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Adsorption and Orientation of Isomeric Phthalic Acids on Alumina Surface Observed by Inelastic Electron Tunneling Spectroscopy

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The vibrational spectra of phthalic, isophthalic and terephthalic acid adsorbed onto the alumina surface have been measured by using inelastic electron tunneling spectroscopy. The tunneling spectra of these acids were obtained by liquid-phase doping with water or various alcohol solutions. The detailed assignments for these spectra are given, together with a comparison of their infrared and Raman spectra. It has been found that both phthalic and isophthalic acid are adsorbed onto the alumina surface mainly as the dicarboxylate ions. However, a comparison between the tunneling spectra of terephthalic and *p*-acetylbenzoic acid shows that terephthalic acid is adsorbed predominantly as the monocarboxylate ion onto the surface when doped with alcohol solutions. Hydrogen bonding is observed among the adsorbed hydrogen terephthalate ions. These results show a difference in their orientation and different probabilities of chemical interaction between the alumina surface and the carboxyl groups of the adsorbed isomeric phthalic acids.

A great deal of interest has been paid to a new technique for investigating the adsorbed species on metal surfaces. The vibrational spectra of such species should give important information on their structure and the adsorption mechanism. Inelastic electron tunneling spectroscopy (IETS), discovered in 1966 by Jaklevic and Lambe,[1] reveals the vibrational spectrum of adsorbed species on the oxide surface of a metal–oxide–metal tunneling junction at cryogenic temperatures, as is shown in Fig. 1. Several authors[2–7] have reviewed the principle, apparatus and application; they have demonstrated the potential of IETS.

When a dc-bias voltage is applied across the junction, electrons can tunnel from one electrode through the oxide into the opposite electrode. A vibrational mode of frequency, ν, appears as a peak in the second derivative of the characteristic current-voltage (I–V) function of the junction, d^2I/dV^2, at a voltage of $V=h\nu/e$, where h is Planck's constant and e is the electron charge. Both infrared and Raman-active vibrational modes appear in the IET spectrum. The useful spectral range extends from 400 to 4000 cm^{-1} and includes all molecular vibrations. The high sensitivity and resolution of IETS enable us to measure the detailed spectrum of a fraction of a monolayer of adsorbed species. In general, the oscillating dipole moment perpendicular to the oxide surface couples to tunneling electrons more strongly than that parallel to the surface. Thus, IETS may be expected to be a powerful analytical technique for investigating the chemical interaction and the structure of molecules adsorbed onto the oxide surfaces.

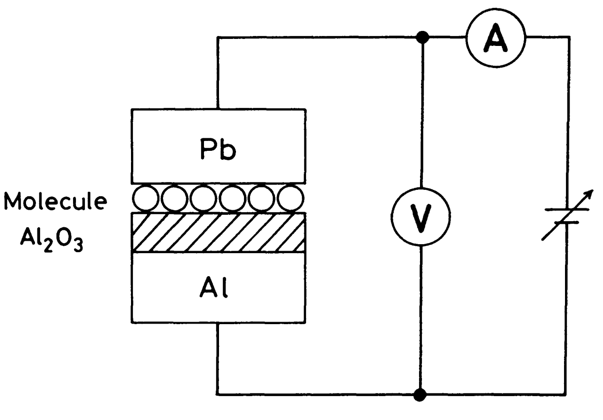

Fig. 1. Schematic representation of the tunneling junction.

The tunneling spectra of benzoic acid,[8] phenol,[9] and benzenesulfonic acid[10] have been measured and indicated their structures on the oxide surfaces. These molecules are found to be adsorbed onto the alumina as anions. The tunneling spectrum of benzaldehyde shows that this molecule reacts with alumina to give the adsorbed benzoate ion.[3,11] In the cases of molecules with two functional groups, however, not so many studies have been carried out. Lewis *et al.*[12] have observed the tunneling spectra of the isomers of catechol, *i.e.*, *o*-, *m*-, and *p*-$C_6H_4(OH)_2$, on Al_2O_3. They found that both catechol and resorcinol are adsorbed as dianions, whereas hydroquinone is adsorbed predominantly as a monoanion. Oxley *et al.*[13] have previously reported that the isomeric phthalic acids are adsorbed onto Al_2O_3 as benzenedicarboxylate ions. Monjushiro *et al.*[14] have studied the adsorption of some *o*-substituted benzoic acids onto Al_2O_3.

The vibrational spectra of isomeric phthalic acids[15] and their ions[16] were measured by means of infrared and Raman spectroscopy. Detailed diagrams for the atom motions involved in these modes can be found in the book by Varsânyi.[17] A comparison between these spectra and the tunneling spectra gives valuable information on these molecules adsorbed onto Al_2O_3. Since alumina is widely used as a catalyst or catalyst support,[18] it is important to know the orientation and structure of adsorbed species in order to understand the reaction mechanism on the catalyst. The isomeric phthalic acids have two carboxyl groups. Their structure on the alumina surface can easily be clarified by examining the characteristic C=O group. In our previous paper,[19] it has been shown that terephthalic acid is adsorbed predominantly as the monocarbox-

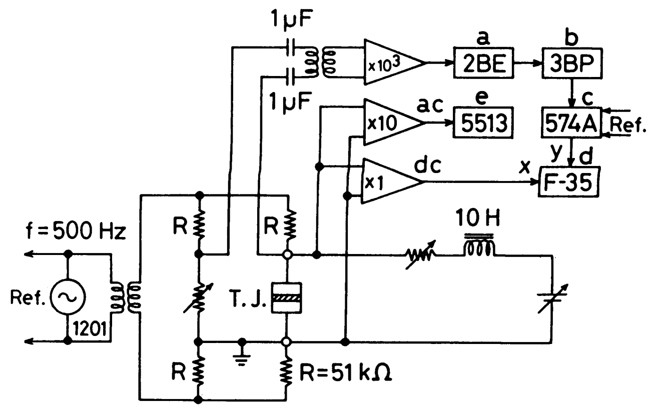

Fig. 2. Schematic diagram of the circuit. One arm of the bridge contains the tunneling junction (T. J.). a) notch filter b) bandpass filter c) lock-in amplifier d) X-Y recorder e) oscilloscope.

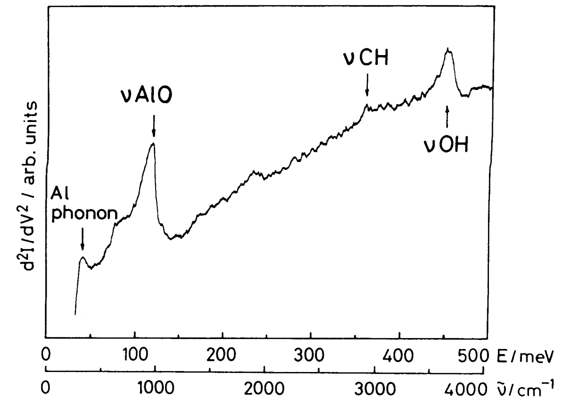

Fig. 3. Tunneling spectrum of the undoped Al–Al_2O_3–Pb junction made by an oxygen glow discharge. Junction resistance: 63 Ω; modulation voltage: 4 mVpp; time constant of the lock-in amplifier: 30 s; trace time: 109 min.

ylate ion onto the alumina surface when doped with alcohol solutions. In this paper, we will consider the tunneling spectra of phthalic, isophthalic, and terephthalic acid, together with their detailed assignments. The structure of these molecules on the alumina surface is clarified. The chemical interaction between the carboxyl groups and the surface is also discussed.

Experimental

The method of junction preparation involves evaporation and oxidation techniques in a liquid nitrogen-trapped diffusion-pumped bell jar. Aluminium (99.999%, Mituwa Chemicals) was evaporated from a molybdenum boat on a clean glass slide (13X37X1 mm) to form three strips (1 mm wide) at a pressure of 10^{-5} Torr (1 Torr=133.322 Pa). The strips were oxidized by exposure to pure oxygen (99.8%, 1 atom) or in an oxygen-dc glow discharge (400—800 V, 30 mTorr, 5 mA, 10—60 s) in the bell jar.[20]

The slide was removed from the vacuum system, dipped into a solution containing the sample molecules, and left for about 3 min to complete the adsorption. The phthalic, isophthalic, and terephthalic acid (Kanto Chemicals) were purified by recrystallization from water. Guaranteed-reagent grade methanol, ethanol and 1-propanol, and distilled water were used as the solvents.

The slide was returned to the vacuum system, and the junctions (1X1 mm area) were completed with an evaporated Pb (99.999%, Wako Chemicals) cross strip (1 mm wide). The resistance of the junction was measured with a digital multimeter (Kikusui 1502). The operations mentioned above were done in a class 10000 clean room (Airtech Japan AER-233C). The slide was mounted in a sample holder and preliminarily cooled with liquid nitrogen at 77 K. Silver paint and solder were used for attaching the leads to the junctions. The sample holder was then inserted into a liquid helium Dewar (Osaka Sanso Hi·CRIC-10), where the junctions were cooled at 4.2 K.

The tunneling spectrum was obtained by measuring the second derivative of the tunneling current through the junction at the liquid helium temperature. A diagram of the circuit is shown in Fig. 2. A 500 Hz ac modulation signal of 2.0—4.0 mV peak-to-peak from a low-distortion oscillator (NF E-1201) and a slowly varying dc voltage from a bias supply were applied to the junction. The aluminium electrode was negatively biased with respect to the Pb electrode. The modulation signal through an amplifier (LM 308H) was monitored with an oscilloscope (Kikusui 5513). The second harmonic signal was differentially amplified (LM 308AH) and detected with a lock-in amplifier (NF LI-574A), with a notch filter (NF 2BE) and a bandpass filter (NF 3BP), preceded by the bridge circuit developed by Adler and Jackson.[21] The bridge circuit achieved an ac rejection of 50 dB. The output of the lock-in amplifier was then applied to the y axis of an x-y recorder (Rikendenki F-35). The dc voltage across the junction was applied through a buffer amplifier (LM 308H) to the x axis. Acceptable resistances for the junctions were in the range of 30—3000 Ω, while matched resistances were in the range of 50—500 Ω.

Results

Performance Test of the Apparatus and Procedures. The tunneling spectrum of an undoped Al–Al_2O_3–Pb junction made by an oxygen glow discharge is shown in Fig. 3. There is a smoothly varying background due to the change in the elastic conductance as the bias voltage is increased. The features and the peak positions of the spectrum agree well with those previously reported.[1–7,22,23] The peaks at about 300 and 940 cm^{-1} are due to the aluminium phonon and the vibrational mode of the aluminium oxide respectively.[22,23] The broad peak at about 3600 cm^{-1} arises from the stretching vibration of the surface hydroxyl species. The OH bending mode appears at about 700 cm^{-1} as the shoulder of the strong peak at 940 cm^{-1}. The weak and broad structure at 1300—1900 cm^{-1} is caused by both the second harmonics of the bending mode of OH and the vibrational mode of AlO.[22] Recently, Gauthier *et al.*[23] have proposed other assignments: the structure near 1900 cm^{-1} and the shoulder at about 700 cm^{-1} are caused by the vibrational and bending mode of an aluminium hydride located near the Al–

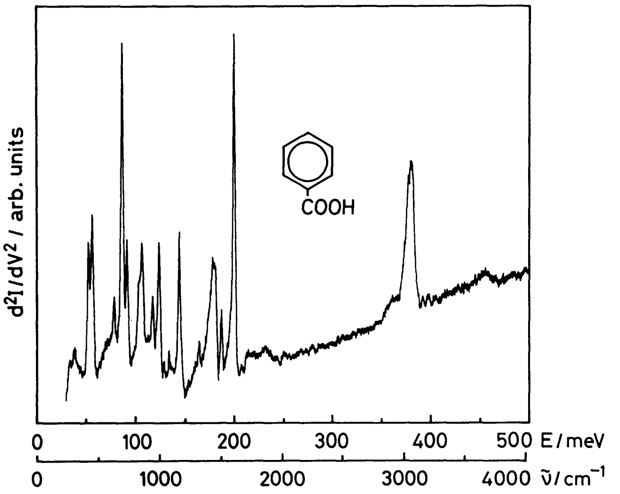

Fig. 4. Tunneling spectrum of benzoic acid doped with a methanol solution of 1.0 mg/ml. Junction resistance: 81 Ω; modulation voltage: 3 mVpp; time constant: 10 s; trace time: 154 min.

TABLE 1. VIBRATIONAL FREQUENCIES (cm^{-1}) FOR BENZOATE IONS ADSORBED ONTO Al_2O_3 MEASURED BY IETS

This work	Oxley *et al.*[a]	Walmsley *et al.*[b]	Hansma[c]	Korman and Coleman[d]
3058 s		3051	3065 m	
3036 sh		3021	3025 m	
2997 sh		2990		
2895 w b			2888 w	
1598 vs	1602 s	1601	1597 vs	1607
1565 sh	1576 sh	1576		1559
	1550 sh			
1487 m	1497 m	1492	1491 m	1500
1448 sh	1451 sh	1447	1450 sh	1453
1426 s	1430 s	1428	1433 m	1437
1309 m	1308 w	1312		1319
		1178		
1154 s	1157 s	1154	1153 m	1161
		1097		
1073 w	1073 w	1070	1068 vw	1072
1026 w	1025 w	1026	1021 vw	1030
987 s	987 s	987	988 m	994
936 m	936 m	938	936 m	940
	885 w			
843 s	850 s	848	847 m	853
825 sh	824 m	823	823 m	827
720 m	722 m	722	723 m	728
684 vs	686 s	687	686 s	690
616 m	618 m	617	617 m	621
434 s	437 s	440	440 m	440
406 s	402 s	404	406 m	407
301 m			307 w	

vs=very strong, s=strong, m=medium, w=weak, vw=very weak, sh=shoulder, b=broad. a) Ref. 13. b) Ref. 11. c) Ref. 3. d) Ref. 8.

Al_2O_3 interface respectively. The peak of the OH bending mode is involved in the strong peak at 940 cm^{-1}.[23] The small peak at around 2900 cm^{-1} is due to the CH stretching mode of a hydrocarbon contamination; its very weak intensity shows that the contamination of the junction is negligible.

The tunneling spectra of benzoic acid have shown that benzoic acid is adsorbed onto the alumina surface as benzoate ion.[8,13] Tunneling spectroscopy shows that benzaldehyde reacts with Al_2O_3 and is also adsorbed as benzoate ion onto the surface.[3,11] Because of the clear features of its spectrum and the detailed assignment, the benzoate ion is a good sample for examining our apparatus and procedures.

The tunneling spectrum of benzoic acid is shown in Fig. 4. The junction was made by liquid doping with a methanol solution of 1.0 mg/ml. The spectrum was measured with a 10-s time constant of the lock-in amplifier and a 2.5-h trace time. In order to obtain a spectrum of good quality, a long trace time should be taken; it is important to spend six time constants per resolution element of the spectrum. Hansma[7] has shown that, if traces are swept faster than these times, shifts in peaks are observed. At 4.2 K, the top lead electrode is superconducting and a correction of −1 meV (−8 cm^{-1}) for the energy gap should be made to measure peak positions accurately.[24] The top lead electrode also causes the peak shifts due to the image dipole effect. The peak of the vibrational mode of the adsorbed hydroxyl species on the surface has a large shift. However, it has been shown that the shifts are less than of the order of 0.5 meV (4 cm^{-1}) for the peaks of the benzoate ion on Al_2O_3.[24] Oxley *et al.*[13] suggested that peaks may shift because of parasitic resistances of electrodes and connection leads when two-point probe measurements are carried out.

The resolution of the tunneling spectrum depends on two broadening contributions: modulation voltage broadening and thermal broadening. The tunneling spectrum in Fig. 4 was measured with a modulation voltage of 3 mV peak-to-peak at 4.2 K. The resolution was estimated to be 2.5 meV (20 cm^{-1}) by measuring the narrowest peak width in the spectrum. The peak positions of the spectrum are in good agreement with those of the spectra reported previously[3,8,11,13] as is shown in Table 1. The accuracy of the peak position of our spectrum is estimated to be ±0.5 meV (±4 cm^{-1}). These results show that our apparatus and procedures are suitable for the accurate measurement of a tunneling spectrum.

Spectra and Peak Assignments for Isomeric Phthalic Acids. The tunneling spectra of phthalic, isophthalic, and terephthalic acid doped from an ethanol solution of 0.5 mg/ml are shown in Fig. 5. For the sake of comparison, the tunneling spectrum of the ethanol solvent is also shown in the same figure. Evans and Weinberg[25] have reported that ethanol is adsorbed as ethoxide ion onto the alumina surface at room temperature. However, the weak peak intensity in the tunneling spectrum of ethanol shown in Fig. 5 indicates almost no contribution from this solvent to the tunneling spectra of isomeric phthalic acids. The tunneling spectra of methanol and 1-propanol have been measured; it has been found that their peak

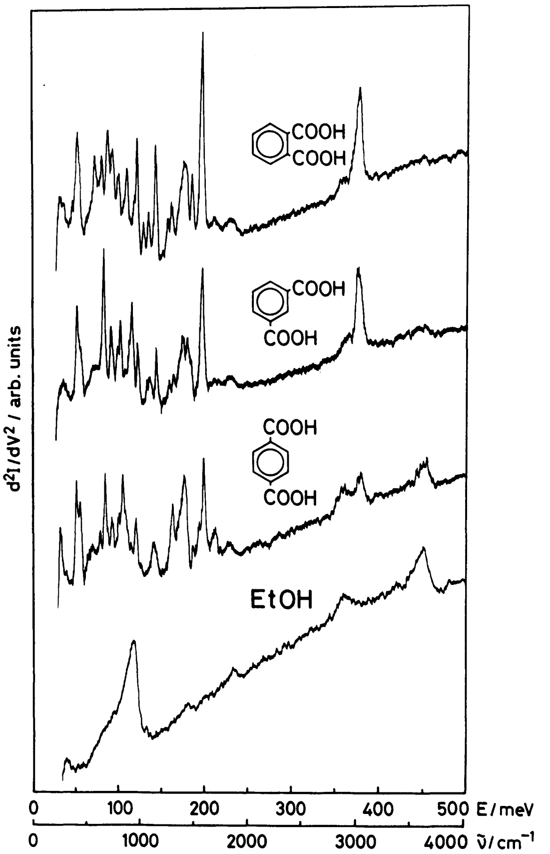

Fig. 5. Tunneling spectra of phthalic, isophthalic and terephthalic acid doped with an ethanol solution of 0.5 mg/ml. Junction resistances: 42—78 Ω; modulation voltage: 3 mVpp; time constant: 10 s; trace times: 145—200 min.

Table 2. Vibrational frequencies (cm^{-1}) and mode assignments for phthalic acid on Al_2O_3 measured by IETS

IETS	Phthalate Ion[a)] Infrared	Phthalate Ion[a)] Raman	Assignment
3596 w b			νOH (surface)
3037 s	3025 vw	3025 vw	νCH (20b)
2894 w b			(contamination)
1704 vw			νC=O
1588 vs	1584 s	1582 w	νCC (8a)
1486 m	1478 m	1479 w	νCC (19b)
1422 s b	1418 vs	1420 s	$\nu_s COO^-$
1296 m	1287 w	1288 w	βCH (3)
1260 w	1259 w	1260 w	νCX (7a)
1149 s	1145 w	1146 m	βCH (15)
1081 m	1082 m	1082 vw	βCH (9b)
1035 m	1035 m	1041 s	βCH (18b)
980 s	980 w		γCH (5)
957 sh	956 w		γCH (10a)
881 m	882 w	895 vw	γCH (10b)
802 m	825 s	826 s	νCC (1)
744 m	753 s		γCH (11)
702 m	694 s		γCC (4)
644 m	649 s	654 s	$\gamma_s COO^-$
582 m	579 m	589 vw	βCC (6b)
422 s	423 s	423 m	$\beta_{as} COO^-$
374 sh			?
285 w			Al phonon
259 m		262 w	βCX (9a)

a) Ref. 16.

intensity is also weak enough to be neglected. Because the tunneling spectrum reveals both infrared and Raman-active vibrational modes, useful information on the adsorbed molecule is obtained by comparing the tunneling spectrum with its infrared and Raman spectrum.

Phthalic Acid: The tunneling spectrum of phthalic acid has a very weak C=O peak at 1704 cm^{-1}. The weak and broad peak at 3596 cm^{-1} is due to the vibrational mode of the surface OH species, as has been mentioned before. Instead, the tunneling spectrum has a strong symmetric stretching, a medium wagging, and a strong rocking mode of the COO^- groups at 1422, 644, and 422 cm^{-1} respectively. When a carboxylic acid is adsorbed onto the alumina surface as a carboxylate ion, the asymmetric vibrational mode of the COO^- group shares a change in the dipole moment parallel to the surface. The peak intensity of this vibrational mode in the tunneling spectrum is weak because of the orientational selection rule.[8,11)] The peak of the asymmetric stretching mode of the COO^- groups of the phthalate ion is considered to be involved in the very strong peak at 1588 cm^{-1}. There is no peak corresponding to the scissoring mode of the COO^- groups. The tunneling spectra of phthalic acid doped with solutions of water, methanol, and 1-propanol are identical with that doped with an ethanol solution. The spectrum is also independent of the acid concentration (0.1—1.0 mg/ml). These results show that phthalic acid reacts with Al_2O_3 by loosing the protons of the COOH groups and is adsorbed onto the surface as the benzenedicarboxylate ion.

The peak assignments for the tunneling spectrum are shown in Table 2, together with those for the vibrational modes of the ion obtained by means of infrared and Raman spectroscopy.[16)] In this table, stretching vibrations are denoted by ν, in-plane bending modes are designated by β, and out-of-plane bending vibrations perpendicular to the plane, by γ. The symmetric or asymmetric vibration is indicated by the subscript of s or as respectively. Of the bending modes of the COO^- group, β_s designates the scissoring vibration, β_{as} denotes the rocking, and γ_s, the wagging mode. In parenthesis is shown the Wilson number for the normal vibration of the benzene ring.[16,17)]

The COO^- groups of the phthalate ion are assumed to be rotated 33° with respect to the plane of the aromatic ring.[16)] The phthalate ion has C_s symmetry and 42 normal vibrations, which are classified as 30 ring vibrations and 12 vibrations of the substituents. These modes are both infrared and Raman-active.[16)] The ring vibrations are divided into 21 in-plane and 9 out-of-plane vibrations.[17)]

Isophthalic Acid: A detailed analysis of the tunneling spectrum and a comparison with the infrared and Raman spectrum show that isophthalic acid is also

Table 3. Vibrational frequencies (cm^{-1}) and mode assignments for isophthalic acid on Al_2O_3 measured by IETS

IETS	Isophthalate Ion[a)] Infrared	Raman	Assignment
3621 w b			νOH (surface)
3038 s	3033 vw		νCH (7a)
2888 w b			(contamination)
1684 vw			νC=O
1587 s	1584 sh	1585 m	νCC (8b)
1467 sh	1477 m		νCC (19b)
1441 s	1429 m	1437 s	νCC (19a)
1402 s b	1391 m	1405 s	ν_sCOO$^-$
1311 w	1315 sh		νCC (14)
1281 vw	1262 w		βCH (3)
1151 m	1157 vw	1159 m	βCH (9b)
1088 w	1085 w	1083 w	βCH (18b)
1061 vw	1069 m	1074 vw	βCH (18a)
980 m	980 w		γCH (5)
930 s	932 w		νCX (7b)
824 m	818 m	820 s	νCC (1)
801 sh			?
737 m	733 s		β_sCOO$^-$
672 s	674 w		γCC (4)
582 w b	553 w	555 vw	βCC (6b)
440 sh			?
418 s	401 m	402 vw	β_{as}COO$^-$
294 m b			Al phonon

a) Ref. 16.

adsorbed onto the alumina surface as the benzenedicarboxylate ion. The tunneling spectrum is independent of the solvent used (water, methanol, ethanol, and 1-propanol) and the acid concentration (0.1—1.0 mg/ml). The peak assignments are shown in Table 3, together with those for the vibrational modes of the ion. The tunneling spectrum has a strong ν_s, a medium β_s, and a strong β_{as} COO$^-$ peak at 1402, 737, and 418 cm^{-1} respectively. The ν_{as}COO$^-$ peak is considered to be involved in the strong peak at 1587 cm^{-1}, as in the case of phthalic acid. There is no peak corresponding to the γ_sCOO$^-$ mode.

The isophthalate ion has 42 normal vibrations with C_{2v} symmetry. These vibrations are both infrared and Raman-active, and are classified as 30 ring vibrations and 12 vibrations of the substituents, as in the case of the phthalate ion.[16)]

Terephthalic Acid: The tunneling spectrum of terephthalic acid has a medium νOH (3623 cm^{-1}) and a medium νC=O (1699 cm^{-1}) peak. The strong peak at 1423 cm^{-1} is due to the βOH and/or the ν_sCOO$^-$ mode. The peaks at 867, 619, and 436 cm^{-1} are caused by β_s, γ_s, and β_{as} of the COO group for the acid and/or the COO$^-$ group for the ion. The spectrum has a very weak ν_{as}COO$^-$ peak at 1550 cm^{-1}. This finding that the tunneling spectrum of terephthalic acid has the C=O peak and the COO$^-$ peaks indicates the presence of the monocarboxylate ion on the alumina surface. The peak assignments are shown in Table 4 with those for the vibrational modes of terephthalic acid[15)] and its ion.[16)]

Terephthalic acid and the terephthalate ion with a D_{2h} point group have 48 and 42 normal vibrations respectively. Of these vibrations, 30 are due to ring vibrations. In the case of these molecules, the mutual-exclusion principle holds and a vibrational mode with

Table 4. Vibrational frequencies (cm^{-1}) and mode assignments for terephthalic acid on Al_2O_3 measured by IETS

IETS	Terephthalic Acid[a)] Infrared	Raman	Terephthalate Ion[b)] Infrared	Raman	Assignment
3623 m b					νOH
3042 m	3066 w			3062 w	νCH (20b, 7b)
2873 w b					(contamination)
1699 m	1682 s b	1632 vs			νC=O
1594 s		1615 s		1597 sh	νCC (8b)
1550 sh			1575 s b	1549 w	ν_{as}COO$^-$
1493 w	1575 m		1497 m		νCC (19a)
1423 s b	1422 s	1452 m	1380 s b	1413 vs	βOH, ν_sCOO$^-$
1302 m	1315 w		1311 w		νCX (13)
1136 m		1126 s		1127 s	βCH (9a)
1003 vw	1018 m		1012m		βCH (18a)
963 m	997 w			968	γCH (17a)
916 vw				910	γCH (10b)
867 sh	881 m		882 m		β_sCOO, β_sCOO$^-$
839 s		835 s		857 s	νCC (1)
797 vw		804 m			βCH-βCX (18b-15)
736 m	734 s		745 s		βCC (12)
677 s		675 m		707 w	γCC (4)
619 w		635 s	620 w	633 m	γ_sCOO, γ_sCOO$^-$
540 w b	525 m				γCC (16b)
436 s	449 m		449 m		β_{as}COO, β_{as}COO$^-$
400 s			412 w	412 vw	γ_{as}COO$^-$+γCH (5)
298 sh		287 m		277 vw	βCX (9b), Al phonon
242 m		272 s		252 m	γCX (5)

a) Ref. 15. b) Ref. 16.

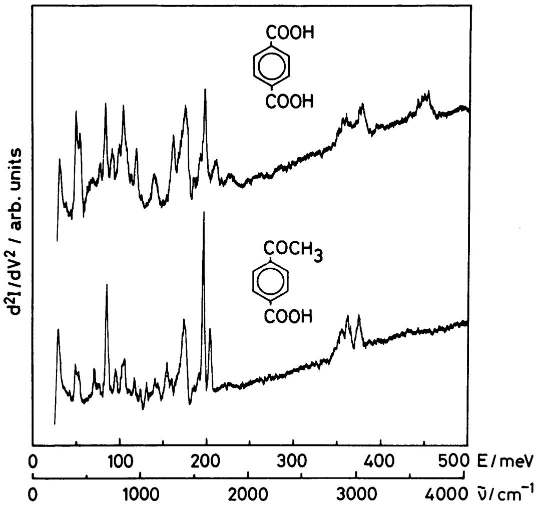

Fig. 6. Tunneling spectrum of *p*-acetylbenzoic acid doped with an ethanol solution of 0.5 mg/ml. Junction resistance: 376 Ω; modulation voltage: 3 mVpp; time constant: 10 s; trace time: 152 min. Tunneling spectrum of terephthalic acid is also shown for a comparison. The relative intensity of the C=O peak of terephthalic acid is similar to that of *p*-acetylbenzoic acid.

a symmetry species appears either in the infrared or Raman spectrum.[15,16] In Table 4, however, this principle is neglected for reasons of simplicity.

Discussion

Comparison of Tunneling Spectrum of Terephthalic and p-*Acetylbenzoic Acid.* Most peaks in the tunneling spectra of isomeric phthalic acids can be clearly identified, and their peak positions agree closely with those of the infrared and Raman spectra. This indicates that the phthalate ions on Al_2O_3 are not strongly perturbed by adsorption. However, these tunneling spectra show a difference in the chemical interaction between the COOH group and the alumina surface. It is found that both phthalic and isophthalic acid react with Al_2O_3 by loosing the protons of two COOH groups and are adsorbed onto the surface as benzenedicarboxylate ions. On the other hand, the tunneling spectrum of terephthalic acid clearly shows the unreacting COOH group, thus indicating the presence of the monocarboxylate ion on the surface. It seems that terephthalic acid is adsorbed onto Al_2O_3 as both the monoanion and the dianion.

The tunneling spectrum of *p*-acetylbenzoic acid (Aldrich Chemicals) is shown in Fig. 6, with that of terephthalic acid. The spectrum of *p*-acetylbenzoic acid has a strong νC=O (1663 cm^{-1}) and νCOO^- (1418 cm^{-1}) peak, showing that this molecule is adsorbed onto Al_2O_3 as the monocarboxylate ion.[26] The relative intensities of the νC=O to the νCOO^- peaks in both the tunneling spectra of terephthalic and *p*-acetylbenzoic acid are similar to each other. This similarity indicates that terephthalic acid is adsorbed predominantly as the monocarboxylate ion onto the Al_2O_3 such as *p*-acetylbenzoic acid.

Oxley *et al.*[13] have previously measured the tunneling spectra of terephthalic acid doped with solutions of both water and ethanol onto Al_2O_3 formed by an oxygen glow discharge. Their spectra, however, have no C=O peak, and they concluded that terephthalic acid is adsorbed onto the surface as the dicarboxylate ion. We examined the experimental conditions in detail and found that the tunneling spectra of terephthalic acid doped with a solution of 1-propanol or methanol onto Al_2O_3 formed by both exposure to oxygen and a glow discharge also have the C=O peak. The relative intensity of the C=O peak is almost independent of the acid concentration (0.01—1.5 mg/ml); this shows saturation coverage. In the case of a methanol solution, however, the relative intensity is somewhat weak. The spectrum from an aqueous solution has the very weak C=O peak. This finding may suggest that terephthalic acid is adsorbed as the dicarboxylate ion when doped with an aqueous solution. It is found that the tunneling spectrum of terephthalic acid strongly depends on the solvent used. Thus, judging from the results of a comparison between the tunneling spectra of terephthalic and *p*-acetylbenzoic acid, we conclude that terephthalic acid is adsorbed predominantly as the monocarboxylate ion onto the alumina surface at almost saturation coverage when doped with either ethanol or 1-propanol solution.

The tunneling spectrum of *p*-acetylbenzoic acid has no νOH peak, but it has the sharp and clear νC=O peak. It seems that the C=O group interacts with neither the adsorbed *p*-acetylbenzoic acid nor the alumina surface. On the other hand, the spectrum of terephthalic acid has the broad νOH and νC=O peak. Judging from the asymmetric tailing of the OH peak and the broadness of the C=O peak, hydrogen bonding seems to be present. Two types of hydrogen bonding seem to be important: hydrogen bonding among the adsorbed hydrogen terephthalate ions and hydrogen bonding between the hydroxylated alumina surface. Because terephthalic acid is adsorbed with its benzene ring nearly perpendicular to the surface at saturation coverage, as will be discussed later, and because it has the unreacting COOH group at the para position, hydrogen bonding among the adsorbed hydrogen terephthalate ions seems to be more important. A similar result has been obtained in the case of diphenol in IETS;[12] both catechol and resorcinol are adsorbed predominantly onto the alumina surface as diphenolate ions, while hydroquinone is adsorbed mainly as the monophenolate ion and extensive hydrogen bonding is observed.

Adsorption and Orientation of Isomeric Phthalic Acids. The adsorption mechanism and orientation of the isomeric phthalic acids on the alumina surface were

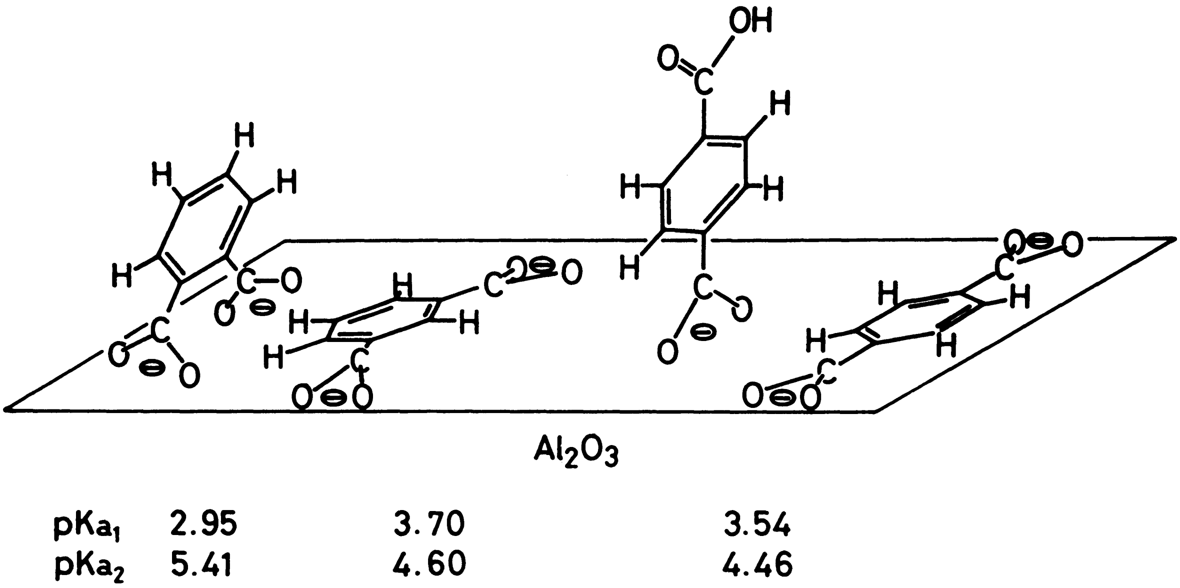

Fig. 7. Schematic representation of the adsorbed isomeric phthalic acids on Al_2O_3. Their dissociation constants in water are also shown.

studied by using a molecular model. A schematic representation of these acids on Al_2O_3 is shown in Fig. 7, with their dissociation constants in water. The isomeric phthalic acids have two carboxyl groups and they dissociate stepwise in water. For phthalic acid, the first dissociation constant is larger and the second is smaller than the others. Thus, phthalic acid may be expected to be adsorbed mainly as the monocarboxylate ion, if a similar tendency in the difference of dissociation constants holds in alcohol solutions. However, the tunneling spectra show that the structures of these acids adsorbed onto the surface are not explained by their dissociation constants; both phthalic and isophthalic acid are adsorbed mainly as dicarboxylate ions, while terephthalic acid is adsorbed predominantly as monocarboxylate ion. This finding indicates a difference in the geometry of the interaction between the alumina surface and the COOH groups of the adsorbed isomeric phthalic acids.

In the cases of phthalic and isophthalic acid, when they are adsorbed at one of the COOH groups, the other groups seem to be very close to the surface. Thus, the COOH group dissociates more easily than would be expected from their second dissociation constants. The tunneling spectra of these acids are independent of the solvent and their concentrations. These acids are considered to be adsorbed at saturation coverage. It seems that the benzene ring of the phthalate ion has a relatively large angle with respect to the surface, even if the COO^- groups are rotated, since the carbon and hydrogen atoms of the ring are not expected to interact with the alumina surface. On the other hand, because of the molecular model, the ring of the isophthalate ion is considered to be nearly parallel to the surface. The close agreement of the peak positions of the benzene ring of the tunneling spectrum of the isophthalate ion with those of the infrared and Raman spectrum shows that the ring has almost no interaction with the surface. A comparison of the tunneling spectra of the two acids indicates that the peak intensity of the out-of-plane and in-plane ring vibrational modes are comparable: Vibrations 4, 11, 10b, 5 (out-of-plane) and 6b, 1 (in-plane) for phthalic acid, and Vibrations 4, 5 (out-of-plane) and 1, 7b (in-plane) for isophthalic acid. This finding is unexpected in view of the orientational selection rule.

Kirtley and Hall27) have calculated the peak intensity of the tunneling spectrum of the methanesulfonate ion adsorbed onto Al_2O_3 by using a transfer Hamiltonian theory. They have found that the calculated peak intensity depends strongly on the distance of the dipole from the Pb electrode; the orientational selection rule is favorable for a mode vibrating perpendicular to the surface when molecules are situated close to the interface. However, this rule does not hold for molecules deep within the insulator. Though no such calculation has been done for isomeric phthalic acids, it seems that the result of Kirtley and Hall is applicable qualitatively to the benzenedicarboxylate ions. Because the benzene rings of adsorbed phthalate and isophthalate ion are at some distance from the interface of the Pb electrode, the orientational selection rule is not expected to hold strictly. These results suggest that care must be taken to use the selection rule in discussing the orientation of the adsorbed species in tunneling spectroscopy.

In the case of terephthalic acid, since the molecule has the COOH groups at the para position, the molecule must fall and become parallel to the surface in order to be adsorbed as the dicarboxylate ion. If this process takes a longer time than the first process of adsorption, many molecules will remain on the surface as monocarboxylate ions. The tunneling spectra doped with various alcohol solutions are independent of their concentrations and indicate saturation coverage. Langan and Hansma[28] have measured the surface concentration of the adsorbed benzoate ion on Al_2O_3. They have reported that this molecule occupies an area of 15 Å^2 at saturation coverage. This area is almost equal to that calculated from the diameter of the benzene ring (5 Å). According to this result, the adsorbed hydrogen terephthalate ion is also considered to occupy the same area of the surface and thus can not fall at saturation coverage. Therefore, the terephthalic acid remains on the surface as the monocarboxylate ion. The observed hydrogen bonding also supports the predominance of the hydrogen terephthalate ion on the surface.

Concluding Remarks. The detailed analysis of the vibrational spectra of the isomeric phthalic acids adsorbed onto Al_2O_3 from alcohol solutions makes it possible to clarify the difference in chemical interaction between the COOH group and the surface. This difference is caused by their orientations and the different probabilities of chemical interaction between the COOH group and the surface. These results suggest the importance of the orientation of adsorbed species for their reactivity and selectivity on an alumina catalyst. Inelastic electron tunneling spectroscopy is a useful analytical tool for investigating the adsorbed species on the oxide surface and their chemical interaction with it.

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