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First-principles investigation of organic molecules on metal surfaces as model systems for laser-induced surface reactions

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Abstract

Organic–metal interfaces have been studied for decades, yet directly imaging the motion of electrons within molecular orbitals and its influence on molecular functionality remains a major challenge. The orbital-cinema project [1] aims to address this challenge, and the present work contributes to this goal by investigating two model systems, the tetracene–maleic anhydride Diels–Alder adduct (4A-MAD) and heptahelicene (7HC) adsorbed on Ag(110). The focus is placed on their adsorption geometries, electronic structures, and, for 7HC, their response to a few-cycle mid-infrared laser field. Density functional theory (DFT) is used to investigate the ground-state properties, while time-dependent density functional theory (TDDFT) is employed to study the time-dependent response.

For 4A-MAD/Ag(110), the investigation is motivated by the potential use of the system to study retro-[4+2] cycloaddition dynamics on metal surfaces. Several adsorption geometries are investigated, and their electronic structures are calculated. The theoretical photoemission data obtained using photoemission orbital tomography (POT) are then compared with experimental angle-resolved photoemission spectroscopy (ARPES) data to further assess the adsorption geometries. The comparison provides insight into the adsorption geometry and identifies the configurations that are most consistent with the experimental data.

For 7HC/Ag(110), the spiral structure and chiral nature of the molecule motivates the investigation of light-induced helical currents. The adsorption geometry and electronic structure are first characterized using ground state DFT. Subsequently, TDDFT calculations are performed for the free-standing molecule under excitation with a few-cycle mid-infrared laser field. The calculations reveal an induced current with a spiral-like spatial structure and provide a first assessment of the associated magnetic response. These results establish 7HC as a promising model system for investigating light-induced helical currents and provide a basis for future investigations of the molecule–surface system.

Kurzfassung

Grenzflächen zwischen organischen Molekülen und Metallen werden seit Jahrzehnten untersucht, doch die direkte Abbildung der Bewegung von Elektronen innerhalb der Molekülorbitale und deren Einfluss auf die Funktionalität von Molekülen stellt jedoch nach wie vor eine große Herausforderung dar. Das "Orbital-Cinema"-Projekt [1] verfolgt das Ziel, diese Herausforderung zu bewältigen. Die vorliegende Arbeit trägt zu diesem Ziel bei, indem zwei Modellsysteme untersucht werden: das Tetracen-Maleinsäureanhydrid-Diels-Alder-Addukt (4A-MAD) und Heptahelicen (7HC), jeweils adsorbiert auf Ag(110). Der Schwerpunkt liegt auf den Adsorptionsgeometrien und elektronischen Strukturen der beiden Systeme sowie für 7HC, auf dessen Reaktion auf ein wenige Zyklen umfassendes Laserfeld im mittleren Infrarotbereich. Zur Untersuchung der Eigenschaften im Grundzustand wird die Dichtefunktionaltheorie (DFT) verwendet, während die zeit-abhängige Dichtefunktionaltheorie (TDDFT) zur Untersuchung der zeitabhängigen Antwort eingesetzt wird.

Im Fall von 4A-MAD/Ag(110) steht die Frage im Mittelpunkt, ob sich das System zur Untersuchung der Dynamik einer Retro-[4+2]-Cycloaddition auf Metalloberflächen eignet. Dazu werden mehrere Adsorptionsgeometrien untersucht und ihre elektronischen Eigenschaften berechnet. Die mithilfe der Photoemissions-Orbitaltomographie (POT) erhaltenen theoretischen Photoemissionsdaten werden anschließend mit experimentellen Daten der winkelaufgelösten Photoelektronenspektroskopie verglichen, um die verschiedenen Adsorptionsgeometrien weiter zu beurteilen. Der Vergleich liefert Einblicke in die Adsorptionsgeometrie und ermöglicht die Identifikation jener Konfigurationen, die am besten mit den experimentellen Daten verträglich sind.

Bei 7HC/Ag(110) motiviert die spiralförmige und chirale Struktur des Moleküls die Untersuchungen zu lichtinduzierten helikalen Strömen. Zunächst werden die Adsorptionsgeometrie und die elektronischen Eigenschaften mittels DFT charakterisiert. Anschließend werden TDDFT-Berechnungen für das freistehende Molekül, wobei ein wenige Zyklen umfassendes Laserfeld im mittleren Infrarotbereich das System anregt. Die Berechnungen zeigen einen induzierten Strom mit einer spiralförmigen räumlichen Struktur und geben einen ersten Einblick in die damit verbundene magnetische Antwort. Diese Ergebnisse zeigen, dass 7HC ein vielversprechendes Modellsystem für die Untersuchung lichtinduzierter helikaler Ströme darstellt, und bilden eine Grundlage für zukünftige Untersuchungen des Molekül-Oberflächen-Systems.

Disclaimer usage of AI

Generative AI and machine-learning-based tools, including ChatGPT, Gemini, UniGPT, DeepSeek, Microsoft Copilot, and DeepL, have been used by myself and, most likely, by colleagues at various stages of the research and writing process. Their use included code generation and debugging, translation, grammar and language improvement, literature searches, and assistance in understanding new concepts.

Due to the integration of these tools into the research process and the difficulty of tracking their use precisely across different stages and contributors, a complete line-by-line account of their influence on this master thesis cannot be provided.

As the author of this Master's thesis, I take full responsibility for its content, including all scientific interpretations and conclusions.

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List of Acronyms and Symbols

4A-MAD tetracene–maleic anhydride Diels–Alder adduct. 3, 13, 15, 19, 21, 38–41, 44–46, 48–53, 55, 56, 58, 71, 72

7HC heptahelicene. 3, 13, 19, 21, 51, 52, 56, 58, 59, 63, 71, 72

ARPES angle-resolved photoemission spectroscopy. 3, 19, 21, 30–32, 49, 51, 58, 71

ASC Austrian scientific computing. 37

ASE atomic simulation environment. 52

CISS chirality-induced spin selectivity. 21, 51

DFT density functional theory. 3, 23–25, 28, 29, 31–33, 37, 38, 46, 47, 51, 71

GGA generalized gradient approximation. 28, 29

H hollow. 20, 39

HOMO highest occupied molecular orbital. 46, 55, 56

k-map photoemission momentum map. 55

KS Kohn–Sham. 26–28, 31, 33

LB long-bridge. 20, 39

LDA local density approximation. 28, 29

LUMO lowest unoccupied molecular orbital. 46, 56

MOPDOS molecular orbital projected density of states. 13, 45, 46, 56, 59

PBE Perdew, Burke, Ernzerhof. 29

pDOS projected density of states. 13, 44, 45, 55

PEEM photoemission electron microscope. 49

PES photoemission spectroscopy. 30

POT photoemission orbital tomography. 3, 19, 23, 71

SB short-bridge. 20, 39

SCF self-consistent field. 27

T top. 20, 39

TDDFT time-dependent density functional theory. 3, 20, 21, 23, 32–34, 38, 51, 63, 71, 72

TDKS time-dependent Kohn-Sham. 33, 34

VASP Vienna ab initio simulation package. 37, 45

1 Introduction

Over the past decades, molecular orbitals have become an important concept for describing and understanding the electronic structure of atoms and molecules. Their spatial distribution provides an intuitive picture of how electrons are arranged within a molecule and can be used to rationalize chemical bonding and reactivity. In particular, the orbital picture has proven useful for understanding how the electronic structure of a molecule influences chemical reactions and how changes in molecular geometry can be connected to changes in its electronic properties [2, 3, 4]. While theoretical descriptions of molecular orbitals have become well established, their experimental observation and characterization remain an important challenge.

One promising approach to access molecular orbital information experimentally is photoemission orbital tomography (POT). Pioneered by Puschnig, Ramsey, Tautz and co-workers, POT combines angle-resolved photoemission spectroscopy (ARPES) with electronic-structure calculations to obtain information about the spatial structure of molecular orbitals [5, 6, 7]. The method has successfully been applied to a variety of molecular systems and provides a direct connection between experimentally measured photoemission patterns and theoretically calculated molecular orbitals. However, conventional POT measurements provide predominantly energy- and momentum-resolved information under static conditions. Accessing the evolution of molecular orbitals on ultrafast timescales therefore remains a significant challenge.

This idea inspired the "orbital cinematography" project [1], which aims not only to make static images of molecular orbitals accessible, but also to obtain snapshots of orbital images during excited state dynamical evolution. The long-term goal is to observe how electronic states evolve on femtosecond, and potentially sub-femtosecond timescales, thereby providing insight into fundamental processes such as charge transfer, electron motion within molecules, and the electronic mechanisms underlying chemical reactions. Establishing such a technique requires a step-by-step development of both the experimental methodology and the theoretical understanding of suitable model systems.

The present work contributes to this development by investigating two different organic molecules adsorbed on a Ag(110) surface. The two molecules considered are the tetracene–maleic anhydride Diels–Alder adduct (4A-MAD) and heptahelicene (7HC). Both systems are considered as potential model systems for future time-resolved investigations, but they are motivated by different physical questions. The 4A-MAD system is investigated as a potential platform for further studying retro-[4+2] cycloaddition dynamics, while 7HC is studied to explore its potential to support light-induced helical currents arising from its spiral and chiral structure.

As a first step, the adsorption geometry and electronic structure of each system are investigated in order to establish a reliable understanding of the molecule-surface interface.

Depending on the properties identified in this initial characterization, further analyses are performed to investigate the suitability of the respective system for future experiments. For the heptahelicene system, this includes an investigation of its response to an external ultrashort laser pulse using time-dependent density functional theory (TDDFT).

Substrate

Both molecular systems investigated in this work are adsorbed on a Ag(110) surface. The choice of this substrate is motivated by several experimental and theoretical considerations. The Ag(110) surface exhibits a two-fold symmetric surface structure and is therefore known to favour a uniaxial alignment of molecules during the formation of a molecular monolayer using typical experimental growth conditions [8, 9]. Furthermore, the surface has been extensively studied and is well established as a model system for investigations of organic molecules on metal surfaces [10, 11]. The experience available within the research group provides additional knowledge that can be used when selecting and evaluating possible adsorption geometries.

Throughout this work, several high-symmetry adsorption sites of the Ag(110) surface are considered. These are denoted as **hollow (H)**, **top (T)**, **short-bridge (SB)**, and **long-bridge (LB)** sites. Their positions relative to the principal crystallographic directions, [001] and [1-10], of the surface are illustrated in figure 1.1.

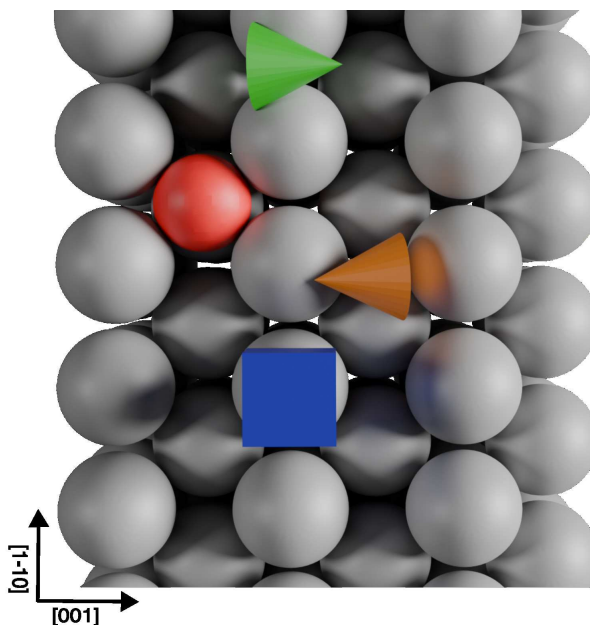


Figure 1.1: Visualisation of the high-symmetry adsorption sites on the Ag(110) surface

4A-MAD

The first molecular system investigated in this work is the tetracene-maleic anhydride Diels–Alder adduct (4A-MAD). This molecule is considered as a model system for

investigating light-induced retro-[4+2] cycloaddition reactions on surfaces [12, 13]. The molecular structure contains a Diels-Alder adduct formed between tetracene and maleic anhydride. Upon excitation with light, the reverse reaction could potentially lead to cleavage of the newly formed carbon-carbon bonds and the recovery of the tetracene backbone.

Understanding the adsorption geometry and molecule-surface interaction is an important prerequisite for investigating such a light-induced reaction. The first part of this work therefore focuses on identifying energetically favourable adsorption configurations and comparing their calculated electronic structure with experimental ARPES data. This provides a basis for assessing whether 4A-MAD is a suitable model system for future investigations of light-induced bond cleavage and retro-[4+2] cycloaddition dynamics.

7HC

The second molecular system studied in this work is heptahelicene (7HC). Heptahelicene consists of seven ortho-fused benzene rings arranged in a helical structure, resulting in a chiral molecular geometry. This structural chirality makes 7HC particularly interesting as a candidate system for investigating light-induced helical currents.

In addition, chiral molecules have attracted considerable interest in the context of the chirality-induced spin selectivity (CISS) effect. CISS describes the experimentally observed dependence of electron spin transport on molecular chirality, making chiral molecules potential candidates for spin-selective electron transport [14, 15]. The present work does not directly investigate whether 7HC exhibits CISS or acts as a spin filter, rather, its properties make it a promising candidate for investigating whether such behaviour can be observed in a controlled model system.

After establishing the adsorption geometry and electronic structure of 7HC, its response to an external time-dependent laser field is investigated using TDDFT. In particular, the induced current density and resulting orbital magnetic moment are analysed to determine whether light-induced currents with a helical or circulating character can arise. These calculations provide a first theoretical assessment of the suitability of 7HC for future experiments aimed at investigating ultrafast electronic dynamics and, ultimately, orbital cinematography.

The remainder of this thesis is structured as follows. First, the theoretical foundations relevant to this work are introduced, including density functional theory (DFT), time-dependent density functional theory (TDDFT), and photoemission orbital tomography (POT). The theoretical background is followed by the results for the two investigated molecular systems, beginning with 4A-MAD and subsequently discussing heptahelicene (7HC). Finally, the results are discussed in a broader context and the main conclusions of this work are summarized.

2 Theory

This theory section provides an introduction to the fundamental concepts required to understand the computational methods and analysis techniques employed in this work. First, the quantum-mechanical many-electron problem is introduced, followed by an overview of density functional theory (DFT) as a widely used approach to treat this complex problem. Subsequently, time-dependent density functional theory (TDDFT) is briefly discussed, including the theoretical framework required to describe the time-dependent response of electronic systems and the quantities analyzed in this work.

Finally, the principles of photoemission orbital tomography (POT) are introduced. This provides the necessary background for understanding the connection between calculated electronic structures, momentum-resolved photoemission measurements, and the experimental data used throughout this thesis.

2.1 Quantum mechanical many electron problem

Throughout this work, the focus lies on the electronic properties of organic molecule/metal interfaces which are addressed by seeking a solution for the underlying many-electron problem. The starting point is the many-body Hamiltonian H_{mb} , which is expressed in atomic units ($m_e = \hbar = 1$, $\frac{e^2}{4\pi\epsilon_0} = 1$) as

$$H_{\text{mb}} = - \underbrace{\sum_i \frac{1}{2} \nabla_i^2}_{\hat{T}_e} - \underbrace{\sum_a \frac{1}{2m_a} \nabla_a^2}_{\hat{T}_n} - \underbrace{\sum_{a,i} \frac{Z_a}{|\vec{r}_i - \vec{r}_a|}}_{\hat{V}_{en}} + \underbrace{\sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\hat{V}_{ee}} + \underbrace{\sum_{a<b} \frac{Z_a Z_b}{|\vec{r}_a - \vec{r}_b|}}_{\hat{V}_{nn}} \quad (2.1)$$

The first $\hat{T}_e$ and second $\hat{T}_n$ terms denote the kinetic energy of the electrons and nuclei, respectively. The electron-nucleus interaction is described by the attractive Coulomb term $\hat{V}_{en}$. The remaining two terms account for the repulsive electron-electron interaction $\hat{V}_{ee}$ and nucleus-nucleus interaction $\hat{V}_{nn}$, respectively. The summations over $i < j$ and $a < b$ include all electron-electron and nucleus-nucleus pairs while avoiding self-interactions and double counting of equivalent pairs.

For extended systems, such as molecule-metal surface interfaces, a direct solution of this many-body Hamiltonian quickly becomes computationally infeasible. Therefore, further approximations are required. The first simplification is introduced by the Born–Oppenheimer approximation, which exploits the large mass difference between nuclei and electrons. Since nuclei are significantly heavier, their motion occurs on a much slower timescale compared to the electronic motion. Consequently, the nuclear kinetic energy term $\hat{T}_n$ can be neglected when solving the electronic problem [16].

Furthermore, within the clamped-nuclei approximation, the nuclear positions are treated as fixed parameters. As a result, the nucleus-nucleus interaction term which does not depend on the electronic coordinates contributes only as a constant energy shift. The resulting electronic Hamiltonian H_e can therefore be written as

$$H_e = - \underbrace{\sum_i \frac{1}{2} \nabla_i^2}_{\hat{T}_e} + \underbrace{\sum_i v(\vec{r}_i)}_{\hat{V}_{ext}} + \underbrace{\sum_{i < j} \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\hat{V}_{ee}}, \quad (2.2)$$

where V_{ext} represents the external potential generated by the fixed nuclei acting on the electrons. This potential is given by

$$v(\vec{r}) = - \sum_a \frac{Z_a}{|\vec{r} - \vec{r}_a|} \quad (2.3)$$

The resulting electronic Hamiltonian can then be used in the time-independent Schrödinger equation to obtain the stationary states of the system

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

For the electronic problem with fixed nuclear positions, this leads to the stationary many-electron Schrödinger equation

$$\hat{H}_e \Psi_q(\{\vec{r}_i, \sigma_i\}, \{\vec{r}_a\}) = E_q(\{\vec{r}_a\}) \Psi_q(\{\vec{r}_i, \sigma_i\}, \{\vec{r}_a\}) \quad (2.5)$$

Here, $\vec{r}_i$ denotes the spatial coordinate of electron i , while σ_i represents its spin degree of freedom. The many-electron wavefunction therefore depends on both the spatial and spin coordinates of all electrons. Although this formulation provides a complete description of the electronic system, solving this equation directly remains computationally extremely difficult for systems containing many electrons. In fact, as shown by Kohn, the complexity of the many-electron wavefunction increases exponentially with the number of electrons N , making a direct treatment impossible even for moderately sized systems [17]. Therefore, an alternative approach based on the electron density rather than the full many-electron wavefunction is introduced in the following section.

2.2 Density functional theory

2.2.1 The electron density as the fundamental variable

Instead of solving the many-electron Schrödinger equation directly, DFT reformulates the problem in terms of the electron density, which serves as the fundamental variable. The key idea is that the ground-state energy can be expressed as a functional of the electron spin density $n_\sigma(\vec{r})$, rather than the many-electron wavefunction. The spin-dependent electron density is defined as

$$n_\sigma(\vec{r}) = N \sum_{\sigma_2 \dots \sigma_N} \int d^3r_2 \dots \int d^3r_N |\psi(\vec{r}\sigma, \vec{r}_2\sigma_2, \dots, \vec{r}_N\sigma_N)|^2 \quad (2.6)$$

The foundation of DFT is provided by the first Hohenberg-Kohn theorem, which states that the external potential $v(\vec{r})$ is uniquely determined by the ground-state electron density $n(\vec{r})$, up to an arbitrary additive constant [18]. Consequently, the electronic Hamiltonian is also uniquely determined by the ground-state density.

The proof proceeds by assuming the opposite and showing that this leads to a contradiction. Assume that two different external potentials $v(\vec{r}), v'(\vec{r})$, differing by more than a constant, produce the same ground-state density $n(\vec{r})$. The corresponding ground-state wavefunctions are denoted by ψ and ψ' , respectively [18]. The total energies of the two systems can then be written as

$$E = \langle \psi | \hat{H} | \psi \rangle = \underbrace{\int d^3r v(\vec{r}) n(\vec{r})}_{\langle \psi | \hat{V}_{\text{ext}} | \psi \rangle} + \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle \quad (2.7)$$

and energy E'

$$E' = \underbrace{\int d^3r v'(\vec{r}) n(\vec{r})}_{\langle \psi' | \hat{V}_{\text{ext}} | \psi' \rangle} + \langle \psi' | \hat{T} + \hat{V}_{ee} | \psi' \rangle \quad (2.8)$$

Applying the minimal principle to this we arrive at the following inequality

$$E < \int d^3r v(\vec{r}) n(\vec{r}) + \langle \psi' | \hat{T} + \hat{V}_{ee} | \psi' \rangle = E' + \int [v(\vec{r}) - v'(\vec{r})] n(\vec{r}) d^3r \quad (2.9)$$

and, analogously for E'

$$E' < E + \int [v'(\vec{r}) - v(\vec{r})] n(\vec{r}) d^3r \quad (2.10)$$

Combining these two inequalities leads to the contradiction

$$E + E' < E + E'. \quad (2.11)$$

Therefore, the initial assumption must be false, proving that no two different external potentials can give rise to the same ground-state electron density. Hence, the ground-state density uniquely determines the external potential and, consequently, the Hamiltonian of the system [18].

2.2.2 Variational principle and the ground-state energy

The ground-state energy of an electronic system can, in principle, be obtained by solving the many-electron Schrödinger equation. Alternatively, it can be determined using the Rayleigh–Ritz variational principle, which states that the expectation value of the Hamiltonian is minimized by the exact ground-state wavefunction

$$E = \min_{\psi} \langle \psi | \hat{H} | \psi \rangle. \quad (2.12)$$

The second Hohenberg–Kohn theorem extends this variational principle from many-electron wavefunctions to the electron density. Instead of minimizing the energy with respect to the many-electron wavefunction, the energy can be expressed as a functional of the electron density $n(\vec{r})$. To formally define this functional, the constrained-search formulation is introduced [19]. For a given density $n(\vec{r})$, all possible many-electron wavefunctions Ψ that yield this density are considered. Within this set, the expectation value of the internal energy contribution, consisting of the kinetic energy and electron–electron interaction, is minimized

$$F[n(\vec{r})] = \min_{\psi \rightarrow n} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle. \quad (2.13)$$

This universal functional $F[n(\vec{r})]$ is independent of the external potential and contains all contributions arising from the kinetic energy of the electrons and their mutual interaction. The total energy functional can therefore be written as

$$E[n(\vec{r})] = \min_{\psi \rightarrow n} \langle \psi | \hat{H} | \psi \rangle = \min_{\psi \rightarrow n} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle + \int d^3r v(\vec{r}) n(\vec{r}) = F[n(\vec{r})] + \int d^3r v(\vec{r}) n(\vec{r}) \quad (2.14)$$

The energy functional (equation (2.14)) is subsequently minimized with respect to the electron density, which yields the ground state total energy E

$$E = \min_{n(\vec{r})} E[n(\vec{r})] = \min_{n(\vec{r})} \left\{ F[n(\vec{r})] + \int d^3r v(\vec{r}) n(\vec{r}) \right\} \quad (2.15)$$

This result represents the second Hohenberg–Kohn theorem, which states that the ground-state density minimizes the energy functional and that the corresponding minimum equals the exact ground-state energy $E = E[n(\vec{r})]$ [18]. Although the existence of the functional is guaranteed, its explicit form is unknown, which motivates the introduction of the Kohn–Sham (KS) formalism.

2.2.3 The Kohn–Sham equations

As discussed previously, the exact form of the universal functional $F[n(\vec{r})]$ is unknown. However, if an approximation to this functional can be found, the ground-state density can, in principle, be determined by minimizing the corresponding energy functional. To overcome this challenge, Kohn and Sham introduced an auxiliary system of non-interacting electrons that reproduces the same ground-state electron density as the original interacting system. In this auxiliary system, the electron–electron interaction is neglected, i.e. $\hat{V}_{ee} = 0$, and the effects of the interaction are incorporated into an effective single-particle potential, the KS potential $\hat{v}^{\text{KS}}$ [20]. This allows the many-electron problem to be transformed into a set of single-particle Schrödinger equations

$$\left[-\frac{1}{2} \nabla^2 + \hat{v}^{\text{KS}}(\vec{r}) \right] \varphi_j^{\text{KS}}(\vec{r}) = \varepsilon_j \varphi_j^{\text{KS}}(\vec{r}). \quad (2.16)$$

where ε_j are the Kohn-Sham eigenvalues and $\varphi_j^{\text{KS}}(\vec{r})$ are the corresponding KS orbitals. The term "orbital" should be interpreted carefully in this context. Although KS orbitals often resemble molecular orbitals and can provide valuable insight into the electronic structure, they do not correspond to the exact orbitals of the interacting many-electron system [4]. Similarly, the Kohn-Sham eigenvalues do not generally represent true excitation energies. Nevertheless, they can provide useful information about the electronic structure, and their interpretation is supported by results such as Janak's theorem [21].

In equation (2.16), the effective Kohn-Sham potential $\hat{v}^{\text{KS}}(\vec{r})$ was introduced. This potential accounts for all interactions experienced by an electron in the auxiliary non-interacting system. It can be decomposed into three physically distinct contributions,

$$\hat{v}^{\text{KS}}(\vec{r}) = v_{\text{ext}}(\vec{r}) + v_H([n], \vec{r}) + v_{xc}([n], \vec{r}) = v_{\text{ext}}(\vec{r}) + \frac{\delta U[n(\vec{r})]}{\delta n(\vec{r})} + \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}. \quad (2.17)$$

The first contribution, $v_{\text{ext}}(\vec{r})$, describes the external potential generated by the nuclei. The second term, $v_H([n], \vec{r})$, is the Hartree potential, which represents the classical electrostatic interaction of an electron with the total electron density. It is obtained as the functional derivative of the Hartree energy $U[n(\vec{r})]$:

$$U[n(\vec{r})] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}. \quad (2.18)$$

The remaining contribution, $v_{xc}([n], \vec{r})$, is the exchange-correlation potential. It contains all many-body effects not included in the classical Hartree description, such as exchange interactions and electron correlation. Since no exact analytical expression for this term is known, it has to be approximated. The exchange-correlation functional which is employed in this work is discussed in the following subsection. Using the KS-potential, the total energy functional can be written as

$$E[n] = T_s[n] + U[n] + E_{xc}[n] + \int d^3r v(\vec{r})n(\vec{r}) \text{ with } T_s[n] = \sum_{i=1}^N \langle \varphi_i | -\frac{1}{2}\nabla^2 | \varphi_i \rangle. \quad (2.19)$$

The electron density is finally obtained by summing over all the occupied KS-orbitals according to

$$n(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2. \quad (2.20)$$

Together, the KS-equation (2.16), the definition of the effective KS-potential equation (2.17), and the expression for the electron density equation (2.20) form a set of coupled equations that must be solved self-consistently. Starting from an initial guess for the electron density, the effective KS-potential is constructed and the KS-equations are solved to obtain a new set of KS-orbitals. These orbitals are subsequently used to calculate an updated electron density, from which a new effective potential is determined. This self-consistent field (SCF) cycle is repeated until the input and output electron

densities, or equivalently the total energy, differ by less than a predefined convergence criterion. Once self-consistency has been achieved, the resulting electron density represents the ground-state density of the system, while the corresponding KS-orbitals and eigenvalues provide access to a wide range of electronic properties.

2.2.4 The exchange correlation energy

As discussed in the previous section, the Kohn-Sham formalism is, in principle, an exact reformulation of the many-electron problem. In practice, however, the exact form of the exchange-correlation functional $E_{xc}[n(\vec{r})]$ is unknown [22]. Consequently, the accuracy of a DFT calculation is largely determined by the approximation chosen for this functional. Over the past decades, numerous exchange-correlation functionals have been developed, which can broadly be classified into empirical approaches, where parameters are fitted to high-level theoretical data, and non-empirical approaches, whose parameters are determined from exact theoretical constraints. Throughout this work, only non-empirical functionals are employed.

LDA

The simplest and historically first approximation is the local density approximation (LDA), which was already proposed in the original work of Kohn and Sham [20]. In the LDA, the exchange-correlation energy is approximated by assuming that each point in the system behaves locally like a homogeneous electron gas with the same electron density. The corresponding functional is given by

$$E_{xc}^{\text{LDA}}[n] = \int d^3r \, n(\vec{r}) e_{xc}^{\text{unif}}(n(\vec{r})), \quad (2.21)$$

where $e_{xc}^{\text{unif}}(n(\vec{r}))$ denotes the exchange-correlation energy per electron of a uniform electron gas with density $n(\vec{r})$. Thus, the total exchange-correlation energy is obtained by integrating the local contribution of a homogeneous electron gas evaluated at the density of the real, spatially varying system. Although this approximation neglects density gradients, it performs remarkably well for systems in which the electron density varies only slowly in space, such as many bulk metals.

GGA

Although the LDA provides a remarkably successful description for many systems, its assumption of a homogeneous electron gas becomes less accurate for systems with strongly varying electron densities. To overcome this limitation, extensions of the LDA were developed that include additional information about the spatial variation of the electron density. The generalized gradient approximation (GGA) introduces the gradient of the electron density as an additional variable. While the LDA depends only on the local density $n(\vec{r})$, GGA functionals also consider the density gradient $\nabla n(\vec{r})$, resulting in the general form

$$E_{xc}^{\text{GGA}}[n] = \int d^3r \, f(n(\vec{r}), \nabla n(\vec{r})). \quad (2.22)$$

The inclusion of the density gradient allows GGA functionals to account for inhomogeneities in the electron density and generally improves the description of systems such as molecules, surfaces, and interfaces. Since the gradient dependence is not uniquely defined, various different GGA functionals have been developed, each based on different approaches to approximate the exchange-correlation energy. In this work, the Perdew, Burke, Ernzerhof (PBE) functional is employed, which is one of the most widely used GGA functionals [23]. PBE is a non-empirical functional designed to satisfy known constraints of the exact exchange-correlation functional while preserving the successful properties of the LDA. Due to its good balance between accuracy and computational efficiency, PBE is commonly applied for the description of molecular systems, surfaces, and molecule-metal interfaces, as investigated in this work.

2.2.5 Van-der-Waals corrections

The functionals discussed above are local or semilocal DFT functionals and therefore do not properly account for nonlocal, long-range dispersion interactions. They can be particularly relevant for the systems investigated in this work, where organic molecules are adsorbed on a metal surface. Such interactions originate from correlated fluctuations of the electron density between the two subsystems. Even in the absence of permanent dipoles, instantaneous fluctuations in the electron density can give rise to temporary dipoles. These fluctuations induce a response in the electron density of the other subsystem, resulting in an attractive interaction that lowers the total energy of the combined system. This interaction is commonly referred to as dispersion or van der Waals interaction [24].

Several approaches have been developed to account for these interactions within DFT. In this work, an a-posteriori dispersion correction is employed, in which an additional dispersion energy E_{disp} is added to the exchange-correlation energy

$$E_{xc} = E_{xc}^{SL} + E_{\text{disp}}. \quad (2.23)$$

Several a-posteriori dispersion correction schemes have been developed, with the approach introduced by Grimme et al. being one of the most widely used [25]. In this work, the DFT-D3 method with zero damping is employed [26]. The DFT-D3 approach accounts for dispersion interactions through geometry-dependent dispersion coefficients, allowing the correction to adapt to the atomic environment during structural relaxation. In the zero-damping formulation used here, the dispersion correction is combined with the underlying DFT functional according to the original DFT-D3 formulation.

2.2.6 Adsorption energy as analysis tool

As will be shown later in this work, different organic molecules are studied on an Ag(110) surface. These molecules are investigated in various adsorption positions and orientations, which can also require different Ag(110) slab sizes depending on the configuration considered. Therefore, a quantity that allows the energetic stability of different adsorption configurations to be compared is required. One such quantity is the adsorption energy, which provides a measure of the energetic stability of a molecule adsorbed on a surface.

It is defined as the energy difference between the combined molecule-surface system and the sum of the corresponding isolated subsystems

$$E_{\text{ad}} = E_{\text{mol+sub}} - [E_{\text{mol}} + E_{\text{sub}}]. \quad (2.24)$$

Here, $E_{\text{mol+sub}}$ denotes the total energy of the combined molecule-substrate system, while E_{mol} and E_{sub} correspond to the energies of the isolated molecule and substrate, respectively. For the latter two energies, the atomic configurations are taken directly from the relaxed combined system. The corresponding subsystem is then isolated by removing either the molecule or the substrate while keeping the remaining atoms fixed at their relaxed positions. This procedure ensures that the adsorption energy reflects the energetic difference between the combined system and its constituent subsystems in the geometries adopted upon adsorption, without introducing additional contributions from relaxing the isolated components.

With this definition, a negative adsorption energy, $E_{\text{ad}} < 0$, indicates that the combined molecule-substrate system is energetically more favourable than the corresponding separated subsystems. Thus, within a consistent set of calculations, more negative adsorption energies indicate energetically more favourable adsorption configurations. The adsorption energy therefore provides a convenient criterion for comparing the different molecular positions and orientations investigated throughout this work.

2.3 Theoretical description of photoelectron spectroscopy

2.3.1 General principles

Before introducing photoemission orbital tomography, a brief overview of the underlying experimental technique, photoemission spectroscopy (PES), is given. PES is based on the photoelectric effect, in which electrons are emitted from a material following the absorption of photons with sufficient energy. The theoretical description of the photoelectric effect was established by Einstein [27]. The kinetic energy of a photoemitted electron is related to the energy of the absorbed photon according to

$$E_{\text{kin}} = \hbar\omega - E_B = \hbar\omega - \phi - E_i, \quad (2.25)$$

where $\hbar\omega$ denotes the photon energy, E_{kin} the kinetic energy of the emitted electron, and E_B its binding energy with respect to the vacuum level. The binding energy can be expressed as the sum of the work function ϕ and the initial-state energy E_i relative to the Fermi level.

In addition to the kinetic energy, the emission angle of the photoelectron can be measured. The combination of energy and angular information provides access to the electronic structure of the investigated material. When the angular dependence of the emitted electrons is explicitly resolved, the technique is referred to as angle-resolved photoemission spectroscopy (ARPES). The experimental data used throughout this work were obtained using ARPES, providing both the energy and momentum dependence of the photoemitted electrons.

2.3.2 Photoemission orbital tomography

To complement the experimental data with theoretical insight, a theoretical description of the photoemission process is required. The necessary information about the electronic structure, including the energies, k -dependent dispersion, and KS wavefunctions, is obtained from the DFT calculations introduced previously. To describe the photoemission process, the one-step model is employed in which photoemission is treated as a single coherent transition from an occupied electronic state to an unoccupied continuum state induced by the absorption of a photon. Within this framework, the photoemission intensity can be expressed using Fermi's golden rule [5, 7]

$$I \propto |\langle \Psi_f | \hat{H}_{\text{int}} | \Psi_i \rangle|^2 \times \delta(E_{\text{kin}} + \phi + E_i - \hbar\omega), \quad (2.26)$$

where I denotes the photoemission intensity and $|\langle \Psi_f | \hat{H}_{\text{int}} | \Psi_i \rangle|^2$ describes the transition matrix element between the initial state Ψ_i and the final state Ψ_f . The Dirac delta function enforces energy conservation during the photoemission process.

Since the focus of this work is on the qualitative comparison of experimental and theoretical momentum maps rather than on an exact quantitative description of the measured intensity, further approximations can be introduced. Within the dipole approximation, the interaction with the electromagnetic field is described by the vector potential $\vec{A}$. Furthermore, the initial states are represented by Bloch states $\psi_{n\vec{q}}$, where n denotes the band index and $\vec{q}$ the crystal momentum within the Brillouin zone. Assuming a plane-wave final state then leads to the following expression for the photoemission intensity [5, 7]

$$I(k_x, k_y, \hbar\omega, \vec{A}) \propto \sum_n^{\text{occ}} \sum_{\vec{q}}^{\text{BZ}} |\vec{A}\vec{k}|^2 |\langle e^{i\vec{k}\vec{r}} | \psi_{n\vec{q}} \rangle|^2 \times \delta(\varepsilon_{n\vec{q}} + \phi + E_{\text{kin}} - \hbar\omega). \quad (2.27)$$

Here, $\vec{k}$ denotes the momentum of the emitted photoelectron. The overlap between the plane-wave final state, $e^{i\vec{k}\vec{r}}$, and the initial-state wavefunction determines the momentum-dependent contribution to the photoemission intensity. This relation forms the basis for connecting the calculated electronic states to the experimentally measured momentum maps.

The plane-wave approximation provides a simple and computationally efficient description of the final state. However, it does not consider inelastic scattering events that give rise to the finite mean free path of the photoelectrons and thereby are responsible for the pronounced surface sensitivity of ARPES. To mimic this behaviour, it has been suggested to introduce an empirical damping term. This damped plane wave final state takes the following form [28]:

$$|\psi_f\rangle_d = \begin{cases} e^{i\vec{k}\vec{r}} e^{\gamma(z-z_0)}, & z < z_0, \\ e^{i\vec{k}\vec{r}}, & z \geq z_0. \end{cases} \quad (2.28)$$

where γ is the damping parameter and z_0 defines the position at which the damping is introduced. For the systems investigated in this work, z_0 is chosen in the region

between the molecule and the substrate. Consequently, contributions originating from the substrate are attenuated while the molecular contributions remain comparatively unaffected. This allows the calculated momentum maps to more closely emphasize the molecular electronic states relevant for comparison with the experimental ARPES data.

2.4 Time-dependent density functional theory

As one of the goals of this work is to gain insight into the time-dependent behavior of a helical molecule on a substrate, TDDFT is employed. The following chapter therefore provides a brief introduction to the theoretical framework of TDDFT and the quantities relevant for the subsequent analysis.

2.4.1 From DFT to TDDFT

The electronic Hamiltonian introduced in equation (2.2) can be extended to include an explicitly time-dependent external potential. The resulting time-dependent Hamiltonian is given by

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \underbrace{\sum_i v(\vec{r}_i) + \sum_i v_{\text{TD}}(\vec{r}_i, t)}_{\sum_i v_{\text{ext}}(\vec{r}_i, t)}, \quad (2.29)$$

where $v_{\text{TD}}(\vec{r}_i, t)$ denotes the time-dependent contribution to the external potential. Together with the previously introduced external potential $v(\vec{r}_i)$, it can be combined into the total time-dependent external potential $v_{\text{ext}}(\vec{r}_i, t)$. The time evolution of the many-electron system is then governed by the time-dependent Schrödinger equation

$$\hat{H}|\Psi(\{\vec{r}_i\}, t) = i\partial_t|\Psi(\{\vec{r}_i\}, t). \quad (2.30)$$

Solving this equation for a many-electron system is subject to the same fundamental complexity as the time-independent many-body problem. In ground-state DFT, the Hohenberg-Kohn theorems provide the basis for replacing the many-electron wavefunction by the electron density as the central variable, leading to the Kohn-Sham formulation. For a time-dependent system, however, the Hohenberg-Kohn framework does not provide the required mapping between the time-dependent density and the external potential. A corresponding foundation for the time-dependent case is provided by the Runge-Gross theorem [29, 30, 31].

Runge-Gross theorem

The Runge-Gross theorem establishes a one-to-one correspondence between the time-dependent electron density and the external potential for a given initial many-electron state, subject to the conditions of the theorem [29]. Consequently, the time-dependent density contains, in principle, the information required to determine the time evolution of the system. Physical observables can therefore be expressed as functionals of the time-dependent density and the initial state. The Runge-Gross theorem thus provides

the fundamental basis for extending the density functional framework to time-dependent systems. Analogously to ground-state DFT, the interacting many-electron problem can subsequently be mapped onto an auxiliary system of non-interacting electrons that reproduces the time-dependent electron density. This leads to the time-dependent Kohn-Sham formulation, which is introduced in the following section [29, 30, 31].

2.4.2 Time-dependent Kohn-Sham equations

Analogously to the time-independent Kohn-Sham approach, the interacting many-electron system can be mapped onto an auxiliary system of N non-interacting electrons that reproduces the time-dependent electron density. The resulting time-dependent Kohn-Sham (TDKS) equations are obtained by requiring the Kohn-Sham orbitals $\varphi_j^{\text{KS}}(\vec{r}, t)$ to satisfy the time-dependent Schrödinger equation:

$$i \frac{\partial}{\partial t} \varphi_j^{\text{KS}}(\vec{r}, t) = \left[-\frac{1}{2} \nabla^2 + \hat{v}^{\text{KS}}[n, \Psi_0, \Phi_0](\vec{r}, t) \right] \varphi_j^{\text{KS}}(\vec{r}, t), \quad (2.31)$$

where $\varphi_j^{\text{KS}}(\vec{r}, t)$ denotes a time-dependent KS orbital. In contrast to the ground-state case, the KS potential is now explicitly time-dependent and, in general, depends not only on the time-dependent density $n(\vec{r}, t)$ but also on the initial interacting state Ψ_0 and the corresponding initial Kohn-Sham state Φ_0 . The KS potential can be separated into three contributions:

$$\hat{v}^{\text{KS}}[n, \Psi_0, \Phi_0](\vec{r}, t) = v_{\text{ext}}(\vec{r}, t) + \int d^3 r' \frac{n(\vec{r}', t)}{|\vec{r} - \vec{r}'|} + v_{xc}[n, \Psi_0, \Phi_0](\vec{r}, t) \quad (2.32)$$

where $v_{\text{ext}}(\vec{r}, t)$ denotes the time-dependent external potential, the second term represents the time-dependent Hartree potential, and $v_{xc}[n, \Psi_0, \Phi_0]$ is the time-dependent exchange-correlation potential.

An important difference to the ground-state formulation is therefore that the Kohn-Sham potential depends on the instantaneous density $n(\vec{r}, t)$ rather than on a static ground-state density alone. In addition, the exact time-dependent exchange-correlation potential may depend on the initial interacting and Kohn-Sham states. In practical TDDFT calculations, this dependence is approximated through the chosen time-dependent exchange-correlation functional. The time-dependent electron density is obtained from the occupied time-dependent Kohn-Sham orbitals in analogy to the ground-state formulation:

$$n^{\text{KS}}(\vec{r}, t) = \sum_i |\varphi_i^{\text{KS}}(\vec{r}, t)|^2 \quad (2.33)$$

The TDKS equations are therefore coupled through the time-dependent density: the evolving orbitals determine $n(\vec{r}, t)$, which in turn determines the time-dependent Kohn-Sham potential. Their solution consequently requires the Kohn-Sham equations to be propagated self-consistently in time.

2.4.3 Time-dependent observables

The TDDFT calculations performed in this work provide access to several time-dependent quantities that are used to characterize the response of the system to the external driving field. In particular, the induced current density and the resulting orbital magnetic moment are analysed. This subsection briefly introduces these quantities and their physical meaning. Details of their numerical implementation can be found in the Octopus documentation [32].

Total current density

One of the main questions investigated in this work is whether a helical molecule can support light-induced currents and, in particular, whether a current with a helical or ring-like character can be induced. The time-dependent current density therefore provides a central quantity for the analysis.

In Octopus, the current density is calculated according to [31]

$$\vec{j}(\vec{r}, t) = -\frac{i}{2} \sum_{i=1}^N (\varphi_i^*(\vec{r}, t) \nabla \varphi_i(\vec{r}, t) - (\nabla \varphi_i(\vec{r}, t))^* \varphi_i(\vec{r}, t)) \quad (2.34)$$

where $\varphi_i(\vec{r}, t)$ are the TDKS orbitals. The first contribution describes the usual current-density term, while the second accounts for the contribution arising from the nonlocal potential.

The spatially resolved current density $\vec{j}(\vec{r}, t)$ allows the direction and spatial distribution of the induced current to be investigated. In addition to the local current density, its spatial integral can be used to obtain the cell-integrated current density,

$$\vec{J}(t) = \int d^3r \vec{j}(\vec{r}, t). \quad (2.35)$$

This quantity is used later to quantify the overall current response and to investigate its dependence on the strength and frequency of the external driving field.

Orbital magnetic moment

In addition to the current density, the induced orbital magnetic moment is of interest. A circulating current generates an orbital magnetic moment, making this quantity particularly relevant when assessing the potential experimental detectability of the light-induced response.

The orbital magnetic moment can be related to the angular momentum of the electronic system. In terms of the current density, the orbital magnetic moment is given by

$$\vec{\mu}(t) = \frac{1}{2} \int d^3r \vec{r} \times \vec{j}(\vec{r}, t). \quad (2.36)$$

Although Octopus provides a direct calculation of the angular momentum through the corresponding output functionality, the magnetic moments analysed in this work are

obtained using the MagJell post-processing tool [33]. This provides the magnetic moment from the calculated time-dependent current and was used here as a computationally convenient post-processing approach.

3 Results

3.1 Computational Setup

The results presented below were obtained using two ab initio electronic structure packages: VASP [34, 35, 36] and Octopus [37]. Computational workflows for both codes were executed on the Austrian scientific computing (ASC) 4 and 5 infrastructure. While Octopus is an open-source software package, VASP requires a commercial license. In the following sections, we briefly outline the implementation and specific application of each code within this work.

3.1.1 VASP

The Vienna ab initio simulation package (VASP) is a widely used software suite for atomic scale materials modeling from first principles, encompassing electronic structure calculations and quantum-mechanical molecular dynamics. VASP applies density functional theory (DFT) and numerically solves the Kohn-Sham equations. Central quantities in VASP—including one-electron orbitals, electronic charge densities, and local potentials—are expanded in a plane-wave basis set, while electron-ion interactions are treated using norm-conserving or ultrasoft pseudopotentials, or the projector-augmented-wave (PAW) method [38].

In this work VASP was primarily employed for geometry optimization to obtain the ground-state electronic structures required for subsequent k-map calculations in a postprocessing step. To perform structural relaxation, the INCAR tag `IBRION` was set to 3, selecting the damped molecular dynamics approach. In this mode, VASP solves a damped, second-order equation of motion [39]:

$$\ddot{\vec{x}} = -2\alpha\vec{F} - \mu\dot{\vec{x}} \quad (3.1)$$

This equation introduces two key parameters: the damping factor μ , controlled via the `SMASS` tag, and the scaling factor α , adjusted via `POTIM`. In VASP the differential equation is discretised using a simple velocity Verlet algorithm which leads to:

$$\vec{v}_{N+1/2} = \frac{(2 - \mu)\vec{v}_{N-1/2} - 4\alpha\vec{F}_N}{2 + \mu} \quad (3.2)$$

$$\vec{x}_{N+1} = \vec{x}_N + \vec{v}_{N+1/2}. \quad (3.3)$$

From these relations, it is evident that $\mu = 2$ corresponds to maximal damping (critical damping), whereas $\mu = 0$ implies no damping. A standard initial choice of `SMASS` = 0.4 ($\mu = 0.4$) was used for all geometry relaxations in this study. Furthermore, while it is

generally recommended to set POTIM as large as possible without inducing divergence, stability tests on our systems indicated that POTIM = 0.12 provided optimal convergence [39]. The remaining convergence parameters employed for the geometry optimization were NSW and EDIFFG. The maximum number of ionic relaxation steps was limited to 3000 (NSW = 3000), while the threshold for the Hellmann-Feynman forces acting on the atoms was defined by setting EDIFFG = -0.001 (eV/Å). Additionally, the tag IVDW = 11 is applied to all calculations to enable Grimme-D3 van der Waals corrections. This is essential because standard local and semilocal DFT functionals fail to account for long-range, nonlocal van der Waals interactions [26].

3.1.2 Octopus

The Octopus code implements time-dependent density functional theory (TDDFT) within the Kohn–Sham formalism. It is a real-space, pseudopotential-based package designed to simulate electron–ion dynamics in finite or periodic systems, where periodic boundary conditions can be imposed in one-, two-, and three directions. The simulations are performed in real time using a regular real-space grid, where external time-dependent electromagnetic fields can be considered. Octopus has been successfully applied to a wide range of problems, including the calculation of linear and nonlinear absorption spectra, high-harmonic generation spectra, and laser-induced fragmentation, among many other applications across diverse physical and chemical systems [40].

In this work, Octopus is primarily utilized to investigate the time-dependent electronic response of systems subjected to a THz laser pulse. The specific parameters and settings configured for each calculation are detailed below.

3.2 4A-MAD on Ag(110)

3.2.1 Motivation

The first system studied in this work is the tetracene–maleic anhydride Diels–Alder adduct (4A-MAD) molecule adsorbed on Ag(110) (see figure 3.1), because of its potential application for the investigation of light-induced chemical reactions. The 4A-MAD molecule is comprised of a tetracene (4A) backbone to which a maleic anhydride Diels–Alder (MAD) adduct is connected. Specifically, this adduct can undergo light induced reactions and therefore serves as a model system to study retro 4+2 cycloadditions on surfaces. In the corresponding experiments, a monolayer of 4A-MAD molecules is grown on Ag(110). Subsequently, a laser pulse triggers the breaking of the bonds between the molecular backbone and the adduct molecule leaving behind tetracene on the surface, while MAD escapes into the vacuum. In order to ensure a steady state, MAD molecules from the gas phase are re-adsorbed on the surface and eventually bind to the reacted 4A molecules. In order to find out, whether this envisioned scenario is indeed realistic, and the planned experiment is possible, this work studies the geometric and electronic properties of the 4A-MAD/Ag(110) interface by means of density functional calculations to reveal important key properties of this system.

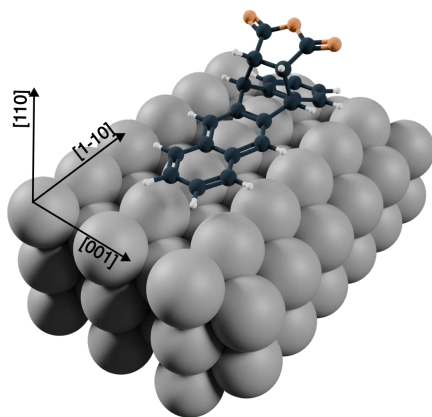


Figure 3.1: Structural model showing the adsorption of 4A-MAD on Ag(110). Note that the long molecular axis of its tetracene backbone is aligned along the $[1-10]$ direction.

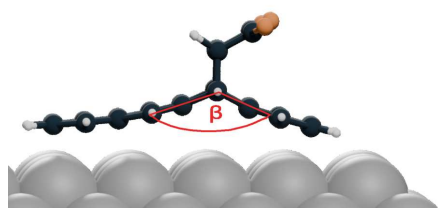
3.2.2 DFT - geometry optimization

To understand the adsorption behaviour of the system, the first step was to investigate how the molecule binds to the surface. Since geometry optimizations, using a damped molecular dynamics scheme introduced in Eqs. 3.1–3.3 generally, converge to a local minimum rather than the global minimum several initial geometries were considered. This approach increases the likelihood of identifying the globally most stable adsorption configuration. Before discussing the results, the terminology for characterizing the various initial starting configurations is introduced.

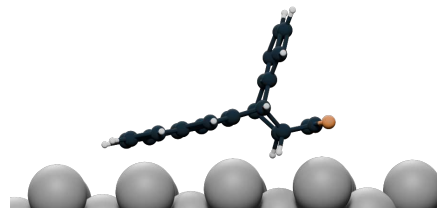
Throughout the following sections, the term MAD-up refers to a configuration in which the MAD group points away from the surface (left panel of figure 3.2), whereas MAD-down denotes the corresponding configuration in which the MAD group points towards the surface (right panel of figure 3.2). Finally, MAD-edge indicates a configuration where the molecule is laying sideways on the substrate (lower panel of figure 3.2).

The high-symmetry adsorption sites of the Ag(110) surface, hollow (H), top (T), long-bridge (LB) and short-bridge (SB), as already defined in figure 1.1 are used to distinguish between different adsorption configurations. Note that the H-atoms at the end of the long axis, away from the adduct molecule, of the tetracene backbone are used as reference atoms to define the molecule's position at the different adsorption sites. Furthermore azimuthal alignments of the molecule of 0° , 15° , 45° , 75° and 90° were tested indicating how the long axis of the tetracene backbone is oriented with respect to the $[1-10]$ direction (see figure 3.3).

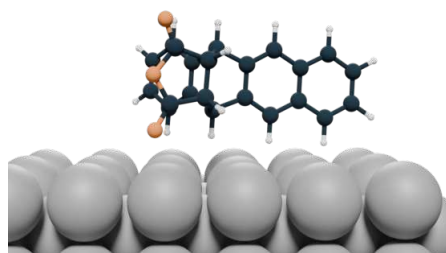
Note that with 3 molecular configurations (up, down, edge), 4 adsorption sites (H, T, LB, SB) and 5 alignments (0° , 15° , 45° , 75° , 90°), there are $3 \times 4 \times 5 = 60$ possible starting geometries to be tested. As a first analysis step, a subset of 14 different starting POSCAR-files were generated using the python library atomic simulation environment (ase) [41].



(a) 4A-MAD *up* configuration and indication of the dihedral angle



(b) 4A-MAD *down* configuration



(c) 4A-MAD *edge* configuration

Figure 3.2: Visualisation of the 4A-MAD molecule on Ag(110) in the (a) *up* and (b) *down* and (c) *edge* configuration.

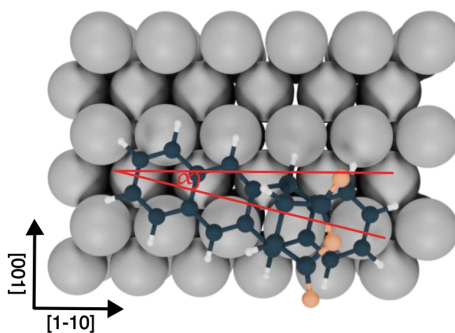


Figure 3.3: Top view of the structural model indicating the azimuthal orientation of the 4A-MAD molecule on the Ag (110) surface.

In order to be able to compare the resulting structures among each other, the adsorption energy is calculated according to equation (2.24). The energies of the most promising candidates are plotted in figure 3.4. Note that we use upward (downward) triangles for up (down) and circles for edge configurations. The different azimuthal alignments α are colour-coded, while the two adsorption sites, H and SB, are distinguishable by solid and dashed lines, respectively. It is important to note that the legend in figure 3.4 refers to

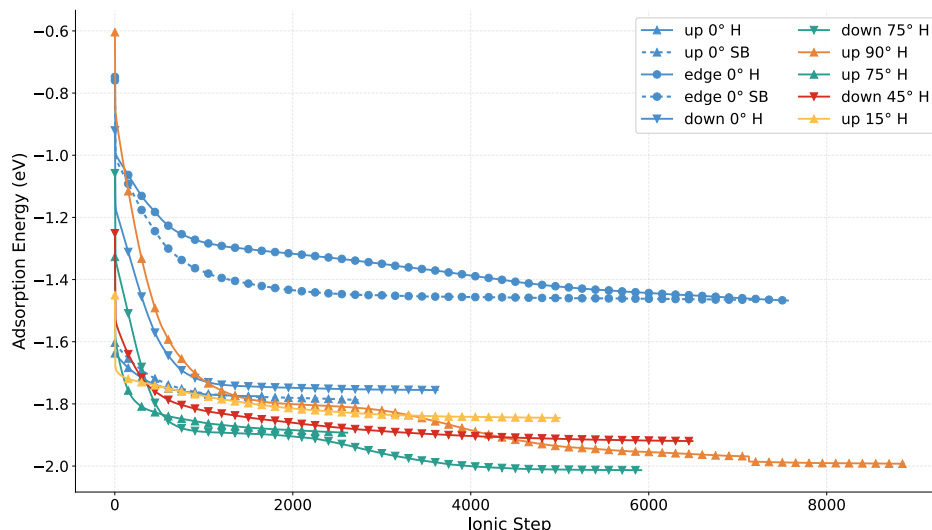


Figure 3.4: Adsorption energy as function of the ionic step for different starting configurations of 4A-MAD on Ag(110). The results show that there are two distinct configurations which are similarly favourable.

the initial configurations, which may differ from the final configuration after geometry optimization. Consequently, two different starting positions may have converged to the same local minimum, resulting in identical energies. In addition, the edge configuration can be ruled out as a likely adsorption geometry due to its comparatively unfavourable adsorption energy.

The two configurations with the most favourable adsorption energies ($E_{ad} = -1.99$ eV for MAD-up 90° H and $E_{ad} = -2.01$ eV for MAD-down 75° H) exhibit distinctly different orientations and require further investigation. To begin with, it is important to note that the non-planar geometry of the isolated 4A-MAD molecule originates from the interruption of the π -conjugated 4A backbone by the MAD adduct. As a consequence, the carbon atoms binding the MAD group adopt an approximately sp^3 -like hybridization, resulting in a finite dihedral angle between the molecular fragments. Upon adsorption on the Ag(110) surface, a stronger molecule-surface interaction could induce a planarization of the molecular backbone. Such a structural rearrangement would be accompanied by a transition toward sp^2 -like hybridization, thereby restoring the conjugated π -system and potentially weakening the bond between the 4A backbone and the MAD group. Indeed a comparison of the relaxed geometries reveals changes in both the dihedral angles and the

carbon bond lengths connecting the MAD group to the tetracene core. The evolution of the dihedral angle and bond length during the ionic relaxation were analysed and plotted in (see figure 3.5 and figure 3.6), respectively.

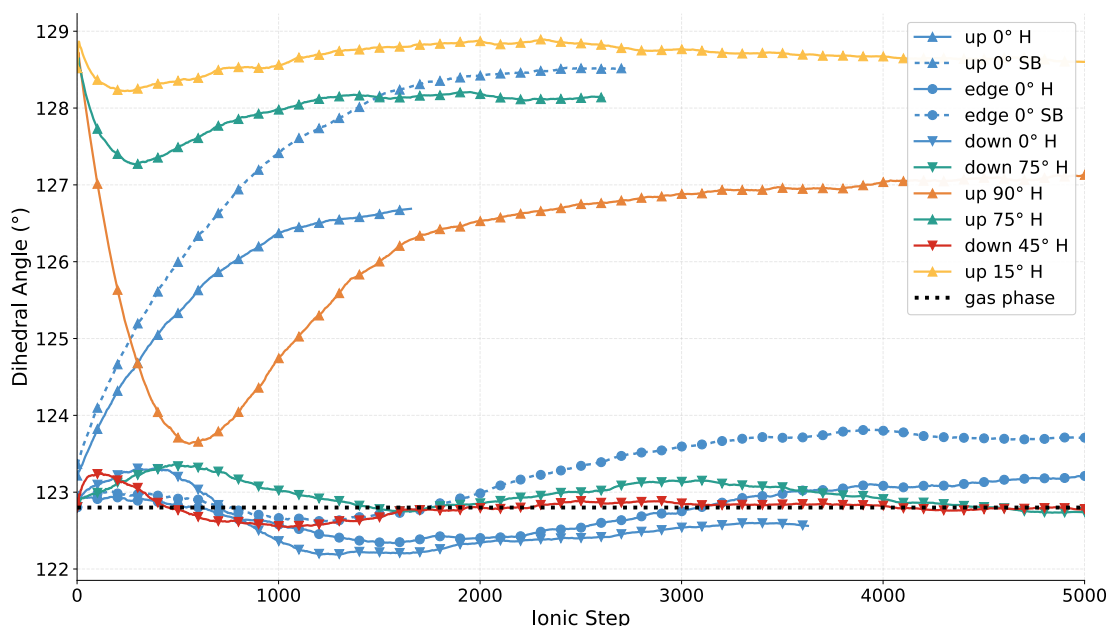


Figure 3.5: Change of the dihedral angle during the ionic relaxation for different starting configurations.

The relaxation trajectories, however, show that this effect remains limited. Although the MAD-up configurations exhibit a noticeable increase in the dihedral angle towards the planar value of 180° , the structural distortion remains insufficient to induce bond cleavage. While the interaction with the surface partially planarizes the molecule, the final adsorption geometry remains distinctly non-planar, indicating that the hybridization of the affected carbon atoms is only weakly modified.

The different initial dihedral angles arise because, once a relaxed configuration had been obtained, the optimized molecular geometry was reused as the starting point for subsequent calculations. This procedure significantly reduces the computational cost by decreasing the number of relaxation steps required for convergence. However, transferring relaxed geometries requires careful positioning of the molecule relative to the surface, as an unsuitable initial placement can introduce artificial features into the relaxation trajectory.

Such a behaviour can be observed for the MAD-up 90° H configuration (orange line). Here, the reused relaxed geometry was initially positioned too far from the surface, causing the molecule to first relax toward a geometry resembling its gas-phase structure before approaching the surface and subsequently adopting the characteristic flattening observed for the remaining MAD-up configurations. This transient reorientation is therefore an artifact of the chosen starting geometry rather than an intrinsic feature of the adsorption

process.

In contrast to the slight flattening of the molecular backbone in the up-configurations, the MAD-down configurations exhibit no comparable increase of the dihedral angle during relaxation. Their adsorption geometries remain essentially unchanged, indicating a substantially weaker structural response to the surface interaction. Consequently, while the MAD-up configurations undergo a moderate degree of planarization, the MAD-down configurations largely retain their initial molecular geometry. In neither case is the structural distortion sufficiently pronounced to promote bond cleavage, in agreement with the adsorption energies discussed above.

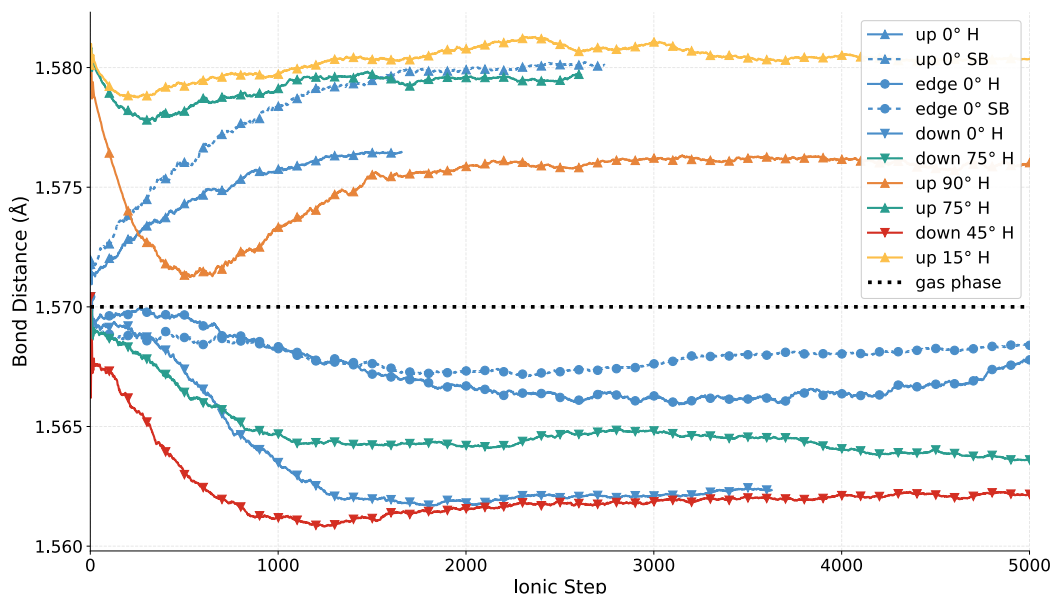


Figure 3.6: Change of the bond distance as function of the ionic step for different starting configurations.

A consistent picture emerges from the evolution of the affected bond length during structural relaxation. If the partial planarization observed for the MAD-up configurations were accompanied by a significant weakening of the bond between the 4A backbone and the MAD group, a substantial bond elongation would be expected. Instead, only a slight increase in bond length is observed for the MAD-up configurations, mirroring the moderate reduction of the dihedral angle. The magnitude of this elongation remains small, and the bond length converges to a stable equilibrium value during relaxation, indicating that the adsorption-induced structural distortion does not significantly weaken the corresponding chemical bond.

For the MAD-down configurations, the bond length remains essentially constant throughout the relaxation, reflecting the absence of pronounced molecular reorientation or deformation. The bond distances therefore remain close to their initial values for all investigated configurations.

A comparison of the final relaxed structures shows a small but distinct difference in

the relevant bond length between the MAD-up and MAD-down configurations. The bond length increases from 1.565 Å in the MAD-down configuration to 1.575 Å in the MAD-up configuration, corresponding to an elongation of approximately 0.01 Å. While this difference indicates that the two adsorption geometries experience somewhat different interactions with the Ag(110) surface, the absolute change remains small compared with the bond length itself. Together with the observed evolution of the dihedral angle, these results indicate that adsorption modifies the molecular geometry but does not drive the molecule towards a fully planar, sp^2 -like configuration. In particular, the calculated bond elongation does not provide evidence for a substantial weakening of the 4A–MAD bond that would suggest bond cleavage under the investigated conditions.

3.2.3 Projected density of states and charge density rearrangements

In order to get deeper insight into the properties of the adsorbed 4A-MAD species, the discussion now turns to their electronic structure. Since the structural analysis alone does not provide evidence for bond cleavage or a pronounced weakening of the molecule–substrate interaction, the electronic properties of the energetically most favorable configurations are investigated to obtain further insight into the nature of the adsorption process on Ag(110).

Furthermore, the calculated DOS serves as a direct link to experiment through comparison with valence band photoemission spectroscopy. Characteristic molecular states predicted by the calculations can be identified in the measured valence band spectra, allowing the electronic structure of the adsorbed system to be assessed experimentally. While the agreement between calculated and measured spectra alone is generally insufficient to uniquely identify the adsorption geometry, it provides valuable complementary evidence for evaluating the proposed adsorption configurations.

A central quantity for this analysis is the electronic density of states (DOS), which describes the distribution of electronic states as a function of energy. In particular, pronounced features in the DOS can be associated with molecular orbitals or substrate-derived bands, while changes in peak position and broadening upon adsorption provide information about hybridization effects.

To disentangle contributions from the Ag(110) surface and the 4A-MAD molecule, a projected density of states (pDOS) analysis is performed. Here, the Kohn–Sham states are projected onto atomic orbitals. This decomposition provided by the VASP PROCAR output enables an orbital-resolved view of the electronic structure and allows molecule-derived states to be distinguished from substrate states through their spatial and orbital character.

The resulting pDOS of the system, which is calculated using the `postvasp.py` python library, is shown in figure 3.7. First, it is evident that the theoretical onset of the Ag (d)-band is located approximately (3 eV) below the Fermi level, which does not coincide exactly with the experimental spectrum. This discrepancy arises from the approximations inherent to density functional theory, in particular the use of the PBE exchange-correlation functional, which does not reproduce binding energies with quantitative accuracy. The resulting offset of approximately (1 eV) also provides an estimate of the expected shift of

the molecular states relative to the experimental spectrum.

Although the DOS of the MAD-up and MAD-down configurations exhibit very similar overall characteristics, subtle differences can still be identified. In particular, a slight relative energy shift of the molecular contributions is observed between the two adsorption geometries, reflecting their different electronic interactions with the Ag(110) substrate.

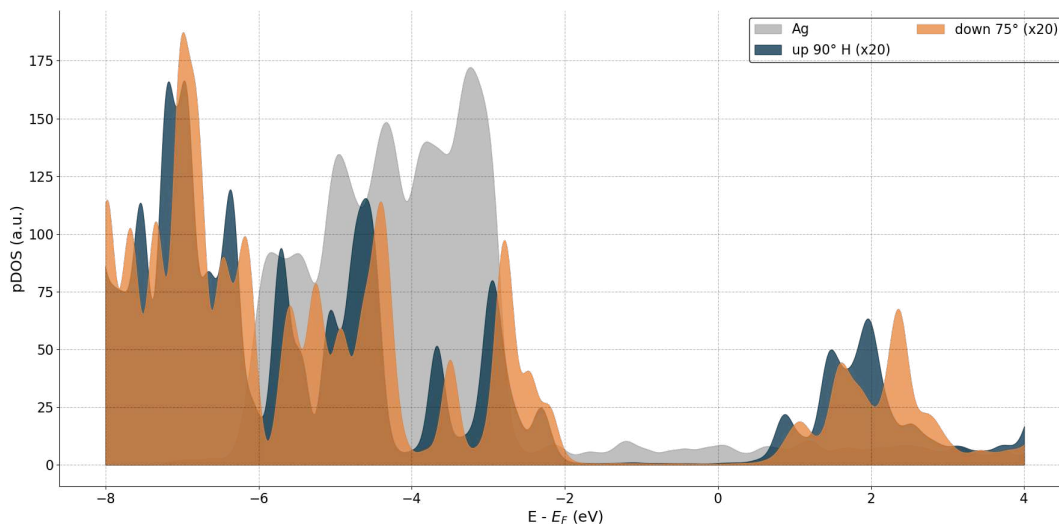


Figure 3.7: PDOS of the two most promising configurations, up 90° H and down 75° compared to the pDOS of the Ag(110) substrate. Important to note here is that the projection of the molecule pDOS has been multiplied with a constant factor (of 20) to enhance visualisation. All atoms of the 4A-MAD molecule were used in this projection.

While the atomic orbital-resolved pDOS provides valuable information on the distribution of electronic states between molecule and substrate, it does not directly allow for tracking individual molecular orbitals upon adsorption, due to strong hybridization and orbital mixing.

To overcome this limitation, additionally a molecular orbital projected density of states (MOPDOS) analysis is performed [28]. In this approach, the Kohn–Sham wave functions of the full adsorption system (obtained from the VASP `WAVECAR` file) are projected onto the molecular orbitals of the isolated 4A-MAD molecule. The latter are obtained from a separate single-point calculation of the freestanding molecule, serving as a well-defined reference for the gas-phase electronic structure.

By combining both datasets, the evolution of individual molecular orbitals upon adsorption can be traced, allowing for a direct assessment of energetic shifts, broadening effects, and hybridization with the Ag(110) substrate. In total, three calculations are required to construct a consistent picture: the full molecule–surface system, the clean Ag(110) slab, and the isolated molecule in vacuum, which also ensures consistent energy alignment between the different contributions. [28]

The MOPDOS of the 4A-MAD-up 90° H/Ag110 system is shown in figure 3.8.

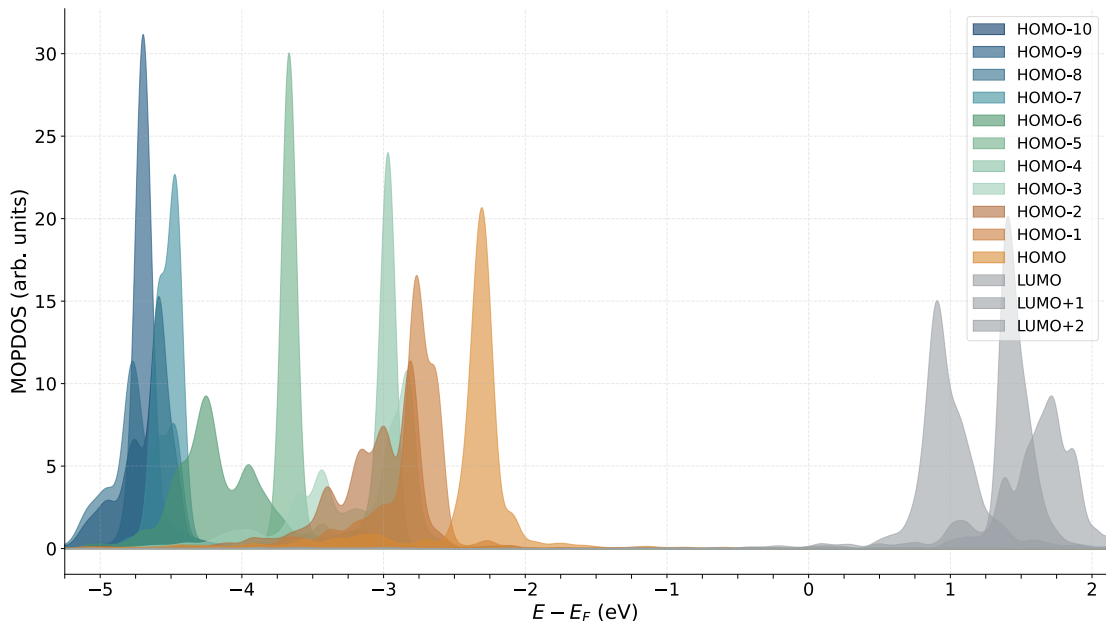


Figure 3.8: MOPDOS for the energetically most favorable 4A-MAD-up 90° H configuration.

The MOPDOS reveals the calculated energy level of the highest occupied molecular orbital (HOMO). Notably, due to the various approximations inherent in DFT (see section 2.2), the predicted energetic position typically deviates quantitatively from the experimental value. Nevertheless, the DFT results provide valuable insights and serve as a reliable qualitative indicator to identify the HOMO features in theoretical k-maps to be discussed next. As shown in figure 3.8, the HOMO is located at approximately 2.4 eV. The lowest unoccupied molecular orbital (LUMO), in contrast, remains unoccupied. This indicates that no significant net charge transfer between the molecule and the substrate occurs upon adsorption. The absence of a substantial occupation of the LUMO suggests that the molecule does not acquire a pronounced additional electronic charge from the Ag(110) surface.

While the density of states provides insight into the energetic distribution of electronic states, it does not directly reveal how the electronic charge is redistributed upon adsorption. To obtain a more complete picture of the molecule–surface interaction, the charge rearrangements at the interface are therefore analyzed. This analysis also provides the basis for understanding the change in the work function induced by molecular adsorption.

The work function is defined as the minimum energy required to remove an electron from the Fermi level of the system to the vacuum level. Upon adsorption, the work function may change due to modifications of the surface dipole. A clean metal surface exhibits an intrinsic surface dipole originating from the finite electron density extending beyond the last atomic layer [42]. When a molecule adsorbs on the surface, this dipole

is altered by two competing mechanisms. The first mechanism is the so-called *Pauli push-back effect*. As the molecular electron density overlaps with the electronic states of the metal, the Pauli exclusion principle forces electrons of the substrate back into the bulk. This redistribution reduces the surface dipole and consequently lowers the work function [43, 44]. The second mechanism is charge transfer across the molecule–surface interface. Depending on the direction of the transferred charge, this process can either increase or decrease the work function. In the present case, charge transfer from the Ag(110) substrate to the adsorbed molecule would increase the work function, thereby opposing the effect of Pauli push-back.

To identify which mechanism dominates the adsorption process, the charge density difference is calculated. It is defined as the difference between the charge density of the fully relaxed adsorption system, ρ_{tot} , and the sum of the charge densities of the isolated substrate, ρ_{sub} , and the isolated molecule, ρ_{mol} ,

$$\Delta\rho(\mathbf{r}) = \rho_{\text{tot}}(\mathbf{r}) - [\rho_{\text{sub}}(\mathbf{r}) + \rho_{\text{mol}}(\mathbf{r})]. \quad (3.4)$$

To ensure that only electronic effects are captured, the atomic positions of both the isolated substrate and the isolated molecule are fixed to the relaxed geometry of the full adsorption system when evaluating ρ_{sub} and ρ_{mol} . Consequently, the charge-density analysis requires three separate DFT calculations: one for the complete adsorbate–substrate system, one for the isolated Ag(110) slab, and one for the isolated molecule.

The charge redistribution is then averaged over the surface plane, yielding the plane-averaged charge density difference $\Delta\rho(z)$ which is shown in figure 3.9. This representation clearly reveals the accumulation and depletion of electronic charge normal to the surface and forms the basis for analysing the adsorption-induced interface dipole and the associated change in the work function.

Since molecular adsorption modifies the electronic structure and charge distribution at the molecule–metal interface, the work function provides an additional quantity with which these adsorption-induced changes can be characterized. In particular, comparing the work function of the clean surface with that of the adsorbed system allows the change induced by adsorption to be quantified

$$\Delta\Phi = \Phi_{\text{tot}} - \Phi_{\text{sub}}. \quad (3.5)$$

Here, $\Delta\Phi$ denotes the adsorption-induced change in the work function, while Φ_{tot} and Φ_{sub} are the work functions of the complete molecule–substrate system and the clean Ag(110) substrate, respectively.

Table 3.1 summarizes the calculated work functions for the two configurations, MAD-up 90° H and MAD-down 75°, together with the work function of the clean slab and the resulting changes. For both configurations, adsorption leads to a reduction of the work function. However, the magnitude of this reduction differs between the two structures. The MAD-up 90° H configuration exhibits a work-function change of -0.18 eV, whereas the MAD-down 75° configuration shows a larger reduction of -0.36 eV. For the MAD-up configuration, the charge-density difference shown in figure 3.9 reveals a potential change of approximately -0.5 eV, which is attributed to the bond dipole formed at

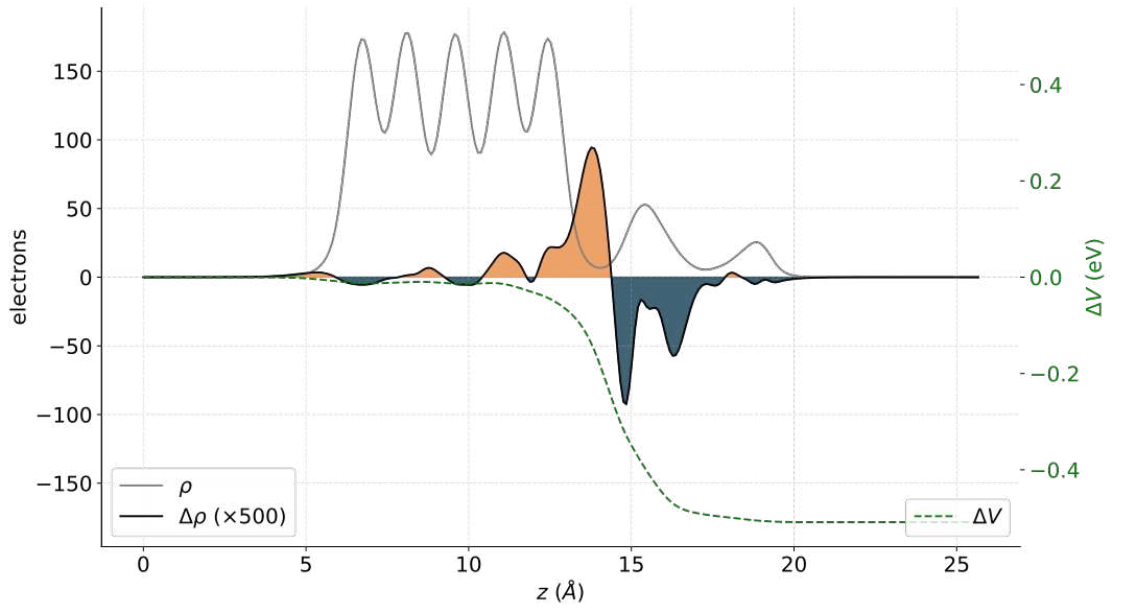


Figure 3.9: Plane-averaged total charge density ρ of the full 4A-MAD up 90° H system (gray line). $\Delta\rho$ denotes the plane-averaged charge density difference and shows an accumulation of electron charge (orange) in the surface region, indicating that the Pauli push-back effect dominates. Also shown is the corresponding change in the electrostatic potential ΔV (green, dashed line).

the molecule–surface interface. The difference between this contribution and the total work-function change can be associated with the dipole of the molecular monolayer, which is referred to as the bend dipole in the following. A similar separation of the adsorption-induced work-function change into contributions from the bond dipole and the molecular monolayer dipole has been reported in [44]. Thus, the work-function change provides an additional quantity that distinguishes the two adsorption configurations. Since the work function can also be determined experimentally, it could provide an additional means of assessing the plausibility of the different adsorption geometries if corresponding experimental data are available.

Table 3.1: Calculated work functions Φ and adsorption-induced work-function changes $\Delta\Phi$ for the clean Ag(110) slab and two 4A-MAD adsorption configurations.

system	Φ / eV	$\Delta\Phi$ / eV
Ag110	4.17	-
MAD up 90° H	3.99	-0.18
MAD down 75°	3.81	-0.36

3.2.4 Photoemission momentum maps: simulation vs. experiment

As a final validation step of the theoretical results, photoemission momentum maps (k-maps) are calculated and compared with the experimental angle-resolved photoemission spectroscopy (ARPES) data introduced in section 2.3.2. With the goal to provide an additional discriminator to identify the experimental adsorption geometry, 8 out of 14 adsorption configurations have been further considered for this analysis.

Before discussing the simulated momentum maps, the experimental conditions of the ARPES measurements are briefly outlined. The experimental data, measured by Eric Fackelman in the group of F. Stefan Tautz at the Forschungszentrum Jülich, Germany [45], were acquired using a HIS 14 HD UV source with a photon energy of $E = 22.21$ eV, corresponding to the He I α emission line. The incident light consisted of 20% (s)-polarized and 80% (p)-polarized components. Photoelectrons were detected using a NanoESCA MARIS momentum microscope, which combines a photoemission electron microscope (PEEM) with two consecutive hemispherical energy analysers [46].

The measurements were performed within a binding-energy range of $E_b = 2.7$ – 3.1 eV. The resulting experimental momentum map has been integrated over this energy window, and is compared with the simulated k-map in figure 3.10. To facilitate the comparison, the experimental data are displayed in the upper half of the figure, while the simulated data are shown in the lower half. This representation exploits the twofold symmetry of the system.

To reproduce the experimental conditions as closely as possible, the same illumination geometry was employed in the simulations. Specifically, an azimuthal angle of 90°, corresponding to the light incident along the [001] crystallographic direction at an angle

of 65° with respect to the surface normal, and a polarization ratio of 20% (s)-polarized to 80% (p)-polarized light were used when calculating the theoretical momentum maps.

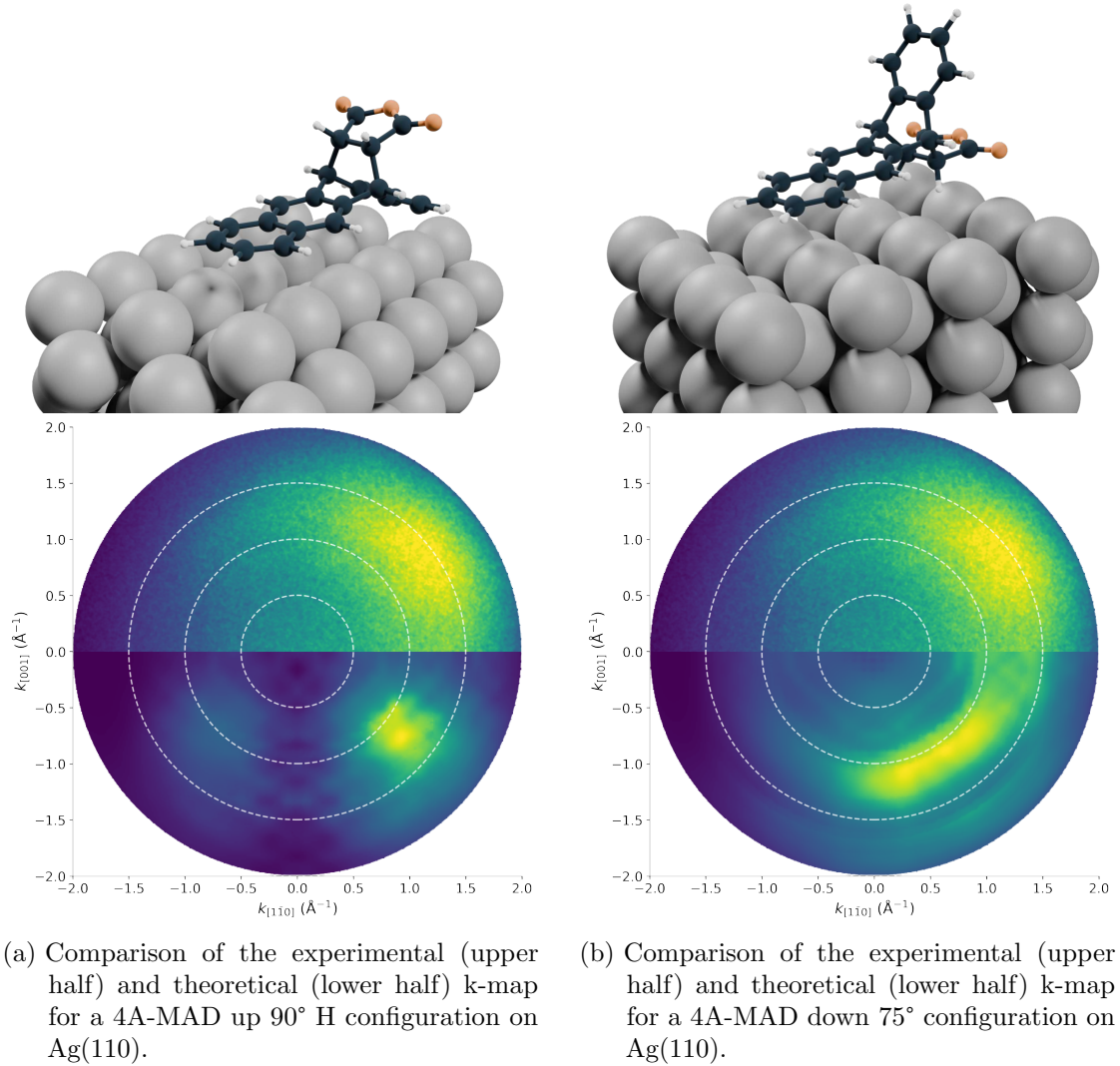


Figure 3.10: Comparison of two different theoretical 4A-MAD configurations to the same experimental data to get some insight of which configuration is present in the experiment.

As shown in figure 3.10, the two candidate configurations which are energetically most favourable (MAD-up 90° H and MAD-down 75°) reproduce several characteristic features of the experimental momentum map, yet neither results in a perfect agreement with the measured data. Consequently, the comparison does not allow a unique adsorption geometry to be identified.

Several factors may account for the remaining discrepancies between theory and

experiment. First, although fourteen adsorption geometries were investigated, it cannot be excluded that the true global minimum was not sampled. In this case, the experimentally realized adsorption geometry—and consequently the corresponding k-map—would not be represented among the calculated configurations.

A second possible explanation arises from the experimentally determined unit cell, which suggests the presence of two molecules per unit cell. This raises the possibility that different adsorption geometries coexist within the same unit cell, for example one 4A-MAD-up and one 4A-MAD-down configuration. Since the measured ARPES signal represents the combined photoemission intensity of all molecules within the illuminated area, such a coexistence would lead to a superposition of the corresponding momentum maps, which is not captured by the present calculations.

Distinguishing between these scenarios requires complementary experimental information on the adsorption geometry, for instance, as obtained from scanning tunnel microscopy. However, such data were not available at the time of writing, preventing a more definitive assignment of the experimentally observed electronic structure.

3.3 Heptahelicene on Ag(110)

3.3.1 Motivation – what do we expect from the system?

The second molecule/substrate system investigated in this work is comprised of a heptahelicene molecule adsorbed on the Ag(110) surface (see figure 3.11). heptahelicene (7HC) is an organic molecule which consists of seven ortho-fused benzene rings arranged in a helical structure, resulting in an intrinsically chiral molecule. Owing to its pronounced helicity, it is considered a promising candidate for supporting light-induced spiral currents and has been proposed as a potential platform for investigating the chirality-induced spin selectivity (CISS) effect, and molecular spin filtering [14, 15].

The CISS effect describes the spin-dependent transport of electrons through chiral molecular systems. In this phenomenon, the structural handedness of a molecule can lead to a preferential transmission of electrons with a specific spin orientation, effectively allowing chiral molecules to act as molecular spin filters. The origin of this effect is related to the coupling between the electron motion through the chiral molecular structure and its spin degree of freedom, which can result in spin-selective transport even in the absence of an external magnetic field. Although the CISS effect has been experimentally observed for various chiral systems, its microscopic origin and the conditions required for efficient spin filtering remain the subject of ongoing investigations [47, 48].

As for the 4A-MAD system, the present DFT study begins with an analysis of the geometric and electronic properties of the adsorbed molecule. In particular, the adsorption energy is calculated to identify the most promising adsorption geometry. Subsequently, the density of states is examined to characterize the electronic structure and the interaction with the Ag(110) substrate. Additionally, the system is studied under excitation by a pulsed laser field using TDDFT. This allows the time-dependent electronic response of the adsorbed molecule to be investigated and provides a basis for assessing its suitability for future time-resolved pump-probe experiments.

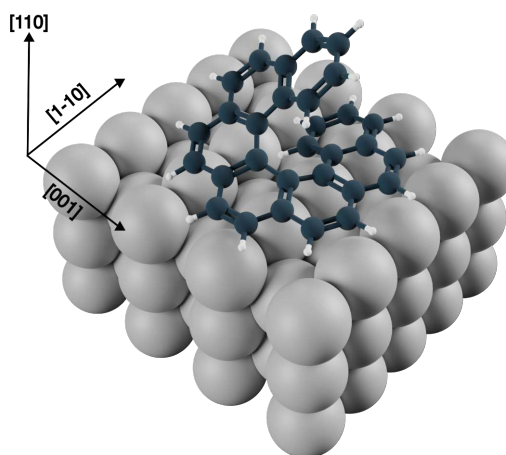


Figure 3.11: Structural model of heptahelicene on Ag(110).

3.3.2 DFT geometry optimization

Following the procedure established for the 4A-MAD system, a geometry optimization was first performed to determine the energetically favourable adsorption configurations of 7HC on Ag(110). A set of different initial adsorption geometries was generated using the atomic simulation environment (ASE) package [41]. As in the previous case, the high-symmetry adsorption sites of the Ag(110) surface were used to define the initial positions, where the benzene ring of 7HC closest to the metal surface (the "first" ring) serves as the reference for defining the adsorption site.

In addition to the adsorption site, the azimuthal orientation of the molecule with respect to the substrate's high symmetry directions was considered. For this purpose, the orientation of the zig-zag pattern formed by the second and third benzene rings was aligned along selected crystallographic directions of the Ag(110) surface (see figure 3.12). Note that due to the symmetry of the molecule, flipping the molecule upside down results in an equivalent adsorption configuration. Furthermore, an edge-on adsorption geometry was considered unlikely due to the expected stronger interaction between the extended aromatic backbone and the surface, and was therefore not included in the configuration search.

The adsorption energies were calculated according to equation (2.24), and the resulting values for the investigated configurations are summarized in figure 3.13. To improve the visualization of the different adsorption geometries, designated colours are used to distinguish between molecular orientations, while different marker shapes represent the corresponding initial adsorption sites. In addition, a separate calculation for the left-handed enantiomer (L) of 7HC was performed denoted by the open symbols in figure 3.13. This comparison demonstrates that, for identical adsorption positions and molecular orientations, the adsorption energy is equivalent for the left-handed and right-handed (R) enantiomers, as expected for a non-chiral substrate such as Ag(110).

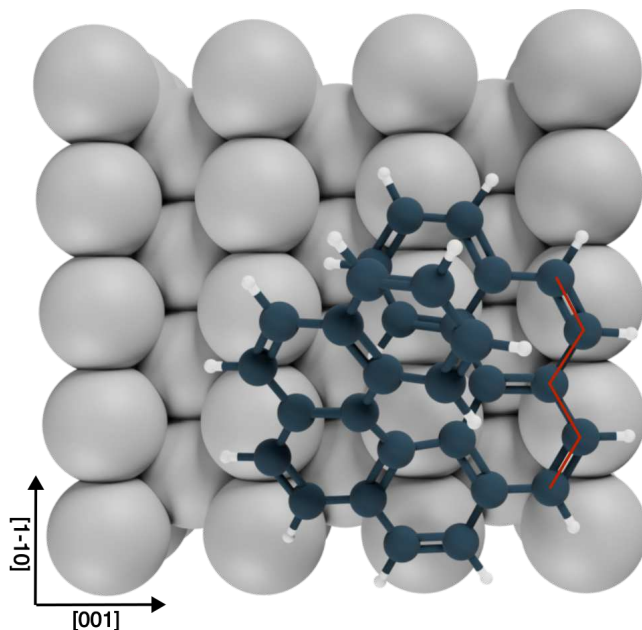


Figure 3.12: Top view of the structural model including a indicator to better visualize the zig-zag of ring 2 and 3 which is aligned in specific crystal directions during geometry optimization.

In contrast to the 4A-MAD system, figure 3.13 reveals a clearly preferred adsorption configuration. The configuration with the zig-zag axis aligned along the $[1-10]$ direction and the reference ring located at the top (T) site exhibits the lowest adsorption energy, differing by approximately 0.2 eV from the remaining configurations. For the remaining part of this chapter, the focus lies on this $[1-10]$ T (R) configuration, also depicted in figure 3.12.

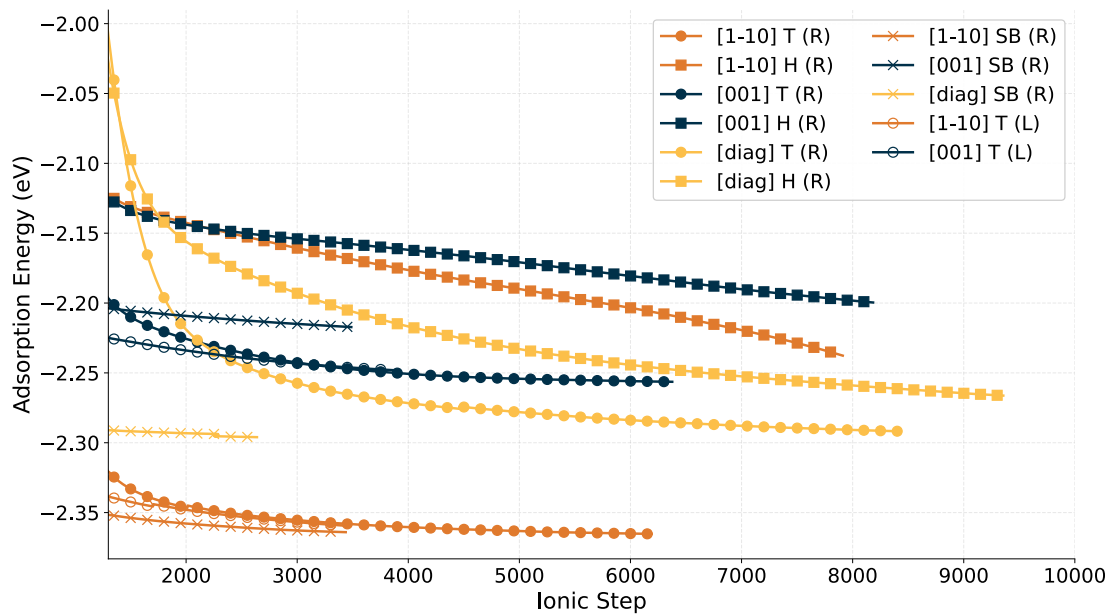


Figure 3.13: Adsorption energy as a function of the ionic step for different starting configurations of 7HC on Ag(110). The results indicate the presence of a preferred adsorption site on the surface, corresponding to the most energetically favourable configuration. The graph also shows that the left-handed (L) and right-handed (R) enantiomers exhibit nearly identical adsorption energies for equivalent adsorption positions and molecular orientations.

3.3.3 pDOS, MOPDOS and charge density rearrangements

The electronic structure of the heptahelicene–Ag(110) system is analysed using the pDOS introduced in the previous section. Here, the focus lies on how the molecular azimuthal orientation and different adsorption geometries influence in the electronic structure. The pDOS for two configurations, corresponding to the two investigated crystallographic alignments of the molecule, are shown in figure 3.14.

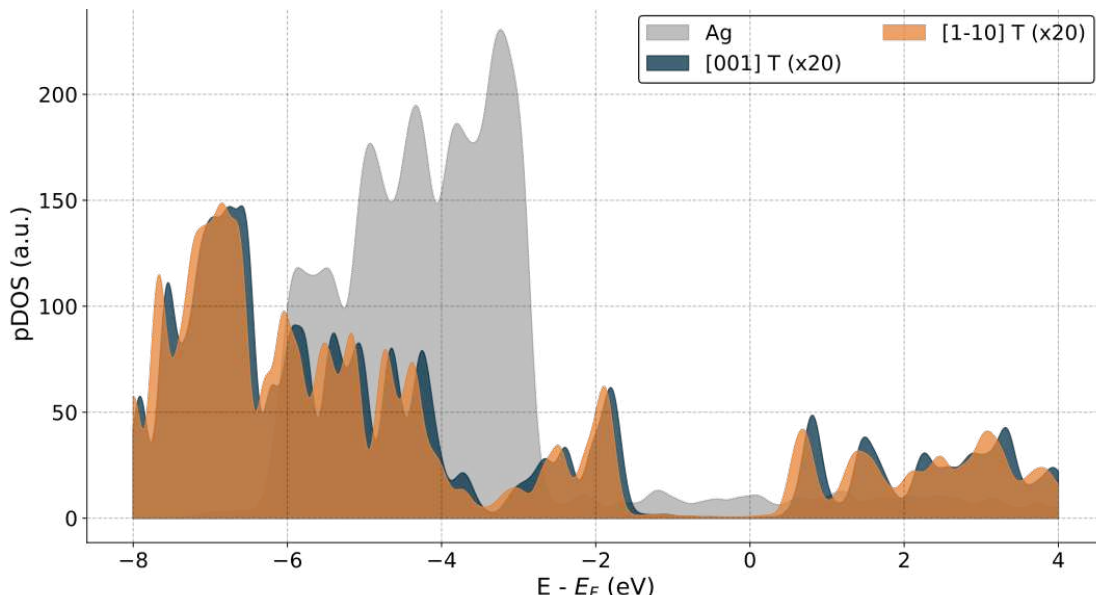


Figure 3.14: Calculated pDOS for two different configurations to investigate the influence of the molecule to the DOS and what role different configurations might play.

As observed for the 4A-MAD system, the onset of the Ag (d)-band is located approximately (3 eV) below the Fermi level. The two heptahelicene configurations exhibit very similar pDOS characteristics, which is expected since the molecular geometry remains essentially unchanged and only the azimuthal orientation with respect to the Ag(110) surface is modified. Nevertheless, there appears to be a slight, almost rigid shift of 0.1 eV to larger binding energies when changing the alignment from [001] to the energetically most favourable direction [1-10], indicating a subtle influence of the adsorption orientation on the molecule–substrate interaction.

Interestingly, the first pronounced molecular features appear at energies above the Ag (d)-band region. This energetic separation reduces the overlap between molecular states and substrate (d)-states in the relevant energy range of the HOMO, which is expected to simplify the interpretation of the molecular contributions in the subsequent momentum-map analysis.

In a subsequent step, photoemission momentum map (k-map) are calculated to investigate the orbital contributions to the photoemission signal. To facilitate their interpre-

tation, first a MOPDOS analysis is performed. The MOPDOS of the most promising adsorption configuration, [1-10] T, is shown in figure 3.15. The relevant molecular orbitals are labelled according to their energetic position, allowing the corresponding theoretical orbital energies to be identified and directly correlated with features observed in the calculated k-maps. The HOMO and HOMO-1 are separated by only a small energy difference, which may complicate to resolve them experimentally. As in the 4A-MAD system, the LUMO remains unoccupied, indicating that no significant charge transfer into the molecular LUMO occurs upon adsorption. This suggests that the molecule does not undergo substantial electron transfer from the Ag(110) substrate.

In addition to the electronic structure analysis, the adsorption-induced charge redistribution is investigated using the charge density difference introduced in the previous section. The resulting charge rearrangement at the 7HC–Ag(110) interface is shown in figure 3.16. The charge density difference reveals a redistribution of electron density upon adsorption, with a depletion of the electron spill-out region of the Ag surface and a corresponding accumulation of charge closer to the substrate. This behaviour is consistent with the Pauli push-back effect discussed previously, where the overlap between molecular and metallic states leads to a compression of the surface electron density. The observed redistribution confirms a finite electronic interaction between the 7HC molecules and the Ag(110) substrate.

A corresponding work-function analysis is performed for the 7HC system to assess whether the two investigated adsorption configurations, [1-10] T and [001] T, can be distinguished by their adsorption-induced changes in work function. The calculated values are summarized in table 3.2.

Table 3.2: Calculated work functions Φ and adsorption-induced work-function changes $\Delta\Phi$ for the clean Ag(110) slab and two 7HC adsorption configurations.

system	Φ / eV	$\Delta\Phi$ / eV
slab	4.17	-
[1-10] T	3.67	-0.50
[001] T	3.74	-0.43

For both configurations, adsorption results in a reduction of the work function relative to the clean Ag(110) slab. The [1-10] T configuration exhibits a change of -0.50 eV, while the [001] T configuration shows a slightly smaller reduction of -0.43 eV. The difference of only 0.07 eV between the two configurations is comparatively small, however, and therefore makes the work-function change less suitable as an additional indicator for distinguishing between the two adsorption geometries.

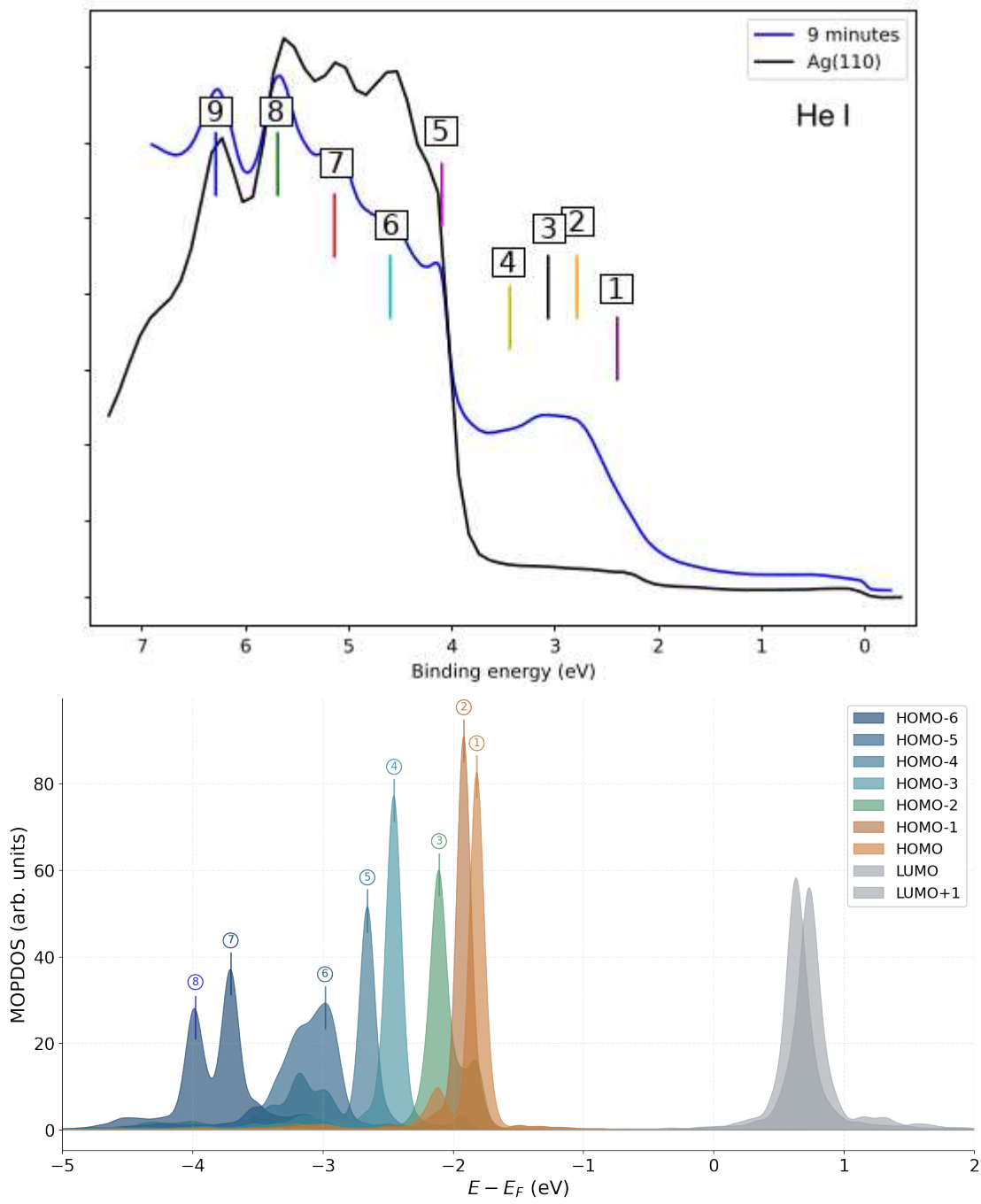


Figure 3.15: Experimental DOS for the 7HC/Ag(110) system provided by [49] (upper panel). MOPDOS for the 7HC [1-10] T (R) configuration (lower panel). The labels indicate the peak maxima of the HOMO, HOMO-1 etc.

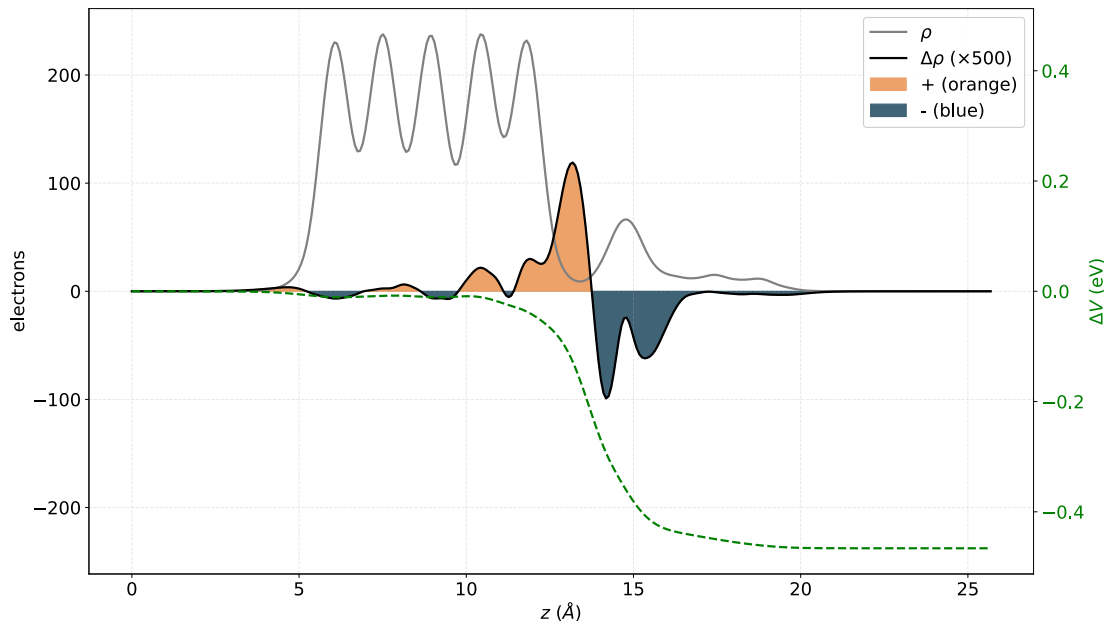


Figure 3.16: Charge difference plot comparing a clean substrate with the full system of the 7HC [1-10] T (R) configuration.

3.3.4 Simulation of photoemission angular distribution maps (k-maps)

To further assess whether the energetically most favourable adsorption geometry corresponds to the experimentally realized structure, the k-map analysis introduced previously is applied also to the heptahelicene–Ag(110) system. The experimental ARPES data were provided by Andrei Matetskii and Serguei Soubatch from the Forschungszentrum Jülich, Germany [49]. In contrast to the 4A-MAD system, the measurements cover a broader energy range, allowing several molecular orbitals to be compared directly with the experimental momentum maps. This enables a more comprehensive evaluation of the agreement between theory and experiment. The remaining experimental parameters are identical to those described in section 3.2.4.

For the theoretical k-map calculations, a damped final-state approach is employed. However, the comparison between the experimental data and both the isolated molecular contribution and the full molecule–substrate system indicates that the assignment of the experimentally observed emission patterns to the molecular orbitals is facilitated when comparing the experimental k-maps to simulated ones, obtained for a freestanding 7HC-molecules, thus disregarding the Ag(110) substrate in the calculation of the momentum maps. Note that for these ARPES simulations, we have simply removed the Ag atoms from the relaxed molecule/Ag(110) unit cell, but kept the 7HC in its adsorption configuration. A comparison between momentum maps simulated for the full 7HC/Ag(110) and the freestanding 7HC is depicted in figure 3.17.

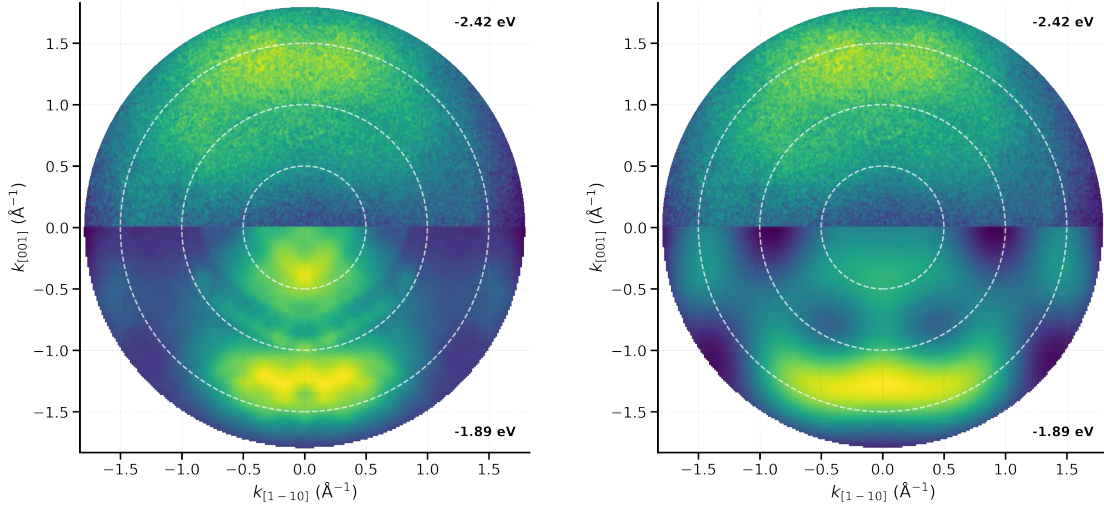


Figure 3.17: Simulated momentum maps (lower halves) for the full 7HC/Ag(110) system (left) and the freestanding 7HC (right). The upper halves show the corresponding experimental data. The respective binding energies are indicated.

Furthermore, the complex three-dimensional geometry of 7HC introduces additional challenges for the interpretation of the calculated momentum maps. In particular, the plane-wave final-state approximation cannot fully capture all effects associated with the curved molecular structure. Therefore, the following analysis should be regarded as a first indication of the electronic behaviour of the system rather than a complete description of the experimental photoemission response. The main objective is to identify promising adsorption configurations and molecular orbitals for future, more detailed investigations.

Momentum maps, computed of the eight binding energies labelled in the MOPDOS plot (figure 3.15), are depicted in figures 3.18 and 3.19, where we also include a comparison with the respective experimental data. For nearly all binding energies, the calculated k-maps show a qualitatively good agreement with the experimental data. In particular, the comparisons for the first three binding energies exhibit features at the outermost ring that agree well in both shape and position. For energy positions 4, 6, and 8, the overall shape of the calculated k-space patterns is also in good agreement with experiment, although their positions show a slight deviation. The comparisons for energies 5 and 7 are less convincing, but still exhibit characteristic similarities between the calculated and experimental maps. Note that for these two energies, the agreement is further improved when the substrate is included in the calculation, indicating that substrate contributions may play a more significant role for these states. Overall, the observed similarities across the different molecular orbitals provide further support for assigning the investigated adsorption configuration, [1-10] T, as a likely structure present on the Ag(110) surface.

To further support this proposed assignment of the energetically most favourable adsorption geometry, figures 3.20 and 3.21 show the k-map comparison for an alternative molecular orientation (zig-zag along the [001] direction). In contrast to the previously discussed configuration, the agreement between the calculated and experimental momen-

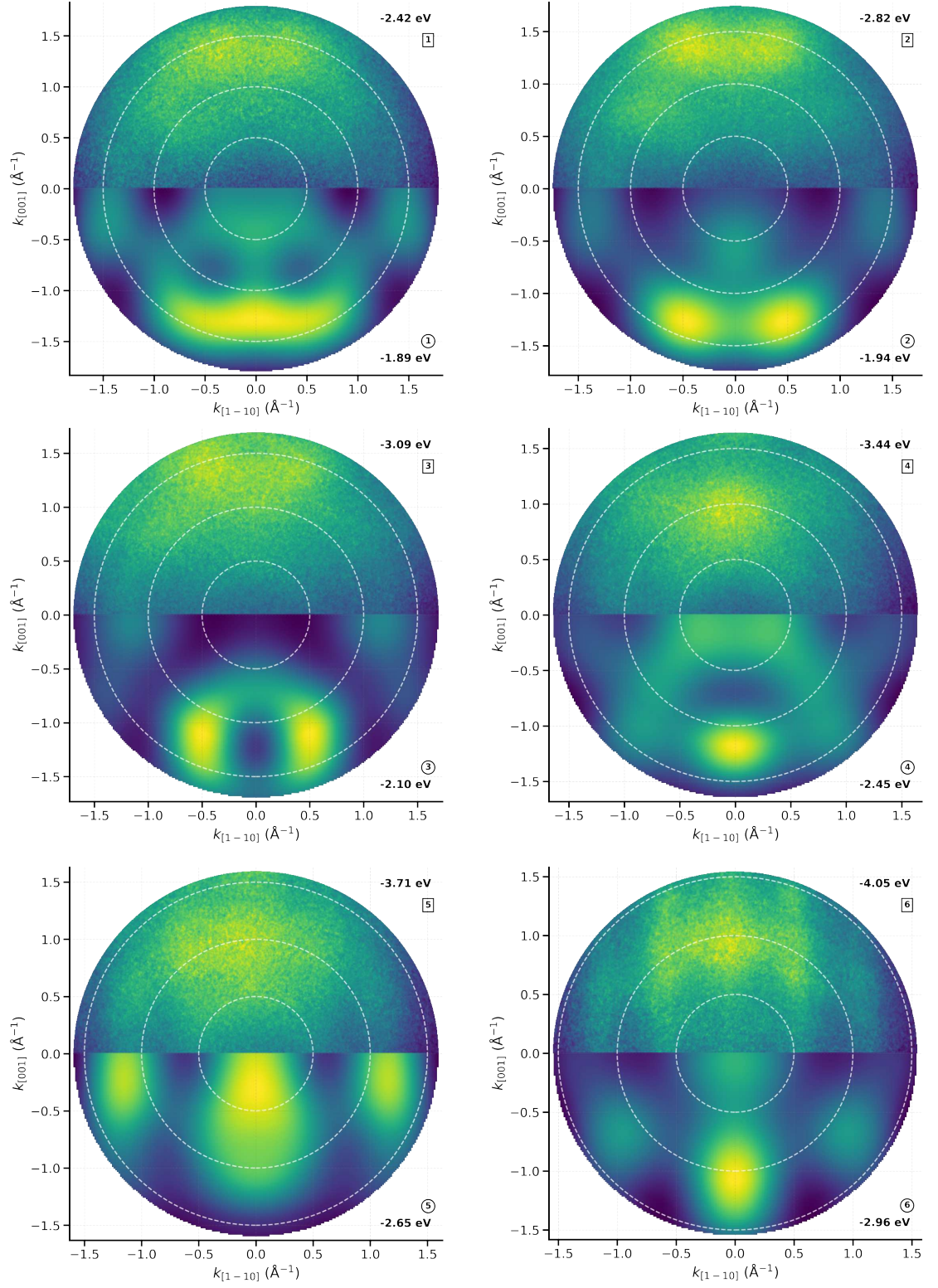


Figure 3.18: Comparison of the free standing relaxed molecule, [1-10] T (R), to the experimental data at 6 of 8 different energy cuts which show qualitative good agreement to the data.

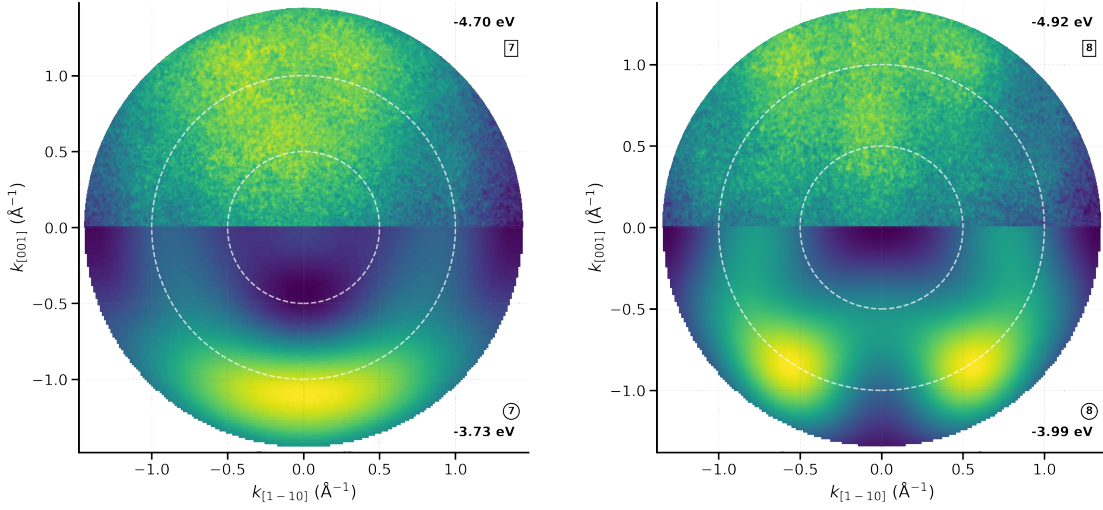


Figure 3.19: Comparison of the free standing relaxed molecule, [1-10] T (R), to the experimental data at the last 2 of 8 different energy cuts which shows qualitative good agreement to the data.

tum maps is considerably poorer, with only limited qualitative similarities. To illustrate the poorer agreement more explicitly, for instance the first three slices show pronounced intensity around $k_{[001]} \approx -0.5 \text{ \AA}^{-1}$ in the theoretical data, whereas no corresponding intensity is observed in the experimental data. For cuts 4, 6, and 7, the overall shape of the calculated emission features also deviates more strongly from the experimental data than for the previously discussed configuration. In particular, several characteristic features observed experimentally are either absent from the calculation or occur at different positions in momentum space. These discrepancies indicate that the [001] configuration provides a less satisfactory description of the experimentally observed electronic structure. This comparison lends additional support to the conclusion that the energetically most favourable adsorption geometry ([1-10] T) is indeed the configuration most likely realized on the Ag(110) surface.

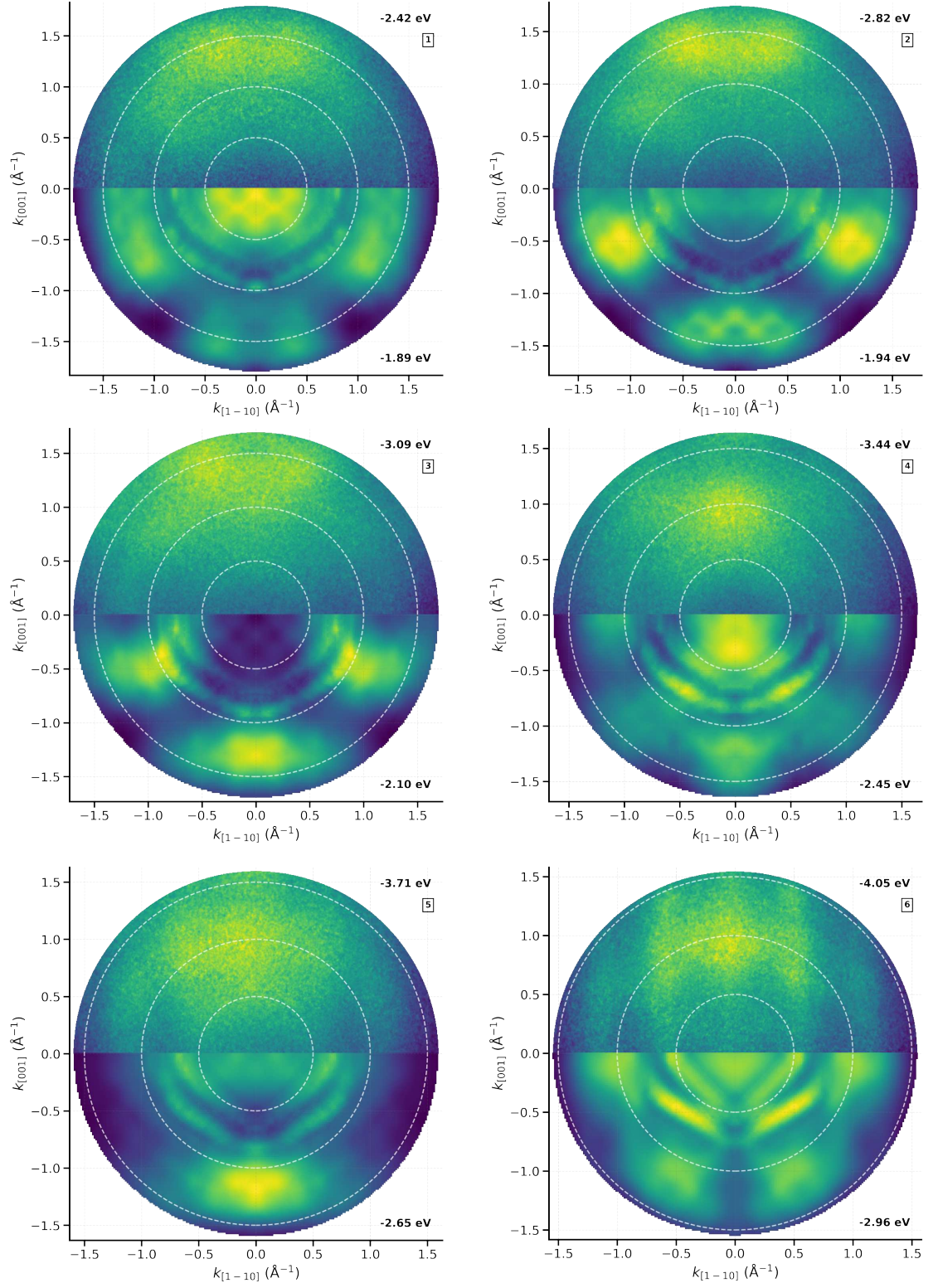


Figure 3.20: Comparison of the alternative configuration ([001] T (R)) to the experimental data at 6 of 8 different energy cuts which shows qualitative worse agreement to the data than before.

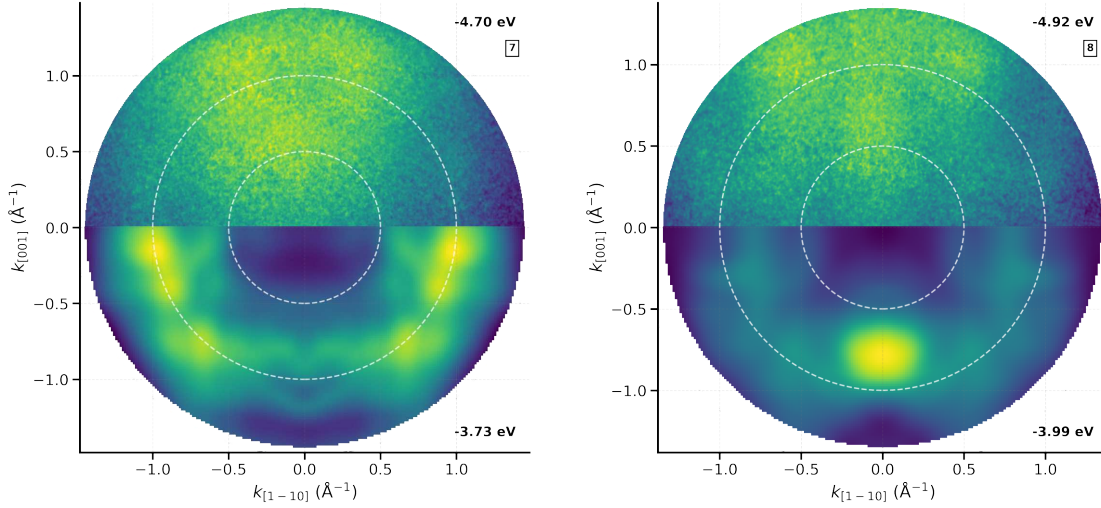


Figure 3.21: Comparison of the alternative configuration ([001] T (R)) to the experimental data at the last 2 of 8 different energy cuts which shows qualitative worse agreement to the data than before.

3.3.5 TDDFT: Induced current and angular momentum

To gain further insight into the response of the 7HC to time-dependent external perturbations, additional simulations based on time-dependent density functional theory (TDDFT) are performed using the approach described in see section 2.4. In particular, the aim is to investigate the electronic response of the system to a few-cycle mid-infrared laser pulse and to assess whether light-induced electronic currents are generated and, if so, to characterize their nature.

Since TDDFT calculations are computationally considerably more demanding than ground-state calculations, the simulations presented in the following are restricted to the isolated gas-phase heptahelicene molecule. Consequently, effects arising from the Ag(110) substrate, such as charge transfer, hybridization, and screening, are not included and may lead to quantitative differences compared to the adsorbed system. The present calculations should therefore be regarded as a first qualitative investigation, providing insight into the types of currents that can be induced and their potential relevance for future studies of the complete molecule–surface system.

The TDDFT simulations are carried out using the OCTOPUS code. As a first step, a ground-state calculation is performed using the optimized molecular geometry (from [50]) stored in an .xyz file. The most relevant computational parameters are summarized below:

- **Spacing:** Controls the spatial discretization of the real-space grid. A grid spacing of 0.24 Å is employed.
- **BoxShape:** Defines the geometry of the simulation domain. A spherical simulation box is chosen.

- **PseudoPotentialSet:** Specifies the pseudopotential library. The `pseudodojo_1da` pseudopotentials are used throughout this work.
- **ExtraStates:** Determines the number of additional unoccupied Kohn–Sham states included in the calculation. Four extra states are considered.
- **MixField:** Defines the quantity mixed during the self-consistent field (SCF) cycle. Here, the electronic density is mixed.

Following the ground-state calculation, the electronic system is propagated in time under the influence of a time-dependent external perturbation. Within OCTOPUS, this perturbation is introduced using the `TDEexternalFields = vector_potential` option, which allows the temporal profile and polarization of the laser pulse to be defined. In the present work, the laser pulse is described by the following envelope function $f(t)$ [51]:

$$f(t) = -\frac{c}{\omega} \sqrt{\frac{I}{3.509470 \times 10^{16}}} \sin^2\left(\frac{\pi t}{p}\right) [1 - \theta(t - p)], \quad (3.6)$$

where p denotes the total pulse duration, θ is the Heaviside step function, t is the propagation time, I is the laser intensity, and ω is the angular frequency of the applied field. Figure 3.22 visualizes this envelope function.

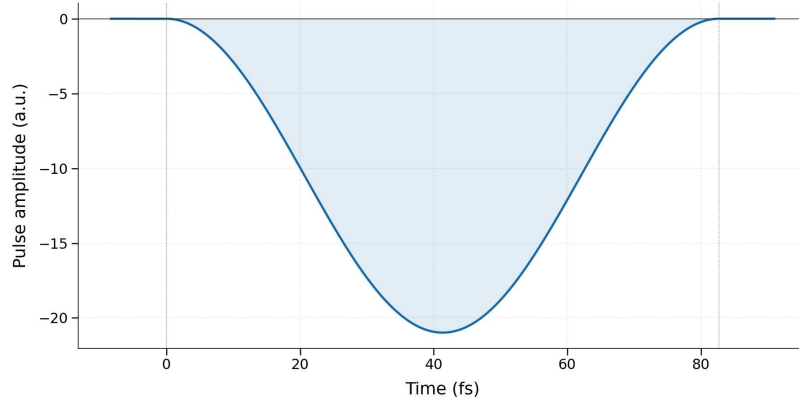


Figure 3.22: Visualisation of the envelope function $f(t)$ defined in equation (3.6).

The first quantity calculated with OCTOPUS is the cell-integrated current density (for further details, see section 2.4.3). This quantity can be obtained directly by enabling the `total_current` tag within the `TDOutput` settings. To investigate the dependence of the induced current on the external driving field, simulations were performed for different field amplitudes and frequencies. The corresponding combinations of field parameters are summarized in table 3.3.

The induced cell-integrated current densities (see equation (2.35)) are shown in figure 3.23 and figure 3.24, where the lower panels display the calculated current density and the upper panels show the applied vector potential of the external field. The influence

Table 3.3: Summary of the different simulation cases used to investigate the influence of the external field amplitude I , the electric field E and frequency f on the induced current response.

case	$E / \frac{\text{MV}}{\text{cm}}$	$I / \frac{\text{W}}{\text{cm}^2}$	f / THz
1	6.1	5×10^{10}	72.5
2	8.7	10^{11}	72.5
3	12.3	2×10^{11}	72.5
4	8.7	10^{11}	35
5	8.7	10^{11}	72.5
6	8.7	10^{11}	125

of the field amplitude on the induced current is presented in figure 3.23. A nearly linear relationship between the amplitude of the applied field and the resulting current density can be observed (see figure 3.25). This indicates that increasing the driving field strength leads to a proportional enhancement of the induced current, suggesting that stronger excitation fields could improve the detectability of the current response in future experiments. We also notice that the induced current is in phase with the vector potential.

The effect of varying the frequency of the external field is shown in figure 3.24. While changing the frequency modifies the amplitude of the resulting current density, the overall magnitude remains within the same order of magnitude for the investigated range. This observation is particularly relevant for the planned experimental setup, where the accessible excitation frequencies are limited to values below approximately 40 THz. The simulations further indicate a proportional behaviour between the applied frequency and the current that is induced which remains observable within the experimentally accessible frequency regime.

These initial results indicate the presence of an induced current while the molecule is exposed to an external driving field. Under the assumption that the employed model system captures the relevant physical mechanisms, this current response is expected to be accompanied by the generation of magnetic moments (see equation (2.36)) associated with the time-dependent charge motion. Similar to the current-density analysis, the influence of the field amplitude and frequency was investigated, with the corresponding results shown in figure 3.26 and figure 3.27. Although a magnetic moment is indeed induced during the excitation, its magnitude, on the order of only a few percent of the Bohr magneton, raises questions regarding its experimental detectability. Nevertheless, the trends observed for the induced magnetic moment are consistent with those identified for the current response. In particular, increasing the driving-field amplitude leads to an approximately linear increase in the magnitude of the induced magnetic moment, as expected from the corresponding dependence of the current on the field strength. Furthermore, the magnetic moment remains of the same order of magnitude for lower excitation frequencies. These results suggest that sufficiently sensitive detection methods,

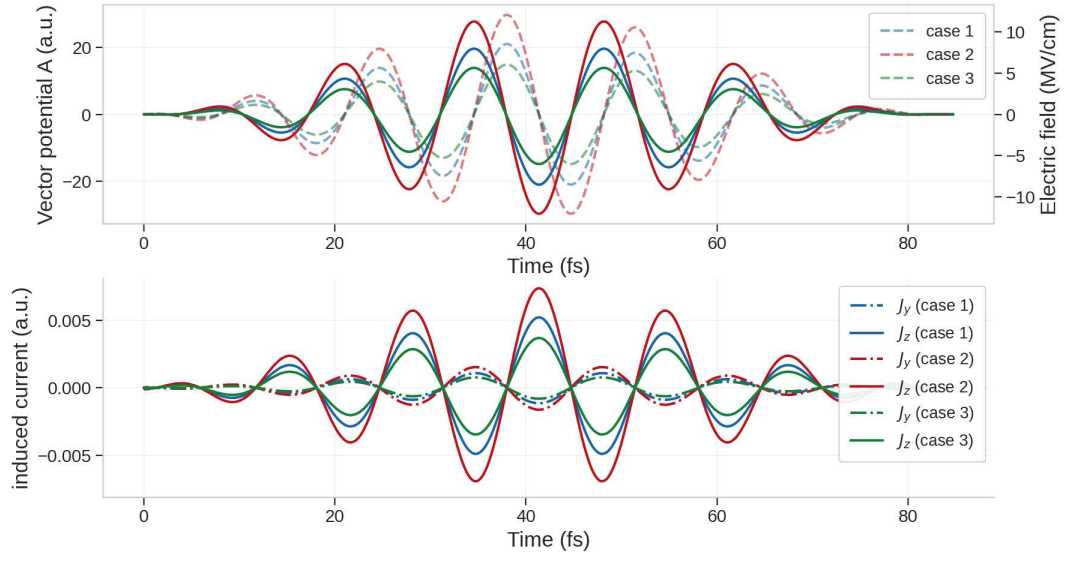


Figure 3.23: Influence of the external electric field amplitude on the induced cell-integrated current density. Top panel shows the input vector potential as well as the corresponding E-field. Bottom panel shows the induced current components J_y (dashed) and J_z (full lines) respectively (cases see table 3.3).

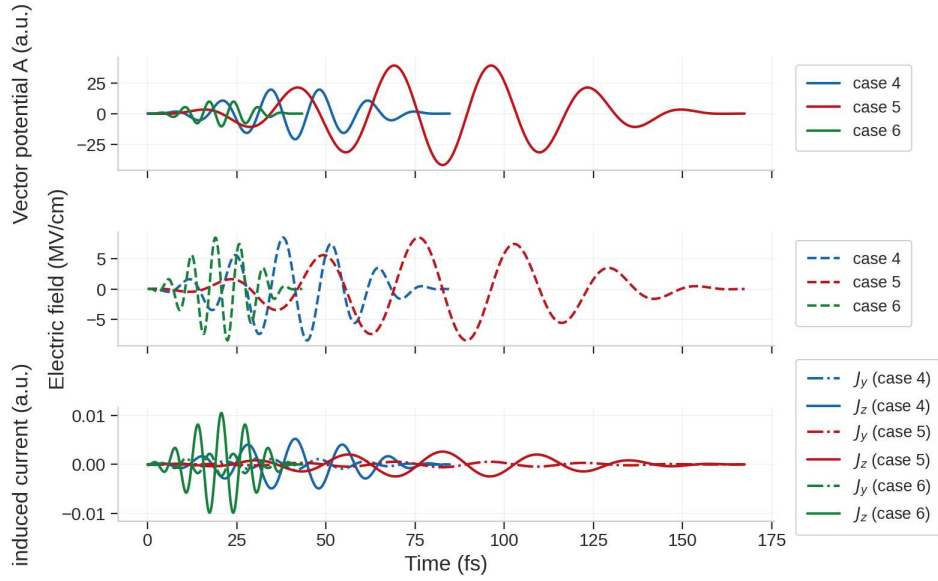


Figure 3.24: Dependence of the induced cell-integrated current density on the frequency of the external driving field. The first panel shows the vector potential while the second panel displays the corresponding E-field. The bottom panel shows the induced cell-integrated current components J_y (dashed) and J_z (full lines) respectively (cases see table 3.3).

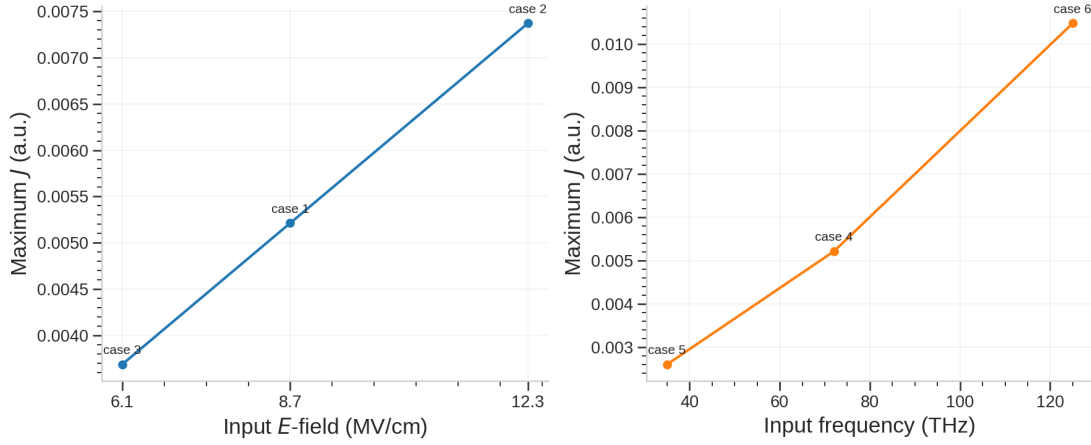


Figure 3.25: Visualisation of the maximum induced cell-integrated current density J per case. The left panel displays the dependency on the input electric field while the right panel displays the frequency dependency.

together with a strong driving field, would be required to enhance the experimental detectability of the induced magnetic moment. This suggests that the induced magnetic response persists within the frequency range relevant for the planned experimental setup.

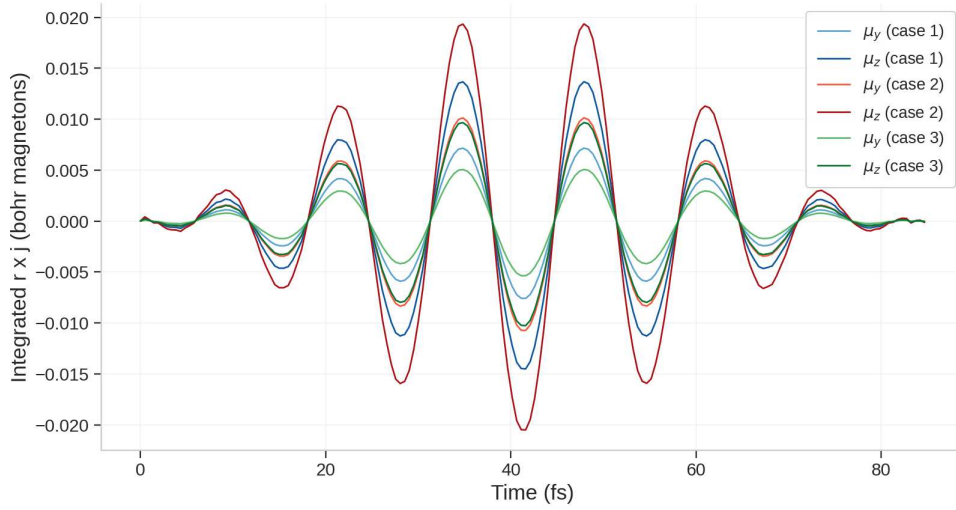


Figure 3.26: Influence of the external electric field amplitude on the induced magnetic moment (cases see table 3.3).

After establishing the presence of an induced current, the next step is to investigate its spatial distribution and determine whether the current exhibits a characteristic pattern,

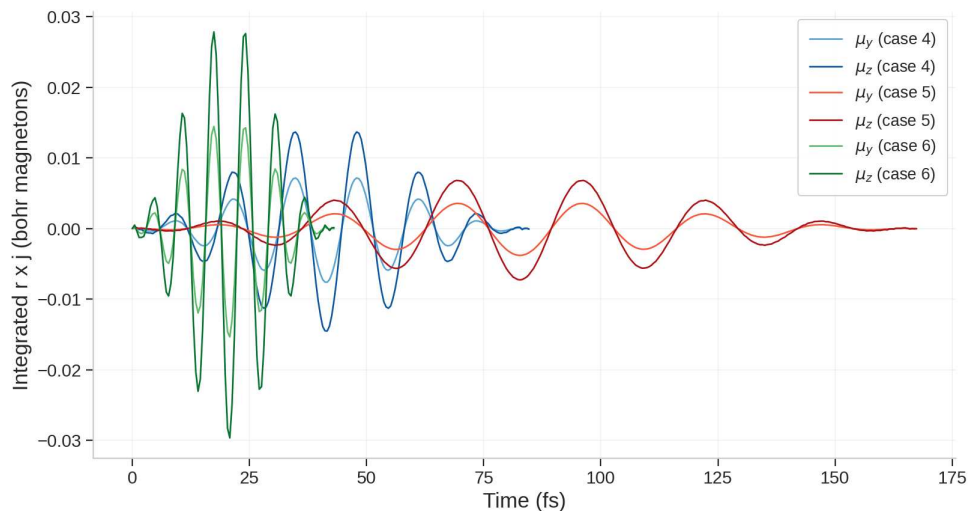


Figure 3.27: Dependence of the induced magnetic moment on the frequency of the external driving field (cases see table 3.3).

such as a light-induced ring current within the heptahelicene backbone. One possible approach for analysing this behaviour is the visualization of the time-dependent current density as a three-dimensional representation, where the current direction is indicated by arrows and the magnitude is represented by the corresponding arrow length and size.

However, a time-dependent three-dimensional visualization is difficult to represent within a written thesis. Therefore, selected time steps of the current-density evolution are extracted and presented as individual snapshots (see figure 3.28), illustrating the temporal development of the current distribution. For visualization purposes, the z -component is suppressed in these snapshots to enhance the visibility of the x - and y -components, which reveal the spiral-like structure of the current. The vectors indicate the local direction of the current, while their size and colour represent its magnitude.

The three selected time steps illustrate the evolution of the current in response to the driving field. In the first snapshot, no external field is applied and, correspondingly, no significant induced current is observed. In the second snapshot, the driving field has a positive sign, resulting in current vectors oriented in a counter-clockwise direction. When the sign of the driving field changes, the induced current reverses its direction and becomes clockwise oriented. These snapshots therefore provide a qualitative illustration of the spiral-like current and its reversal with the driving field.

In addition, a more quantitative representation is obtained by evaluating the current density j along the z -axis at $x = 0$ and $y = 0$ for different z -positions and time steps, using the Octopus tag `axis_z`. Here, $x = 0$ and $y = 0$ correspond to the center of the molecule, while z is varied over the height of the molecule. This allows the current contributions along the z -axis to be examined at different points in the time evolution.

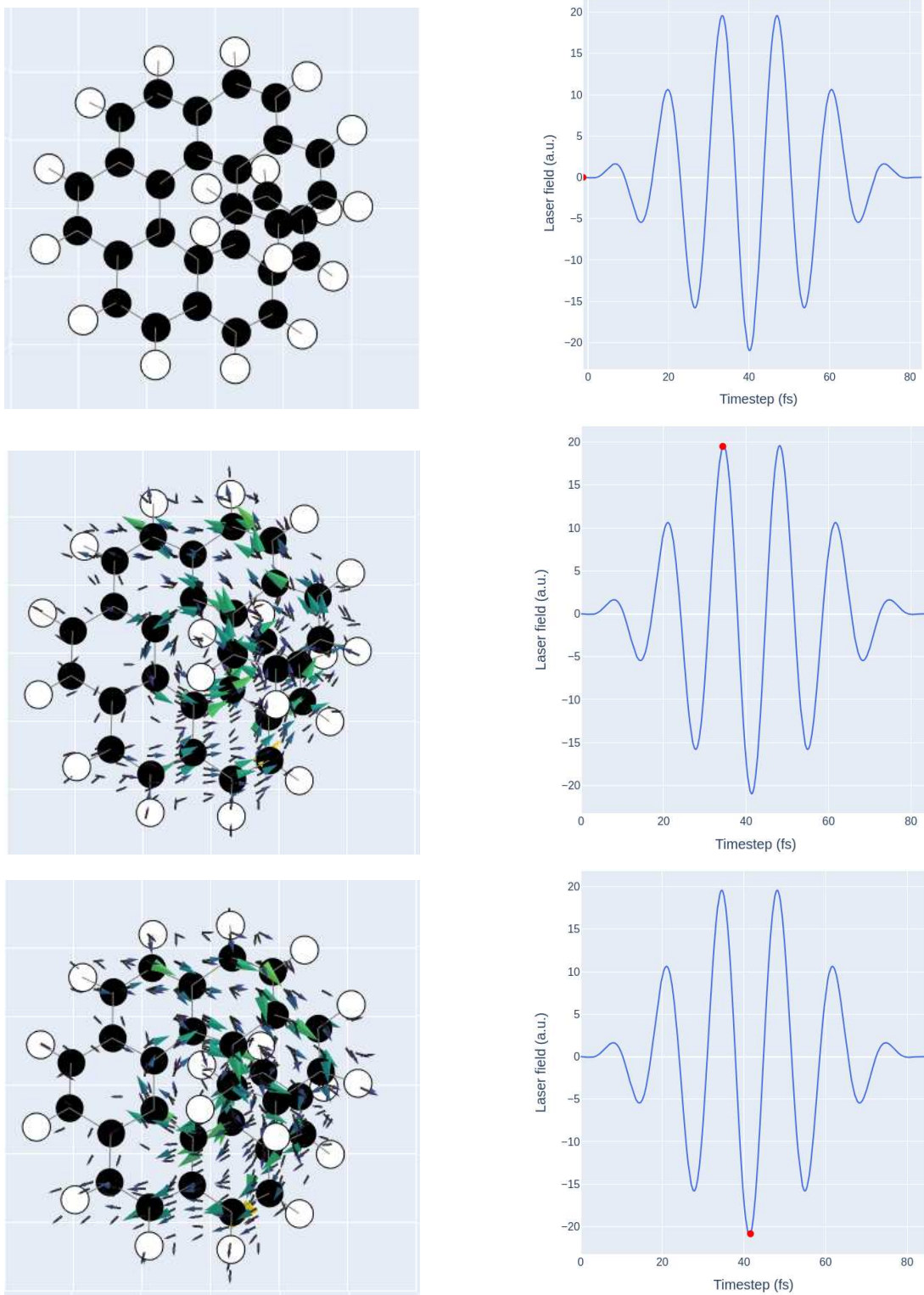


Figure 3.28: Snapshots of the time evolution of the induced current density. **Left:** Top-view of the molecular current density. The z-component has been omitted for visualization purposes to highlight the in-plane current distribution. **Right:** Corresponding applied laser field ($E = 8.7 \frac{\text{MV}}{\text{cm}}$, $f = 72 \text{ THz}$).

The resulting heatmaps, shown in figure 3.29, allow the individual current components and their temporal evolution to be analyzed. Since only the current density along this one-dimensional slice is considered, rather than the full three-dimensional current distribution, the corresponding current magnitudes are smaller.

As expected, the (z)-component of the current density is significantly larger than the in-plane components, with an amplitude approximately one order of magnitude higher. This behaviour follows from the polarization of the external driving field, which is applied along the (z)-direction. Furthermore, the (x)-component exhibits opposite signs for different (z)-positions. This antisymmetric behaviour explains the absence of a significant net (x)-directed contribution in the total current, as the individual contributions compensate each other.

Overall, both the three-dimensional current-density evolution and the extracted current-density slices show a spatial redistribution of the induced current that is consistent with the formation of a spiral-like current pattern within the heptahelicene molecule.

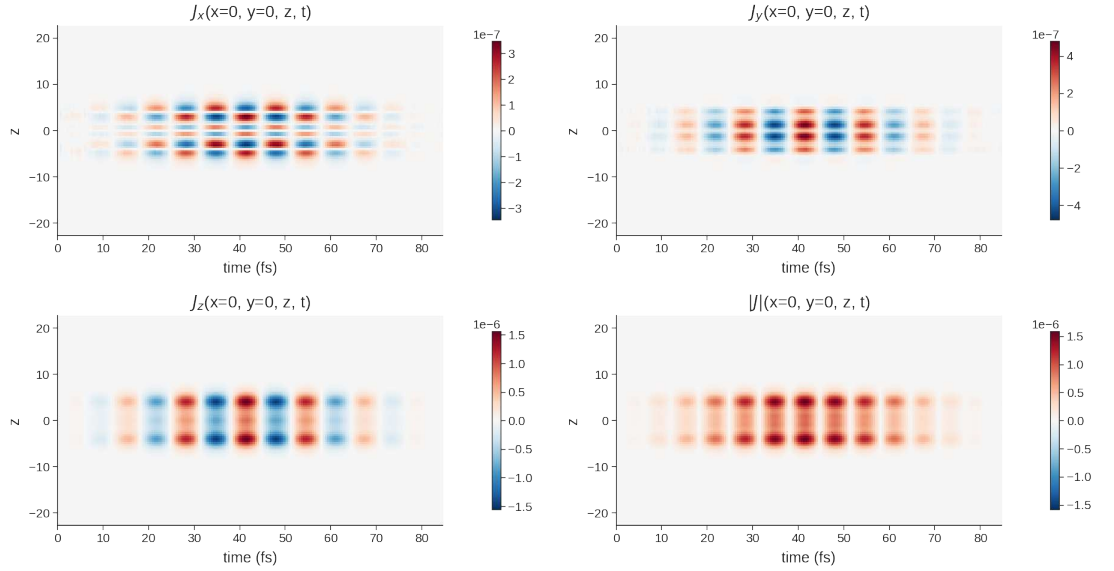


Figure 3.29: Heatmap of the induced cell-integrated current density along the z-axis $\vec{J}(x = 0, y = 0, z, t)$ for case 1 (see table 3.3).

4 Conclusion

The aim of this thesis was to assess the suitability of two molecular systems, the tetracene–maleic anhydride Diels–Alder adduct (4A-MAD) and heptahelicene (7HC) adsorbed on Ag(110), as model systems for future investigations within the orbital cinematography project. To this end, the adsorption geometries and electronic structures of both systems were investigated using density functional theory (DFT), while photoemission orbital tomography (POT) and angle-resolved photoemission spectroscopy (ARPES) were used to assess the agreement between theoretical predictions and experimental observations. For 7HC, the investigation was further extended using time-dependent density functional theory (TDDFT) to explore its response to an external driving field in the mid infrared (mid-IR) regime.

For the 4A-MAD/Ag(110) system, the large number of possible molecular orientations and adsorption geometries resulted in a comparatively extensive structural search. In total, 14 initial trial configurations were investigated and subsequently relaxed. The calculated adsorption energies showed that several configurations are energetically competitive, preventing the identification of a single structure solely on the basis of energetic stability. Additional analysis of the electronic structure, including the projected density of states and calculated momentum maps, was therefore performed. Although the comparison with the experimental ARPES data provided indications for several promising configurations, it did not allow an unambiguous assignment of a single adsorption geometry. Consequently, the theoretical investigation narrows down the number of plausible structures but cannot fully resolve the experimental structure at this stage. Further experimental characterization, in particular atomic force microscopy (AFM) measurements planned by the experimental collaborators, will therefore be important to clarify the molecular arrangement on the surface. These measurements were not yet available within the timeframe of this thesis.

The 7HC/Ag(110) system, in contrast, yielded a more conclusive result. The structural search identified one particular-adsorption configuration which was significantly favoured over the others. This finding is not only supported by its adsorption energy but also by the comparison of calculated and experimental momentum maps. The qualitative agreement observed for several molecular orbitals provides additional evidence that this configuration is representative of the experimentally realized structure. Conversely, the comparison with an alternative molecular orientation, exhibiting the second best adsorption energy, showed substantially poorer agreement, further supporting the assignment of the energetically favourable configuration. The work-function analysis also demonstrated a clear adsorption-induced reduction of the work function, although the difference between the two investigated orientations was too small to serve as a strong discriminating criterion on its own. Taken together, the structural and electronic analyses therefore provide a consistent picture of the adsorption geometry of 7HC on Ag(110).

Based on these results, the 7HC system was selected for a first TDDFT investigation of its response to an external mid-IR field. Since the computational cost of the time-dependent calculations prevented a corresponding treatment of the full molecule–substrate system within the scope of this work, the initial simulations were performed for the isolated gas-phase molecule. The resulting calculations therefore do not account for possible substrate-induced modifications of the electronic response and should be interpreted as a first assessment rather than a complete description of the experimental system.

Nevertheless, the TDDFT calculations provide several interesting indications. An induced current was observed in response to the applied mid-IR field, and an analysis of its spatial and temporal evolution revealed a circulating current pattern consistent with the presence of a helical or ring-like current in the 7HC molecule. The corresponding orbital magnetic moment was also quantified and found to be on the order of a few percent of the Bohr magneton. While a more detailed investigation including the substrate will be required before making a definitive statement about experimental observability, the magnitude obtained here indicates that the effect is not necessarily negligible from an experimental perspective. The dependence of the current response on the field amplitude and frequency further showed that the induced current remains within the same order of magnitude even when the driving frequency is reduced towards the range accessible to the planned experimental setup.

Overall, the results demonstrate the potential of 7HC/Ag(110) as a promising model system for future time-resolved investigations of light-induced helical currents. At the same time, the present TDDFT calculations should be regarded as a first theoretical indication rather than a complete description of the experimental situation. In particular, the influence of the Ag(110) substrate, charge transfer, screening, and the molecule–surface interaction on the induced current and magnetic response remains to be investigated. Extending the TDDFT calculations to the full adsorbate–substrate system would therefore be a natural next step. Further investigations could also address the dependence of the response on molecular orientation, laser polarization, pulse duration, and frequency, as well as establish a more direct connection between the time-dependent electronic response and experimentally accessible observables.

For 4A-MAD, the immediate next step is the experimental determination of the adsorption geometry, which will provide an important basis for assessing its suitability for future studies of light-induced retro-[4+2] cycloaddition dynamics. For 7HC, the combination of a well-supported adsorption geometry and the predicted light-induced helical current provides a strong basis for further theoretical and experimental investigations. Thus, the original objective of identifying promising model systems was achieved: 7HC/Ag(110) emerges as a particularly promising candidate for subsequent time-resolved studies, while the 4A-MAD system remains a promising candidate whose suitability requires further experimental clarification.

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