Lateral Interactions and Order-Disorder Phase Transitions of Metal Phthalocyanines on Ag(111)

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Abstract

The intermolecular interaction among phthalocyanine molecules deposited on Ag(111) has been investigated at submonolayer coverages. By means of IRAS and SPA-LEED unambiguous evidence for an attractive interaction between neighboring TiOPc molecules is found for dilute layers, which is in contrast to the intermolecular repulsion reported for the CuPc/Ag(111) system. Accordingly, the formation of dense 2D islands of TiOPc molecules with well-defined long-range order (commensurate phase) is observed upon cooling to temperatures below 75 K while a disordered arrangement is retained for adsorbed CuPc. Using DFT calculations as a guide, these differences have been traced to the competition of attractive van der Waals and repulsive electrostatic interactions. Specifically, the vertically oriented molecular dipoles are substantially smaller for adsorbed TiOPc as compared to CuPc due to a compensation of the oppositely oriented dipole moments arising from the Pauli push-back effect on the one hand and the internal molecular dipole associated with the axial Ti-O group on the other. A detailed account and comparison of the molecule-substrate interaction, molecular binding geometries and intermolecular interactions of TiOPc and CuPc on the Ag(111) surface is provided in a theoretical analysis based on DFT.

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1. Introduction

For molecule-metal contact layers the electronic and optical properties are closely related to the structural characteristics of the grown molecular films. Thereby, lateral intermolecular interactions compete with the (vertical) molecule - metal interaction that comprises the ubiquitous van der Waals interactions, often supplemented by more site-specific chemical affinities. The adsorption energy of large molecules usually ranges at 2-4 eV and in general displays a distinct but nonetheless weak preference for particular sites and azimuthal orientations. Quantification of lateral interactions between neighboring molecules is less straightforward, because the net interaction is the sum of various contributions (van der Waals, electrostatic, hydrogen bonding) that may be either repulsive (leading to disordered films) or attractive (yielding island formation at relatively low coverages). Upon adsorption, the intramolecular multipole moments additionally receive a vertical dipole moment induced by (i) charge transfer between the metal and the molecule and (ii) the Pauli push-back effect [1-3], adding a repulsive component to the total lateral interaction (from vertically oriented, equally aligned induced dipoles in neighboring molecules). Refining our understanding of the underlying mechanisms facilitates the tailoring of individual contributions, eventually generating an effective tool to adjust the net interaction and to engineer novel molecular structures.

A promising approach is to modify deposited molecules by adding or replacing functional groups. For example, starting with pentacene, replacement of selected hydrogens by oxygen atoms (e.g. PEN – P2O – P4O) will alter the adsorption energy as well as the molecule - metal bonding distance and most likely the preferred adsorption sites [4]. In another approach a versatile class of molecules, phthalocyanines, are modified by exchanging the central metal complex. In this way, specific molecular properties like planarity, reactivity, magnetization, dipole moment, and electronic structure can be tuned [5], while leaving the molecule's periphery untouched.

Upon adsorption of phthalocyanines (Pc) on coinage metal substrates such as Ag, Au or Cu a variety of phases within the first monolayer (ML) have been reported. At low coverage (submonolayer regime) the formation of a 2D gas phase is commonly observed where adsorbed molecules diffuse and rotate freely on the metallic surface (with some weak preference regarding adsorption site and azimuthal orientation), even at cryogenic

temperatures [5]. As the mobility of the molecules is essentially determined by thermally activated processes within the potential energy landscape defined by the molecule-substrate interaction, one concludes that the heights of the corresponding kinetic barriers are rather low.

For denser layers, lateral motion of adsorbed species becomes more and more constrained, either by island formation (net attractive intermolecular interactions) or by means of enhanced steric hindrance (net repulsion), which causes an enlargement of the kinetic barrier heights, thereby curbing lateral mobility. When approaching saturation of the monolayer short range repulsive intermolecular interactions become dominant, rendering the preference of Pc for particular sites and local adsorption geometries less important. Molecules then have to arrange adequately in order to optimize their positions in the layer, and point-on-line (POL) or incommensurate phases are commonly formed [6].

At present, the long-range order of molecular layers and its dependence on coverage is investigated using imaging or scattering techniques, e.g. by spot-profile analysis low energy electron diffraction (SPA-LEED); thereby, similar diffraction patterns were observed for the various Pc molecules like CuPc [7, 8], H₂Pc [9], SnPc [10], or TiOPc [11-13] on Ag(111). Experimental studies focusing on the temperature dependence of long-range order, e.g. dilute systems forming a 2D gas-phase at high T and a 2D condensate at low T, are rare, though. In the case of SPA-LEED the primary cause is the interference of the electron trajectories and electric/magnetic fields generated by the heating currents. For real space methods, that is, scanning probe microscopy techniques, the study of dilute systems in a wide range of temperatures represents a challenge as well, due to thermal drift and the high mobility of the Pc molecules at elevated T.

Besides, spectroscopic methods such as infrared absorption spectroscopy (IRAS) may qualify as adequate techniques for the study of dilute molecular layers and their phase transitions in a broad temperature range (30 – 500 K). Vibrational line positions react sensitively to the local environment, that is, the type and number of neighboring species, as well as distances [13-15]. In this way semi-quantitative information regarding the prevalence of the various phases of deposited molecular species, e.g., with increasing temperature, becomes available. Additionally, structural information (bonding geometry and/or molecular orientation) can be extracted from the absorption bands in the IR spectra [16, 17].

In this investigation the main focus will lie on the disordered phases of the polar titanyl-phthalocyanine (TiOPc) and planar copper-phthalocyanine (CuPc) on Ag(111) at submonolayer coverages. Here, SPA-LEED measurements serve as the main tool to explore the long-range ordering of these adsorbate layers, in addition to IR-spectroscopy. Thereby, we provide unequivocal evidence for an attractive interaction between TiOPc molecules that leads to the formation of well-ordered islands upon cooling the sample to temperatures below 75 K. At variance hereto the 2D gas phase is retained for CuPc molecules on Ag(111), which are known to experience repulsive intermolecular interactions [7], even after cooling to temperatures of $T \approx 30$ K. These findings might be considered somewhat surprising, in view of the relatively large dipole moment of the TiOPc molecules, projected to add a repulsive component to the intermolecular interactions.

In order to elucidate the role of the molecule-substrate interaction beyond the experimental observations using IRAS and LEED, the TiOPc/Ag(111) as well as the CuPc/Ag(111) systems have been explored by density functional theory calculations (DFT). In this way fundamental aspects for the intermolecular interactions like the extent of charge transfer and charge redistribution within the system, as well as dipole moments of the adsorbed species can be derived. This information is then used to create a simplified model of the intermolecular interaction and to set up the 2D phase diagram as a function of the (vertical) dipoles of the adsorbed species.

2. Methods

2.1. Sample preparation and experimental measurements

Samples have been prepared in an ultra-high vacuum (UHV) chamber at a base pressure of 7×10^{-11} mbar. The chamber is equipped with an Omicron Spot-Profile Analysis *Low Energy Electron Diffraction* (SPA-LEED) optics, and a Bruker (IFS 66v/S) Fourier transform infrared absorption spectrometer (FT-IRAS) with evacuable optics ($P < 10$ mbar). A Ag(111) single crystal was used as substrate, that was cleaned by cycles of Ar^+ sputtering ($E_{\text{kin}} = 0.7$ keV) and annealing to 780 K (direct current heating). The temperature of the substrate was measured using a K-type thermocouple welded to the edge of the Ag(111) crystal, providing an accurate sample temperature reading. CuPc and TiOPc molecules have been evaporated on the Ag(111) surface with deposition rates of 0.2 ML/min for CuPc and 0.05 ML/min for TiOPc; background

pressure readings during evaporation were 9×10^{-11} mbar (CuPc) and 3×10^{-10} mbar (TiOPc). The deposition rate was monitored using a quadrupole mass spectrometer; completion of one monolayer is probed sensitively using LEED and IRAS, allowing for a precise calibration of the evaporators. The substrate temperature during CuPc evaporation was set to 300 K, while for TiOPc the optimal substrate temperature was 450 K.

IRAS measurements can be performed in a broad temperature range (28 - 600 K). Typically, 1000-2000 scans were coadded at a spectral resolution of 2 cm^{-1} . In order to obtain SPA-LEED data (2D images and 1D line scans) at variable sample temperatures, a chopped heating procedure (after Kury et al. [18]) has been implemented. Thereby, the sample heating current is modulated with a square wave ($f \approx 100 \text{ Hz}$) instead of applying a constant current, and the scattered electron signal is collected exclusively when the heating current is turned off. In this way distortions of the diffraction image due to electric and magnetic fields associated with the heating current can be avoided. The SPA-LEED versus temperature image shown in Fig. 2(a) was obtained after flashing the sample to 400 K; the measurement began as the sample started to slowly cool down. In the critical temperature range (50 – 100 K) the cooling rate was about 1 K/s. The vertical temperature axis is obtained by recording the respective temperature readings while the LEED image is collected line-by-line.

2.2 Density functional theory calculations

DFT calculations were done using the Vienna *ab initio* simulation package (VASP) [19] and the PBE-GGA functional [20]. Long-range van der Waals interactions were incorporated using the D3 Grimme approximation [21]. We used a 400 eV plane-wave cut-off as well as the projected-augmented-wave (PAW) method to describe the atomic cores [22].

The lattice constant obtained for bulk Ag was $4.073 \text{ \AA}$, in good agreement with the experimental result $4.056 \text{ \AA}$ [23]. A $25 \times 25 \times 25$ Monkhorst-Pack grid was used in these bulk calculations to sample the Brillouin zone. Using this lattice parameter a Ag(111) slab containing 3 layers was created. Only the topmost surface layer was allowed to relax. The relaxation of the system was performed until the forces acting on all the atoms were smaller than $0.03 \text{ eV/\AA}$. We kept a large vacuum distance ($\sim 20 \text{ \AA}$) to avoid interaction between periodic replicas of the slab along the z-direction. This distance was increased to $40 \text{ \AA}$ in some test calculations, with negligible impact in the results.

In order to study molecular adsorption on different sites and for different molecular orientations in the low coverage regime, a $7 \times 4\sqrt{3}$ lateral supercell in conjunction with a $3 \times 3 \times 1$ k-point grid sampling was used. For the most stable bridge- adsorption configuration we performed additional calculations using a larger $(9 \times 5\sqrt{3})$ lateral supercell with the purpose of obtaining a better description of the induced charge distribution around the molecule. These charge distributions were later used to compute the electrostatic contribution to the intermolecular interaction potentials of the adsorbed molecules.

Adsorption energies were obtained as usual by subtracting the energies of the independently relaxed adsorbate and substrate from the total energy of the combined relaxed system. Heights listed in the tables were obtained using the topmost surface layer as a reference. The population analysis was calculated using the Bader charge analysis [24] as implemented in the program developed by G. Henkelman *et al.* [25-27]. The induced electron density for the system was calculated as

$$n_{induced} = n_{system} - n_{adsorbate'} - n_{surface'},$$

where n_{system} is the total electron density of the full system (adsorbed molecule) in its relaxed geometry, and $n_{adsorbate'}$ and $n_{surface'}$ are the electron densities obtained from two separate calculations: (i) a gas phase molecule (adsorbate') keeping the geometry from its adsorbed configuration and, (ii) a clean Ag(111) surface (surface') keeping the metal atoms at the relaxed positions obtained when the molecule was adsorbed on top.

3. Results and Discussions

3.1. Lateral ordering of TiOPc and CuPc on Ag(111) at submonolayer coverages

At a sample temperature of 80 K three types of long-range ordered phases have been identified for increasing amounts of deposited TiOPc: (i) a 2D gas phase, (ii) a commensurate phase (c-phase), and (iii) a point-on-line (POL) phase at full saturation [11, 12]. The latter two phases are readily identified by their sharp diffraction spots that reveal a distinct long-range order with (close to) rectangular unit cells.

For CuPc/Ag(111) a similar sequence of LEED patterns, again starting with a disordered phase which transforms into a commensurate and, at full coverage, to a point-on-line phase has been reported [7, 8]. Despite these similarities some differences do exist; for example, the TiOPc c-phase contains two inequivalent molecules per unit cell, whereas all molecules are

equivalent for CuPc/Ag(111). More importantly, the TiOPc/Ag(111) disordered phase is characterized by a disc-like LEED-pattern [11, 12], while a uniform ring is found for CuPc/Ag(111) [7, 8].

The dissimilar appearances of the CuPc and TiOPc (electron) diffraction patterns at low coverages suggest fundamentally different intermolecular interactions. Specifically, the disc-like pattern indicates random locations of TiOPc and a broad distribution of intermolecular distances; the radius of the disc thereby defines the minimum distance between molecules, which is given by the dimensions of parallel oriented TiOPc molecules. A ring-like pattern of scattered electrons, on the other hand, can be ascribed to more or less uniform intermolecular distances but lacking any azimuthal preference. Changing the CuPc coverage (0.3 – 0.7 ML) alters the ring radius ($r \sim \sqrt{\text{coverage}}$); according to Kröger et al. such behavior points at repulsive interactions among neighboring CuPc molecules [7].

We have now conducted LEED experiments at different sample temperatures in order to elucidate the influence of thermal energy on the arrangement of molecules. Specifically, in Figure 1 (a-d) SPA-LEED images have been taken at 80 K as well as 40 K, for TiOPc and CuPc on Ag(111) at submonolayer coverages (0.5 ML).

Figure 1: SPA-LEED patterns of CuPc (a, b) and TiOPc (c, d) deposited on Ag(111) at submonolayer coverages (0.5 ML), obtained using kinetic energies of 30 eV and 50 eV, respectively. Images on the left (right) hand side have been obtained at a sample temperature of 80 K (40 K). The radius of the inner ring of CuPc (a, b), and the inner disc of TiOPc (c) are marked in yellow. (d) Commensurate phase of TiOPc described by matrix $\begin{pmatrix} 7 & 0 \\ 4 & 8 \end{pmatrix}$ [11, 12], measured at 40 K. The surface unit cell of TiOPc is highlighted in yellow; Ag(111) high symmetry directions are indicated by dashed lines (black).

By cooling down to 40 K the characteristic ring-pattern of CuPc/Ag(111) with its well-defined radius is largely retained (Figs. 1a and b). Additionally, six weak intensity maxima within the ring in the direction of the Ag reflexes are discernible at low T. They indicate a trend away from a purely random arrangement towards correlated positions of neighboring CuPc, most likely comprising a preferential alignment of the CuPc molecules with respect to the Ag atom rows of the Ag(111) surface.

The prevalence of a disordered 2D gas phase for the CuPc/Ag(111) system even at low T differs markedly from TiOPc/Ag(111), where emerging sharp LEED reflexes manifest a qualitative change in the long-range order at low T (Figure 1d); specifically, the observed pattern unequivocally reveals the formation of a TiOPc/Ag(111) c-phase [12]. Note that the local density of the c-phase (0.92 ML) is substantially higher than the actual amount of deposited TiOPc (0.5 ML). We suggest that upon cooling to cryogenic temperatures, the disordered 2D gas phase of TiOPc reorganizes into islands that display an internal c-phase structure. As will be described in the following, the transition temperature T_c from the 2D gas phase to the c-phase of TiOPc can be derived from LEED images taken at variable temperatures. A detailed description of the temperature-dependent LEED measurements is given in the Methods section.

Figure 2 (a) depicts, on the left side, the reference LEED pattern, obtained at constant $T_{\text{sample}} = 40$ K. On the right side the evolution of the LEED pattern with temperature is displayed, measured during the cool-down of the sample from 400 K to 40 K. Thanks to the high density of sharp diffraction spots the onset of long-range order formation can be visualized: At about 75 K a transition of the disc-like pattern, characteristic of a disordered 2D gas phase, to the ordered c-phase, is observed. Such a behaviour provides unequivocal evidence for an attractive net interaction among TiOPc molecules, that contrasts the repulsion prevailing for CuPc/Ag(111) dilute layers. Since the periphery of TiOPc and CuPc is virtually identical, the disparate intermolecular forces call for a more detailed discussion of lateral interactions between molecular species adsorbed on a metal substrate.

In a more elaborate effort, the order-disorder phase transition has been examined more quantitatively. Individual SPA-LEED line scans covering the (0,0) reflection as well as a characteristic spot of the c-phase have been collected as a function of temperature and merged into a gray-scale coded 2D plot that is shown in Figure 2 (b). From their intensity evolution a transition temperature of 75 K has been extracted. Interestingly, the vanishing of

the selected c-phase spot is correlated with a distinct weakening of the intense (0,0) reflex. This is attributed to an enhanced diffuse scattering of the incident electrons as the density of TiOPc molecules within the 2D gas phase increases at elevated temperatures.

Figure 2: SPA-LEED analysis of TiOPc deposited on Ag(111) at a coverage of 0.5 ML. (a) On the left hand side the reference LEED pattern obtained at $T_{\text{sample}} = 40 \text{ K}$ is shown. This image was taken right before annealing of the sample to realize the LEED image on the right hand side; here, the experiment was conducted during the cool-down of the sample from 400 K to 40 K. The temperature scale on the right refers to the actual sample temperature as the respective line of the LEED image is acquired. The kinetic energy of the electron beam was 50 eV. (b) Gray-scale 2D plot of a SPA-LEED 1D line scan along the yellow line in (a), intersecting the (00) reflection of the Ag(111) lattice and a c-phase spot of TiOPc/Ag(111) at 0.5 ML coverage. The individual line scans were recorded in the temperature range 40 - 140 K while the sample was cooled down linearly at a rate of -0.1 K/s (note that cooling slowed down below this rate at $T < 50 \text{ K}$). The kinetic energy of the electron beam in (b) was 28.6 eV.

A thorough discussion of lateral interactions among organic adsorbates on a metallic surface, namely free-base porphine (2H-P) on Ag(111) has been conducted by Bischoff et al. [28]. They discuss various contributions that may overturn the attractive van der Waals forces between molecules, eventually resulting in a net molecular repulsion: (i) Friedel oscillations in the surface state electron density [29], (ii) elastic deformations of the substrate that may induce

electrostatic interactions [30], (iii) repulsive dipole-dipole interactions that affect polar as well as non-polar molecules [31, 32], and (iv) the entropy as a quantity counteracting island formation [31, 33]. In addition to this list of possible contributions, one should also consider the effect of electrostatic multipole moments carried by some molecules and that can be either attractive [34] or repulsive [35] depending on the azimuthal orientation of interacting species.

For the various porphyrins or phthalocyanine species the fourfold symmetry of the parallel-adsorbed molecule renders in-plane dipole and quadrupole moments negligible, leaving the very short range octupole moment as the lowest order electrostatic interaction. Note however, that there will always exist a dipole moment perpendicular to the surface plane, which is produced when a molecular species is adsorbed on a surface as a result of the so-called Pauli push-back effect [1-3]; for chemisorbed species this dipole moment may receive an additional contribution due to molecule-metal charge transfer. In the case of TiOPc yet another contribution to the vertical dipole moment comes from the strong intrinsic axial dipole moment ($0.6 \text{ e}\cdot\text{\AA}$) associated with the titanyl unit. For CuPc/Ag(111) that latter component is evidently absent; the interaction with the Ag(111) substrate may lead to slight deviations from planarity, though. The quoted lateral interactions associated with the molecule's multipole moments will then add up on top of that.

According to Fig. 1 and in the particular case of TiOPc the role of the entropy seems to be important as well; specifically, the formation of islands with an internal c-phase is impeded at temperatures higher than about 75 K, and a quasi-random distribution of adsorbed species is found instead. In the case of CuPc the influence of entropy is less obvious as the ring-like LEED pattern, signalling a disordered arrangement, is only weakly altered upon variation of temperature.

3.2. Dipole Moments and Lateral Interactions

In a previous publication we have conducted a comprehensive study on the adsorption of TiOPc on Ag(111) [12]. The most stable adsorption geometry was investigated using DFT, considering both, the central metal ion adsorption site and the molecular azimuthal angle with respect to the Ag surface. Thereby, it turned out that the preferred adsorption site for TiOPc on Ag(111) is the so-called bridge₊ (lobes of TiOPc aligned along and perpendicular to the Ag atom rows), with a calculated adsorption energy (E_{ads}) of 3.74 eV [12].

Following the same methodology, we have found that for CuPc/Ag(111) the preferred adsorption geometry is also bridge₊, with an E_{ads} of 3.95 eV. In Table 1 various DFT findings obtained for CuPc and TiOPc adsorbed at bridge₊ sites are listed. As reference, the corresponding values calculated for CuPc in the gas-phase have been included. Other calculated adsorption geometries for CuPc/Ag(111) that are energetically less preferred are summarized in the Supporting Information.

Configuration	^a E_{ads} (eV)	^b $S(\mu_B)$	^c h_1 (Å)	^d h_2 (Å)
CuPc gas-phase	-	0.94	0.00	-
CuPc bridge₊	3.95	0.84	-0.160 ± 0.003	3.200 ± 0.018
TiOPc gas-phase	-	-	0.707 ± 0.009	-
TiOPc bridge₊	3.74	-	0.645 ± 0.009	3.289 ± 0.020

^a E_{ads} : adsorption energy per molecule in eV. ^b S : magnetization per molecule in Bohr magnetons. ^c h_1 : height difference (including its standard deviation) between the central metal atom and the phthalocyanine molecular plane (aromatic backbone) in Å. ^d h_2 : distance (including its standard deviation) between the top-most Ag(111) surface layer and the phthalocyanine molecular plane in Å.

Table 1: Calculated quantities of CuPc/Ag(111) in the low coverage regime, namely a single CuPc molecule adsorbed on a $(7 \times 4\sqrt{3})$ supercell (area 405 Å²) in a bridge₊ configuration, with the molecule aligned along the (110) symmetry direction. To aid comparison, the respective values for TiOPc/Ag(111) [12], as well as CuPc and TiOPc in the gas phase have been included.

The adsorbed CuPc molecule on Ag(111) does not show a noteworthy distortion compared with the CuPc molecule in gas-phase. Thus, it largely keeps its planar geometry with the metallic centre located slightly closer to the surface. Adsorbed TiOPc molecules display a slightly larger adsorption distance, while retaining their pyramidal shape with the Ti atom relatively far away from the surface. Regarding the magnetization of adsorbed CuPc, we find that the magnetic moment is only slightly reduced with respect to CuPc in the gas-phase. This robustness of the CuPc magnetic moment upon adsorption on metallic substrates has been already observed in several experimental works, and it contrasts with other metallic Pc species like e.g. CoPc or FePc, which display a quenching or strong reduction of the magnetic moment in the first monolayer [36-38]. Moreover, the derived value of approximately 1 μ_B is similar to that found by Huang et al. using PBE-GGA [39] and consistent with most previous experimental publications available of adsorbed CuPc [36-38].

By comparing our theoretical results for CuPc on Ag(111) to those reported by Huang et al. [39], we notice that the molecule - surface bonding distance is larger by ~ 0.2 Å in our case.

This is most probably caused by the different approximation used to introduce the effect of van der Waals interactions and, therefore, can be taken as an indication of the order of magnitude of the uncertainties associated with current standard computational techniques. The experimental bonding distance $d_{\text{NIXSW}} \approx 3.08 \text{ \AA}$ for the carbon backbone deduced from normal-incidence X-ray standing wave (NIXSW) results [7] is compatible with both theoretical values.

Figure 3: CuPc adsorbed on the Ag(111) surface in a bridge+ configuration. (a) PDOS projected onto the copper atom (black) and the molecular frame (red). The inset shows the spin-resolved PDOS projected onto the Cu atom, α spin (red) and β spin (blue) contributions. Energies are referred to the Fermi level. (b) Top and side views of the isosurface (isovalue = $\pm 2 \times 10^{-4} e/\text{Bohr}^{-3}$) of the induced electron charge. Red and blue surfaces indicate electron accumulation and depletion, respectively. (c) Induced electron density $\Delta n(z)$, averaged in the xy plane and plotted along z . Besides the bridge+ configuration (green), we also show data for the fccx (red), topx (blue), top+ (magenta) and bridgex (orange) structures.

Figure 3(a) shows the projected density of states (PDOS) on the metal centre and on the molecular framework for CuPc/Ag(111). We note that this PDOS displays an only weak dependence on the adsorption site, similar to the case of TiOPc/Ag(111) [12]. The population analysis reveals that CuPc takes 0.2 electrons from the surface, again similar to TiOPc/Ag(111). The interaction with the surface thus induces a partial filling of the LUMO for both molecules. The molecular orbital distribution of CuPc/Ag(111), however, displays notable differences with respect to the TiOPc system. In the case of TiOPc only the molecular backbone

contributes to the molecular orbitals around the Fermi level. For CuPc/Ag(111), on the other hand, both the molecular framework and the central metal ion are found to contribute.

Top and side views of the induced electronic density upon CuPc adsorption are depicted in Fig. 3(b). We identify an electron accumulation beneath the metal core and at the periphery of the molecule (in red), while the region of the molecule itself is subject to electron depletion (in blue). This is a clear signature of the Pauli repulsion between the electrons located in the molecule and of the surface below, an effect that is known as Pauli push-back effect [1-3]. A more quantitative picture is obtained from the plane-integrated charge density rearrangement, shown in Fig. 3(c). In the interface region ($z \approx 5-8$ Å) the electron rearrangement due to Pauli repulsion is evident; quite clearly there is an electron accumulation close to the surface and a depletion in the molecule. Using the calculated induced electronic density, $\Delta\rho(z)$, the dipole moment along the z direction was evaluated and the results listed in Table 2 for the bridge₊ adsorption configuration. The calculated dipole moments for different adsorption geometries of CuPc/Ag(111) are summarized in the Supporting Information.

Configuration	d_{mol} (e·Å)	$^b d_{\text{ind}}$ (e·Å)	$d_{\text{tot}} = d_{\text{mol}} + d_{\text{ind}}$ (e·Å)
CuPc gas-phase	0.00	-	-
TiOPc gas-phase	-0.59	-	-
CuPc bridge₊	-0.01 ^a	1.49 (1.13)	1.48 (1.12)
TiOPc bridge₊	-0.63 ^a	0.91 (0.89)	0.28 (0.26)

^a d_{mol} (molecular dipole) corresponds to the dipole of the (free) molecule computed using the molecular geometry obtained after adsorption. ^b d_{ind} denotes the induced dipole computed using the charge density distributions equivalent to Figure 3c

Table 2: Calculated vertical dipole moments (e·Å) of CuPc adsorbed on Ag(111), consistent with the results in Table 1. To aid comparison, the respective values for TiOPc/Ag(111) [12], as well as CuPc and TiOPc in the gas phase have been included. The data in parenthesis were computed using a larger (rectangular) lateral supercell ($9 \times 5\sqrt{3}$) in order to minimize the overlap of the induced charge distributions from neighboring molecules.

Although the CuPc molecule does not have a dipole moment in the gas phase, it acquires a total dipole moment d_{tot} larger than 1 e·Å along the surface normal (see Table 2) after adsorption on Ag(111) due to the already mentioned push-back effect. TiOPc/Ag(111), on the other hand, displays a much smaller total dipole moment of about 0.26 e·Å, the primary reason being the opposite sign of the contributions that arise from the push-back effect and the intrinsic molecular dipole associated with the axial Ti-O unit [12]. Moreover, the different

adsorption heights for CuPc and TiOPc may also contribute. CuPc, and particularly its metal center, lies closer to the surface, which leads to an increase of the induced dipole. It is apparent from our analysis that the vertical dipole moment represents a key difference between adsorbed CuPc and TiOPc molecules. In this respect, it is interesting to note that just by considering the electrostatic interaction of an array of vertically oriented dipoles we can expect a larger repulsion for CuPc that would contribute to prevent their self-assembly at low coverages for CuPc, in accordance with our experimental observations.

In order to elucidate the influence of the dipole moment of the adsorbed Pc molecules on the formation of 2D islands, we have modelled the intermolecular interaction. To do so, we have combined the electrostatic interaction obtained from *ab initio* DFT electron density distributions with a universal force field (UFF) that accounts for both, short-range repulsion and long-range van der Waals (vdW) attraction [40]. We have checked that for our Pc molecules the vdW tail given by the UFF force field is very similar to that obtained using the Grimme D2 model [41].

We have modelled our Pc molecules as neutral objects that combine the valence electron density computed for free-standing molecules with the adsorbed geometry, the ionic charges

(as spherical Gaussian radial distributions $\rho(r) = 8 / (L_c \sqrt{\pi})^3 \exp\left[-\left(2r/L_c\right)^2\right]$ with $L_c = 2.3$ Bohr

for Ti and Cu, 1.5 Bohr for C, N, and O, and 1.0 Bohr for H), and the distribution of induced charge upon adsorption on the Ag(111) substrate [see Fig. 4 (a)]. The electrostatic potential created by this object is then computed using a multipolar expansion including angular momenta up to $l_{\max} = 45$. Additionally, the potential was computed by straightforward numerical integration in the grid along specific directions to check the accuracy of the expansion. The comparison was found to be satisfactory, with the potential converged well within 1% for the relevant distances ($D > 15$ Å, with D the distance between the centers of neighboring molecules). Fig. 4(a) displays the charge distribution of an isolated TiOPc molecule with its electronic charge distribution in yellow (left), and the distribution of induced charge upon adsorption on Ag(111) (right) that extends beneath the surface and forms a rim around the molecular frame, displaying positively charged (electron depletion, in blue) and negatively charged (electron accumulation, in yellow) regions. In order to achieve a more precise description of this induced charge density, and avoiding overlap of the clouds caused by

periodic copies of the molecule in neighboring unit cells, a $(9 \times 5\sqrt{3})$ lateral supercell was used for the most relevant bridge+ configuration. Using this larger supercell gives rise to a reduction of the induced dipole moment as compared to the values obtained with the smaller $7 \times 4\sqrt{3}$ lateral supercell (see Table 2). Thus, the total dipole moments of TiOPc and CuPc on Ag(111) are estimated to be, respectively, 0.26 eÅ and 1.12 eÅ using the larger cell.

Figure 4: (a) On the left, in yellow, an isosurface of the electron density of an isolated TiOPc molecule, keeping the adsorbed geometry, is displayed. On the right, the induced charge density upon adsorption of TiOPc on a Ag(111) surface is shown. Negatively charged areas are represented in yellow, while areas with deficiency of electrons are represented in blue color. (b) Averaged effective pair intermolecular potential for CuPc (solid black line) and TiOPc (solid red line) of the most relevant molecular configurations [xx] and [x+]. The pronounced barrier potential at short-range distances of CuPc is evident. The dashed lines represent effective potentials that only consider the effect of the total point dipole, instead of the Coulomb interaction derived from the ab initio density distributions in panel (a). (c) The two highly symmetric pair configurations, most relevant for molecules in close proximity.

Moreover, we have to bear in mind that the resulting effective intermolecular pair potentials strongly depend on the relative orientation of the molecules. In order to allow for a simplified treatment below, we average the interaction potential over the most relevant high symmetry configurations when the molecules are in close proximity, shown in Fig. 4 (c) and denoted as xx and x+, obtaining an effective potential that only depends on the distance between the molecular centers D. The average is done according to the formula

$$V_{avg}(D) = \frac{1}{3} [2V_{x+}(D) + V_{xx}(D)] \quad (\text{Eq.1})$$

where we have taken into consideration that averaging over the azimuthal angle of *both* molecules means that the configuration x+ appears twice as often as xx. One should note here that the highly symmetric configuration ++ is too repulsive when molecules are close and, thus, it is not considered very relevant. Furthermore, an averaged effective potential of configurations xx and x+ seems meaningful since their minima and electrostatic barriers appear for both potentials at similar intermolecular distances D. In the supporting information one can find the individual effective potentials of the three high symmetry configurations (xx, x+ and ++) discussed in this paragraph.

The comparison between the averaged effective potentials computed for TiOPc (solid red line) and CuPc (solid black line), displayed in Fig. 4 (b), evidences a barrier potential at intermediate distances that is relatively pronounced for CuPc. The latter may explain the dominance of a disordered phase at relatively low temperatures for this molecule, as observed experimentally. The barrier appears due to the dominant repulsive character of the electrostatic interactions at large and intermediate distances. Fig. 4 (b) also displays the effective potentials when the electrostatic contribution is approximated by the interaction between point dipoles (with the same size as the *ab initio* total dipoles and located at the center of the molecules), instead of Coulomb interactions derived from the full *ab initio* charge distribution. As expected, both potentials behave similarly at long-range distances; at intermediate distances, however, the point-dipole severely underestimates the electrostatic repulsion resulting in a reduced barrier. At shorter distances we find an attractive potential well due to the van der Waals tail of the force field, and finally we encounter a short-range strong repulsion coming from both, the force field and the additional electrostatic component. Here, we postulate a simple 2D version of the van der Waals equation of state

$$S = \frac{nk_B T}{1 - nb} - an^2, \quad (\text{Eq.2})$$

describing a 2D molecular gas that is under an isotropic stress σ , where n is the areal density of Pc molecules and T the temperature. The constant b is the excluded area per molecule $\rho r_c^2 / 2$, where $r_c \sim 15 \text{ \AA}$ for both CuPc and TiOPc. Within the mean field approximation in the high temperature limit we obtain a simple expression for a in terms of the interaction potential,

$$a = -\pi \int_{r_c}^{r_{\max}} dr r V_{\text{avg}}(r) - \pi \frac{d_{\text{tot}}^2}{r_{\max}}. \quad (\text{Eq.3})$$

Here, the effective intermolecular potential has been replaced by the repulsion between two parallel point dipoles d_{tot} at distances larger than $r_{\max} = 90 \text{ \AA}$. For CuPc we obtain $a \sim 2341 \text{ meV \AA}^2$, while for TiOPc we get a value approximately twice larger $4587 \text{ meV \AA}^2$.

We can now extract the critical temperature for coexistence of the gas and condensed phases

$k_B T_c = 8a / 27b$, i.e., above this temperature the condensed phase does not appear. We obtain a T_c of approximately 23 K for CuPc, while for TiOPc T_c is almost double, with a value of 44 K. This provides clear evidence that the formation of a condensed phase takes place at lower temperatures for CuPc than for TiOPc, in accordance with experimental observations (Section 2.1). Specifically, a condensed phase has been observed for 0.5 ML TiOPc at $T < 75 \text{ K}$, while no evidence for such a transformation is found for CuPc, even at the minimum temperature of 40 K. Note that absolute T_c values obtained from the model may differ from the experimental values due to several simplifications that we have assumed in this approach; however, on a qualitative level our theoretical findings that feature a larger Coulomb repulsion for CuPc than for TiOPc are well supported. Our model reveals that the electronic density induced by Pc molecules adsorbed on the Ag(111) surface plays a crucial role in determining the total molecular dipole, and therefore represent a crucial factor in the intermolecular interactions and formation of molecular condensates for dilute systems (2D gas phase).

One interesting observation is that the short-range part of the interaction potentials in Fig. 4 (b) is very similar for both CuPc and TiOPc. The main difference stems from the electrostatic repulsion at intermediate (barrier) and long-range (dipolar) distances. Thus, we can encode the main ingredients in a simplified version of the potential, as shown in Fig. 5 (a), where only

the total molecular dipole is left as a free parameter. Here the long-range behavior is given by the total dipole d_{tot} , while the width r_d and depth V_0 of the attractive potential well are chosen to obtain reasonable values of the potential barrier and the parameter a in the equation of state. The explicit expression for a is

$$a = \frac{\rho V_0}{2} (r_d^2 - r_c^2) - \frac{\rho d_{tot}^2}{r_d}. \quad (\text{Eq. 4})$$

Using the dipole moments extracted from the DFT calculations ($d_{tot}^{CuPc} = 1.12 \text{ eÅ}$ and $d_{tot}^{TiOPc} = 0.26 \text{ eÅ}$), we find values of a similar to those computed above by adjusting the parameters in Eq. 4 to $V_0 = 11.4 \text{ meV}$ and $r_d = 22.2 \text{ Å}$ for both, CuPc and TiOPc.

Figure 5: (a) The lateral interaction between Pc molecules can be approximated by a simplified potential that contains an attractive potential well of depth V_0 and width $r_d - r_c$ at short range distances, and by dipole-dipole repulsion at long-range distances. (b) Phase diagram that displays the variation of T_c with the total molecular dipole of a Pc molecule upon adsorption on a Ag(111) surface. T_c is the critical temperature for the appearance of the condensed phase. The total dipole considers the intrinsic molecular dipole (if present) and the induced dipole upon adsorption on a Ag(111) surface.

As a result, Fig. 5 (b) shows the phase diagram of the 2D gas of Pc molecules as a function of the total dipole moment d_{tot} (upon adsorption)

$$T_c = \frac{8}{27k_B} \left\{ V_0 \left[\left(\frac{r_d}{r_c} \right)^2 - 1 \right] - 2 \frac{d_{tot}^2}{r_d r_c^2} \right\}. \quad (\text{Eq. 5})$$

As expected there is a quadratic dependence (reduction) of T_c on the total dipole of the adsorbed molecules and, for a total dipole larger than about 1.5 eÅ, the condensed phase eventually disappears. It is also interesting to note the stronger dependence of T_c on the total dipole moment for values close to those obtained for CuPc. Thus, uncertainties in the computed total dipole translate into larger uncertainties of T_c for CuPc than for TiOPc. We have seen that the Pauli push back effect induces a dipole of around +1 eÅ for CuPc as well as TiOPc; we suspect that a similar order of magnitude can be expected for other Pc molecules that absorb at similar distances from the substrate and with similar interaction strengths. Therefore, in the absence of detailed calculations for a given Pc molecule on Ag(111) we suggest that a rough estimate of the total dipole after adsorption that may allow positioning the molecule in the diagram in Fig. 5 (b) can be given by $d_{tot} \sim (\hat{n} \cdot \vec{d}_{mol} + 1 \text{ eÅ})$, where $\hat{n}$ is the outward-pointing normal unit vector. Of course, this expression will require additional modifications in case of a substantial charge transfer [42], or if bonding to the surface is stronger than that of the species explicitly considered here.

In the literature, the formation of 2D islands similar to TiOPc/Ag(111) has been observed for other phthalocyanine species as well, *e.g.* for Cl-MnPc adsorbed on Ag(111) [43]. At variance hereto the related MnPc molecules stay well separated from each other despite a similar molecule - metal charge transfer of about 0.7 e^- , as well as similar dipoles for adsorbed MnPc (0.53 eÅ) and Cl-MnPc (-0.47 eÅ) [44, 45]. A noteworthy difference, however, is found in the calculated adsorption energies, 3.58 eV for MnPc and 3.38 eV for Cl-MnPc. This enhanced molecule-metal interaction for MnPc correlates well with its shorter vertical bonding distance of 3.084 Å (distance between the average molecular plane and the Ag surface), as compared to 3.122 Å for Cl-MnPc. Even more significantly, the Mn atom is located much closer to the Ag(111) surface for MnPc (2.74 Å) than for Cl-MnPc (3.05 Å), which most likely is the main factor contributing to an accordingly enlarged corrugation ($\rightarrow$ diffusion barrier) regarding lateral motion for MnPc.

In order to understand the dissimilar behavior of MnPc and Cl-MnPc we have to consider what will happen as the sample is cooled down, and in particular to consider whether the experimentally observed spatial distribution corresponds to the thermodynamic equilibrium at all temperatures. Quite clearly, all species, including TiOPc and Cl-MnPc that do form 2D islands at low T, will be distributed statistically in the high T limit. This is because of entropy governing the occupancy of the various sites and adsorption geometries. Upon cooling, lateral mobility is gradually slowing down until at some point all motion has come to an end. In an experiment (performed at low T) the actually observed distribution of molecules will then correspond to the temperature at which diffusion of this particular type of molecule has vanished; this temperature will naturally depend on the diffusion barriers of the respective species. As these diffusion barriers can be expected to be substantially higher for MnPc with respect to the other compounds, MnPc motion will stop at considerably higher T as compared to, e.g., Cl-MnPc or CuPc. Given that the lateral interaction (attraction) between MnPc is rather weak, it is justified to assume that the statistical distribution still prevails at the temperature when MnPc lateral motion is freezing out. The observed distribution of well-separated MnPc thus reflects a kinetically limited situation, rather than that corresponding to the true thermodynamic equilibrium of the system.

Whether MnPc might form 2D islands at low T as well, given that restrictions regarding lateral mobility could be lifted, is tedious as we cannot tell. In view of the diagram in Figure 5b, that question is related to whether lateral mobility of MnPc on Ag(111) remains sufficiently high that the phase boundary can be reached. We conclude that the reason for the absence of island formation is different for MnPc and for CuPc, taking into account that the total dipole moment of adsorbed MnPc is much smaller than for CuPc/Ag(111), and more importantly, is very similar to Cl-MnPc that does form islands.

3.3. Vibrational spectroscopy as a monitor for the 2D gas-phase to 2D island phase transition

3.3.1. Dilute layers of CuPc and TiOPc on Ag(111)

From an analysis of IRAS spectra obtained at submonolayer coverages [8, 12] it became clear that CuPc and TiOPc molecules can unambiguously be discriminated from their characteristic

vibrational modes, even though both of them are phthalocyanines with a similar basic structure and are adsorbed with their backbone oriented planar to the Ag(111) surface.

In Fig. 6 IR spectra of dilute layers (0.5 ML) of CuPc and TiOPc on Ag(111) are shown. The selected spectral ranges in the left (a) and right (b) panels thereby cover modes with out-of-plane and in-plane character, respectively. The most obvious difference in the two displayed spectra refers to the axial Ti-O unit of TiOPc, which gives rise to a prominent band at 993.5 cm^{-1} that is evidently missing for adsorbed CuPc. In the left panel, C-H bending modes located at the periphery of the phthalocyanine species are observed at frequencies of about 720 and 770 cm^{-1} (cartoons of their character are depicted in the insets of Fig. 7, below). The two prominent bands display similar frequencies for CuPc and TiOPc, i.e. their line positions are only weakly dependent on the metal atom located in the molecule's center. As will be detailed below, these C-H bending modes are sensitive to the local environment of the molecules, offering valuable information related to the arrangement of molecules and the prevailing phases in the adlayer.

Figure 6: Comparison of IR spectra obtained from 0.5 ML of CuPc (top spectrum) and TiOPc (bottom spectrum) adsorbed on Ag(111). The left panel (a) covers the spectral region dominated by out-of-plane vibrational modes, while the right panel (b) exclusively contains in-plane modes. The spectra have been obtained at 80 K using a spectral resolution of 2 cm^{-1} . The indicated line positions for CuPc and TiOPc in the right panel have been determined by a line shape analysis using Fano-type line profiles [46].

In Figure 6(b) the CuPc/Ag(111) spectrum reveals a number of intense in-plane vibrational modes, all of them exhibiting strongly asymmetric line shapes. They can be ascribed to modes with A_{1g} – type of symmetry which have gained in intensity due to interfacial dynamical charge transfer (IDCT): vibrational motion in conjunction with a partially filled molecular orbital (e.g. the former LUMO) induces correlated charge oscillations between molecule and metal

substrate [8]. We note beforehand that for both molecular species we could not identify any E_u type of vibrational modes that should show up in case that the molecular plane is tilted. The vibrational modes' pronounced asymmetry is a clear indication for non-adiabatic processes governing these excitations and the associated coupling of vibrational motion and molecule - metal charge flow [8, 46-48].

Interestingly, these prominent modes of the phthalocyanine species are barely visible for TiOPc/Ag(111), signalling a significantly reduced IDCT. This might be a consequence of a weaker bonding to the Ag(111) substrate and the slightly larger vertical bond distance for TiOPc as compared to adsorbed CuPc, according to our DFT calculations. Our theoretical results further suggest that in the case of TiOPc the main interaction is between the molecular framework and Ag(111), complemented by a much weaker interaction between the Ti atom and the substrate, most likely due to the slight pyramidal shape of the TiOPc molecule. For CuPc, on the other hand, we find a quite strong interaction between the central Cu atom and the Ag substrate, promoted by its planar geometry and with the Cu atom slightly displaced closer to the substrate. Despite these differences the (static) charge transfer ($\sim 0.2 e^-$) from the metal substrate to the molecules is found to be about the same, as stated in our DFT calculations.

According to photoemission measurements of TiOPc/Ag(111) and CuPc/Ag(111) at coverages close to completion of the monolayer [49], the position of the former LUMO is slightly closer to ε_F in the case of CuPc (0.16 eV) as compared to TiOPc/Ag(111) (0.26 eV). This can be interpreted as a lower density of states at ε_F for TiOPc/Ag(111), resulting in an accordingly reduced intensity of TiOPc in-plane vibrational modes, i.e. IDCT is less effective for TiOPc/Ag(111).

3.3.2. 2D gas-phase to 2D island phase transition: coverage dependence

In the following we will look in more detail at the C-H bending modes introduced above, as they may offer in-depth information on the local environment of the molecular species. In a first set of experiments we have investigated whether the coverage-dependent transition of TiOPc on Ag(111) from isolated molecules (2D gas phase) towards TiOPc islands (2D condensate phase with well-defined long-range order) [11, 12] leads to an according signature in TiOPc vibrational spectra. In Fig. 7 the evolution of the prominent bands at 700 - 800 cm^{-1} with increasing TiOPc coverage (coverage range 0.3 - 0.8 ML) is shown. Thereby, we clearly

identify a transition of the 716.2 cm^{-1} band towards a new band at 713.7 cm^{-1} ; a similar trend is found for the mode at $760 - 770\text{ cm}^{-1}$. According to a normal mode analysis it is evident that both of them refer to C-H bending modes. As these are located at the periphery of the molecules, they react sensitively to changes in their local environment; accordingly, the Ti-O stretching mode at 993.5 cm^{-1} associated with the Ti-O unit in the center of TiOPc displays a negligible line shift ($< 0.2\text{ cm}^{-1}$) [12]. We conclude that changes in the arrangement of adsorbed molecules can indeed be detected from details in vibrational spectra. Specifically, the c-phase is characterized by distinct modes at 713.7 and 764 cm^{-1} , while for the 2D gas phase according bands are observed at 716.2 and 767 cm^{-1} . This interpretation is corroborated by the observation of TiOPc aggregates (mostly disordered) in addition to the prevalent TiOPc 2D gas phase, as shown in [12] (supporting information) using STM. Alternative explanations for the discrete frequency shifts and double-peak appearances of the C-H bending modes, such as occupation of two different adsorption sites for TiOPc on Ag(111), or the lifting of the degeneracy of these modes due to symmetry breaking ($C_{4v} \rightarrow C_{2v}$), induced by adsorption on the preferred bridge adsorption site [50], appear less likely.

Figure 7: Evolution of the C-H bending modes with increasing coverage (coverage range 0.3 - 0.8 ML) for TiOPc adsorbed on Ag(111). The spectra have been obtained at 80 K using a spectral resolution of 2 cm^{-1} .

From the coverage-dependent shift of the C-H bending mode frequencies towards the red we can further conclude that its origin is not due to dynamical dipole coupling, as an increased density of TiOPc molecules within the islands should produce a blue shift [51]. Rather, its primary cause is a 'chemical shift', induced by neighboring molecules. For CuPc/Ag(111) we

have observed a similar red shift of the modes at about 720 and 770 cm^{-1} for increasing coverages, that is, for more closely spaced 2D gas-phase molecules [8], confirming our interpretation.

3.3.3. 2D gas to 2D island phase transition: temperature dependence

In section 2.1 we have shown that no long-range order is observed in LEED at 80 K for TiOPc/Ag(111) low coverage layers at $\Theta_{\text{TiOPc}} \approx 0.5$ ML and below; cooling to 40 K, however, leads to the formation of 2D islands with c-phase internal structure. This can be taken as unequivocal evidence for an attractive intermolecular interaction among the TiOPc molecules. Moreover, it demonstrates that lateral mobility of TiOPc/Ag(111) is still substantial at 80 K; this probably holds for other Pc species as well, at least for those that adsorb at similar distances from the substrate and with similar interaction strength.

According to our findings, TiOPc 2D-clusters or islands are formed at temperatures below 75 K, reaching sizes large enough to generate a well-defined and sharp LEED pattern. No such condensation effects have been found for CuPc/Ag(111), which is ascribed to repulsive intermolecular forces as evidenced by coverage dependent SPA-LEED images provided by Kröger et al. [7] and corroborated by our observations and calculations.

We have now examined a series of IR spectra obtained at different sample temperatures in order to correlate the thermally induced transformation in the molecular long-range order (see Fig. 2) to according changes in the vibrational spectra. This set of spectra complements the series in figure 7 that yielded distinct spectral changes associated with the coverage dependent transition 2D gas-phase $\rightarrow$ commensurate c-phase. Hereby, we focus on the thermal evolution of the TiOPc C-H bending mode located at about 765 cm^{-1} (right panel of Fig. 8). As a reference, and in order to confirm our findings, the observations obtained for the dilute TiOPc/Ag(111) are compared to corresponding spectra of CuPc/Ag(111) for which no such T-dependent transformation does occur (left panel of Fig. 8).

In our experiments the 765 cm^{-1} vibrational band displays a marked splitting at low temperatures ($T < 100$ K) that we ascribe to TiOPc molecules experiencing different local environments. Specifically, the observed double-peak appearance of this band suggests that the TiOPc/Ag(111) layer at 0.5 ML coverage is characterized by the coexistence of dense 2D islands and a disordered 2D gas phase of TiOPc molecules. From our series it is apparent that their relative ratio varies with sample temperature, as evidenced by the T-dependent intensity

shift from the low frequency to the high frequency component of this feature. As the temperature is raised to $T > 100$ K it transforms into a single band with broadened line shape produced by the overlap of the two vibrational components, associated with isolated molecules and dense 2D islands. Interestingly, a narrowing is observed at temperatures 120 K - 150 K; this unusual behavior is, however, ascribed to the continued diminution of the low frequency component of the broad band (located at about 764.8 cm^{-1} , and associated with TiOPc 2D islands), and to the prevalence of isolated TiOPc molecules at elevated T (high frequency component). This interpretation is fully supported by the pronounced intensity gain of the 767.5 cm^{-1} band associated with isolated TiOPc/Ag(111), observed at $T = 40 - 100$ K. A direct comparison to the corresponding C-H vibrational band of CuPc [Fig. 8(a)], measured in the temperature range 28 - 200 K reveals a single absorption peak at about 769 cm^{-1} , which we take as clear evidence that all CuPc molecules experience an identical local environment. The band gradually shifts to lower frequencies and broadens for increasing temperatures. This is attributed to anharmonic coupling of this mode to thermally excited low frequency modes of adsorbed CuPc molecules. In the past such phenomena have been observed and analyzed in detail for small molecular species, e.g. adsorbed CO on various transition metal surfaces; an exhaustive description and analysis of anharmonic coupling effects can be found in the literature [47, 52, 53].

Figure 8: Temperature dependence of a C-H vibrational mode obtained from dilute layers of CuPc (a) and TiOPc (b) on Ag(111). The sample temperature during measurements is given in the figure; spectral resolution was 2 cm^{-1} , except for the 28 K and 80 K spectra of CuPc which used 0.5 cm^{-1} .

At variance to CuPc/Ag(111), however, no such T-dependent red-shift of the displayed broad band seems to occur for TiOPc/Ag(111) in Fig. 8b; rather, its center even experiences a blue-shift. As a matter of fact, this apparent oppositely directed T-dependent line shift is primarily caused by the vanishing of the 764.5 cm^{-1} component of the broad TiOPc band at elevated T. Actually, the band at about 767 cm^{-1} due to isolated molecules does experience a T-dependent red-shift, very similar to CuPc/Ag(111), and it can likewise be attributed to anharmonic coupling to thermally excited low frequency modes.

4. Conclusions

The intermolecular interaction within dilute layers of TiOPc and CuPc molecules adsorbed on Ag(111) have been investigated by means of IRAS and SPA-LEED in the temperature range 30 - 200 K. At variance to CuPc molecules repelling each other, neighboring TiOPc are found to experience an attractive intermolecular interaction, leading to an order-disorder phase transformation. Specifically, LEED measurements clearly demonstrate that TiOPc molecules, while arranged statistically at elevated $T > 75\text{ K}$ (2D gas), adopt a definite long-range order (c-phase) at low temperatures $T < 75\text{ K}$ (2D-condensate), minimizing the abundance of isolated molecules in the system. The considerably tighter packing within the c-phase as compared to the average density of deposited TiOPc implies that this transition proceeds via the formation of islands of the c-phase at low T.

The effect of intermolecular and molecule-substrate interactions on vibrational spectra has been examined by IR spectroscopy. According to these data the c-phase islands of TiOPc/Ag(111) are found to coexist with isolated molecules at low T; their relative abundances, as deduced from the relative intensity ratio of the respective vibrational bands, depends strongly on temperature at 30 - 150 K. This means that the attractive interaction between the TiOPc molecules is only weak, in accordance with the vanishing of the characteristic c-phase LEED reflexes already at $T > 75\text{ K}$.

The comparison of TiOPc/Ag(111) with CuPc/Ag(111) shows that the prevailing intermolecular interactions differ markedly for the two systems despite a virtually identical footprint and periphery of both molecules, resulting in repulsion for the one (CuPc) and a net attraction for the other (TiOPc) species.

Based on DFT calculations various contributions related to the specific interactions of the two molecules with the Ag(111) substrate have been identified that, while present for both systems, add up differently for adsorbed CuPc and TiOPc. Most prominently, a quite substantial vertical dipole moment is created upon adsorption for CuPc (Pauli push-back effect), adding a repulsive term to the intermolecular interactions, while a compensation of an according dipole by the intrinsic molecular dipole moment renders this component negligible for TiOPc. The virtual absence of such a repulsive contribution leads to an overall more attractive intermolecular interaction between adjacent TiOPc molecules and 2D island formation at low T. Thus, by modifying the total vertical dipole moment of an adsorbed species it is possible to tune the lateral interactions between adsorbed species (from repulsive to attractive), enabling us to modify and tailor novel molecular structures. Adding an axial component with an intrinsic dipole moment thereby represents an efficient way to achieve this.

Interestingly, the PDOS for CuPc/Ag(111) shows a marked contribution of the metallic ion to the molecular orbitals located at the Fermi level, while this is not the case for adsorbed TiOPc. This might explain the substantially stronger IDCT for CuPc as compared to TiOPc on Ag(111) despite a similar molecule-metal charge transfer of about $0.2e^-$.

Associated Content

Supporting Information

Additional results using DFT calculations on adsorption geometries and associated vertical dipole moments for CuPc/Ag(111); computed intermolecular interaction potentials for highly symmetric molecular configurations of CuPc and TiOPc on Ag(111).

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