Raman Spectroscopic Study of Monodentate Dopamine Adsorbed on Silver and Copper Adatoms

Min Young Youn†, Yunsoo Kim†, and Nam-Soo Lee*

†*Advanced Materials Division, Korea Research Institute of Chemical Technology, Taejon 305-600, Korea*
Department of Chemistry, Chungbuk National University, Cheongju 361-763, Korea
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Catecholamines, such as dopamine, norepinephrine, and epinephrine are neurotransmitters and/or systemic hormones in peripheral tissues and in the central and the sympathetic nervous system for the regulation of heart beat rate, or blood pressure, and so forth.[1] Dopamine, the precursor of norepinephrine in the biological synthesis pathway, has biological activities in peripheral tissues, and serves as a neurotransmitter in several important pathways in the central nervous system. Biosynthesis, storage, release, transport and reuptake of catecholamines have been rigorously characterized than those for any other neurotransmitters. These small charged hydrophilic compounds interact with cell surface receptors which have their binding sites with high affinity for a particular signaling substance. At least six classes of receptors for catecholamines have been so far classified in the brain. Postsynaptic receptors for dopamine and norepinephrine/epinephrine are distinct in chemical species. In general, the catechol moiety is essential for a hormone to elevate the concentration level of cytosolic cAMP, Ca^{2+} ion or other substances in the cellular system, that is, for a hormone to be an agonist. The NH-containing side chain has been known to determine the affinity of a hormone to the cell surface receptors. The conformational studies of NH-containing side chains of catecholamines have been extensively investigated with various kinds of experimental techniques and theoretical calculation methods.[2] The free ionic species, the divalent metal ion chelates, as well as the complexed species with substrates of catecholamines have been studied in prospect of possible pathway intermediates of the storage and the transport of neurotransmitters. From the surface enhanced Raman spectroscopic studies, active species of catecholamines adsorbed on the silver electrode was proposed to be a bidentate complex holding two hydroxyl groups of the catechol moiety.[3] It was also supposed to be dianionic electrically deprotonated at hydroxyl groups of the catechol moiety from experimental evidences of Fourier transform Raman scattering of sodium salts of catecholamines using Nd : YAG cw 1064 nm excitation. High resolution NMR studies proved that the NH-containing side chains of catecholamines experiences its conformational change from the *trans* conformer to the *gauche* conformer except that of dopamine.[4]

Recently, surface enhanced Raman spectra obtained on the silver electrodes polished using alumina powders or other polishing powders were carefully reexamined whether polishing powders embedded into the silver metal surface might play important roles for the adsorption of surface active species. They showed a possibility of complexed species,[5] plausibly an aluminum complex, at adsorption sites generated from the embedded alumina powders. Silver-coated alumina/glass substrate prepared by a chemical reduction method or a vacuum evaporation method was proven effective for strong surface enhanced Raman scattering for several dye compounds.[6]

In an attempt of presenting Raman spectrum of dopamine species adsorbed on the metal surface without alien mediators for adsorption, we chose to apply an electrochemical reduction method for the deposition of silver adatoms or copper adatoms on the silver electrode surface adapting the technique of the underpotential deposition.[7] This electrode surface was not applied any oxidation-reduction cycle which has been an usual procedure for surface enhanced Raman scattering. It would exhibit less enhancing effects of Raman scattering or less concentration of adsorbed species, but should remove any interference of polishing powders embedded, *i.e.*, the adsorption sites.

Experimental Section

Measurements of Raman scattering were conducted with a Jovin-Yvon U-1000 double spectrophotometer (focal length 1000 mm, F/8) equipped with two 1800 grooves/mm holographic gratings, Coherent Model Innova 70 series Ar^+ ion laser, Spectralink control system, Hamamatsu photoncounter Model C1230, and Hamamatsu photomultiplier tube (R943-02, cooled to -30 °C by a photomultiplier cooler, Hamamatsu Model C2761) operated in single-photon counting mode at -800 V. Each slit width, the scan speed, and the gate time were 300 μm, 100 cm^{-1}/min and 1.0 sec, respectively. The laser power of 514.5 nm line was kept to about 100 mW through narrow band pass filter and tightly focused at sample. The laser was irradiated to sample with 60° of incident angle, and Raman scattering was collected in perpendicular to the working electrode surface.

Electrode potentials were controlled in a conventional three electrode system, using a home-built potentiostat. Saturated calomel electrode (SCE) and a platinum wire (diameter 1 mm) were chosen as a reference electrode and an auxiliary electrode, respectively. The working electrode was made of a silver ribbon (width 2.0 mm and 99.99% purity from Niraku). Silver ribbon of about 5 cm long was cemented on a glass rod using a torr seal. Silver electrode surface was covered with an epoxy resin except an area of about 2×2 mm which served as an active surface of a silver electrode. Its surface was polished using sandpaper (No. 1500) and then rinsed thoroughly in an ultrasonic bath with distilled water. It was then electrochemically cleaned in a deaerated (through 99.999% N_2 gas bubbling for 20 minutes) 0.1 M KCl solution at -0.7 V *vs* SCE for 20 minutes. The electrode potential at -1.0 V *vs* SCE was applied to de-

posit the silver adatoms in 0.01 M silver nitrate solution or the copper adatoms in 0.01 M copper acetate solution, respectively. Then, this working electrode rinsed throughly in the distilled water was immersed immediately to the sample cell under study.

Sample solutions were buffered to pH 7.2 using a phosphate buffer solution, and contained 1 mM dopamine · HCl, 0.1 M potassium chloride, and 1 mM L(+)-ascorbic acid to prohibit the oxidation reaction. Sample solution was contained with three electrodes in a quartz cell (10×10×45 mm), which is usually a UV-VIS spectrophotometer cell. During collection of scattered light, N_2 gas (99.999%) was kept gassing downward from the top of the cell to prevent an air oxidation reaction of dopamine to *o*-quinone, leucoaminochrome, aminochrome or a mixture of three. The electrode potential was maintained at −0.9 V *vs* SCE during data acquisition because Raman scattering of dopamine in this condition is strong in intensity near this potential. Dopamine · HCl was purchased of the highest purity from Tokyo Kasei and other chemicals were used as received without further purification.

Results and Discussion

Raman spectra of dopamine · HCl adsorbed on the silver adatoms (A) and on the copper adatoms (B) deposited to the surface of the silver electrode are presented in Figure 1. Raman shifts in the range 1100-1700 cm^{-1} of dopamine and catechol in different environments are tabulated in Table 1. Raman bands obtained from this experiment are shown in the last two columns of Table 1, and display quite distinct characteristics from surface enhanced Raman spectra of dopamine.[3] SERS of dopamine adsorbed on the roughened silver electrode had shown three strong bands at 1269, 1331, and 1479 cm^{-1}. SERS on the silver hydrosol[11] is essentially the same as that on an electrode above, and was observed at 1271, 1325, and 1480 cm^{-1}.[8]

These bands were also observed in resonance Raman spectrum of a dianionic iron-catechol complex species, $[Fe(cat)_3]^{3-}$, deprotonated from two hydroxyl groups of catechol.[9,10] The band at 1480 cm^{-1} was considered the ring stretching vibration, ν_{19b}, contributed mainly from the stretching of the carbon-carbon bond to which the oxygens are attached. The band at 1271 cm^{-1} was assigned to the stretching of the C-O$^-$ bond of catechol complexed to the metal ion, Fe^{3+}, and the band at 1325 cm^{-1} was assigned to the ring stretching vibration, ν_3.

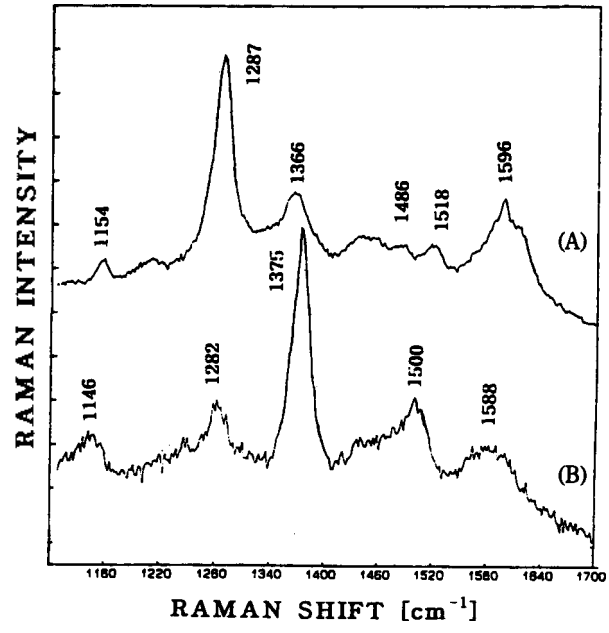

Figure 1. Raman spectra of dopamine adsorbed on Ag adatoms (A) and on Cu adatoms (B) deposited on the silver electrode at −0.9 V *vs* SCE. (λ_{ex}=514.5 nm, 1 mM dopamine concentration in pH 7.2 phosphate buffer).

The spectrum (A) presented, however, has relatively weak bands near 1486 cm^{-1}, and two strong bands at 1287 and 1366 cm^{-1}. These bands at 1287 and 1366 cm^{-1} upshifted from 1270 and 1330 cm^{-1} observed in SERS were

Table 1. Raman shifts in cm^{-1} of Dopamine (DA) and Catechol (Cat) in different environments

Bands[k]	DA Cationic Solid State[a]	DA Dianionic Solid Salt[b]	DA Adsorbed on Silver Hydrosol[c]	DA Adsorbed on Silver Electrode[d]	Cat Bidentate Complex State[e]	Cat monodendate Complex[f]	DA In Aqueous Solution[g]	DA Adsorbed on Ag Adatoms[i]	DA Adsorbed on Cu Adatoms[j]
ν_{15}			1155	1152	1155	1155		1154	1146
$\nu_{C\text{-}O}$	1285	1313	1271	1269	1273	1287	1295	1287	1282
ν_3	1320	1338	1325	1331	1323				
$\nu_3/\delta_{O\text{-}H}$	1341					1375	1378	1366	1375
ν_{19a}	1449	1436	1428	1424	1475	1450	1448		
ν_{19b}	1498	1462	1480	1479	1491	1489		1486	1500
ν_{8a}	1600	1568	1562	1572	1567	1591		1596	1588
ν_{8b}	1616		weak	1584	1591	1603	1618	1608	shoulder

[a] DA Fourier transform Raman of cationic species in the solid state (λ_{ex}=1024 nm) from ref 4. [b] DA Fourier transform Raman of dianionic salt in the solid state (λ_{ex}=1024 nm) from ref 4. [c] DA surface enhanced Raman on Ag hydrosol (λ_{ex}=829 nm) from ref 8. [d] DA surface enhanced Raman on Ag electrode (λ_{ex}=514.5 nm) from ref 3. [e] Iron-catechol dianionic complex resonance Raman in solid state (λ_{ex}=657.1 nm) from ref 10. [f] Iron-catechol monoanionic complex resonance Raman in the solid state (λ_{ex}=657.1 nm) from ref 10. [g] DA Raman in aqueous solution (λ_{ex}=829 nm, 7×10^{-1} M) from ref 8. [i,j] DA surface Raman on silver and copper adatoms (λ_{ex}=514.5 nm) from this experiment. [k] Wilson numbering from ref 11.

identified characteristic to the vibrations of the monoanionic catechol-iron complex investigated by resonance Raman scattering.[10] The resonance Raman spectra of monoanionic catechol had shown two bands at 1287 and 1375 cm^{-1}, and Raman spectrum[8] of 7×10^{-1} M aqueous dopamine · HCl had also shown two bands at 1295 and 1378 cm^{-1}. Because the pK_1, pK_2 and pK_3 constants of dopamine were known to be near 9, 10 and 13, respectively, dopamine is a weak polyprotic acid. Therefore, two hydroxyl groups of catechol moiety readily hold almost all their protons in aqueous solution of 7×10^{-1} M dopamine · HCl. In acidic or neutral solution, dopamine has one or two hydroxyl protons attached to catechol moiety. With only one hydroxyl proton attached and the other deprotonated, it would be a zwitterion-like species. At higher pH values, however, the zwitterion-like species or the deprotonated dianionic species of dopamine would be dominant. So, a considerable possibility may be paused on that the Raman bands at 1375 and 1378 cm^{-1} in both cases are strongly attributed to a deformation vibration due to the in-plane O-H bending motion. Adsorbed perpendicular to the metal surface, in particular, the in-plane O-H bending vibration could exhibit a dipole scattering to result in its moderate intensity on the silver adatoms. Otherwise this vibration would be very weak or almost not seen in normal Raman scattering. The in-plane O-H bending vibration of neat phenol does not show any significant intensity near 1370 cm^{-1} in Raman scattering,[11] but it gains substantial intensity to be broad enough near 1370 cm^{-1} implying a hydrogen bonding interaction between a hydroxyl proton and a hydroxyl oxygen atom of neighbouring molecule in infrared absorption.

Raman spectrum obtained by A. Otto *et al.*[12] of surface formate and formic acid adsorbed on the cold-deposited copper film had also shown a band at 1368 cm^{-1}, which was not assigned definitely to an in-plane C-H bending vibration of surface formate or to an in-plane O-H bending vibration of surface formic acid by comparison with literature data of surface formate, formate salts, and solid formic acid. Raman spectrum (B) of dopamine on Cu adatoms has similar characteristics to that on Ag adatoms, but the intensities of two bands are quite different to spectrum (A). The band at 1375 cm^{-1} in spectrum (B) is very strong unlikely to other dopamine species. Right now, it is not clearly understood why the in-plane O-H bending vibration is so intense on the Cu adatoms. We could take account into several points, *i.e.*, a moderate modification of the electronic charge of surface dopamine due to its interaction with the metal surface, a short range effect in consequence due to a closer distance to the Cu metal surface, and as well a dipole scattering due to a rigid orientation of O-H group by a weak interaction to the metal surface through its oxygen atom. In this experiment, we can easily exclude the possibility of assigning the band at 1375 cm^{-1} to the in-plane C-H bending motion because it is much farther than the O-H from the surface.

The band intensities in the range of 1480 to 1650 cm^{-1} in Figure 1(A) and 1(B) are relatively weak compared with other spectra of dopamine. This reduced intensities in this range were also observed at lower pH in SERS of dopamine.[9] These bands are mainly contributed from the ring vibrations of catechol moiety as seen in Table 1. The zwitterion-like species of dopamine would be dominant near pH 9 and 10. At lower than pH 7 value, therefore, one of two hydroxyl groups of catechol moiety holds its proton, but the other is deprotonated to attach to the metal surface, *i.e.*, monodentate species.

These spectroscopic evidences demonstrate that active species of dopamine on the metal surface is monoanionic adsorbed perpendicular on the metal surface, and the catechol moiety loses only one proton upon binding to the metal surface.

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