Structure, energetics, and vibrational spectra of perylene adsorbed on Si(001):
First-principles calculations compared with STM and HREELS

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The adsorption of perylene on the Si(001) surface is studied by means of first-principles density-functional theory calculations. Our results indicate that perylene adsorbs in an upright way in accordance with experimental observations. A number of conceivable geometries are considered and compared with respect to their adsorption energies, to their behavior in scanning tunnelling microscopy experiments and to their spectral response in an electron energy loss setup. Only the combination of these three aspects allows for the unique identification of the realized adsorption structure. In order to obtain complete energy loss spectra that can be related directly to experiments a recently developed method is used which allows for the easy calculation of both vibrational frequencies and intensities.

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I. INTRODUCTION

Organic functionalization is becoming an increasingly versatile tool in the development of semiconducting devices.1–4 Despite enhanced experimental resolution in techniques like scanning tunnelling microscopy (STM), atomic force microscopy (AFM), and high-resolution electron energy loss spectroscopy (HREELS) the more subtle details of the molecule-substrate-interface remain obscure in many instances.

By probing spectroscopic fingerprints for structural candidates density-functional theory (DFT) calculations have proven helpful for the interface exploration. Known to yield accurate energies and geometries, the determination of vibrational frequencies within the harmonic approximation is also well within the reach of this method. Using advanced exchange-correlation functionals experimental wave numbers are usually reproduced with an error of less than 4%. Together with the corresponding oscillator strengths of the fundamental transitions it is possible to predict complete infrared (IR) or HREEL spectra that aid in the interpretation of the experimental data.

Perylene is an interesting model system because it consists of five six-membered carbon rings which define its aromaticity and \( \pi \)-conjugated character. Moreover, perylene constitutes the core of the widely known organic semiconductor 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA), but is easier in that it lacks the carboxylic anhydride functionality. Many studies5–7 have shown that PTCDA adsorsbs in an essentially flat-lying fashion on many different substrates where the interaction between adsorbate and substrate is mainly mediated by dispersion forces.8,9 Perylene, on the other hand, apparently adsorbs on Si(001) more or less vertically and establishes a strong covalent bond to the surface.10 In order to contribute to a better understanding of the molecule-surface interaction process, in this work we employ the state-of-the-art pseudopotential method, within a generalized gradient approximation to the density functional theory, to propose a model for the interaction of perylene with the Si(001) surface.

The paper is organized as follows. In Sec. II the general computational approach used in this work is presented, together with a brief comment on the recently developed method for the calculation of HREEL spectra. Section III starts with a part on the vibrational properties of gas-phase perylene and then proceeds with the discussion of the calculated structures of perylene adsorbed on Si(001) in terms of geometry, energetics, STM images and electron energy-loss response. Sec. IV concludes with a summary.

II. COMPUTATIONAL METHOD

The total-energy and electronic-structure calculations are performed using the Vienna \textit{ab initio} simulation package (VASP) implementation11 of the gradient-corrected (PW91)12 density functional theory (DFT). The electron-ion interaction is described by non-normconsuming ultrasoft pseudopotentials,13 allowing for the accurate quantum-mechanical treatment of first-row elements with a relatively small basis set. We expand the electronic wave functions into plane waves up to an energy cutoff of 25 Ry, which has been demonstrated to be sufficient in previous studies on small organic molecules in the gas phase14 and adsorbed on Si(001).15,16
Our calculations employ the residual minimization/direct inversion in the iterative subspace (RMM-DIIS) method\textsuperscript{17,18} to minimize the total energy of the system. The molecular atomic structure is considered to be in equilibrium when the Hellmann-Feynman forces are smaller than 10 meV/Å. According to our tests this value is small enough to yield accurate forces and dipole moments. Isolated perylene is arranged in a hexagonal supercell with edge lengths of 20 Å. This size is necessary to get rid of spurious interactions between the periodically repeated images of the molecules.

The Si(001) surface in the $2 \times 1$ reconstruction with buckled dimers is modeled with periodically repeated slabs where each supercell consists of six Si double layers plus adsorbed perylene molecules and a vacuum region equivalent in thickness to eight double layers. To permit the description of well-separated, noninteracting rows of perylene molecules we consider sections of the Si(001) surface with nominal $2 \times 6$, $6 \times 2$, and $4 \times 4$ periodicity. The corresponding slab bottom layers are hydrogen-saturated and kept frozen during the structure optimization whereas all other atoms are allowed to relax. All surface calculations are performed with the theoretical Si lattice constant of $a_{\text{Si}} = 5.456$ Å. The Brillouin zone integrations are carried out using the $\Gamma$ point in case of the isolated molecules and one (two) special $k$ point(s) in the irreducible part of the Brillouin zone in case of the $2 \times 6$ and $6 \times 2$ ($4 \times 4$) surface calculations. The method for the calculation of the IR and HREEL spectra is sketched as follows. The dynamic dipole is the basic quantity that determines the strength of vibrational transitions. In IR as well as specular HREEL spectroscopy it is directly related to the intensity,

$$I_i \propto \left| \frac{\partial \mu}{\partial q_i} \right|^2.$$  \hfill (1)

Here $q_i$ is the generalized normal mode coordinate of the $i$th vibrational mode so that kinetic and potential energy of the harmonic potential are strictly quadratic in $q_i$ and $q_i$, respectively. The normal modes and the corresponding frequencies are the solutions of the dynamical problem of the ions driven by the dynamical matrix, or Hessian, that is constructed with the Hellmann-Feynman forces resulting from displacements of the ions from their equilibrium positions. Accompanyingly, the dipole moment of the system is calculated for each distorted geometry so that, after a little algebra, the intensity according to Eq. (1) can be obtained. Details of this approach are described elsewhere.\textsuperscript{19}

III. RESULTS AND DISCUSSION

A. Vibrational spectrum of perylene

Perylene ($C_{20}H_{12}$) has been calculated and geometry-optimized using a hexagonal supercell with primitive basis vectors $a = a(1, 0, 0)$, $b = a(-1/2, \sqrt{3}/2, 0)$, and $c = (0, 0, c)$ with $a = c = 20$ Å. The molecule plane was aligned parallel to the $a-b$ plane, and the long perylene axis parallel to the $a$ axis. This arrangement results in C-C bond lengths between 1.377 Å and 1.465 Å and C-H bond lengths between 1.086 Å and 1.090 Å, cf. Fig. 1(a), in very good agreement with previous \textit{ab initio} studies.\textsuperscript{20} The $D_{2h}$ point group symmetry of perylene manifests itself also in the shape of the frontier orbitals depicted in Fig. 1.

Each normal mode of vibration can be regarded as a basis for an irreducible representation of the respective point group. In case of perylene one expects the following classification of the 90 ($3 \times 32 - 6$) internal molecular vibrations, employing the standard notation of the $D_{2h}$ character table:\textsuperscript{21}

$$\Gamma_{\text{vib}} = 16A_g + 15B_{1g} + 6B_{2g} + 8B_{3g} + 7A_u + 8B_{1u} + 15B_{2u} + 15B_{3u}. \hfill (2)$$

All “undegenerate” ($u$) $B$ modes are expected to appear in an IR spectrum because they are symmetry allowed. So despite the high symmetry of perylene the IR spectrum with (potentially) 38 allowed modes will show a rich structure, especially taking into account that no modes are degenerate. The calculated IR spectrum is shown in Fig. 2 with the wave numbers of the strongest transition indicated. In perylene, in-plane and out-of-plane modes are strictly separated; the
latter have nonvanishing oscillator strengths only below 817 cm$^{-1}$. It is noteworthy that perylene exhibits six low-frequency vibrations (not shown in the spectrum) between 6.6 cm$^{-1}$ ($B_{3u}$) and 224.4 cm$^{-1}$ ($A_u$), three of which are allowed, but have very low oscillator strengths. This is an indication of the softness of this molecule as these low-frequency vibrations are associated mostly with slight ring deformations. So it is to be expected that perylene easily could change its planar gas-phase geometry substantially when it interacts with the Si surface though it remains essentially intact.

The displacement patterns of the vibrations that contribute mainly to the gas-phase spectrum are sketched in Fig. 3. The strongest out-of-plane vibrations (not shown in the spectrum) are excited at 543 cm$^{-1}$, 770 cm$^{-1}$ and 817 cm$^{-1}$ (all $B_{1u}$). These are predominantly out-of-plane wagging motions of the H atoms. Ten out of the 11 most important in-plane modes (from 251 cm$^{-1}$ to 1601 cm$^{-1}$) are characterized mainly by bendings of the C-H bond and strong collective deformations of the carbon rings. The high-frequency mode at 3135 cm$^{-1}$, on the other hand, consists quasi solely of asymmetric stretches of the C-H bonds, in accordance with the expectations from experience.

Compared to the experimental C-H stretch frequency vibrations are associated mostly with slight ring deformations. Ten out of the 11 most important in-plane modes ($251$ cm$^{-1}$ to $1601$ cm$^{-1}$) are characterized mainly by bendings of the C-H bond and strong collective deformations of the carbon rings. The high-frequency mode at 3135 cm$^{-1}$, on the other hand, consists quasi solely of asymmetric stretches of the C-H bonds, in accordance with the expectations from experience.

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tion that may have been believed to occur due to previous observations for the adsorption of aromatic molecules on solid surfaces. Therefore we have included this possibility in our calculations although it seems not to be consistent with experiment. Despite the very large adsorption energy of almost 7 eV this structure must be discarded, see below. It is interesting to note that there are rearrangements in the molecular framework that resemble those seen in the case of benzene adsorption on Si(001), see, e.g., Ref. 19: The constituting six-membered rings of perylene that are closest to a Si dimer adopt a frustrated butterfly geometry, the full completion of which is hampered by the strong intramolecular bonding.

The group of cross-dimer (CD), long-axis bonding structures, denoted lo-CD, is depicted in Figs. 4(c)–4(e). The coverage is defined such that two molecules per 2×6 surface unit cell correspond to one monolayer (ML). The six-fold repetition in [110] direction is necessary to separate the perylene chains in order to avoid mutual interaction. The first two structures in this group, lo-CD-facing with half and full monolayer coverage, share the feature that they give rise to perylene rows perpendicular to the dimer rows like in Fig. 6 and therefore show the observed long-range behavior. The zigzag structure is included for completeness. The three models have in common that the perylene molecules are subject to strong distortions upon adsorption: the left two and the right two rings of the molecule are twisted against each other by nearly 11°, determined as the angle between least-squares planes fitted against the carbon atoms in the left and the right part of the distorted molecule, respectively. This may explain the inclination of the molecules concluded from the STM observations.

The adsorption energies for the lo-CD and sh-CD structures lie between 1.07 eV and 3.25 eV. In Table I two values, $E_{\text{ad}}$ and $E'_{\text{ad}}$, for the adsorption energy in case of full monolayer coverage are given. The first one is the average adsorption energy per molecule that results if two molecules are thought to approach the surface at the same time. The second one is the energy gained upon adsorption of the second perylene molecule when the first molecule is already adsorbed at the surface.

**TABLE I.** Adsorption energies $E_{\text{ad}}$ (in eV) per molecule with respect to the clean 6×2 (top-dimer model, TD) or 2×6 (cross-dimer models, CD) Si(001) surface for the adsorption models considered in Fig. 4. For full monolayer (ML) coverage the value $E'_{\text{ad}}$ denotes the energy gain upon adsorption of the second perylene molecule when the first molecule is already present.

<table>
<thead>
<tr>
<th>Model</th>
<th>$E_{\text{ad}}$ (eV)</th>
<th>$E'_{\text{ad}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) lo-TD-facing, 1/2 ML</td>
<td>3.16</td>
<td></td>
</tr>
<tr>
<td>(b) flat</td>
<td>6.90</td>
<td></td>
</tr>
<tr>
<td>(c) lo-CD-facing, 1/2 ML</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>(d) lo-CD-facing, 1 ML</td>
<td>1.15</td>
<td>1.07</td>
</tr>
<tr>
<td>(e) lo-CD-zigzag, 1 ML</td>
<td>1.24</td>
<td>1.25</td>
</tr>
<tr>
<td>(f) sh-CD-facing, 1/2 ML</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>(g) sh-CD-facing, 1 ML</td>
<td>2.45</td>
<td>3.25</td>
</tr>
<tr>
<td>(h) sh-CD-zigzag, 1 ML</td>
<td>1.69</td>
<td>1.73</td>
</tr>
</tbody>
</table>

**FIG. 4.** Models of adsorption of perylene on Si(001) considered in this work in topview and in sideview. Large (small) white circles correspond to Si (H) atoms, medium gray circles to C atoms, and large gray circles to Si dimer atoms. Surface unit cells are indicated by rectangles. The multiplicators in parentheses indicate the nominal periodicity.
Therefore, the average adsorption energy in case of full monolayer coverage is recovered by 
\[ \bar{E}_{\text{ad}}(E_{\text{ad}}+E_{\text{ad}})/2 \]
This value is lowest, 1.07 eV, for the apparently experimentally observed adsorption model lo-CD-facing, and highest for the sh-CD-facing model, 3.25 eV. But adsorption energies are not always sufficient to assess the probability of formation because there may be huge energy barriers that thwart the realization of one or the other structure. In principle the height of these barriers could be estimated by constrained-realization of one or the other structure. In principle because there may be huge energy barriers that thwart the formation of either structure. To calculate STM images we employ the Tersoff-Hamann approach and show the integrated charge density between and .

The locally integrated density of states as probed by STM may give further hints to decide which structure is the one that actually occurs. To calculate STM images we employ the Tersoff-Hamann approach and show the integrated charge density between and , energy corresponding to the desired bias voltage) mapped to a plane. In order to avoid redundancy only STM images of the flat 4×4 and the full monolayer lo-CD-facing and sh-CD-facing structures are shown in Fig. 5. The top-dimer structure could be discarded in the first place due to the differing orientation of the perylene rows compared to experiment, the zigzag structures do not form tightly packed, well-separated rows at all, and the molecule-molecule distances in the half-monolayer structures are too large to give rise to nearly overlapping bright spots. The flat adsorption structure appears in the simulated STM image as shown in Fig. 5(a): it does not remotely resemble the experimental image (Fig. 6) as no distinguishable row-structure emerges. So this structure, too, must now be finally rejected as a candidate for the experimentally observed adsorbed structure. The sh-CD-facing geometry, Fig. 5(b), shows a very regular and symmetric pattern, a result of the retaining flatness of the adsorbed species, that comes close to the experimental image and is as such a very hopeful aspirant for the realized geometry. But up to this point also the lo-CD-facing model cannot be fully ruled out, although the spot structure is slightly alternating: it is not uncommon that in STM experiments the contrast between two spots of different brightnesses is averaged out.

To allow for an unambiguous decision on the actual interface structure we measured HREEL spectra and compared the data (see right-hand part of Fig. 7) with calculations for candidate structures. The method used for the calculation is briefly outlined in Sec. II and elaborated in more detail in Ref. 19. To set up the dynamical matrix including the substrate influence on the vibrations we include the complete adsorbate and two substrate layers in these calculations, corresponding to 56 and 88 atoms for half and full monolayer coverage, thus resulting in a 168- and 264-dimensional Hessian, respectively. The obtained spectra for the half monolayer lo-CD-facing and lo-TD-facing as well as the full monolayer sh-CD-facing and lo-CD-zigzag models are shown in the left-hand part of Fig. 7. Whereas the line shapes are similar in the high-frequency region that is dominated by C-H stretches in the adsorbate, there are pronounced differences between 500 cm−1 and 2000 cm−1. None of the left spectra, however, bears even qualitative resemblances to the

![Color online] (Filled-state STM image of perylene on Si(001)-2×1 at low coverage recorded at a bias voltage of –2.225 V and 0.065 nA. The bright spots correspond to perylene molecules, the rows of weak spots indicate Si dimers.)
experimental spectrum. That leaves, from the structures considered here, only one structure that can possibly be the actual surface geometry. Indeed, the full monolayer lo-CD-facing model gives rise to a calculated HREEL spectrum (Fig. 7, right-hand panel) which exhibits the same basic features as the experimental one and reproduces the line shape with good accuracy. We attribute the systematically lower oscillator strengths of the calculated spectrum in the region between 500 cm\(^{-1}\) and 1600 cm\(^{-1}\) to a homogeneous diffuse background due to unordered perylene molecules present in the experiment that are not included in our model. Nevertheless, for most of the peaks we can find a one-to-one correspondence between measured and calculated frequencies, a part of which will be discussed in the following with respect to the corresponding displacement patterns (and compared to those of the isolated molecule where applicable) that are shown in Fig. 8. In order not to overload the graphical representation the patterns in only one half of the surface unit cell seen in [110] direction are depicted. The movements in the other half can be derived by the newly introduced clas-

![HREEL spectra](image)

**FIG. 7.** Left-hand side: Calculated HREEL spectra for selected models of adsorption of perylene on Si(001). Right-hand side: experimental and calculated HREEL spectrum for the lo-CD-facing (1 ML) adsorption structure of perylene on Si(001). Important transitions are labeled with their respective wave numbers.

![Displacement patterns](image)

**FIG. 8.** Sketch of the displacement patterns of the normal modes with strong oscillator strengths that contribute to the calculated HREEL spectrum of the full monolayer lo-CD-facing model of perylene on Si(001) with wave numbers and their classification according to translation (T) or antisymmetry (A), see text for details of this scheme. Si (C, H) atoms are shown as large (medium, small) circles. Movements out of the perylene plane are depicted in such a way that atoms bearing dots (crosses) are displaced forwards (backwards). Atomic displacements in the perylene plane are indicated with arrows.
sification scheme of translation (T) and antisymmetry (A). This notation indicates that the individual vibrations in the two parts of the unit cell blend into each other by either a translation or a point reflection in the surface plane. The latter is to be understood in such a way that the vibrations of the two molecules are antisymmetric to each other with respect to a rotation by 180° around the surface normal. Note that this classification eases discussion but is somewhat approximate because the perylene molecules are not inherently vibrationally coupled. This is especially true for the 649 cm⁻¹ mode and the 3137 cm⁻¹ mode where the amplitude of the normal mode vibration is larger in one molecule than in the other.

A first skim over the depicted patterns shows that not only the high-frequency modes, but also the low- and medium-frequency modes are dominated by vibrations within the adsorbate, contrary to the case of, e.g., benzene adsorbed on Si(001). The reason for this is the already mentioned softness of the perylene molecule as indicated by its pronounced low-frequency modes that are easily excited. In the following calculated frequencies are given in midtext and experimental values in parentheses where a clear-cut assignment is possible. We find a notable Si-Si-stretch and a Si-C-bending type of vibration only in the A mode at 527 cm⁻¹ (513 cm⁻¹), but even here the adsorbate performs large-amplitude ring deformations. The out-of-plane T mode excited at 649 cm⁻¹ (629 cm⁻¹) is at least partially similar to the B₁u mode at 543 cm⁻¹ of isolated perylene, Fig. 3. There are also out-of-plane vibrations of the Si-substrate atoms, albeit with small amplitude. The 811 cm⁻¹ A-mode (818 cm⁻¹) of the system (a shoulder in the spectra) can be seen to come very close to the 817 cm⁻¹ B₁u mode of perylene in terms of the displacement pattern and frequency. The frequency shift is very small and as such indicative of the already strongly reduced substrate influence. The complicated ring-deformation present in the T modes at 1043 cm⁻¹ and 1095 cm⁻¹ may both be derived from the 1045 cm⁻¹ B₃g mode of the isolated molecule where due to the interaction between the two molecules on the surface a frequency splitting has occurred. The C-H-bending vibrations of the 1490 cm⁻¹ T mode (1470 cm⁻¹) correspond almost exactly to those of the 1499 cm⁻¹ B₃g mode of perylene; these vibrations are not strongly affected by the distortion from planarity of the adsorbed molecules. Comparing frequencies, we relate the 1607 cm⁻¹ T mode (1582 cm⁻¹ or 1656 cm⁻¹) to the 1601 cm⁻¹ B₁u mode of the isolated molecule. A close inspection reveals that in the latter the vibrations on the left-hand and right-hand parts of the molecule are in phase, whereas in the former they are opposite in phase. Not surprisingly, the C-H-stretch excited at 3137 cm⁻¹ can be traced back to the C-H-stretch at 3135 cm⁻¹ (3046 cm⁻¹) of gas-phase perylene. As the two molecules on the surface interact with each other the displacement pattern does not reflect the D₂h symmetry like the corresponding mode of the gas-phase molecule. The mode that indicates hydrogen abstraction from perylene upon formation of the bonds to the surface is the Si-H-stretch mode at 2085 cm⁻¹ (2098 cm⁻¹).

IV. SUMMARY

We have studied the adsorption of the aromatic molecule perylene on the Si(001) surface by means of density-functional theory calculations. A number of conceivable bonding scenarios has been investigated with respect to their geometries, energetics, STM signals and HREEL spectra. By a combination of these methods we were able to single out the adsorption geometry lo-CD-facing that is most probably realized in experiment.

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