

Theoretical and Experimental Study of Surface-Enhanced Raman Scattering of 4,4'-bipyridine Molecule on Graphene

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Abstract. In present work, we investigated the surface-enhanced raman scattering(SERS) of 4,4'-bipyridine on Graphene surface with a quasi-analytical approach based on density functional perturbation theory(DFPT). Three different configurations were considered to simulate the adsorption structures on the Graphene surface. The interaction between 4,4'-bipyridine molecule and Graphene surface depends on the adsorption structure, which also results in the distinct spectroscopy. The relationship between the configurations and SERS spectroscopy were interpreted. We also performed the experimental SERS spectroscopy of 4,4'-bipyridine molecule on Graphene. Comparing with the experimental SERS spectroscopy, the landscape of 4,4'-bipyridine on Graphene has been revealed.

1. Introduction

Since the discovery of Graphene in 2004 [1], it has become one of the most attractive organic materials in 21th century. The 2-dimensional geometric structure of Graphene makes it with the unique electronic structure, as well as the mechanical, optical, thermal properties. These unique properties bring broad application prospect in the fields of microelectronics, quantum physics, materials and chemistry [2–4]. Recently, Graphene has been widely applied as the Surface-Enhanced Raman Spectroscopy (SERS) substrate due to its distinctive properties [5, 6].

Raman spectroscopy is a kind of useful technique for studying the molecular structure and properties by means of molecular vibration. Due to the 'fingerprint' feature of Raman spectroscopy, this wonderful technique could be used for detection at single molecule level. While the intensity of Raman spectroscopy is very low, hence the SERS was developed and widely applied for molecular detection. As we know there are two kinds of enhancement mechanisms for Raman spectroscopy. One is electromagnetic enhancement, the other one is chemical enhancement. There is only chemical enhancement mechanism exists on Graphene substrate. So far, a lot of experimental researches of chemical enhancement mechanism on Graphene substrate have been carried on [7, 8]. While there is hardly any theoretical research about it. Before the simulation of SERS spectroscopy, the modeling of the probe molecule on Graphene should be constructed. In the previous theoretical SERS spectroscopy study of metallic surface, there are two different models. One is a cluster model in which several metal atoms are used for mimicing the substrate. The other one is the model with periodic condition

boundary (PCB). These two models both have their disadvantages, the cluster model with finite atoms obviously cannot well describe the electronic structure of surface. For the later model, the lack of numerical stability and the time consuming bring the application limit when the purely numerical third derivative was calculated for Raman tensor. Recently, Hu and coworkers developed a quasi-analytical approach based on density functional perturbation theory for calculating the Raman spectroscopy in periodic systems [9]. This low-cost quasi-analytical approach could effectively simulate the SERS on metal surface, and furthermore investigate the surface landscape by means of the relationship between the spectroscopy and the geometric structure.

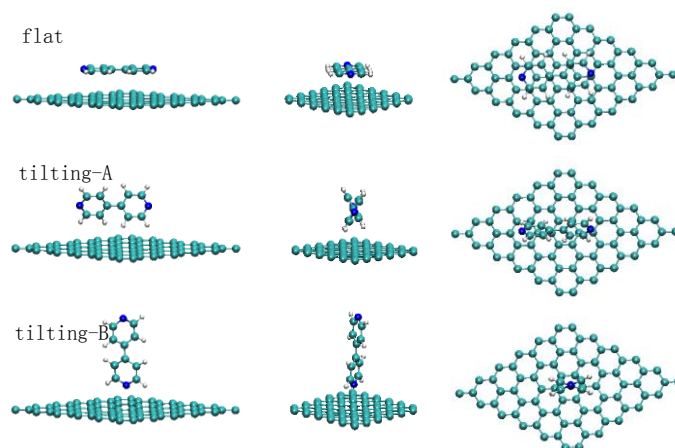


Figure 2.1: The geometric structures of three different configurations, flat, tilting-A and tilting-B.

In this work, the 4,4'-bipyridine molecule was chosen as a probe molecule. 4,4'-bipyridine molecule is a simple molecule but widely used for studying SERS, especially metal substrate. The performance of 4,4'-bipyridine molecule on Graphene surface is rarely investigated. Therefore, the SERS spectroscopy, as well as the enhancement mechanism is of much significance. At present, the possible geometric

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structures of 4,4'-bipyridine on Graphene was optimized, then we calculated the SERS on Graphene with the quasi-analytical approach [9]. The experimental SERS spectroscopy of 4,4'-bipyridine molecule on Graphene was also performed. The relationship between the SERS and the geometric structures was revealed. Comparing with the available experimental SERS, the landscape of 4,4'-bipyridine molecule on Graphene was accurately illustrated.

2. Computational details

The geometric structure of isolated 4,4'-bipyridine molecule in gas phase was optimized in DFT level with GAUSSIAN09 program package [10]. The BP86 functional [11, 12] and 6-31G(d,p) [13] basis set were used. Furthermore, the frequency analysis and the analytical Raman spectrum were carried out in the same level. The BP86 functional was chosen in present work because it could give harmonic frequencies close to experimental results without using the scaling factor [14]. The calculated Raman spectrum was convoluted with a Gaussian function with a full-width-at-half-maximum (fwhm) of 10 cm⁻¹. When 4,4'-bipyridine molecule locates on the surface of Graphene, the PBC model should be applied during the calculation. The geometric structures of 4,4'-bipyridine molecule on Graphene surface were optimized using the PBC model implemented in the Vienna abinitio simulation package (VASP) [15]. Three different adsorption configurations of 4,4'-bipyridine molecule on Graphene were considered, named flat, tilting-A and tilting-B, shown in Figure 2.1. The Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA-PBE) [16] was performed to describe the exchange-correlation potential. A planewave basis cutoff of 400 eV was applied during the calculation. The special K-point sampling only with a Gamma point of Monkhorst-Pack scheme was used for the Brillouinzone integrations approximately. The Graphene surface was constructed by a slab model with 5×5 unit cells. The lattice constant of unit cell was fixed by experimental value 2.46 Å and the bond length of C-C bond was set 1.42 Å as well. The vacuum layer was set 30 Å for this slab model. The atomic coordinates in the superlattice model were fully relaxed until the force on each atom was less than 0.02 eV/Å. Based on the optimized geometric structures, the vibrations of the molecule were calculated under the condition of fixing Graphene substrate. Then the SERS spectra were calculated by a Quasi-analytical approach developed by Hu et al [9]. Standardly, the differential Raman cross section was calculated by [17]

$$\left(\frac{d\sigma}{d\Omega}\right)_k = \frac{\pi^2}{\epsilon_0^2} (\tilde{\nu}_{in} - \tilde{\nu}_k)^4 \frac{\hbar}{8\pi^2 c \tilde{\nu}_k} |\vec{\epsilon}_i \cdot \hat{R} \cdot \vec{\epsilon}_s|^2 \times \frac{1}{1 - \exp(-hc\tilde{\nu}_k / k_B T)}, \quad (1)$$

Where \hat{R} is the Raman tensor, a third derivative of energy [17]

$$R_{\alpha\beta}^k = -\frac{\partial^3 E}{\partial \epsilon_\alpha \partial \epsilon_\beta \partial Q_k}, \quad (2)$$

α and β denote the cartesian direction, Q_k is the normal mode, ϵ is the external electric field. Since the Born effective charge [18]

$$Z_{\beta i} = -\frac{\partial^2 E}{\partial \epsilon_\beta \partial x_i}, \quad (3)$$

can be analytically calculated by the density functional perturbation theory [18,19], the Raman tensor could be reduced by the Born effective charge and written as

$$R_{\alpha\beta}^k = \sum_i \frac{l_{ik}}{\sqrt{m_i}} \frac{\partial Z_{\beta i}}{\partial \epsilon_\alpha}, \quad (4)$$

where

$$\frac{\partial Z_{\beta i}}{\partial \epsilon_\alpha} = \frac{Z_{\beta i}(\Delta \epsilon_\alpha) - Z_{\beta i}(-\Delta \epsilon_\alpha)}{2\Delta \epsilon_\alpha}, \quad (5)$$

The wavelength of the incident light and the temperature were 514 nm and 298 K, respectively. All calculated cross sections were convoluted with a Gaussian function with fwhm of 10 cm⁻¹ with a scale factor of 1.01 [20].

3. Experimental details

Raman spectroscopy was carried to study the SERS behaviors of substrates using a Raman spectrometer (Horiba HR Evolution 800) with laser wavelength of 532 nm, laser power of 48mW, the diffraction grid of 1800 gr/mm and the spatial resolution of 400 nm. A 50× objective (N.A.=0.50) was used throughout the experiment.

The Graphene grown on copper foils by chemical vapor deposition was transferred onto the SiO₂ substrate using wet-transfer method. After successfully fabricated the substrate, 1μL 4,4'-bipyridine with concentration 10⁻³ was dropped on the Graphene/SiO₂ to study the SERS performance by using a Raman spectrometer with laser excitation at 532 nm (2.33 eV). The excitation laser spot was about 0.5 μm and the incident laser power kept at 0.5 mW. The laser light was coupled through an objective lens of 50× and the Raman spectra from all substrates were measured under the same conditions. SERS measurements were taken from at least five random points that were more than 2 mm apart.

4. Results and discussion

Our calculated result shows that the 4,4'-bipyridine molecule in gas phase is not a planar molecule. The dihedral angle between the two pyridine plane is about 35°. Figure 4.1 shows the analytical Raman spectrum of 4,4'-bipyridine molecule in gas phase within BP86/6-31G(d,p) level. One can see that there are five main Raman peaks locating at about 980, 1215, 1285, 1493 and 1593 cm⁻¹. The corresponding vibration modes are all in-plane vibrations, which are also shown in Figure 4.1. When the 4,4'-bipyridine molecule is adsorbed on Graphene surface, its geometric structure changes since the interaction between them. In the flat configuration, the 4,4'-bipyridine becomes a planar molecule. The distance between 4,4'-bipyridine plane and Graphene surface is around 3.3 Å. In the two tilting configurations, the two pyridine rings of 4,4'-bipyridine molecule keeps crossing. While the dihedral angles

between two pyridines in the two tilting configurations are different. In tilting-A and tilting-B, the dihedral angles are about 54.1° and 39.6° , respectively. They are both larger than that of 4,4'-bipyridine molecule in gas phase.

The interaction between the 4,4'-bipyridine and Graphene brings not only the difference of the geometric structure, but also the change of the electronic structure. Therefore the intensity of Raman spectroscopy will show distinct features after the 4,4'-bipyridine molecule adsorbed on Graphene. Figure 4.2 shows the calculated SERS of three different configurations of 4,4'-bipyridine molecule on Graphene. In general, one can see that the vibrational frequencies have been shifted after the adsorption. The main peaks of the three different configurations also show distinct features. The intensities of flat configuration is the lowest among them. When the 4,4'-bipyridine molecule is tilting on the Graphene surface, the SERS intensity is much stronger. For the flat configuration, the peak at 980 cm^{-1} is the strongest but the peak at 1593 cm^{-1} is very weak. When the 4,4'-bipyridine molecule is parallel to Graphene surface, all the vibrations are also parallel to Graphene surface, therefore the polarization changes caused by the vibrations are mainly along the plane of Graphene surface. The electronic field of the plasma on the surface of Graphene caused by the incident light has large intensity in the direction perpendicular to Graphene surface. Therefore the Raman spectroscopy of flat configuration can't be strongly enhanced. Figure 4.3 shows the charge density difference of these three different clusters. We can see that for the flat configuration, the charge transfer mainly occurs inside of Graphene. While for the two tilting configurations, the obvious charge transfer is shown between 4,4'-bipyridine molecule and Graphene surface. For the two tilting configurations, most of the vibrations are perpendicular to Graphene surface. The large polarization charge caused by the vibrations is parallel to the electronic field, hence the enhancement for these two configurations are stronger than that of flat configuration. For these two tilting configurations, different orientations bring distinct landscapes of SERS. For the configuration tilting-A, the peaks at 1240 cm^{-1} (1215 cm^{-1} for isolated molecule) and 1593 cm^{-1} are the strongest two peaks, since the symmetrical C-H bending will result the change of polarization in the direction perpendicular to Graphene surface. While for the configuration tilting-B, the

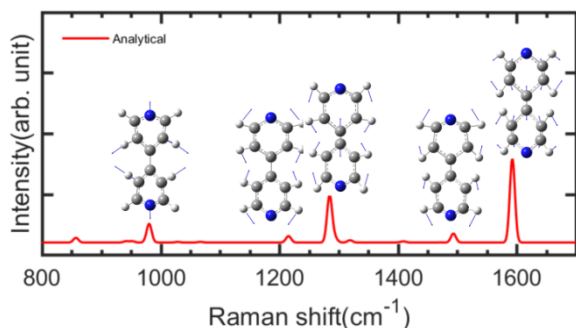


Figure 4.1: The analytical Raman spectrum of 4,4'-bipyridine single molecule (SM) broadened with a Gaussian having a fwhm of 10 cm^{-1} , as well as the vibrational modes of five feature peaks at 980 , 1215 , 1285 , 1493 and 1593 cm^{-1} .

vibrations at 1285 cm^{-1} and 1593 cm^{-1} have strong Raman scattering. The main difference between these two vibrations and the others is that some heavy atoms are involved and the displacements of these involved heavy atoms are also along the direction of the electronic field. Comparing with the experimental spectroscopy, one can see that the calculated SERS spectroscopy of configuration tilting-B matches the experimental spectroscopy very well. It is believable that the 4,4'-bipyridine molecule would prefer the tilting-B configuration on Graphene surface.

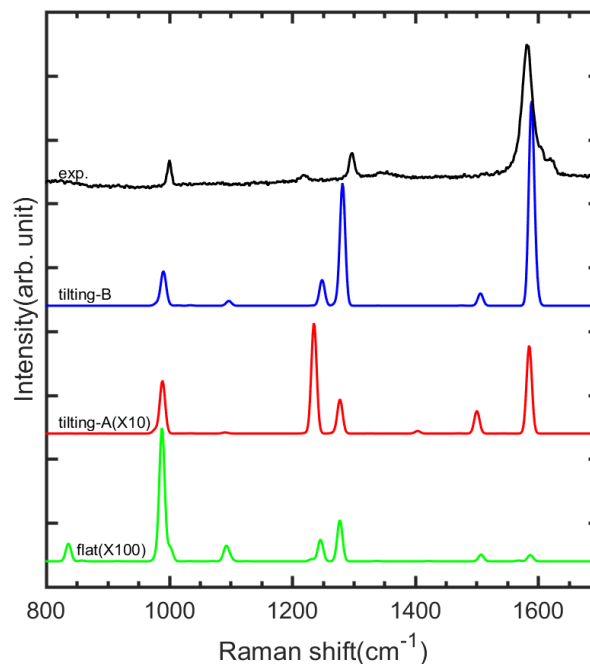


Figure 4.2: The calculated SERS of the configurations flat, tilting-A and tilting-B.

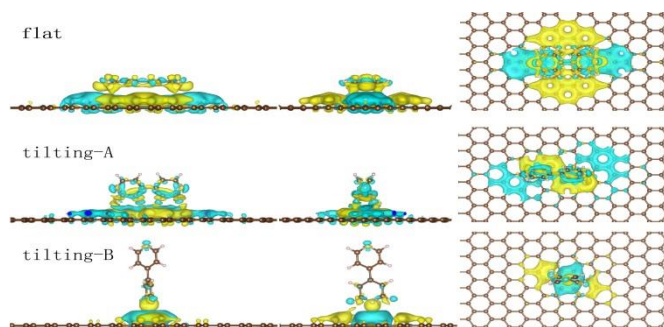


Figure 4.3: The calculated charge density difference of these three configurations.

5. Conclusion

In summary, the surface-enhanced Raman scattering (SERS) spectroscopy of 4,4'-bipyridine molecule on Graphene was investigated theoretically and experimentally. A quasi-analytical method based on density functional perturbation theory (DFPT) was applied to calculate the SERS spectroscopy. Three possible configurations flat, tilting-A and tilting-B were considered to simulate the adsorption structure of 4,4'-

bipyridine on Graphene. The relationship between the SERS spectroscopy and the configuration was revealed. The agreement of theoretical and experimental spectroscopy nicely illustrate the landscape of the 4,4'-bipyridine on Graphene.

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