdew, Burke and Ernzerhof (PBE) for the exchange correlation functional. The deviations in the distances, angles and interaction energy are 1%, 7% and 5%, respectively. Larger deviations are found in the case of the hybrid HF-DFT method B3LYP. Particularly, the interaction energy is underestimated by about 5 kJ/mol. The structural parameters obtained by the SCC-DFTB method show some deviation to the MP2/cc-pvdz results. The H· · ·N distance \(d\) is underestimated by 0.4 Å (16%) and the CH· · ·N angle is overestimated by 17° (11%). However, the interaction energy (21.5 kJ/mol) is in good agreement with the MP2 result.

Bearing in mind that different basis sets cause similar deviations, we conclude that the SCC-DFTB method and the DFT functionals investigated here provide a reasonable description of the CH· · ·NC hydrogen bond interaction. In particular, for the investigation of very large systems, which are computationally too demanding to be calculated using MP2, these methods are appropriate alternatives.

Influence of substituents

The influence of substitution in 3-position on the geometry and strength of the CH· · ·NC hydrogen bond interaction is studied by means of MP2/cc-pvdz calculations. In particular, we investigate the substituents \(R = \text{CH}_3\), \(\text{C}_4\text{H}_9\), \(\text{OCH}_3\), \(\text{NH}_2\) and \(\text{NO}_2\) (Figure 4.1). The alkyl groups are electron-donating by inductive effects, whereas \(\text{OCH}_3\), \(\text{NH}_2\), \(\text{NO}_2\) and \(\text{Cl}\) are electron-withdrawing groups. Thus, the former are supposed to increase the acceptor strength of the CN group by increasing the electron density in the ring system. On the contrary, the latter are supposed to decrease the electron density in the π-system and, therefore, are expected to increase the CH acidity.

In Table 4.2, we summarise the calculated interaction energies, distances \(d\) and angles \(\beta\) of the optimised dimers. We note that the effect of substitution is quite small. The parameters \(d\), \(\beta\) and \(E_{\text{int}}\) vary by 0.1 Å, 20° and 9 kJ/mol, respectively. However, we still can work out some general trends. In most cases, the strength of the hydrogen bond is increased with increasing linearity, e.g. increasing angle \(\beta\). The conventionally electron-withdrawing \(\text{NO}_2\) and \(\text{Cl}\) substituents decrease the linearity of the hydrogen bond, but still slightly increase the strength of the hydrogen bond interaction. \(E_{\text{int}}\) is decreased with increasing length of the alkyl group, i.e. the hydrogen bond becomes stronger. The methoxy group strengthens the CH· · ·NC hydrogen bond most pronouncedly by about 9 kJ/mol, whereby the CH· · ·NC hydrogen bond becomes nearly linear \((\beta = 170°)\) and the distance \(d\) is slightly reduced by 0.03 Å compared with the nonsubstituted molecule.
Table 4.2: Substituted 1-cyano-thiophene derivates: Parameters $\beta$, $d$ and $E_{\text{int}}$ in the optimised dimers (cf. Figure 4.1). The differences with respect to 1-cyano-thiophene are given in parentheses. The calculations were performed using MP2/cc-pvdz + BSSE counterpoise correction.

<table>
<thead>
<tr>
<th>R</th>
<th>$\beta$ [$^\circ$]</th>
<th>$d$ [Å]</th>
<th>$E_{\text{int}}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>150</td>
<td>2.43</td>
<td>$-21.73$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>154 (4)</td>
<td>2.46 (0.03)</td>
<td>$-22.47$ (-0.74)</td>
</tr>
<tr>
<td>C$_4$H$_9$</td>
<td>159 (9)</td>
<td>2.44 (0.01)</td>
<td>$-23.95$ (-2.22)</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>170 (20)</td>
<td>2.40 (-0.03)</td>
<td>$-30.81$ (-9.08)</td>
</tr>
<tr>
<td>Cl</td>
<td>144 (-6)</td>
<td>2.48 (0.05)</td>
<td>$-23.13$ (-1.40)</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>159 (9)</td>
<td>2.44 (0.01)</td>
<td>$-24.89$ (-3.16)</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>141 (-9)</td>
<td>2.49 (0.06)</td>
<td>$-22.75$ (-1.02)</td>
</tr>
</tbody>
</table>

Next, we focus on the charge distribution in the substituted 1-cyano-thiophene derivates to further evaluate the effect of the different functional groups. The net charges of a natural population analysis [225] in different parts of the optimised monomers corresponding to Figure 4.1 are listed in Table 4.3. The electron density is decreased in the thiophene ring by substitution and is increased at the respective substituents. On the other hand, the charges of the CN group and the H atom, which form the hydrogen bond, are only marginally affected. The expected electron-donating character of the alkyl groups is not reflected in the charge distribution. The alkyl groups decrease the electron density in the thiophene ring and increase the electron density at the H atom of the hydrogen bond, i.e. it decreases the CH acidity. Hence, the charge distribution does not explain the reason for the increased strength of the hydrogen bond in case of 1-cyano-3-methyl-thiophene or 1-cyano-3-butyl-thiophene compared with the nonsubstituted 1-cyano-thiophene molecule. The electron-withdrawing substituents, OCH$_3$, NH$_2$, NO$_2$ and Cl, significantly decrease the electron density in the thiophene ring. Thereby, the CH acidity, i.e. the donor strength of the H atom is slightly increased, but in almost the same manner the acceptor strength of the CN group is weakened.

In general, each molecule acts both as donor (CH) and acceptor (CN) of the hydrogen bond. Substituents that, on the one hand, increase the CH acidity, on the other hand, reduce the acceptor strength of the CN group in the same molecule and vice versa. Thus, both effects cancel out each other, leading to only small changes in the hydrogen bond parameters. The NH$_2$ group can act as hydrogen bond donor itself. It is supposed to form a NH$\cdot\cdot\cdot$NC hydrogen bond with the CN group of the second molecule that is probably much stronger than the CH$\cdot\cdot\cdot$NC hydrogen bond investigated here.

In conclusion, we state that the strength of the hydrogen bond is increased most pronouncedly in case of the methoxy group as substituent. It changes the electron density in the ring, but does not influence the charges on the CN group and H atom, which form the hydrogen bond.
4.3.3 Hydrogen bond interaction between DCNDBQT molecules

In this subsection, we will investigate the CH⋯NC hydrogen bond interaction in DCNDBQT dimers using the SCC-DFTB method. As we found above, this method can qualitatively describe the most important features of hydrogen-bonded systems at much lower computational effort compared with MP2. Therefore, it can be applied for larger systems to study, e.g., the properties of the hydrogen bond interaction in chains of DCNDBQT molecules.

The hydrogen bond distance and angle in the optimised DCNDBQT dimer are 2.04 Å and 170°. They are similar to those in 1-cyano-thiophene. The interaction energy is \(-23.5\) kJ/mol. Thus, the interaction is stronger than in case of 1-cyano-thiophene by 2 kJ/mol. Obviously, the attached butyl chains are mainly responsible for the increase of the hydrogen bond strength, since the gain in energy is similar to that obtained for the related 1-cyano-3-butyl-thiophene by MP2 calculations (cf. Table 4.2). In general, the interaction energy in the DCNDBQT dimer is small. However, referring to Rozas [216], cooperativity effects might further increase the strength of the hydrogen bond interaction. Thereby, hydrogen-bond cooperativity means that a chain of several molecules connected through hydrogen bonds is kept together more strongly than expected from the interaction energy of a single hydrogen bond in a dimer. This effect is attributed to the polarisation induced in each monomer by the presence of the other monomers in the hydrogen bond complex, cf. Ref. [216].

To evaluate these cooperativity effects for the CH⋯NC hydrogen bond interaction, we investigated chains of \((\text{DCNDBQT})_n\) molecules with \(n = 2–6, 8, 12\). We can see from Table 4.4 that the structural parameters \(\beta\) and \(d\) are independent of the number of molecules in the chain. They retain the values of the dimer. The (total) interaction energy in the chain decreases linearly with increasing number of DCNDBQT molecules and the interaction energy per hydrogen bond does not change significantly. Hence, a single hydrogen bond in a
Table 4.4: DCNDBQT. Structural parameters, $\beta$ and $d$, interaction energy, $E_{\text{int}}$, interaction energy per hydrogen bond, $E_{\text{int}}^{\text{hh}}$, HOMO-LUMO-gap energy, $E_{\text{gap}}$, and energy of the HOMO and LUMO levels, $E_{\text{h}}$ and $E_{\text{l}}$, in the optimised chains of (DCNDBQT)$_n$ calculated using SCC-DFTB.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\beta$ [°]</th>
<th>$d$ [Å]</th>
<th>$E_{\text{int}}$ [kJ/mol]</th>
<th>$E_{\text{int}}^{\text{hh}}$ [kJ/mol]</th>
<th>$E_{\text{gap}}$ [eV]</th>
<th>$E_{\text{h}}$ [eV]</th>
<th>$E_{\text{l}}$ [eV]</th>
</tr>
</thead>
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<tr>
<td>1</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>170</td>
<td>2.04</td>
<td>-23.50</td>
<td>-23.50</td>
<td>1.72</td>
<td>-5.41</td>
<td>-3.70</td>
</tr>
<tr>
<td>3</td>
<td>170</td>
<td>2.04</td>
<td>-46.95</td>
<td>-23.48</td>
<td>1.66</td>
<td>-5.29</td>
<td>-3.63</td>
</tr>
<tr>
<td>4</td>
<td>170</td>
<td>2.04</td>
<td>-70.40</td>
<td>-23.47</td>
<td>1.66</td>
<td>-5.28</td>
<td>-3.63</td>
</tr>
<tr>
<td>5</td>
<td>170</td>
<td>2.04</td>
<td>-93.81</td>
<td>-23.45</td>
<td>1.65</td>
<td>-5.28</td>
<td>-3.63</td>
</tr>
<tr>
<td>6</td>
<td>170</td>
<td>2.04</td>
<td>-117.26</td>
<td>-23.45</td>
<td>1.65</td>
<td>-5.27</td>
<td>-3.63</td>
</tr>
<tr>
<td>8</td>
<td>170</td>
<td>2.04</td>
<td>-164.13</td>
<td>-23.45</td>
<td>1.65</td>
<td>-5.27</td>
<td>-3.63</td>
</tr>
<tr>
<td>12</td>
<td>170</td>
<td>2.04</td>
<td>-257.87</td>
<td>-23.44</td>
<td>1.64</td>
<td>-5.27</td>
<td>-3.62</td>
</tr>
</tbody>
</table>

chain of DCNDBQT molecules is not stronger than that in the dimer. From this analysis, we expect no cooperativity effects here. This was also found for the related CH· · · O hydrogen bond between imidazole and water molecules [226].

Next, we focus on the Mulliken atomic-charge distribution in the monomer, the dimer and the longer DCNDBQT chains. Due to the atomic orbital basis within DFTB, the Mulliken population analysis is an appropriate method to determine the charge distribution here. Our calculated charges in different molecular parts are summarised in Figure 4.3. The main differences between the monomer and the dimer occur for the two interacting thiophene moieties. In particular, the charges at the interacting CN group and the H atom as well as at the thiophene ring are (slightly) affected by the hydrogen bond interaction. This charge distribution does not change significantly when going to the longer (DCNDBQT)$_n$ chains ($n \geq 3$). Therefore, we conclude that the forces in the CH· · · NC hydrogen bond interaction of DCNDBQT molecules are highly local. This was also demonstrated by Guzman et al. [13] for $\alpha,\omega$-dicyano-terthiophene employing DFT calculations.

In Figure 4.4, we show the topologies and energies of the molecular orbitals around the gap for (DCNDBQT)$_n$ ($n = 1$−$4$). We note that the topologies of the frontier molecular orbitals of the chains resemble those of the HOMO and LUMO of the monomer. Moreover, $n$ occupied and $n$ unoccupied molecular orbitals arise around the HOMO-LUMO gap that have similar energies. Moreover, always two of them are degenerated. The orbitals are each localised on one molecule for those (DCNDBQT)$_n$ chains with an odd number of molecules. The HOMO and the HOMO-1 as well as the LUMO+$n$-2 and LUMO+$n$-1 are localised on the two central DCNDBQT molecules for even numbers of molecules in the oligomer. The total changes in the energies of the frontier molecular orbitals and of the gap are quite small, cf. Table 4.4. Hence, we expect that also the optical properties of the monomer and of the chain are similar and molecule-dominated.

In conclusion, we found no evidence for the presence of cooperativity effects on the CH· · · NC hydrogen bond interaction in the (DCNDBQT)$_n$ chains. Furthermore, the geome-
try and the strength of the hydrogen bond as well as the charge distribution, the gap energy and the topologies and energies of the frontier molecular orbitals are only slightly or negligibly affected by the CH⋅⋅⋅NC interaction independent of the chain length. Thus, from our present results, we conclude that the weak CH⋅⋅⋅NC hydrogen bond interaction found in the DCNDBQT chains promotes the desired orientation of the DCNDBQT molecules in the film perpendicular to the substrate by linking the molecules into extended ribbons. However, we think that further effects must participate significantly to enable the highly ordered and stacked molecules in the film like for example the π-π-stacking interactions, which are the scope of the next section.

4.4 π-π-Stacking interaction

4.4.1 π-π-Stacking parameters

The π-stacking arrangement that we considered for the calculations of the thiophene and 1-cyano-thiophene dimers is shown in Figure 4.5. The relevant intermolecular parameters are indicated according to Rodriguez et al. [227] as follows: The distance \( R \) refers to the distance between the two centers of mass of the thiophene rings and indicates the separation between them. \( \theta \) is the rotational angle between the two rings, i.e. it denotes the relative orientation of the rings. The thiophene rings are considered as parallel and antiparallel when \( \theta = 0^\circ \) and \( 180^\circ \), respectively. \( \phi \) is the tilting angle between the two planes of the thiophene monomers. The two rings are coplanar when \( \phi = 0^\circ \), while \( \phi = 180^\circ \) corresponds to a perpendicular configuration. The parameter \( \Delta d \) defines the displacement between the centers \( C_1 \) and \( C_2 \). The centers \( C_1 \) and \( C_2 \) and the resultant relevant stacking parameters \( R \), \( \theta \) and \( \Delta d \) for the DCNDBQT dimer are illustrated in Figure 4.9.
Figure 4.4: Orbital-isosurfaces and energies of the frontier molecular orbitals around the gap for (DCNDBQT)$_n$ with $n = 1–4$. Yellow, blue, green and grey spheres indicate S, N, C and H atoms, respectively.

Figure 4.5: Structure of the π-stacked thiophene dimer and indication of the relevant intermolecular parameters according to Ref. [227].
Intermolecular interactions between thiophene-based molecules

4.4.2 π-π-Stacking interactions in thiophene dimers

Tsuzuki et al. [62] found for the thiophene dimer by CCSD(T) calculations that the perpendicular arrangement of the thiophene rings is more favored than the parallel one. However, thiophenes with, e.g., alkyl or cyano groups as substituents are shown to prefer the π-stacked structure. Since these thiophene derivates are of special interest in this work, we restricted our investigation to the parallel sandwich (π-stacked) arrangement of the rings [11, 12, 62, 207]. Moreover, this arrangement is the most relevant for application in OFET devices.

In Figure 4.6 (a) the interaction energy $E_{\text{int}}$ of the thiophene dimer is plotted as a function of the stacking distance $R$ ($\theta=180^\circ$) that we obtained by SPE calculations using MP2 with several basis sets. It is compared to the interaction energy calculated at the CCSD(T) level of theory [62]. In agreement with the results of Tsuzuki et al. [62], the MP2 interaction energy depends strongly on the basis set, and a large basis set is necessary for an accurate description of the π-π-stacking interaction. We found that the 6-311++G** basis agrees best with the high level CCSD(T) results. Therefore, we chose the MP2/6-311++G** data as a benchmark for the further investigation.
Table 4.5: Interaction energies, $E_{\text{int}}$, and structural parameters $R$, $\Delta d$, $\theta$ and $\Phi$ of optimised stacked thiophene dimers according to MP2 and DFT-based calculations.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis/Disp.</th>
<th>$R$ [Å]</th>
<th>$\Delta d$ [Å]</th>
<th>$\theta$ [°]</th>
<th>$\Phi$ [°]</th>
<th>$E_{\text{int}}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2</td>
<td>6-31G*</td>
<td>3.39</td>
<td>1.80</td>
<td>65</td>
<td>3</td>
<td>$-1.72^a$</td>
</tr>
<tr>
<td></td>
<td>6-311G*</td>
<td>3.27</td>
<td>1.78</td>
<td>62</td>
<td>3</td>
<td>$-4.72^a$</td>
</tr>
<tr>
<td></td>
<td>6-311G**</td>
<td>3.33</td>
<td>1.93</td>
<td>(180)</td>
<td>(0)</td>
<td>$-3.64^{a,b}$</td>
</tr>
<tr>
<td></td>
<td>6-31+G**</td>
<td>3.79</td>
<td>1.39</td>
<td>57</td>
<td>6</td>
<td>$-7.29^{a,c}$</td>
</tr>
<tr>
<td></td>
<td>6-311++G**</td>
<td>3.24</td>
<td>1.88</td>
<td>88</td>
<td>2</td>
<td>$-9.55^a$</td>
</tr>
<tr>
<td></td>
<td>cc-pvdz</td>
<td>3.30</td>
<td>1.77</td>
<td>63</td>
<td>2</td>
<td>$-5.32^a$</td>
</tr>
<tr>
<td>BLYP-D</td>
<td>TZVPP</td>
<td>3.77</td>
<td>–</td>
<td>(180)</td>
<td>(0)</td>
<td>$-8.33^d$</td>
</tr>
<tr>
<td>B97D</td>
<td>6-311++G**</td>
<td>3.37</td>
<td>1.98</td>
<td>79</td>
<td>2</td>
<td>$-9.65^a$</td>
</tr>
<tr>
<td>wB97xD</td>
<td>6-311++G**</td>
<td>3.62</td>
<td>1.33</td>
<td>145</td>
<td>12</td>
<td>$-9.85^a$</td>
</tr>
<tr>
<td>SCC-DFTB-DC</td>
<td></td>
<td>3.69</td>
<td>0.11</td>
<td>60</td>
<td>8</td>
<td>$-15.23$</td>
</tr>
</tbody>
</table>

$^a$ Energies are with BSSE counterpoise correction. $^b$ Data from Ref. [62]. The CCSD(T) calculated interaction energy estimated at the basis set limit is $-7.16$ kJ/mol. $^c$ Data from Ref. [227]. The CCSD(T)/6-31+G** calculated interaction energy is $-1.01$ kJ/mol. $^d$ Data from Ref. [228].

In Figure 4.6 (b), the MP2/6-311++G** interaction energy is compared with results that we calculated using dispersion-corrected DFT-based methods. We obtain a reasonably good agreement for the DFT functionals, B97D and wB97xD, with respect to MP2. In particular, the dispersive $R^{-6}$ energy dependence at large distances is nicely reproduced. The minimum is localised accurately at $R = 4.0$ Å. The SCC-DFTB-DC method shifts the minimum to a smaller distance (3.6 Å) and overestimates the strength of the $\pi$-stacking interaction by about 10 kJ/mol. We found that the energy dependence of the dimer on the dihedral angle $\theta$ is very small, as it was already stated in Ref. [227]. The parallel ($\theta=0^\circ$) and antiparallel ($\theta=180^\circ$) arrangements differ by less than 1 kJ/mol in case of MP2.

In Table 4.5, the calculated interaction energies and intermolecular structural parameters of the optimised thiophene dimers according to our MP2 and DFT calculations are summarised and compared with results reported in the literature [62, 227, 228]. The minimum energy arrangement obtained with our benchmark calculation (MP2/6-311++G**) has an interaction energy of 9.55 kJ/mol. The rotational angle is $\theta=88^\circ$. The ideal sandwich arrangement of the thiophene rings ($\Delta d=0$ Å and $\phi=0^\circ$) changes to a displaced $\pi$-stacked geometry with $\Delta d=1.88$ Å and $\phi=2^\circ$. The stacking distance $R$ is reduced by 0.76 Å with respect to the starting structure. We can see in Table 4.5 that the interaction energy and the structural parameters are very sensitive to the applied basis set. The deviation in the distances, angles and energies are 0.5 Å ($R$, $\Delta d$), 31° ($\theta$), 4° ($\phi$) and 8 kJ/mol ($E_{\text{int}}$). However, we note the good agreement of our calculated interaction energy using MP2/6-311++G** with the CCSD(T) result of Tsuzuki et al. [62] that was estimated at the basis set limit ($E_{\text{int}} = -7.16$ kJ/mol).

Among DFT, the B97D functional shows the best agreement with the MP2/6-311++G**
results. The wB97xD functional significantly overestimates the stacking distance $R$ and the angle $\theta$. The SCC-DFTB-DC method particularly overestimates the stacking distance $R$ and the interaction energy $E_{\text{int}}$. Additionally, it underestimates the displacement $\Delta d$. However, as already mentioned above, even the MP2 results are quite dependent on the chosen basis set and the deviations in the distances, angles and energies are similar to those obtained by the DFT-based methods. Hence, we conclude that the DFT-based methods used here give reasonable results.

4.4.3 $\pi$-$\pi$-Stacking interactions in 1-cyano-thiophene dimers

We use the MP2/6-311++G**, the B97D/6-311++G** and the SCC-DFTB-DC method to study the $\pi$-$\pi$-stacking interaction in dimers of 1-cyano-thiophene. Two starting configurations are considered, in which the CN groups are either on the same site (syn orientation: “cns”) or on opposite sites (anti orientation: ”cna”), see Figure 4.7 (a) and (b), respectively.

In Figure 4.8 (a), the calculated interaction energy $E_{\text{int}}$ is plotted as a function of the distance $R$. We found a qualitatively good agreement of the B97D and the SCC-DFTB-DC results with the MP2 data. In particular, the SCC-DFTB-DC method accurately localises the minimum at 3.6 Å. However, in contrast to the thiophene dimer, it underestimates the interaction by about 15 kJ/mol compared with MP2. In Figure 4.8 (b), the energy dependence on the relative orientation of the two rings is shown resulting from MP2 SPE calculations. It is ten times larger than in the thiophene dimer due to the insertion of the CN group. The minima are localised around 180° and 60° for the two configurations cnT2x-cns and cnT2x-cna, respectively. We note that all employed DFT-based methods describe the energy dependence upon rotation qualitatively well. The minima and maxima are correctly defined, although the SCC-DFTB-DC methods underestimates the energy dependence by about 5 kJ/mol.

In Figure 4.7 (b) and (c), we illustrate the optimised geometries of the two arrangements of the 1-cyano-thiophene dimers resulting from MP2/6-311++G** calculations. The corresponding structural parameters and interaction energies are given in Table 4.6. In comparison with the optimised thiophene dimer, the stacking distances $R$ are only slightly
increased by 0.2 Å (cnT2x-cns) and 0.1 Å (cnT2x-cna). Again, the ideal sandwich arrangements of the monomers change to a displaced, slightly tilted π-stacked structure in the optimised dimers. The interaction energy is significantly larger by 13-14 kJ/mol than for the thiophene dimer. Obviously, the CN groups increase the dispersion interaction in the π-stacked dimer. Moreover, the CN substituent stabilises the parallel dimer with respect to the perpendicular one according to Refs. [12, 207]. Similar observations were reported for methyl-substituted thiophene dimers [62]. The optimised configurations of cnT2x-cns-opt and cnT2x-cna-opt correspond to θ=180° and θ=6°. In both dimers, the CN groups of the stacked molecules are on opposite sites and, thus, localised farthest from each other, cf. Figure 4.7 (b) and (c). The S atoms in the cnT2x-cns-opt dimer are on opposite sites, too, and this configuration is slightly more stable than the cnT2x-cna-opt dimer by 1 kJ/mol.

We found a reasonably good agreement for the structural parameters and interaction energies calculated using the two DFT-based method in comparison with the MP2/6-311++G** results, see Table 4.6. Furthermore, the structural parameters and interaction energies agree better to the benchmark data after optimisation of the dimer than for the SPE calculation. Also, the agreement of the B97D and SCC-DFTB-DC results with MP2 is much better in case of 1-cyano-thiophene than in case of the nonsubstituted thiophene. This further validates the applicability of especially the SCC-DFTB-DC methods to study the π-π-stacking interaction.

### 4.4.4 π-π-Stacking interactions between DCNDBQT molecules

The SCC-DFTB-DC method is applied to study the π-π-stacking interaction in stacks of DCNDBQT molecules. As we showed above, this method gives reliable results for the
**Table 4.6:** 1-cyano-thiophene: Interaction energies, $E_{\text{int}}$, and structural parameters $R$, $\Delta d$, $\theta$ and $\Phi$ of optimised stacked dimers according to MP2 and DFT-based calculations. The MP2 and B97D energies are with BSSE counterpoise correction.

<table>
<thead>
<tr>
<th>Model</th>
<th>Method</th>
<th>$R$ [Å]</th>
<th>$\Delta d$ [Å]</th>
<th>$\theta$ [°]</th>
<th>$\Phi$ [°]</th>
<th>$E_{\text{int}}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cnT2x-cns</td>
<td>MP2/6-311++G**</td>
<td>3.42</td>
<td>1.21</td>
<td>180</td>
<td>0</td>
<td>−23.89</td>
</tr>
<tr>
<td></td>
<td>B97D/6-311++G**</td>
<td>3.58</td>
<td>1.34</td>
<td>180</td>
<td>0</td>
<td>−23.67</td>
</tr>
<tr>
<td></td>
<td>SCC-DFTB-DC</td>
<td>3.52</td>
<td>0.44</td>
<td>203</td>
<td>8</td>
<td>−25.04</td>
</tr>
<tr>
<td>cnT2x-cna</td>
<td>MP2/6-311++G**</td>
<td>3.34</td>
<td>1.39</td>
<td>6</td>
<td>8</td>
<td>−22.70</td>
</tr>
<tr>
<td></td>
<td>B97D/6-311++G**</td>
<td>3.68</td>
<td>1.25</td>
<td>88</td>
<td>19</td>
<td>−23.20</td>
</tr>
<tr>
<td></td>
<td>SCC-DFTB-DC</td>
<td>3.44</td>
<td>1.44</td>
<td>53</td>
<td>19</td>
<td>−23.83</td>
</tr>
</tbody>
</table>

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**Figure 4.9:** DCNDBQT: a) Parallel and b) antiparallel arrangement of the $\pi$-stacked molecules in the dimer and indication of the relevant intermolecular parameters.

The structural parameters and interaction energies of the four optimised dimer configurations are summarised in Table 4.7. The interaction energy is significantly increased by more than 100 kJ/mol in comparison to the (1-cyano-)thiophene dimers. This we mainly attribute to the extension of the aromatic $\pi$-electron system by increasing the number of thiophene rings in the molecule. Indeed, the interaction energy per thiophene ring is about $-35$ kJ/mol and, thus, similar to $E_{\text{int}}$ of 1-cyano-thiophene. The intermolecular distance $R$ is slightly increased at maximum by 0.2 Å in comparison with the 1-cyano-thiophene dimer. We ascribe this to the steric hindrance of the butyl chains in the DCNDBQT dimers, which also causes the displacement of $\Delta d=1.15$ Å in the dcndbqt2x-ss-bnp dimer. The model
Table 4.7: DCNDBQT2x: Interaction energies, $E_{\text{int}}$, and structural parameters $R$, $\Delta d$ and $\theta$ of optimised stacked dimers according to SCC-DFTB-DC calculation.

<table>
<thead>
<tr>
<th>Model</th>
<th>$R$ [Å]</th>
<th>$\Delta d$ [Å]</th>
<th>$\theta$ [°]</th>
<th>$E_{\text{int}}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>dcndbqt2x-ss-bp</td>
<td>3.61</td>
<td>0.00</td>
<td>16</td>
<td>-145.14</td>
</tr>
<tr>
<td>dcndbqt2x-sa-bp</td>
<td>3.47</td>
<td>0.00</td>
<td>59</td>
<td>-155.50</td>
</tr>
<tr>
<td>dcndbqt2x-ss-bnp</td>
<td>3.56</td>
<td>1.15</td>
<td>22</td>
<td>-136.24</td>
</tr>
<tr>
<td>dcndbqt2x-sa-bnp</td>
<td>3.64</td>
<td>0.06</td>
<td>29</td>
<td>-134.30</td>
</tr>
</tbody>
</table>

$dcndbqt2x-sa-bp$ is the most stable one, since it has the most negative interaction energy (strongest interaction) of the four optimised dimers. In this configuration, the butyl groups are oriented in the plane of the quarterthiophene moiety and the S atoms of stacked thiophene rings in the dimer are in antiparallel arrangement. The optimised structure of this configuration is shown in Figure 4.10. Due to the intermolecular rotation of $\theta=59^\circ$, the thiophene rings in the dimer are not ideally $\pi$-stacked. The optimised structure is characterised by intermolecular interactions between the butyl chain and the cyano-thiophene moiety at the edges and between the S atoms of stacked thiophene rings in the center.

We chose the optimised structure of the most stable dimer configuration ($dcndbqt2x-sa-bp$) to build stacks of (DCNDBQT)$_n$ with $n=2$–6, 8, 12, 18, 26 and 36, which were then optimised at the SCC-DFTB-DC level. The knowledge of the $\pi$-stacking structure is essential for the later investigation of the hopping transport properties of the organic thiophene-based film [9, 10]. Therefore, we plot the intermolecular structural parameters $R$ and $\theta$ as a function of the number $n$ of molecules in the stack in Figure 4.11. For each stack size, the averaged distances and angles are given as well as the $R$ and $\theta$ values between the two DCNDBQT molecules at the edges and in the center of the stack. We also include the evolution of the intermolecular distances and angles in the stack of (DCNDBQT)$_{36}$.

In general, the intermolecular distance at the edge of the stacks is smaller than in the center (for $n>3$), see Figure 4.11 (a). Its value slightly increases with increasing number $n$.
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of molecules in the stack. For stack sizes with \( n \geq 12 \), the intermolecular distances at the edge and in the center have constant values of about 3.53 Å and 3.65 Å, respectively. The intermolecular angle \( \theta \) [Figure 4.11 (b)] fluctuates for small stack sizes more than for larger ones. However, the angles at the edge and in the center both have constant values of about 58° for stack sizes with \( n \geq 12 \).

The calculated interaction energy per DCNDBQT molecule, \( E_{\text{int}}^{\text{qt}} \), as a function of the stack size is shown in Figure 4.12 (a). In particular, \( E_{\text{int}}^{\text{qt}} \) is the parameter that gives an indication of the strength of the \( \pi-\pi \)-stacking interaction in the stack. It strongly decreases and converges to a value of -155 kJ/mol for \( n > 12 \); i.e. the interaction becomes stronger with increasing number \( n \) of molecules in the stack. Hence, contrary to our finding for the CH \( \cdot \cdot \cdot \) NC hydrogen bond, there are cooperativity effects in the strength of the \( \pi-\pi \)-stacking interaction, in the sense that a stack of several molecules is kept together more strongly than a dimer. Moreover, the \( E_{\text{int}}^{\text{qt}} \) of the \( \pi-\pi \)-stacking interaction is, even for the dimer, significantly larger than for the CH \( \cdot \cdot \cdot \) NC hydrogen bond interaction (−23 kJ/mol). Therefore, we state as a main conclusion, that the \( \pi \)-stacking interaction is the main driving force for the growth and self-assembly of the DCNDBQT monolayer.

Next, we focus on the electronic properties of the \((\text{DCNDBQT})_n\) stacks. In particular, we examine the HOMO-LUMO gap energy and the energies and topologies of the frontier molecular orbitals as a function of the stack size. The gap energy strongly decreases with increasing number \( n \) of molecules in the stack from 1.73 eV (\( n = 1 \)) to 1.55 eV (\( n = 12 \)), as we can see in Figure 4.12 (b). For larger stack sizes, it gradually approaches to about 1.53 eV. A similar behaviour was found for the energies of the HOMO and LUMO levels, see Figures 4.13 (a) and (b), respectively. The energies of the molecular orbitals strongly decrease for \( n \leq 12 \) and gradually converge to −5.48 eV (HOMO) and −3.95 eV (LUMO) for \( n \geq 12 \).

We illustrate the topologies of the HOMO and LUMO levels in \((\text{DCNDBQT})_n\) stacks
4.4 \(\pi-\pi\)-Stacking interaction

Figure 4.12: \((\text{DCNDBQT})_n\): a) Interaction energy per DCNDBQT molecule, \(E_{\text{int}}\), and b) HOMO-LUMO gap energy, \(E_{\text{gap}}\), as a function of the stack size \(n\) according to SCC-DFTB-DC calculations.

Figure 4.13: \((\text{DCNDBQT})_n\): Energy splitting between a) the highest occupied molecular orbitals and b) the lowest unoccupied molecular orbitals as a function of the stack size \(n\) according to SCC-DFTB-DC calculations. For each \((\text{DCNDBQT})_n\) stack, there are \(n\) occupied and \(n\) unoccupied orbitals around the gap with similar topologies. Here, only the energies of the HOMO (LUMO) and the HOMO-\((n-1)\) [LUMO+\((n-1)\)] are given. They are drawn as continuous and dashed lines, respectively.
for \( n = 1-5 \) in Figure 4.14. It is obvious that the topologies of the frontier molecular orbitals in the stack resemble the HOMO and LUMO of the monomer. Furthermore, there are \( n \) occupied and unoccupied orbitals around the gap that are each localised at different molecules in the stack. For example, the HOMO of \((\text{DCNDBQT})_5\) is mainly localised at the two molecules at the edge, whereas the HOMO-4 is mainly localised at the three molecules in the center; vice versa we found for the LUMO and LUMO+4 level, cf. Figure 4.14. The energy splitting between the HOMO and HOMO-\((n-1)\) levels is shown in Figure 4.14 (a). The energy of the HOMO-(n-1) strongly decreases – even more pronouncedly than in case of the HOMO energy level – and converges to \(-5.67 \text{ eV}\) for \( n \geq 12 \). The difference in energy to the HOMO amounts to about 0.19 eV. Analogous, we found for the LUMO and LUMO+(n-1) level, see Figure 4.14 (b). For large stack sizes the energy of the LUMO+(n-1) level approaches to \(-3.72 \text{ eV}\) and the energy splitting to the LUMO is 0.23 eV.

In conclusion, we could demonstrate the presence of cooperativity effects on the \( \pi-\pi \)-stacking interaction in a \((\text{DCNDBQT})_n\) stack. Moreover, the geometry, the interaction energy, the gap energies and the topologies and energies of the frontier molecular orbitals are significantly affected by the \( \pi-\pi \)-stacking interaction. Up to \( n = 12 \), they depend on the number \( n \) of molecules in the stack. For larger stack sizes the examined parameters converges to specific values that we expect to be similar to those of a periodic stack of DCNDBQT molecules.

### 4.5 Final conclusions

In this chapter, we investigated in detail the CH\( \cdots \)NC hydrogen bond and \( \pi-\pi \)-stacking interaction in dimers and oligomers of various thiophene-based molecules by means of quantum-mechanical MP2 and DFT-based calculations. At first, we examined (1-cyano-) thiophene dimers. We found, that the SCC-DFTB(-DC) method and the DFT functionals investigated here provide a reasonably good description of the intermolecular structural parameters and interaction energies in comparison with the MP2 results. Hence, they are an efficient alternative to investigate the intermolecular interaction in larger and/or more complex thiophene-based molecular systems.

The interaction energy of the CH\( \cdots \)NC hydrogen bond in 1-cyano-thiophene dimers is small (\(-21.7 \text{ kJ/mol}\)), but is in the range of hydrogen bonds. Moreover, we found several further indications for the formation of a hydrogen bond like interaction. The hydrogen bond is directional, close to linearity (150°) and the N\( \cdots \)H distance is 2.43 Å. We also studied dimers of substituted 1-cyano-thiophene using MP2. Altogether, we found that the effect of substitution on the strength and geometry of the hydrogen bond is quite small, but is largest in case of the methoxy group.

Concerning the \( \pi-\pi \)-stacking interaction in 1-cyano-thiophene dimers, we established that the stacking distance is only slightly increased in comparison to the thiophene dimer. Analogous to the thiophene dimer, the initial ideal sandwich arrangement of the monomers
Figure 4.14: Topologies and energies of the frontier molecular orbitals in stacks of (DCNDBQT)$_n$ ($n = 1–5$). Colors of the atoms are as in Figure 4.7.
changes to a displaced slightly tilted \( \pi \)-stacked structure in the optimised dimers. The CN groups in the most stable dimer are located farthest from each other, and the S atoms of the thiophene rings are on opposite sites. We also found that the CN groups increase the dispersion interaction in the \( \pi \)-stacked dimer. This is reflected in a significantly larger interaction energy and might be the reason for the stabilisation of the parallel compared to the perpendicular arrangement \([12, 207]\), as it was also found for methyl-substituted thiophene dimers \([62]\).

For very large molecular systems, MP2 and even standard DFT methods are computationally too demanding. Hence, we employed the very efficient SCC-DFTB(-DC) method to investigate the CH···NC hydrogen and \( \pi-\pi \)-stacking interaction in chains respective stacks of DCNDBQT molecules. We demonstrated the highly local character of the hydrogen bond interaction between the molecules in the chain having an interaction energy of about \(-23.5 \text{ kJ/mol}\). Furthermore, we found no indication for the presence of cooperativity effects that would further increase the strength of the hydrogen bond. The electronic properties of the monomer and of the chain are similar. Contrary to this, we established that the geometry, interaction energy and the electronic properties are significantly affected by the \( \pi-\pi \)-stacking interaction in the (DCNDBQT)\(_n\) stacks. Up to \( n = 12 \), they depend on the number of molecules in the stack. The examined parameters converge to constant values for larger stack sizes that are expected to be similar to those of a periodic stack of DCNDBQT molecules. We also noted that the interaction energy of the hydrogen bond is significantly smaller than that of the \( \pi-\pi \)-stacking interaction. Therefore, we conclude that the hydrogen bond interaction links the molecules into extended ribbons, but the \( \pi-\pi \)-stacking interaction is the main driving force in the self-assembly of the DCNDBQT molecules in the film [Figure 1.1 (c)].
5 Field-sensitivity of the functional thiophene-based molecules

5.1 Introduction

In an organic, ferroelectric field effect transistor (OFFET) [5, 19, 20], the dielectric gate element of a conventional OFET setup is substituted by a ferroelectric substrate such as BaTiO$_3$ or Pb(Zr,Ti)O$_3$, see Figure 1.1 (b). The ferroelectric material spontaneously polarises below a material-dependent critical temperature. The corresponding electric field can serve as gate field in the OFFET device and controls the charge injection and charge density inside the device. The maximum strength of an unscreened electric field above, e.g., the ferroelectric surface of BaTiO$_3$ was calculated to $10^{10}$ V/m [19, 20]. In the ideal case, the ferroelectric material forms domains with two preferable directions of polarisation, in-plane and orthonormal. The polarisation and associated electric field ($E_{F_{\perp}}$) oriented parallel to the surface normal is expected to have the largest influence on the adsorbed organic layer. Thus, the organic semiconducting material adsorbed on the ferroelectric substrate must be polarisable in this orthonormal direction. Moreover, the organic molecules must be well-ordered and appropriately aligned with respect to the electric field.

The two thiophene-based molecules, DCNDBQT and CNBTPA, synthesised by Haubner et al., cf. Figure 1.1 (c), are very attractive candidates with good prospects for application as the field-sensitive organic semiconductor in the ferroelectric OFET due to their extended polarisable $\pi$-electron system. The phosphonic acid headgroup of the CNBTPA molecule binds the molecules to the ferroelectric substrate and well-anchored, robust self-assembled monolayers are formed [11]. In particular, the high affinity of the phosphonic acid molecule to form strong and stable bonds to various metal oxide surfaces was demonstrated in detail in Chapter 3. The self-organisation of the DCNDBQT molecules in a $\pi$-stacked arrangement with their long molecular axis oriented perpendicular to the substrate surface, i.e. parallel to the (orthonormal) electric field induced by the ferroelectric material, is promoted further by the formation of intermolecular CN···HC hydrogen bonds and $\pi$-$\pi$-stacking interactions, as we discussed in Chapter 4 and as can be seen in Figure 1.1 (c).

In the present chapter, we investigate the interaction of these organic molecules with the electric field induced by the ferroelectric substrate to assess their potential as the field-sensitive organic semiconducting component in a ferroelectric OFET device. At first, we
calculated the polarisabilities of a set of phosphonic acids and quarterthiophene-based molecules shown in Figure 5.1 using DFT. The results of these calculations give a first qualitative estimation of the field-sensitivity of the molecules with respect to the orientation of the electric field in general. Moreover, the calculated results can be compared to experimental data. Second, to quantify further the influence of the electric field on the thiophene-based molecules, the HOMO-LUMO gap energy and the energies of the frontier molecular orbitals of quarterthiophene and their derivatives are calculated as a function of the strength of an external electric field by employing various DFT-based methods. The electric field was applied separately along the three molecular axis, i.e. in x-, y- and z-direction according to Figure 5.1 (e). The field-induced variation of the HOMO and LUMO is of particular interest because these orbitals correspond to the valence and conduction band of an inorganic semiconductor. They represent the conduction channel for the hopping transport of the charge carriers (electrons or holes) in the OFET device.

5.2 Computational details

The geometries of all molecules were optimised at the respective level of theory in the Gaussian03 program suite [229] using the 6-31G* basis set. The static electric dipole polarisabilities of the molecules were calculated in the program package DeMon [230] by employing the finite field method [74] and using an electric field strength of 0.0032 a.u. The DFT functional of Perdew, Burke and Ernzerhof (PBE) [48] and the triple-zeta-valence basis set with polarisation and field-induced polarisation functions (TZVP-FIP1) [231] were applied. The calculated polarisability is a symmetric second order tensor with nine components (α_{ij}, i,j = x,y,z). For the comparison with experimental data, the average (isotropic) polarisibility is calculated as:

\[ \bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \]  

(5.1)

Moreover, we restrict our discussion on the diagonal components of the polarisability tensor (α_{xx}, α_{yy}, α_{zz}), which correspond to the electric field applied in x-, y- and z-direction and which we denote as the longitudinal, transversal and perpendicular component of the polarisability, respectively. The optimised molecules are oriented with respect to the electric field vectors as shown in Figure 5.1.

The field-induced variation of the HOMO-LUMO gap energy and the HOMO and LUMO energy levels of the quarterthiophene derivatives [Figure 5.1 (e)] were calculated employing the SCC-DFTB method [49–56], the HF-DFT hybrid functional, B3LYP [218, 219], and the two full DFT functionals, SVWN [36, 37, 41, 232] and PBE [48]. The electric field was applied separately in x-, y- and z-direction and the electric field strength was appropriately increased up to \( 10^{10} \) V/m, which is the typical range for the electric field strength of an unscreened ferroelectric surface [19, 20]. The SCC-DFTB calculations were performed using the DFTB+ program package [110]. The Gaussian03 program suite [229] is used for the (hybrid) DFT calculations. Moreover, we applied the 6-31G* basis set in case of B3LYP,
5.3 Polarisability of the α-oligothiophenes

DFT-PBE and DFT-SVWN, whereas an atomic orbital valence basis was used in the SCC-DFTB method. This minimal basis employed in the SCC-DFTB scheme does not allow for a polarisation of the orbitals perpendicular to the molecular plane, as we discussed in Section 2.2.5. Thus, we obtained no field dependency in z-orientation of the electric field with this method for the planar molecules.

5.3 Polarisability of the α-oligothiophenes

The calculated diagonal components of the polarisability tensor and the average polarisability of the α-oligothiophenes as a function of the number of thiophene monomers \( n = 1-6 \) are plotted in Figure 5.2 (a). The average polarisability \( \bar{\alpha} \) increases approximately linear with increasing number of thiophene rings in the oligomer. Moreover, \( \alpha_{xx} \) is largest and \( \alpha_{zz} \) is smallest. Thus, the molecule is most polarisable in direction of the extension of the thiophene system and less polarisable in direction perpendicular to the molecular plane.

Furthermore, we note from Figure 5.2 (b) that the perpendicular and transversal polarisability components per thiophene ring, \( \alpha_{zz}/n \) and \( \alpha_{yy}/n \), are constant for \( n \geq 2 \), corresponding to the linear increase of these components with increasing chain length in Figure 5.2 (a). However, the value of the longitudinal component, \( \alpha_{xx}/n \), does not converge to a fixed value in the investigated range of \( n \). It increases with growing number \( (n) \) of thiophene
units due to the delocalization of the $\pi$-electrons along the chain. Since $\alpha_{xx}/n$ is much larger than the other two components, it determines the overall shape of the $\overline{\alpha}/n$. Therefore, $\overline{\alpha}/n$ does also not converge for $n \leq 6$. This is in agreement with the experimental finding that the average polarisability tends to increase linearly only at longer oligomers ($n \geq 7$) [233–235]. Also, it was found by Thienpont et al. [235] that the onset of saturation in the polarisability of the $\alpha$-oligothiophene series agrees with the convergence of the band gap as a function of the molecular size. According to our calculations, the HOMO-LUMO gap energy is not converged for $n \leq 6$, see Figure 5.5 (b) ($E_{FV}=0$ V/m).

In Table 5.1, the calculated $\overline{\alpha}/n$ results are compared with other theoretical and experimental data. A very good agreement with experimental and theoretical results is found for the thiophene monomer. Hartree-Fock in some cases, significantly underestimates the polarisability. The $\overline{\alpha}/n$ increases with increasing number ($n$) of thiophene units, but not as much as in experiment. However, the experimentally determined polarisabilities are very sensitive to the nature and physical state of the chains and depend quite strongly on the surrounding media and, thus, on the inter- and intramolecular interactions [233–235]. The calculated polarisabilities are more correct for “isolated” molecules.

### 5.4 Polarisability of the quarterthiophene derivates

The influence of the cyano group on the polarisability components of quarterthiophene is shown in Figure 5.3. The cyano and the butyl group both increase the average polarisability by 125 a.u. (DCNQT) and 130 a.u. (DBQT), due to the extension of the molecule.
Table 5.1: Comparison of the calculated and experimental average polarisabilities per thiophene ring ($\bar{\alpha}/n$) in [a.u.] for the $\alpha$-oligothiophenes.

<table>
<thead>
<tr>
<th>Method</th>
<th>Ref.</th>
<th>No. of thiophene rings $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>PBE/TZVP-FIP1</td>
<td>This work</td>
<td>66.0</td>
</tr>
<tr>
<td>HF/3-21G*</td>
<td>[236]</td>
<td>44.3</td>
</tr>
<tr>
<td>B3PW91/aug-cc-pVTZ</td>
<td>[236]</td>
<td>63.5</td>
</tr>
<tr>
<td>HF/6-31G**</td>
<td>[234]</td>
<td>49.4</td>
</tr>
<tr>
<td>HF/Sadlej</td>
<td>[234]</td>
<td>63.1</td>
</tr>
<tr>
<td>HF/aug-cc-pVTZ</td>
<td>[236]</td>
<td>61.5</td>
</tr>
<tr>
<td>B3LYP/6-31+G**</td>
<td>[237]</td>
<td>64.3</td>
</tr>
<tr>
<td>B3LYP/6-311++G**</td>
<td>[238]</td>
<td>60.7</td>
</tr>
<tr>
<td>AM1/TDHF</td>
<td>[239]</td>
<td>45.0</td>
</tr>
<tr>
<td>THF solut., $\lambda = 589$ nm</td>
<td>[233]</td>
<td>66.9</td>
</tr>
<tr>
<td>THF solut., $\lambda = \infty$ nm</td>
<td>[234, 235]</td>
<td>55.9</td>
</tr>
<tr>
<td>Thin film, $\lambda = 632.8$ nm</td>
<td>[233]</td>
<td>66.0</td>
</tr>
<tr>
<td>PMMA matrix, $\lambda = 632.8$ nm</td>
<td>[235]</td>
<td>-</td>
</tr>
</tbody>
</table>

The phosphonic acid [HPO(OH)$_2$, Figure 5.1 (a)] is the least polarisable of all studied molecules ($\bar{\alpha}=39.3$ a.u.) and shows nearly no anisotropy of the polarisability ($\alpha_{xx}=37.1$ a.u., and the substitution on two sites. However, the gain by extension of the well-polarisable thiophene system from thiophene to quarterthiophene is significantly larger ($\Delta\bar{\alpha}=312$ a.u.). The cyano group extends the molecular system in $x$-direction. Therefore, the polarisability component $\alpha_{xx}$ is most affected by this substituent (cf. DCNQT). The butyl group extends the molecular system in $y$-direction and to some extent by its all-trans zig-zag CH$_2$ units also in $z$-direction, i.e. perpendicular to the plane of the thiophene rings. Thus, this group increases in particular the polarisability components $\alpha_{yy}$ and $\alpha_{zz}$ (cf. DBQT). If both groups are included in the molecule (cf. DCNDBT), both effects are combined and the polarisability becomes significantly larger in all molecular directions.

From the calculated polarisabilities, we can draw the following three qualitative predictions concerning the field-sensitivity of the thiophene-based molecules studied here: First, the influence of the external field is generally largest in $x$-direction, i.e. parallel to the extension of the thiophene ring system and smallest in $z$-direction, i.e. perpendicular to the molecular plane. Second, the influence of the electric field in $x$-direction is further increased by extension of the molecular system in this direction, e.g., by attachment of the cyano group or by increasing the number of thiophene rings. Third, the influence of the electric field in $y$- and $z$-direction is increased by the attachment of the butyl group.

5.5 Polarisability of the phosphonic acids

The phosphonic acid [HPO(OH)$_2$, Figure 5.1 (a)] is the least polarisable of all studied molecules ($\bar{\alpha}=39.3$ a.u.) and shows nearly no anisotropy of the polarisability ($\alpha_{xx}=37.1$ a.u.,
Field-sensitivity of the functional thiophene-based molecules

Figure 5.3: Polarisability of the quarterthiophene derivates calculated using DFT-PBE/TZVP-FIP1. Lines are drawn to guide the eyes. The molecules are oriented with respect to the electric field vectors according to Figure 5.1 (e).

\( \alpha_{yy} = 40.6 \text{ a.u.}, \alpha_{zz} = 39.3 \text{ a.u.} \). The polarisability of the alkyl phosphonic acids \([C_nH_{2n+1}PA, \text{Figure 5.1 (d)}]\) is plotted as a function of the length of the alkyl chain in Figure 5.4 (a). The average polarisability increases linearly with increasing chain length. The average increment of growth per CH\(_2\) groups is 14 a.u. The increase of \( \Delta \alpha_{xx} \) is largest (\( \Delta \alpha_{xx} = 17 \text{ a.u.} \)) and approximately twice as large as \( \Delta \alpha_{yy} \) (\( \Delta \alpha_{yy} = 10 \text{ a.u.} \)), since the extension of the chain takes place mainly in x-direction.

The attachment of a thiophene unit to the phosphonic acid molecule also increases the average polarisability (\( \overline{\alpha} = 103.3 \text{ a.u.} \)). The value of \( \overline{\alpha} \) agrees with the sum of the average polarisabilities of the thiophene (\( \overline{\alpha} = 66.0 \text{ a.u.} \)) and phosphonic acid molecules. In Figure 5.4 (b), we show the calculated polarisability of the 2-(alkyl phosphonic acid)-thiophene molecule \([TC_nH_{2n}PA, \text{Figure 5.1 (b)}]\) as a function of the length of the alkyl chain, which is inserted between the phosphonic acid headgroup and the thiophene ring. In agreement with the above results of the alkyl phosphonic acids, the average polarisability and the polarisability components increase linearly with increasing chain length. The average increments are 36, 20, 28 and 28 a.u. for \( \alpha_{xx}, \alpha_{yy}, \alpha_{zz} \) and \( \overline{\alpha} \), respectively. They are approximately twice as large as the polarisabilities of the alkyl phosphonic acids. Hence, the thiophene moiety significantly influences the polarisability and its increase with extension of the alkyl chain.

In total, the phosphonic acids studied are not very sensitive towards the external electric field at a ferroic surface. Their field-sensitivity is significantly smaller in comparison with the quarterthiophenes. However, the phosphonic acids act as the anchoring molecules, that bind the more polarisable quarterthiophenes to the ferroelectric support and that promote the self-assembled alignment of the quarterthiophene molecules parallel to the induced electric field above the ferroic substrate \([11]\). They can also be used as spacer molecules to
adjust the distance between the quarterthiophene overlayer and the ferroelectric surface, and hence, to tune the electric field strength acting on the field-sensitive molecules.

5.6 Field-sensitivity of the quarterthiophene derivates

To quantify the influence of the electric field on the quarterthiophene derivates (QT, DC-NQT, DBQT, DCNDBQT), cf. Figure 5.1 (e), the field-induced variation of the HOMO-LUMO gap energy as well as the topologies and energies of the frontier molecular orbitals are calculated in dependence on the strength and orientation of the electric field using the SCC-DFTB method and the DFT-functionals B3LYP, SVWN and PBE. These results were the basis for the calculation of the electronic transport of electrons and holes through stacks of DCNDBQT molecules as part of an ferroelectric OFET device modelled by means of the program MOLED [5].

In Figure 5.5 (a), we plot the HOMO-LUMO gap energy of quarterthiophene as a function of the strength of the external electric field that was applied in x-direction. At zero electric field, the gap energy is calculated to about 1.9 eV in case of the SCC-DFTB and the two full DFT functionals PBE and SVWN, but the HOMO-LUMO gap energy is shifted by 1.1 eV to higher energies when using the B3LYP hybrid functional (3.0 eV). We attribute this to the Hartree-Fock part of this functional. A Hartree-Fock calculation within a 6-31G* basis gives a HOMO-LUMO gap of 8.6 eV. The strongest observed visible absorption in organic solution is about 3.2 eV [240]. It is predominantly built up from the HOMO-LUMO
Figure 5.5: HOMO-LUMO gap energy as a function of the electric field $E_F$ calculated a) for quarterthiophene using different DFT-based methods and b) for the $\alpha$-oligothiophenes ($n=1–6$) using DFT-PBE. The molecules are oriented with respect to the electric field vectors according to Figure 5.1.

transition and agrees with the B3LYP gap value. However, as we can see from Figure 5.5, all four methods give qualitatively the same trend of the HOMO-LUMO gap energy over a wide range of the electric field strength. Therefore, we restrict the further discussion on the DFT-PBE results.

As expected from the polarisability (see above), the strongest field-sensitivity of the HOMO-LUMO gap energy is obtained, if the external electric field is aligned parallel to the chain direction ($E_{Fx}$), cf. Figure 5.6 (a). The gap energy decreases with increasing electric field strength ($\leq 10^{10}$ V/m). Moreover, we obtain an increasing field-sensitivity in $x$-direction with increasing number of thiophene rings in the oligomer, see Figure 5.5 (b). In contrast, it can be seen in Figure 5.6 (b) and (c), that there is no field-induced variation of the HOMO-LUMO gap energy of quarterthiophene in $y$- ($E_{Fy}$) and $z$-direction ($E_{Fz}$) in the region of realisable electric field strengths of up to $10^{10}$ V/m. The gap energy increases for $E_{Fy}$ and decreases in case of $E_{Fy}$ only at even higher field strengths of about $E_{Fy} \geq 1.5 \cdot 10^{10}$ V/m and $E_{Fz} \geq 5 \cdot 10^{10}$ V/m, respectively.

At zero electric field, the attachment of the CN groups at $\alpha, \omega$-position of quarterthiophene (DCNQT) shifts the HOMO-LUMO gap by 0.2 eV to lower energy (1.7 eV). This red-shift through the presence of cyano groups was reported also by others [12, 13, 241]. Contrary to this, the substitution at $\beta, \beta'$-position of quarterthiophene by butyl groups (DBQT) does not change the gap energy (1.9 eV). Thus, the gap energy of DCNDBQT is almost the same as that of DCNQT.

In Figure 5.6, the calculated HOMO-LUMO gap energies of the four quarterthiophene derivates are plotted as a function of the strength and orientation of the external electric
field. The strongest field-sensitivity of the HOMO-LUMO gap is obtained, if the external electric field is applied in x-direction, as it can be seen in Figure 5.6 (a) and as it was predicted from the calculated polarisabilities [cf. Figure 5.2 (b)]. The gap energy of all investigated quarterthiophene derivates decreases with increasing strength of the electric field in x-direction. Moreover, the decrease in case of the substituted derivates is qualitatively, but also almost quantitatively, the same as for the pure quarterthiophene, though the curve of DCNQT and DCNDBQT is red-shifted by 0.2 eV. Figure 5.8 (a) illustrates that the π-electron system is strongly deformed along the DCNDBQT molecule with increasing $E_Fx$, thus, polarising the molecule towards one edge. Moreover, the energies of the HOMO and LUMO come closer to each other, see Figure 5.7 (a). This corresponds to a compensation of the polarisation in the molecule induced by the electric field component $E_Fx$. Also, we note the remarkable change in the orbital isosurface of the HOMO at $E_Fx = 9 \cdot 10^9$ V/m [Figure 5.8 (a)] due to the proximity of this energy level with lower energetically deformed occupied states, [Figure 5.7 (a)].

The gap energy of DCNQT shows the same trend with increasing strength of the electric field in y-direction as obtained for quarterthiophene, but it is red shifted, see Figure 5.6 (b). In contrast, the presence of the butyl group in the molecules β, β'-dibutyl-quarterthiophene and DCNDBQT causes a decrease of the gap energy for $E_Fy \geq 7 \cdot 10^9$ V/m. This is mainly attributed to the (avoided) crossing of the HOMO and LUMO energy levels with lower respective higher molecular orbitals [Figure 5.7 (b)], which is also reflected in the orbital isosurface of the HOMO that mixes with lower deformed states localised at the butyl chain similar to the case obtained for an applied electric field $E_Fx$ [Figure 5.8 (b)]. The influence of the electric field in z-direction is negligible in the range of electric field strength of up to $10^{10}$ V/m, independently on the substitution, see Figure 5.6 (c).

In conclusion, we state that both substituents have no significant influence on the field-induced variation of the HOMO-LUMO gap energy of the quarterthiophene molecule.
Field-sensitivity of the functional thiophene-based molecules

Figure 5.7: Energies of the occupied (solid line) and unoccupied (dashed line) orbitals around the gap of DCNDBQT in dependence on the strength and orientation of the electric field calculated using DFT-PBE/6-31G*. The molecule is oriented with respect to the electric field vectors according to Figure 5.1 (e).

Hence, all investigated quarterthiophene derivates are equally suitable with respect to their field-sensitivity for application in ferroelectric OFET devices.

5.7 Final conclusions

In the present chapter, we studied in detail the field-sensitivity of a set of phosphonic acid and thiophene-based molecules by means of DFT calculations to evaluate their potential as field-sensitive organic semiconducting material in a ferroelectric OFET device. In particular, we focussed on the polarisabilities of the molecules to get a first qualitative estimate of the influence of an external electric field on the molecular electronic structure. To quantify further the influence of the electric field, we calculated the HOMO-LUMO gap energy and the topologies and energies of the frontier molecular orbitals of quarterthiophene and their derivates as a function of the strength and orientation of an external electric field employing DFT-based methods.

We found that the phosphonic acids themselves are not polarisable enough towards the external electric field at a ferroic surface to be a optimal candidate as the field-sensitive organic component in an ferroelectric device. However, they can function as anchoring molecules that bind the more field sensitive quarterthiophene molecules to the ferroelectric substrate. Moreover, the strength of the electric field acting on the quarterthiophene-based overlayer can be tuned by varying the length of the alkyl chain of the anchoring phosphonic acid, i.e. by varying the distance between the ferroelectric material and the field-sensitive
5.7 Final conclusions

a) \( HOMO \quad LUMO \)

\[ EF_x = 0 \text{ V/m} \]

\[ EF_y = 0 \text{ V/m} \]

\[ EF_x = 3 \cdot 10^9 \text{ V/m} \]

\[ EF_y = 3 \cdot 10^9 \text{ V/m} \]

\[ EF_x = 6 \cdot 10^9 \text{ V/m} \]

\[ EF_y = 6 \cdot 10^9 \text{ V/m} \]

\[ EF_x = 9 \cdot 10^9 \text{ V/m} \]

\[ EF_y = 9 \cdot 10^9 \text{ V/m} \]

b) \( HOMO \quad LUMO \)

Figure 5.8: Orbital isosurfaces of the frontier molecular orbitals of DCNDBQT in dependence on the strength and orientation of the electric field. Yellow, blue, green and grey spheres indicate S, N, C and H atoms, respectively.
organic film.

For the quarterthiophene derivates, we found that the influence of the electric field in z-direction, i.e. perpendicular to the molecular plane, is negligible at least in the range of realisable electric field strengths up to $10^{10}$ V/m. But, in agreement with other theoretical and experimental results, the field-sensitivity is strongest for an external electric field $E_{Fx}$ aligned parallel to the well-polarisable x-direction of the thiophene ring. It further increases with increasing number of thiophene rings in the oligomer. However, neither the attachment of the butyl nor of the cyano group strengthens or weakens the influence of the electric field significantly in comparison to the ordinary quarterthiophene. This holds especially for the most relevant x-direction and for typical electric field strength of an unscreened ferroelectric surface ($\leq 10^{10}$ V/m). Consequently, the quarterthiophene derivates are suitable to operate as the field-sensitive component in devices that take advantage of a band-gap engineering, e.g. (optical) switches or ferroelectric OFET devices. In particular, our results were used further to investigate the electronic transport and device properties of an ferroelectric OFET device with the help of a phenomenological model MOLED [5]. Our calculations also emphasise the importance of the adsorption morphology, because the field-sensitivity can be exploited best if the molecules self-organise in a π-stacked arrangement with their longitudinal molecular axis oriented parallel to the (orthonormal) electric field induced by the ferroelectric substrate, cf. Figure 1.1 (c).
6 Summary

In this thesis, we investigated the structural and electronic properties of thiophene-based molecules with respect to their application as organic semiconducting component in organic-based electronic devices, e.g. (ferroelectric) OFETs (Figure 1.1). We also studied the adsorption of the phosphonic acid on metal oxide surfaces to demonstrate the applicability of this anchoring group to bind the functional thiophenes to the gate substrate. The investigations in this work are performed employing quantum-chemical *ab initio* and DFT-based methods.

Our first results presented in this work were dedicated to the adsorption of phosphonic acid on aluminium oxide and titanium oxide surfaces that we studied by means of density-functional based calculations. In case of aluminium oxide, we focussed on hydroxylated surface models based on corundum \(\alpha\)-Al\(_2\)O\(_3\) (0001), bayerite \(\beta\)-Al(OH)\(_3\) (001) and boehmite \(\gamma\)-AlOOH (010). On these, we studied monodentate, bidentate and tridentate adsorption of phosphonic and ethyl phosphonic acid on all possible adsorption sites considering two different surface coverages. By comparing the energies of the adsorption complexes, we determined the favored adsorption sites for each coordination mode and surface structure. We found that the preference of an adsorption site is strongly influenced by its geometry and that the regioselectivity increases when going from monodentate, bidentate and tridentate adsorption complexes. Moreover, the energetically favored sites for mono-, bi- and tridentate binding of the acids allow a logical adsorption sequence that strongly supports a step-by-step condensation reaction between the acid and the substrate surface. The phosphonic acid also tends to bind to structural similar sites on the three surfaces and, the attachment of the ethyl chain has no influence on the preference of an adsorption site.

Furthermore, we examined the structural organisation of some long-chain alkyl phosphonic acids on the three aluminium oxide surfaces in dependence on their binding mode, on the length of the alkyl chain, on the surface structure and on the surface coverage. We established that the alkyl chains of the molecules are always tilted with respect to the surface normal and that the tilt angles are similar for the mono-, bi- and tridentate adsorption complexes. Thus, we conclude that the binding modes cannot be determined by the tilt angle. The tilt angles at full surface coverage are similar to the angles observed for the single adsorbed molecules. Hence, we state that the maximum packing of the alkyl chains is not reached and that the density of adsorption sites on the surface limits the concentration of phosphonic acids in the monolayer. The distortion of the alkyl chains in the full-coverage
situation indicates the presence of lateral interactions between the alkyl chains.

In case of titanium oxide, we studied the adsorption of phosphonic acid on TiO$_2$ anatase (101) and rutile (110) surfaces. In particular, we focused on the adsorption energies as well as on the geometrical and electronic properties of several adsorption complexes. We found that several adsorption structures are likely to be present on the specific TiO$_2$ surfaces. Those complexes have exclusively bidentate configuration. They have similar adsorption energies, but different geometries. Even the monodentate complexes tend to relax towards a bidentate adsorption structure. This might explain at least to some extend the difficulties and the discrepancies in the experimental and theoretical findings of a preferred binding mode.

We compared the adsorption of phosphonic acid with the results for the coupling related formic acid. The preferred adsorption modes of both formic and phosphonic acid on both surfaces are dissociated bridging bidentate complexes. However, we found that phosphonic acid binds more strongly to TiO$_2$ than formic acid. A detailed analysis of the Mulliken charge distribution and the electronic structure properties showed that the surface atoms experience a bulk-like situation upon adsorption. This effect is more developed in the bidentate complexes and in the adsorption models involving phosphonic acid. It strongly supports the obtained preference of the bidentate complexes and the more stable adsorption complexes in case of phosphonic acid. Therefore, we conclude that for the design of robust and well-anchored organic films on TiO$_2$ substrates, phosphonic acids are the preferable choice as anchoring molecules in comparison to carboxylic acids. A proper coupling between the support and the organic film can help to re-establish bulk electronic properties at the substrate side of the interface. Our results also open the perspective to tune the electronic properties of an organic/inorganic system by the inclusion of a suitable spacer group and the design of a proper terminal functional molecule.

In this thesis, we performed optimizations of adsorbed phosphonic acid in vacuum and at 0 K temperature using rather small test systems. However, in experiment the adsorption of (organo) phosphonic acids takes place in aqueous solutions or other polar solvents at various temperatures (T $\neq$ 0) [17, 86, 97–102, 104]. The presence of water and/or other solvents might considerably influence the activation barriers for elementary steps of the adsorption reaction as well as the selectivity of the preferred adsorption site and binding mode. Thus, for a further detailed, comprehensive and realistic description of the adsorption of phosphonic acid or similar on AlO- or TiO-based surfaces, the usage of much more complex systems are necessary. The efficiency of the SCC-DFTB method allows the calculation of such complex and extended structures with some thousands of atoms. We extensively demonstrated the reliability of the SCC-DFTB method for this chemical system in the present work. Hence, this thesis opens the way for studies of adsorption on more complex metal oxide materials, e.g. including surface protonation and hydroxylation, solvent effects, larger adsorbate molecules or defect diffusion in the surface materials.

The second main objective of this work was the investigation of the CN···HC hydrogen bond and the $\pi$-$\pi$-stacking interaction between functional thiophene-based molecules
by MP2 and DFT-based calculations. These molecules are potentially applicable as the organic semiconducting material in OFET devices due to their high structural ordering. We found that the DFT-based methods employed here provide a reasonably good description of the intermolecular interaction in the present system. Hence, especially the SCC-DFTB(-DC) method provides an efficient alternative to investigate the intermolecular interaction in larger thiophene-based molecular systems. Furthermore, we put special focus on the influence of the intermolecular interactions and of the number of molecules in a chain respective stack of DCNDBQT molecules on the technologically relevant structural and electronic properties. We found that the CN···HC hydrogen bond interaction possess a highly local character and that the geometry and the electronic properties are only affected marginally by this interaction. The interaction energy of the hydrogen bond is significantly smaller than that of the π-π-stacking interaction. Therefore, we conclude that the CN···HC hydrogen bond link the molecules into extended ribbons, but the π-π-stacking interaction is the main driving force in the self-assembly of the DCNDBQT molecules. Indeed, the π-π-interaction stabilises the parallel stacked arrangement of the molecules compared to the perpendicular, herringbone one. Furthermore, we established that the intermolecular structure, the interaction energy, the gap energies and the topologies and energies of the frontier molecular orbitals are significantly influenced by the π-π-stacking interaction. For small stack sizes, they depend on the number of molecules in the stack. The examined parameters converge to specific values for larger stack sizes that might correspond to those of a periodic stack of DCNDBQT molecules.

In the last part of this thesis, we evaluated in detail the influence of the electric field on the phosphonic acid anchoring molecule and the quarterthiophene derivates in order to asses their potential as the field-sensitive organic semiconducting component in ferroelectric OFET devices. We found that the polarisabilities of the phosphonic acid based molecules are significantly smaller than those of quarterthiophene and its derivates. Thus, we conclude that the phosphonic acid is not sensitive enough towards the external electric field at a ferroelectric substrate to be used as the field-sensitive organic component in a ferroelectric OFET device. However, it can well anchor the more field-sensitive quarterthio- phenes to the ferroic surface. Also, they can be employed to tune the electric field strength acting on the bonded thiophene molecules by the length of the alkyl chain (inserted in between the anchoring phosphonic acid headgroup and the functional field-sensitive thiophene molecular part) that determines the distance between the ferroelectric substrate and the field-sensitive organic film.

For the quarterthiophene derivates, we obtained the strongest field-sensitivity for an external electric field aligned parallel to the extension of the thiophene framework. This emphasises the importance of the adsorption morphology of the molecules in the film in a π-stacked fashion with their longitudinal axis oriented parallel to the (orthonormal) electric field induced by the ferroelectric substrate. We also found that the butyl and the cyano groups in the DNCDBQT molecule have no influence on the field-sensitivity in comparison with the ordinary quarterthiophene molecule, especially for the most relevant longitudinal
direction and for typical electric field strength of an unscreened ferroelectric surface ($\leq 10^{10}$ V/m). Therefore, we conclude that all studied quarterthiophene derivates are suitable to act as the field-sensitive organic components in devices that take advantage of a band-gap engineering e.g. (optical) switches or ferroelectric OFET devices.

In the present thesis, we demonstrated in detail the applicability of functional thiophene-based molecules to operate as the (field-sensitive) organic semiconducting component in a (ferroelectric) OFET device. We also showed that the phosphonic acids can bind the organic molecules to the dielectric or ferroelectric material and well-anchored, robust self-assembled monolayers are formed. Hence, this thesis opens the way for the further research and development of a (ferroelectric) OFET based on functional thiophenes in general. Indeed, the present results are the basis for the determination of the hopping transport parameters and the calculation of the charge transport (conductivity) of the organic thiophene-based material in the device. First calculations were already performed using the phenomenological model called multilayer organic-light-emitting diodes (MOLED) [5] and the surface Green function method [8–10]. Therein, Morawetz et al. [9] demonstrated the shaping of the conductance and the current fluctuations as a function of the lead barrier height. Also, a nonlinear electric and thermal conductance and thermopower at high bias voltage was found. These results make the investigated thiophene-based molecules interesting not only for OFETs but also as elements for thermoelectric applications.


7 List of publications related to this thesis

1. Infrared spectra of alkylphosphonic acid bound to aluminium surfaces
   R. Luschtinetz, G. Seifert, E. Jähne, and H.-J. P. Adler,

2. Adsorption of phosphonic and ethylphosphonic acid on aluminum oxide surfaces

3. Self-assembled monolayers of alkylphosphonic acid on aluminum oxide surfaces – A theoretical study

4. Adsorption of phosphonic acid on TiO$_2$ anatase (101) and rutile (110) surfaces
   R. Luschtinetz, J. Frenzel, T. Milek, and G. Seifert,

5. Anchoring functional molecules on TiO$_2$ surfaces: a comparison between the carboxylic and the phosphonic acid group
   R. Luschtinetz, S. Gemming, and G. Seifert,

6. Current without external bias and diode effect in shuttling transport of nanoshfts
   K. Morawetz, S. Gemming, R. Luschtinetz, L. M. Eng, G. Seifert, and A. Kenfack,

7. Transport and noise in organic field-effect devices
   K. Morawetz, S. Gemming, R. Luschtinetz, T. Kunze, P. Lipavsky, L. M. Eng, G. Seifert,
   V. Pankoke and P. Milde,
8. **The role of homophase and heterophase interfaces on transport properties in structured materials**  
   S. Gemming, T. Kunze, K. Morawetz, V. Pankoke, R. Luschtinetz, and G. Seifert,  

9. **Theoretical studies on the π-π-stacking in functional thiophene-based molecules**  
   R. Luschtinetz, and G. Seifert,  
   in preparation.

10. **Theoretical study on the CH···NC hydrogen bond interaction in thiophene-based molecules**  
    R. Luschtinetz, S. Gemming and G. Seifert,  

11. **Polymorphism in ferroic functional elements**  

12. **Modelling ferroic functional elements**  
    S. Gemming, R. Luschtinetz, W. Alsheimer, G. Seifert, C. Loppacher, and L. M. Eng,  

13. **Electronic transport properties through thiophenes on switchable domains**  
    T. Kunze, S. Gemming, V. Pankoke, K. Morawetz, R. Luschtinetz, and G. Seifert,  

14. **Theoretical studies on the field-sensitivity of functional thiophene-based molecules**  
    R. Luschtinetz, S. Gemming, and G. Seifert,  
    in preparation.
Versicherung nach § 5 Abs. 1 Nr. 5

Versicherung nach § 5 Abs. 1 Nr. 5 der Promotionsordnung der Fakultät Mathematik und Naturwissenschaften an der Technischen Universität Dresden in der Fassung vom 23. Februar 2011:

a) Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

b) Die vorliegende Arbeit wurde in der Professur für Physikalischen Chemie I der Fachrichtung Chemie und Lebensmittelchemie an der Fakultät Mathematik und Naturwissenschaften der Technischen Universität Dresden unter der wissenschaftlichen Betreuung von Prof. Gotthard Seifert angefertigt.

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