Probing Intermolecular Vibrational Symmetry Breaking in Self-Assembled Monolayers with Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy

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Supporting Information

ABSTRACT: Ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS) combines the atomic-scale imaging capability of scanning probe microscopy with the single-molecule chemical sensitivity and structural specificity of surface-enhanced Raman spectroscopy. Here, we use these techniques in combination with density functional theory to reveal insights into the influence of intermolecular interactions on the vibrational spectra of a N'-N'-bis(2,6-diisopropylphenyl)-perylen-3,4,9,10-tetra-carboxylic dianhydride (PDI) self-assembled monolayer adsorbed on single-crystal Ag substrates at room temperature. In particular, we have revealed the lifting of a vibrational degeneracy of a mode of PDI on Ag(111) and Ag(100) surfaces, with the most strongly perturbed mode being that associated with the largest vibrational amplitude at the periphery of the molecule. This work demonstrates that UHV-TERS enables direct measurement of molecule–molecule interaction at nanoscale. We anticipate that this information will advance the fundamental understanding of the most important effect of intermolecular interactions on the vibrational modes of surface-bound molecules.

INTRODUCTION

Self-assembled monolayers (SAMs) provide a unique way of tailoring interfacial properties of metals, oxides, and semiconductor surfaces. The detailed behavior of molecular self-assembly is governed by molecule–molecule and molecule–substrate interactions. Strong molecule–substrate interactions, i.e., chemisorption or strong charge-transfer interaction with the substrate, may result in different packing structures on different substrates. However, strong molecule–molecule interactions can form similar assemblies on different surfaces since the structure is mainly stabilized by intermolecular forces.

Molecular vibrations are extremely sensitive to the local molecular environment. A strong interaction with the surrounding environment can lead to vibrational symmetry breaking. Depending on the nature of the interaction, vibrational symmetry breaking in molecular systems may result in different spectroscopic selection rules, modifications to band intensity, and enhanced transfer of vibrational coherence in photodissociation.

Tip-enhanced Raman spectroscopy (TERS) is a powerful technique for characterizing surface-bound molecular systems. It combines the chemical selectivity and sensitivity of surface-enhanced Raman spectroscopy (SERS) with the atomic resolution of scanning probe microscopy to achieve the ultimate spatial resolution: Ångstrom-scale resolution. By overcoming the optical diffraction limits, deeper insight into phenomena otherwise unattainable due to limited spatial resolution are revealed, including the subensemble behavior of adsorbates on plasmonic surfaces, local electric field distribution, and single-molecule surface-induced chemistry. Ultrahigh vacuum TERS (UHV-TERS) interrogates fundamental surface interactions and dynamics in the ultimate controlled environment. Recently, TERS under electrochemical environments has also been demonstrated.

Herein, we report additional insights into the nature of intermolecular interactions in a perylene diimide monolayer adsorbed on single crystal Ag substrates at room temperature. More specifically, we have interrogated the lifting of the vibrational degeneracy of N'-N'-bis(2,6-diisopropylphenyl)-perylen-3,4,9,10-tetra-carboxylic dianhydride (PDI) on Ag(111) and Ag(100) surfaces. In combination with time-dependent density functional theory (TDDFT) simulations, we assess the nature of intermolecular interactions on the vibrational modes of surface-bound molecules.

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of the vibrational normal modes that are directly responsible for the doublets observed in the TER spectra reported herein.

### EXPERIMENTAL SECTION

#### In Vacuo Sample Preparation.

The Ag(111) and Ag(100) single crystals (Princeton Scientific Corp.) were cleaned by repeated cycles of Ar⁺ ion sputtering (−2 × 10⁻⁷ Torr) and annealing at 750 K. PDI molecules were thermally sublimed in UHV at ~510 K onto the clean Ag(111) and Ag(100) samples. Electrochemically etched Ag tips were cleaned by Ar⁺ ion sputtering before all experiments.

**UHV-STM and TERS.** STM imaging and TERS were performed with a home-built optical UHV-STM equipped with a thermoelectrically cooled CCD (Princeton Instruments PIXIS 400BR). A laser power stabilizer (Brockton Electro-Optics Corp. LPC) maintains the excitation power at 1.00 mW to avoid sample degradation due to the strong plasmonic field (Figure S1 of the Supporting Information, SI). All TER spectra were acquired for 30 s with 6 accumulations and at $V_b = 0.1$ V since it gave the strongest intensity (Figure S2).

**TDDFT Simulation.** The Raman scattering cross sections of gas-phase PDI were calculated with the Amsterdam Density Functional (ADF) software package at the density functional level of theory. The triple-$ζ$ with polarization (TZP) basis set and the Becke-Perdew exchange-correlation were chosen. Harmonic vibrational frequencies calculated at this level of theory closely match experimental results without incorporating a scaling factor. The C₂ point group was enforced during geometry optimization and the numerical calculation of the vibrational modes. The σ and inversion operations, although valid for gas phase PDI, would not be valid for the case when PDI is bound to the metal surface and that symmetry is broken.

The AOResponse module implemented in ADF and developed by Jensen et al. was used to calculate the real and imaginary components of the polarizability tensors. In AOResponse module, the short time approximation proposed by Lee and co-workers is made to the Kramers, Heisenberg, and Dirac formulation of Resonance Raman scattering. The wavelength of the perturbation was 785 nm, the damping parameter was set to 0.004 au (approximately 0.1 eV), the zero-order regular approximation (ZORA) was applied to the calculation, and the convergence for the AOResponse module was set to $10^{-7}$ a.u. These parameters are consistent with previous work.

### RESULTS AND DISCUSSION

The molecular structure of PDI (Figure 1a) consists of a center perylene-3,4,9,10-tetracarboxylic-3,4,9,10-diimide (PTCDI) with two bis-2,6-diisopropylphenyl functional groups on the two ends. The center PTCDI governs the main electronic absorption in the UV–vis spectrum (Figure 1b). This particular functionalization of PTCDI is chosen because the diisopropylphenyl groups are expected to lift the molecule away from the surface and consequently align better with the plasmonic dipole of the tip–sample junction. For a mostly planar molecule like this, the in-plane Raman modes have higher than expected intensities, probably because the molecules are thermally activated to tilt away from being parallel to the surface. Additionally, the diisopropylphenyl groups also fine-tune the absorption spectrum so that the main absorption peak is at ~532 nm which enables strong resonance enhancement in Raman scattering when excited with a 532 nm laser. Although PDI is known for its ability to generate excited triplet states through singlet fission, we do not expect to observe Raman spectra from the excited-states because no sensitizers were used, and the PDI molecules were in direct contact with metal surfaces.

The formation of a large stable PDI molecular island (Figure 1c) at room temperature is a direct result of strong lateral molecule–molecule interactions. On open terraces (top right corner in the STM image), individual PDI molecules cannot be resolved due to surface diffusion. This rapid diffusion further reveals that the interaction between PDI and the Ag substrate is weak, as expected from the addition of diisopropylphenyl groups.

The detailed molecular packing structure can be slightly altered by changing the underlying symmetry of the Ag single-crystal facet. Figure 2a,c shows submolecular resolution STM images of PDI islands formed on Ag(111) and Ag(100), respectively. The PDI packing structures on different Ag facets
packing structures suggests that the direct π−π structural interactions between the end diisopropylphenyl groups of neighboring molecules, and between the methyl groups in the diisopropylphenyl group of one PDI molecule and a side of the perylene ring of the other are the driving forces for the self-assembling on Ag substrates.

TDDFT simulated Raman spectrum of a gas phase PDI molecule is shown in Figure 3. The simulated spectrum reveals several weak modes below 1100 cm⁻¹, and most intense modes are located between 1200 cm⁻¹ to 1600 cm⁻¹. The relative intensities in the simulated spectrum are in good agreement with the experimentally observed TER spectra in Figure 2 and on other metal substrates (Figure S3). Since the simulation did not account for any substrate-effects, the simulation supports the experimental observation that the molecule−surface interaction is indeed weak.

In order to gain detailed fundamental insights into the intermolecular interaction, Raman-active vibrational normal modes are assigned based on the naming conventions shown in Figure 4. The π systems were divided into four types of rings based on the molecular symmetry (Figure 4a). The vibrational modes of those rings can be characterized by 6 distinct motions (Figure 4b): ring breathing, Kekulé, quinoidal, ring distortion with bond stretching, bonds bending asymmetrically, and bonds bending symmetrically.

Figure 5a shows a zoomed-in UHV-TER spectrum of PDI on Ag(111) above the simulated spectrum in the 1200 cm⁻¹ to 1600 cm⁻¹ spectral region. Three pairs of doublets were observed experimentally but only 5 peaks (assigned in Figure 5b) were present in the simulation. The doublet at ∼1550 cm⁻¹ is assigned as a combination of symmetric ring A bending, ring B Kekulé, and symmetric ring C bending, and the vibrational mode at ∼1370 cm⁻¹ (exp: 1371 cm⁻¹, calcd: 1342 cm⁻¹) is assigned as a
A combination of a ring A breathing, ring B quasi Kekulé, and ring C distortion bending. The \(~30\) cm\(^{-1}\) shifts of the 1371 cm\(^{-1}\) peak in the TDDFT simulation with respect to experiment could possibly be due to strong lateral intermolecular interactions which were not considered in the simulation of the gas-phase PDI.

Only one Raman peak was predicted near \(~1300\) cm\(^{-1}\) in the simulation although this consists of two degenerate vibrational modes, both involving ring A breathing, ring B distortion stretching, ring C no motion, and ring D Kekulé mode (exp: 1293 and 1301 cm\(^{-1}\), calc: 1286 cm\(^{-1}\)). The top and bottom phenyl rings are perpendicular to the plane of the PDI in the optimized geometry, leading to weak interactions with the in-plane modes. Ring D was mixed in opposite way for the two modes (1286\(^a\) and 1286\(^b\) cm\(^{-1}\)). The degeneracy is therefore an accidental degeneracy\(^{12}\) due to weak coupling of different vibrations, rather than a degeneracy that arises from intrinsic symmetry effects. Consequently, when ring D of one PDI molecule interacts strongly with ring B of another molecule, the degeneracy of the 1286 cm\(^{-1}\) modes was lifted due to an intermolecular coupling between the two. This prediction is consistent with the UHV-STM and TERS observations in Figure 2. The methyl–π (green-lines) and methyl–methyl (red-lines) interactions identified were mainly between the methyl groups in one diisopropylphenyl end group (ring D in Figure 4a) of a PDI molecule and a side of the perylene ring (ring B in Figure 4a) of another molecule. The vibrational mode amplitudes in Figure 5b show that the modes at 1342 cm\(^{-1}\) and the top mode at 1286 cm\(^{-1}\) have the largest amplitude at the periphery of the ring system that overlaps with the green/red lines in Figure 2b,d. It is therefore understandable that these are the modes that will be most strongly perturbed by intermolecular interactions. The methyl–methyl interactions can be on the order of few kcal/mol\(^{53,54}\) which are strong enough to perturb the molecular vibrations. The methyl–π interaction is difficult to quantify. Other Raman-mode assignments can be found in Table 1 with the degenerate modes highlighted in red.

### CONCLUSIONS

In summary, we have used a combination of UHV-TERS and TDDFT simulations to reveal vibrational symmetry breaking of a self-assembled PDI island, which was induced by the intermolecular interactions, on single-crystal Ag substrates. Through careful examinations of the packing structures on different Ag facets and with consideration of the nature of the Raman active vibrational normal modes, we conclude that lifting of the vibrational degeneracy of the 1286 cm\(^{-1}\) modes originates from strong lateral intermolecular interactions between the diisopropylphenyl end groups and the center perylene rings. This provides direct insight into the strength of...
Table 1. Raman Peak Assignments for PDI

<table>
<thead>
<tr>
<th>experiment (cm⁻¹)</th>
<th>TDDFT simulation (cm⁻¹)</th>
<th>vibration description</th>
</tr>
</thead>
<tbody>
<tr>
<td>540</td>
<td>533</td>
<td>PDI ring breathing mode. A, B, C breathing symmetrically</td>
</tr>
<tr>
<td>1059</td>
<td>1046</td>
<td>A: “Quinoidal” like mode, B: ring distortion bending, C: bending asymmetrically</td>
</tr>
<tr>
<td>1293, 1301</td>
<td>1286, 1286</td>
<td>A: breathing, B: ring distortion stretching, C: no motion, D: Kekulé mode. D mixed in opposite way for the two modes</td>
</tr>
<tr>
<td>1371</td>
<td>1343</td>
<td>A: breathing, B: quasi Kekulé, C: ring distortion bending</td>
</tr>
<tr>
<td>1383</td>
<td>1384</td>
<td>A: Bending symmetric, B: Kekulé, C: symmetric bending</td>
</tr>
<tr>
<td>1452</td>
<td>1439</td>
<td>A: symmetric bending, B: antisymmetric bending, C: ring distortion bending</td>
</tr>
<tr>
<td>1572</td>
<td>1555</td>
<td>A: Quinoidal like mode, C: ring distortion bending mode from carbon #3 in the C ring. Rings B have very similar ring distortions as seen in 1566 cm⁻¹</td>
</tr>
<tr>
<td>1587</td>
<td>1566</td>
<td>A: Ring breathing mode C: ring distortion bending mode from carbon #3 in the C ring. Rings B have very similar ring distortions as seen in 1555 cm⁻¹</td>
</tr>
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</table>

“The degenerated modes are in italic.

intermolecular interactions for SAM formation at submolecular scales. We anticipate that this information will advance the fundamental understanding of the critical effect of intermolecular interactions on the vibrational modes of surface-bound molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b10645.

Laser excitation power-dependence and STM bias-dependence of UHV-TERS of PDI on Ag(111)/Ag(100), UHV-TERS of PDI on Cu(111) and Au(111), Lorentzian fitted TER spectra for Figures 2 and 5 (PDF)

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Notes

The authors declare no competing financial interest.

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