Adsorption-induced symmetry reduction of metal-phthalocyanines studied by vibrational spectroscopy

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We investigate the vibrational properties of Pt- and Pd-phthalocyanine (PtPc and PdPc) molecules on Ag(111) with high resolution electron energy loss spectroscopy (HREELS). In the monolayer regime, both molecules exhibit long range order. The vibrational spectra prove a flat adsorption geometry. The red shift of vibrational modes and the presence of asymmetric vibrational peaks suggest a moderate interaction of the molecules with the substrate, accompanied by a static charge transfer from the metal to the molecules. The appearance of a particular vibrational mode, which (i) belongs to the $B_{1g}$ representation of the original fourfold $D_{4h}$ molecular symmetry group and which (ii) exhibits interfacial dynamical charge transfer (IDCT), proves that a preferential charge transfer from the Ag surface into one of the originally doubly degenerate lowest unoccupied molecular orbitals (LUMOs) of $E_g$ symmetry takes place, i.e. the electronic degeneracy is lifted and the molecule-surface complex acquires the twofold symmetry group $C_{2v}$. The vibration-based analysis of orbital degeneracies, as carried out here for PtPc/Ag(111) and PdPc/Ag(111), is not restricted to these cases. It is particularly useful whenever the presence of multiple molecular in-plane orientations at the interface makes the analysis of orbital degeneracies with angle-resolved photoemission spectroscopy difficult.

I. INTRODUCTION

Organic molecules with $\pi$-conjugated electron systems have been intensively studied in recent years. Apart from a fundamental interest in their electronic properties, this activity is motivated by the wide range of possible applications in the fields of optoelectronic,1,2 and spintronic.3 Among these molecules, metal-phthalocyanines (MPc), i.e. tetrabenzoporphyrazine macrocycles with a metal atom in their center, play an important role, because of their planar geometry, their thermal stability, their suitability for organic molecular beam epitaxy, and their chemical versatility that its brought about by very diverse central metal atoms.4 In fact, MPc molecules have been employed in organic light emitting diode,5 field effect transistors,6,7 and solar cells.8

The interaction of MPc with metal surfaces is interesting both from a fundamental point of view, in particular regarding the balance between the contributions of the central metal atom and the $\pi$-electron system, and for applications, in which such interfaces are the primary functional elements. For MPc with almost filled $d$-shells, the molecule-substrate interaction is dominated by the chemisorptive or physisorptive interaction of the macrocycle with the metal surface.9 If there is a chemisorptive contribution to this bond, this often leads to charge transfer from the metal into the lowest unoccupied molecular orbital (LUMO) of the molecule.9 This is also true in the case of PtPc and PdPc on Ag(111), as we show in this paper.

An interesting issue in relation to the molecule-substrate interaction in general and the charge transfer in particular is the symmetry of adsorbed MPc molecules. Except for a few cases, e.g., SnPc10 the central metal fits into the inner cavity and the corresponding isolated MPc belongs to the $D_{4h}$ symmetry group.11 Because of the presence of the surface, the symmetry of the molecule is lowered to $C_{4v}$. However, a further molecular symmetry reduction to a twofold symmetry is often observed in scanning tunneling microscopy (STM).12,14

The symmetry reduction of MPc molecules from fourfold to twofold symmetry raises an intriguing question regarding the charge transfer into the molecule. The LUMO of isolated MPc is twofold degenerate and belongs to the irreducible representation $E_g$ of the $D_{4h}$ symmetry group. This degeneracy is closely related to cross-conjugation in the central porphyrazine macrocycle of phthalocyanine molecules.15,16 When charge is transferred into the LUMO, two situations are conceivable: either both orbitals remain degenerate and receive the same amount of charge, or the degeneracy is lifted and charge is transferred preferentially into one of the two. Degeneracy lifting has been invoked in certain cases to explain the symmetry reduction of MPc molecules,11,14,16 while in other cases equal filling of both $E_g$ orbitals was conjectured,17,18 or the symmetry reduction was assigned to structural effects.19,20

At first glance, STM seems to be the method of choice for symmetry analysis of molecular adsorbates, because any symmetry breaking should become immediately obvious in the image. However, in STM purely electronic as well as purely geometric effects can both lead to a symmetry reduction in the image, and there are only a few cases in which the origin of the broken symmetry can be determined on basis of STM alone (e.g. Ref. 16). Of course, in most cases geometric and electronic effects will be coupled to each other, because a geometric distortion of the molecule by the influence of the external environment will also break the electronic symmetry within the molecule, and vice versa an electronic symmetry reduction will generally lead to a structural distortion (Jahn-Teller effect).13,16,21,22 Yet, it is still an important question...
to ask which is the dominant of the two effects. For example, a strong geometric distortion may lead to a negligible symmetry break of electronic states.

For this reason, additional experimental methods have been employed to settle the issue of a possible lifting of the degeneracy. These include core level spectroscopy\(^\text{13}\), near-edge x-ray absorption spectroscopy (NEXAFS)\(^\text{21}\), or density functional theory (DFT)\(^\text{22}\). Recently, also photoemission tomography\(^\text{22,23}\) has been applied to this problem: In the case of FePc/Ag(111) no splitting of the LUMO was found\(^\text{24}\), while for CuPc/Ag(110) a clear splitting was observed\(^\text{25}\). Photoemission tomography has the unique advantage that if a degeneracy lifting takes place, the actual orientation of the filled orbital can be determined\(^\text{22}\). However, this orientational sensitivity can also be a drawback, if many molecules with many different orientations are present at the surface. In this case, photoemission tomography results become difficult to analyze\(^\text{21}\).

Here we present an approach that does not suffer from the presence of multiple orientations, because only the internal symmetry of the molecule-surface complex matters. Yet at the same time, if applicable, it leads to unambiguous results regarding electronic symmetry breaking, i.e. degeneracy lifting. This approach is based on vibrational spectroscopy. Specifically, we employ high resolution electron energy loss spectroscopy (HREELS) which in its dipole scattering mechanism is sensitive to infrared (IR) active vibrational modes\(^\text{23}\). Due to the surface selection rule, only totally symmetric modes of the molecule-surface complex are IR active\(^\text{23}\). Any reduction of the molecular symmetry group upon adsorption may imply that formerly inactive modes can become IR active.

Because, as mentioned above, the symmetry reduction can be effected both by geometric and electronic effects, also the corresponding IR activation can have these two distinct origins. However, if additionally the line shape of an activated mode is taken into account, it is (under favorable conditions) possible to unambiguously link the activation of certain vibrational modes to an electronic symmetry breaking. More specifically, we argue here that if a mode that indicates a particular symmetry reduction has a Fano line shape, this proves an electronic contribution (i.e. degeneracy lifting) to this symmetry reduction, because the Fano line shape indicates an interfacial dynamical charge transfer (IDCT), and for an IDCT to be observable in a MPc molecule, there must exist an imbalance in the occupation of the two E\(_g\) LUMOS. Hence, their degeneracy must be broken.

II. EXPERIMENTAL DETAILS

The experiments were performed in an ultra-high vacuum (UHV) system consisting of a preparation and an analysis chamber equipped with low electron energy diffraction (LEED) and HREELS. The pressures in the chambers were \(4 \times 10^{-9}\) and \(4 \times 10^{-10}\) mbar, respectively. The Ag(111) crystal surface was prepared by \(\text{Ar}^+\) sputtering at 1 keV followed by annealing to 730 K until a sharp LEED pattern was observed. Thin films of PdPc and PtPc were prepared in UHV by depositing the molecules, evaporated from a home-made Knudsen cell, on the crystal kept at room temperature. The sublimation temperatures were 770 K and 670 K for PdPc and PtPc, respectively. A multilayer phase, which does not exhibit a LEED pattern, is prepared by sublimating PtPc more than ten times longer than the sublimation time necessary to obtain the ordered monolayer phase. The pressure in the preparation chamber did not exceed \(1 \times 10^{-8}\) mbar during sublimation.

After the layer was prepared, its long range order was checked by LEED. Vibrational features were recorded with a primary electron beam energy of 6.3 eV in both specular and off-specular geometries. The incoming beam is directed to the sample with an angle of 45° with respect to surface normal. In the specular (off-specular) geometry the electrons are detected at an angle of 45° (60°) with respect to the surface normal. The energy resolution, estimated from the full width at half maximum (FWHM) of the elastic peak, is in the range of \(16 - 22\) cm\(^{-1}\) (2 - 2.7 meV). In order to interpret the complex vibrational spectra, we performed theoretical calculations of isolated PtPc and PdPc molecules using GAUSSIAN\(^\text{26}\). The DFT calculations of their electronic structure and of their vibrational eigenfrequencies were carried out using the LanL2DZ basis set and the B3LYP functional. The theoretical vibration energies were compressed by a factor 0.945\(^\text{27,28}\).

III. PLATINUM-PHTHALOCYANINE ON AG(111)

A. Long range order

PtPc molecules form ordered two-dimensional structures on the Ag(111) surface. Like for most of the MPc molecules, two diffuse rings are detected at room temperature in LEED at low coverage after annealing a thick layer up to 730 K (see Ref. 29). This two-dimensional disordered phase has already been observed in the case of, for example, CuPc on Ag(111) and Au(111)\(^\text{24,31}\). Stadler et al. interpreted the presence of this two-dimensional gas phase at low coverage as the result of an intermolecular repulsion\(^\text{32}\). As the density of the PtPc molecules on the surface increases, diffraction spots are detected in LEED at room temperature (ordered phase). According to high resolution structural measurements for CuPc, the unit cell formed by the CuPc molecules decreases continuously in size as the coverage is increased. Our LEED measurements indicate a similar behavior for PtPc on Ag(111).
B. Vibrational properties of the multilayer and mode assignment

PtPc has $3N - 6 = 165$ distinct vibrational modes ($N = 57$ is the number of atoms in the molecule). Its symmetry group is $D_{18h}$, its vibrational representation is $\Gamma = 14A_{1g} + 13A_{2g} + 14B_{1g} + 14B_{2g} + 26E_u + 56E_u + 8A_{2u} + 6A_{1u} + 7B_{1u} + 7B_{2u}$. Modes transforming according to the irreducible representations $A_{2u}$ and $E_u$ are IR active modes, i.e., the motion of the atoms produces a dynamic dipole moment $\vec{\mu}_{\text{dyn}}$. Depending on the direction of $\vec{\mu}_{\text{dyn}}$, the IR active modes can be classified as in-plane modes, in which $\vec{\mu}_{\text{dyn}}$ lies in the molecular $xy$-plane ($E_u(x,y)$ modes), and as out-of-plane modes, in which $\vec{\mu}_{\text{dyn}}$ is oriented perpendicular to the molecular plane along the $z$-direction ($A_{2u}(z)$ modes). The $A_{1g}$, $E_u$, $B_{1g}$ and $B_{2g}$ modes are Raman (R) active modes, i.e., the atomic vibration induces a change of the molecular polarizability.

In this work we are interested in IR active modes, because HREELS is sensitive to the dynamic dipole moment $\vec{\mu}_{\text{dyn}}$. According to the surface selection rule, modes for which $\vec{\mu}_{\text{dyn}}$ is oriented perpendicular to the surface are excited in the dipole scattering mechanism.
Table I. List of the experimental vibrational modes present in the PtPc multilayer and ordered monolayer phase specular spectra on Ag(111) accompanied by their description and symmetries. The theoretical frequencies are compressed by a factor 0.9456. The acronyms stand for: OP=out-of-plane, IP=in-plane; bend=bending mode, deform=deformation mode, sciss=scissoring mode, stretch=stretching mode, rock=rocking mode. All values are given in cm$^{-1}$.

| Modes | Multilayer | Ordered monolayer | DFT | Symmetry | Description |
|-------|------------|-------------------|-----|----------|-------------|
| a     | 145        | 145               | 136 | A$_{2u}$ | OP bend: Molecule |
| R1    | -          | 255               | -   | -        | -           |
| b     | 310        | -                 | 301 | A$_{2u}$ | OP bend: Molecule |
| c     | 380        | 350               | 382 | A$_{2u}$ | OP bend: N atoms |
| d     | 430        | 430               | 434 | A$_{2u}$ | OP bend: N + C atoms |
| e     | 505        | -                 | 490 | E$_u$    | IP sciss: N + C atoms |
| R2    | -          | 565               | -   | -        | -           |
| f     | 575        | -                 | 574 | E$_u$    | IP deform: Molecule |
| R3    | -          | 655               | -   | -        | -           |
| g     | 730        | 715               | 738 | A$_{2u}$ | OP bend: Main ring |
| h     | 765        | 765               | 770 | A$_{2u}$ | OP bend: N atoms + Phenyl groups |
| i     | 880        | -                 | 869 | E$_u$    | IP deform: Molecule |
| j     | 925        | -                 | 956 | A$_{2u}$ | OP bend: Phenyl groups |
| k     | 1075 – 1200| -                 | 1031 – 1159 | E$_u$ | IP deform/stretch: Molecule |
| F1    | -          | 1075 – 1200       | -   | -        | -           |
| l     | 1285 – 1375| -                 | 1260 – 1323 | E$_u$ | IP rock/stretch: N atoms + Phenyl groups |
| F2    | -          | 1285 – 1375       | -   | -        | -           |
| m     | 1410 – 1530| -                 | 1376 – 1465 | E$_u$ | IP stretch: Main ring |
| F3    | -          | 1410 – 1530       | -   | -        | -           |
| n     | 1585 – 1640| -                 | 1546 – 1574 | E$_u$ | IP stretch: Phenyl groups |
| o     | 3010 – 3030| -                 | 3025 – 3064 | E$_u$ | IP stretch: H atoms |

( speculative geometry), whereas modes having a dynamic dipole oriented parallel to the surface are suppressed, because the $\vec{\mu}_{\text{dyn}}$ produced by the image charges in the substrate is anti-parallel to $\vec{\mu}_{\text{dyn}}$, leading to a cancellation of the two. In the language of group theory, the surface selection rule states that only totally symmetric modes (A$_1$, A’ and A representations) of the molecule-substrate complex may be visible in HREELS. In contrast, all modes can be excited in the impact scattering regime (off-specular geometry). The appearance and/or disappearance of specific modes in the HREELS spectrum, depending on the measurement geometry, give important information on the symmetry of the molecule-substrate complex. Therefore, an accurate assignment of the vibrational features is necessary.

The assignment is carried out by comparing the experimental peaks in the spectrum of a multilayer with calculated frequencies of the isolated PtPc molecule. In the multilayer, the effect of the substrate is reduced and thus the spectral properties are expected to be similar to the isolated molecule. Fig. 1(a) shows the experimental spectrum of a PtPc multilayer on Ag(111), acquired in specular geometry, in comparison with the calculated spectrum of the isolated PtPc molecule (Fig. 1(b)). The calculated spectrum contains a gaussian broadening of 20 cm$^{-1}$, similar to the experimentally observed one, and is composed of A$_{2u}$ (blue lines) and E$_u$ (red lines) modes only, because these are the sole IR active vibrations. We note that all experimental features can be identified in good agreement with theory. A simplified description of the modes is given in Tab. I (see Ref. 29 for details). The spectrum is dominated by the A$_{2u}$ modes, with dynamic dipole moments perpendicular to the molecular plane, such as the strongest vibrations a at 145 cm$^{-1}$ (out-of-plane bending of the whole molecule except Pt) and g at 730 cm$^{-1}$ (out-of-plane bending of the central ring of alternating C and N atoms around the metal porphyrazin macrocycle together with the H atoms, Fig. 1(d)). Compared to experiment, the theoretical E$_u$ mode intensities appear reduced, suggesting a predominantly flat adsorption orientation of the molecules in the multilayer. However, the intensity ratio of the in-plane modes (E$_u$) and out-of-plane modes (A$_{2u}$) is conserved in the off-specular spectrum (not shown). This can be caused by a residual contribution of the dipole scattering in the off-specular geometry due to, e.g., surface roughness.

C. Vibrational Properties of the ordered monolayer phase and molecular symmetry reduction

The vibrational properties of the ordered monolayer phase are discussed in comparison with those of the multilayer. Fig. 2(a) shows specular HREELS spectra of the
ordered monolayer phase and the multilayer. In the ordered monolayer, most of the $E_u$ in-plane modes are absent, especially between 1000 and 1600 cm$^{-1}$. But in this range three asymmetric peaks ($F_1$, $F_2$ and $F_3$) are detected. Their origin will be discussed later. The absence of the in-plane vibrations indicates that the surface selection rule strongly attenuates the in-plane $E_u$ modes in comparison to the out-of-plane $A_{2u}$ modes. We conclude that the molecules in the monolayer are oriented strictly parallel to the Ag surface.

1. **Out-of-plane $A_{2u}$ modes**

Like in the multilayer, all of the out-of-plane $A_{2u}$ modes are detected in the spectrum of the ordered monolayer phase. However, in the latter the $c$ and $g$ modes are shifted to lower wavenumbers. The shift of the $c$ mode ($\simeq 30$ cm$^{-1}$) is larger than that of the $g$ mode ($\simeq 15$ cm$^{-1}$). The $c$ mode is associated with the out-of-plane bending of the aza bridge N atoms against the pyrrole N atoms (Fig. 1(c)), while in the $g$ mode all N atoms move in-phase against the C atoms in the porphyrin macrocycle and the H atoms in the phenyl groups (Fig. 1(d)). We assign the sizable shifts of these two modes to the molecule-substrate interaction. In contrast to FePc and CoPc on Ag(111)\cite{33,34}, for which the central metal forms a covalent bond with the substrate, the molecule-substrate interaction in PtPc takes place through the porphyrin macrocycle, because neither the $c$ nor the $g$ modes, which are the ones that are most strongly influenced by the substrate, involve the central metal atom, unlike the $a$ mode for example, which involves the metal atom but does not show an appreciable shift. This observation is in agreement with the general trend of a reduced metal participation in the molecule-substrate bond as the number of $d$-electrons increases.\cite{35}

The observation that the shift of $c$ is larger than that of $g$, in conjunction with the fact that the $c$ mode displacement is due to the N atoms only while in the $g$ mode the displacements of N atoms are relatively small, suggests that most of the interaction between the molecule and

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**Figure 2.** (a) The comparison of the specular HREELS spectra of the PtPc ordered monolayer phase and multilayer on Ag(111). The simulated vibrational modes of the isolated molecule are indicated as color bars. Note that the vibrational properties of the ordered monolayer phase do not change with the coverage. (b) The calculated charge density of the two degenerate LUMOs of isolated PtPc. (c) Representation of the Raman mode of $B_{1g}$ symmetry at 1509 cm$^{-1}$ (marked with * in panel (a)) that is used to fit the Fano peak $F_3$ at approximately 1500 cm$^{-1}$ (see text).
of the molecule is broken. With the help of so-called correlation tables it is possible to deduce how the modes (representations) of the isolated molecule ($D_{4h}$) relate to the ones of the molecule-substrate system of reduced symmetry ($C_{4v}$ or lower). An adaptation of the correlation tables of the $D_{4h}$ group from Ref. 25 considering the observed R modes (and the F modes), is given in Tab. [11].

In principle, there is a chance that the observation of the R modes allows us to deduce the symmetry of the molecule-substrate complex. For example, a B$_{2g}$ mode would become activated for HREELS dipole scattering only if the $D_{4h}$ symmetry was reduced to $C_{2v}(\sigma_d)$ upon adsorption (Tab. [1]). Hence, we must look for a single reduced symmetry group in which the vibrational modes of the free molecule which we assign to R1, R2 and R3 map onto a totally symmetric representation (A$_1$, A’ or A). However, since it is a possibility that R1, R2 and R3 could all originate from A$_{1g}$ modes (see Tab. [1]), all three would in this case be visible in dipole scattering HREELS irrespective of the symmetry of the molecule-substrate complex ($C_{4v}$, $C_{2v}(\sigma_v)$ or $C_{2v}(\sigma_d)$). Hence, it is not possible to conclude on the basis of R1, R2 and R3 alone whether PtPc preserves its fourfold symmetry upon adsorption ($C_{4v}$) or lowers its symmetry to a twofold one ($C_{2v}(\sigma_v)/C_{2v}(\sigma_d)$).

3. Asymmetric peaks

In order to identify the symmetry of the PtPc molecule on the Ag surface, we now turn to the analysis of the F modes. Between 1000 and 1600 cm$^{-1}$, where the E$_u$ modes are excited in the multilayer spectrum (Fig. [2]a), three asymmetric features, labeled F1, F2 and F3 in Fig. [2]a, are visible in the spectrum of the ordered monolayer. Asymmetric line shapes of Fano type are well known for molecular and atomic adsorbates on metallic surfaces in the presence of an IDCT [18][22]. A prerequisite for the occurrence of IDCT is the partial filling of an orbital that couples to a molecular vibration. Then, as the vibration is excited, the associated distortion of the molecule along the vibrational coordinate modulates the orbital energy periodically, leading to an oscillatory charge flow between the molecule and the substrate that is effectively pumped by the vibration. In the presence of IDCT, the dynamical dipole moment $\mu_{\text{dyn}}$ of the vibration is the sum of the ionic and the electronic contributions, $\mu_{\text{ion}}$ and $\mu_{\text{DCT}}$. If the dynamic electron transfer between the orbital and the substrate, yielding $\mu_{\text{DCT}}$, is not in phase with the ion movement, leading to $\mu_{\text{ion}}$, i.e. if the Born-Oppenheimer approximation breaks down, $\mu_{\text{dyn}}$ acquires an imaginary part ($\mu_{\text{dyn}} = \mu_1 + i\mu_2$). This leads to a damping of the adsorbate vibration and yields an asymmetric Fano line shape. By introducing the asymmetry parameter $\omega_0^\tau = \mu_2/\mu_1$ the resulting line shape can be expressed as [43][45]:

\begin{table}[h]
\begin{center}
\begin{tabular}{|c|c|c|c|}
\hline
$D_{4h}$ & $C_{4v}$ & $C_{2v}(\sigma_e)$ & $C_{2v}(\sigma_d)$ \\
\hline
$E_u(x,y)$ & $E(x,y)$ & $B_1(x)+B_2(y)$ & $B_1(x)+B_2(y)$ \\
$A_{1g}$ & $A_1(z)$ & $A_1(z)$ & $A_1(z)$ \\
$E_g$ & $E(x,y)$ & $B_1(x)+B_2(y)$ & $B_1(x)+B_2(y)$ \\
$B_{2g}$ & $B_2$ & $A_2$ & $A_1(z)$ \\
$B_{1g}$ & $B_1$ & $A_1(z)$ & $A_2$ \\
\hline
\end{tabular}
\end{center}
\caption{Correlation tables of the $D_{4h}$ symmetry group limited to the possible modes assignment of the R and F modes. The notation ($x,y$) and (z) define the in-plane and out-of-plane character of the representation. The other representations are not IR active.}
\end{table}

\begin{table}[h]
\begin{center}
\begin{tabular}{|c|c|}
\hline
Mode & Symmetry \\
\hline
R1 & $A_{1g}/E_u(x,y)/E_g$ \\
R2 & $A_{1g}/E_u(x,y)/B_{1g}$ \\
R3 & $A_{1g}/B_{2g}$ \\
F1 & $A_{1g}/E_u(x,y)/B_{1g}$ \\
F2 & $A_{1g}/E_u(x,y)/B_{1g}/B_{2g}$ \\
F3 & $B_{1g}$ \\
\hline
\end{tabular}
\end{center}
\caption{Possible assignments of the R and F modes observed in the ordered monolayer phase of PtPc on Ag(111). The F modes assignments are based on the fit results presented in Ref. 29.}
\end{table}

the Ag substrate occurs via the N atoms.

2. Raman modes

Another noteworthy difference between the vibrational properties of the ordered monolayer phase and the multilayer is the appearance of new modes labeled R1, R2 and R3 in Fig. 2(a). Based on their frequencies, the R1 peak at 255 cm$^{-1}$ can be interpreted either as an E$_u$, A$_{1g}$ or as an E$_g$ mode, while the R2 peak at 565 cm$^{-1}$ may be attributed to either an E$_u$, A$_{1g}$ or a B$_{1g}$ mode. Finally, the R3 peak at 655 cm$^{-1}$ can either be ascribed to a A$_{1g}$ or a B$_{2g}$ mode. The possible assignments are summarized in Tab. [11]. Ruling out the E$_u$ modes, because as in-plane IR modes they should be screened by the metal surface, only the A$_{1g}$, E$_g$, B$_{1g}$ and B$_{2g}$ modes remain as possible assignments. However, they are R active modes and as such not expected to contribute to the spectrum of an isolated molecule. But they can be activated if the molecular symmetry is reduced. Thus, a symmetry reduction of the molecule in contact with the surface must be considered.

When a PtPc molecule adsorbs with its plane parallel to the surface, its molecular symmetry is reduced from the original $D_{4h}$ group. Specifically, at least the in-plane-plane ($x,y$) mirror symmetry is broken. A PtPc molecule lacking its ($x,y$)-plane symmetry belongs to the C$_{4v}$ group. However, further symmetry reductions are possible, e.g., to the C$_{2v}$ group, if the fourfold symmetry of the molecule is broken.
In order to identify which vibrational modes are involved in the IDCT that produces F1, F2 and F3, Eq. 1 is used to fit these features, using values of ω0 that are determined by DFT calculations of an isolated molecule. All the calculated ω0 frequencies in the range from 900 to 1800 cm⁻¹ have been tested (Fig. 3(a)). The fits can be found in the supplement. The few modes that yield reasonable fits for F1 and F2 are summarized in Tab. III. Because both features may possibly be assigned to a A1g mode, whose representation in the D4h group transforms into a totally symmetric one in both the C4v or C2v groups, it is not possible to identify the symmetry of the molecule-substrate complex by considering these modes. Interestingly, however, F3 at about 1500 cm⁻¹ can only be fitted well when using a B1g vibrational mode, namely the one at ω0 = 1509 cm⁻¹, see Fig. 3(c). The fitted value of γ (77 ± 5 cm⁻¹) compares well to the results for ZnPc/Ag(110) (60 cm⁻¹) [29]. For comparison, an example of a bad fit using an A1g mode (ω0 = 1481 cm⁻¹) is also shown in Fig. 3(b). Since the R active B1g mode of the D4h symmetry group transforms into an IR active A1 mode only in the C2v(σv) group (Tab. I), we conclude that the molecular symmetry must be reduced to twofold. The full symmetry of the PtPc molecule on the Ag(111) surface is schematically shown in the inset of Fig. 3.

However, the mere appearance of the B1g mode in the spectrum does not yet clarify the origin of the symmetry reduction D4h → C2v(σv). In principle, it is possible that because of a geometric distortion of the molecule μdyn is tilted out of the surface plane and acquires a perpendicular contribution. But in this case μdyn would necessarily remain real, and we would observe a conventional, symmetric line shape for F3. This is evidently not the case. Its Fano line shape shows that μdyn of F3 is complex. Hence, there must be a phase-shifted electronic contribution μIDCT to its overall dynamical dipole moment μdyn.

We have already mentioned above that for PtPc/Ag(111) the LUMO is the most likely partner in IDCT, because it becomes filled upon adsorption and straddles the Fermi energy. Moreover, a comparison of the elongation pattern of F3, which predominantly involves the stretching of the C-N bonds in the porphyrazine macrocycle (Fig. 2(c)), with the lobular structure of the LUMO (Fig. 2(b)) shows that the ionic motion of F3 should indeed couple well to the LUMO. Comparing Figs. 2(b) and (c) moreover shows that exciting F3 with positive amplitude has the same effect on the B1-LUMO as exciting F3 with negative amplitude has on the B2-LUMO. Hence, if B1 and B2

\[
L(\omega) = a + c\gamma\omega_0\left[1 - \left(\frac{\tau}{\gamma}\right)(\omega^2 - \omega_0^2)\right]^2\left(\omega^2 - \omega_0^2\right)^2 + (\gamma\omega)^2, \tag{1}
\]

where a and c are constants, and \(\gamma\) denotes the width of the Fano profile. \(\omega_0\) is the vibrational frequency of a given mode and \(\tau\), the asymmetry ratio, is (negative) positive if \(\mu_2\) is (anti-) parallel to \(\mu_1\).

Figure 3. (a) Zoom of the ordered monolayer phase spectrum of PtPc on Ag(111) showing the asymmetric peaks F1, F2 and F3 together with the theoretical vibrational modes (vertical bars). Each peak has been fitted using all the theoretical vibrations visible in panel (a), and all the ω0 values which give reasonable fits of F1, F2 and F3 are shown with dotted lines. An example of bad fit of F3 is shown in panel (a) using ω0 = 1481 cm⁻¹, and the best fit of F3 is shown in panel (c) using ω0 = 1509 cm⁻¹. The symmetry (C2v(σv)) of the PtPc molecule in contact with Ag(111) is depicted in the inset of (c).
were still degenerate, dynamic filling and depletion of the two would be 180° out of phase (assuming that the phase lag relative to the ionic movement is the same for both LUMOs, which is expected to be a good approximation, in spite of the observed symmetry breaking, see below). In other words, in one half of the vibrational oscillation cycle the B₁-LUMO would be filled, while the B₂-LUMO would be depleted, and vice versa in the other half. Overall, no μDCT would prevail (small differences between the IDCT in the B₁- and B₂-LUMOs notwithstanding).

However, in the experimental spectrum a substantial μDCT is observed, as argued above. This can mean two things. Either the two LUMOs are still degenerate and their dynamic couplings to the F3 vibration are different, or the LUMO levels B₁ and B₂ are indeed split. We consider it unlikely that the static level positions of the LUMOs are not affected by symmetry breaking, while their dynamic couplings to F3 are. Therefore, we conclude that the B₁- and B₂-LUMO levels must be split, i.e. the degeneracy of the PtPc LUMO is lost upon adsorption on Ag(111). One may speculate that this LUMO splitting proceeds via a geometric distortion that is induced by the environment (the Ag(111) surface), enhanced by a Jahn-Teller-like internal stabilization of this external geometric distortion via the splitting of the electronic LUMO state.

### IV. Palladium-Phthalocyanine on Ag(111)

PdPc molecules adsorbed on Ag(111) show similar long range order as PtPc/Ag(111). A two-dimensional gas phase is found after annealing the thick layer up to 730K and an ordered phase is detected in LEED for lower annealing temperatures, that is at higher coverages.

In Fig. 4 the specular HREELS spectrum of the PdPc ordered monolayer phase is shown together with the simulated results for the isolated molecule. The assignment of the experimental vibrational frequencies can be found in the supplement. As in the case of PtPc, the in-plane Eₘ modes are absent and only the dipole scattering allowed out-of-plane A₂ₙ modes of the isolated molecule are present. This indicates an essentially flat adsorption geometry. The c, g and h modes are shifted to lower frequencies by approximately 45, 15 and 15 cm⁻¹ with respect to theory, respectively. The larger shift of the c mode for PdPc (45 cm⁻¹) than for PtPc (30 cm⁻¹) suggests a stronger interaction of PdPc with the Ag(111) substrate.

The presence of R modes in Fig. 4 suggests that a reduction of the molecular symmetry upon adsorption.

| Mode Symmetry | R1   | R2   | R3   | R4   |
|---------------|------|------|------|------|
|               | A₁₈/Eₖ | A₁₈/Eₘ(x,y)/B₁₈ | A₁₈/B₂₈ | A₁₈/Eₘ(x,y)/B₂₈/E₆ |
| F1            | A₁₈/Eₘ(x,y)/B₁₈ |
| F2            | A₁₈/Eₘ(x,y)/B₁₈/B₂₈ |
| F3            | B₁₈ |

Table IV. Possible assignments of the R and F modes observed in the ordered monolayer phase of PdPc on Ag(111). The F modes assignments are based on the fit results.

to modes with a A₁₈ representation (since R₄ is very broad, it is rather difficult to assign it and a designation as a A₁₈ mode cannot be excluded); they would then be detectable in HREELS in specular geometry irrespective of the symmetry group of the molecule-substrate complex (Cᵥ or C₄ᵥ), cf. Tab. II.

Three asymmetric peaks (F1, F2 and F3) are observed between 1000 and 1600 cm⁻¹, which indicates that several vibrational modes are involved in an IDCT. Using Eq. 1, we single out vibrational frequencies given by DFT calculations for isolated PdPc (ω₀) that yield the best fit of the experimental data as explain in Sec. III C 3.

As in the case of PtPc, several modes yield a reasonable fit for F1 and F2, while F3 can be fitted only with ω₀ = 1506 cm⁻¹, a mode which belongs to the B₁₈ representation of the D₄h symmetry group (see Fig. 5), and a B₁₈ mode can only be detected in HREELS in the specular direction if the molecular symmetry is reduced to Cᵥ (σᵥ) (see Tab. I). As in the case of PtPc, this demonstrates that a preferential charge transfer occurs into one of the two LUMOs. Thus, the Ag(111) substrate lifts the degeneracy of the LUMO also in the case of PdPc.

### V. Summary and Conclusion

In conclusion, the vibrational properties of Pt- and Pd-phthalocyanine molecules on the Ag(111) surface show that both molecules adsorb with their molecular plane parallel to the surface in the ordered monolayer phase. The red shift of some of the out-of-plane modes reflects a moderate interaction between the meso-tetraazaporphin (porphyrizin) macrocycle of the molecule and the Ag substrate. The presence of Raman vibrational modes proves the lowering of the molecular symmetry from the D₄h group of the isolated molecule upon adsorption on Ag(111). The asymmetrical line shape of some of the molecular vibrational modes further demonstrates that the charge transfer to the molecule is involved in the symmetry reduction to Cᵥ (σᵥ). Therefore, this study shows that HREELS is a valuable tool to determine the origin of the molecular degeneracy lifting upon adsorption on a metal surface.
Figure 4. Specular HREELS spectra of the PdPc ordered monolayer phase on Ag(111). The simulated vibrational modes of the isolated molecule are shown as colored vertical bars.

Figure 5. Best fit of F3 using $\omega_0 = 1506$ cm$^{-1}$, for the ordered monolayer PdPc phase on Ag(111).

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1 R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, and W. R. Salanek, “Electroluminescence in conjugated polymers,” Nature 397, 121 (1999).

2 P. W. M. Blom, V. D. Mihailetchi, L. J. A. Koster, and D. E. Markov, “Device Physics of Polymer : Fullerene Bulk Heterojunction Solar Cells,” Adv. Mater. 19, 1551 (2007).

3 S. Sanvito, “Molecular spintronics,” Chem. Soc. Rev. 40, 3336 (2011).

4 J. M. Gottfried, “Surface chemistry of porphyrins and phthalocyanines,” Surf. Sci. Rep. 70, 250 (2015).

5 J. Blochwitz, M. Pfeiffer, T. Fritz, and K. Leo, “Low voltage organic light emitting diodes featuring doped phthalocyanine as hole transport material,” Appl. Phys. Lett. 73, 729 (1998).

6 B. Crone, A. Dodabalapur, Y. Y. Lin, R. W. Filas, Z. Bao, A. La Duca, R. Sarapeshkar, H. E. Katz, and W. Li, “Large-
scale complementary integrated circuits based on organic transistors,” Nature 403, 521 (2000)

7 G. Horowitz, “Organic Field-Effect Transistors,” Adv. Mater. 10, 365 (1998)

8 J. C. Conboy, E. J. C. Olson, D. M. Adams, J. Kerimo, A. Zaban, B. A. Gregg, and P. F. Barbara, “Impact of Solvent Vapor Annealing on the Morphology and Photophysics of Molecular Semiconductor Thin Films,” J. Phys. Chem. B 102, 4516 (1998)

9 Y. Wang, J. Kröger, R. Berndt, and W. Hofer, “Structural and Electronic Properties of Ultrathin Tin-Phthalocyanine Films on Ag(111) at the Single-Molecule Level,” Angew. Chem. Int. Ed. 48, 1261 (2009)

10 S.-H. Chang, S. Kück, J. Brede, L. Lichtenstein, G. Hoffmann, and R. Wiesendanger, “Symmetry reduction of metal phthalocyanines on metals,” Phys. Rev. B 78, 233409 (2008)

11 H. Karacuban, M. Lange, J. Schaffert, O. Weingart, T. Wagner, and R. Möller, “Substrate-induced symmetry reduction of CuPc on Cu(111): An LT-STM study,” Surf. Sci. 603, L39 (2009)

12 Y. Wang, X. Ge, C. Manzano, J. Kröger, R. Berndt, W. A. Hofer, H. Tang, and J. Cerda, “Supramolecular Patterns Controlled by Electron Interference and Direct Intermolecular Interactions,” J. Am. Chem. Soc. 131, 10400 (2009)

13 R. Cuadrado, J. I. Cerda, Y. Wang, G. Xin, R. Berndt, and H. Tang, “CoPc adsorption on Cu(111): Origin of the C4 to C2 symmetry reduction,” J. Chem. Phys. 133, 154701 (2010)

14 O. Snezhkova, J. Lieder, A. Wiengarten, S. R. Burema, F. Bischof, Y. He, J. Rusz, J. Knudsen, M.-L. Bocquet, K. Seufert, J. V. Barth, W. Auwärter, B. Brena, and J. Schnadt, “Nature of the bias-dependent symmetry reduction of iron phthalocyanine on Cu(111),” Phys. Rev. B 92, 075428 (2015)

15 N. F. Phelan and J. Orchin, “Cross conjugation,” J. Chem. Educ. 45, 633 (1968)

16 C. Uhligmann, I. Swart, and J. Repp, “Controlling the Orbital Sequence in Individual Cu-Phthalocyanine Molecules,” Nano Lett. 13, 777 (2013)

17 V. Feyer, M. Graus, P. Nigge, M. Wießner, R. G. Acres, C. Wiemann, C. M. Schneider, A. Schöll, and F. Reinert, “Adsorption geometry and electronic structure of iron phthalocyanine on Ag surfaces: A LEED and photoelectron momentum mapping study,” Surf. Sci. 621, 64 (2014)

18 T. Niu, M. Zhou, J. Zhang, Y. Feng, and W. Chen, “Dipole Orientation Dependent Symmetry Reduction of Chloroaluminum Phthalocyanine on Cu(111),” J. Phys. Chem. C 117, 1013 (2013)

19 H. A. Jahn and E. Teller, “Stability of Polyatomic Molecules in Degenerate Electronic States. I. Orbital Degeneracy,” Proc. Roy. Soc. A 161, 220 (1937)

20 H. Köpper, D. R. Yarkony, , and H. Berentzen, The Jahn-Teller Effect (Springer-Verlag Berlin Heidelberg, 2009).

21 P. Borghetti, A. El-Sayed, E. Goiri, C. Rogero, J. Lobo-H. Köpper, D. R. Yarkony, , and H. Berentzen, “Impact of Solvent Vapor Annealing on the Morphology and Photophysics of Molecular Semiconductor Thin Films,” J. Phys. Chem. B 102, 4516 (1998)

22 P. Buschig, S. Berkebile, A. J. Fleming, G. Koller, K. Entset, T. Seyller, J. D. Riley, C. Ambrosch-Draxl, F. P. Netzer, and M. G. Ramsey, “Reconstruction of Molecular Orbital Densities from Photoemission Data,” Science 326, 702 (2009)

23 P. Buschig, E.-M. Reinisch, T. Ules, G. Koller, S. Soubatch, M. Ostler, L. Romaner, F. S. Tautz, C. Ambrosch-Draxl, and M. G. Ramsey, “Orbital tomography: Deconvoluting photoemission spectra of organic molecules,” Phys. Rev. B 84, 235427 (2011)

24 K. Schönauer, S. Weiss, V. Feyer, B. Lüftner, D. Stadtmüller, C. Kumpf, P. Buschig, M. G. Ramsey, F. S. Tautz, and S. Soubatch, “Charge transfer and symmetry reduction at the CuPc/Ag(110) interface,” Submitted to Phys. Rev. B (2016).

25 H. Ibach and D. L. Mills, Electron Energy Loss Spectroscopy and Surface Vibrations (Academic Press, New York, 1982).

26 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. J. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowsi, and D. J. Fox, “Gaussian09 Revision D.01,” Gaussian Inc. Wallingford CT 2009.

27 Z. Liu, X. Zhang, Y. Zhang, and J. Jiang, “Theoretical investigation of the molecular, electronic structures and vibrational spectra of a series of first transition metal phthalocyanines,” Spectrochim. Acta. 67A, 1232 (2007)

28 V. G. Maslov, “Interpretation of the electronic spectra of phthalocyanines with transition metals from quantum-chemical calculations by the density functional method,” Opt. Spectrosc. 101, 853 (2006)

29 “See supplemental material”.

30 I. Kröger, B. Stadtmüller, C. Stadler, J. Ziroff, M. Kochler, A. Stahl, F. Pollinger, T.-L. Lee, J. Zegenhagen, F. Reinert, and C. Kumpf, “Submonolayer growth of copper-phthalocyanine on Ag(111),” New J. Phys. 12, 083038 (2010)

31 B. Stadtmüller, I. Kröger, F. Reinert, and C. Kumpf, “Submonolayer growth of CuPc on noble metal surfaces,” Phys. Rev. B 83, 085416 (2011)

32 C. Stadler, S. Hansen, I. Kröger, C. Kumpf, and E. Umbach, “Tuning intermolecular interaction in long-range-ordered submonolayer organic films,” Nat. Phys. 5, 153 (2009)

33 N. Ohta, R. Arafune, N. Tsukahara, N. Takagi, and M. Kawai, “Adsorbed states of iron(II) phthalocyanine on Ag(111) studied by high-resolution electron energy loss spectroscopy,” Surf. Interface Anal. 46, 1253 (2014)

34 J. D. Baran and J. A. Larsson, “Theoretical Insights into Adsorption of Cobalt Phthalocyanine on Ag(111): A Combination of Chemical and van der Waals Bonding,” J. Phys. Chem. C 117, 23887 (2013)

35 Y. J. Chabal, “Electronic Damping of Hydrogen Vibration on the W(100) Surface,” Phys. Rev. Lett. 55, 845 (1985)
36 J. Kröger, S. Lehwald, and H. Ibach, “EELS study of the clean and hydrogen-covered Mo(110) surface,” Phys. Rev. B 55, 10895 (1997).

37 F. S. Tautz, M. Eremtchenko, J. Schaefer, M. Sokolowski, V. Shklover, and E. Umbach, “Strong electron-phonon coupling at a metal/organic interface: PTCDA/Ag(111),” Phys. Rev. B 65, 125405 (2002).

38 P. Amsalem, L. Giovanelli, J.-M. Themlin, and T. Angot, “Electronic and vibrational properties at the ZnPc/Ag(110) interface,” Phys. Rev. B 79, 235426 (2009).

39 W. Dou, Y. Tang, C. S. Lee, S. N. Bao, and S. T. Lee, “Investigation on the orderly growth of thick zinc phthalocyanine films on Ag(100) surface,” J. Chem. Phys. 133, 144704 (2010).

40 I. Kröger, Adsorption of phthalocyanines on noble metal surfaces, Ph.D. thesis (2010).

41 C. R. Braatz, G. Ohl, and P. Jakob, “Vibrational properties of the compressed and the relaxed 1,4,5,8-naphthalene-tetracarboxylic dianhydride monolayer on Ag(111),” J. Chem. Phys. 136, 134706 (2012).

42 P. Rosenow, P. Jakob, and R. Tonner, “Electron-Vibron Coupling at Metal-Organic Interfaces from Theory and Experiment,” J. Phys. Chem. Lett. 7, 1422 (2016).

43 D. Langreth, “Energy Transfer at Surfaces: Asymmetric Line Shapes and the Electron-Hole-Pair Mechanism,” Phys. Rev. Lett. 54, 126 (1985).

44 Z. Criljen and D.C. Langreth, “Asymmetric line shapes and the electron-hole pair mechanism for adsorbed molecules on surfaces,” Phys. Rev. B 35, 4224 (1987).

45 J. Kröger, “Electron-phonon coupling at metal surfaces,” Rep. Prog. Phys. 69, 899 (2006).