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Vibrational Spectroscopic Investigation of Benzoic Acid Adsorbed on Silver

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The surface-enhanced Raman scattering (SERS) of benzoic acid has been investigated in aqueous silver sol and at a silver electrode. The adsorption behavior of benzoic acid seemed very dependent on the nature of substrate. On the electrode surface, the molecule was found to adsorb preferentially, after deprotonation, via the oxygen lone pair electrons, assuming a perpendicular orientation with respect to the surface. In contrast, the benzoate species appeared more likely to take a flat or tilted orientation on the sol surface. The same observation could be made for 4-methylbenzoic acid. According to the *ab initio* quantum mechanical calculation which modeled the silver surface as an Ag_5^+ cluster, the perpendicular orientation appeared to be energetically more favorable than the flat orientation. Although the origin of such a different adsorption mechanism could not be clarified, it was tentatively ascribed to the different surface morphology along with the intrinsic difference in the nature of SERS active sites on the two surfaces.

Introduction

In recent years, much attention has been devoted to Langmuir–Blodgett (LB) and self-assembled (SA) films consisting of organized molecular assemblies in the form of ultrathin films. Carboxylic acids^{1–5} and thiols^{6–10} are known as the most effective surfactant molecules to form the LB and SA films, respectively, on the metallic surfaces. In LB deposition, the structure of multilayers is affected by the orientation of the first layer anchored directly on the substrate. Although the fatty acid tail of the adsorbed monolayer is known to be inclined at an angle of 8–25° to the normal of the surface,^{3,11,12} the detailed interaction mechanism of carboxylic acid with the metal surfaces has not been established.

Carboxylic acid can bind to metal via either the oxygen lone pair electrons or the carboxylate π systems.^{13–16} Depending on the binding mechanism, the adsorbed carboxylic acid will assume different orientations on the surface. In order to deepen our understanding of the interaction of carboxylic acid with the metal surface, a more thorough investigation than that hitherto performed seems necessary.

Owing to its rather rigid structure, benzoic acid can be regarded as a good model compound in the investigation of interaction of carboxylic acids with metal surfaces. Accordingly, numerous researchers have examined its adsorption mechanism.^{17–19} However, a controversy still remains on the nature of its interaction with surfaces. For instance, Pagannone et al.¹⁷ reported that the molecule adsorbs on the silver surface via the oxygen lone pair electrons with the benzene ring oriented perpendicular to the surface. On the other hand, the same molecule was reported by Stern et al.¹⁸ to adsorb on platinum via the π system of carboxylate with a flat orientation and by Gao and Weaver¹⁹ to adsorb on gold via only the benzene ring π orbitals with the carboxylic group being pendent to the surface. It is surprising and rather unlikely that the adsorption mechanism of such a simple acid depends so much on the kind of noble metals. Such controversial claims on the adsorption mechanism of benzoic acid drawn from vibrational spectroscopy may be caused by the misinterpretation of the spectral data.

In conjunction with the above implication, we have intended to reinvestigate the adsorption of benzoic acid on a silver surface by surface-enhanced Raman (SER) spectroscopy. In addition,

the reflection–absorption infrared spectrum was also recorded for benzoic acid self-assembled on an evaporated silver film, and an *ab initio* quantum mechanical calculation has been carried out.

Experimental Section

The method for silver sol preparation and details of Raman scattering measurements were reported previously.²⁰ A small amount (10 μL) of 2×10^{-2} M benzoic acid or 4-methylbenzoic acid in methanol was added to 1 mL of silver sol solution to obtain a final concentration of 2×10^{-4} M. When the sol solution had changed color from yellow to red, poly(vinylpyrrolidone) (PVP, MW 40 000) was added as a colloid stabilizer. The pH of a sol solution was adjusted with NaOH or H_2SO_4 as needed. Glass capillaries were used as sampling devices for recording the SER spectra. When the SER spectra were recorded at the silver electrode, the previously reported electrochemical system was used.²¹ The method of electrode preparation was described therein. The electrode was roughened by performing sequential oxidation–reduction cycles (ORCs) in 0.1 M KCl. All the potentials are quoted versus a saturated calomel electrode (SCE).

A Japan Spectroscopic Model R-300 Raman spectrometer operated with 514.5 nm radiation from an argon ion laser (Spectra-Physics Model 164-06) was used to obtain the Raman spectra. Raman scattering was observed at 90° geometry using a photon counting system interfaced with a personal computer. In a typical experiment, the laser power was 50 mW at the sample position and the spectral slit width was 10 cm^{-1} .

The silver substrates used for the self-assembling (SA) of benzoic acid were prepared by evaporating silver at 10^{-5} – 10^{-6} Torr on batches of previously sonicated 2.5×3.7 cm glass slides. After a near 200 nm deposition, the evaporator was back-filled with nitrogen to reduce the ambient contamination. The self-assembled monolayer was prepared by dipping the silver substrate into 10^{-3} M benzoic acid in ethanol for 1 h. After being taken out from the solution, the substrate was rinsed with ethanol. The soaking solution was initially bubbled with nitrogen, and the whole SA system was kept in the N_2 -purged drybox during the film deposition.

The infrared spectra were obtained with a Bruker Model IFS 113v FT-IR spectrometer equipped with a mercury cadmium telluride detector. To record the reflection–absorption IR spectrum, a specular reflection attachment (Harrick VRA) was used in conjunction with a Harrick wire grid polarizer. The angle

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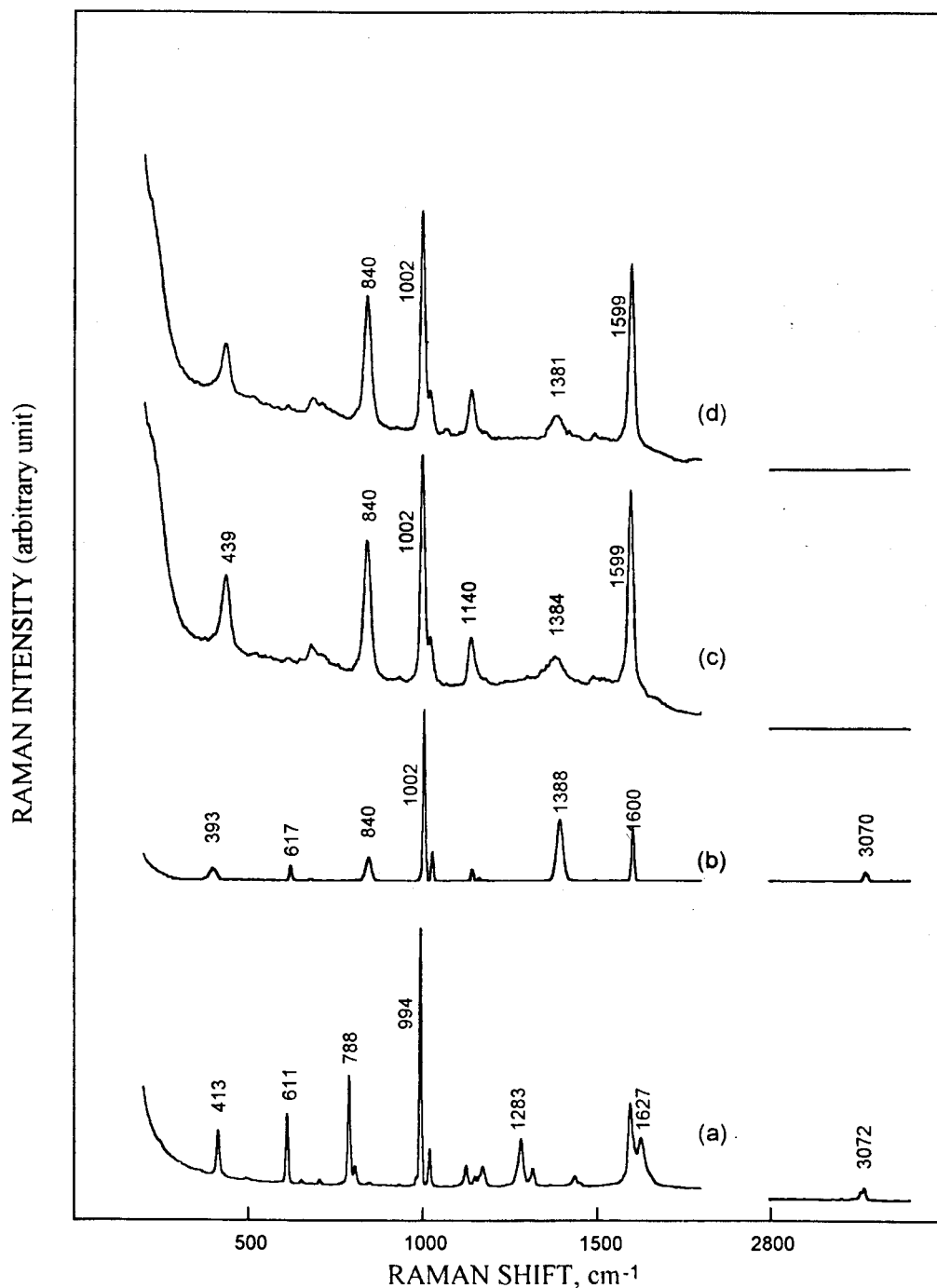


Figure 1. Ordinary Raman spectra of benzoic acid obtained (a) in the solid state and (b) in aqueous solution at pH 13. (c) SER spectrum of 2×10^{-4} M benzoic acid obtained in silver sol. (d) SER spectrum of 2×10^{-4} M benzoic acid in silver sol in the presence of 10^{-3} M BH_4^- .

of incidence for the p-polarized light was set at 80° . Each spectrum was obtained by averaging 2048 interferograms at 4 cm^{-1} resolution. To reduce the effect of water vapor rotational lines on the absorption spectra, the sample and reference interferograms were recorded alternately every 32 scans. The Happ-Genzel apodization function was used in Fourier transforming the interferograms. The absorption spectrum is reported as the $-\log(R/R_0)$, where R and R_0 are the reflectivities of the sample and the bare clean silver substrate, respectively. The IR spectrum of BA in aqueous phase was obtained with a nine-reflection ZnSe prism liquid cell (Harrick Model PLC-19M). All chemicals were reagent grade, and triply distilled water was used throughout.

Results and Discussion

The ordinary Raman (OR) spectra of benzoic acid (BA) obtained in solid state and in highly basic aqueous solution are

shown in Figure 1a and 1b, respectively. Existence of BA as benzoate in basic medium can be evidenced from the presence of the $\nu_s(\text{COO}^-)$ band at 1388 cm^{-1} in Figure 1b. The $\nu(\text{C=O})$ band of the acid form which appears at 1627 cm^{-1} in Figure 1a is barely seen in Figure 1b. In Table 1 the positions of peaks and their vibrational assignments are collectively summarized. The present vibrational assignments are made by referring to the works of Varsanyi²² and Lewandowski and Baranska.²³

The SER spectrum of BA obtained in a silver sol is shown in Figure 1c. As reported by Pagannone et al.,¹⁷ the SER spectral pattern is seen to be significantly different from the OR spectrum of neat BA (Figure 1a) but resembles the OR spectrum of dissolved benzoate (Figure 1b). In the SER spectrum, the acid C=O stretching band is completely absent while the symmetric stretching and bending vibrations of the carboxylate group appear distinctly at 1384 and 840 cm^{-1} , respectively. This implies that BA is adsorbed on the sol surface as benzoate. Considering further

TABLE 1: Spectral Data and Vibrational Assignments for Benzoic Acid^a

ORS		SERS				assignment ^d
solid	basic ^b	sol	electrode ^c			
			-0.2	-0.6	-1.0	
413	393					16a
		439		429	429	16b
611	617					6b
651	675	679		681	681	1
		709		726	725	$\gamma_s(\text{COO}^-)$
788						11
	840	840	840	837	837	$\delta(\text{COO}^-)$
994	1002	1002	1002	1002	1002	12
1021	1025	1025	1025	1025	1025	18a
1126						18b
1149	1138	1140	1140	1138	1137	9b
1172			1177	1177	1176	9a
1283						$\nu(\text{C—O})$
1317						14
	1388	1384	1388	1386	1384	$\nu_s(\text{COO}^-)$
1437	1444					19b
			1491	1490	1490	19a
1597	1600	1599	1597	1597	1597	8a
1627						$\nu(\text{C=O})$
3073	3072		3060	3062	3062	$\nu(\text{C—H})$

^a Wavenumbers in cm^{-1} . ^b Taken at pH 13. ^c Potentials quoted versus SCE. ^d Denoted in terms of Wilson notation given in ref 22.

that the $\nu_s(\text{COO}^-)$ band is broadened one and half times more than others upon surface adsorption, the carboxylate group is thought to interact directly with the surface. Namely, the mode of adsorption to the sol surface should be chemisorptive through the carboxylate group.

Pagannone et al.¹⁷ assigned the asymmetric stretching vibration of the carboxylate group to the 1548 cm^{-1} band in the OR spectrum of benzoate. However, we could not identify the $\nu_{as}(\text{COO}^-)$ band in the OR spectrum albeit the band could be seen clearly at 1541 cm^{-1} in the IR spectrum. Pagannone et al. claimed further that the $\nu_{as}(\text{COO}^-)$ band appeared at 1450 cm^{-1} in the SER spectrum. In contrast, we could not observe any band attributable to the $\nu_{as}(\text{COO}^-)$ mode in the SER spectrum. Considering that the symmetric and bending modes of carboxylate group shift at best 4 cm^{-1} upon surface adsorption, assignment made by Pagannone et al. for the $\nu_{as}(\text{COO}^-)$ mode in the SER spectrum seems to be erroneous.

Although the SERS selection rule has not been established unequivocally, the benzene ring C—H stretching vibration was demonstrated to be an unambiguous probe in the determination of surface orientation of aromatics. Namely, in accordance with the electromagnetic surface selection rule proposed by Creighton²⁴ and by Moskovits and Suh,²⁵ the C—H stretching vibration should be relatively more enhanced when the C—H bond is perpendicular to the surface plane than when it lies parallel to the surface. In this regard, Pagannone et al.¹⁷ suggested that adsorbed benzoate do not lie flat on the surface on the basis of the presence of the $\nu(\text{CH})$ band in their SER spectrum. From the intensity changes of the ring modes, they claimed, on the other hand, that the orientation of the adsorbate must be different from an end-on type. The adsorbed benzoate was thus concluded to be oriented with its C_2 axis canted with respect to the surface.

The SER spectral pattern shown in Figure 1c is much the same as that reported by Pagannone et al. Nonetheless, we could not ascertain the existence of the $\nu(\text{CH})$ band unequivocally even though the band was occasionally observable in the sol SER spectrum with a red-sensitive detector. This may suggest that the adsorbed benzoate on the sol surface is more inclined to a flat orientation rather than to a perpendicular one. Such a possibility could be inferred further by comparing the SER spectrum obtained in a silver sol with that obtained at a silver electrode.

Figure 2 shows the SER spectra of BA obtained at a silver electrode. The present SER spectral quality is superior to that

reported by Shin and Kim.²⁶ The peak positions observed in Figure 2 are also summarized in Table 1. The complete absence of the $\nu(\text{C}=\text{O})$ band dictates that BA should chemisorb at the electrode surface as benzoate, as is the case on the sol surface. However, a few remarkable differences exist between the SER spectra obtained at the electrode and in the sol. First of all, the number of peaks in the electrode spectrum is larger than that in the sol spectrum. The newly observable peaks are nonetheless attributable to the ring modes of adsorbed benzoate species, i.e. ν_{9a} (1177 cm^{-1}) and ν_{19a} (1491 cm^{-1}). These peaks are readily observable in the IR spectrum but indiscernible in the OR spectrum taken at basic conditions. The appearance of IR-active but Raman-inactive modes in the SER spectrum is frequently reported in the literature.²¹ This may be rendered to the symmetry reduction caused by the surface adsorption and/or to the different enhancement mechanisms operating at the electrode and sol surfaces.

Another noticeable difference between the electrode and sol spectra concerns the peak positions as well as the relative intensities of the COO^- group related modes. In the sol spectrum the $\nu_s(\text{COO}^-)$ band appears at 1384 cm^{-1} with a rather weak intensity. However, the band becomes one of the most intense bands in the electrode spectrum, appearing at 1388 cm^{-1} at -0.2 V and at 1384 cm^{-1} at -1.0 V . On the other hand, the $\delta(\text{COO}^-)$ band appearing at around 840 cm^{-1} becomes weaker along with a slight red shift as the electrode potential decreases. This may indicate that the adsorption mechanism of BA on the sol surface is different from that on the electrode surface. On the other hand, the C—H stretching band could be identified clearly at 3060 cm^{-1} in the electrode spectra. This dictates that benzoate should preferably assume a perpendicular stance on the electrode surface. The species responsible for the sol spectrum may then be conjectured to assume more likely a flat stance. Then, the packing density at the electrode surface will be somewhat larger than that at the sol surface. Although the exact value cannot be presented, the packing density of benzoate is expected to be around 5×10^{14} molecules/ cm^2 if one assumes that the surface area occupied by each benzoate species is similar to those (ca. 20 \AA^2) of cyclohexanethiolate²⁷ and other related aliphatic thiolates^{28–31} adsorbed on the silver surfaces via their sulfur atoms (in fact, from the density of benzoic acid in the crystalline state and the reported interatomic distances in benzoate,³² the packing density of benzoate with a perpendicular stance is computed to be 6.7×10^{14} molecules/ cm^2 , but for a closed-packed flat stance, the packing density of benzoate is calculated to be 2.9×10^{14} molecules/ cm^2).

Referring to the previous SERS studies on 4-aminobenzoic acid (4ABA)²¹ and 4-(methylthio)benzoic acid (4MTBA),¹³ the $\nu_s(\text{COO}^-)$ mode should have red-shifted by as much as $13\text{--}19\text{ cm}^{-1}$ from the value in a free state when the carboxylic acid adsorbs on the highly negatively charged surface via the π orbital of the carboxylate group. With the knowledge that the same mode red-shifts for BA only by 4 cm^{-1} at -1 V , BA can be thought to be bound to the electrode surface via the oxygen lone pair electrons rather than via the π orbitals. Such a bonding will more favorably occur with a perpendicular orientation. In that case, the electron donation from metal to the antibonding π^* orbital of the carboxylate group will be ineffective as actually observed. On the other hand, the observations made for 4ABA and 4MTBA suggest that the SER spectral pattern should be retained as far as the adsorption mechanism is invariably maintained. The substantial difference in the SER spectral pattern of BA observed in the sol and at the electrode may then be thought to arise from different adsorption behaviors. Considering that the $\nu_s(\text{COO}^-)$ mode red-shifts only by 4 cm^{-1} upon adsorption on the sol surface, BA can be thought to be adsorbed on the sol surface with a nearly flat or slightly canted orientation, such that the π orbital of the carboxylate group can participate

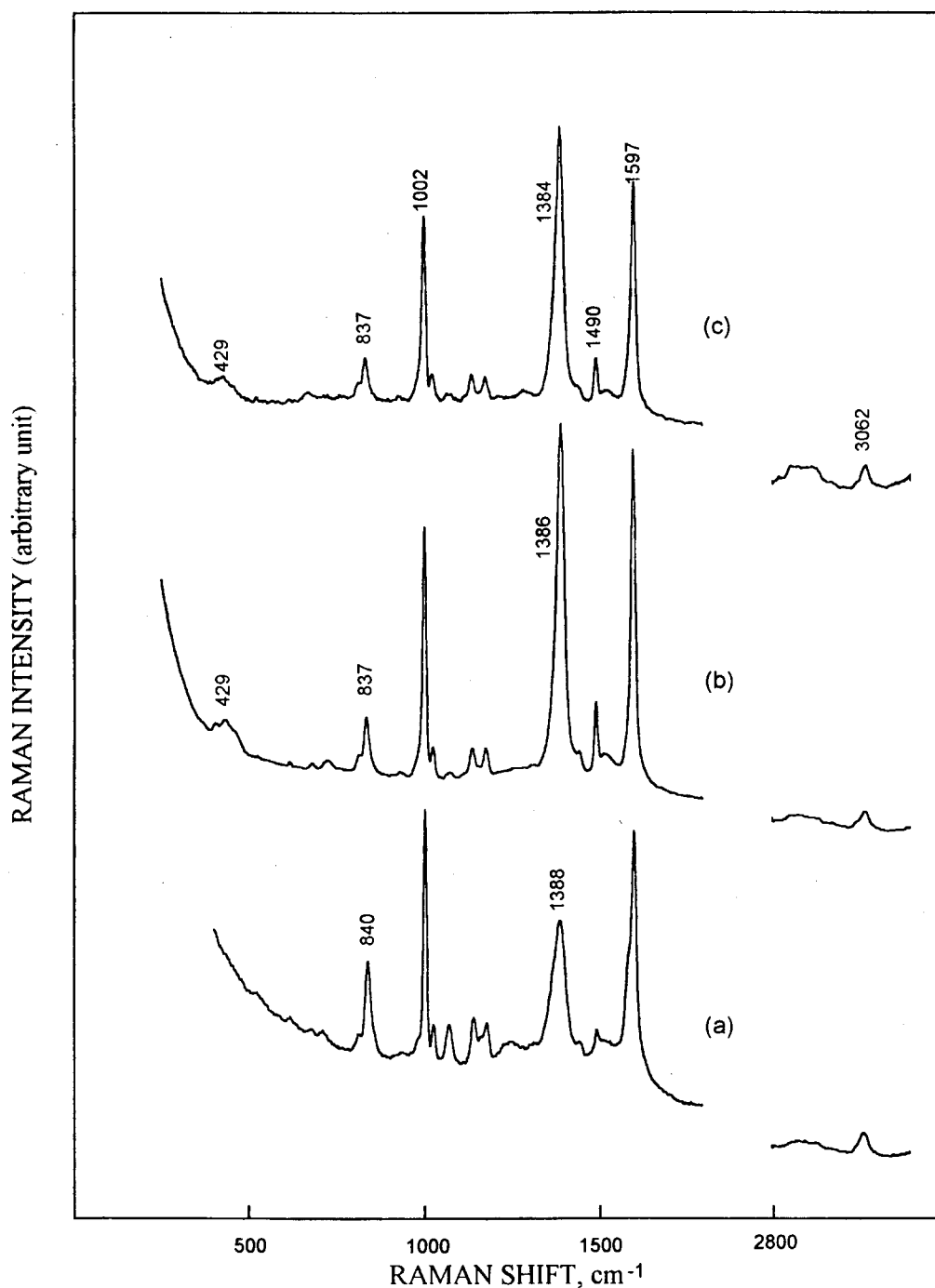


Figure 2. SER spectra of benzoic acid obtained at a silver electrode at (a) -0.2 , (b) -0.6 , and (c) -1.0 V versus SCE.

in the surface bonding. The fact that the out-of-plane mode, i.e. ν_{16b} , is more distinct in the sol spectrum than in the electrode spectrum may also support the above argument.

The potential dependence of the $\delta(\text{COO}^-)$ mode of BA appeared also somewhat different from those of 4ABA and 4MTBA. At the electrode surface, the $\delta(\text{COO}^-)$ mode of BA became weakened upon the potential lowering. In contrast, for 4ABA and 4MTBA the corresponding modes became more or less stronger upon the potential lowering. The accompanying peak shift was to some extent greater in the latter case than that in the former. This may be attributed once again to the different adsorption mechanisms for these molecules. One intriguing observation concerns the intensity of the $\nu_s(\text{COO}^-)$ mode. For 4ABA and 4MTBA, the $\nu_s(\text{COO}^-)$ modes appeared distinctly in both the sol and electrode spectra. However, the mode became slightly weakened for 4ABA but more or less intensified for 4MTBA as the surface potential decreased. For the case of BA, the $\nu_s(\text{COO}^-)$ mode became considerably stronger as the electrode potential

was lowered, albeit the mode appeared very weak in the sol spectrum. Hence, it seems that the intensity of the $\nu_s(\text{COO}^-)$ mode is not directly related to the adsorption mechanism.

Naturally, a question arises whether the different adsorption behavior observed on the sol and electrode surfaces is intrinsic to BA. In this regard, the SER spectra of 4-methylbenzoic acid (4MBA) were recorded in a silver sol and at a silver electrode. In the sol spectrum, the $\nu_s(\text{COO}^-)$ mode appeared at 1386 cm^{-1} , implying a 4 cm^{-1} downshift from that in a free state. In the electrode spectrum, the same mode appeared at 1401 cm^{-1} at -0.4 V and at 1398 cm^{-1} at -0.8 V . The mode has thus blue-shifted by $8\text{--}11\text{ cm}^{-1}$ upon adsorption at the electrode. Although the ring C—H stretching band was hardly seen in the sol spectrum, the $\nu(\text{CH})$ band could be identified clearly at 3070 cm^{-1} in the electrode spectra. These spectral features are almost the same as those observed for BA. Hence, the adsorption mechanism of 4MBA seems very similar to that of BA.

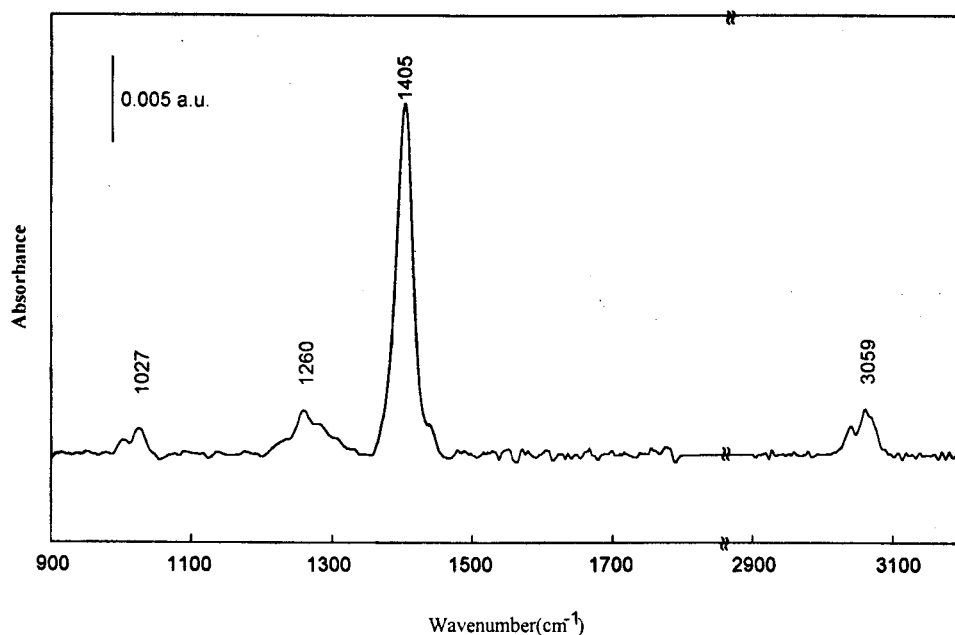


Figure 3. Reflection-absorption infrared spectrum of benzoic acid self-assembled on evaporated silver film.

It is difficult to manifest the origin of the different adsorption mechanism found at the sol and electrode surfaces. From an experimental point of view, such a difference may be thought to be connected with the potential applied to the electrode. In fact, numerous cases have been reported in the literature.^{33–36} regarding the changes in the surface orientation of adsorbates as a function of applied potential. The phenomenon observed for BA seemed, however, to have nothing to do with the surface potential. Acknowledging that sodium borohydride lowers the sol surface potential,³⁷ we have attempted to record the SER spectrum of BA in a silver sol in the presence of BH_4^- . The SER spectra thus obtained (see Figure 1d) were barely different from those obtained without BH_4^- . Nonetheless, it is informative to note that the $\nu_s(\text{COO}^-)$ mode downshifted by 3 cm^{-1} when the sol surface potential reached down to -0.3 V by the addition of BH_4^- to a final concentration of 10^{-3} M .

Various adsorbates have been reported to assume different orientations, depending on their surface coverages. For instance, 2-naphthoic acid adsorbing on the silver sol surface via the carboxylate group was reported to have a perpendicular orientation at high surface concentration but to have a parallel one at low surface concentration.³⁸ As far as an orientational change can be induced by the variation of surface concentration, a perpendicular orientation is favorable at a full monolayer coverage limit. Since the SER spectral patterns for BA and 4MBA are hardly dependent on their bulk concentrations, the spectral difference observed at the sol and electrode surfaces seems also to have nothing to do with the surface concentration.

At this moment, it may be informative to discuss the infrared spectral feature for BA adsorbed on the flat silver surface. Figure 3 displays the reflection-absorption infrared (RAIR) spectrum of BA self-assembled on an evaporated silver film. All the peaks in the RAIR spectrum can be rendered to the adsorbed benzoate species. The $\nu(\text{C}=\text{O})$ peak was completely absent. This absence, together with the presence of symmetric stretching band of the COO^- group at 1405 cm^{-1} , dictates that the adsorption process results in the formation of carboxylate salt. The fact that the corresponding asymmetric stretching band [$\nu_{as}(\text{COO}^-)$] is hardly detectable in the RAIR spectrum suggests further that the line joining two oxygen atoms of the carboxylate group lies parallel to the silver substrate. Namely, the carboxylate head group should be bound at the silver substrate symmetrically. Moreover, the benzoate species should assume a perpendicular stance with respect to the surface rather than a flat stance. This conclusion

is based on the well-known infrared surface selection rule^{39–41} that vibrational modes whose dipole moment derivatives possess components normal to the metal surfaces are preferentially excited. In this sense, with a flat orientation, only the out-of-plane ring modes will appear in the RAIR spectrum. All the peaks in Figure 3 can be attributed, however, to the in-plane ring modes, implying a perpendicular stance. Nonetheless, it is not clear whether the carboxylate group binds to the silver surface as a bridging or a bidentate form. The distance between the two oxygen atoms in the carboxylate group³² is generally about 2.23 \AA , and the diameter of the silver atom⁴² is 2.88 \AA so that either form seems to be feasible in the adsorbed state. Considering that most silver salts are reported from X-ray crystallographic studies^{43–45} to be composed of a bridging structure, the adsorbed benzoate may be assumed to exist as a bridging form.

It is intriguing that the frequency of the $\nu_s(\text{COO}^-)$ mode observed in the RAIR spectrum is larger by 18 cm^{-1} than that in the OR or IR spectrum taken at basic conditions. This may imply that the oxygen lone pair electrons of the carboxylate group have strongly antibonding character and that the silver-to-benzoate electron back-donation hardly occurs with an upright orientation. Although there exists a noticeable difference in the peak frequency of the $\nu_s(\text{COO}^-)$ mode, the RAIR result seems, however, to correspond more closely to that from the electrode SER spectra. Namely, the benzoate species should assume more likely a perpendicular orientation with respect to the silver electrode surface. This conclusion contrasts apparently with that made from the sol SER spectrum.

In order to judge which of the two possibilities, perpendicular or flat stance with respect to the surface, is more favorable, the calculation of their relative energies has been attempted by an *ab initio* quantum mechanical method. In this calculation, the silver surface was modeled by constructing an Ag_5^+ cluster. Two limiting cases were considered, one being benzoate (the actual surface species) adsorbed via its oxygen lone pair electrons with a perpendicular orientation and the other being benzoate adsorbed via the π systems of carboxylate and the benzene ring, assuming a flat orientation with respect to the silver surface (see Figure 4). The interatomic distances in Ag_5^+ were frozen in complying with the value for bulk material.⁴⁶ The interatomic distances in benzoate were also fixed in the calculation by referring to the previously reported values.³² The geometry optimization was performed by varying the distance between the adsorbate and the silver cluster, using the GAUSSIAN 92 Program for Windows⁴⁷

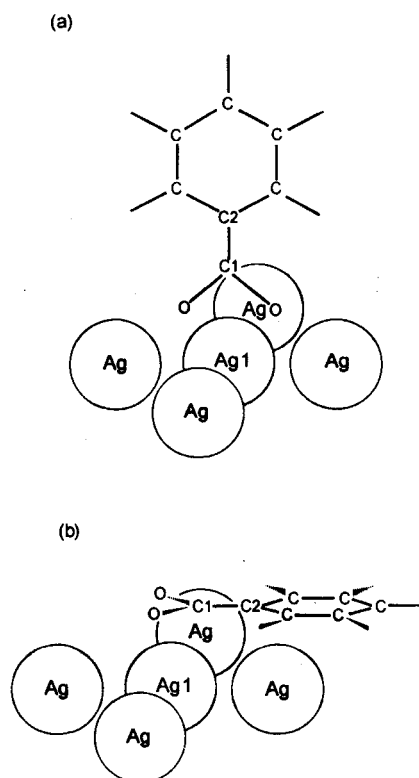


Figure 4. Schematic diagram of benzoate adsorbed on a Ag_5^+ cluster with (a) perpendicular and (b) flat orientations, modeled by ab initio quantum mechanical calculations.

TABLE 2: Optimized Geometry of Benzoate Adsorbed on a Ag_5^+ Cluster^{a-c}

Ag_5^+ -benzoate(perpendicular)		Ag_5^+ -benzoate(flat)	
$r(\text{C}_1-\text{Ag}_1)$	2.8707	$r(\text{ring}-\text{Ag})^d$	2.70
$r(\text{C}_1-\text{O})$	1.2794	$r(\text{C}_1-\text{O})$	1.270
$r(\text{C}_1-\text{C}_2)$	1.4985	$r(\text{C}_1-\text{C}_2)$	1.525
$\angle(\text{O}-\text{C}_1-\text{O})$	123.0	$\angle(\text{O}-\text{C}_1-\text{O})$	127.8

^a Distances are in angstroms, angles in degrees. ^b See Figure 4 for the numbering of atoms. ^c Interatomic distances not mentioned in this table are fixed in complying with the reported values in ref 32. ^d Distance between the benzene ring and the Ag_5^+ cluster plane.

with the LANL1DZ basis set, i.e. Dunning/Huzinaga valence double- ζ (DZ) for the adsorbate and Los Alamos ECP + DZ for the silver cluster. The best optimized results are summarized in Table 2. The perpendicular geometry is determined to be more stable by 105 kJ/mol over the flat geometry. In comparison with the sum of unbound state energies, i.e., $E(\text{Ag}_5^+) + E(\text{BA}^-)$, the energy of the perpendicularly adsorbed state is lower by 418 kJ/mol. It is interesting that the horizontally adsorbed state is also lower by 313 kJ/mol than the unbound state. This suggests that the flat orientation as well as the perpendicular orientation can occur although the former is less favorable than the latter.

Invoking the previous SERS study,⁴⁸ both the silver electrode and sol surfaces should be present in equilibrium with solution, being covered preferentially with a chemical species that adsorbs more strongly to silver. The substantial enhancement of Raman scattering upon the addition of benzoic acid to either sol or electrolyte implies that the strength of benzoic acid adsorption to silver is much stronger than any other species present in the bulk phase. With the assumption that the perpendicular orientation is more feasible than the flat orientation, it is, however, very difficult to rationalize the different SER spectral feature observed in the sol medium. One plausible explanation would render the different spectral pattern as arising from either the different surface structure or the different adsorption site. The electrode surface is known to be covered with nearly hemispherical

islands^{49,50} of diameter 10–100 nm. Although the colloidal particles have diameters within this same length scale, much larger SERS signals are obtainable if the particles having slightly positive charges are aggregated into stringlike clusters.^{51,52} Considering that the atomic scale roughness of the sol surface will be quite different from that of the electrode surface, the different adsorption behavior may have relevance to the difference in the detailed microstructure of adsorption sites on the two surfaces. On the other hand, it has been proposed by many investigators^{49,50,53,54} that the electrode surface which has experienced ORCs was composed of the so-called "adatom sites" that could form a complex with an adsorbed species. The function of the surface complex was claimed to stabilize a particular arrangement of adsorbate such that a resonant Raman scattering could occur at the metal surface. The electrochemically stabilized surface complexes were reported also to be excited by a charge transfer mechanism.⁵⁴⁻⁵⁶ The intensification of the $\nu_s(\text{COO}^-)$ band upon the potential lowering may then be understood in terms of the availability of charge transfer excitation. Although the above explanation may seem plausible, the exact cause of SER spectral difference between the two silver substrates remains a matter of conjecture at the moment.

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