

Surface-Enhanced Raman Scattering and DFT Study of 4,4'-Biphenyldithiol on Silver Surface

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Surface-enhanced Raman scattering (SERS) of 4,4'-biphenyldithiol (BPDT) has been investigated at a silver island film. Ordinary Raman (OR) spectra of neat sample in solid state and in basic solution have also been taken for comparison. The spectral feature in the SERS spectrum was similar to that for the OR spectrum in basic solution, except for the broadening of ring stretching bands indicative of the presence of surface-phenyl ring π interaction. In contrast, only absence of the C-H stretching band with very small Raman scattering cross-section seemed not pertinent in judging the definitive orientation of molecule. The observed vibrational bands in the SERS spectrum have been assigned by referring to the normal modes and wavenumbers from density functional theory (DFT) calculations of the simple model as 4,4'-biphenyldithiolates bound to two Ag atoms at the both ends. Excellent agreement between the experimental and the calculated results was achieved, which is remarkable considering the level of theory applied.

Key Words : SERS, Biphenyldithiol (BPDT), DFT, Silver island film

Introduction

Surface-enhanced Raman scattering (SERS) is the phenomenon that the Raman scattering cross-section of the molecule adsorbed on noble metal surface is substantially increased.^{1,2} Then, lots of experimental and theoretical studies have been made to elucidate the exact nature on the mechanism of the Raman scattering enhancement. Although the enhancement of the Raman scattering of molecules on the metal surfaces has been known to be induced by mainly the electromagnetic and/or chemical mechanisms,³⁻⁵ its definite comprehension has not been fully accomplished yet. Nonetheless, it has become one of the most powerful spectroscopic techniques for investigating the orientation and the adsorption behavior of molecules on the metal surfaces, because only the adsorbates show their significant Raman scattering enhancement.⁶ In addition, the relative enhancement of certain Raman bands in the SERS spectra could be interpreted in relation to the orientation of the polyatomic molecules such as biphenyl derivatives on the surfaces by invoking the surface selection rules,^{7,8} even still contradictory.

Detailed investigations on the structures of some biphenyl derivatives at the metal surfaces and their adsorption behaviors have been performed by SERS. Bae et al. reported that 4-biphenyl isocyanide adsorbs on the silver and gold surface *via* the carbon lone pair electrons with standing geometry whereas it should have more vertical orientation on Ag than on Au, which is determined through the detailed analysis of the shift and relative enhancement of the distinctive vibrational bands in the spectra.⁹ On the other hand, the same molecule self-assembled monolayers on Ag result-

ed in both the low surface coverage and the orientational disorder even at room temperature, because of the weakness of isocyanide-metal bond examined by the near-edge X-ray absorption fine structure spectroscopy.¹⁰

Self-assembled monolayers (SAMs) prepared from aromatic dithiols on metal surfaces have been attracted as model for exploring and comprehending the charge transport mechanism between the metal and molecule junctions in nanoscale.^{11,12} In particular, oligophenyl dithiols have recently been investigated with respect to the properties and the potential as a reconfigurable switch in future molecular electronics.^{13,14} Accordingly, the structure of the adsorbed oligophenyl dithiols should be very important to test the eligibility in microelectronics. Adsorption behaviors of molecules adsorbed on the metal surfaces and their structures were investigated by utilizing the SERS selection rule and the spectral correlation among the derivatives without a reliable theoretical guideline, in general. For instance, aromatic dithiols were known to chemisorb on Ag with a flat orientation by forming the two S-Ag bonds whereas they chemisorbed on Au with a perpendicular orientation by forming a single S-Au bond,¹⁵⁻¹⁸ which is determined through the detailed analysis on the shift and relative enhancement of the distinctive vibrational bands in the spectra. Also, such an analysis suggested that 1,2-benzenedithiol is chemisorbed by forming two S-metal bonds with the different tilt angles of the phenyl ring, which were estimated to be *ca.* 51° on gold and 38° on silver, respectively, with respect to the surface normal.¹⁸ It is widely accepted that the adsorption behavior of molecules is mainly affected by the surface characteristics of the SERS active substrates. However, the detailed adsorption mechanism depending on the kind of the

metal surfaces has not been established yet. A recent investigation even showed that the torsion angle thus the degree of the π - π coupling between the two phenyl rings of biphenyldithiol sandwiched between the Au nanoparticles and the single crystal gold (100) surface could be controlled by applying electrochemical gate field.¹⁹ Nonetheless, detailed studies on the structural characteristics of biphenyldithiol on gold as well as on silver have not been reported yet to our knowledge.

In this report, structure and adsorption behavior of 4,4'-biphenyldithiol on a silver island film have been investigated by measuring the SERS spectra for the first time. Quantum chemical density functional theory (DFT) calculations have also been performed to identify the structure and to analyze the observed Raman bands in the spectra.

Experimental Section

Preparation of the silver island film and its surface characteristics were described elsewhere in detail.²⁰ Briefly, 30 mL of 0.12 M AgNO_3 solution was mixed with 2 mL of 1.32 M NaOH to produce dark brown AgOH precipitate. Ammonium hydroxide solution was added drop-wise until the precipitate dissolved and the solution became transparent. Then, 9 mL of 0.56 M D-glucose solution was added as a reducing agent in the presence of the cleaned substrate. The substrate was pre-cleaned with nitric acid and sonicated successively in several solvents before chemical deposition. The prepared silver film was dipped in 1 mM KCl solution for 4-5 min and rinsed with methanol, for improving the surface quality of the film such as the reproducibility of SERS activity. Then, the film was dipped in 2 mM of 4,4'-biphenyldithiol (BPDT) in methanol solution for 10 min. The remaining solution on the film was sufficiently removed by rinsing in methanol. BPDT was purchased from Aldrich and used without further purification. All other chemicals were of the reagent grade and the de-ionized water was used all through.

Raman scattering was measured by utilizing a triple grating imaging monochromator (Princeton Instruments, SP-2500i) equipped with a back-illuminated CCD (Princeton Instruments, 100B_eXcelon). The 632.8 nm of a He-Ne laser was used as the excitation source. The excitation source used was the 632.8 nm line of a He-Ne laser (Melles Griot, R54-168). Typical laser power at the sample position was 12 mW. Raman scatterings were collected at 90° through a holographic Notch filter (Edmund Optics) set in front of the entrance slit of the spectrometer. The holographic grating of 1200 grooves/mm and the slit opening of 100 μm allowed the spectral resolution of 1 cm^{-1} . The spectrometer was calibrated with the lines from a mercury lamp as references and the typical data acquisition time in Raman experiments was 0.5 s.

Results and Discussion

Ordinary Raman (OR) spectra of 4,4'-biphenyldithiol (BPDT) in solid state and in basic solution have been taken

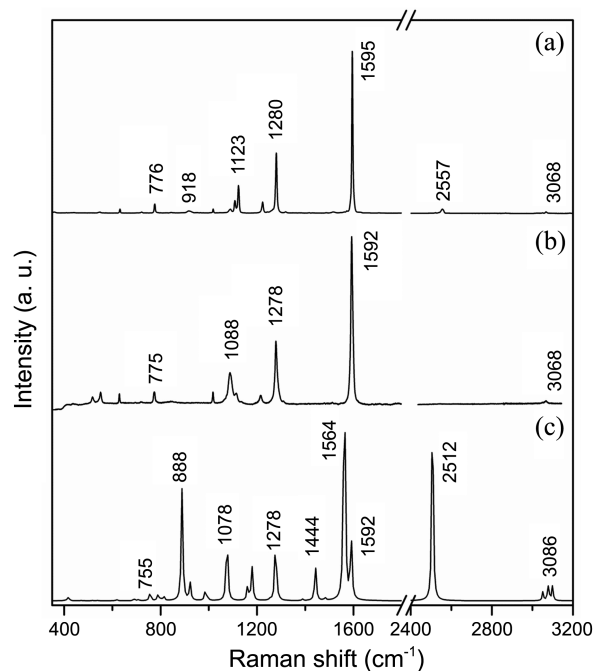


Figure 1. (a) Ordinary Raman spectrum of 4,4'-biphenyldithiol (BPDT) in solid state. (b) Ordinary Raman spectrum of BPDT in basic solution. (c) Calculated Raman spectrum of free BPDT in anionic form at one end from density functional theory (DFT) calculations.

for finding the correlation with the SERS spectrum and shown in Figure 1(a) and 1(b), respectively. The apparent difference between the OR spectra is the absence of the vibrational bands in the basic solution, which appear at 2557 and 918 cm^{-1} in solid state. Consulting the assignments for many aromatic thiols,¹⁵⁻¹⁸ two bands can be assigned to the $\nu(\text{S-H})$ and the $\beta(\text{S-H})$, respectively. Namely, two spectra clearly indicate that BPDT exists in dithiolate form in basic solution. As a result, the peak at 551 cm^{-1} in basic solution appears distinctively, assignable to the $\nu_s(\text{C-S})$. Another feature in the spectra is appearing to be negligible for the C-H stretching bands at ~ 3060 cm^{-1} , probably owing to the small Raman scattering cross-section. This means that absence/presence of the C-H stretching vibration might be not pertinent in determining the orientation of molecule adsorbed on the metal surface.

The surface-enhanced Raman scattering spectrum of BPDT for the first time adsorbed on a silver island film is shown in Figure 2(a). The observed SERS spectrum correlates well with the one obtained in basic solution except for some distinctive, the broadening and red-shifted of certain vibrational bands. This suggests that BPDT chemisorb on the silver surface *via* the Ag-S bond formation, assuming a flat orientation with respect to the surface. The prominent peaks observed at 1590, 1286, 1204, and 1085 cm^{-1} , which are broad and shifted to lower wavenumbers compared to the ones in basic solution, are indicative of the interaction between the π system of phenyl rings and the metal surface. In contrast, the absence of vibrational bands in the C-H stretching region seemed not to be a definite criterion in

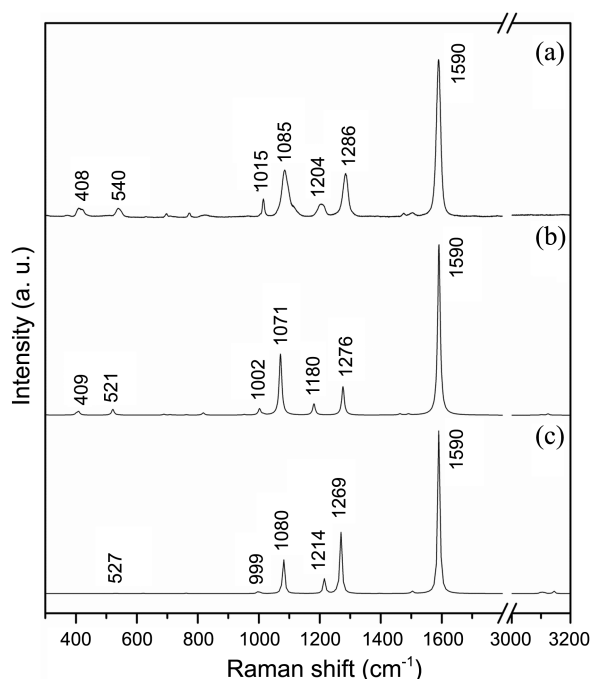


Figure 2. (a) Surface-enhanced Raman scattering (SERS) spectrum of 4,4'-biphenyldithiol (BPDT) adsorbed on silver surfaces. Calculated Raman spectra of the anionic BPDT bound to two Ag atoms at both ends from density functional theory (DFT) calculations: (b) 36 and (c) 0 for the tilt angles between the two phenyl rings of BPDT.

determining an orientation of BPDT on the surface as has been mentioned above, although the same case for aromatic molecules adsorbed on metal surfaces, in general, reveals the parallel orientation of the phenyl ring on the surface according to the surface selection rules.

For the definite assignment of the observed peaks in the SERS spectrum, the density functional theory (DFT) calculations have been performed at the B3LYP/DGDZVP level.²¹ First, free BPDT was optimized with the DFT level and its Raman spectrum was obtained for the optimized structure. Then, the same calculations were performed for BPDT in a thiolate form, BPDT in dithiolate form, and the anionic BPDT bound to two Ag atoms at both ends, respectively. The calculated wavenumbers in Raman spectra were scaled by a single factor of 0.97. In addition, to elucidate the spectral change induced by the interactions between the π systems of two phenyl rings and the metal surface, the Raman spectra for the structures with the tilt angles of 0–50° between two phenyl rings in the anionic BPDT bound to two Ag atoms belonging to the C_2 point group were calculated. Even though the Raman spectra except for the equilibrium geometry with the tilt angle of 36° involve the imaginary frequencies, the calculated results were sufficient to notice the difference in the Raman spectra according to the change in the tilt angle of the phenyl rings. As have been expected in the biphenyl derivatives, only the difference is shifted for the C-H in-plane bands according to degree of the π - π interaction between the two phenyl rings of biphenyl. In the present work, the normal modes calculated for the anionic BPDT

bound to two Ag atoms at both ends were adopted for the assignment of the vibrational bands in the SERS spectrum and the Raman spectra calculated for the two tilt angles of 36° and 0° between two phenyl rings in BPDT are presented in Figure 2(b) and Figure 2(c), respectively. The agreement between the observed spectrum in Figure 2(a) and the calculated spectrum in Figure 2(b) is very remarkable considering the level of theory applied and the simple assumption of chemical bonds of the two thiolate groups with two Ag atoms. Relative intensities of the peaks in the three spectra represented in Figure 2 were normalized with respect to the largest peak at 1590 cm^{-1} . The peak at 2512 cm^{-1} in the calculated spectrum of free BPDT in anionic form at one end (Figure 1(c)), which is identified to the SH stretching band, is absent in the SERS spectra. Also, it is reasonable to show no peak at 2512 cm^{-1} in basic solution, because of expecting BPDT in dithiolate form.

On the basis of the normal mode vectors and the wavenumbers calculated with our simple model, the observed peaks in the SERS spectrum of BPDT are first identified and then peaks in the spectra in solid state and in basic solution are assigned by referring the calculated wavenumbers and the ring modes broadened and peak-shifted with the respect to a surface-ring π interaction in the SERS spectrum. Assignments of the vibrational bands in the SERS spectra of some biphenyl derivatives on the metal surfaces have been performed by comparing the normal modes of benzene derivatives denoted by the Wilson notation so far. In the present work, it seems to be unreasonable that the vibrational assignment is carried out through the analysis of only the partial vibrational modes without understanding whole the vibrational modes of BPDT. This may make some mismatch in the vibrational assignment. Therefore, the Mulliken notations have been denoted by referring with the calculated normal modes and wavenumbers for explicitly spectral

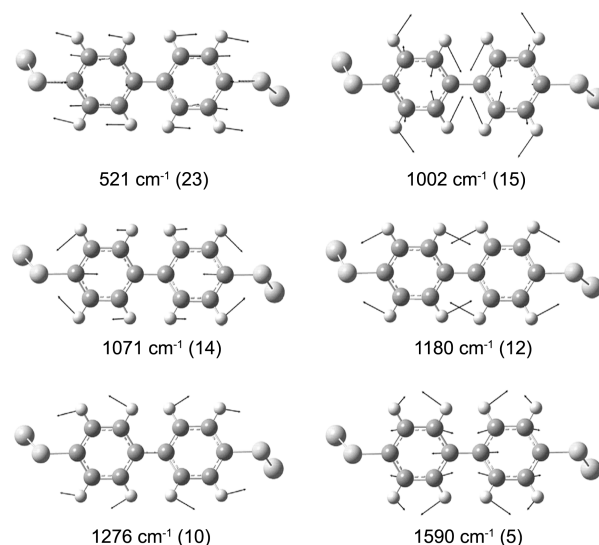


Figure 3. Normal mode vectors for the observed prominent Raman bands in Figure 2(b) obtained by density functional theory calculations. Vibrational wavenumbers and representative assignments according to the Mulliken notation are provided.

Table 1. Experimental and calculated vibrational wavenumbers (cm^{-1}) of the Raman bands in the spectra of 4,4'-biphenyldithiol (BPDT) and their assignments

| OR spectra | | SERS spectra | | Assignment ^a |
|------------|------------|--------------|------|---|
| Solid | dithiolate | Exp | Cal | |
| | | 408 | 401 | 59 ($\nu_{as}(\text{C-S})$) |
| | | 421 | 409 | 26 (Out-of-plane skeletal) |
| 547 | 551 | 540 | 521 | 23 ($\nu_s(\text{C-S})$) |
| 630 | 629 | 628 | 689 | 55 (ring deformation) |
| 718 | | 697 | 709 | 21 (Out-of-plane skeletal) |
| 776 | 775 | 770 | 763 | 20 (ring deformation) |
| 842 | 842 | 816 | 818 | 18 (C-H out-of-plane) |
| 918 | | | | $\beta(\text{S-H})$ |
| 1017 | 1017 | 1015 | 1002 | 15 (ring deformation) |
| 1088 | 1088 | 1085 | 1071 | 14 ($\text{C}_{\text{ring-S}}$ in-plane) |
| 1106 | 1114 | 1112sh | 1074 | 47 ($\text{C}_{\text{ring-S}}$ in-plane) |
| 1123 | | | | |
| 1221 | 1215 | 1204 | 1180 | 12 (C-H in-plane) |
| 1280 | 1278 | 1286 | 1276 | 10 (inter-ring C-C stretching) |
| | | 1472 | 1463 | 41 (C-C stretching) |
| 1517 | | 1502 | 1490 | 7 (ring stretching) |
| 1595 | 1592 | 1590 | 1590 | 5 (C-C stretching) |
| 2557 | | | | $\nu(\text{S-H})$ |
| 3068 | 3067 | | 3123 | 1 (C-H stretching) |

^aDenoted in terms of Mulliken notation by referring the normal modes and wavenumbers obtained from DFT calculations for the anionic BPDT binding two Ag atoms with C_2 symmetry.

assignments.^{23,24}

The calculated normal modes associated for the prominent peaks in the SERS spectra and their Mulliken notations are presented in Figure 3. Experimental and calculated vibrational wavenumbers and the assignment are listed in Table 1. Thus, the C-H stretching bands at 3067 cm^{-1} in basic solution that are absent in the SERS spectrum can be assigned as ν_1 . The strong peaks appearing at 1590, 1286, 1204, and 1085 cm^{-1} in Figure 2(a), are broader rather than the others and can be assigned as the ring modes, indicating an interaction of the π -systems of the rings lying flat against the surface of Ag. As a results, those are assigned to ν_5 (C-C stretching), ν_{10} (inter-ring C-C stretching), ν_{12} (C-H in-plane), and ν_{14} ($\text{C}_{\text{ring-S}}$ in-plane), respectively. Then, the distinct peaks at 1015, 770, and 628 cm^{-1} are assignable to the ring deformations, ν_{15} , ν_{20} , and ν_{55} , respectively. The relatively large peak at 421 cm^{-1} can be assigned as ν_{26} , the out-of-plane skeletal vibration mode whose intensity was similar enhanced compared to the calculated one. In this regard, BPDT adsorbed on silver island film seems not to be definitely flat-oriented for the phenyl rings with small tilted angle at least.

Conclusions

To obtain information on the surface adsorption mechanism from SERS spectra of aromatic thiols, it is generally necessary to find the correlation with the corresponding ordinary Raman spectra. The spectral changes induced by

the adsorption should be thus analyzed. In this respect, vibrational assignment of the Raman bands observed from the SERS spectrum is needed to be preceded. Such an analysis might be accomplished with the qualitative spectral correlation between the spectra for a lot of congeners. However, the SERS spectral analysis of a molecule with a large number of normal mode such as 4,4'-biphenyldithiol can be suffered and also attribute to some major mismatch, especially when the surface selection rule does not work unequivocally. Our previous work in SERS of 4,4'-biphenyl dicarboxylic acid on Ag surface has demonstrated that use of the normal modes and wavenumbers from the DFT calculation for a simple model led to nearly complete assignment for its SERS spectrum and intuitive understanding for the adsorption behavior.²⁵ Adopting the same strategy for the SERS study of the BPDT, the agreement between the observed and the calculated is remarkably made. In this regard, the present analysis of the SERS spectrum will be a useful guideline rather in the case that no additional information is available in the literature.

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