

Adsorption Characteristics and Structure of 4,4'-Bis(mercaptomethyl)biphenyl on Silver by Surface-enhanced Raman Scattering and Density Functional Theory Calculations[†]

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Adsorption of 4,4'-bis(mercaptomethyl)biphenyl (44BMBP) on silver nanoparticles has been investigated by surface-enhanced Raman scattering (SERS) spectroscopy. In addition, the Raman spectra of 44BMBP in solid state and in basic condition have been obtained for comparative study to elicit the characteristics of adsorption. The observed Raman and SERS spectra were analyzed comparing with the normal modes and vibrational frequencies from density functional theory (DFT) calculations performed for the feasible structures of 44BMBP molecule. On the basis of excellent agreement between the calculated and the experimental results, the molecule is found to have both the *cis*- and *trans*-forms for the mercaptomethyl groups in the solid state as well as in the basic condition. In contrast, the molecule is found to be chemisorbed on the silver surface by forming two Ag-S linkages only in the *cis*-form but not in the *trans*-form due to the steric interruption, which indicates the parallel orientation of molecules on the surface. Particularly, the spectral features in the SERS spectra such as the absence of the C-H stretching band and enhancement for the out-of-plane skeletal modes are confirmatory for the parallel geometry through π interaction between the phenyl rings and the metal surface, based on the electromagnetic surface selection rule.

Key Words : SERS, DFT, 4,4'-Bis(mercaptomethyl)biphenyl (44BMBP), Adsorption, Silver nanoparticles

Introduction

Biphenyl derivatives consisting of two phenyl rings connected by σ bond have greatly attracted the attentions because of their high applicability and suitable size in electronic nanoscale devices.¹⁻³ Especially, it was recently considered as a potential molecular switch from the fact that the π systems of two phenyl rings can represent the on-off molecular switch in a way of either in-plane or twisted to each other.⁴⁻⁶ In addition, further studies showed that the torsion angle between the two phenyl rings of biphenyldithiol inserted between the Au nanoparticles and the single crystal gold (100) surface could be altered by applying electrochemical gate field.⁷ In this regard, the correlations between molecular structures and charge transport properties needed to be comprehended and hence the studies on the structure and orientation of molecules linked on the metal have been investigated experimentally and theoretically.⁸⁻¹³ 4,4'-Biphenyl dicyanide is flatly adsorbed on both Ag and Au through direct interaction between the π -systems of the phenyl rings and the metal.⁸ 4,4'-Biphenyl diisocyanide is, however, known to be bridged between the two gold nanoparticles at low concentrations whereas it should be vertically bonded on gold *via* one of the two isocyanide groups at higher concentrations.

⁹ Aromatic dithiols as well as aliphatic dithiols are usually adsorbed on the Au surface as a monolayer by forming only a single S-Au bond, while they are adsorbed forming the two S-Ag bonds on the Ag surface.¹⁰⁻¹² 1,3-Benzenedimethanethiol is found to be adsorbed through two S-Au bonding at low concentration, but to have a vertical geometry at high concentration. However, 1,3-benzenedithiol is found to be adsorbed by forming two S-Au linkages at any concentration.¹¹ Also, the tilt angle of the phenyl ring with respect to the surface normal in 1,2-benzenedithiol is found to be $\sim 51^\circ$ on Au but $\sim 38^\circ$ on Ag.^{12,13} It is to be noted that the structures and adsorption behavior of molecules on the metal surfaces should depend upon the circumstances such as the concentration and substrate. Now, it becomes generally known that the adsorption behavior of molecules can be mainly affected by the surface characteristics although the definite influence of the metal surface has not been clarified yet.

Since discovery of the phenomenon that the Raman scattering of molecules adsorbed on the metal surfaces is tremendously enhanced, surface enhanced Raman scattering (SERS) has widely been used to investigate the adsorption behavior and molecular geometry on the surface.¹⁴ The enhancement of the Raman scattering was known to be accomplished due to chemical and electromagnetic reasons.^{15,16} In addition, it was found that the relative enhancement of certain bands in the SERS spectrum should appear in relation to the

[†]This paper is to commemorate Professor Myung Soo Kim's honourable retirement.

orientation of the molecules with respect to the surfaces, namely, the surface selection rules.^{17,18} Therefore, vibrational assignment for the peaks observed in the SERS spectrum could have been performed by utilizing the SERS selection rule and the spectral correlation among the derivatives. However, it is still contradictable in assigning the Raman bands for polyatomic molecules such as biphenyl derivatives with more than 60 normal modes. In such investigations, the vibrational assignments in Wilson notation used for hundreds of benzene derivatives would be ambiguous when applied to biphenyl derivatives possessing low symmetry.¹⁹ As a means of circumventing the ambiguity in the assignment, Kwon and coworkers showed that the reliable analyses for the SERS spectra of 4,4'-biphenyl dicarboxylic acid and 4,4'-biphenyl dithiol were successfully accomplished through simple model calculations at density functional theory (DFT) level.^{20,21}

In this paper, the structure and adsorption behavior of 4,4'-bis(mercaptomethyl)biphenyl (44BMBP) on silver nanoparticles is investigated by measuring the SERS spectra for the first time. Particularly, the same strategy used in our previous works is adopted to determine the structure and to characterize the adsorption behavior by assigning the peaks observed in the SERS spectrum.

Experimental Section

The details on preparation and characteristics of the silver nanoparticle for effective SERS substrate have been described in the previous work.²² Briefly, 30 mL of 2×10^{-3} M NaBH₄ solution at ice temperature was prepared with stirring at 1500 rpm and 8×10^{-3} M AgNO₃ solution at ambient temperature was added drop by drop with a dispenser. As reduction in solution proceeds, its color turned yellow and afterwards the solution became turbid with precipitates. The reduction was terminated adding 1 mL of NaBH₄ solution for stabilization. The addition rate of AgNO₃ solution was varied by varying the number of droplets per second with the droplet volume of 50 μ L. The optimum rate for the maximum SERS signal was determined to be 0.4 μ mol/s and the substrate thus generated consisted of the aggregates of two or three Ag nanoparticles of about 30 nm sizes, providing hot-spots for enhancement of the Raman signal. A sample to obtain the SERS spectra was prepared by adding 44BMBP (2×10^{-3} M, 20 μ L) and PVP (2×10^{-4} M, 20 μ L) as a stabilizer to 1 ml of the prepared Ag solution. 44BMBP was purchased from Aldrich and used without further purification. All other chemicals were of the reagent grade and 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 excitation source was the 632.8 nm line of a He-Ne laser (Melles Griot, R54-168). Typical laser power at the sample position was 10 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 holo-

graphic grating of 1200 grooves/mm and the slit opening of 100 μ m 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 5 s.

Results and Discussion

Ordinary Raman (OR) spectra of 4,4'-bis(mercaptomethyl)biphenyl (44BMBP) in solid state and basic condition shown in Figure 1(a) and Figure 2(a), respectively, were recorded to acquire the basic information on its vibrational modes and to compare with the ones in the SERS spectrum. In the observed OR spectra, most notably, the peaks appearing near 2550 cm^{-1} in solid state are absent in the basic condition. Referring to the assignments for some aromatic thiols,¹⁰⁻¹² those peaks can be clearly assigned as $\nu(\text{S-H})$ and hence the lack of this feature in the OR spectra in basic condition indicates that 44BMBP exists in dithiolate form in basic solution. It is also notable that the doublet at 2550 and 2559 cm^{-1} for $\nu(\text{S-H})$ appears in the OR spectrum of 44BMBP in solid state.

To account for the spectral feature observed in the OR spectrum, we performed the density functional theory (DFT) calculations at the B3LYP level with the 6-311+G (d,p) basis

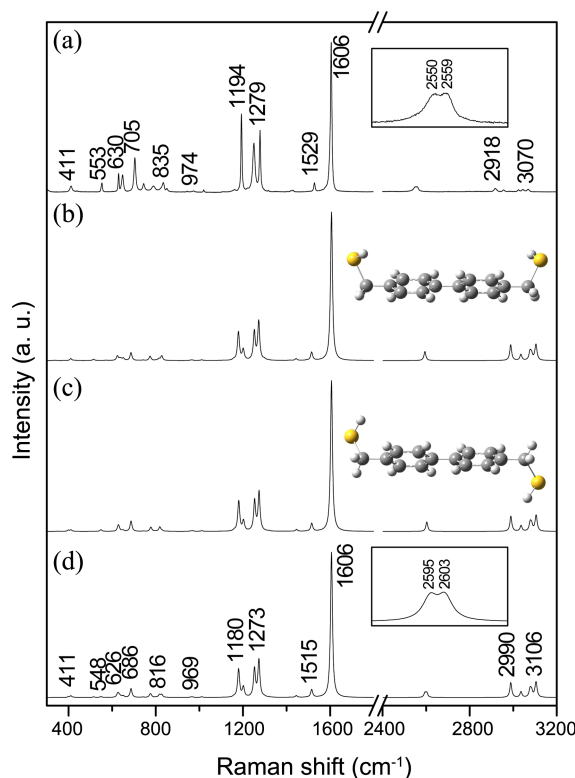


Figure 1. (a) Ordinary Raman spectrum of 4,4'-bis(mercaptomethyl)biphenyl (44BMBP) in solid state. Calculated Raman spectra of (b) free *cis*-44BMBP and (c) *trans*-44BMBP with respect to the SH groups from density functional theory (DFT) calculations. (d) Raman spectra simulated for the two isomers under the assumption of equal composition in equilibrium were summed. Insets in figure display the enlarged peaks in the region of the SH stretching vibration.

Table 1. Experimental and calculated vibrational wavenumbers (cm^{-1}) of the peaks observed in the spectra of 4,4'-bis(mercaptomethyl)-biphenyl (44BMBP) and vibrational assignment

Solid	OR Spectra					SERS spectra			Assignment ^c
	Cal		Basic	Cal		Exp	Cal ^b		
	<i>cis</i>	<i>trans</i>		<i>cis</i>	<i>trans</i>		Ag ₁	Ag ₃	
403	384	399	396	384 ^a	399		387		76(out-of-plane skeletal)
411	410	411	408	414	412 ^a	412	405	406	33(out-of-plane skeletal)
						504	506		31(out-of-plane skeletal)
553	515	548				550	557	544	73(out-of-plane skeletal)
						627	616		30(out-of-plane skeletal)
630	624	628	634	644	643	638	627	659	29(ring deformation)
648	651	651	662	671	650	649	642	583	71($\nu_{\text{as}}(\text{C-S})$)
705	686	686	702	694	692	685	675	575	28($\nu_{\text{s}}(\text{C-S})$)
			733	731		723	719	720	27(out-of-plane skeletal)
744	742	743	752	749 ^a	750	748	740	737	70(out-of-plane skeletal)
790	773	778							$\beta(\text{S-H})$
835	814	818	818	821	815	801	791	791	69(ring deformation)
851	827	829	838	829	844	832	813	826	25(C-H out-of-plane) ^d
							835	826	23($\beta_{\text{as}}(\text{CH}_2)$) ^d
974	968	969							$\beta(\text{S-H})$
1020	1010	1011				1017	1004	987	20(ring deformation)
1194	1179	1181	1190	1178	1178	1188	1172	1172	17(C-H in-plane)
1221	1201	1202	1211	1201	1205		1209	1205	15($\nu_{\text{ring-Cmethyl}}$ stretching) ^e
1251	1252	1253	1230	1205	1202	1224	1194	1162	16($\gamma_{\text{s}}(\text{CH}_2)$) ^e
1279	1272	1274	1280	1276	1276	1283	1271	1271	14(inter-ring C-C stretching)
						1362	1306	1311	12($\gamma_{\text{as}}(\text{CH}_2)$)
1430	1444	1446	1425	1456	1455	1425	1443	1444	10($\beta_{\text{s}}(\text{CH}_2)$)
						1490	1484		52(C-C stretching)
1529	1515	1515	1522	1520	1520	1521	1511	1510	9(ring stretching)
1606	1606	1606	1606	1606	1606	1604	1604	1604	7(C-C stretching)
2550	2595								$\nu(\text{S-H})$
2559		2603							$\nu(\text{S-H})$
2918	2989	2990	2931	2927	2928		2983	2992	6($\nu_{\text{s}}(\text{Cmethyl-H})$)
2955	3036	3037	2940	2953	2955		3045	3057	48($\nu_{\text{as}}(\text{Cmethyl-H})$)
3025	3077	3079	3021	3090	3091		3078	3076	4($\nu_{\text{as}}(\text{C}_{\text{ring-H}})$)
3045	3085	3086					3083		3($\nu_{\text{as}}(\text{C}_{\text{ring-H}})$)
3070	3105	3106	3070	3115	3116		3104	3102	1($\nu_{\text{s}}(\text{C}_{\text{ring-H}})$)

^aThe Raman scattering cross-sections of the 384, 412, and 749 cm^{-1} modes in the Raman spectra simulated for anionic 44BMBP were very small.

^bVibrational frequencies of the bands in the Raman spectra simulated at the B3LYP/DGDZVP level for anionic *cis*-44BMBP bound to each one Ag atom (Ag₁) and three Ag cluster (Ag₃) at both ends, respectively. ^cDenoted in terms of Mulliken notation by referring to the normal modes calculated for anionic *cis*-44BMBP bound with the angle, $\angle\text{CSAg}$ of 160° to each one Ag atom (Ag₁) in the C₂ symmetry. ^dPeak at 832 cm^{-1} in the SERS spectrum can be alternatively assigned as $\nu_{25}(\text{C-H out-of-plane})$ or $\nu_{23}(\beta_{\text{as}}(\text{CH}_2))$. ^ePeak at 1224 cm^{-1} in the SERS spectrum can be alternatively assigned as $\nu_{15}(\text{C}_{\text{ring-Cmethyl}}$ stretching) or $\nu_{16}(\gamma_{\text{s}}(\text{CH}_2))$.

set employing the GAUSSIAN 09 program package.²³ First, the DFT calculations were performed for geometry optimization of free 44BMBP in equilibrium and the Raman spectra for the optimized structures were simulated. Then, the same calculations were performed for the anionic 44BMBP. The calculated frequencies in Raman spectra were scaled by a single factor of 0.975 and the relative intensities of the peaks were normalized with respect to the largest peak near 1600 cm^{-1} . After optimization of the equilibrium geometry for a single 44BMBP molecule, we have found two isomers of the *cis*- and *trans*-forms with respect to the two mercaptomethyl groups in equilibrium (as insert in Figure 1(b) and 1(c)). The calculated results revealed that the latter is more stable by

only 23 cm^{-1} than the former, which means that both isomers can exist in solid state. The calculated Raman spectra for the optimized isomers look very similar to each other as shown in Figure 1(b) and 1(c), except for the difference between the calculated frequencies for the band near 2550 cm^{-1} in the experimental spectrum. Namely, the frequencies for the SH stretching vibration were calculated as 2595 and 2603 cm^{-1} for the *cis*- and *trans*-forms, respectively, in excellent agreement with the peak separation at 2550 and 2559 cm^{-1} observed in the OR spectrum of 44BMBP in solid state. It suggests that 44BMBP in solid state might be in both *cis*- and *trans*-forms. Then, the peaks at 790 and 974 cm^{-1} can be assigned as $\beta(\text{S-H})$ referring to the calculated frequencies for

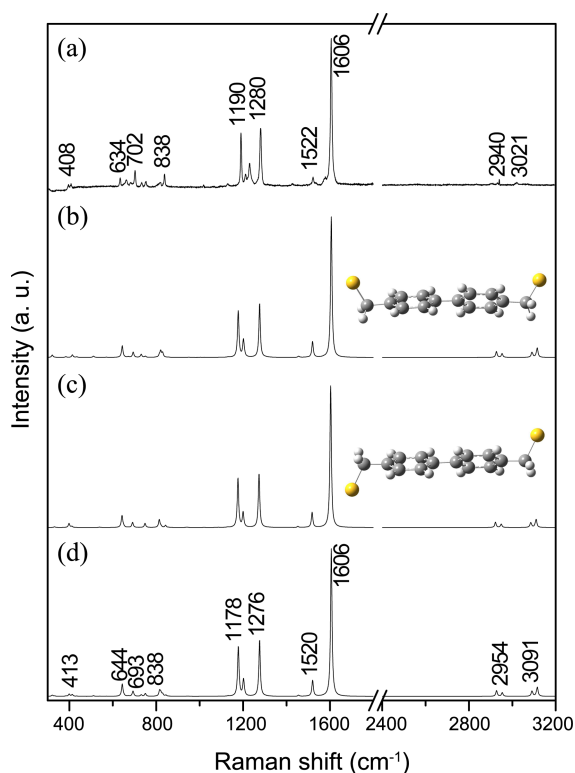


Figure 2. (a) Ordinary Raman spectrum of 4,4'- bis(mercaptomethyl)biphenyl (44BMBP) in basic condition. Calculated Raman spectra of (b) free *cis*-44BMBP and (c) *trans*-44BMBP in anionic form from density functional theory (DFT) calculations. (d) Raman spectra simulated for the two isomers under the assumption of equal composition in equilibrium were summed.

the two isomers (as listed in Table 1), which are absent in the OR spectrum of 44BMBP in basic condition.

Based on equilibrium geometries plausible for the 44BMBP molecule, Raman spectra of anionic 44BMBP were simulated as shown in Figure 2(b) and 2(c) for comparison with the experimental spectrum. It is worth noting that the twin peaks at 396 and 408 cm^{-1} and the ones at 733 and 752 cm^{-1} due to the out-of-plane skeletal modes can be completely simulated by summing the calculated spectra for the two anionic 44BMBP isomers as shown in Figure 2(d). Then, it has been found that the weak peak due to the $\text{C}_{\text{ring}}\text{-C}_{\text{methyl}}$ stretching vibration was red-shifted to 1211 cm^{-1} with distinct intensity, while the intense peak due to $\gamma_{\text{s}}(\text{CH}_2)$ was red-shifted to 1230 cm^{-1} with the small intensity as the SH groups in 44BMBP were deprotonated.

We report the surface-enhanced Raman spectrum of 44BMBP adsorbed on Ag surface for the first time. The SERS spectrum shown in Figure 3(a) basically seems similar to the one obtained in basic condition except for the distinctive features broadened and red-shifted for some vibrational modes. In addition, the fact that the vibrations related to the SH group completely disappears in the SERS spectrum suggests that the resulting dianion should interact with the silver surface through the two sulfur atoms. Accordingly, this means that 44BMBP adsorbs on the silver surface by forming two Ag-S bonds after deprotonation. However, since

this does not imply that any specific isomer is preferentially adsorbed on the Ag surface, it is additionally needed to examine the Raman scattering intensities for some vibrational modes using the surface selection rules in order to conclusively determine the molecular orientation on the silver surface although the quantum chemical calculations were performed to determine the corresponding structure upon adsorption.

The surface selection rules for Raman scattering of molecules adsorbed on metal surfaces state that the vibrational modes of the Raman tensor components involving the two axes in the surface plane are expected to exhibit the least enhancement, while the ones parallel to the surface normal would experience large enhancement. Although the surface selection rules have not been explicitly established, the enhancements for the C-H stretching bands in the SERS spectra have been used to determine the molecular orientation on the surface as a reliable probe. In this regard, the absence of the C-H stretching bands originating from the phenyl rings of 44BMBP in the SERS spectrum indicates the parallel orientation of the phenyl rings on the surface. Such parallel orientation is possible only for the geometry of the *cis*-form because of the steric hindrance from the two phenyl rings decussated against the Ag surface for the *trans*-form. Therefore, the Raman spectra were simulated for anionic *cis*-44BMBP bound to either Ag atom (Ag_1) or a cluster of three Ag atoms (Ag_3) at both ends at the B3LYP/DGDZVP

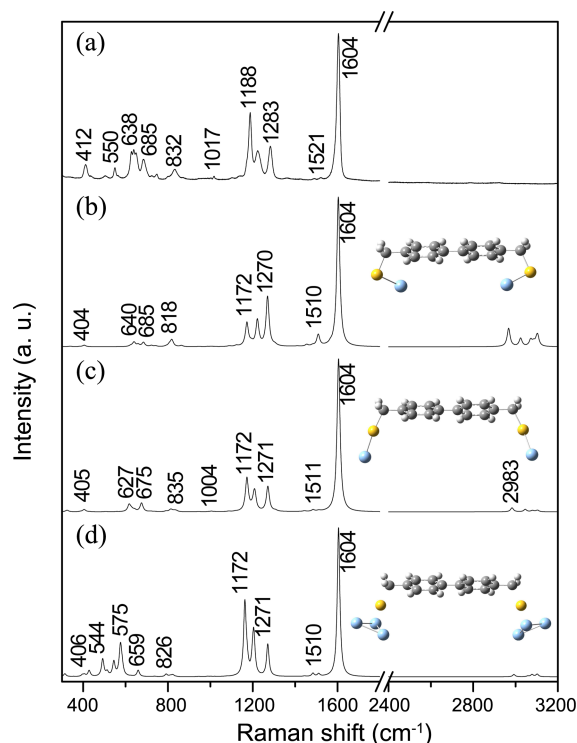


Figure 3. (a) Surface-enhanced Raman scattering (SERS) spectrum of 4,4'-bis(mercaptomethyl) biphenyl (44BMBP) adsorbed on silver nanoparticles. Calculated Raman spectra of anionic 44BMBP bound with the angle, $\angle\text{CSAg}$ of (b) 100° and (c) 160°, respectively, to each one Ag atom (Ag_1) at both ends from density functional theory (DFT) calculations. (d) Calculated Raman spectrum of anionic 44BMBP bound to each three Ag cluster (Ag_3) at both ends.

level and utilized to definitely assign the observed peaks in the SERS spectrum. First, the anionic *cis*-44BMBP bound to two Ag atoms at both ends was optimized and the Raman spectrum was simulated for the optimized structure as shown in Figure 3(b).

However, the calculated Raman spectrum seems slightly different in the region of $\sim 1200\text{ cm}^{-1}$ compared to the SERS spectrum in Figure 3(a). This mismatch might arise because the sulfur atoms having the $\angle\text{CSAg}$ of 100° are too close to the surface. Then, considering the realistic geometry of the molecule adsorbed on the Ag surface, the calculated Raman spectrum was obtained from density functional theory (DFT) calculations for the anionic *cis*-44BMBP bound with the $\angle\text{CSAg}$ of 160° to Ag atoms (Ag) at both ends as shown in Figure 3(c). An excellent agreement between the calculated and the experimental results was then achieved by simply adjusting the $\angle\text{CSAg}$ to be larger. Then, as an effort to obtain better results in the simulation, we calculated the SERS spectrum at the higher B3LYP/Gen (C, H, O=cc-pVTZ, Ag=LanL2DZ) level. Yet, the agreement with the experimental spectrum was similar to the one with the result calculated at B3LYP/DGDZVP level. In order to better understand the interaction between the molecule and the metal surface, the Raman spectra were calculated for the structures with the tilt angles of $0\text{--}90^\circ$ between the two phenyl rings in the anionic *cis*-44BMBP bound to the two Ag atoms with the C_2 symmetry. In such investigations, even though the Raman spectra except for the equilibrium geometry with the tilt angle of 37° reveal the imaginary frequencies, the calculated spectra were informative enough to account for the change in the Raman spectrum according to the change in the tilt angle of the phenyl rings. As have been expected in the biphenyl derivatives, only the C-H in-plane bands shift in frequency depending on the degree of $\pi\text{--}\pi$ interaction between the two phenyl rings of biphenyl. Besides, the C-H stretching bands in the simulated spectra (not shown here) distinctly appear, even for parallel as well as twisted orientations of the two phenyl

rings in 44BMBP with respect to the Ag surface. In addition, further calculations were performed for the anionic *cis*-44BMBP bound with the fixed $\angle\text{CSAg}$ of 150° to each cluster consisting of three Ag atoms (Ag_3) and the simulated spectrum is shown in Figure 3(d), although the calculation with metal cluster is very time consuming. Accordingly, we adopted the calculated results of anionic *cis*-44BMBP bound with the angle, $\angle\text{CSAg}$ of 160° to each one Ag atom (Ag) at both ends for the assignment of the vibrational bands in the SERS spectrum. Relative intensities of all the peaks represented in Figure 3 were normalized with respect to the largest peak at 1604 cm^{-1} . The intensities of the peaks at $412, 550, 627, 649, 685, 832,$ and 1188 cm^{-1} are larger in the experimental spectrum compared to the calculated ones, which will be considered later for the peak assignments.

Based upon the vibrational frequencies and normal mode vectors obtained from the DFT calculations, all the peaks observed in the experimental spectra of 44BMBP were identified and the results are listed in Table 1. For spectral assignments, the Mulliken notations²⁴ have been employed to indicate the normal modes in the SERS spectrum. The calculated normal modes associated with the prominent peaks in the SERS spectra and their Mulliken notations are presented in Figure 4. The normal mode vectors were examined for the peaks observed in the spectra and the assignments are given in comparison with the most similar modes in the Mulliken notation (Table 1). Thus, the most intense peaks observed at 1606 cm^{-1} in solid state and basic condition were broadened and red-shifted to 1604 cm^{-1} in the SERS spectrum, which can be assigned as ν_7 (ring C-C stretching). The strong peaks at 1188 and 1283 cm^{-1} in the SERS spectrum are assigned as ν_{17} (C-H in-plane) and ν_{14} (inter-ring C-C stretching), respectively. It indicates that the phenyl rings should interact *via* their π -systems lying flat against the surface of Ag. Then, the broad and distinct peak at 1224 cm^{-1} in the SERS spectrum can be alternatively assigned as ν_{16} ($\gamma_s(\text{CH}_2)$) or ν_{15} ($\text{C}_{\text{ring}}\text{--C}_{\text{methyl}}$ stretching), which

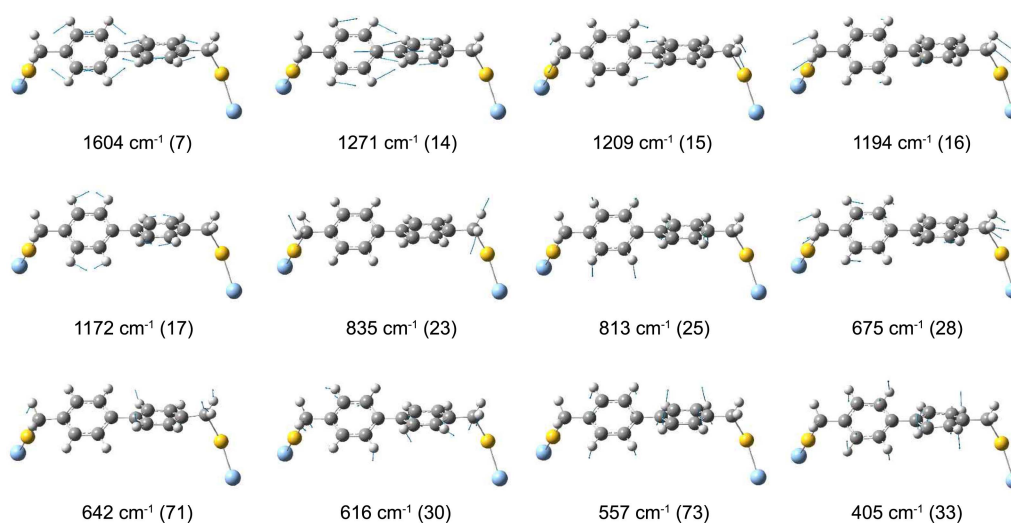


Figure 4. Normal mode vectors for the observed prominent Raman bands in Figure 3(a) obtained by density functional theory calculations. Vibrational wavenumbers and representative assignments according to the Mulliken notation are provided.

appeared at 1251 and 1221 cm^{-1} in solid state and at 1230 and 1211 cm^{-1} in basic condition, respectively. It was found that the relative intensities between ν_{16} and ν_{15} are inverted upon deprotonation in the SH groups. The prominent peaks observed at 649 and 685 cm^{-1} are assigned as ν_{71} ($\nu_{\text{as}}(\text{C-S})$) and ν_{28} ($\nu_{\text{s}}(\text{C-S})$), respectively, which are broad and red-shifted compared to the ones in basic condition. In addition, the distinct peak at 832 cm^{-1} in the SERS spectrum can be alternatively assigned as ν_{25} (C-H out-of-plane) or ν_{23} ($\beta_{\text{as}}(\text{CH}_2)$). Finally, the intense peak at 412, 550, and 627 cm^{-1} can be assigned as ν_{33} , ν_{73} , and ν_{30} , the out-of-plane skeletal vibration modes, respectively. It is to be emphasized that the intensities of the out-of-plane modes were greatly enhanced compared to the ones in basic condition and the calculated results due to flat orientation of the phenyl rings in anionic *cis*-44BMBP on the surface.

Conclusion

To characterize adsorption behavior of a molecule on the Ag surface, it is necessary to obtain information on normal modes from molecular structure and hence to analyze particular spectral changes arising from surface adsorption. In this respect, vibrational assignment of the Raman bands observed in the SERS spectrum is needed.

The qualitative spectral correlation between the spectra of many derivatives is generally utilized in such vibrational assignment. However, the SERS spectral analysis of a polyatomic molecule with large number of normal modes such as 4,4'-bis(mercaptomethyl)phenyl (44BMBP) should be a formidable work and also cause some major mismatch. In our previous works on SERS of 4,4'-biphenyl dicarboxylic acid and 4,4'-biphenyl dithiol on the Ag surface, the use of normal modes and their frequencies from the DFT calculation for a simple model allowed nearly complete assignment of the peaks observed in the spectra and intuited the comprehension on adsorption behavior. Adopting the same strategy for the SERS study of 44BMBP, the excellent agreement between the experimental and the calculated spectra was remarkably accomplished. In this regard, the adoption of the quantum chemical calculations will be very helpful for assigning the vibrational bands in the observed Raman spectra, even in the case that vibrational information is not available at all.

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