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Studies on the Inelastic Electron Tunneling Spectroscopy of *o*-Hydroxy-, *o*-Amino-, and *o*-Mercaptobenzoic Acid on Aluminium Oxide

Hideaki Monjushiro,* Katsuo Murata, and Shigero Ikeda
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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Inelastic electron tunneling (IET) spectra were obtained for *o*-hydroxybenzoic acid (OHBA), *o*-aminobenzoic acid (OABA) and *o*-mercaptobenzoic acid (OMBA) adsorbed on aluminium oxide (AlO_x) grown on aluminium film and were analyzed by referring IR results. OHBA is adsorbed on AlO_x with both two functional groups, carboxyl and hydroxyl radicals. In the case of OABA, the adsorption occurs mainly with carboxyl group and the interaction between amino group and AlO_x is rather weak. Mercapto group of OMBA forms two kinds of hydrogen bonding, and a dissociated species on AlO_x. These results indicate that the surface of AlO_x used in this study is highly hydrated and hydroxyl groups on the oxide are reactive with the proton donating sites of the chemical species. IET spectra of *o*-fluoro- and *o*-chlorobenzoic acid were also observed for comparison.

Inelastic electron tunneling spectroscopy (IETS) is a kind of energy loss electron spectroscopy. The principle of IETS is based on the interaction between tunneling electrons and molecules on the interface of an insulating oxide layer and the metal. An excitation mode of a molecule is obtained as a function of energy of tunneling electrons. With respect to the molecular vibrations, both infrared and Raman active modes can be observed in IETS. The details of the principle, techniques and applications of IETS have been well reviewed by several authors.[1–3] Since this spectroscopy is very sensitive, vibrational spectra of molecules adsorbed on the insulating oxide layer with submonolayer coverage could be observed.[4] Therefore IETS is applicable to the state of arts analysis for trace amounts of chemical species. One should note in this case that chemical species containing various functional groups interact with the oxidized aluminium insulating surface, leading to the partial modification of the vibrational spectra of the active sites of a free molecule. And these studies are also helpful to understand the surface property such as acidity and basicity of aluminium oxide grown on aluminium metal.

This paper presents IETS studies on the molecules of bifunctional benzene derivatives: *o*-hydroxy-, *o*-amino-, and *o*-mercaptobenzoic acid on aluminium oxide grown on aluminium film. These compounds possess two different functional groups in single molecule. Comparative analysis on the difference of molecular vibrations between IETS and IR or Raman spectra was carried out to elucidate the adsorbed structure of the proposed compounds and to analyze the reactivity of the functional groups. The study was also attempted to understand the property of the aluminium oxide utilized for IETS measurement.

Experimental

Preparation of Tunneling Junction. Tunneling junctions of Al–Al oxide–Pb sandwich structure were prepared in a specially designed home-made vacuum chamber for this study as shown in Fig. 1. The chamber was evacuated with oil diffusion pump through liquid N_2 trap as low pressure as 2×10^{-5} Pa. It consists of two rooms, an evaporation room for the preparation of metal electrodes and a sample loading room where oxidation of aluminium electrode surface and sample loading are carried out. The entire process of junction preparation was accomplished in this chamber as follows. First, aluminium was evaporated onto a thoroughly cleaned glass slide under a pressure of 5×10^{-4} Pa or below. The oxidation of aluminium film was carried out by exposing it to oxygen gas saturated with water vapor for 5 min. And then 4 μl of sample solution was dropped on the oxide. During the loading procedure, the pressure of the evaporation room was maintained below 1×10^{-3} Pa. This enabled rapid performance of next evaporation process. Lead was evaporated finally to make film strips across the aluminium strip. Loaded junctions with a resistance of 40 to 1000 ohm at room temperature with 1 mm×1 mm junction area were available for measurements of IET spectra.

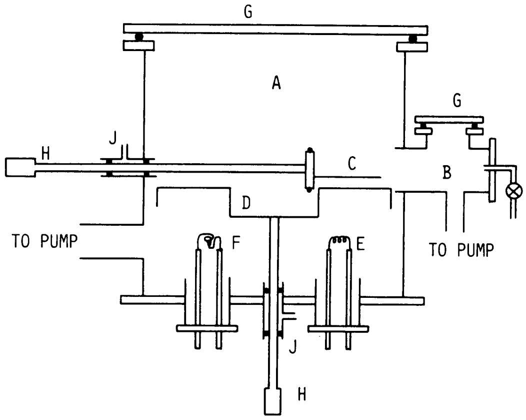

Fig. 1. Sample preparation chamber.
A: Evaporation room, B: sample loading room, C: substrate, D: mask, E : W spiral for Al evaporation, F : W basket for Pb evaporation, G: glass window, H: motion feedthrough, I : O_2 introducing cock, J: differential pumping.

Measurement of IET Spectra. IET spectra were measured by the device with circuit similar to that of Adler and Jackson[5] as shown in Fig. 2. The bias voltage (20 to 500 mV d.c.) across the junction was applied by low frequency function generator, and an a.c. modulation signal of 1.2 kHz was superimposed on the d.c. bias. The second harmonics of the modulation frequency, being proportional to d^2V/dI^2, was detected with a lock-in amplifier (NF model LI-574). Tunneling spectra were taken at liquid helium temperature 4.2 K, in a standard double glass liquid helium cryostat to obtain sufficient resolution.[1-3] Peak positions were read with digital voltmeter and the values were converted from millivolt to wavenumber with correlation of 1 mV=8.065 cm^{-1} and then a correction of -7 cm^{-1} was made to cancel out the superconducting energy gap of lead electrode. The observed line-width of the spectral peaks at half maximum was *ca.* 20 cm^{-1} with modulation voltage of 0.6 mV rms.

Chemicals. Chemicals used were obtained from Wako Pure Chemical Ind. or Nakarai Chemical Co. They were recrystallized before use. Acetone was used as solvent for sample loading.

Results and Discussion

IET Background Spectra. There appear invariably some peaks which contribute to insulating aluminium oxide and metal electrodes in IET spectra.[6] And there is a fear of observing additional peaks due to solvent molecule. In order to subtract these peaks, IET spectrum of the junction treated with acetone was compared with that obtained from the junction with sample solution. Figure 3 shows the IET spectrum obtained from the junction treated with acetone. The spectral feature is similar to that of unloaded junction and peaks due to adsorbed acetone are not present in the spectrum. Thus it is clear that acetone has no influence on the IET spectrum.

Although the surface property of aluminium oxide could be evaluated from the surface hydroxyl stretching frequency,[7] the observed hydroxyl stretching peak position in IET spectrum is thought to be shifted to lower wavenumber from substantial value due to image dipole effect of top lead electrode,[8,9] and the exact magnitude of the shift could not be estimated. However, the oxide used in this study is considered to be hydrated surface, because oxygen containing water vapor was employed to oxidize the aluminium surface at room temperature.[7]

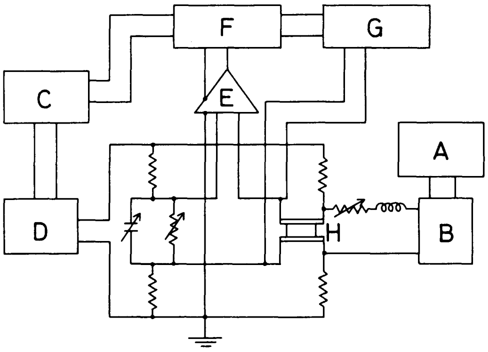

Fig. 2. Block diagram of IETS measurement circuit. A: Low frequency function generator, B : d.c. voltage supply, C: oscillator, D: attenuator, E: pre-amplifier, F: lock-in amplifier, G: X-Y recorder, H: tunnel junction.

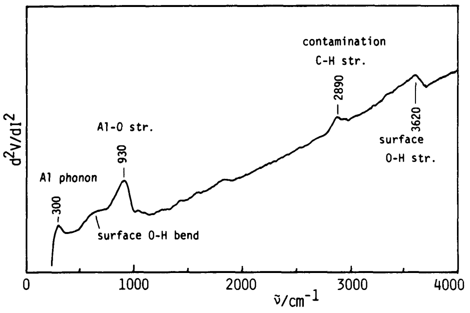

Fig. 3. IET background spectrum of Al–Al oxide–Pb junction.

IET Spectra of o-Substituted Benzoic Acids. The IET spectra of *o*-fluorobenzoic acid (OFBA), *o*-hydroxybenzoic acid (OHBA), and *o*-aminobenzoic acid (OABA) adsorbed on aluminium oxide are shown in Fig. 4. Figure 5 shows the IET spectra of *o*-chlorobenzoic acid (OCBA) and *o*-mercaptobenzoic acid (OMBA) adsorbed on aluminium oxide.

These spectra were obtained from junction loaded from 1 mg/cm^3 acetone solution. The observed spectral

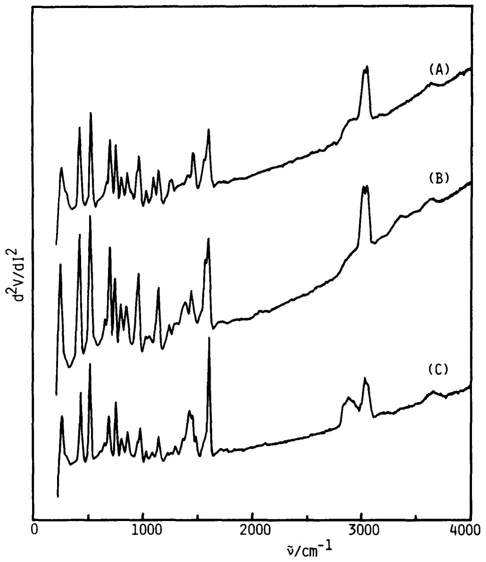

Fig. 4. IET spectra of (A): *o*-hydroxybenzoic acid, (B): *o*-aminobenzoic acid, and (C): *o*-fluorobenzoic acid adsorbed on aluminium oxide. Modulation voltage= 1.2 mV rms.

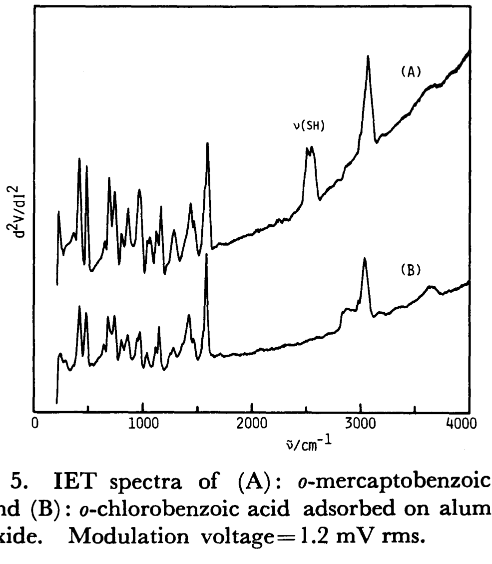

Fig. 5. IET spectra of (A): *o*-mercaptobenzoic acid and (B): *o*-chlorobenzoic acid adsorbed on aluminium oxide. Modulation voltage=1.2 mV rms.

range is from 230 to 4000 cm^{-1}. In these spectra each peak position is reproducible within experimental error of ±0.5 mV (±4 cm^{-1}). The observed values (peak positions and relative intensity) and their mode assignments are listed in Tables 1 and 2. The values of IR data (*o*-fluoro- and *o*-chlorobenzoate) are also listed for comparison. Each peak was assigned by referring to the IR and Raman spectra of *o*-disubstituted benzenes,[10,11] *o*-substituted benzoic acids and their alkali metal salts.[12]

Benzene Ring Modes: The vibrational modes of these compounds can be classified into two groups, namely the vibrational modes of benzene ring system and that of substituent groups. Since *o*-substituted benzoic acids are assigned to the C_s point group, the ring system would have 30 normal vibrations comprised of 21 a′ modes (in-plane modes) and 9 a″ modes (out of plane modes) and all modes are both IR and Raman active. Peaks observed in IET spectra of the proposed compounds could be easily identified with the corresponding normal vibrations of the related *o*-disubstituted benzene ring system. Of the expected four aromatic CH stretching modes, two or three peaks are found at a region of 3000 cm^{-1}, and the peak positions

Table 1. IET spectral data of *o*-fluoro-, *o*-hydroxy- and *o*-aminobenzoic acid on aluminium oxide

Symmetry class	Peak position[a)]/cm^{-1}				Approximate description[b)]
	o-F		*o*-OH	*o*-NH$_2$	
	IR[c)]	IETS	IETS	IETS	
a′				3480 w-b	$\nu_a(\mathrm{NH_2})$
				3350 w-b	$\nu_s(\mathrm{NH_2})$
	3076 m	3058 m	3050 m	3062 s	ν(CH)
	3036 m	3034 m	3023 s	3022 s	
		3001 sh			
	1617 s	1612 vs	1606 s	1612 s	ν(CC) 8a
	1569 s		1575 m-b	1581 s-b	ν(CC) 8b
		1579 sh			
	1600 vs		1560 sh	1570 sh	ν_a(COO)
	1485 s	1491 w	1477 sh	1486 w	ν(CC) 19b
	1452 s	1458 m	1461 s	1458 m	ν(CC) 19a
	1410 vs	1430 m	1410 w-b	1405 w-b	ν_s(COO)
	1309 w	1301 w	1324 w-b	1316 w-b	Kekulé 14
	1264 w	1262 w	1258 w	1251 w	β(CH) 3
	1222 m	1225 w-b	1201 sh	1210 sh	X-sens.
	1163 w			1156 s	β(CH) 9a
		1149 m	1151 m-b		
	1144 w			1130 sh	X-sens.
	1099 m	1100 w	1099 w	1074 w	X-sens.
	1038 m	1033 w	1033 w	1037 w	β(CH) 18b
	861 s	868 w[d)]	862 m[d)]	860 m[d)]	X-sens.
	811 m	808 w[d)]	809 m[d)]	813 m[d)]	X-sens.
	660 m	652 w	671 w	666 w	X-sens.
	569 m	619 w	595 w	564 w	ρ(COO)
	544 w	522 vs[d)]	536 vs[d)]	531 vs[d)]	X-sens.
	403 m	412 sh			X-sens.
a″	975 w	982 m	971 s	972 s	γ(CH) 5
	950 w	956 w	957 sh	955 sh	γ(CH) 17b
	(861)	868 w[d)]	862 m[d)]	860 m[d)]	γ(CH) 10b
	800 s	808 w[d)]	809 m[d)]	813 m[d)]	γ(COO)
	746 vs	758 s	761 s	755 m	γ(CH) 10a
	693 m	693 m	708 s	708 s	ϕ(CC) 4
	521 m	522 vs[d)]	536 vs[d)]	531 vs[d)]	ϕ(CC) 16a
	443 m	437 s	429 vs	432 vs	ϕ(CC) 16b
		262 m	260 m-b	258 s-b	?
			895 w		?

a) Peak positions corrected as in the text, relative intensity also shown; s = strong, m = medium, w = weak, v = very, sh = shoulder, b = broad. b) Description of the modes based on Ref. 11; ν = stretching, ν_a = antisymmetric stretching, ν_s = symmetric stretching, β,ρ = in-plane deformation, γ,ϕ = out of plane deformation, X-sens. = associated with motion of substituent group. c) The IR data listed are of sodium *o*-fluorobenzoate, Ref. 12. d) Wavenumber used twice.

are down-shifted from IR data of the corresponding compounds, respectively. This is presumably due to the effect of top electrode of lead.[9] At the energy region below 1620 cm^{-1}, where the peak shift is negligible, 23 peaks are observed for OCBA, 22 for OMBA, 21 for OFBA and OABA and 20 for OHBA comparing to the expected 26 peaks for normal vibrational modes. Taking into account the coincidence of the wavenumber observed and the number of the peaks below IET spectral range, almost all modes of benzene ring system are observed in IET spectra. The close agreement of the frequency of ring modes between the IETS and IR data indicates that each benzene ring of these compounds has no strong interaction with aluminium oxide surface in chemisorbed structure. On the other hand, the vibrations of substituent functional groups observed in IET spectra show significant difference from those of parent molecules. This fact implies that substituent functional groups to be deformed by junction formation and interaction with aluminium oxide surface could be expected. The bond formation and interaction between the functional groups of sample molecules and aluminium oxide will be discussed below for each compounds.

Table 2. IET spectral data of *o*-chloro- and *o*-mercaptobenzoic acid on aluminium oxide

Symmetry class	Peak position a)/cm^{-1}			Approximate description b)
	o-Cl		*o*-SH	
	IR c)	IETS	IETS	
a′			3079 sh	ν(CH)
	3075 m	3040 m	3038 vs	
	3050 m	2980 m	3009 sh	
			2540 m-b	ν(SH)
			2490 e)	
	1600 s	1592 vs	1587 vs	ν(CC) 8a
	1559 s			ν(CC) 8b
		1567 sh	1560 m-b	
	1589 vs			ν_a(COO)
	1472 s	1475 w	1466 w	ν(CC) 19b
	1431 s		1433 s-b	ν(CC) 19a
		1431 s-b		
	1400 vs		1400 sh	ν_s(COO)
	1313 w	1288 w	1287 w-b	Kekulé 14
	1260 w	1262 w	1270 w	β(CH) 3
	1162 w			X-sens.
		1158 m	1159 s	
	1152 w			β(CH) 9a
	1124 m	1125 w	1122 m	X-sens.
	1050 s		1066 m	X-sens.
		1047 w-b		
	1042 m		1041 w	β(CH) 18b
	842 s	858 sh	864 m d)	X-sens.
	721 s	723 w	745 m d)	X-sens.
	647 m	650 w	655 w	X-sens.
	552 m	529 w	612 w	ρ(COO)
	453 m	430 s d)	427 vs d)	X-sens.
a″	975 w	981 m	971 s	γ(CH) 5
	945 w	955 m	961 sh	γ(CH) 17b
	867 w	871 m	864 m d)	γ(CH) 10b
	805 m	811 m	812 w	γ(COO)
	742 vs	751 s	745 m d)	γ(CH) 10a
	693 m	690 s	695 s	ϕ(CC) 4
	490 w	486 s	494 vs	ϕ(CC) 16a
	408 w	430 s d)	427 vs d)	ϕ(CC) 16b
		367 w	364 w-b	?
		245 w-b	238 m-b	?
			911 vw	δ(CSH)

a) Peak positions corrected as in the text, relative intensity also shown; s = strong, m = medium, w = weak, v = very, sh = shoulder, b = broad. b) Description of the modes based on Ref. 11; ν = stretching, ν_a = antisymmetric stretching, ν_s = symmetric stretching, β,ρ,δ = in-plane deformation, γ,ϕ = out of plane deformation, X-sens. = associated with motion of substituent group. c) The IR data listed are of sodium *o*-chlorobenzoate, Ref. 12. d) Wavenumber used twice. e) Relative intensity of this peak shows sample to sample variation, see text.

o-Hydroxybenzoic Acid (OHBA): In the IET spectrum of OHBA chemisorbed on aluminium oxide, the most characteristic mode of carboxylic acid at *ca.* 1700 cm^{-1} corresponding to the C=O stretching vibration is absent. Instead, antisymmetric stretching mode of carboxylato group; ν_a(COO) is observed at 1560 cm^{-1} as a shoulder on the side of intense peak at 1575 cm^{-1} due to benzene ring skeletal stretching mode, and its symmetric stretching mode; ν_s(COO) appears at 1410 cm^{-1} as a broad peak. This indicates that OHBA is adsorbed on aluminium oxide as carboxylate similar to other carboxylic acids.[13,14]

Another characteristic feature of the IET spectrum of OHBA is that there appear no vibrational modes corresponding to hydroxyl group. Solid OHBA has its OH stretching band at 3240 cm^{-1} and in the case of alkali metal salts of OHBA, OH stretching band appears in the range of 2500 to 2900 cm^{-1} owing to the strong intramolecular hydrogen bonding with carboxylate ion.[15] In the IET spectrum, however, no peak due to OH stretching mode is observed in the 2500 to 3600 cm^{-1} region. In-plane bending mode of OH group expected to appear at *ca.* 1200 cm^{-1} is also missing in IET spectrum. A small shoulder at 1201 cm^{-1} in IET spectrum is assigned to substituent group sensitive mode of the ring system, because similar peaks are also observed in IET spectra of OFBA and OABA. These facts imply the formation of phenolate species on aluminium oxide surface in analogy to other phenols.[16] Then, two functional groups in the single molecule of OHBA might interact with aluminium oxide surface.

Two kinds of interaction mode would be presumed for the adsorption of OHBA on aluminium oxide surface. One would coordinate to a single aluminium atom with two active sites of a molecule to form a chelate ring, and the other is the coordination of each functional group to different aluminium atoms to form a bridge structure. If both functional groups coordinate to a single aluminium atom to form a surface chelate, the carboxylato group should have unidentate structure as shown in Fig. 6 (A). It is known that in

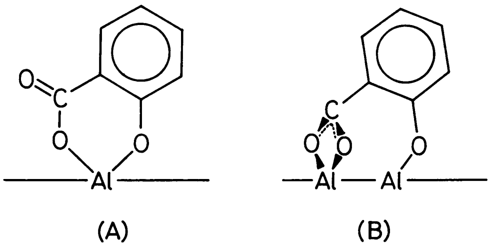

Fig. 6. Schematics of the chemisorption structure of *o*-hydroxybenzoic acid on aluminium oxide.
(A): Chelating structure, (B): bridging structure.

unidentate carboxylate, the wavenumber of ν(C=O) is higher than that of ν_a(COO$^-$) of free carboxylate ion and ν(C–O) is lower than that of ν_s(COO$^-$).[17] Peak positions for carboxylato stretching in IET spectrum of OHBA; ν_a(COO) at 1560 cm^{-1} and ν_s(COO) at 1410 cm^{-1} are in good agreement with IR data of *o*-hydroxybenzoate ion;[15,18,19] ν_a(COO$^-$) at 1546 cm^{-1} to 1593 cm^{-1} and ν_s(COO$^-$) at 1373 to 1410 cm^{-1}. Thus the carboxylato group of adsorbed OHBA is considered to be symmetrical structure like free ion and not unidentate structure. This suggests the adsorption of OHBA on aluminium oxide to form a bridge structure as shown in Fig. 6 (B).

o-*Aminobenzoic Acid (OABA)*: Similar to the case of OHBA, in the IET spectrum of OABA, there observed no feature due to carboxyl group but carboxylato stretching modes appear at 1570 cm^{-1} and at 1405 cm^{-1}. Thus the adsorption of OABA with carboxyl group on aluminium oxide is evident to form surface carboxylate. Close similarity of those carboxylato stretching peak positions with those of OHBA indicates that surface carboxylate has symmetrical structure and chelation does not take place.

Most characteristic vibrational modes reflecting the nature of amino group is its stretching vibrations. In the case of OABA, free amino group gives symmetric and antisymmetric stretching modes in 3300 to 3500 cm^{-1} region,[20,21] amino group coordinated to metal ions such as Cu^{2+} exhibits two or three bands in 3100 to 3300 cm^{-1} region[22] and protonation of amino group would cause further down-shift of the bands. Figure 7 shows the expanded low-noise IET spectrum of OABA in the range of 2500 to 4000 cm^{-1}. Beside the peaks due to aromatic CH stretching modes at 3022 cm^{-1} and at 3062 cm^{-1} and surface OH stretching mode at *ca.* 3620 cm^{-1}, two broad and weak peaks are observed at 3350 cm^{-1} and 3480 cm^{-1}. These peaks could be assigned to symmetric and antisymmetric stretching modes of free amino group respectively. This fact implies that there are no strong interactions between amino group of OABA and aluminium oxide surface such as coordination to surface aluminium atom on the oxide or protonation by surface hydroxyl group observed for other amines by IETS.[23–25]

However, the both observed peaks corresponding to amino stretching vibrations are very broad (the linewidth at half maximum is at least 120 cm^{-1}). This suggests the existence of weak interaction between the amino group and the oxide surface. Formation of hydrogen bonding is most probable to explain the broadening of the amino stretching peaks. However, generally in IR spectra, hydrogen bonding causes the down-shift of corresponding stretching mode,[26] whereas IET spectrum shows no shift from free state frequency. This fact will not be explained by the simple hydrogen bonding assumption. Another modes of amino group expected to lie below 1650 cm^{-1} could not be assigned because of the complexity of the spectrum in this region. Thus further interpretations for the surface interactions between amino group and aluminium oxide surface is quite difficult in the present.

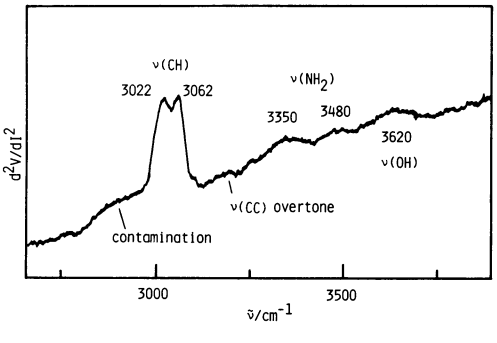

Fig. 7. Expanded IET spectrum of *o*-aminobenzoic acid adsorbed on aluminium oxide in the range of 2500 to 4000 cm^{-1}.

o-*Mercaptobenzoic Acid (OMBA)*: In the IET spectrum of OMBA, there observed carboxylato stretching modes at *ca.* 1559 cm^{-1} and at 1400 cm^{-1}. Both peaks are considered to coincide with ring modes and accurate positions are not found from the spectrum. However, OMBA is considered to be adsorbed on aluminium oxide as carboxylate, because of missing of the carboxyl group vibrations. Although the IET spectrum of OMBA has been published by Hall and Hansma,[14] no data was given so far on the mercapto group frequency observed by IETS and no discussion has been done on the nature of mercapto group.

In IR spectroscopy, the free SH stretching modes of aromatic thiols generally appear near 2585 cm^{-1} and the steric and electronic effects have no influence on the SH stretching frequency.[27] In IET spectrum of OMBA, SH stretching modes appear at 2490 cm^{-1} and at 2540 cm^{-1}. The peak splitting indicates the presence of two kinds of species on the oxide. The down-shift of the peaks referred to IR data is to be due to either image dipole effect of top lead electrode[8,9] or hydrogen bonding of mercapto group. In the case of down-shift caused by top metal, the magnitude of the shift should be relate to the oscillating dipole moment strength of the mode. Whereas SH stretching mode of OMBA observed in IR spectrum is quite weak,[27] indicating a small oscillating dipole moment. Therefore the shift must be due not to the top metal effect, but to hydrogen bonding. And the both two SH stretching peaks in IET spectrum are broad on comparing with other peaks corresponding to the ring modes. This fact also supports the presence of hydrogen-bonded mercapto species on the oxide.

Hydrogen bonding of mercapto group of adsorbed OMBA could be classified into either of following three categories; (**I**) intermolecular hydrogen bonding, (**II**) intramolecular hydrogen bonding, and (**III**) hydrogen bonding with aluminium oxide surface. If the intermolecular hydrogen bonding(**I**) is presumed, the number of species(**I**) should be increase with increasing the surface concentration of OMBA. Consequently, the relative intensity of the peak corresponding to species(**I**) should increase. However, no correlation was found between the relative intensity of either peak at 2490 cm^{-1} or at 2540 cm^{-1} and the surface concentration of OMBA. Thus it is clear that species(**I**) is not present on the oxide.

OMBA in solid state or in solution is known to form intramolecular hydrogen bonding(**II**) between mercapto group and oxygen of carboxyl group. Mori *et al.* have studied the mercapto hydrogen bonding in solution by IR spectroscopy in detail.[27)] They observed two bands in mercapto stretching wavenumber at 2558 cm^{-1} and at 2530 cm^{-1} in dilute carbon tetrachloride solution of OMBA, and assigned them to the mercapto species having hydrogen bonding with the ethoxyl and carbonyl oxygen atom, respectively. On the contrary, OMBA adsorbed on aluminium oxide forms carboxylate, and the two oxygen atoms of carboxylato group are considered to be equivalent character. Hence when the species(**II**) is formed on the oxide, only a single configuration must be allowed for OMBA and resulting in a single peak in IET spectrum. The peak position can be expected to appear at around the wavenumber between 2530 cm^{-1} and 2558 cm^{-1}. This assumption leads us to conclude the peak at 2540 cm^{-1} observed in IET spectrum to be due to the stretching mode of intramolecular hydrogen-bonding species(**II**).

The relative intensity of the peak at 2490 cm^{-1} varies by sample to sample. This variation indicates the high surface sensitivity of the interaction in nature. Thus the peak at 2490 cm^{-1} is considered to be due to mercapto group, which forms hydrogen bonding with oxide surface(**III**). Formation of hydrogen bonding between mercapto group and aluminium oxide surface has been already observed for methanethiol molecule by the use of IR spectroscopy.[28)] The hydrogen-bonding species has its stretching mode at 2470 cm^{-1}. The peak position observed at 2490 cm^{-1} in IET spectrum of OMBA is close to this IR value. Therefore we assign the peak at 2490 cm^{-1} to be due to mercapto species(**III**).

In the course of the study on OMBA, we noticed that the intensity of the peak at 2490 cm^{-1} had a tendency to be stronger when the surface hydroxyl stretching peak appeared stronger in IET spectra. To make sure of this, water molecules were introduced into the complete junction by using infusion doping technique,[29)] because the water infusion is expected to increase surface hydroxyl group on the oxide.

Figure 8 shows the expanded IET spectra of OMBA before(A) and after(B) infusion of water. By introducing water molecule into the junction, the peak at *ca.* 3620 cm^{-1} due to surface hydroxyl stretching mode and the peak at 2490 cm^{-1} due to mercapto species(**III**) are both intensified, although the intensities of other peaks remain unchanged. This result indicates that not only the number of surface hydroxyl group but that of mercapto group of struture(**III**) in the junction increase by water infusion. This phenomenon could be explained by assuming the presence of coordination species *via* sulfur atom to surface aluminium atom of the oxide before infusion of water. And this S-bonded species may react with water molecule introduced to form mercapto species(**III**). Consequently, there are three kinds of mercapto species on the aluminium oxide, namely intramolecular hydrogen-bonding species(**II**), species which forms hydrogen bonding with surface oxygen atom(**III**) and S-bonded species.

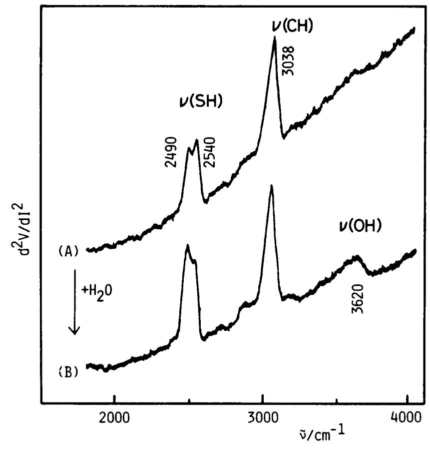

Fig. 8. Expanded IET spectrum of *o*-mercaptobenzoic acid (A): before and (B): after infusion of water.

Property of Aluminium Oxide Surface. The adsorbed feature of the proposed compounds may lead to a suggestion on the surface property of aluminium oxide grown on evaporated aluminium film. In IET spectra of *o*-substituted benzoic acids, it is found that the surface hydroxyl stretching intensity is less than that in back ground spectrum. This indicates the consumption of surface hydroxyl groups with the adsorption reaction of carboxyl group. A presumable reaction is that carboxyl group leaves proton and the proton reacts with surface hydroxyl group to form water. The water produced would be evacuated out during the junction preparation, since the vibrational modes of molecular water are absent in IET spectra. Similar surface reactions are considered to take place on the hydroxyl group of OHBA and partly on the mercapto group of OMBA with surface hydroxyl group.

As discussed above, OHBA is adsorbed on the oxide through both carboxyl and hydroxyl group to form bridge structure, and both functional groups are considered to react with surface hydroxyl groups. Therefore it is thought that there are many neighboring hydroxyl groups on the oxide used. In the case of OABA, amino group of ortho position does not coordinate to the oxidized aluminium despite the possible steric configuration. Then there must be few or no exposed aluminium ion (Lewis acid site)[30)] around the carboxylate adsorption site on the oxide.

Consequently, we conclude that the surface of aluminium oxide grown by wet oxygen is highly hydrated and has many neighboring surface hydroxyl groups. The surface hydroxyl groups tend to react with Brϕnsted acids such as carboxyl group to form water, in other words, the oxide surface behaves as Brϕnsted base with respect to the proposed compounds.

Conclusion

The IETS of three kinds of *o*-substituted benzoic acid with functional groups, -OH, $-NH_2$, and -SH were studied. All compounds are adsorbed on aluminium oxide as benzoate. The second substituent functional groups show various types of interaction with the oxide surface.

The type of the adsorption reaction of these functional groups on the oxide of IET junction is specifically defined to be acid-base reaction. In this case, the oxide surface behaves as base (OH donor) and the functional groups behave as acid (H donor). The reactivity of the functional groups is the order of

$$-COOH, -OH > -SH \gg -NH_2.$$

The results show that the character of aluminium oxide surface utilized for IETS is quite different from that of γ-alumina, which is known to have acidic property.

On the other hand, these surface reactions affect negatively for the utilization of IETS to the identification of unknown chemical species. Further experiences to pile up more IETS data for various compounds are needed as well as the more precise analysis for the characterization of aluminium oxide of IET junction.

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