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Surface-Enhanced Raman Scattering of 4-Cyanobiphenyl on Gold and Silver Nanoparticle Surfaces

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The adsorption behavior of 4-cyanobiphenyl (CNBP) has been investigated by means of surface-enhanced Raman scattering (SERS). CNBP appeared to assume a tilted orientation on silver and gold. The presence of the ring C–H band denoted a rather vertical orientation of the biphenyl ring on Ag and Au. On the other hand, considerable red shifts of the ring-breathing modes with the increase in their bandwidths indicated a substantial π -type interaction between the benzene rings and metal substrates. On gold, the concentration-dependent SERS experiment showed CNBP to have a slightly perpendicular stance at its high surface coverage. The presence of the BH_4^- ion in sols was found to affect the adsorption reaction and surface orientation of CNBP. The spectral band analysis based on electromagnetic selection rule indicated that CNBP should have a slightly more vertical orientation on gold than on silver at the concentration of $\sim 10^{-4}$ M.

1. Introduction

Adsorption of nitriles on metal substrates has attracted much interest due to its potential applications in many areas including liquid crystal thin films^{1,2} and molecular electronics.^{3,4} In organometallic chemistry, nitriles are generally known to have a σ -type coordination to metal atoms via the nitrogen lone-pair electrons.^{5,6} Our compiled spectroscopic data^{7–16} have lead to a conclusion that a majority of aromatic nitriles were adsorbed on silver surface via a $\text{C}\equiv\text{N}$ π system.

Numerous cases have been reported indicating that the adsorption behavior depends on the substrates.^{17,18} Dithi-

ols are known to adsorb on gold as monothiolates by forming one single Au–S bond^{19–25} whereas they are usually adsorbed on silver by forming two Ag–S bonds.^{19–21} Our recent surface-enhanced Raman scattering (SERS) study indicated that 4-biphenylisocyanide has different orientations on Au and Ag sol surfaces.²⁶ The detailed origins of the different adsorption characteristics on Ag and Au have not been fully clarified, however.

Among the various spectroscopic methods, SERS has been utilized as a convenient technique to investigate self-assembled monolayers (SAMs) on metal surfaces.²⁷ The analysis of spectral features has provided detailed information on adsorption mechanism and chemical reactions on surfaces. We have recently studied surface-catalyzed polymerization reactions^{19–21} and the surface orientation of adsorbates^{26,28} by means of SERS.

The structure of biphenyl has been investigated in both theoretical and experimental ways.^{29–35} There have been

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several studies on the adsorption behaviors of biphenylthiols^{36–38} and surface orientation of 4-biphenylcarboxylic acid³⁹ on gold. 4-*n*-Pentyl-4'-cyanobiphenyl as a mesogenic unit in liquid crystal thin films have been recently investigated using time-resolved Fourier transform infrared spectroscopy.¹ Our recent SERS study has shown 4,4'-dicyanobiphenyl to have a rather flat geometry on Ag and Au surfaces.²⁸ In this article we present a SERS study of 4-cyanobiphenyl on silver and gold sols for a better understanding of adsorption behaviors and surface reactions of biphenyl monocarbonitriles.

2. Experimental Section

The silver and gold sols were prepared by following the recipes in the literature.⁴⁰ Approximately, 10 mL of 10^{-3} M AgNO_3 solution was added dropwise to 30 mL of 2×10^{-3} M NaBH_4 solution which was cooled to ice temperature. A 133.5 mg portion of KAuCl_4 (Aldrich) was initially dissolved in 250 mL of water, and the solution was brought to boiling. A solution of 1% sodium citrate (25 mL) was then added to the KAuCl_4 solution under vigorous stirring, and boiling was continued for ca. 20 min. The resulting Au sol solution was stable for several weeks. To 1 mL of Au sol or Ag sol solution was added a $\sim 10^{-2}$ M methanolic solution of 4-cyanobiphenyl (CNBP, Sigma Aldrich) dropwise to a final concentration of 10^{-5} to 5×10^{-4} M using a micropipet. All the chemicals otherwise specified were reagent grade, and triply distilled water, of resistivity greater than $18.0 \text{ M}\Omega \text{ cm}$, was used in making aqueous solutions. To estimate the sizes of sol particles, their TEM images were obtained with a JEM-200CX transmission electron microscope at 200 kV after placing sequentially a drop of colloidal solutions onto Ni/Cu grids. Raman spectra were obtained using a method described in the previous literature.¹⁹

3. Results and discussion

3.1. Raman Spectra. Figure 1 shows the ordinary Raman (OR) spectrum of CNBP in neat solid state, the Ag sol SERS spectrum, and the Au sol SERS spectrum, respectively. In the OR spectrum, the major bands associated with the ring vibrational modes can be divided into four symmetry species. The A_1 ring modes appeared at 995 (ν_{12}), 1039 (ν_{18a}), 1181 (ν_{9a}), 1513 (ν_{19a}), 1605 (ν_{8a}), and 3069 (ν_2) cm^{-1} . The bands at 788 (ν_{10a}), 807 (ν_{11}), and 1285 (ν_3) cm^{-1} could be ascribed to A_2 , B_1 , and B_2 , respectively. It was rather straightforward to correlate the OR bands with the Ag and Au SERS bands. Their peak positions are listed in Table 1 along with the appropriate vibrational assignments. Our assignment is based on the previous literature.^{26,41}

The concentration of CNBP in the sol was $\sim 10^{-4}$ M. Transmission electron microscopy (TEM) measurements showed the average diameters of silver and gold particles to be ~ 10 and ~ 17 nm, respectively. This implies that the SERS spectra shown in Figure 1b,c should correspond to CNBP on silver and gold at the concentration above a full-coverage limit by assuming that the adsorbate was oriented perpendicularly with respect to the colloidal surfaces.¹⁹

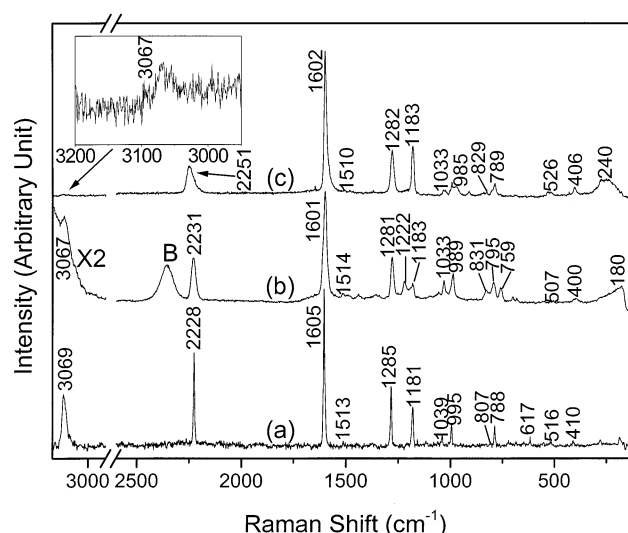


Figure 1. (a) OR spectrum of CNBP in the solid state. SERS spectra of $\sim 10^{-4}$ M CNBP in (b) silver sol and (c) gold sol. The ring C–H band was observed weakly in the Au SERS spectrum as shown in the inset of Figure 1c. The spectral region between 3100 and 2950 cm^{-1} in Figure 1b was magnified by a factor of 2 for a better presentation. The band labeled B at $\sim 2350 \text{ cm}^{-1}$ in Figure 1b was due to the BH_4^- species. The spectral region between 2950 and 2600 cm^{-1} was omitted due to the lack of any information.

Table 1. Spectral Data and Vibrational Assignment of CNBP^a

CNBP OR	CNBP Ag sol SERS ($\sim 10^{-4}$ M)	CNBP Au sol SERS ($\sim 10^{-4}$ M)	assignment ^b
In-Plane			
617 w	c	c	6b(B_2)
995	989	985 b	12(A_1)
1039	1033	1033	18a(A_1)
1181	1183	1183	9a(A_1)
	1222		7a(A_1)
1285	1281	1282	3(B_2)
1513 w	1514 w	1510 vw	19a(A_1)
1605	1601	1602	8a(A_1)
3069	3067	3067 w	2(A_1)
Out-of-Plane			
	759		4(B_1)
788	795	789 w	10a(A_2)
807 w	831	829	11(B_1)
Substituent			
410	400	406	$\gamma_s(\text{CN})$
516	507 w	526	$\delta_{as}(\text{CN})$
2228	2231	2251	$\nu(\text{CN})$

^a Unit in cm^{-1} . Abbreviation: vw, very weak; w, weak; b, broad.

^b In Wilson notation with symmetries based on C_{2v} point group.

^c Not found.

As shown in Figure 1b,c, it is noteworthy that the ring C–H stretching bands were identified at $\sim 3067 \text{ cm}^{-1}$, albeit weakly, both in the Au sol and in Ag sol SERS spectra. It has been well documented in the literature that the presence of the ring C–H stretching band in an SERS spectrum is indicative of a vertical (or at least tilted) orientation of the aromatic ring moiety on a metal substrate.⁴²

On the other hand, the ring-breathing mode ν_{12} which appeared at 995 cm^{-1} in the OR spectrum exhibited a substantial red shift in the Au SERS spectrum with the increase of its bandwidth as shown in Figure 1c. This result may indicate a direct interaction of the benzene

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rings on the gold surface.⁴³ The Ag sol SERS spectrum also showed a red shift and broadened bandwidth. In addition, the position of the ν_{8a} band varied from 1605 cm^{-1} in its neat state to 1601 and 1602 cm^{-1} in the Ag and Au SERS spectra, respectively. Except for the ν_{9a} band at $\sim 1180 \text{ cm}^{-1}$ and the ν_{19a} band at $\sim 1510 \text{ cm}^{-1}$, most in-plane vibrational modes were red shifted by 2–10 cm^{-1} in the SERS spectra. It is noteworthy that neither a substantial red shift nor a significant band broadening of the ring breathing modes was observed for the case of 4-biphenylisocyanide where the molecule is assumed to have a standing orientation on Ag and Au.²⁶ It seemed that a tilted orientation of CNBP was to occur on Ag and Au as proposed in the previous SERS study⁴⁴ of phthalic acid on a silver sol surface.

The band positions of both Ag and Au SERS spectra looked quite comparable except the two bands at 759 and 1222 cm^{-1} . These bands observed only in the Ag SERS spectrum could be ascribed to the ν_4 and ν_{7a} bands, respectively. Although it was uncertain why these bands did not appear in OR and Au SERS spectra, it may suggest different orientations of CNBP upon adsorption on Ag and Au.

The CN stretching frequencies at 2231 and 2251 cm^{-1} in Figure 1b,c were blue shifted by 3 and 23 cm^{-1} at $\sim 10^{-4}$ M, respectively, from that at 2128 cm^{-1} in the OR spectrum of a free state in Figure 1a. Considering the fact that the $\nu(\text{CN})$ bands were considerably broader in the SERS spectra, the cyano group seemed to directly interact with metal surfaces. The bandwidth (fwhm, full width at half-maximum) of the $\nu(\text{CN})$ band of a free state CNBP became broadened from 6 cm^{-1} into ~ 24 and $\sim 35 \text{ cm}^{-1}$ upon adsorption on silver and gold surfaces, respectively. The blue shifts of the $\nu(\text{CN})$ band were explained in coordination chemistry by invoking the fact that the nitrogen lone pair electrons have antibonding character and the electron donation to the metal surfaces may increase the strength of the CN bond.⁵ In our previous SERS studies,^{7–15} however, such blue shifts on a silver sol surface were mainly ascribed to the disruption of conjugation induced by the π coordination of the nitrile group to metals. Yet it seems a matter of conjecture to dictate the exact adsorption mechanism from our SERS spectra.

The broad band at 2350 cm^{-1} in the Ag sol SERS spectrum as shown in Figure 1b could be ascribed to BH_4^- species.¹⁴ We have to notice that the BH_4^- peak was observed only in Ag sol, since sodium citrate was used as a reducing agent for the preparation of Au sol. As reported in previous literature,^{14,16} the adsorption of aromatic nitriles seemed to be affected by the presence of the BH_4^- ion. In fact the peak positions of the $\nu(\text{CN})$ band were changed along with the BH_4^- peak at 2350 cm^{-1} in the Ag sol SERS spectra. Also, the $\nu(\text{CN})$ band was found to be quite red shifted and the SERS spectral quality became deteriorated considerably, when we added the BH_4^- ion into the Au sol. These results indicate that the adsorptions of CNBP on Ag and Au were considerably affected by the presence of the BH_4^- ion. It seems problematic to explain the differences in adsorption mechanism on Ag and Au merely by our spectral analysis, since the adsorption characteristics were found to change upon the BH_4^- ion present in the sols.

3.2. Surface Orientation. Since an unequivocal selection rule is not available for SERS, the exact tilt angle cannot be determined for CNBP at present. According to

Table 2. Relative Enhancement Factors of SERS Bands of CNBP at $\sim 10^{-4}$ M

symmetry type ^a	tensor element ^b	normal mode ^c	rel intens ($I_{\text{SERS}}/I_{\text{OR}}$) ^d	
			Ag	Au
A ₁	α_{xx} α_{yy} α_{zz}	2	0.543	0.121
		12	2.23	0.893
		8a	1.38	2.18
		9a	0.766	2.81
		18a	1.00	1.00
		19a	1.24	0.632
A ₂	α_{xy}	10a	1.74	1.55
B ₁	α_{xz}	11	4.40	2.17
B ₂	α_{yz}	3	1.42	1.80
$\gamma_s(\text{CN})$			2.58	4.56
$\delta_{as}(\text{CN})$			1.24	2.52
$\nu(\text{CN})$			0.887	1.04

^a Symmetry types corresponding to the C_{2v} point group. ^b Subscripts, i.e., x , y , and z , correspond to the conventional molecular axes. The x -axis lies perpendicular to the two benzene rings, and the z -axis passes through the CN group. ^c See Table 1 for the vibrational assignment. ^d Normalized to 1.00 for the 18a band at ca. 1033 cm^{-1} in the SERS spectra.

the electromagnetic (EM) theory on the SERS selection rule,^{45–47} vibrations along the direction perpendicular to the surface are expected to be more enhanced than vibrations in the parallel direction. This rule suggested that the in-plane vibration modes should be more enhanced than the out-of-plane ones. For CNBP at $\sim 10^{-4}$ M, most ring modes were found to belong to the in-plane mode except the ν_{10a} and ν_{11} bands. As shown in Table 2, the relative intensity of the ν_{11} band on silver was measured to be approximately twice larger than that on gold. The ν_{10a} band intensity was also found to be slightly stronger on silver. Moreover the ν_4 band was observed only in the Ag sol SERS spectrum. These results may imply that CNBP at $\sim 10^{-4}$ M has a more parallel orientation on silver sol.

Moskovits proposed that the relative enhancement should be in the order of $A_1 > B_1 \approx A_2 > B_2$ for flat orientation and of $A_1 > B_1 \approx B_2 > A_2$ for vertical orientation.^{9,46} In addition, Creighton has shown on the grounds of the EM surface selection rule that for molecules with C_{2v} symmetry, the relative enhancement factors for A_1 , A_2 , B_1 , and B_2 modes would be 1–16, 1, 4, and 4 for edge-on orientation whereas these would be 1–16, 4, 4, and 1 for face-on orientation.⁴⁷

On these grounds, the relative surface enhancements have been evaluated for the normal modes of CNBP. The ring mode intensities were normalized to the intensity of the ring 18a mode in both the OR and SERS spectra, and then the SERS-to-OR intensity ratios were computed for each peak regarding them as the relative enhancement factors. Table 2 lists the intensity ratios with the relevant molecular polarizability elements. The subscripts, i.e., x , y , and z , in Table 2 correspond to the conventional molecular axes as shown in Figure 2a. Namely, the x -axis lies perpendicular to the ring and the z -axis passes through the cyano group.

For CNBP, the intensities of the ring modes on Au seemed quite comparable with those on Ag. Although not definitive due to insufficient ring modes, it seemed to suggest that the CNBP has a tilted stance on both the Ag and Au surfaces. For CNBP at $\sim 10^{-4}$ M, the relative band enhancements were found to be in the order of $B_1 > B_2 >$

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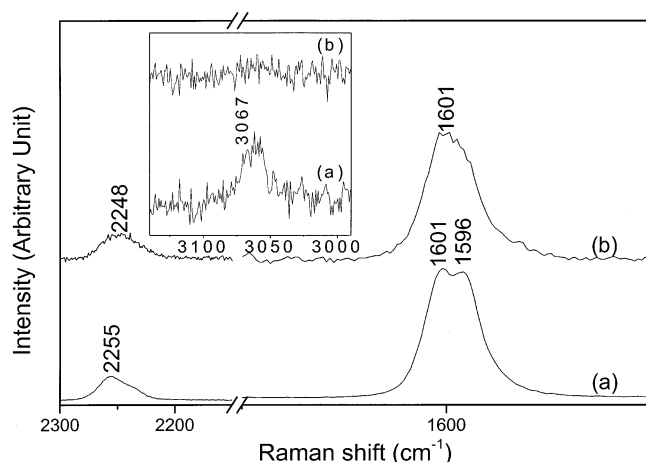


Figure 2. SERS spectra taken at (a) a high bulk concentration ($\sim 5 \times 10^{-4}$ M) and (b) a low concentration ($\sim 10^{-5}$ M) of CNBP in gold sol. The spectral regions in 2300–2150 and 1650–1550 cm^{-1} were expanded to compare the differences of the $\nu(\text{CN})$ and ν_{8a} bands, respectively. The inset is drawn to show the ring $\nu(\text{C-H})$ region at ~ 3060 cm^{-1} .

A_2 on gold and $B_1 > A_2 > B_2$ on silver as shown in Table 2. Moreover the relative band enhancement ratio of the two $\nu_{11}(B_1)$ and $\nu_3(B_2)$ modes is close to 4:4 on gold indicating a more perpendicular orientation, whereas it is near to 4:1. These results may suggest a more parallel orientation on Ag and support our previous conclusion that the biphenyl ring has a more vertical orientation on Au at $\sim 10^{-4}$ M. The relative enhancement factors of the $\nu(\text{CN})$, $\delta_{as}(\text{CN})$, and $\gamma_s(\text{CN})$ bands on Au were found to be a little larger than those on Ag as shown in the Table 2.

The tilted structure of CNBP on Ag and Au also suggests a possibility that its two benzene rings have a twisted structure on the surfaces as in the previous reports.^{29–35} For CNBP, the ν_{6b} band was not observed in the Ag or Au SERS spectrum. The absence of the in-plane quadrant bending mode ν_{6b} may suggest a substantial ring π interaction of the two benzene rings on Ag and Au.³⁹ As evidenced in the SERS spectra, a direct π -interaction between the two benzene rings and the metals also existed on the surfaces, however.

Figure 2a,b shows the SERS spectra in the wavenumber regions of 2300–2150 and 1650–1550 cm^{-1} , taken in gold sol at the concentrations of $\sim 5 \times 10^{-4}$ and $\sim 10^{-5}$ M, respectively. This result indicates that CNBP did not adsorb well to show SERS enhancement on Au at concentrations lower than $\sim 10^{-5}$ M. Although it was difficult to conduct more systematic concentration-dependent SERS experiments in a wider concentration range due to a weak binding of the nitrile on Au sol, these results have suggested a possibility of different structures of CNBP depending on the surface coverage. As seen in Figure 2a, the spectral feature at ~ 1600 cm^{-1} was split into the two bands at 1596 and 1601 cm^{-1} . The feature at 1596 cm^{-1} became stronger at higher concentrations of CNBP. Although it is tempting to assign the ring $\nu_{8b}(B_2)$ mode at ~ 1596 cm^{-1} , we prefer to assign the same $\nu_{8a}(A_1)$ band, since no peak is separately identified in this wavenumber region, when the concentration is lower than $\sim 10^{-4}$ M in the gold sol or in the OR spectrum. The splitting is presumably caused by different enhancements of the two benzene rings of CNBP on Au since they did not lie

in the same plane. Along with this splitting, the frequency position of the $\nu(\text{CN})$ band was blue shifted at high concentrations. As shown in the inset, the $\nu(\text{CH})$ band prominent at ~ 3060 cm^{-1} almost disappeared at the low concentration of $\sim 10^{-5}$ M. This result may indicate that CNBP has a more vertical orientation at the high concentration. On silver, the asymmetric line shape at ~ 1600 cm^{-1} also suggested a multiple structure, although such a noticeable splitting as in Au was not observed under our experimental condition. For a time-dependent study, we took SERS spectra on Au after a certain time was elapsed. Our spectra indicated almost no change at 10^{-5} – 10^{-4} M in Au sol for ~ 1 h, due to a weak aggregation of CNBP and gold sol. On silver, we could not obtain a consistent result since the spectrum was greatly affected by the sol condition.

Considering that the benzene rings of CNBP were found to have a tilted orientation on gold and silver substrates, the association between the exact bonding mechanism and the adsorbate orientation seems still a matter of conjecture. Our recent SERS study has shown that 4,4'-dicyanobiphenyl showed comparable blue shifts with those of CNBP, although it was assumed to have a flat orientation on Ag and Au.²⁸ It seems difficult to explain the adsorption mechanism only by referring the $\nu(\text{CN})$ band. The simultaneous involvement of σ - and π -type coordination may explain that CNBP has to assume a tilted orientation on the surfaces.

The detailed origins in different adsorption characteristics of CNBP on Au and Ag are not still clear yet. Energetic or kinetic factors may also result in different adsorption behaviors on Ag and Au.¹⁹ Since the experiment was conducted in the solution phase and the Raman spectra appeared to depend on the sol condition as well as the bulk concentration, we have to mention that our spectral data mainly provide information on the adsorption pathways occurring at the surface rather than on the electronic interaction between the adsorbate and substrate. We plan to conduct electrochemical studies combined with infrared reflection absorption spectroscopy and theoretical calculations in order to firmly understand the adsorption characteristics and surface orientations of CNBP on Ag and Au.

4. Summary and Conclusion

The spectral evidence in silver and gold sols indicated that the biphenyl ring group should have a tilted orientation with respect to both the surfaces. The adsorption characteristics of CNBP on Ag and Au were found to depend on the sol condition as well as the bulk concentration. The frequency positions of the $\nu(\text{CN})$ bands were affected by the presence of the BH_4^- ion. On gold, the concentration-dependent SERS spectra have shown CNBP to have different orientations depending on its surface coverage. On the basis of the electromagnetic SERS selection rule, we also attempted to study the orientation of CNBP on Ag and Au sol surfaces by analyzing the relative enhancement factors of the vibrational bands. The band analysis indicated that the two benzene rings should take a slightly more vertical stance on Au at the same bulk concentration of $\sim 10^{-4}$ M when the BH_4^- ion was present only in the Ag sol solution.

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