Scand., **25,** 1 (1971).

9. S. Scheibye, B. S. Pedersen, and S.-O. Lawesson, *Bull. Soc., Chim. Belg.,* **87,** 299 (1978).

10. C. S. Marvel, and J. Dec, H. G. Cooke, J. C. Cowan, *J. Am. Chem. Soc.,* **62,** 3495 (1940).

Surface-enhanced Raman Scattering(SERS) of Benzylcyanide in Silver Sol

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The surface-enhanced Raman scattering(SERS) of benzylcyanide in a silver sol was investigated. It was concluded that the molecule adsorbed onto the silver surface via the π system of the CN group. The molecule was assumed to coordinate with either a single atom or two silver atoms. According to the SERS selection rule, the benzene ring of the adsorbed species seemed to assume a flat stance with respect to the silver surface.

Introduction

The observation of vibrational spectra of molecules adsorbed on metal surfaces at monolayer or submonolayer coverages can be made by virtue of surface-enhanced Raman scattering (SERS)[1]. The ability to perform vibrational spectroscopy under these conditions has led to a new understanding about the chemical identity, geometry, and bonding of adsorbed material at a level previously unaccessible.

Organic cyanide(or nitrile) has a very interesting character in that several binding sites, *i.e.* π-bond of $C \equiv N$ group, lone pair electrons of nitrogen atom, and other functional groups in the molecule, are available for the adsorption on metal surface. In the SERS study, benzonitrile appeared to adsorb on the silver surface via the nitrogen lone pair electrons[2]. It would then be worthwhile to investigate other structurally similar system in order to understand the detailed nature of the interaction between the organic cyanide(or nitrile) molecule and the metal surface. In this respect, we present here the SER spectrum of benzylcyanide adsorbed on aqueous silver sol particle.

Experimental

Details of the apparatus for Raman measurements have been described previously[3]. Preparation and spectral properties of silver sol solution have also been described. Since benzylcyanide is insoluble in water, it is difficult to introduce the material to the sol solution. Hence, a small amount of neat benzylcyanide (Merck) was dropped directly into the sol solution in this work. The color of the aqueous layer changed slowly from yellow to green. About 10 min. after the addition of benzylcyanide, the aqueous layer was sampled to record its Raman spectrum. The SER spectrum obtained in this manner hardly changed upon the amount of neat benzylcyanide initially dropped into the sol solution.

Results and Discussion
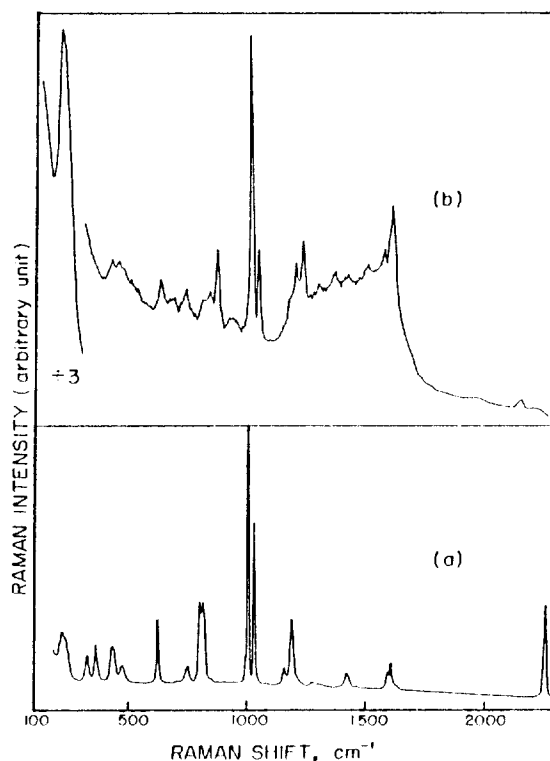
The ordinary Raman spectrum of neat benzylcyanide and

Figure 1. (a) Ordinary Raman spectrum of benzylcyanide (514.5 nm excitation at 100 mW, 4.2 cm^{-1} bandpass). (b) SER spectrum of benzylcyanide in a silver sol (514.5 nm excitation at 20 mW, 12 cm^{-1} bandpass).

its SER spectrum in a silver sol are shown in Figure 1(a) and 1(b), respectively. The latter spectrum has a broad background in the 1100-1600 cm^{-1} region. That may be due to carbon overlayers on the silver particles as reported by Cooney *et al.*[4] Nevertheless, it is rather straightforward to correlate the vibrational lines between the two spectra. For instance, the major bands associated with the benzene-ring vibrational modes[5,6] appeared at $428(\nu_{6a})$, $620(\nu_{6b})$, $701(\nu_4)$, $748(\nu_{11})$, $847(\nu_{10a})$, $1005(\nu_{12})$, $1031(\nu_{18a})$, $1186(\nu_{13})$, and

$1605(\nu_{8a})$ cm^{-1} in the ordinary Raman spectrum. The corresponding peaks occurred in the SER spectrum at 415, 620, 702, 728, 858, 1004, 1031, 1187, and 1599 cm^{-1}, respectively.

A number of vibrational studies of benzene and alkylbenzene adsorbed on metal surfaces have been reported[7-9]. It has generally been known for the ring breathing mode that 10 cm^{-1} or more red shift as well as substantial band broadening occur as the molecule is adsorbed on metal surfaces via the π system 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 antibonding π^* 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 benzylcyanide, the ν_{12} trigonal ring breathing mode red-shifted only by 1 cm^{-1} upon the adsorption of the molecule on silver. As noted above, this band appeared at 1005 and 1004 cm^{-1}, respectively, in the ordinary Raman and SER spectra. In addition, the bandwidth was measured to be 5 and 6 cm^{-1}, respectively, in the ordinary Raman and SER spectra. It thus appears that the benzylcyanide molecule is bound to the silver surface via its cyano group rather than via the benzene ring itself. With this veiw, we now consider the spectral changes associated with the ν_{CN} mode.

In the ordinary Raman spectrum, the band due to the ν_{CN} mode appeared at 2250 cm^{-1} with 11 cm^{-1} bandwidth. It is very interesting to observe, in the SER spectrum, two different bands both of which can be assigned to the ν_{CN} mode. They appeared at 2205 and 2148 cm^{-1} with 20 and 29 cm^{-1} bandwidths, respectively. The ν_{CN} bands in the SER spectrum have thus red-shifted by 45 and 102 cm^{-1} from its position in the ordinary Raman spectrum. In addition, substantial band broadening occurred, implying the direct interaction of the cyano group with the silver surface.

Rather significant frequency shift in the CH$_2$ rocking mode is also supposed to support the above argument. This mode blue-shifted by 13 cm^{-1} as the benzylcyanide molecule adsorbed to the silver surface, appearing at 829 and 816 cm^{-1}, respectively, in the SER and ordinary Raman spectra. The CH$_2$ rocking plus twisting mode, which is Raman inactive but can be observed at 1230 cm^{-1} in the infrared spectrum of neat benzylcyanide, appeared at 1218 cm^{-1} in the SER spectrum. The 12 cm^{-1} red-shift of this band may, as well, reflect the direct interaction between the cyano group and the silver surface.

From the studies of the metal-nitrile complexes and the nitrile adsorbed on the metal surface using EELS, XPS, UPS, and other techniques[10-14], it has generally been accepted that the linear coordination (σ-bonding) through the nitrogen lone pair electrons results in an increase in the C $\equiv$ N stretching frequency from the free molecule. On the other hand, coordination through the C $\equiv$ N π system is known to result in a decrease in the C $\equiv$ N stretching frequency from that of free molecule. The red-shift of the ν_{CN} mode in the SER spectrum may then indicate that the benzylcyanide molecule is adsorbed to the silver surface via the C $\equiv$ N π system. The direct coupling of the C $\equiv$ N π system to the silver surface is believed to exert a significant effect upon the widths of the ν_{CN} bands.

The cause for the appearance of two bands, instead of one, assignable to the ν_{CN} modes is uncertain. However, by analogy with the studies of adsorption of CO on various metals, the two bands may arise because benzylcyanide adsorbs on two or more different sites on the silver surface. The relative influence on the C-O bond strength of metal d-band electron concentration versus the coordination number of the adsorption site, *i.e.*, the number of surface metal atoms with which the CO molecule interacts, has been a debate of considerable interest[15-18]. Generally, high frequency bands above 2000 cm^{-1} are associated with CO coordinated with a single metal atom in a linear or terminal manner, whereas 2-fold(bridged) or other forms of multiple-bonded CO results in lower frequency bands below 2000 cm^{-1}. On this basis, we tentatively ascribe the bands at 2205 and 2148 cm^{-1} in the SER spectrum of benzylcyanide to the ν_{CN} modes arising, respectively, from the coordination of the molecule with a single atom and from the two fold bridged coordination.

If the two bands have nothing to do with the coordination number of the adsorption site but arise from two different geometries of the adsorbed species with respect to the silver surface, the SER spectrum should exhibit more complex feature than that observed here. If two adsorption geometries which result in 57 cm^{-1} difference in the ν_{CN} frequency are involved, other band such as the benzene ring modes and the CH$_2$ rocking mode are also expected to appear at different positions. Or, if the frequency differences are not large, at least the bandwidths in the SER spectrum should be substantially larger than those in the ordinary Raman spectrum. In fact, only one peak was observed in the SER spectrum for each of the benzen ring modes and the CH$_2$ rocking mode. Moreover, the bandwidth of each mode in the SER spectrum was hardly different from that of the corresponding mode in the ordinary Raman spectrum. These observations suggest that the two ν_{CN} bands in the SER spectrum are not due to the different geometries of the adsorbed species.

As can be seen in Figure 1(b), a rather broad peak centered at 227 cm^{-1} appeared in the SER spectrum of benzylcyanide. Such a band was not observed in the absence of benzylcyanide. That band is unusually intense so that it is not reasonable to assign the band to one of the CH$_2$CN group vibrations. Rather, it seems to be more appropriate to assign the above band to the stretching modes of Ag-C and Ag-N bonds formed through binding of the CN group via its π system to Ag. This picture is consistent with the two-fold bridged attachment of the π bond of CN group to silver. In that case, the composite character of the Ag-C and Ag-N stretching modes will result in a single broad band as observed.

Although the benzylcyanide molecule adsorbs onto the silver surface via its π system, the orientation of the benzene ring with respect to the surface plane is still undetermined. According to the surface selection rule[19-20], the vibrational mode with its normal mode component perpendicular to the metal surface is much more enhanced than the parallel mode. In this respect, we have classified the benzene ring modes into two parts, *i.e.* out-of-plane modes and in-plane modes. For benzylcyanide, the bands such as ν_4, ν_{10a}, and ν_{11} belong to the out-of-plane modes, whereas ν_{6a}, ν_{6b}, ν_{8a}, ν_{12}, ν_{13}, and ν_{18a} modes belong to the in-plane modes.

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 in-

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

Class[a]	Frequencies(cm^{-1})[b]		Vibrational assignment[c]	Relative enhancement factors[d] I_{SERS}/I_{ORD}
	Oridinary	SERS		
in-plane modes	428(3.8)	415(4.7)	6a	1.2
	620(7.5)	620(8.1)	6b	1.1
	1005(100)	1004(100)	12	1.0
	1031(21)	1031(29)	18a	1.4
	1186(7.9)	1187(18)	13	2.3
	1605(3.2)	1599(24)	8a	7.5
out-of-plane modes	701(0.33)	702(3.4)	4	10
	748(2.3)	728(6.8)	11	3.0
	847(0.31)	858(26)	10a	84

[a]See text. This classification is based on refs.(5,6,23). [b]Values in parentheses are the normalized peak intensities. [c]Taken from refs.(5,6). [d]Normalized to 1.0 at 1004 cm^{-1}.

tensity of the ν_{12} mode in each spectrum. The SERS-to-ordinary Raman intensity ratios for each Raman peak were then evaluated. It is seen from the Table that surface enhancement for the out-of-plane modes are, in general, larger than those for the in-plane modes. Hence, it seems that the benzene ring of the adsorbed benzylcyanide molecule assumes a flat stance with respect to the silver surface.

In summary, we have performed a detailed SERS study on the benzylcyanide molecule in aqueous silver sol. It was concluded that the molecule adsorbed onto the silver surface via the π system of the CN group. The molecule was assumed to coordinate with either a single atom or two silver atoms. According to the SERS selection rule, the benzene ring of the adsorbed species appeared to be face-on to the silver surface.

References

1. R. K. Chang and T. E. Furtak, Eds., Surface-Enhanced Raman Scattering, Plenum Press, New York (1982).
2. D. W. Boo, K. Kim and M. S. Kim, Bull. Kor. Chem. **8,** 251 (1987).
3. T. H. Joo, K. Kim and M. S. Kim, Chem. Phys. Lett. **112,** 65 (1984).
4. R. P. Cooney, M. R. Mahoney and M. W. Howard, Chem. Phys. Lett. **76,** 448 (1980).
5. G. Varsanyi, Ed., Vibrational Spectra of Benzene Derivatives, Academic Press, New York (1969).
6. S. Chattophdhyay, Indian J. Phys. **41,** 759 (1967).
7. M. Moskovits and D.P. Dilella, J. Chem. Phys. **73,** 6068 (1980).
8. P. Gao and M. J. Weaver, J. Phys. Chem. **89,** 5040 (1985).
9. P. Avouris and J. E. Demuth, J. Chem. Phys. **75,** 4783 (1981).
10. C. M. Friend, J. Stein and E. L. Muetterties, J. Am. Chem. Soc. **103,** 767 (1981).
11. C. M. Friend, E. L. Muetterties and J. Gland, J. Phys. Chem. **85,** 3256 (1981).
12. K. Kishi and S. Ikeda, Surface Sci. **107,** 405 (1981).
13. B. A. Sexton and N. R. Avery, Surface Sci. **129,** 21 (1983).
14. R. M. Wexler and E. L. Muetterties. J. Phys. Chem. **88,** 4037 (1984).
15. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York (1978).
16. H. Ibach and D. L. Mills, Electron Energy Loss Spectroscopy and Surface Vibrations, Academic Press, New York (1982).
17. M. A. Vannice, Catalysis, Vol. 3(J. R. Anderson and M. Boudart, Eds.), Springer-Verlag, New York (1982).
18. T. E. Mady, J. T. Yates, Jr., D. R. Sandstrom, and R. J. H. Voorhoeve, Treatise on Solid State Chemistry, Vol. 6B(N. B. Hannay, Ed.), Plenum Press, New York (1983).
19. H. Nichols and R. M. Hexter, J. Chem. Phys. **75,** 3126 (1981).
20. M. Moskovits, J. Chem. Phys. **77,** 4408 (1982).
21. J. A. Creighton, Surface Sci. **124,** 209 (1983).
22. V. M. Hallmark and A. Campion, J. Chem. Phys. **84,** 2942 (1986).
23. F. R. Dollish, Characteristic Raman Frequencies of Organic Compounds, Wiley, New York (1974).