Reorganization energy and polaronic effects of pentacene on NaCl films

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Due to recent advances in scanning-probe technology, the electronic structure of individual molecules can now also be investigated if they are immobilized by adsorption on non-conductive substrates. As a consequence, different molecular charge-states are now experimentally accessible. Thus motivated, we investigate as an experimentally relevant example the electronic and structural properties of a NaCl(001) surface with and without pentacene adsorbed (neutral and charged) by employing density functional theory. We estimate the polaronic reorganization energy to be $E_{\text{reorg}} \simeq 0.8 - 1.0$ eV, consistent with experimental results obtained for molecules of similar size. To account for environmental effects on this estimate, different models for charge screening are compared. Finally, we calculate the density profile of one of the frontier orbitals for different occupation and confirm the experimentally observed localization of the charge density upon relaxation of the substrate from ab-initio calculations.

Keywords: NaCl; pentacene; polarons; reorganization energy; density functional theory; scanning tunneling microscope

The interaction of individual molecules with surfaces and interfaces constitutes one of the central topics of surface science since this field was launched. In the past, most of the interest focused on metallic surfaces, partially because of the relevance to catalysis, but also because experimental techniques such as the scanning tunneling microscope (STM) could not operate on non-conductive substrates. It was only relatively recently that this situation changed and STM-related techniques became available also for individual molecules adsorbed on insulating films, which in turn are deposited on a metallic substrate;1 for an illustration see Fig. 1. Since then scanning-probe studies of individual molecules on insulating films, such as sodium chloride (NaCl), have received a growing amount of attention (see, e.g., [2–6] and references therein). The main reason is that molecules tend to hybridize much more weakly with insulators than with metals and therefore new physical regimes become available. If sufficiently thick insulating substrates are used, the electron transfer from the adsorbed atoms or molecules is quenched and they can exhibit different metastable (long-lived) charge-states.2 Combination of STM techniques with atomic force microscopy (AFM), has allowed to experimentally obtain the energy gain of the system after charging a single-molecule3, analyze the differences in the orbital shape with angstrom resolution4 or measure geometrical changes of single-molecules induced by electron transfer5. Partially motivated by these experimental developments, calculations of the physical properties of atomic and molecular adsorbates on insulating substrates have been attempted1–15. These calculations are very challenging due to the large number of electrons (especially from the substrate layers) involved. Most notably, only approximate density functional theory (DFT) calculations13–15 have been performed for single molecules adsorbed on insulating films. The additional simplification in these calculations is achieved by not explicitly including the metallic layer which is replaced by a perfectly conducting ideal plane. The electrostatic interaction between the localized charge in the molecule and its image charge is self-consistently included by considering the energy of two charge distributions separated by an homogeneous insulating film.

In this paper, we present an extensive computational study of a single pentacene molecule adsorbed on a NaCl surface. We focus on the understanding of the interplay between charging the molecule and the structural relaxation of the substrate. To address this issue, we first comprehensively characterize the free surface (NaCl slab). Already this arrangement, as it turns out, is nontrivial because, as we show, the crystal structure of the bulk lattice is reached only very slowly with in-

FIG. 1. Schematic representation of a scanning-probe setup for single-electron transfer between a metallic tip and a pentacene molecule adsorbed on a NaCl film (violet: Na\(^{+}\), green: Cl\(^{-}\)). Single-electron transfer between the tip and the molecule are indicated with black arrows.
creasing the slab thickness.

Depositing a single neutral pentacene molecule alters the alternating free surface by shifting away the nearby $\text{Cl}^-$ ions towards the inside of the film by $\sim 8.5\%$ of the bulk lattice spacing. Upon adding an electron to the molecule, the main structural effect on the surface is that nearby $\text{Na}^+$ ions are attracted and bulge out towards the molecule at the expense of the $\text{Cl}^-$ ions that go deeper inside. Importantly, the charge state of the molecule is experimentally found to be metastable if the NaCl-film with sufficient thickness is deposited on a copper substrate. We estimate $0.8-1\text{ eV}$ for the corresponding reorganization energy. To illustrate the effects of screening at the underlying metallic substrate different screening models have been compared.

To connect to previous experimental work, scanning tunneling profiles along the charged molecule have been simulated. We find that the charge-induced lattice relaxation enhances the tunneling probability around the center of the molecule. Our computational results are consistent with published experimental data.9

RESULTS AND DISCUSSION

Models for metal substrate

As mentioned above, including in addition to the NaCl film a metallic layer in ab-initio calculations is computationally prohibitive. We note that the main physical effects of these metal layers is to ensure, via screening, charge neutrality when charged atoms or molecules are adsorbed on the substrate. This behaviour can be conveniently included in simplified models. We compared here some of those models for the NaCl slab with a charged pentacene adsorbed.

**Jellium-model.** The simplest approach employs the jellium model, which ensures charge neutrality by adding a uniformly charged compensating background to the supercell, see Fig. 2 (a). In band-structure codes, the model is often implemented by omitting the zero-wavenumber component of the Coulomb interaction. For slab calculations, the background extends also into the vacuum layer.

As a consequence, the unit cell carries an electric dipole, while the shape of the associated field is a modeling artifact In the literature, two methods have been proposed to compensate for this: (i) extrapolation to the dilute limit by finite-size scaling; (ii) a posteriori corrections based on dielectric models.

**Shaped counter-charge distribution.** The artifact of the jellium model results from distributing the compensating background charge ("counter charge") homogeneously over the unit cell. More realistic arrangements are easily possible, though not standard in every band structure code. Alternative choices are to arrange the counter-charges as a two-dimensional sheet, Fig. 2(b), to contract them into a point, Fig. 2(c) or any intermediate geometry, Fig. 2(d) that can mimic the form of the image charge. On the technical level, the counter charges can be modeled as an ensemble of $N_{\text{counter}}$ ion cores, with an individual fractional charge $q_{\text{counter}}$ each, and with a total charge matching the charge of the surface layer $Q$, i.e. $Q = q_{\text{counter}}N_{\text{counter}}$.

We mention that the sheet geometry, Fig. 2 (b), was adopted by Sinai et al. 23 to describe surfaces of doped semiconductors, where the transfer of free charge carriers between the doped material and the surfaces leads to a space-charge region. In modelling, this region was contracted to a thin sheet that produces the associated electric field - hence the name charge-reservoir electrostatic sheet technique (CREST).

**Dimerization effects on pristine NaCl films**

The reference geometry for our investigation on the effect of adsorbates on insulating substrates will be a clean NaCl(001) film. We therefore first extensively characterize the atomic geometry of this system.
Atomic geometry and relaxation. The NaCl slab consists of two types of ionic slabs, denoted A and B, showing an alternation of Na\(^+\) and Cl\(^-\) ions along the \(\hat{z}\) direction (see Fig. 3). The “surface relaxation” describes the structural change of the crystal lattice that occurs due to the existence of a vacuum interface. This change is characterized by the displacement of neighboring ions from each other measured relative to the bulk position; specifically we consider the mean layer separation

\[
\bar{d}_{ij} = \frac{1}{2} \left[ (z_i^A - z_j^A) + (z_i^B - z_j^B) \right],
\]

where \(z_i^{A/B}\) is the \(z\)-coordinate of ion \(i\) in the stack \(A/B\), and the intralayer buckling

\[
\Delta_i := z_i^A - z_i^B.
\]

In our calculations, only the relaxation normal to the surface has been accounted for, while the transverse coordinates are bulk-like and not relaxed. Lateral relaxations are not expected from symmetry considerations.

Depending on the physical situation at hand, thin films - freely suspended or on substrates - or thick films, different boundary conditions are appropriate for modeling. For example, with freely suspended films the upper and the lower sides of the film can relax freely (“symmetric slabs”); in contrast, when modeling the surface of a thicker film, the ions of one side of the slab can be fixed to the bulk values (“asymmetric slabs”). We have ensured in detailed separate calculations that our conclusions do not change for this asymmetric situation (not shown).

Mean layer separation. Our main results are summarized in Fig. 4. We compare two slabs with even \((L = 24)\) and odd \((L = 25)\) number of layers to investigate even-odd effects. For comparison, in Tab. I we also reproduce results for \(L = 12\). The data allows for the following conclusions:

Qualitatively, we observe that the inter-layer distances oscillate when going from the surface into the bulk, see blue traces in Fig. 4, (a) and (b). We attribute the effect to the reduced coordination number of the surface atoms, which tends to strengthen the remaining bonds to the second layer. The second layer in turn coordinates more strongly with the first layer and so binding to the third is less pronounced. This mechanism – well-known from closed-packed metal surfaces – results in an oscillating inter-layer spacing, with the amplitude of these oscillations decaying within few layers into the bulk.

To illustrate this, we compare in Tab. I the mean layer separation of first-second and second-third layers for two different thicknesses, \(L=12,24\). Quantitatively, the impact of surface relaxation on the mean layer separation is of the order of 0.5% in terms of the bulk interlayer distance, \(d_{\text{bulk}}\), for the first and second layers and a factor of two smaller for the second and third.

Intralayer Buckling. Qualitatively, Cl\(^-\) ions of the first layer relax outwards of the surface compared to the Na\(^+\) ions. There, the buckling is stronger, up to almost 4% in units of \(d_{\text{bulk}}\) and has a negative sign, indicating that the Cl\(^-\) ions always relax outwards while the Na\(^+\) ions inwards. Together with the alternating stacking of ions in NaCl this behavior is a manifestation of dimerization in NaCl where Na\(^+\) and Cl\(^-\) ions come closer in alternating way along \(\hat{z}\). We show a sketch of the dimerization occurring in the central region of the slab in Fig. 4 (c). The NaCl dimers originated by surface creation are marked with red rectangles. As compared to the
### Table I. Mean layer separation in percentage of the bulk lattice spacing.

| Method               | $\delta d_{12} [%]$ | $\delta d_{23} [%]$ | $\Delta_1/\Delta_{bulk} [%]$ | $\Delta_2/\Delta_{bulk} [%]$ | $\Delta_3/\Delta_{bulk} [%]$ |
|----------------------|----------------------|----------------------|-----------------------------|-----------------------------|-----------------------------|
| PBE (12 lay.)        | -0.786               | 0.334                | -3.472                      | -1.297                      | -0.210                      |
| PBE (24 lay.)        | -0.793               | 0.337                | -3.437                      | -1.333                      | -0.175                      |
| PBE-TS-CM (12 lay.)  | -0.255               | 0.362                | -3.924                      | -1.490                      | -0.327                      |
| PBE [25]             | -0.600               | 0.020                | -3.860                      | -1.053                      | 0.000                       |
| Experiment [24]      | -1.430               | 0.100                | -5.0 ± 0.1                  | -0.7 ± 0.1                  | 0.0 ± 0.1                   |

From a DFT-relaxed structure we extract the optimal adsorption distance, $d_{opt}$, and the adsorption energy, $E_{ads}$.

mean layer separation, the buckling and the associated dimerization decay much slower: $\Delta/\Delta_{bulk}$ keeps a value of $\sim 0.1%$ even 10 layers deep into the bulk of the slab. Indeed, we have checked (not shown here) that slabs of up to 50 layers still present dimerization between Na$^+$ and Cl$^-$ ions along a stack.

**Relation to experiments and earlier DFT studies.** Finally, as inferred from Table I our results are in good qualitative agreement with experimental measurements, with quantitative deviations that can reach a factor of 2-3. Comparing to earlier computational work$^{25}$, we report a relatively large discrepancy of around 24% difference (roughly 0.3 pm) for $\delta d_{12}$ and 94% difference (roughly 0.6 pm) for $\delta d_{23}$. We attribute these deviations to methodological differences in DFT-implementations of FHI-aims (all electron, localized basis set) versus CASTEP (pseudopotentials, plane waves).

**Discussion of functional dependencies.** One infers from the data given in Tab. I that the *ab-initio* obtained geometries have a residual dependency on the DFT functional. Specifically, we have tested the effect of dispersive interactions; our numerical data in Tab. I shows they can have a significant quantitative but no qualitative effect.$^{26}$

**Surface energy.** We turn to the investigation of the surface energy per area, $\gamma$. It derives from the scaling of the total energy of a slab with $L$ layers:

$$\frac{E_{slab}(L)}{L} - E_{bulk} := \gamma A \frac{1}{L} + \Delta. \quad (3)$$

Here, $A$ denotes the surface area of the slab unit cell and $E_{bulk}$ is obtained from a separate bulk calculation (see Supporting Information for technical details). The value for $\gamma$ can be obtained fitting the numerical data as a function of $1/L$. The parameter $\Delta$ is kept as a sanity check: correct fitting must result in an estimate for $\Delta$ consistent with zero.

We show the numerical results for odd- (red line) and even-layered (blue line) slabs in Fig. 5. Fitting to Eq. (3) yields parameters reproduced in Tab. II. As one would expect, in the limit of thick slabs both yield identical results within the error bars (given by the accuracy of the total energy with respect to the vacuum spacing). Our results for $\gamma$ are in excellent agreement with previous DFT calculations$^{25}$, which give a substantially broader interval $9 - 10$ meV/Å$^2$.

**Molecule-induced surface reorganization**

We turn to the investigation of the NaCl surface reorganization after physisorption of a single pentacene molecule.

| $\gamma$ [meV/Å$^2$] | $\Delta$ [meV] |
|-----------------------|----------------|
| odd                   | 9.6 ± 0.2      | -0.1 ± 0.4 |
| even                  | 9.6 ± 0.2      | -0.1 ± 0.4 |

**Adsorption energy and binding geometry.** We first report on the adsorption properties of neutral pentacene on NaCl. From a DFT-relaxed structure we extract the optimal adsorption distance, $d_{opt}$, and the adsorption energy, $E_{ads}$.
We rationalize our result in the following way: An important contribution from electrostatics stems from the interaction between the surface ions and the charge distribution on the molecule. Since most of the electronic charge lies on the benzene rings, the electrostatic repulsion can be minimized by having a string of Cl$^{-}$ ions to be located along the long symmetry axis of the molecule and thus further apart from the C atoms. This way, also a larger number of Na$^+$ ions are allowed to be closer to the molecular charge on the C atoms. The collinear geometry is also favorable for reducing the Pauli repulsion. Here, the reason is that the ionic radii of Cl$^{-}$ ions are larger than Na$^+$ and therefore the Pauli repulsion occurs for Cl$^{-}$ at larger distances. This then also favors Cl$^{-}$ to be located further away from the C atoms.

The quantitative estimates for the binding energy and optimal adsorption distance are summarized in Tab. III and Fig. 6. Without vdW-corrections, we find an unrealistically flat binding curve with a small adsorption energy, $-0.25$ eV, and a binding distance $d_{\text{opt}}$ approximately 20% bigger than the experimental estimations. Including vdW dispersion increases the curvature of the binding both for PBE-TS and PBE-TS-CM. The binding distance agrees with experiment and previous DFT calculations using the optimized non-local exchange correlation functional optB86b-vdW.\textsuperscript{15}

**Detailed response of pentacene/NaCl adsorption geometry.** While binding energies in Tab. III are seen to exhibit a rather strong functional dependency (by almost a factor of two), the binding geometries of the vdW-corrected calculations are rather close. In the following, we therefore use the computationally inexpensive PBE-TS treatment for pentacene/NaCl structure optimization and subsequently check our calculations with PBE-TS-CM.

We turn now to the investigation of the response of the NaCl film geometry upon adsorption of neutral and charged pentacene. In Fig. 7, we show the atomic displacements for a $7 \times 5$ supercell cell size in the $x-y$ plane. As one would expect, most of the substrate reaction to the adsorption of the neutral molecule occurs in the topmost layer of the NaCl film; the second layer show a similar pattern with significantly smaller displacements. The Na$^+$ ions are attracted by the molecule and relax – predominantly laterally – by an amount of $\sim 6$ pm, i.e., roughly 2% of the NaCl layer spacing, $d_{\text{bulk}}$. The Cl$^{-}$ ions that are located along the molecular long axis are pushed deeper into the substrate by 8.51\% (roughly 24.2 pm) [see Fig. 7 (b) and (c) respectively]. Note that this trend is opposite to the trend given by the buckling of the clean NaCl surface, as seen in Fig. 4, thus partly ironing out the uppermost layer. We observe also a small bending of outer rings in the molecule upon adsorption by 2\% (roughly 10\%).

Upon charging the molecule, the pentacene molecule dives deeper into the NaCl surface by 2\% $d_{\text{bulk}}$ (\sim 6 pm) due to electrostatic interaction. In addition, trends observed for adsorption of neutral pentacene are enhanced, see Fig. 8: The excess charge attracts the Na$^+$ ions even more, and now bulge out of the surface towards the molecule. The Cl$^{-}$ ions are pushed further downwards, inverting the sign of the buckling near the molecule.

For charged pentacene/NaCl systems, we have checked that different models for the metal substrate yield the same qualitative response of the pentacene/NaCl surface after charging. The quantitative difference found is small: we find a maximum displacement of the ions of 5.42\% for CREST, 5.73\% for point-shaped charge distribution and 4.92\% for the

![Graph showing binding energy of pentacene on a NaCl(001) surface over the distance of the molecule over the surface. DFT-calculations employ PBE-functionals without (blue circles) and with vdW-corrections (PBE-TS, orange triangles; PBE-TS-CM, green squares). Energies, $E_{\text{tot}}$, are given relative to the energy of the fully relaxed system, $E_{\text{min}}$.](image)

**TABLE III.** Adsorption energies, $E_{\text{ads}}$, and distances, $d_{\text{opt}}$, estimated experimentally and calculated with different functionals and vdW dispersion schemes.

| Functional | $E_{\text{ads}}$ [eV] | $d_{\text{opt}}$ [Å] |
|------------|----------------------|----------------------|
| PBE       | -0.25                | 3.56                 |
| PBE-TS    | -2.71                | 3.12                 |
| PBE-TS-CM | -1.55                | 2.95                 |
| optB86b-vdW [15] | -1.65              | 3.05                 |
| Experiment [1] | -                | $\approx$ 3.0       |

computed from the total energy as

$$E_{\text{ads}} = E_{\text{Pc-NaCl}}(d_{\text{opt}}) - E_{\text{NaCl}} - E_{\text{P}}. \quad (4)$$

Here, $E_{\text{Pc-NaCl}}$ is the energy of pentacene adsorbed on NaCl, $E_{\text{NaCl}}$ the energy of the NaCl slab and $E_{\text{P}}$ the energy of isolated pentacene. The binding potential is obtained from the total energy by varying the distance between the molecule and the surface of the NaCl slab without relaxation of the ionic coordinates. We monitor directly the atomic geometry (nuclear coordinates) of relaxed pentacene on NaCl after geometry optimization.

After geometry optimization, we find the central benzene ring of pentacene located on top of a Cl$^{-}$ ion and the molecular long axis symmetry axis oriented along the polar direction of the surface (i.e. along a string of Cl$^{-}$ ions). Our computational results are consistent with experimental adsorption geometry\textsuperscript{1}. The optimal geometry results from a competition of several forces including electrostatic, e.g. Hartree-type, forces, the van der Waals attraction and the Pauli repulsion.

We rationalize our result in the following way: An important contribution from electrostatics stems from the interaction between the surface ions and the charge distribution on the molecule. Since most of the electronic charge lies on the benzene rings, the electrostatic repulsion can be minimized by having a string of Cl$^{-}$ ions to be located along the long
FIG. 7. Displacements of Na$^+$, Cl$^-$ ions and C atoms upon adsorption of pentacene; only the first two top-layers out of four are displayed. Atomic displacements are shown for (a) the molecular and top surface layer in the $x$–$y$ plane, and red-boxed areas across (b) $x$–$z$ plane and (c) $y$–$z$ plane. The displacement is given as a percentage with respect to the bulk interlayer distance, $d_{\text{bulk}}$, of the NaCl crystal. The displacement arrows are scaled by a factor of 50 in panel (a) and a factor of 100 in panels (b) and (c).

jellium-model in units of $d_{\text{bulk}}$. For comparison, we get a maximum displacement of 5.61% for the image-shaped charge distribution (shift of $\sim$ 16 pm), see Fig. 8. Maximal deviations in each layer parallel to the molecular plane are small (0.1%). Ionic displacements between the metal models with explicit charge compensation that create a realistic dipole inside the supercell agree better with each other compared to the uniform background model. Small quantitative differences between them can be readily understood from different spatial distribution of the dipole fields.

We also have investigated the effect of including CM corrections to the vdW dispersion at the PBE level (not shown). We report, both for neutral and charged pentacene/NaCl systems, a residual dependency on the vdW-scheme. The displacements out of the molecular plane are larger by $\sim$ 1% (neutral) and $\sim$ 4% (charged pentacene). Parallel to the molecular plane, the atomic displacements are very similar compared to PBE-TS. We also observe a stronger bending of the molecule at both ends by 4.87% - roughly 13 pm for neutral adsorption. Stronger finite size effects and surface reaction are expected from the larger CM corrections to the polarizability of the NaCl surface.

**Electronic structure of pentacene adsorbed on NaCl.**

The molecular density of states (DoS) and relevant molecular orbitals of neutral free pentacene and neutral pentacene/NaCl
HOMO LUMO
HOMO LUMO
a)
b)
c) DoS [eV V\text{unit cell}]^{-1}
FIG. 9. (a) Highest occupied (HOMO, $-4.50$ eV) and lowest unoccupied (LUMO, $-3.35$ eV) molecular orbital of the isolated pentacene molecule and (b) corresponding density of states (DoS, blue solid curve). Also shown is the DoS of the 4-layer NaCl slab (orange dashed curve) and of pentacene adsorbed on NaCl (green dotted curve) in the NaCl band gap region. For each DoS curve the energy is referred to the Fermi energy defined as $(E_{\text{LUMO}} + E_{\text{HOMO}})/2$ (and equal to $-3.92$ eV for neutral pentacene, $-4.51$ eV for NaCl and $-4.70$ eV for pentacene-NaCl). The DoS peaks were broadened using Gaussians with broadening of 0.1 eV. (c) HOMO ($-5.29$ eV) and LUMO ($-4.11$ eV) of adsorbed pentacene molecule on NaCl.

are displayed in Fig. 9. The frontier orbitals (HOMO/LUMO) in free and adsorbed pentacene exhibit the same nodal structure and similar spatial distribution. Furthermore, the Kohn-Sham gap is almost insensitive to adsorption, 1.15 eV for gas-phase pentacene vs. 1.18 eV for pentacene/NaCl. While these values are in very good agreement with previous DFT calculations\(^{15}\) ($\pm 0.01$ eV), note that they strongly disagree with the experimental transport gap (which is measured close to 4.4 eV for 3-layered NaCl films\(^{1}\)). This is due to the missing derivative discontinuity\(^{27,28}\) and absence of substrate-induced renormalization\(^{29}\) in the exchange-correlation functionals employed here.

Finally, we observe that the frontier orbitals lie within the large band gap of NaCl far from the conduction and valence band edges, as seen in the DoS, Fig. 9 (b). Therefore, as one would expect for an insulating substrate any excess charge is expected to remain localized on the molecule.

Reorganization energy. The reorganization energy (also polaronic shift) quantifies the energy gain that results from the reaction of the pentacene/NaCl geometry upon charging. Experimentally, it can be accessed, e.g., by means of the scanning probe setup shown schematically in Fig. 1. Formally, the reorganization energy can be defined as

$$E_{\text{reorg}} := [E_-(N) - E_0(N)] - [E_0(N+1) - E_-(N+1)], \quad (5)$$

where $N$ denotes the number of electrons in the neutral system and the suffix indicate the whether the total energy corresponds to the structurally relaxed charged ($-$) or uncharged (0) geometry. The bracketed terms in Eq. (5) are identified as relaxation energies from the neutral, $\lambda_0 := E_-(N) - E_0(N)$, and charged, $\lambda_{-} := E_0(N+1) - E_-(N+1)$, system. A sketch representing the calculation procedure is given in Fig. 10.

The polaronic shifts obtained for the different models of metal substrate with explicit counter-charges (CREST, point, shaped) are summarized in Fig. 11. We show $E_{\text{reorg}}$ as a function of $L_{\text{eff}}^{-3}$, where $L_{\text{eff}} = \sqrt{L_x L_y}$ is an effective lateral size (here $L_{x/y}$ is the length of the supercell in the $x/y$ direction). We compare these results to the polaronic shift computed with the jellium-model in the Supporting Information.

We note that our calculations operate with periodic replicas of the system and thus do not represent a single molecule but instead a molecular lattice with the supercell size as a lattice constant. Due to its long-range nature, the Coulomb interaction introduces interactions - roughly of a dipolar nature - between the charged molecule and its periodic replicas. Dipolar interactions manifest in $E_{\text{reorg}}$ as finite-size corrections that converge slowly with increasing the effective supercell lateral size. To explore the single-molecule limit, we extrapolate the reorganization energy using a form $E_{\text{reorg}}(L_{\text{eff}}) = a/L_{\text{eff}}^3 + E_{\text{reorg}}(\infty)$, which is motivated by assuming parallel dipole-dipole interaction.\(^{30}\) We extract a polaronic shift, $E_{\text{reorg}}(\infty)$, for CREST of 878 $\pm$ 9 meV; for point
charge, $877.8 \pm 0.3$ meV and for the shaped image charge distribution, $870.4 \pm 0.4$ meV.

Similar to the situation of the atomistic structure, we have checked the importance of including CM corrections into the vdW dispersion forces for the reorganization energy. We find that the scaling with the lateral dipole correction yields a polaronic shift increased by $\sim 7\%$, which amounts to $E_{\text{reorg}}(\infty) = 928.6 \pm 0.1$ meV for the shaped image charge distribution. The increase in this value is simply a manifestation of the larger ionic displacements after charging due to larger polarizability of the NaCl surface.

So far we have not considered the dependence of the reorganization energy on the number of NaCl layers, $N_l$, which was 4 in our simulations and $\sim 20$ in experiments.9 From simple electrostatic considerations, and taking into account that for large $N_l$ the interaction between the charged molecule and its image charge becomes point-like, we expect $E_{\text{reorg}}$ to slowly decay with a dominant $1/N_l$ functional dependency. We observe, nevertheless, that the impact of different models for the electrostatic interaction between the charged molecule and its image charge is small, as seen in Fig. 11, and therefore, the impact on the reorganization energy is predicted to be quantitatively also small. Note that as a difference to the lateral dipole correction to the reorganization energy, the dependency on the number of layers is not a consequence of periodicity of the present in single-molecule calculations if the number of NaCl layers would be modified.

Comparison to experiment

Experimental measurement of orbital line shapes. We turn to the interpretation of the experimental results reported in Patera et al. [9]. In this experiment an individual pentacene molecule adsorbed on thick ($>20$ monolayers) NaCl film was repeatedly charged and discharged by tunneling from and to the conductive tip of an atomic force microscope. The Coulomb forces from the charged pentacene act on the oscillating tip and thereby lead to a measurable additional disposition of the cantilever. By measuring this quantity, the spatially resolved probability to induce different charge transitions by tunneling can be mapped out. With this method, dubbed alternating-charging STM (AC-STM), the electronic transitions $0 \rightarrow 1^-$ and $1^- \rightarrow 0$ have been mapped, which can be associated to tunneling into and out of the former LUMO. As the tunneling process occurs much faster than ionic relaxations the former and latter transitions proceed in the relaxed geometry of neutral (for $0 \rightarrow 1^-$) and charged (for $1^- \rightarrow 0$) pentacene/NaCl, respectively. In the following, these geometries we denote as $\text{geo}^0$ and $\text{geo}^{-1}$, respectively. The slow response to the charge in $\text{geo}^{-1}$ then manifests as an increase of the amplitude in the central lobe of the signal at the expense of a simultaneous decrease in the outer lobes (“orbital confinement”) as compared to $\text{geo}^0$. These differences were attributed to substrate-ion relaxation after electron transfer (“polaron formation”).

Computational results. To simulate the experimental results for polaron formation, we first obtain the former LUMO orbital, $\Psi(x,y,z)$, for a charged pentacene/NaCl system before (neutral geometry) and after charge-induced geometry relaxation (charged geometry). We use the same computational settings as in previous section For simplicity, we consider line cuts along the main molecular axis (here by convention the $\hat{k}$ axis) obtained from the 3D wavefunction,$\Psi(x) \equiv \Psi(x,y_0,z_0)$.

We show in Fig. 12 the probability density of the former LUMO (orbital designation refers to the neutral molecule) for
charged pentacene/NaCl with (a) neutral geometry (geo0) and (b) charged geometry (geo−1) along the main molecular axis. They are both characterized by seven lobes and are qualitatively similar to the LUMO of uncharged pentacene/NaCl, as expected. In Fig. 12 (c) we also show the line cuts, \(|\Psi(x)|^2\), for the geometries in (a) and (b). We note that taking into account the relaxation of the NaCl film leads to a decrease of the density in the outer lobes together with a small increase for the central lobe only. We attribute the increase of the amplitude of the central lobe to the fact that the underlying Cl− ions below that peak moves deeper into the surface and therefore the hybridization is locally reduced.

**Simulation of tip effects.** To simulate effects of the STM tip, we adopt a conventional procedure\(^{31,32}\) and convolve the molecular orbital \(\Psi(x)\) with a model wavefunction for the STM tip

\[
[\Psi \ast \Phi_s](x) = \int_{-\infty}^{+\infty} \Psi(y) \Phi_s(x-y) \, dy.
\] (6)

We here adopt the approximation

\[
\Phi_s(x) = \exp \left[ -\frac{x^2}{\sigma^2} \right]
\] (7)

which should be appropriate for s-type tip orbitals. Eq. (6) describes the overlap between the tip and molecular orbitals as the tip slides along the \(x\) axis. In principle, there could be more than one channel (i.e., s-wave, p-wave, etc.) with additive contribution to the total STM signal.\(^{33}\) We have verified that possible p-wave contributions have a negligible contribution to the simulated spatial tunneling amplitude. This is consistent with the fact that the AC-STM signal acquired with a non-functionalized copper tip comes mostly from s-type tip orbitals.

Using Eqs. (6) and (7) with a Gaussian broadening of \(\sigma = 2.5\ \text{Å}\), we obtain the simulated AC-STM spatial tunneling amplitude shown in Fig. 13. As a result of the convolution with the tip orbital, the AC-STM signal shows only three lobes. Before structural relaxation, the central lobe has smaller amplitude compared to the two outer lobes (geo0). After relaxation (geo−1), the situation is reversed: the inner lobe increases the amplitude while the amplitude for the outer lobes diminishes, in very good agreement with the experiment (c.f. Fig. 13).

**CONCLUSION**

To recapitulate, we have investigated structural and energetic properties of NaCl(001) slabs as well as neutral and charged individual pentacene molecules adsorbed on NaCl(001) films. We have analyzed the geometry (mean layer separation and buckling) both for thin and thick NaCl slabs and found pronounced odd-even effects. We find a strong dimerization between Na\(^+\) and Cl\(^-\) ions of neighbouring layers, possessing long range order that goes deep into the NaCl slab. We provide a precise calculation of the surface energy per area from finite-size scaling of the energy per layer to the bulk limit and obtain the value \(\gamma = 9.6 \pm 0.2\ \text{meV/Å}^2\).

We have also investigated the adsorption properties of isolated pentacene/NaCl. We find that the electrostatic interaction between the charge density of charged pentacene and the NaCl surface produces a reversal of the buckling pattern on the first layers of the NaCl film. We have checked the consistency of our results for different models of screening at the metal substrate that have explicit counter-charges and investigated the impact of dispersion forces on the pentacene/NaCl atomistic structure. We have calculated the reorganization energy associated to relaxation of the surface upon charging and found it to be \(E_{\text{reorg}} \approx 870-930\ \text{meV}\); depending on the functional used. This observable has so far not been measured for pentacene/NaCl surfaces but the value is consistent with the known reorganization energy of other molecules of similar size adsorbed on NaCl.\(^8\) Finally, we have studied the spatial changes of the STM signal associated to the LUMO. We have confirmed from \textit{ab-initio} calculations and simple modelling of the tip-sample interaction the localization of the charge density upon relaxation of the surface as observed in a recent
The experimental results are thus interpreted as being of polaronic-like nature.

**Methods**

Our computational study focuses on NaCl films. We perform slab calculations with periodic supercells with (001) surface orientation employing DFT. Our DFT calculations are performed with the FHI-aims package that implements the Kohn-Sham formulation of DFT using a localized basis set. We use a standard generalized-gradient approximation (PBE) for the exchange-correlation functional and incorporate scalar relativistic corrections to the kinetic energy at the level of the zeroth-order regular approximation (ZORA). As basis set, we have routinely employed the optimized “light” settings (approximately equivalent to “double zeta” quality). We have checked the robustness of our most prominent observations against “tight” settings (“double zeta + polarization” quality).

Our standard convergence criteria are $10^{-5}$ electrons/Å$^3$ for the density, $10^{-5}$ eV for the sum of the Kohn-Sham eigenvalues and $10^{-6}$ eV for the total energy. The geometry optimization of the atomic structures start from an initial state in which the atoms and ions are located relatively to their bulk (for the NaCl slabs) or slab (for pentacene on NaCl) positions. They are performed using the energy-based Broyden-Fletcher-Shanno-Goldfarb optimization algorithm and atomic structures are relaxed until every component of the residual force per atom or ion drops below the threshold $10^{-2}$ eV/Å. For organic-inorganic interfaces, the account of dispersive forces in DFT is known to be very important. We treat dispersive forces [van der Waals (vdW) interactions] using the Tkatchenko-Scheffler (TS) approach and the Clausius-Mosotti correction for solids (TS-CM). Unless stated otherwise, we ignore dispersive forces inside the NaCl slabs, i.e. between Na$^+$-Na$^+$, Cl$^-$-Cl$^-$ and Na$^+$-Cl$^-$, but allow vdW interactions between all the other atomic species.

For NaCl(001) slabs, our DFT calculations and geometry optimizations follow the convergence criteria for the SCF cycle detailed above with slightly tighter force convergence parameter (0.005 eV/Å). We consider a vacuum spacing layer of 20 Å (for which total energies are converged with a precision of 0.8 meV per layer). We have verified that the structures are converged with a precision of 0.1 pm and also performed numerous checks of the convergence with respect to the vacuum spacing and $k$-grid discretization (see Supporting Information).

The geometry optimizations for pentacene on NaCl slabs are performed in rectangular supercells of sizes $n \times m \times 1$ ions in the $x$–$y$ plane. We ensure that the distance of the adsorbed molecule to the boundaries of the supercell is the same in both directions. Geometry optimizations start from an initial geometry in which the gas-phase molecule and a four-layered NaCl slab are structurally relaxed independently. The two bottom-most layers are kept frozen (“asymmetric slab”). Next, we place the molecule at a distance of 3.1 Å from the top layer of the slab and perform the minimization of the forces using DFT following the criteria detailed above. Dispersion forces are described within the PBE-TS scheme. For charged pentacene/NaCl systems, the counter-charge distribution in the supercell is located at a fixed distance of 8 Å from the bottom layer of the NaCl film.

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**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

Additional computational data (bulk properties of NaCl, convergence checks, comparison of reorganization energy with the jellium model and different explicit shaped-counter charge distributions in the supercell).
For PBE, the interlayer distance $|\delta \bar{d}_{12}|$ is larger than $|\delta \bar{d}_{23}|$. Surprisingly, this is not the case when including the TS-CM dispersion.
Reorganization energy and polaronic effects of pentacene on NaCl films
Supporting Information

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BULK NaCl

Here, we study the bulk properties of NaCl as reference for our investigation of NaCl films. NaCl is an ionic solid formed by the arrangement of two face-centered cubic lattices; one formed by negatively charged Cl− ions and another by smaller positively charged Na+ ions. The Na/Cl lattices are shifted against each other by (1, 1, 1) a0/2 where a0 is the lattice constant.

Results

Our computed lattice constants are summarized in Tab. S1. The lattice constant from our PBE calculations are in good agreement to previous theoretical studies1–3. Compared to experimental measurements, the lattice constant is overestimated at least 0.06 Å (1% a0). Due to the impact of long-range screening on the polarizability of atoms in solids, we also checked the effect of including vdW dispersion within the TS4 and TS-CM2 approaches. The calculated lattice constants underestimate the experimental one by at least 0.18 Å (for PBE-TS) and 0.065 Å (for PBE-TS-CM). This results from overestimation of the dispersion forces for a bulk solid5.

We show in Fig. S1 the band structure of NaCl obtained using the PBE functional (similar band structures are obtained for PBE-Ts and PBE-TS-CM here not shown). The band gap energy for different functionals obtained at the Γ point is summarized in Tab. S1. This band gap strongly underestimates the experimental optical gap ∼ 8.5 eV8 due to well-known artifacts of local and semilocal functionals.9 For further details on the NaCl band structure, we refer the reader to Ref. 1.

Computational details. For bulk NaCl structural optimizations, we have used the FHI-aims “tight” settings10 (roughly equivalent to “double-zeta plus polarization” quality) and relaxed the unit cell until the residual value for every component of the force acting in each ion was smaller than 0.005 eV/Å. We considered a dense k-point mesh of at least 8 × 8 × 8 sampling in each direction of the Brillouin zone.

CONVERGENCE CHECKS

We report some of the checks used to determine the convergence of our computational setup for the slab calculations. Specifically, we show the dependence of the total energy on the width of the vacuum layer in Fig. S2 and the and k-grid

| a0 [Å] | E_G [eV] |
|-------|----------|
| PBE   | 5.700    | 5.03    |
| PBE-TS| 5.389    | 5.66    |
| PBE-TS-CM | 5.505   | 5.39    |
| PBE [1] | 5.70    | 5.0     |
| Exp.  | 5.576–5.647 | 8.5 (optical)7 |

TABLE S1. Lattice constants, a0, and band-gap energies, E_G, of bulk NaCl obtained using PBE, and van der Waals corrected PBE-TS and PBE-TS-CM functionals. The accuracy in the determination of the lattice constant is 0.1 pm and the band gap is 0.01 eV. For comparison, DFT results from Ref. 1 and experimental values from Refs. 6 and 7 are shown.
FIG. S2. Variation of the total energy of a 12-layer NaCl(001) slab with respect to vacuum layer thickness. The energies are normalized to the reference energy, $E_{\text{ref}} \approx -204072.096449004$ eV, corresponding to the total energy for 30 Å vacuum.

FIG. S3. Variation of the total energy of a 12-layer NaCl(001) slab with respect to $k$-point discretization. The energies are normalized to the reference energy, $E_{\text{ref}} \approx -203227.951979871$ eV, corresponding to the total energy for a $k$-mesh of $15 \times 15$. Similar convergence tests were carried out for slabs of different widths.

**POLARONIC SHIFT: JELLIUM VS EXPLICIT CHARGE-COMPENSATION**

In Fig. S4, we compare the reorganization energy computed using the jellium model and different shaped-counter charge distributions in the supercell (see main paper). As reported in the main text, the explicit counter-charge models for the metallic surface show a convergence with the lateral supercell size. However, no convergence is obtained for the jellium model for which we also report reorganization energies $200 - 300$ meV smaller. The lack of convergence with $L_{\text{eff}}$ is a consequence of the failures of the jellium model to describe properly electrostatic long range Coulomb interactions in charged supercells with vacuum.

1. B. Li, A. Michaelides, and M. Scheffler, Phys. Rev. B 76, 1 (2007).
2. G.-X. X. Zhang, A. Tkatchenko, J. Paier, H. Appel, and M. Scheffler, Phys. Rev. Lett. 107, 245501 (2011).
3. T. Bučko, J. Hafner, S. Lebègue, and J. G. Ángyán, J. Phys. Chem. A 114, 11814 (2010).
4. A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 6 (2009).
5. T. Bučko, S. Lebègue, J. Hafner, and J. G. Ángyán, Phys. Rev. B 87, 064110 (2013).
6. K. Wang and R. R. Reeber, Mater. Sci. Eng. R Reports 23, 101 (1998).
7. D. R. Lide, ed., CRC Handbook of Chemistry and Physics, 76th ed. (CRC Press, Boca Raton, 1996).
8. N. O. Lipari and A. B. Kunz, Phys. Rev. B 3, 491 (1971).
9. J. P. Perdew, International Journal of Quantum Chemistry 28, 497 (1985).
10. V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, Comput. Phys. Commun. 180, 2175 (2009).