Adsorption of PTCDA on NaCl(100) and KCl(100)

H. Aldahhak, W.G. Schmidt, E. Rauls

Abstract

The adsorption of PTCDA on KCl and NaCl(100) surfaces has been investigated by means of first principles calculations. Besides a variety of adsorbate structures for single molecules and a monolayer of flat lying molecules on plain terraces, the influence of monoatomic steps and the different defect site at step edges has been studied in detail.

1. Introduction

Alkali salt surfaces are a promising alternative to the more common metal substrates for studying molecular self organisation. Potassium chloride (KCl) and sodium chloride (NaCl) are the most simple representatives of these materials and considered as prototype insulators with large band gaps of 8.4 eV and 8.5 eV, respectively [1]. Previous theoretical studies reveal a quasiparticle gap of 8.6 eV for NaCl [2]. Experimentally, the treatment of alkali salt surfaces with methods commonly used for the investigation of metal surfaces, like, especially, scanning tunneling microscopy (STM), is a difficult task. The difficulty arises from surface charging and effects like electron-induced dissociation, which appears on insulator surfaces and hampers the detailed spectroscopy of the surfaces [3]. To overcome these difficulties, often ultrathin layers of alkali salts deposited on metallic surfaces are studied.

In this paper, we present the results of our first principles calculations on PTCDA adsorption on NaCl(100) and KCl(100). After a description of the computational methodology, we start by summing up the experimental observations of adsorbates laying flat on the surface (P-type). Then, we present our results for the different P-type adsorption patterns on both surfaces. Finally, we discuss the role of step edges including a number of different defective terminations at these steps for initiating structure growth.

The adsorbate structures have been calculated using first principles density functional theory (DFT) calculations with the Vienna Ab Initio Simulation Package (VASP) [4]. The PW91 functional [5] was used to model the electron exchange and correlation interaction within the generalized gradient approximation (GGA). The electron–ion interaction was described by the projector-augmented wave (PAW) method [6]. A (2 × 2 × 1) scheme was chosen as k-point sampling for the Brillouin zone. Four hundred electron volts was chosen as energy cut-off for the plane-wave basis. Since dispersion forces play an important role in structures like these, we extended the DFT description by a semi-empirical London-type correction as described in Ref. [7]. This approach has proven to yield satisfying results for a variety of molecular adsorption structures (see e.g. in Refs. [8–10]). The salt surfaces were modelled in slabs with six atomic layers, the two lowest of which were kept fixed during structure optimization. All other layers and the adsorbate were allowed to relax freely. A vacuum separation of 40 Å was found to be sufficient for obtaining converged results. The same set up was used to model the step edges in a saw tooth like model system with terraces wide enough to suppress interaction between periodic images of the molecule or the step itself.

The (100) surfaces of KCl and NaCl consist of alternating cation–anion pairs. According to experiments and previous force field and DFT calculations, the ions in the topmost two layers of this surface are slightly displaced from the coplanar layer [11–14]. Our calculations confirm this effect: the surface anions in the first layer are displaced upwards by 0.03 Å (KCl) and 0.06 Å (NaCl), and the surface cations are displaced by the same amount downwards. The second layer exhibits a smaller relaxation than the first one, but in the opposite direction for the surface cations and anions. Using the description of the surface rumpling, employed by Vogt et al. in Ref [11], where a positive rumpling means an outward movement of the anion and a negative value an inward movement, we sum up our results in the top (bottom) part of Table 1 for the (100) surfaces of KCl (NaCl). The quantity Δ expresses...
the shift of the ions in the ith layer, and $d_i$ expresses the distance between layers numbered $i$ and $i + 1$.

The 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) molecule ($C_{24}H_{8}O_{6}$) is – in the context of molecular adsorption studies – one of the most intensely studied organic molecules during the last years [15,16]. Fig. 1 shows a structural model of it and its specific non-equivalent binding sites of either pure donor (sites 2, 4, and 5 where the molecule can form either double or triple hydrogen bonds), pure acceptor (sites 3 and 6) character or both [15] (site 1). Different epitaxial adsorbate structures of PTCDA are observed on different metal or salt surfaces. Among the most common phases are the so-called square structures, the non-equivalent sites of the adjacent PTCDA molecules are combined in different ways [15].

### Table 1

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\Delta_1$</th>
<th>$\Delta_2$</th>
<th>$\Delta_3$</th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>0.00(5)</td>
<td>-0.01(2)</td>
<td>-0.01(4)</td>
<td>3.14(3)</td>
<td>3.15(3)</td>
<td>3.14(4)</td>
</tr>
<tr>
<td>Theory</td>
<td>0.03</td>
<td>-0.01</td>
<td>0.00</td>
<td>3.07</td>
<td>3.13</td>
<td>3.11</td>
</tr>
<tr>
<td>Ref. Benson</td>
<td>-0.06</td>
<td>0.03</td>
<td>-0.01</td>
<td>3.10</td>
<td>3.13</td>
<td>3.12</td>
</tr>
<tr>
<td>This work</td>
<td>0.03</td>
<td>-0.01</td>
<td>0.00</td>
<td>3.13</td>
<td>3.12</td>
<td>3.13</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>$d_1$ [Å]</th>
<th>$d_2$ [Å]</th>
<th>$\phi^\circ$</th>
<th>$m_1$ [Å]</th>
<th>$m_2$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl(100)</td>
<td>2.76</td>
<td>3.40</td>
<td>176.20</td>
<td>0.40</td>
<td>0.17</td>
</tr>
<tr>
<td>NaCl(100)</td>
<td>2.60</td>
<td>3.40</td>
<td>172</td>
<td>0.70</td>
<td>0.37</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Atom number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>On KCl(100)</td>
<td>+0.13</td>
<td>-0.10</td>
<td>-0.10</td>
<td>+0.02</td>
<td>-0.04</td>
</tr>
<tr>
<td>On NaCl(100)</td>
<td>+0.14</td>
<td>-0.10</td>
<td>-0.11</td>
<td>+0.04</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

---

1. As most commonly used in literature, more negative values mean stronger binding and are denoted as higher adsorption energies throughout the work.

**Fig. 1.** Structural model of the PTCDA molecule. The different specific binding sites are marked by the numbered ovals. Sites 3 and 6 have acceptor character, sites 2, 4, and 5 have donor character, and site 1 combines both.

**Fig. 2.** Top-view of PTCDA on (a) KCl(100) and on (b) NaCl(100) in SQ phase. The surface atoms beneath the molecule are labelled from 1 to 5. Their displacements upon adsorption of PTCDA are shown in Table 3.

**Fig. 3.** (a) Top-view and (b) side-view of the induced charge density difference for PTCDA on NaCl(100) in SQ. An isosurface value of ±0.003 e/Å³ was chosen.

**2. Single PTCDA molecule on KCl(100) and NaCl(100)**

The adsorption of PTCDA on plane surfaces of KCl and NaCl [17–24] as well as at step-edges has been thoroughly investigated both experimentally and theoretically [26,16]. To the best of our knowledge, single PTCDA molecules on KCl(100) have only been investigated in the group of M. Sokolowski [24,25]. Their polarization dependent fluorescence spectroscopy investigations suggest single molecules to adsorb parallel to the surface with slightly distorted geometries with the long axis of the molecule parallel to the [110] or [1\bar{T}0] directions of the surface. They expected, but not proved, the center of the molecule to be above a surface anion, its carboxyl oxygen atoms above the surface cations.

Our calculations for the single molecule on KCl confirm the reported experimental observations and can be extended to the case of NaCl. The single PTCDA molecule adsorbs on both KCl(100) and NaCl(100) in a structure which we denote by SQ in the following (see Fig. 2). In this structure, the molecule is parallel to the surface, its long axis parallel to [110], the carboxyl oxygens above cation sites, and the center above an anion site. The adsorption energy of PTCDA on KCl(100) is $-2.49$ eV, while it is $-2.91$ eV on NaCl(100). In both cases, about 72% of the adsorption energy originates from the vdW interactions. On NaCl(100), PTCDA has a higher adsorption energy, and both molecule and surface...
are more strongly distorted (Tables 2 and 3). As reported by Möbus et al. [17] and Schlettwein et al. [18], this result can be understood as a result of the smaller lattice constant of NaCl (5.6 Å) compared to KCl (6.25 Å), offering a better overlap between the carboxyl oxygen atoms of PTCDA molecules and the surface cations on the one hand and between the hydrogen atoms of PTCDA and the surface anions on the other hand (Fig. 2).

The charge distribution for PTCDA on NaCl(100) in SQ resembles that on KCl(100). The electron density is depleted near the perylene rings of the molecule and accumulated near the surface anion beneath and between the carboxyl oxygens and the surface cations (Fig. 3). In the SQ-phase, the adsorption induced total charge redistribution is 0.72 e (0.50 e) on NaCl (KCl).

### 3. Monolayer of PTCDA on KCl(100) and NaCl(100)

Dienel et al. investigated the growth of PTCDA on bulk KCl by atomic force microscopy (AFM) [20], while Müller et al. studied the growth of a monolayer of PTCDA on 10 ML thick of KCl by LEED [24]. They found PTCDA to arrange in a commensurate square-cell structure of dimensions of \( a = b = 12.6 \pm 0.1 \) Å (Fig. 4). In this so-called BW-phase, the molecules adsorb flat and parallel to the surface and to each other with their long axis parallel to [110] or [1\(\overline{1}0\)] (Fig. 4). In neither experiment, the adsorption sites are reported, but it is suggested that the center of the molecule is above an anion site of the surface and the carboxyl oxygens above cation sites.

![Fig. 4.](image1) (a) AFM image of PTCDA on KCl(100) in the so-called BW-structure [20]. The supercell has the dimensions \( a = b = 12.6 \pm 0.1 \) Å, \( \gamma = 90^\circ \) [20]. (b) Structural model of the BW-phase.

![Fig. 5.](image2) Structural model of the Herringbone phase (HB) of PTCDA on KCl(100) (left). Cell dimensions are \( a = 12.5 \) Å, \( b = 18.75 \) Å and \( \gamma = 90^\circ \). (Right) Q-phase model for PTCDA on KCl(100) with cell dimensions \( a = b = 18.75 \) Å and \( \gamma = 90^\circ \).
Our calculations confirm the experimental findings for the BW-phase. In the energetically most favored structures among the models investigated, the molecules adsorb in square-cells with dimensions \(a = b = 12.50\ \text{Å}, \gamma = 90^\circ\) (associated to \(2 \times 2\) surface-cells). The molecule has the same orientation as observed experimentally. Its adsorption energy \((-2.75\ \text{eV})\) is higher than that of the other suggested structures: Herringsbone (HB) \((-2.55\ \text{eV})\) and Q-phase \((-2.63\ \text{eV})\) (Fig. 5). Furthermore, a slight energy gain compared to an isolated adsorbed molecule \((E_{\text{ads}} = -2.49\ \text{eV})\) is found, indicating the presence of stabilizing intermolecular interactions. The registry of the molecule is similar in all these structures. In contrast to the BW-phase, which has one molecule in the unit cell, the HB- and the Q-phase unit cell contain two molecules per unit cell rotated by \(90^\circ\) compared to each other. A monolayer of molecules in the Herringsbone-phase exhibits a commensurate \(p2 \times 3\) film (Fig. 5), while the Q-phase shows a larger strain with a \(p3 \times 3\) film (Fig. 5).

In the BW-phase, the vdW-interactions make up 73\% of the adsorption energy. This adsorption energy can be divided into two terms: \(-0.38\ \text{eV}\) (molecule–molecule interactions) and \(-2.37\ \text{eV}\) (molecule–substrate interactions). Due to the smaller molecule–substrate interaction in the BW-phase, also the distortion of the molecule is smaller than for isolated molecules, cf. Table 4.

Our calculations yield higher adsorption energies than previous force field calculations \((-1.81\ \text{eV})\), but the electrostatic part for both calculations (about \(-0.80\ \text{eV}\)) is almost the same. To our knowledge, no experimental studies for measuring the distance between the PTCDA molecule and the KCl(100) surface either for the isolated molecules or for the monolayer have been reported.

The morphology of submonolayer and higher coverages of PTCDA on bulk NaCl was investigated by Burke et al. by means of the nc-AFM [21]. For coverages below 0.74 ML, their high resolution images show \(p3 \times 3\) adsorption patterns. The center molecule is rotated by \(90^\circ\) compared to those on the corners of the unit cell. They confirmed their experimental investigations by DFT and molecular mechanics (MM) calculations.

Eric Le Moal et al. investigated the growth of PTCDA on 10 monolayer thick NaCl films by spot-profile-analysis low energy electron diffraction (SPA-LEED) and obtained results identical to PTCDA on bulk NaCl. They found a commensurate superstructure of PTCDA molecules arranged in a square unit cell with a calculated lattice-constant of 16.92 Å (associated to \(3 \times 3\) surface cells), which is in a good agreement with the measured value of \(17 \pm 0.1\ \text{Å}\) determined from the SPA-LEED.

Analogous to the case of PTCDA on KCl(100), we calculated the Q-phase arrangement of PTCDA on NaCl(100) (Fig. 6 (c)), the HB-phase and the BW-phase (Fig. 7). The adsorption energies are shown in Table 5. Our calculations (Table 5) deviate from the experimental observations insofar as they suggest the BW-phase to be the most stable phase, while the experiment indicates Q-phase formation. In order to understand this, we studied the molecule–substrate and the molecule–molecule interactions separately for all phases (Table 5).

<table>
<thead>
<tr>
<th>d₁</th>
<th>d₂</th>
<th>(\varphi)</th>
<th>(m₁)</th>
<th>(m₂)</th>
<th>(S₁)</th>
<th>(S₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ-phase</td>
<td>2.76</td>
<td>3.40</td>
<td>176.20</td>
<td>-0.40</td>
<td>-0.17</td>
<td>+0.13</td>
</tr>
<tr>
<td>BW-phase</td>
<td>2.80</td>
<td>3.42</td>
<td>176.90</td>
<td>-0.35</td>
<td>-0.14</td>
<td>+0.12</td>
</tr>
</tbody>
</table>

Fig. 6. PTCDA on NaCl in Q-phase in (a) different submonolayer coverages. At 0.74 ML or below, only monolayer islands are observed [21]. (b) nc-AFM topography of monolayer islands [21]. (c) Structural model of the Q-phase on NaCl(100), cell dimensions are 16.80 Å, \(\gamma = 90^\circ\).
The molecule–substrate interactions are highest in the Q-phase suggesting this phase to form at low coverages. In the smaller unit cell of the BW-phase, the molecule–molecule interactions contribute to a maximum extent to the structural stability, resulting in a high adsorption energy. A possible explanation for the formation of the Q-phase, instead, might be that – due to the small lattice constant of NaCl – the molecules at higher coverages are prevented to rotate by 90° as required for the formation of the BW-phase. There is, however, no hint whether the BW-phase on NaCl can be prepared under some real experimental conditions.

In the Q-phase, the distance between the center of the molecule and the surface anions beneath is 3.37 Å, while it is 2.82 Å between the carboxyl oxygen atoms of the molecule and the surface cations beneath. Our results are in a good agreement with the height of 3.4 ± 0.20 Å measured for the Q-phase by Kelvin probe force microscopy [21]. Their calculated distance is also in good agreement with previous DFT (3.50 Å) [21] and MM calculations (ranging from 2.71 Å to 3.73 Å [21]). The differences between our results and the DFT results from Ref. [21] can be attributed to the neglect of dispersive interactions in the latter.

The total charge redistribution at the molecule–surface interface is 0.79 electrons. As a result of the higher molecule–surface interactions, the isolated molecule is distorted more strongly than the molecules in the Q-phase. The oxygen atoms come closer to the surface, and the surface cations beneath the carboxyl oxygen atoms are pulled up by larger amount (cf. Table 6).

4. PTCDA at NaCl step-edges

The adsorption of organic molecules at surface step-edges of KCl and NaCl surfaces is crucial to initiate the growth of the first layer [18].

Experimentally, Sun and Silly studied the formation of PTCDA films on Au(111)-(22h,√3) covered with NaCl islands at submonolayer and higher coverages of NaCl. At coverages below a complete monolayer of NaCl, their STM investigations suggest the PTCDA molecules to nucleate preferentially at the NaCl island step-edges [26]. In their study of PTCDA on Cu(111) partially covered with NaCl, Karacuban et al. reported that the single PTCDA molecules adsorb at vacancies of (001) and (101) oriented steps of NaCl(100) islands (for the definition of the defective sites, cf. Fig. 10). At coverages of 0.1 ML, they observe that the defect-free non-polar step-edges are not decorated with PTCDA molecules, but the molecules begin to nucleate at the polar step-edges, at defects and at previously adsorbed molecules (Fig. 8(a)). At coverages of 0.4 ML, step-edges are completely decorated with molecules, while the bare substrate remains free of molecules (Fig. 8(b)) [16].

We compared the adsorption energy of single PTCDA molecules at polar and non-polar mono-atomic step-edges with that on the plane surface. The step-edges were modeled in a saw-tooth model with six layers, cf. Fig. 9.

The inequivalent terminations and defective sites of the step-edges are non-polar, Cl-terminated, Na-terminated, kinks and vacancies (Fig. 10, left part). The non-polar step-edges contain alternatively positive and negative ions at the step-edge. They are defect-free and parallel to [100] [16]. All other terminations and sites are parallel to [110] and polar, i.e. containing unequal numbers of sodium and chloride ions.

At all step-edges, the adsorption energy is higher than for the single molecule on the plane surface, suggesting that structure formation starts at these sites. In particular, the high adsorption energy of the molecule at vacancies confirms the experimental observations of Karacuban et al. [16]. After having filled all vacancy sites at low coverages, PTCDA adsorbs preferentially at the other defect sites and polar terminations

### Table 5

Energetic comparison between Q-, HB-, and BW-phase of PTCDA on NaCl(100).

<table>
<thead>
<tr>
<th>Structure</th>
<th>HB-phase</th>
<th>Q-phase</th>
<th>BW-phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption energy [eV]</td>
<td>−3.36</td>
<td>−3.32</td>
<td>−3.49</td>
</tr>
<tr>
<td>Mol-surf contribution [eV]</td>
<td>−2.72</td>
<td>−2.84</td>
<td>−2.77</td>
</tr>
<tr>
<td>Mol-mol contribution [eV]</td>
<td>−0.64</td>
<td>−0.48</td>
<td>−0.72</td>
</tr>
</tbody>
</table>

### Table 6

Comparison between the geometries of the SQ-phase (isolated molecule) and the Q-phase (monolayer of molecules) for PTCDA on NaCl(100). All values in [Å].

<table>
<thead>
<tr>
<th>d₁</th>
<th>d₂</th>
<th>γ</th>
<th>m₁</th>
<th>m₂</th>
<th>S₁</th>
<th>S₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ-phase</td>
<td>2.60</td>
<td>3.40</td>
<td>172</td>
<td>−0.70</td>
<td>−0.37</td>
<td>+0.14</td>
</tr>
<tr>
<td>Q-phase</td>
<td>2.82</td>
<td>3.37</td>
<td>175</td>
<td>−0.48</td>
<td>−0.21</td>
<td>+0.08</td>
</tr>
</tbody>
</table>
of the island, then at previously adsorbed molecules. The non-polar step-edges start to be decorated last, i.e. only at higher coverages, until, finally, structure formation is extended to the flat surface terraces.

Since STM only images the chlorine atoms of the step-edge [16], the measured distance corresponds to the distance between anhydride oxygen atoms of the molecule and the chloride atoms of the step-edge (Fig. 10 (right)). Accordingly, our calculated values fit perfectly (cf. Table 7) to the experimental value of about 4 Å [16] (cf. the dark region between the molecule and the NaCl island in Fig. 8 (a)).

In summary, we performed first principles calculations in order to investigate the different adsorption patterns of PTCDA molecules on KCl and NaCl (100). In agreement with experimental findings, we proved the single molecule to adsorb on KCl with its long axis parallel to the [110]-direction of the surface, and we extended this result to NaCl. The center of the molecule resides above a surface anion with its carboxyl oxygen atoms above the surface cations. The smaller lattice constant of NaCl, compared to KCl, yields a better overlap between the carboxyl oxygen atoms of the molecule and the surface cations. Higher

![Image](image-url)

**Fig. 8.** (a) STM-image of individual PTCDA molecules (≈0.1 ML) decorating the monatomic steps of NaCl islands. The measured distance between the molecule and the step-edge (see inset) is 0.4 nm. (b) Starting phase formation at step edges: PTCDA molecules (≈0.4 ML) at higher coverages [16].

![Image](image-url)

**Fig. 9.** Saw-tooth model of the supercell used to model the non-polar step-edge as an example of defective edges. As atomic radii, the vDW radii are used for illustration.

![Image](image-url)

**Fig. 10.** (Left) Definition of the various possible adsorption positions of a PTCDA molecule at step edges. (Right) Definition of the distance as measured experimentally $d_{\text{exp}}$. 
adsorption energies (NaCl: $-2.91$ eV, KCl: $-2.49$ eV) and a stronger distortion are the consequence.

For one monolayer of PTCDA on KCl, our calculations predict the experimentally observed BW-phase. The same phase is predicted to be formed on NaCl as well. Experimentally, however, the Q-phase is observed, which we calculated to slightly less stable. This deviation might result from the molecule–molecule interactions which are at maximum in the small cell and stabilize the BW-phase compared to the Q-phase. In the monolayer adsorbrates on both KCl and NaCl surfaces, the molecule is less distorted compared to the single molecule. Naturally, in these structures, the molecule–surface interaction is reduced in favor of stronger molecule–molecule interactions. Step edges play an important role in the initiation of structure formation. PTCDA adsorbs preferentially at defect edges of monoatomic steps on the surface. For all such sites, adsorption energies are higher than on terraces. In agreement with experimental observations, adsorption at polar step-edges is preferred over that at non-polar step-edges. Among different polar step-edges, the adsorption of the molecule at step-edge vacancies is preferred. Such sites can, thus, be attributed the role of initiating the ordered growth of PTCDA networks on KCl and NaCl surfaces.

The calculations were performed using grants of computer time from the Paderborn Center for Parallel Computing (PC²). The Deutsche Forschungsgemeinschaft (DFG) and the Ministry for Innovation, Science and Research Nordrhein-Westfalen (MIWF NRW) are acknowledged for financial support. H.A. would like to thank the director general of the AECS, Prof. Dr. I. Othman and Prof. Dr. M. K. Sabra, for their permanent support. We would like to thank M. Sokolowski and T. Wagner for fruitful discussions.

### Table 7

<table>
<thead>
<tr>
<th>Step-edge</th>
<th>$E_{ads}$ [eV]</th>
<th>$d_{mol-step}$ [Å]</th>
<th>$d_{exp}$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-polar</td>
<td>$-3.05$</td>
<td>3.04 (O(A) − Cl)</td>
<td>2.63 (O(C) − Na)</td>
</tr>
<tr>
<td>Cl-terminated</td>
<td>$-3.47$</td>
<td>2.90 (O − Cl)</td>
<td></td>
</tr>
<tr>
<td>Na-terminated</td>
<td>$-3.80$</td>
<td>2.33 (O − Na)</td>
<td>3.89 (H − Cl)</td>
</tr>
<tr>
<td>Kinks</td>
<td>$-3.64$</td>
<td>2.47 (O(A) − Na)</td>
<td>3.80−4.22 (O(C) − Na)</td>
</tr>
<tr>
<td>Vacancy</td>
<td>$-4.13$</td>
<td>2.39</td>
<td>3.75−4.22</td>
</tr>
</tbody>
</table>

The experimentally determined distance, these numbers have to be compared to, is $\approx 4$ Å [16].

### References