Raman Spectroscopic Study of Benzonitrile on Silver Surface

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The surface-enhanced Raman scattering(SERS) of benzonitrile in a silver sol was investigated. It was concluded that the molecule adsorbed onto the silver surface via the nitrogen lone pair electrons. Using the surface selection rule, the orientation of the benzene ring with respect to the surface plane could not be determined conclusively. However, it seemed likely that benzonitrile is adsorbed edge-on to the surface. It was demonstrated that the SERS technique provides a useful method for detailed characterization of the chemisorbed layer.

Introduction

Important advances in experimental and theoretical methods for the study of surface phenomena have been made in the last decade. The thrust of current experimental and theoretical studies is toward a microscopic characterization of the geometric and electronic structure of chemisorbed layers.[1]

It is only within the past 20 years or so that spectroscopic methods for probing surfaces have become generally available for detailed characterization of the chemisorbed layer. The first of these techniques was infrared spectroscopy, followed recently by electron-diffraction, ion scattering, and various electron spectroscopic methods.[2] It has also been shown recently that the surface-enhanced Raman scattering (SERS) provides a useful method for the study of the adsorbate-adsorbent interaction.[3-10]

The benzonitrile molecule has a very interesting character in that three different binding sites(aromatic ring, π-bond of CN group, and lone pair electrons of nitrogen atom) are available for the adsorption of the molecule on the metal surface. In this respect, we present here a detailed SERS study on the benzonitrile molecule in the aqueous silver sol.

With regard to the appropriate binding site(s), we have investigated the spectral changes accompanying the adsorption of the molecule on the silver surface. In specific, changes in the frequencies and bandwidths for both the C≡N stretching and the benzene ring modes are thoroughly studied. In addition, the surface selection rule has been applied to the various vibrational modes to investigate the molecular conformation on the silver surface.

Experimental

Aqueous silver sol was prepared according to the procedure described by Creighton *et al.*[11] The 10 m*l* volume of 10^{-3} M $AgNO_3$ solution was added dropwise to 30 m*l* of 2×10^{-3} M $NaBH_4$ solution. The latter solution was maintained at ice temperature and the mixture was stirred vigorously during the preparation. The resulting sol, which was stable for several weeks, was yellowish in tint with a UV/VIS spectrum displaying a single peak near 392 nm as reported previously.[3]

Raman spectra were obtained with a Japan Spectroscopic Company model R-300 laser Raman spectrophotometer using the 514.5 nm line of an Ar^+ laser (Spectra Physics model 164-06) as an exciting source. Glass capillary tube was used as sampling device and Raman scattering was observed with 90° geometry. Raman signals were detected using a commercial photon counting system.

A 0.03 M aqueous solution of benzonitrile was mixed with the silver sol in the volume ratio of 1:5. Polyvinylpyrrolidone was added to stabilize the solution. A small amount of $NaBH_4$ was then added. Concentration of polyvinylpyrrolidone and $NaBH_4$ were 0.01% and 2.5×10^{-4} M, respectively, in the final solution.

The ordinary Raman spectra were also obtained for the CCl_4 and CH_3OH solutions containing benzonitrile by 1%. The solvent peaks were manually subtracted to get the sole spectrum of benzonitrile.

All the chemicals used in this work were reagent grade, and triply distilled water was used for preparation of solutions.

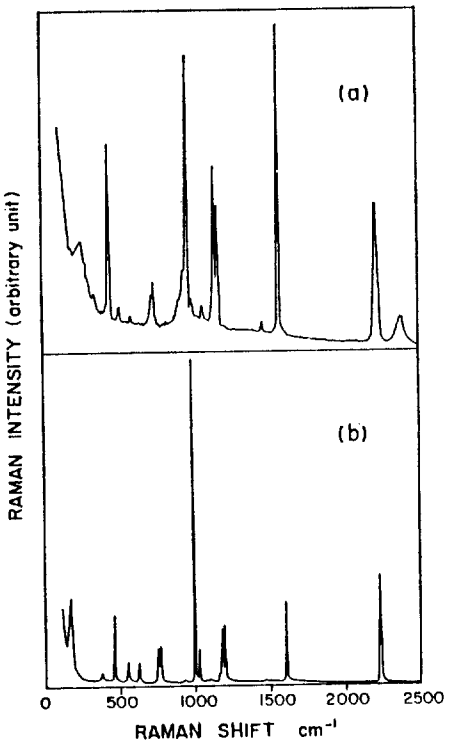

Figure 1. (a) SER spectrum of benzonitrile in a silver sol. (b) Ordinary Raman spectrum of benzonitrile.

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Results and Discussion

The SER spectrum of benzonitrile in silver sol and the ordinary Raman spectrum of benzonitrile are shown in Figure 1(a) and 1(b), respectively. The SER spectrum is nearly identical to the ordinary Raman spectrum. In the ordinary Raman spectrum, the major bands associated with the benzene-ring vibrational modes[12, 13] appeared at 381 (ν_{10b}), 461 (ν_{6a}), 550 (ν_{16b}), 626 (ν_{6b}), 755 (ν_{11}), 769 (ν_1), 1000 (ν_{12}), 1178 (ν_{9a}), 1192 (ν_{13}), and 1599 (ν_{8a}) cm^{-1}. The corresponding peaks occurred in the SER spectrum at 384, 484, 555, 630, 760, 775, 1001, 1182, 1200, and 1597 cm^{-1}, respectively. It is rather straightforward to correlate the vibrational lines between the two spectra. However, it can also be noticed that a few spectral changes occur indeed following the adsorption of benzonitrile to silver. For a few peaks, some changes in the band position and the bandwidth were observed. Such phenomena may be explained as due to a change of the environment for adsorbed molecules.[14,15]

A number of vibrational studies of benzene and alkylbenzene adsorbed at metal surfaces have been reported.[16-18] It has generally been known for the ring breathing mode that 10 cm^{-1} or more red shift as well as band broadening occur as the molecule is adsorbed to metal surfaces via the π bonds of the benzene ring. Such a red shift arises from the bond weakening in the benzene ring system caused by the back donation of the metal d-electrons to the benzene ring π^*-antibonding orbitals. Metal surface is also supposed to provide an extra vibrational relaxation channel resulting in the increase of the bandwidth of the ring breathing mode.

For the benzonitrile molecule, there are two kinds of ring breathing modes, namely ν_1 and ν_{12}.[12,13] The bandwidths of these two modes in the SER spectrum are observed to be hardly different from those in the ordinary Raman spectrum. On the other hand, the ν_1 ring breathing mode was blue-shifted by 6 cm^{-1} in the SER spectrum(775 cm^{-1}) compared with that in the ordinary Raman spectrum(769 cm^{-1}), whereas the ν_{12} trigonal ring breathing mode positions were nearly comparable in the two spectra(1001 and 1000 cm^{-1} for SER and ordinary Raman spectra, respectively).

It is a well-known experimental fact that in mono-substituted benzene the frequencies of ν_1, ν_{6a}, ν_{10b}, ν_{13}, and ν_{16b} modes are more sensitive to the mass of the substituent than other ring modes.[13] The 6 cm^{-1} blue-shift of the ν_1 mode in the SER spectrum is thus supposed to be related with the substituent mass effect rather than with the direct interaction between the benzene ring π orbitals and the metal d orbitals. In the latter case, the ν_1 mode should show red shift, instead of the blue shift described above, as the benzonitrile molecule adsorbs on the silver surface. Moreover, it has been observed that the above-mentioned substituent sensitive modes are more or less shifted from their positions in the ordinary Raman spectrum. For example, the ν_{6a} and ν_{13} bands have blue-shifted by 23 and 8 cm^{-1}, respectively(for ν_{6a}, SERS: 484, ordinary: 461 cm^{-1} and for ν_{13}, SERS: 1200, ordinary: 1192 cm^{-1}). On the other hand, smaller shifts(<5 cm^{-1}) were seen for the substituent insensitive modes such as ν_{9a}, ν_{11}, ν_{12}, ν_{18b}, ν_{19a}, and ν_{19b}. It thus appears that the benzonitrile molecule is bound to the silver surface via the cyano group rather than via the benzene ring itself. In this respect, we now consider the spectral changes associated with the ν_{CN} mode.

In the SER spectrum the ν_{CN} mode appeared at 2244 cm^{-1}. The bandwidth was measured to be 25 cm^{-1}. The corresponding band occurred at 2230 cm^{-1} in the ordinary Raman spectrum with the 9 cm^{-1} bandwidth. Hence, the ν_{CN} band blue-shifted by 14 cm^{-1} and its bandwidth increased by 16 cm^{-1}. The above observation reflects the direct interaction of the CN group with the silver surface. As mentioned in the introductory part, however, the CN group can bind to the metal surfaces through either its π bond or the nitrogen lone pair electrons[19]. It is to be determined which of the two sites is actually involved in the adsorption of the benzonitrile molecule onto the silver surface.

From the studies of the metal-nitrile complexes and the nitriles adsorbed at the metal surfaces using EELS, XPS, UPS, and other techniques[20-24], it has generally been accepted that the linear coordination(σ-bonding) through the nitrogen lone pair electrons results in an increase in the C≡N stretching frequency from the free molecule. On the other hand, coordination through the C≡N π system is known to result in a decrease in the C≡N stretching frequency from that of the free molecule. Hence, the experimental fact that the ν_{CN} mode blue-shifts by 14 cm^{-1} in the SER spectrum may indicate that the benzonitrile molecule is adsorbed to the silver surface via the nitrogen lone pair electrons. The indirect coupling of the C≡N π system to the silver surface is believed to exert an important effect upon the width of the ν_{CN} band. Although the benzonitrile molecule adsorbs onto the silver surface via its nitrogen lone pair electrons, the orientation of the benzene ring with respect to the surface plane is still undetermined.

The orientation of an adsorbed molecule on the silver surface may be investigated by SERS once its selection rule is known. For molecules with C_{2v} symmetry such as benzonitrile, the image model treatment proposed by Nichols *et al.*[14] predicts that the a_1 and a_2 vibrational modes are active for face-on adsorption, while a_1, a_2, b_1 and b_2 modes are active for edge-on adsorption. According to the electromagnetic field enhancement model proposed by Moskovits[25], the relative band enhancements should be in the order of $a_1 > a_2 \approx b_1 > b_2$ for face-on adsorption and of $a_1 > b_1 \approx b_2 > a_2$ for edge-on adsorption. In specific, when the rule proposed by Creighton[26] is used, the relative enhancement factors for the different modes would be a_1: a_2: b_1: b_2 = 1~16:4:4:1 and 1-16:1:4:4 for face-on and edge-on adsorption, respectively. Hallmark and Campion[28] have recently modified the image model, arriving at the same result as that predicted by Moskovits from the electromagnetic field enhancement model. In order to apply the electromagnetic field enhancement model proposed by Moskovits[25] and Creighton[26], bands due to the a_2-type vibrational mode should be prominent in both the SER and ordinary Raman spectra. It is unfortunate that there occurs only one band, ν_{10a}, associated with the a_2-type mode in both spectra of benzonitrile. Furtheromore, the ν_{10a} bands appearing at 848 and 849 cm^{-1}, respectively in the ordinary Raman and SER spectra are extremely weak. Hence, the relative enhancement for the a_2 mode is hardly determinable. Nevertheless, the relative enhancements between the b_1 and b_2 modes may be informative. It was observed for benzonitrile that surface enhancements for the b_2-type modes are smaller than those of the b_1-type modes. Hence, based on Creighton's model it seems that benzonitrile adsorbs face-one to the silver sol particle.

Table 1. Frequencies and Relative Raman Intensities of the Ring Modes in the SER and Ordinary Raman Spectra of Benzonitrile, and the Relative Enhancement Factors for the SER Bands

Class[a]	Frequencies(cm^{-1})[b]		Vibrational assignment[c]	Relative enhancement factors[d]
	Ordinary	SERS		I_{SERS}/I_{ORD}
class I,	381(2.5)	384(5.3)	10b	2.1
out-of-plane	550(5.8)	555(5.8)	16b	< 1
modes	755(9.2)	760(9.3)	11	1.0
	461(19)	484(77)	6a	4.1
	769(9.6)	775(19)	1	2.0
class II,	1000(100)	1001(100)	12	1.0
in-plane modes	1178(16)	1182(64)	9a	4.0
along z-axis	1192(17)	1200(43)	13	2.5
	1491(0.6)	1491(4.7)	19a	8
	1599(25)	1597(140)	8a	5.6
class III,	626(5.8)	630(1.6)	6b	0.28
in-plane mode	1069(0.5)	1065(0.5)	18b	< 1
along y-axis	1448(0.6)	1445(0.3)	19b	< 0.5

[a]See text. This classification is based on refs. (13, 27). [b]Values in parentheses are the normalized peak intensities. [c]Taken from refs. (12, 13). [d]Normalized to 1.0 at 1001 cm^{-1}.

In order to examine the orientation of an adsorbed molecule from a different point of view, we have classified the ring modes into three groups, i.e., out-of-plane mode and two kinds of in-plane modes. The in-plane modes are divided into two groups, depending on the vibrational axis. For benzonitrile, the bands such as ν_{10b}, ν_{11}, and ν_{16b} belong to the out-of-plane mode with the b_1 type symmetry(class I). The bands such as ν_1, ν_{8a}, ν_{9a}, ν_{12}, ν_{13}, and ν_{19a} belong to the in-plane modes with the a_1-type symmetry which has the normal mode component along the molecular principal z axis(class II). The b_2-type modes such as ν_{6b}, ν_{18b}, and ν_{19b} belong to the in-plane vibrations along the molecular principal y-axis (class III).

The surface selection rules proposed independently by Nicohls,[14] Moskovits[25], Creighton[26], and Campion[28] have one common feature. Namely, if the benzene ring is adsorbed face-on to the silver surface, the out-of-plane modes, class I, should be more enhanced than the in-plane modes. On the other hand, if the benzene ring is adsorbed edge-on to the silver surface, the class-II in-plane modes should be more enhanced than other classes.

Table 1 lists the normalized peak intensities and the intensity ratios of the benzene ring modes in the SER spectrum with respect to the corresponding modes in the ordinary Raman spectrum. Peak intensities were normalized to the intensity of the ν_{12} mode in each spectrum. The SERS-to-ordinary Raman intensity ratios for each Raman peak were then computed. It is seen from the Table that surface enhancements for the second class modes are, in general, larger than those for other classes. The third class is the least enhanced. The fact that the second class exhibits the most enhancement suggests that the benzonitrile molecule is adsorbed edge-on to the silver surface. This result excludes the possibility that the benzonitrile molecule adsorbs to the silver surface via either the benzene ring or the C≡N π system. Furthermore, inclined binding through the nitrogen lone pair electrons is hardly likely.

It is very unfortunate that the two approaches considered above do not lead to a unanimous decision on the molecular orientation. Such a conflict result may be explained as due to the coexistence of two kinds of molecules, one with the face-on and the other with the edge-on orientations. However, considering the aforementioned conclusion that the benzonitrile molecule is bound to the silver surface via the nitrogen lone pair electrons rather than via either the benzene ring or the C≡N π system, it is very tempting to say that benzonitrile is adsorbed edge-on to the silver surface.

Finally, it should be mentioned that the SER spectrum obtained in the absence of BH_4^- is slightly different from the one(Figure. 1(a)) recorded in the presence of BH_4^-. In the former spectrum, a broad band appeared in the 1100~1600 cm^{-1} region. Addition of BH_4^-, however, resulted in the disappearance of the broad band even though additional lines appeared at 310 and 2410 cm^{-1}(see Figure 1 (a)). Nevertheless, vibrational peak positions as well as relative intensities of each peak were not changed upon addition of $NaBH_4$. This suggests that BH_4^- affects the silver colloidal particles rather than benzonitrile. The origin of the broad bands as well as the exact role of BH_4^- are uncertain. In analogy with the reports of Cooney *et al.*[29], the broad band may be due to carbon overlayers on the silver particles. As reported by Blatchford *et al.*[30], addition of BH_4^- may change the potential of the Ag sol particles. Then, the surface carbon would be reduced to hydrocarbon and desorbed[29], resulting in the disappearance of the broad band. The two additional lines referred to above are not likely to be due to hydrocarbons, however, considering the absence of C-H stretching peaks in the spectrum. Hence, these peaks were tentatively assigned as due to adsorbed BH_4^- on the Ag particles.

In summary, we have performed a detailed SERS study on the benzonitrile molecule in the aqueous silver sol. In view of the change in the frequencies and the bandwidths of both the C≡N stretching and the benzene ring modes, it was concluded that the molecule adsorbed onto the silver surface via the nitrogen lone pair electrons. Although we could not present concrete evidence, it seemed more likely that the molecule is adsorbed edge-on to the silver surface. Nevertheless, we believe that this kind of data will provide a basis for a firmer understanding of the detailed nature of the adsorbate-adsorbent interaction.

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Palladium Dichloro Complex Catalysed Oxidation of Cyclopentene by Dioxygen in Tetralin†

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Palladium dichloro complexes catalysed the oxidation of cyclopentene by dioxygen in tetralin solvent at ambient temperature. Cyclopentanone formed mainly together with autoxidation products from both cyclopentene and tetralin. The oxidation seems to proceed by co-oxidation mechanism, where tetralin was first oxidized to its hydroperoxide which then oxidized cyclopentene to cyclopentanone. Mechanism of the other by-products formations has been discussed.

Introduction

Oxygen atom transfer reactions using transition metal complexes and some oxygen donors such as dioxygen, hydrogen peroxide and alkyl hydroperoxides, etc., is one of the current interests and many papers have been published from the following two aspects; the first is concerned with the model reactions for monooxygenase catalysed oxygen atom transfer, and the second is its synthetic utility to produce epoxide or ketone[1]. Concerning to olefin oxidation by noble metal catalysts, it has been reported that a rhodium cationic complex shows catalytic activity for oxygen incorporation from dioxygen,[2] while a palladium peroxo complex can work as the catalyst using *t*-butyl hydroperoxide or hydrogen peroxide as the oxygen doner.[3] In both cases, terminal olefin is the sole substrate which can be readily oxidized to methyl ketone, and the oxidation of internal or cyclic olefin to the corresponding ketone does not proceed so easily under the usual conditions.

We have found that cyclic olefin such as cyclopentene or cyclohexene can be oxidized to the corresponding alicyclic ketone by palladium complex-dioxygen couple in alcoholic solvent[4] or palladium complex-*t*-butyl hydroperoxide couple.[5] In the latter case, *t*-butyl hydroperoxide seems to work as the oxygen donor. We examined here a possibility of the cyclopentene oxidation by dioxygen in tetralin solvent, expecting that α-tetralyl hydroperoxide *in situ* formed can work as the oxygen donor to cyclopentene.

† Dedicated to the 60th birthday of Professor Nung Min Yoon.
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