

Adsorption of 4-Biphenylisocyanide on Gold and Silver Nanoparticle Surfaces: Surface-Enhanced Raman Scattering Study

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Received: January 24, 2002; In Final Form: April 30, 2002

The adsorption behavior of 4-biphenylisocyanide (BPNC) has been studied by means of surface-enhanced Raman scattering (SERS). BPNC has been found to adsorb on silver and gold via the carbon lone pair electrons assuming a standing geometry with respect to the surfaces. The presence of the $\nu(\text{CH})$ band in the SERS spectra indicated a vertical orientation of the biphenyl ring of BPNC on Ag and Au. Neither a substantial red shift nor a significant band broadening of the ring breathing modes implied that a direct ring π orbital interaction with metal substrates should be quite low. On the basis of the electromagnetic surface selection rule, we attempted to explain the orientation of the adsorbate on Ag and Au surface by determining the relative enhancement factor of each vibrational band. The band analysis indicated that BPNC should have a slightly more vertical orientation on silver than on gold. The frequency of the $\nu(\text{NC})$ band on gold increased by $\sim 10\text{ cm}^{-1}$ than that on silver surface. Such a higher blue shift of the $\nu(\text{NC})$ stretching vibration in the gold sol SER spectrum may be due to a higher electronegativity of gold.

Introduction

Despite the equivocal selection rule and limited applicability to a few metals, surface enhanced Raman scattering (SERS) phenomena has become one of the most sensitive techniques to monitor the adsorbates on metal substrates at submonolayer coverage limit ever since its discovery by Fleischmann et al.¹ The analysis of spectral features has provided detailed information on adsorption mechanism, surface reactions, and the surface orientation of adsorbates.² Creighton proposed the relative enhancement factors for different orientations of C_{2v} symmetry molecules on surfaces based on electromagnetic (EM) selection rule.³ Gao and Weaver inferred surface orientation of benzene derivatives from the band shift and broadening of the ring modes.⁴

There have been several studies exploring the chemisorption of the organoisocyanide on metals including Ag, Au, Cr, Co, Pt, Pd, and Ru.^{5–17} Using diffuse reflectance infrared Fourier transform spectroscopy, Robertson and Angelici concluded that 1,4-phenylenediisocyanide should adsorb on gold via one N–C bond by observing both coordinated and uncoordinated NC bands at 2181 and 2121 cm^{-1} , respectively.⁶ 4,4'-Biphenyldiisocyanide was also found to adsorb on Au with its one pendant NC group by a reflection–absorption infrared spectroscopy, ellipsometry, and contact-angle measurement study.⁷ The adsorptions of mono-, bi-, and tridentate alkyl isocyanides have

also been investigated on Au powder surface.⁸ Lin and McCarley reported that 1,6-diisocyanohexane could form a robust layer on Pt and Au surfaces.⁹ We recently reported the adsorption characteristics of 1,4-phenylenediisocyanide on silver by means of infrared and Raman spectroscopy.¹⁰ 1,4-Phenylenediisocyanide was found to have a vertical orientation on the silver surface via its carbon lone-pair electrons. Several binding modes such as terminal upright bonding, bridging, and lying flat have been observed for isocyanides adsorbed on metal surfaces.¹² The preparation of aryl isocyanide thin films attracted much attention due to its potential application as a molecular wire.¹⁵ Electronic transport between the metals and 1,4-phenylenediisocyanide has been studied by Chen et al.¹⁷ Understanding of electron transport property in aryl isocyanide self-assembled monolayers on the metal substrates should be important to design a new nanoscale molecular electronic device.

Numerous cases have been reported indicating that the adsorption behavior depends on the substrates. Aliphatic thiols were known to adsorb with the alkyl chain tilted on gold about 30° with respect to the surface and by $\sim 7^\circ$ on silver.¹⁸ By applying the infrared surface selection rule, the benzene ring of 4-methoxybenzylcyanide appeared to have a more parallel orientation on silver.¹⁹ For 1,2-benzenedithiol, the tilt degrees of benzene ring were estimated to be ca. 51° on gold and 38° on silver with respect to the surface normal.²⁰ The detailed origins of the different adsorption characteristics on Ag and Au have not been fully clarified, however. In this report we present SERS study of 4-biphenylisocyanide on silver and gold nanoparticle surfaces for a better understanding of its adsorption characteristics on Ag and Au. The purpose of this study is to apply the symmetry-based electromagnetic selection rule to explain different adsorbate orientation on gold and silver surfaces.

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Experimental Section

Preparation of Samples. BPNC was prepared from 4-aminobiphenyl by a literature method.²¹ The compound 4-aminobiphenyl was purchased from Sigma Aldrich. The prepared BPNC sample was examined by its ¹H NMR spectrum in CDCl₃ solvent using a Bruker AVANCE 300 MHz spectrometer. The citrate stabilized gold sol was synthesized by following the recipes in the literature:²² 133.5 mg of KAuCl₄ (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 KAuCl₄ solution under vigorous stirring, and boiling was continued for ca. 20 min. The resulting Au sol solution was stable for several weeks. For Ag sol, approximately 10 mL of 10⁻³ M AgNO₃ solution was added dropwise to 30 mL of 2 × 10⁻³ M NaBH₄ solution which was chilled to ice temperature. All the chemicals otherwise specified were reagent grade and triply distilled water, of resistivity greater than 18.0 MΩ cm, was used in making aqueous solutions. To estimate the sizes of gold colloidal particles, their TEM images were obtained with a JEM-200CX transmission electron microscope at 200 kV after placing sequentially a drop of Au colloidal solution onto Ni/Cu grids.

Raman Measurements. Raman spectra were obtained using a Renishaw Raman system model 2000 spectrometer equipped with an integral microscope (Olympus BH2-UMA). The 514.5 nm radiation from a 20 mW air-cooled argon ion laser (Spectra Physics Model 163-C4210) and the 632.8 nm from a 17 mW air-cooled He/Ne laser (Spectra Physics Model 127) were used as the excitation sources for the Ag and Au sol SERS experiments, respectively. To 1 mL of Au sol or Ag sol solution was added a 0.05 M ethanolic solution of BPNC dropwise to a final concentration of 5 × 10⁻⁴ M using a micropipet. The yellowish silver and purple gold sols became dark blue and bluish green, respectively, by the addition of BPNC. An appropriate holographic notch filter was set in the spectrometer depending on the excitation source. Raman scattering was detected with 180° geometry using a peltier cooled (-70 °C) CCD camera (400 × 600 pixels). A glass capillary (Chase Scientific) with an outer diameter of 1.1 mm was used as a sampling device. Data acquisition times used in the Ag and Au sol SERS experiments were 90 s. The holographic grating (1800 grooves/mm), and the slit allowed the spectral resolution to be 1 cm⁻¹. The Raman band of a silicon wafer at 520 cm⁻¹ was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be better than 1 cm⁻¹. The Raman spectrometer was interfaced with an IBM-compatible PC, and the spectral data were analyzed using Renishaw WiRE software v. 1.2 based on the GRAMS/32C suite program (Galactic).

X-ray Diffraction Measurements. X-ray diffraction measurements were carried out to examine the crystallinity of Au and Ag nanoparticles. The colloidal nanoparticles were dried in a vacuum oven to evaporate water for the X-ray powder diffraction measurements. The patterns were obtained at a scanning rate of 3° per minute by a Rigaku D-MAX/IIIC diffractometer using Cu Kα radiation at 0.154 nm.

Results and Discussion

OR and Ag sol SERS Spectra of BPNC. Figure 1a,b shows the ordinary Raman (OR) spectrum of BPNC in neat solid state and the Ag sol SERS spectrum, respectively taken using an Ar-ion laser at 514.5 nm. To obtain information on the surface adsorption mechanism, it is necessary to analyze spectral changes according to the adsorption process. A correct vibra-

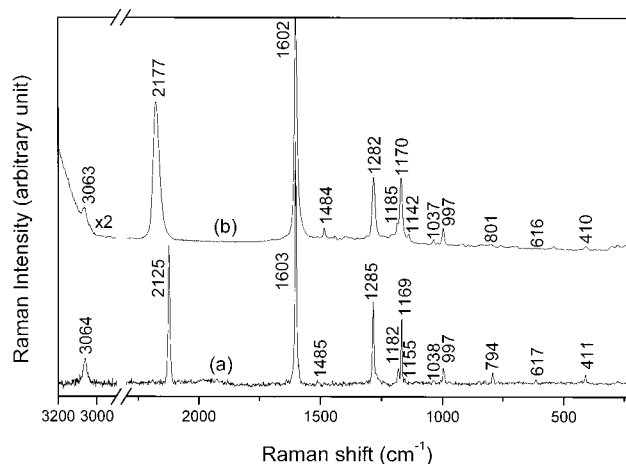


Figure 1. (a) OR spectrum of BPNC in neat solid state and (b) SERS spectrum of $\sim 5 \times 10^{-4}$ M BPNC in aqueous silver sol. Both spectra were taken using the Ar-ion laser at the 514.5 nm radiation. The spectral region between 2900 and 2300 cm⁻¹ was omitted due to the lack of any information. The spectral region between 3200 and 2900 cm⁻¹ in Figure 1b was magnified by a factor of 2 for a better presentation.

TABLE 1: Spectral Data and Vibrational Assignment of BPNC^a

OR	Ag sol SERS	Au sol SERS	assignment ^b
In-Plane			
3064	3063	3064vw	2 (A ₁)
1603	1602	1600	8a (A ₁)
1485w	1484	not found	19a (A ₁)
1285	1282	1282	3 (B ₂)
1182	1185	1188	9a (A ₁)
1169	1170	1173	9b (B ₂)
1155	1142	not found	18b (B ₂)
1038	1037	1038	18a(A ₁)
997	997	998	12 (A ₁)
617	616	616w	6b (B ₂)
Out-of-Plane			
794	801w	804	10a(A ₂)
411	410	411	10b (B ₁)
Substituent			
411	410	411	γ _s (NC)
2125	2177	2187	ν(NC)

^a Unit in cm⁻¹. Abbreviation: vw, very weak; w, weak. ^b Based on ref 27 in Wilson notation. The symmetry in the parenthesis corresponds to C_{2v} point group. ^c The band at 411 cm⁻¹ may be ascribed to either ν_{10b} or γ_s(NC).

tional assignment is prerequisite in this respect. Consulting the earlier vibrational assignments,²³⁻²⁷ we analyzed the Ag sol SERS spectrum in Figure 1b. In the OR spectrum, the major bands associated with the ring vibrational modes can be divided into four symmetry species assuming C_{2v} symmetry.²⁷ The A₁ ring modes appeared at 997 (ν₁₂), 1038 (ν_{18a}), 1182 (ν_{9a}), 1485 (ν_{19a}), 1603 (ν_{8a}), and 3064 (ν₂) cm⁻¹. The bands at 794 (ν_{10a}) and 411 (ν_{10b}) cm⁻¹ could be ascribed to A₂ and B₁ modes, respectively. The B₂ ring modes appeared at 1285 (ν₃), 1169 (ν_{9b}), 1155 (ν_{18b}), and 617 (ν_{6b}) cm⁻¹. It was rather straightforward to correlate the OR bands with the Ag SERS bands. Their peak positions are listed in Table 1 along with the appropriate vibrational assignments.

The concentration of BPNC in the Ag sol was $\sim 5 \times 10^{-4}$ M. According to the TEM measurement, the average diameter of silver particles was ~ 10 nm, so the concentration of BPNC required for the monolayer coverage was estimated to be 3.0×10^{-6} M, assuming that the adsorbate was oriented perpendicularly with respect to the colloidal silver surface.²⁸ This implies

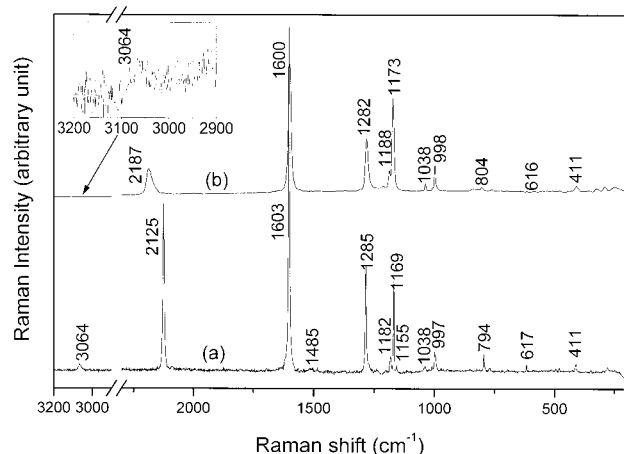


Figure 2. (a) OR spectrum of BPNC in neat solid state and (b) SERS spectrum of $\sim 5 \times 10^{-4}$ M BPNC in aqueous gold sol. The spectral region between 2900 and 2300 cm^{-1} was omitted due to the lack of any information. Both spectra were taken using the He–Ne laser at the 632.8 nm radiation.

that the SERS spectrum shown in Figure 1b corresponds to BPNC on silver at the concentration far above a full-coverage limit.

As shown in Figure 1b, it is noteworthy that the benzene ring CH stretching band is identified at $\sim 3063 \text{ cm}^{-1}$. It has been well documented in the literature that the presence of the ring CH stretching band in an SERS spectrum is indicative of a vertical (or at least tilted) orientation of the benzene ring moiety on a metal substrate.^{4,29} Much the same conclusion was made in the analysis of the SERS spectra of *p*-xylene- α,α' -dithiol²⁸ and 1,4-benzenedithiol³⁰ in an aqueous gold sol. The $\nu(\text{NC})$ stretching frequency at 2177 cm^{-1} in Figure 1b is higher by 52 cm^{-1} than that of a free state in Figure 1a. The bandwidth (fwhm: full width at half-maximum) of the $\nu(\text{NC})$ band of a free state BPNC became broadened from 8 to 30 cm^{-1} upon adsorption on silver surface. This blue shift was explained by invoking the fact that the carbon lone pair electrons have antibonding character and the electron donation to the Ag surface may increase the strength of the NC bond.¹⁰

OR and Au sol SERS Spectra of BPNC. Figure 2a,b shows the ordinary Raman (OR) spectrum of BPNC in neat solid state and the Au sol SERS spectrum, respectively, taken using a He–Ne laser at 632.8 nm. The sample of BPNC for OR spectrum in Figure 2a was identical to that presented in Figure 1a. According to the TEM measurement, the average diameter of gold particles was $\sim 17 \text{ nm}$, so the concentration was also much higher than that required for its monolayer coverage.²⁸ It has been recently reported that methyl isocyanide adsorbs on Pd-(111) has a rather parallel orientation at low surface coverage whereas it has a more perpendicular geometry as the surface coverage increases.¹¹ Our recent SERS study of 1,4-phenylene-diisocyanide on colloidal surface indicated that the adsorbate should have a more vertical orientation particularly at its high surface coverage. Due to a poor spectral quality at low concentrations, we have not attempted to study any orientation change depending on the surface coverage as in the studies of dithiols.^{28,30}

As shown in the inset of Figure 2b the benzene ring CH stretching band was identified very weakly at $\sim 3064 \text{ cm}^{-1}$. This was due to a weak response of the CCD camera at the far wing of the He–Ne laser excitation frequency of 632.8 nm. The position of the ν_{8a} band of BPNC in gold sol appeared at 1600 cm^{-1} while it appeared at 1602 cm^{-1} in silver sol. This result implied a more ring π interaction on Au.^{28,30}

TABLE 2: Relative Enhancement Factors of SERS Bands of BPNC in Ag and Au SERS

			relative enhancement factor ($I_{\text{SERS}}/I_{\text{OR}}$) ^d	
symmetry type ^a	tensor element ^b	normal mode ^c	Ag sol SERS	Au sol SERS
A ₁	α_{xx} α_{yy} α_{zz}	2	2.11	0.392
		12	8.40	8.33
		8a	6.62	2.24
		9a	7.00	7.00
		18a	9.94	9.24
		19a	16.7	not found
A ₂	α_{xy}	10a	0.994	1.19
B ₁	α_{xz} α_{yz}	10b	3.09	4.14
B ₂		3	5.26	2.85
		6b	2.20	0.931
		9b	6.93	6.09
		18b	15.1	not found
$\gamma_s(\text{NC})$			3.09	4.14
$\nu(\text{NC})$			8.01	0.910

^a Symmetry types corresponding to the C_{2v} point group from ref 27.

^b Subscripts, i.e., x , y , and z , correspond to the conventional molecular axes. The x -axis lies perpendicular to the ring, and the z -axis passes through the NC group. ^c See Table 1 for the vibrational assignment.

^d Normalized to 7.00 for the 9a band at ca. 1180 cm^{-1} in the SERS and OR spectra.

The $\nu(\text{NC})$ stretching peak on Au was blue shifted by 62 cm^{-1} from that of a free state. Also, the bandwidth (fwhm: full width at half-maximum) of the $\nu(\text{NC})$ band of a free state BPNC became broadened from 8 into 27 cm^{-1} upon adsorption on gold surface. The frequency of the $\nu(\text{NC})$ mode on gold increased higher by 10 cm^{-1} than that on silver surface. Such a higher blue shift indicated the donation from the $\text{N}\equiv\text{C}$: group to the Au surface was more efficient.³¹ On the other hand, it was found that the $\nu(\text{NC})$ band on Ag was several times more enhanced than that on Au. From the electromagnetic surface selection rule,^{3,24,32,33} the vibrational mode perpendicular to the surface is more enhanced than the parallel mode. It is not absolutely certain however whether the dissimilarity of the $\nu(\text{NC})$ bands should indicate a different orientation of BPNC on Ag and Au. The detailed discussion will be described in the following sections.

Electromagnetic Surface Selection Rule. It is unfortunate that the structural change cannot be analyzed more precisely from the SERS spectra since the set of SERS selection rules established so far is highly dependent on the specific enhancement mechanism.^{3,24,32,33} The conclusion made herein through an analysis of a few selected peaks agrees, at least qualitatively, with the prediction based on the electromagnetic (EM) selection rule. Table 2 lists the intensity ratios with the relevant molecular symmetry elements. The ring mode intensities were normalized to the intensity of the ring ν_{9a} mode in each SERS spectrum.

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.³² For most bands of BPNC, the relative band enhancements were found to be in the order of $A_1 > B_1 \approx B_2 > A_2$ on both gold and silver as shown in Table 2. Although not definite, this result suggested a rather vertical orientation of BPNC with respect to the surfaces.

As mentioned, according to the electromagnetic (EM) theory on the SERS selection rule,^{3,24,32,33} as vibrations along the direction perpendicular to the surface should be more enhanced than the parallel ones. This rule suggested that the in-plane vibration modes of molecules adsorbed in a perpendicular orientation should be more enhanced than the out-of-plane ones. For BPNC, although most ring modes were found to belong to

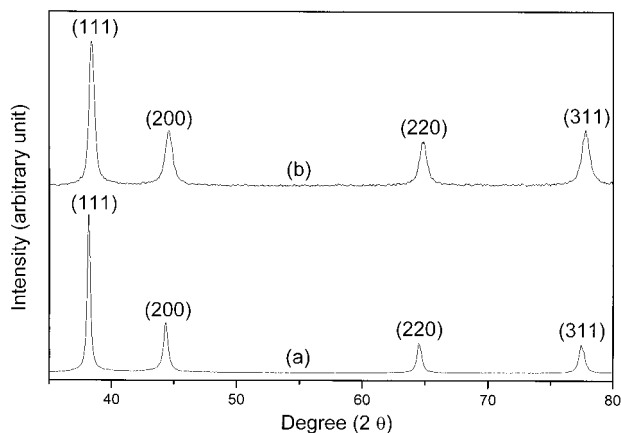


Figure 3. X-ray diffraction patterns of the prepared (a) Ag and (b) Au nanoparticles.

those of in-plane modes, the feature at ~ 410 and ~ 800 cm^{-1} could ascribe to the ν_{10b} and ν_{10a} out-of-plane ring modes. The weakness of the out-of-plane bands suggested that the adsorbate should have a rather vertical structure. As shown in Table 2, the relative intensities of the ν_{10a} and ν_{10b} bands on gold were measured to be slightly larger than those on silver. These results suggested that BPNC should have a slightly more parallel orientation on gold. On silver, the relative enhancement factor of the $\nu(\text{NC})$ stretching band was found to be several times stronger whereas the out-of-plane $\gamma_s(\text{NC})$ bending band was a little smaller as shown in the Table 2. This result also supported a more vertical stance of the isocyanide group on silver.

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.³ On these grounds, the relative intensities have been evaluated for the normal modes of BPNC. First, the relative enhancement factor of the $\nu_{10a}(A_2)$ band was found to be a little stronger on Au. In addition the relative band enhancements of the B_2 modes with respect to that of the B_1 mode were found to be larger on silver. All these results supported a more parallel orientation on gold.

X-ray Diffraction Patterns of Nanoparticles. We should mention that several crystal faces are present on the nanoparticle surfaces due to the variation in the size of particles. X-ray diffraction patterns of the Ag and Au nanoparticles were measured to examine the crystallinity of the nanoparticles as shown in Figure 3a,b. Their diffraction patterns agreed well with the previous reports.^{34,35} The (111), (200), (220), and (311) planes represent a cubic structure of the metallic silver and gold. BPNC may thus have a different orientation due to differences in packing on each crystal face. This result implies that we obtained only an average orientation of the species with respect to the several crystal planes existed on the nanoparticle surfaces. It is a matter of conjecture as to how polycrystalline surfaces of nanoparticles would affect our observed orientation. It is noteworthy that the diffraction patterns of the Ag and Au nanoparticles showed quite analogous features that the (111) planes were most prevalent among the several crystal faces as shown in Figure 3a,b. It is not certain however whether the similar crystal structures in the two Au and Ag nanoparticles may abate an error due to the polycrystalline surfaces. In addition, the absolute size of the nanoparticles may yield a difference in the types of crystal faces. As mentioned, the average diameters of the silver and gold particles were 10 and 17 nm, respectively, for our experiment. We plan to investigate

a change of the crystal faces depending on the size of nanoparticles by high-resolution TEM and X-ray diffraction measurements. A resulting diversification in orientation of BPNC depending on the size will also be examined by a SERS technique.

Comparison with Nitriles. In organometallic chemistry, nitriles are generally known to have a σ -type coordination to metal atoms via the nitrogen lone-pair electrons.^{36,37} The compiled SERS data^{23,38–45} of various aromatic nitriles, however, have led a conclusion that a majority of aromatic nitriles were adsorbed on the silver surface via $\text{C}\equiv\text{N}$ π system by referring to the spectral shifts of the $\nu(\text{CN})$ bands.

We are currently studying the adsorption characteristics of 4-cyanobiphenyl (CNBP), a geometry isomer of BPNC on colloidal silver and gold surface by means of SERS.⁴⁶ CNBP appeared to assume a rather vertical orientation on the silver and gold surfaces with the prominent appearance of the ring CH stretching band. On the other hand, the CN stretching frequencies of CNBP in the Ag sol and Au sol SERS spectra were only blue-shifted by 3 and 23 cm^{-1} , respectively. CNBP was assumed to adsorb on the surfaces also via $\text{C}\equiv\text{N}$ π system. Moreover the ring breathing mode ν_{12} in the OR spectrum exhibited a substantial red shift in the Au and Ag SERS spectra with much broadened bandwidth. This result indicated a direct interaction of the benzene rings on both gold and silver surfaces,⁴ whereas BPNC showed almost no direct interaction between its benzene rings and metal substrates. Another noteworthy point is that the analysis of the relative band intensities based on electromagnetic SERS selection rule suggested that the biphenyl ring of CNBP on gold should take a slightly more perpendicular stance with respect to the gold surface in opposite to the case of BPNC. In addition the relative enhancement factor of the $\nu(\text{CN})$ band in CNBP was larger on Au, whereas the $\nu(\text{NC})$ band of BPNC was several times more enhanced on Ag. Much the same observation has been obtained on the study of 1,4-phenylenediisocyanide¹⁰ and its geometry isomer, 1,4-dicyanobenzene.²³ Although the origin of the different adsorption mechanism is uncertain, it seemed to be advantageous to use aryl isocyanides instead of aromatic nitriles for a molecular wire, considering its more vertical orientation and superior electron donating capability to the metal substrates.

Benzene Rings in BPNC. To better check the role of the additional phenyl ring in the adsorption of aromatic isocyanides on Ag and Au, we examined the SERS spectra of phenylisocyanide (PhNC) on Ag and Au. PhNC was prepared from aniline by a literature method.²¹ The SERS spectra of PhNC have shown that the adsorption characteristics of PhNC were found to be quite analogous with those of BPNC. The presence of the ring CH band at ~ 3060 cm^{-1} in the SERS spectra evidenced a vertical orientation of PhNC on Ag and Au surfaces. The observed $\nu(\text{NC})$ bands were blue-shifted in the Ag and Au sol SERS spectra by 55 and 63 cm^{-1} , respectively, from that of the OR spectrum. Almost no red shifts of the ring breathing modes ν_1 and ν_{12} indicated that a direct interaction between the metal surfaces and benzene ring should be quite low. As in the case of BPNC, the $\nu(\text{NC})$ band of PhNC was much broadened on Ag. These results suggested that the additional phenyl ring in the biphenyl moiety appeared not to give a much influence on the adsorption of BPNC on the Ag and Au surfaces.

It is a matter of conjecture however whether the two benzene rings of BPNC has a twisted angle as found in its gaseous state.^{25,47–52} Considering that the possibility of the interaction between the biphenyl group and metal surfaces is quite low, the two benzene rings of BPNC should not lie on the same plane.

Since SERS selection rules do not provide a precise interpretation of band intensities, we have been currently applying other spectroscopic techniques to reach a more consistent conclusion. Using a grazing angle infrared reflection absorption spectroscopy, it was however difficult to obtain reliable peak intensities of BPNC on the Ag(111) and Au(111) films. Also, it seems difficult to directly compare the SERS or ordinary Raman intensities with that of the infrared transmission spectrum due to the different selection rules and enhancement mechanisms of infrared and Raman spectroscopy. Our future research is to determine a more quantitative orientation of the species on the well-defined crystal plane by combined spectroscopic methods. Thermodynamic, electrochemical, and theoretical studies shall also be beneficial to explain the different adsorption characteristics of BPNC on Ag and Au surfaces.

Summary and Conclusions

The adsorption behavior of 4-biphenylisocyanide (BPNC) on colloidal gold and silver surfaces has been investigated by means of surface-enhanced Raman scattering (SERS). As evidenced from the appearance of the ring CH stretching band, BPNC has a rather vertical stance on silver and gold surfaces. By determining the relative vibrational intensity factors in the Ag and Au SERS spectra, we attempted to explain the adsorption orientation of BPNC on Ag and Au in a more quantitative way based on the electromagnetic surface selection rule. The band analysis indicated that BPNC should have a slightly more vertical orientation on silver than on gold. The observed $\nu(\text{NC})$ bands were blue-shifted in the Ag and Au sol SERS spectra by 52 and 62 cm^{-1} , respectively from that of the OR spectrum. Such high blue shifts of the $\nu(\text{NC})$ stretching vibration in the SERS spectra assumed to be due to the electron donation from the $\text{N}\equiv\text{C}$: group to the metals. The higher blue shift of the $\nu(\text{NC})$ band in the Au sol SERS spectrum suggested that the electron donation should be more efficient for Au due to its higher electro-negativity. On the other hand, a stronger enhancement of the $\nu(\text{NC})$ band supported a more vertical orientation on Ag.

Acknowledgment. The present research was conducted by the research fund of Dankook University in 2001.

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