LETTER

Site-Dependent TERS Study of a Porphyrin Molecule on Ag(100) at 7 K

Atif Ghafoor[a], Ben Yang[a], Yun-jie Yu[a], Yu-fan Zhang[a], Xian-biao Zhang[a], Gong Chen[a,b], Yao Zhang[a*], Yang Zhang[a], Zhen-chao Dong[a*]

a. *Hefei National Laboratory for Physical Sciences at the Microscale and Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei 230026, China*
b. *School of Physics and Engineering, Zhengzhou University, Zhengzhou 450052, China*

Single-molecule tip-enhanced Raman spectroscopy (TERS) has emerged as an important technique for structural analysis at sub-molecular scale. Here in this work, we report a TERS study of an isolated free-base porphyrin molecule adsorbed on the Ag(100) surface at cryogenic temperature ($\sim$7 K). Site-dependent TERS spectra reveal distinct local vibrational information for the chemical constituents within a single molecule. Moreover, distinct spatial features among different Raman peaks can be resolved from the TERS mapping images. These images are found to associate with related vibrational modes, enabling to resolve the mode associated with N$-$H bonds at the sub-nanometer level. This study will provide deep insights into the symmetry of adsorption configurations and local vibrational information within a single molecule.

Key words: Tip-enhanced Raman spectroscopy, Spatial mapping, Adsorption configuration, Porphyrin

Tip-enhanced Raman spectroscopy (TERS) is a versatile technique that integrates the chemical sensitivity of surface enhanced Raman spectroscopy (SERS) with the ultrahigh spatial resolution of scanning probe microscopy (SPM) [1] and enables chemical imaging down to sub-nanometer scale [2]. In general, a sharp metallic tip is used to generate local plasmonic field at the tip apex and enhance the Raman signals from the molecules underneath. This local field can be further confined and enhanced by introducing a metallic substrate to form the gap-mode plasmons. In our previous work, such gap-mode plasmons are implemented by the tunneling junction in a scanning tunneling microscope (STM) and has allowed us to demonstrate TERS mapping of a single porphyrin molecule with sub-nanometer resolution [3]. Different adjacent porphyrin molecules can also be distinguished by this STM based TERS technique [4, 5]. In these earlier studies, experiments were carried out at liquid-nitrogen temperature ($\sim$80 K), and similar spectral features, though different in intensities, were observed at different locations within a single porphyrin molecule. Therefore, an important question for TERS still remains: is it possible to push this technique further to sense the local vibrational information at different parts within a single molecule? Here in this work, by performing experiments at a much lower

liquid-helium temperature ($\sim$7 K), we will demonstrate such capability of TERS to extract local vibrational information within a single porphyrin molecule adsorbed on the Ag(100) surface. Lower temperature is beneficial in two ways: (i) reducing the thermal drift and thus improving the stability of the STM junction, and (ii) suppressing both the molecular diffusion on the surface and the motions of constituent atoms and groups within a molecule and thus improving the stability of the molecule and local molecular orientations under study. TERS spectra measured over a molecule are found to be site-dependent, reflecting the sensitivity of TERS to reveal local structural differences within a single molecule. Such distinction is further demonstrated by the panoramic TERS imaging, which directly provides the spatial distribution of Raman responses for various vibrational modes.

FIG. 1 shows the schematic of STM-controlled TERS setup. All the TERS experiments were implemented on a custom low-temperature and ultrahigh-vacuum STM (Unisoku-1400S) in a confocal-type side-illumination configuration [6] at about 7 K under a base pressure of $\sim$6$\times$10^{-11} torr. Meso-tetrakis (3,5-ditertiarybutylphenyl)-porphyrin (H$_2$TBPP) molecules were thermally sublimed onto the Ag(100) surface which was previously cleaned by cycles of argon ion sputtering and annealing. Silver metal was selected as the material for both the tip and substrate because the nanocavity thus formed can offer very strong plasmonic enhancement due to its low optical losses at visible frequencies as compared with other metals [7]. Tips were
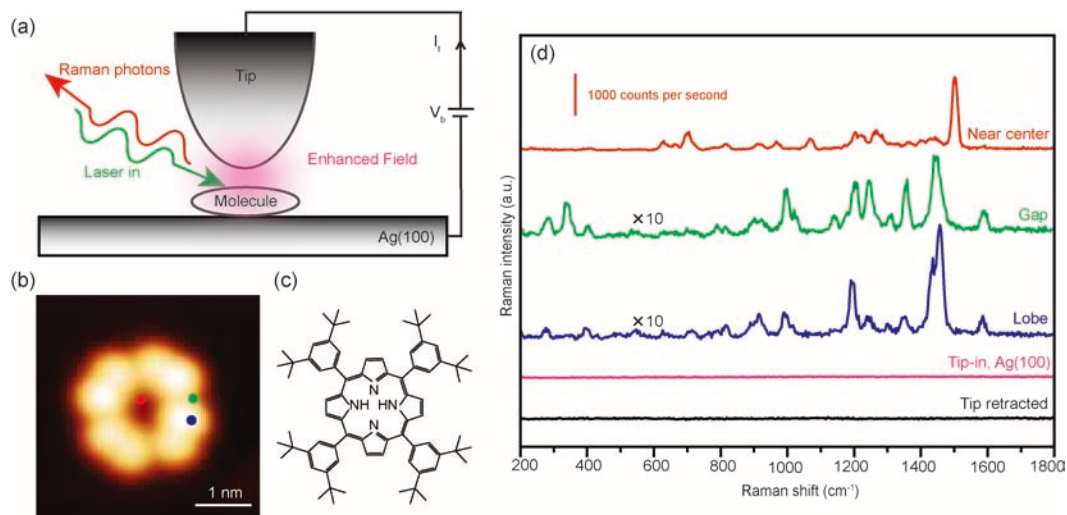
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FIG. 1 (a) Schematic of STM controlled TERS setup. (b) STM topograph of a single H$_2$TBPP molecule adsorbed on Ag(100) (−0.05 V, 2 pA, 4 nm×4 nm). (c) Molecular structure of H$_2$TBPP. (d) TERS spectra (−0.05 V, 4 nA, 5 s) were acquired at the corresponding positions marked in (b), namely, blue for the lobe position, green for the gap position, and red for the near-center position. The magenta spectrum was taken on the bare Ag(100) and the black spectrum was measured when the tip was retracted.

fabricated via electrochemical etching process and further cleaned in ultrahigh vacuum via outgassing and argon ion sputtering. The as-prepared tips were additionally modified by tip indentation and high-voltage pulses [8] to achieve desired TERS-active status. The optical detection systems used in our experiments were described elsewhere [3, 5]. A 532 nm continuous-wave laser with the power of ∼0.4 mW was utilized as an excitation source with the polarization parallel to the tip axis. STM imaging and TERS measurements were made in a constant-current mode with the sample biased and under laser illumination. The structure optimization and Raman frequency calculations were performed with density functional theory (DFT) by using the Gaussian 09 software under the B3LYP/6-31G(d) basis [3].

FIG. 1(b) illustrates the STM topograph of a single H$_2$TBPP molecule adsorbed on Ag(100) with the molecular structure shown in FIG. 1(c). FIG. 1(d) shows TERS spectra measured at three representative sites within the molecule, as indicated in FIG. 1(b) for the tip located above the molecular lobe (blue), gap (green) and near-center (red) positions, respectively. All three spectra are different from each other. Such a spectral distinction suggests the possibility of distinguishing local intramolecular vibrations within a single molecule. A featureless flat continuum spectrum (magenta spectra in FIG. 1(d)) was obtained when the tip was positioned on the bare Ag(100) surface, ensuring that the tip was clean and free from contamination.

Considering that the STM image of a H$_2$TBPP molecule exhibits an approximate eight-lobe (or four-big-lobe) pattern (FIG. 1(b)), TERS spectra on these lobes and four gap-positions as well as near-center po-

sitions were acquired to check if they follow the topographic symmetry, as shown in FIG. 2(a−c). Evidently, four-fold symmetry is definitely not there in these TERS spectra. For molecular lobes, TERS spectra acquired at positions (1, 1*), (2, 2*), (3, 3*) and (4, 4*) are quite similar in each pair in terms of peak positions and intensities. These pairs are almost replica of each other with respect to the mirror plane (or two-fold axis) shown by the grey dotted line in the inset of FIG. 2(a). However, while spectra at positions 1, 2, and 3 are more or less similar to each other, TERS spectra at position 4 (or 4*) are quite different, with a distinctly strong peak at ∼1460 cm^{-1}, which suggests at least a different local orientation for the molecular lobe and thus the absence of even rough four-fold symmetry for the whole molecule. Such symmetry reduction is also clearly revealed by the TERS spectra given in FIG. 2 (b) and (c) for gap and near-center positions. TERS spectra taken at gap positions 1 and 2 are different, although those at (1, 1*) or (2, 2*) are similar in each pair (nevertheless, TERS spectra measured at positions (2, 2*) still exhibit some variations in the relative intensities of some Raman peaks). Dramatic spectral differences were found for the TERS spectra measured at the central or near-center positions, as shown in FIG. 2(c). While the TERS profiles at the exact center position (1), and two other nearby horizontal positions (2, 2*) are relatively similar with weak intensities, the TERS spectra acquired at positions (3, 3*), where the tip is displaced a little (∼0.14 nm) away from the center along the vertical direction, are very different in terms of additional modes and higher peak intensities. A very intense mode around 1500 cm^{-1} emerges at this position, which is barely observable in the spectra at any other positions.
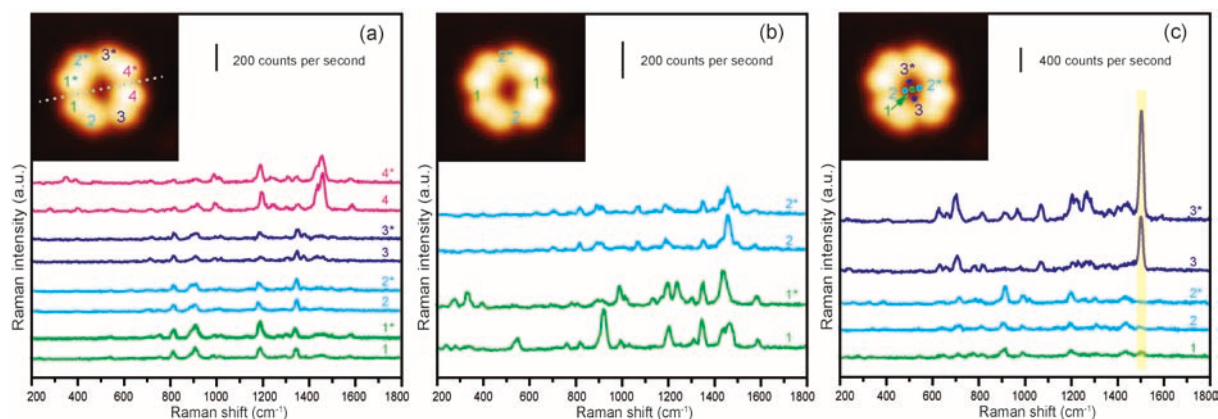

FIG. 2 (a) TERS spectra on different lobes. (b) TERS spectra on different gap positions. (c) TERS spectra at the center and near-center positions. All TERS spectra were acquired with the same conditions (−0.05 V, 4 nA, 5 s). Insets are STM topographs showing positions for TERS measurements.

This suggests a highly confined local vibration within the porphyrin molecule, probably associated with the rocking motion of the N−H bonds around the molecular center [9]. The observation of such a high sensitivity of TERS to local vibrations is quite encouraging and remarkable.

The spectral differences demonstrated above by site-dependent TERS spectra reflect the complex nature of the adsorption configurations when a H_2TBPP molecule is adsorbed on the Ag(100) surface, probably due to the large number of atoms (174) involved in this molecule and its complicated interaction with the Ag(100) substrate. The differences revealed by TERS spectra at different molecular lobes suggest different orientations of two tertiary butyl components within each phenyl group for each lobe, which would lead to different lobe heights, which is corroborated by the STM topographic images of the molecule, as shown in FIG. 3(a, b). Because of the influences of local environments and adsorption configurations on the Raman response as well as the TERS selection rule [10], the observed TERS spectra will be different for different orientations of components contained by that particular site, which could explain the symmetry breaking and pronounced differences in the TERS spectra described above.

In order to obtain a panoramic view of both the spatial distribution of different Raman peaks and spectral differences, we further performed the spatially resolved TERS imaging, as shown in FIG. 3(c−e) for three representative vibrational modes roughly associated with the atomic motions around the lobe, gap, and near-center positions. These TERS imaging results exhibit distinctive spatial features among different modes, which can be explained by different contributions of vibrational motions arising from different parts of the H_2TBPP molecule, as indicated by the colored atoms in FIG. 3(f−h). For example, the vibrations corresponding to the 817 cm^{-1} mode shown in FIG. 3(c) are mainly

contributed by the C−H bonds from the lobe and the modified pyrrole near the center (FIG. 3(f)), giving a feature of approximate four "bright" lobes in the TERS mapping. The vibrations associated with the mode at 1138 cm^{-1} shown in FIG. 3(d) are mainly related to the in-plane vibrations of the porphyrin ring shown in FIG. 3(g), exhibiting some bright feature around the gap and near-center positions (though not symmetric). Of particular interest is the TERS mapping for the 1500 cm^{-1} mode shown in FIG. 3(e), which reveals a vertically aligned "two-dot" pattern with a separation distance of ∼0.4 nm. As we have discussed previously according to the single-point spectra in FIG. 2(c), this mode is likely to associate with the rocking motions of the N−H bonds around the molecular center. The separation between the two dots agrees very well with the distance of ∼0.4 nm estimated between two nitrogen atoms from the theoretically optimized geometry of a H_2TBPP molecule (FIG. 3(h)). Therefore, the observation of such a two-dot pattern in FIG. 3(e) appears to suggest the absence of tautomerization process within a porphyrin ring of the H_2TBPP molecule at ∼7 K even under light illumination. We would like to mention that the calculated normal modes are based on a free-space molecule without considering the influence of substrate and the resultant symmetry breaking upon adsorption. More sophisticated calculations that take into account of the molecule—substrate interaction are needed in further studies to better correlate the observed TERS spectra with precise adsorption conformations of the molecule on a surface.

It should be noted that, in terms of peak positions, most of TERS peaks described above for the H_2TBPP molecule on Ag(100) resemble quite well with the same molecule adsorbed on Ag(111) at 80 K [3], reflecting the chemical connection of Raman spectra with the vibrations of chemical bonds. However, the patterns of relative peak intensities are very different and the present TERS maps reveal much more details of the H_2TBPP
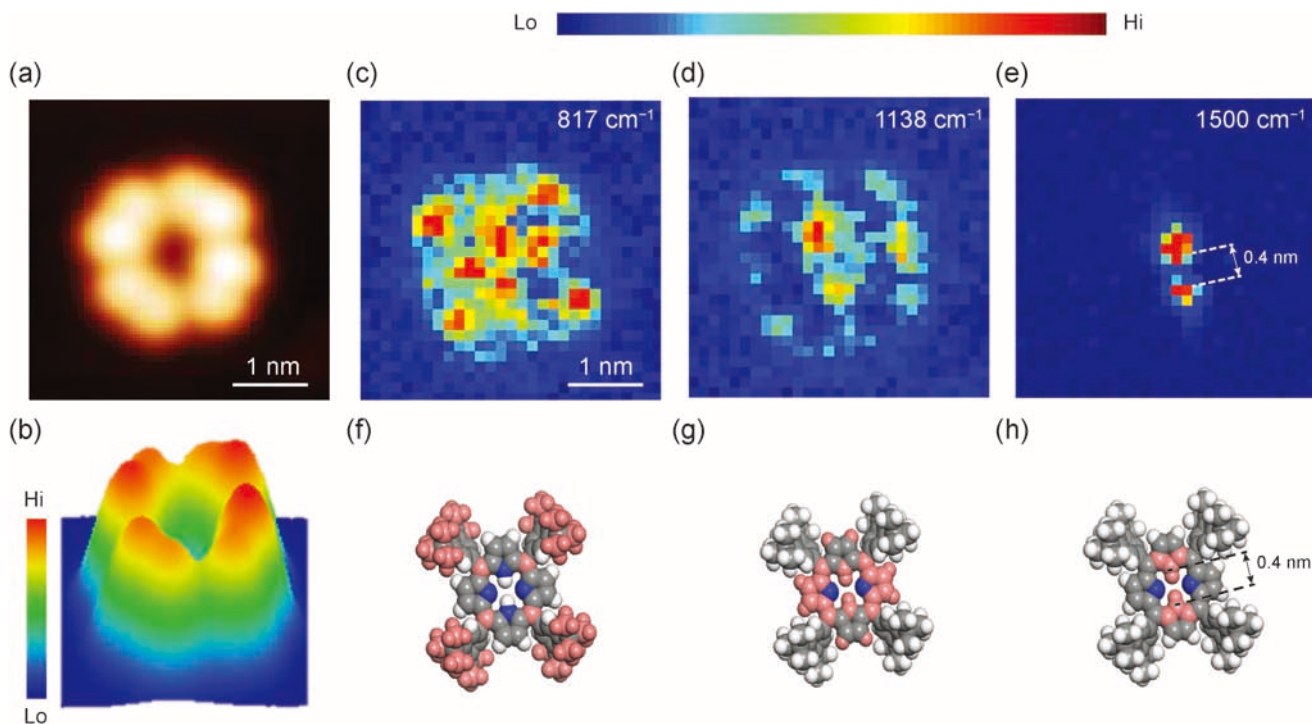
FIG. 3 (a) STM topograph of a single H$_2$TBPP molecule (−0.05 V, 2 pA, 4 nm×4 nm). (b) 3D view of the STM topography of (a) showing different lobe heights. (c, d, e) TERS images of a single molecule for representative Raman modes (−0.05 V, 4 nA, 4 nm×4 nm, 29×29, 1 s/pixel). (f, g, h) Molecular structures highlighting pink-colored atoms involved in vibrational motions based on calculated Raman modes corresponding to (c, d, e).

molecule beyond the four-lobe feature. There are two major reasons for such differences. One is related to the temperature difference. Liquid nitrogen temperature (∼80 K) is perhaps not low enough to suppress both the continuous flip-flop motions of the constituent atoms inside the lobe of the H$_2$TBPP molecule and the tautomerization process within the porphyrin core, resulting in the blurring of the images into four-fold symmetry. By contrast, at liquid helium temperature (∼7 K), the thermal drift in STM and the above-mentioned motions of the H$_2$TBPP molecules are significantly suppressed, providing a more stable STM junction and specific frozen local adsorption conformations for spectral imaging. The other reason is related to the orientation difference of the substrate. The use of the present Ag(100) versus previous Ag(111) might also result in different adsorption configurations and different local environments for different parts within a single molecule due to different chemical reactivity of surface Ag atoms and resultant different molecule-substrate interactions. The lobe heights become non-uniform (or irregular) on Ag(100) as compared with the relatively uniform distribution of the lobe heights for an isolated H$_2$TBPP molecule on Ag(111). The combination of the above two factors leads to different spectral features and spatial mapping images observed. Finally, before closing,

we would like to point out that the spatial resolution of TERS imaging presented in this work, as demonstrated clearly in FIG. 3(e), has reached down to at least ∼0.4 nm. Such ultrahigh spatial resolution appears to experimentally correlate with the highly localized plasmonic field at the tip apex with atomistic sharpness [11], although the physical mechanism behind is still under active debate [10, 12–15].

In summary, we have demonstrated that the STM based TERS technique operated at cryogenic temperature down to ∼7 K is capable of resolving the inner structure of a single H$_2$TBPP molecule associated with its local vibrations. The TERS spectra are site-dependent over the molecule, revealing symmetry information on the adsorption of the whole molecule and local orientation information for the chemical groups directly underneath the tip. Furthermore, mode-specific TERS mapping reveals different patterns for different vibrational modes with sub-nanometer spatial resolution, allowing to directly identify the orientation of N−H bonds around the porphyrin core. Our findings not only have a substantial impact on the fields of plasmonics, surface chemistry and molecular nanotechnology, but also can stimulate theoretical studies to explain the extraordinary spatial resolution and mode-specific TERS imaging.

[1] B. Pettinger, P. Schambach, C. J. Villagómez, and N. Scott, Annu. Rev. Phys. Chem. **63**, 379 (2012).

[2] M. Richard-Lacroix, Y. Zhang, Z. Dong, and V. Deckert, Chem. Soc. Rev. **46**, 3922 (2017).

[3] R. Zhang, Y. Zhang, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang, and J. G. Hou, Nature **498**, 82 (2013).

[4] S. Jiang, X. Zhang, Y. Zhang, C. Hu, R. Zhang, Y. Zhang, Y. Liao, Z. J. Smith, Z. Dong, and J. G. Hou, Light Sci. Appl. **6**, e17098 (2017).

[5] S. Jiang, Y. Zhang, R. Zhang, C. Hu, M. Liao, Y. Luo, J. Yang, Z. Dong, and J. G. Hou, Nat. Nanotechnol. **10**, 865 (2015).

[6] X. Wang, Z. Liu, M. De Zhuang, H. M. Zhang, X. Wang, Z. X. Xie, D. Y. Wu, B. Ren, and Z. Q. Tian, Appl. Phys. Lett. **91**, (2007).

[7] P. R. West, S. Ishii, G. V. Naik, N. K. Emani, V. M. Shalaev, and A. Boltasseva, Laser Photonics Rev. **4**, 795 (2010).

[8] C. Zhang, B. Gao, L. G. Chen, Q. S. Meng, H. Yang, R. Zhang, X. Tao, H. Y. Gao, Y. Liao, and Z. C. Dong, Rev. Sci. Instrum. **82**, 083101 (2011).

[9] N. Chiang, X. Chen, G. Goubert, D. V. Chulhai, X. Chen, E. A. Pozzi, N. Jiang, M. C. Hersam, T. Seideman, L. Jensen, and R. P. Van Duyne, Nano Lett. **16**, 7774 (2016).

[10] S. Duan, G. Tian, and Y. Luo, Angew. Chem. Int. Ed. **55**, 1041 (2016).

[11] M. Barbry, P. Koval, F. Marchesin, R. Esteban, A. G. Borisov, J. Aizpurua, and D. Sánchez-Portal, Nano Lett. **15**, 3410 (2015).

[12] L. Meng, Z. Yang, J. Chen, and M. Sun, Sci. Rep. **5**, 9240 (2015).

[13] C. Zhang, B. Q. Chen, and Z. Y. Li, J. Phys. Chem. C **119**, 11858 (2015).

[14] P. Liu, D. V. Chulhai, and L. Jensen, ACS Nano **11**, 5094 (2017).

[15] S. Duan, G. Tian, Y. Ji, J. Shao, Z. Dong, and Y. Luo, J. Am. Chem. Soc. **137**, 9515 (2015).