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The Adsorption of 1-Propanol, 1-Propylamine, and 3-Amino-1-Propanol on Plasma-Grown Aluminum Oxides; Comparison with Propanoic Acid and β-Alanine

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Inelastic electron tunneling spectroscopy is used to study the adsorption of 1-propanol, 1-propylamine, 3-amino-1-propanol, propanoic acid, and β-alanine on plasma-grown aluminum oxide surfaces. The feasibility of preparing highly deuterated oxide surfaces, and the utility of these surfaces in interpreting tunneling spectra are demonstrated. Tunneling spectra are compared to ir and Raman spectra of the pure materials and of a nickel complex of the amino acid. It is concluded that 1-propanol and 1-propylamine adsorb on the oxide surface in very nearly the same configuration. There is only a slight tendency for 1-propanol to form propanoate ion during the short (≤20 min) exposure times employed. The two bifunctional species, 3-amino-1-propanol and β-alanine, adsorb in a manner that involves both functional groups in binding to the surface.

INTRODUCTION

Aluminum oxide is a tremendously important material because of its use as a support for active metal catalysts and because of its catalytic activity in its own right. Hence, the adsorption of various types of molecules on the aluminum oxide surface has been studied extensively in order to better understand its catalytic properties. Acidic properties of the oxide surface have been probed by observing the adsorption of such basic molecules as ammonia, pyridine, or other nitrogen-containing species (*1–9*). The adsorption of alcohols has been studied since they undergo catalytic reactions on the oxide surface (*9–14*). The methods used in these studies include measurement of adsorption isotherms (*1, 2, 4, 8*), thermal desorption (*1, 4, 8*), ^{13}C NMR (*3*), ir (*1, 5, 10, 11, 13, 14*), and tunneling spectroscopy (*9, 12*). The adsorption of amino acids on silica and silica-supported nickel has been investigated by ir spectroscopy (*15*) and on alumina by tunneling (*16*). There have been few reports on the study of bifunctional molecules other than amino acids adsorbed on aluminum oxide, despite the fact that there is potentially much to be learned from such studies. If competition between the two different functional groups were observed, it would be possible to make inferences about the distribution and relative population of different reactive sites on the surface.

This paper presents a study of the adsorption of a bifunctional molecule, 3-amino-1-propanol, on aluminum oxide. Inelastic electron tunneling spectroscopy, a technique which yields vibrational spectra of the adsorbed species, is used as the primary investigative tool. To facilitate the assignment of the vibrational spectra obtained, β-alanine (3-amino-propanoic acid), 1-propylamine, 1-propanol, and propanoic acid were also studied. In addition 3-amino-1-propanol and β-alanine deuterated at the amine and alcohol or acid positions were employed. Of these additional compounds the adsorption of propylamine has been studied by temperature-programmed de-

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sorption and isothermal adsorption methods (*4*), propanol adsorption has been studied by ir spectroscopy (*10, 11*), and propanoic acid adsorption has been studied by tunneling spectroscopy (*12*).

Tunneling spectroscopy is an effective probe of the structure of molecules adsorbed on certain oxides; it has the advantage over ir in that the tunneling spectrum in the region below ~1000 cm^{-1} is not obscured by the spectrum of the adsorbent, in addition it is sensitive to submonolayer coverages. The technique has been well reviewed (*18, 19*), and will only be described briefly here. Tunneling spectra are obtained from measurement of the electrical properties of metal–insulator–metal tunnel diodes. These diodes, or junctions, are sandwich-like structures composed of a thin metal film, usually aluminum, a thin layer ($\leq$20 Å thick) of grown oxide, the adsorbate, and another metal (usually lead). Tunneling spectra are measured at liquid helium temperatures.

EXPERIMENTAL

Materials. 3-Amino-1-propanol, 1-propanol, and 1-propylamine were purchased from Baker, Mallinckrodt, and M.C.B., respectively. They were distilled before use. $D_2N(CH_2)_3$-OD was prepared as follows: 2 ml of 3-amino-1-propanol (bp 178°C) was placed in a micro-distillation apparatus to which a dropping funnel containing D_2O was attached. Five milliliters of D_2O was added to the amino alcohol, allowed to equilibrate for 45 min, and the resulting H_2O and remaining D_2O were then distilled off. Another 5-ml aliquot of D_2O was introduced, equilibrated, and distilled. This process was repeated until a total of 30 ml of D_2O was consumed, then the deuterated amino alcohol was distilled. Infrared spectra indicated that the isotopic exchange at the amine and alcohol groups was about 95%. Propanoic acid was prepared by extraction and distillation from M.C.B. reagent grade sodium propanoate. β-Alanine from Sigma was used without further purification. $D_2N(CH_2)_2COOD$ was prepared by dissolving 1 g of β-alanine in 5 ml of D_2O, then evaporating the D_2O/H_2O mixture in vacuum over P_2O_5 (*20*). This process was repeated for a total of four times, yielding a material whose ir spectrum indicated an isotopic purity of about 90%. Bis-β-alaninatonickel was prepared by warming a suspension of excess nickel carbonate in an aqueous solution of β-alanine, then filtering off the unreacted carbonate. The complex crystallized from the solution on cooling (*21*). The deuterated complex was formed from the deuterated β-alanine in D_2O. Infrared spectra of these materials agreed well with published spectra (*22*). For the β-alanine and its nickel complex elemental analysis gave: β-alanine predicted (found): C: 40.44% (40.48%); H: 7.92% (8.20%); N: 15.72% (15.94%); $Ni(H_2NCH_2CH_2COO)_2 \cdot 2H_2O$: C: 26.60% (26.43%); H: 5.95% (5.92%); N: 10.34% (10.17%).

METHODS

The diodes used in this study were fabricated in a previously described vacuum system (*23*). Even at low pressures, there was a considerable quantity of water adsorbed on various parts of this system. It was, therefore, necessary to exchange this water with D_2O to preserve the isotopic purity of the deuterated amino alcohol. This was accomplished by thoroughly pumping out the system ($P \leq 5 \times 10^{-7}$ Torr), exposing it to saturation pressure (~12 Torr) of D_2O vapor for several hours, followed by an AC glow discharge with D_2O vapor. Between fabrication runs care was taken to minimize exposure of the vacuum system to air.

Glass microscope slides were used as substrates for diode formation. The temperature of the slides could be controlled by using a quartz lamp heater or a metal block contact heater. Diodes were fabricated in the following manner: a thin aluminum film was deposited on the slide from an aluminum-coated tungsten filament through a stainless-steel mask. A thin film of oxide was grown by exposing the slide to an O_2 glow discharge. Oxidation temperatures of 20 and 200°C were employed.

Following oxidation, the resultant oxides were heated to some predetermined temperature ($T \leq 400°C$) in vacuum, then allowed to cool to the temperature at which vapor phase adsorption occurred. Adsorption pressures were typically 5, 50, 100, and 5 mTorr, for the amino propanol, propanol, propylamine, and propanoic acid, respectively. An exposure time of 1 min was used in the case of propanoic acid and amino propanol. Maximum intensity spectra were obtained with 5 min exposures of propanol or propylamine. Extending the exposure time to 20 min did not increase the amount of propanol adsorbed. Following adsorption, the oxides were allowed to cool in vacuum to $T \leq 30°C$ before the junctions were completed by evaporation of a lead top electrode. This procedure was followed for all the compounds except β-alanine, which was adsorbed from a pH adjusted aqueous solution whose concentration was 1 mg/ml. Completed junctions were 1 mm^2 in area and had resistances ranging from 20 Ω to 1 kΩ.

Tunneling spectra were measured at 4.2°K with a previously described spectrometer (*23*). All of the spectral data were stored by a MINC 11 computer. In addition to storing data the computer was used to actively measure some of the spectra in a multichannel analyzer mode. In this mode the spectrum was scanned quickly (~400 sec), then the computer program interpolated the data to form a file with the intensity data spaced at even intervals in energy. For low resolution spectra, this spacing was typically 5 cm^{-1}, decreasing to 1 cm^{-1} for the highest resolution spectra. After interpolation the spectrum was again scanned; the new data were interpolated and added to the previous data. This process was repeated until the signal-to-noise ratio was acceptable.

Before plotting the spectra, a smooth polynomial curve of third degree or less was subtracted from the data. This improved the presentation of the spectra by reducing the rising background due to elastic conduction. Infrared spectra were taken with a Perkin-Elmer model 283 B spectrophotometer. Instrumental resolution in all cases was less than 7 cm^{-1}. For some of the spectra, samples as KBr wafers were mounted on a liquid nitrogen cooled cell.

RESULTS AND DISCUSSION

The conclusions in this paper are based principally on the interpretation of tunneling spectra. Spectra are assigned utilizing the assumption that the assignments of characteristic vibrational bands observed in the spectra of bulk materials are transferable to bands occurring at similar locations in the tunneling spectrum. This assumption is justified by the high degree of correlation between ir, Raman, and tunneling spectra of a wide variety of species (*18*). Arguments relating to the intensity of bands will generally be based on a comparison of integrated intensities normalized to the intensity of the Al–O stretch.

The first part of this section will discuss the oxides used for the adsorption experiments. The second part will consider the adsorption of 3-amino-1-propanol. The behavior of this species will be discussed by comparison with three monofunctional species, 1-propanol, 1-propylamine, and propanoic acid and with β-alanine, a bifunctional molecule.

Types of Oxides Used

Weinberg *et al.* have studied several types of aluminum oxides used in tunneling spectroscopy (*24,ab*). They showed that many types of oxide preparation yield oxides similar to those which are thermally grown (*24b*); these in turn, have been shown to be similar to γ-alumina (*25*). Hansma *et al.* have demonstrated that thermally grown aluminum oxide films are similar to γ-alumina in their chemical properties (*26*). In addition, an irreversible transition from amorphous to crystalline γ-alumina at about 350°C has been observed for thin oxide films (*27*). The features of the tunneling spectra reported here did not depend greatly on the oxide pretreatment temperature; accordingly the oxide films used in this study are identified as γ-alumina.

Figure 1 presents spectra of three different clean oxide surfaces. Trace A is the spectrum of an oxide grown at room temperature under normal conditions. Trace B is the spectrum obtained from an oxide prepared under identical conditions, except that the vacuum system had been saturated with D_2O. Trace C is also from a junction whose oxide was grown under D_2O saturated conditions, however in this case the oxidation was carried out at 200°C. The band maxima observed and their assignments are collected in Table 1. It should be noted that the extent of deuteration of the oxide surface seen in Fig. 1 is considerably greater than in previously reported deuterated barriers (*24, 25*). This enhanced deuteration is due to the extreme measures taken (see experimental section) to replace background H_2O in the vacuum system with D_2O.

TABLE 1

Band Maxima (cm^{-1}) Observed in the Tunneling Spectra of Undoped Oxides

Heated[a]	Unheated[a]	Unheated	Assignment[b]
3590, vw[c]	3590, w	3590, m	ν(OH)
2665, str	2665, str		ν(OD)
1835, vw	1835, m	1835, w	2ν(Al–O)
1350, m	1350, vw		ν(Al–O) + δ(Al–O–D)
930, str	930, str	930, str	ν(Al–O)
~670, m			See text
		600, m	δ(Al–O–H)
435, vw	430, m		δ(Al–O–D)
303, m	303, m	303, m	Al phonon

[a] Grown under D_2O saturated conditions.
[b] References (*9*) and (*24*).
[c] str, Strong; m, intermediate; w, weak; v, very.

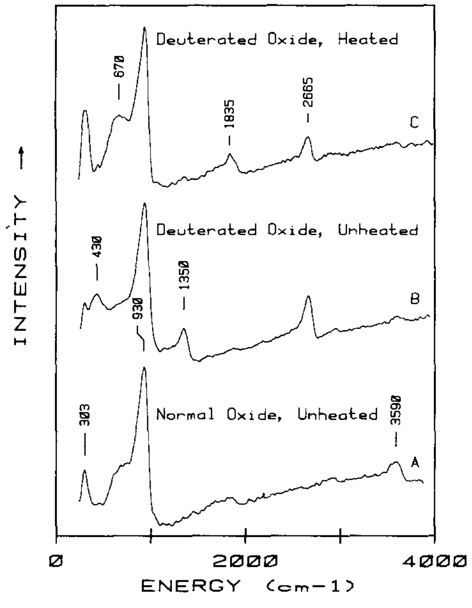

FIG. 1. Tunneling spectra of aluminum oxide films taken with 15 cm^{-1} instrumental resolution. (A) Oxide grown at room temperature under normal conditions. (B and C) Oxides grown in a D_2O-saturated vacuum system; grown at 20°C (B) and at 200°C (C).

In general our results for the clean oxides are fairly consistent with those of Weinberg *et al.* (*24a*) and their assignments have been adopted here. There is one discrepancy, however. The spectrum of the heated deuterated oxide shows a rather broad peak at about 670 cm^{-1} which is less pronounced in the spectrum of the unheated junction. A peak at this position has been assigned to the bending motion of bulk OD groups of oxides grown at low temperatures (*24a*). The increase in intensity of this band with increasing growth temperature brings its assignment into question.

The surface OD bending mode, seen at about 430 cm^{-1}, is more easily identified than the corresponding OH bend near 600 cm^{-1}. The OH bend is seen as a shoulder on the low energy side of the intense Al–O stretching peak, but the OD bend is a distinct peak. There are two causes for this variation in intensity. In order to ensure complete deuteration, the vacuum system was exposed to large amounts of D_2O. There was, therefore, significantly more D_2O available to make surface OD groups than H_2O available to make surface OH groups. This is probably the major cause of the difference in intensity between the two peaks. Overlap of the OH bending mode with the intense Al–O stretching mode at

930 cm^{-1} may also account for the relative weakness of the OH bend.

Adsorption of 3-Amino-1-propanol

This section begins with a discussion of the significant features of the spectrum of 3-amino-1-propanol adsorbed on γ-Al_2O_3. This is followed by comparison of the amino propanol results with spectra of 1-propanol, 1-propylamine, and β-alanine. There are two underlying assumptions that are involved in the interpretation of these tunneling spectra. The first assumption is that the spectrum of a molecule doped from the gas phase is due to a chemisorbed species. It is expected that, at the doping pressures used, there is a large amount of physisorbed material present on the oxide surface. This material is pumped off when the vacuum system is evacuated prior to deposition of the top metal film. Hence, only the strongly held (chemisorbed) material should be present in the completed tunnel diode. The second assumption is that the intensity of the tunneling spectrum is related to the amount of chemisorbed material present on the oxide. This relationship, while certainly not linear, is at least monotonic (*28*).

3-Amino-1-propanol may chemisorb in a variety of ways: the C–OH group may form an alkoxide or a carboxylate, the NH_2 group may coordinate with an aluminum ion, or it may be protonated to form RNH_3^+. Either or both ends of the molecule may be involved in bonding. The primary regions of the spectrum that are informative for determining which of the above possibilities are operative are: the OH stretching region, 3500–3700 cm^{-1}; the NH stretching region near 3300 cm^{-1}; and the region near 1600 cm^{-1}. This last region is not unambiguous; the asymmetric COO^- stretching frequency of carboxylates occurs here, but both NH_2 and NH_3^+ groups also have deformation bands in this region. This ambiguity may be resolved by studying material deuterated at the amine group. Additionally, the region near 1100 cm^{-1} is of importance in identifying alkoxides.

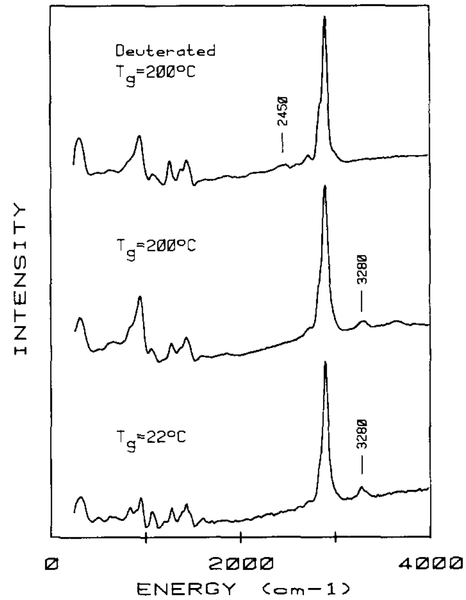

FIG. 2. Spectra of 3-amino-1-propanol on aluminum oxide films grown at various temperatures. Upper trace. $D_2N(CH_2)_3OD$ adsorbed at 185°C on deuterated Al_2O_3 grown at 200°C; 20 cm^{-1} instrumental resolution. Middle trace: $H_2N(CH_2)_3OH$ adsorbed at 185°C on normal Al_2O_3 grown at 200°C, 19 cm^{-1} resolution. Lower trace: $H_2N(CH_2)_3OH$ adsorbed at 85°C on normal Al_2O_3 grown at 22°C; 13 cm^{-1} resolution.

Figure 2 presents spectra of 3-amino-1-propanol on aluminum oxide under various conditions. The lower trace is the spectrum of the amino alcohol adsorbed at 85°C on a 22°C grown oxide, the middle trace is the spectrum of the amino alcohol adsorbed at 185°C on an oxide grown at 200°C, while the upper trace is the spectrum of the deuterated amino alcohol adsorbed at 185°C on an oxide grown at 200°C. Figure 3 presents expanded scale, higher resolution presentations of the spectra in the upper and middle traces and an expanded scale presentation of the lower trace. The assignments of the bands observed from 3-amino-1-propanol and its deuterated analog are collected in Table 2.

Comparison of Fig. 2 with Fig. 1A shows the band at 3590 cm^{-1} is absent or very weak in comparison to the Al–O stretch in

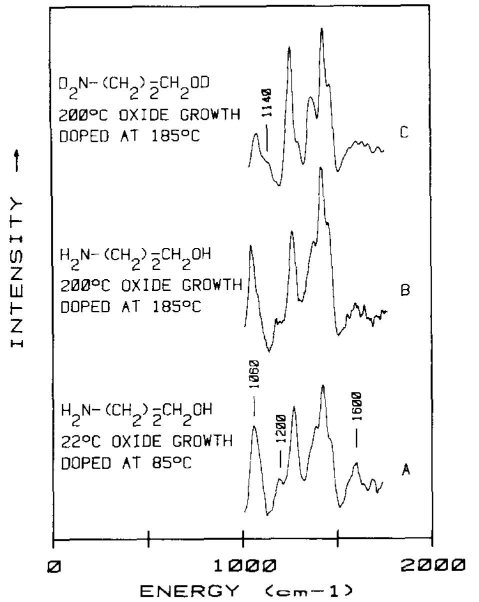

FIG. 3. Expanded scale spectra of 3-amino-1-propanol on Al_2O_3. (A) $H_2N(CH_2)_3OH$ on a room temperature grown oxide; 13 cm^{-1} instrumental resolution. (B) $H_2N(CH_2)_3OH$ on an oxide grown at 200°C; 10 cm^{-1} resolution. (C) $D_2N(CH_2)_3OD$ on a deuterated oxide grown at 200°C; 10 cm^{-1} resolution.

the amino alcohol spectrum. This implies that the alcohol group is not present in the surface species. This implication is corroborated by the absence of an OH bending band expected near 1230 cm^{-1} (*9, 29*). The decrease in intensity of the 3590 band following 3-amino-1-propanol adsorption suggests that surface hydroxyl groups are removed as part of the adsorption process.

The peak at 3280 cm^{-1} in the spectrum of the amino alcohol (Fig. 2) appears at 2450 cm^{-1} in the spectrum of 3-amino-1-propanol deuterated at the amine and alcohol positions. This shift allows the 3280 cm^{-1} band to be unambiguously assigned to an NH_x stretching mode. The energy of this band is outside the region expected for protonated amines whose HN_3^+ stretching bands are expected near 2950 cm^{-1} (*29*). The NH stretching modes for a free (gas phase) RNH_2 group are expected near 3450 cm^{-1} (*29*); thus, it is unlikely that a free NH_2 group is present on the surface. 3280 cm^{-1} is in the proper range for the NH stretching bands of metal–amine complexes (*30–33*). The band at 3280 cm^{-1} is therefore assigned as ν(NH) of an NH_2 group coordinated to an aluminum ion.

In Fig. 3A there is a broad peak at 1600 cm^{-1}. This could be due to the asymmetric stretching vibration of a carboxylate group, or to the scissoring deformation of an NH_2 group. In the spectrum of the deuterated material (Fig. 3C) this band is very weak and is replaced by a shoulder near 1140 cm^{-1}. Accordingly, the peak at 1600 cm^{-1} is assigned to an NH_2 scissoring motion, and the shoulder at 1140 cm^{-1} to the analogous ND_2 motion. Note that the 1600 cm^{-1} band is reduced in intensity in the spectrum of the amino alcohol adsorbed on an oxide grown at 200°C. No other changes attributable to oxide growth temperature were observed. A pronounced shoulder at about 1200 cm^{-1} in Figs. 3A and B is not present in Fig. 3C. This feature is assigned as the NH_2 wagging motion of the amine group (*30–33*).

Comparison with Monofunctional Species

Figure 4 shows the spectra of 1-propanol and 1-propylamine adsorbed on aluminum

TABLE 2

Bands Observed in the Tunneling Spectrum of 3-Amino-1-Propanol

Position (cm^{-1})		Assignment
$D_2NCH_2CH_2CH_2OD$	$H_2NCH_2CH_2CH_2OH$	
	3280	ν(NH)
2895	2895	ν(CH)
2710		ν(OD)
2450		ν(ND)
	1600	$\delta(NH_2)$
1465	1465	$\delta(CH_2)$
1435	1425	$\delta(CH_2)$
1370[a]	1380	CH_2 wag
1260	1270	CH_2 wag
1140		$\delta(ND_2)$
	1200	NH_2 wag
1080	1060	ν(C–O) + ν(C–N)

[a] The distortion of this band compared to the 1380 cm^{-1} band of the proton form is probably due to overlap with the ν(Al–O) + δ(Al–O–D) combination band.

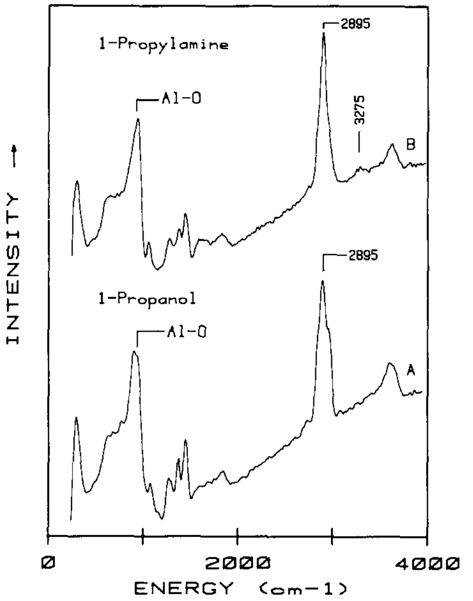

FIG. 4. Spectra of 1-propanol and 1-propylamine on a 20°C grown oxide. (A) Oxide heated to 350°C then doped with 1-propanol at 100°C, 16 cm^{-1} resolution. (B) Oxide heated to 400°C then doped with 1-propylamine at 250°C, 15 cm^{-1} resolution.

oxide. Figure 5 is a more detailed presentation of the low energy region of these spectra. The similarity of these spectra, particularly in the CH deformation region (~1100–1500 cm^{-1}), suggests that the surface species are oriented in like manner (*19*). Assuming that the nitrogen and oxygen atoms are bound to the surface, and that they have tetrahedral bond angles, then both species would have a propyl group extending away from the surface at an angle of about 55°. Assignments for the bands observed in Figs. 4 and 5 are collected in Table 3. These assignments are based on information from the following sources: a normal coordinate analysis of the vibrational spectrum of 1-propanol (*34*), ir investigations of the reaction of 1-propanol with γ-alumina (*10, 11*), the ir spectra of a series of complexes of propylamine with ethylaluminum chlorides (*35*), and vibrational assignments for a series of transition metal complexes of methylamine, ethylamine, and propylamine (*30–33*).

The OH stretching bands, in Fig. 4, near 3600 cm^{-1} are quite pronounced, in contrast to the spectrum of 3-amino-1-propanol (Fig. 2). In the case of propanol adsorption, in

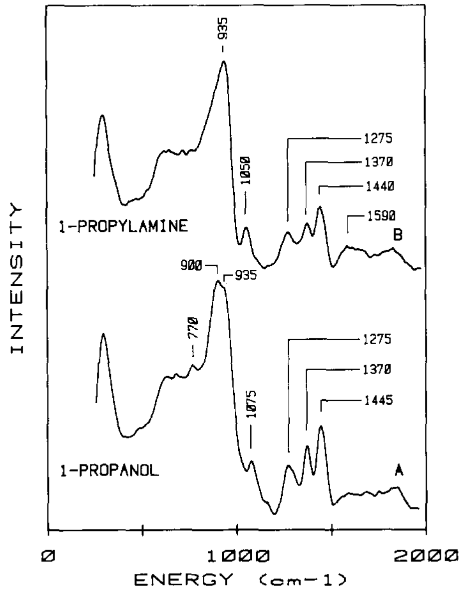

FIG. 5. The 250 to 2000 cm^{-1} region of the spectra of 1-propylamine and 1-propanol on aluminum oxide. Resolution: 16 cm^{-1} (A); 15 cm^{-1} (B).

TABLE 3

Bands Observed in the Tunneling Spectra of 1-Propanol and 1-Propylamine

Position (cm^{-1})		Assignment
1-Propanol	1-Propylamine	
3615	3615	ν(OH)[a]
	3275	ν(NH)[b]
2895	2895	ν(CH)
1590		ν(OCO) (see text)
	1590	NH_2 scissors[b]
1445	1440	CH_2 bend[c]
1370	1370	CH_3 sym def + CH_2 wag
1275	1275	CH_2 wag
1075		ν(CO) (see text)
	1050	ν(CN)
900		CH_3 rock[c] + ν(C–C)[c]
770		CH_2 rock[c]

[a] Ref. (*24*).
[b] Ref. (*35*).
[c] Ref. (*34*).

fact, an increase of ν(OH) relative to ν(Al–O) is observed with alcohol adsorption. Further, a similar comparison shows a marked decrease in ν(OH) intensity following amino propanol adsorption. This implies that neither the alcohol nor the amine dehydroxylates the oxide surface although the amino alcohol does.

Free (gas phase) 1-propylamine has NH_2 stretching bands at 3411 and 3346 cm^{-1} (*36*), while the tunneling spectrum shows a broad band at 3275 cm^{-1}. Two possible explanations of this downshift are: the downshift is due to interactions with the top metal in the tunnel diode structure, or the downshift has a chemical cause. Shifts in vibrational energy due to interactions with the top metal have been observed and accounted for theoretically (*37*). The magnitude of the shift is related to the size of the dipole derivative of the mode. NH stretching vibrations of 1-propylamine are quite weak in the ir (*38*), indicating a small dipole derivative. The shift, therefore, is not due to the top metal. The NH stretching vibrations for propylamine coordinated to Al(III) occur near 3300 cm^{-1} (*35*); this is typical for coordinated primary amine complexes (*30–33*). Chemical intuition and spectroscopic data, therefore, both imply that the nitrogen atom in 1-propylamine coordinates with an aluminum ion when it chemisorbs on alumina.

In their tunneling study of large aromatic amines on plasma grown aluminum oxide Brown *et al.* (*9*) report intense broad peaks centered near 2870 cm^{-1}. They assign these to the NH stretching vibrations of a protonated, ammonium-like species, or to NH stretches of amines highly perturbed by interaction with strong Lewis acid sites. The spectrum of propylamine reported here shows no sign of such a peak. Further there is no evidence of NH_3^+ rocking and symmetric deformation bands expected at 1190 and 1515 cm^{-1} (*39*). There is, however, a distinct peak at 1590 cm^{-1} which is attributed to the scissoring deformation of the complexed NH_2 group. The tunneling spectrum of 1-propylamine (Figs. 2 and 3) also shows a band at 1052 cm^{-1}. This is in the proper range for the C–N stretching vibration of coordinated aliphatic amines (*30–33*), and of 3-amino propanoic acid (*40*). Hence the peak near 1050 cm^{-1} in the propylamine spectrum is assigned to the CN stretching vibration.

The preceding considerations lead to the conclusion that 1-propylamine chemisorbs on aluminum oxide by coordination with an aluminum ion. The near coincidence of the NH stretching frequencies of 3-amino-1-propanol and 1-propylamine (3280 and 3275, respectively) demonstrates that the amine groups of both molecules are similarly bound.

As in the case of amino propanol, no OH bending bands (*9, 29*) are observed in the spectrum of propanol adsorbed on aluminum; instead, a strong band near 1075 cm^{-1} is seen. In tunneling studies of ethanol adsorption, a similar band near 1050 cm^{-1} was reported (*9, 12*). This latter band was assigned to either CH_3 rocking (*9*), or CH_2 bending and Al–O–C stretching (*12*). Al(III) alkoxides display bands in this region which have been convincingly assigned as C–O stretching motions (*11, 41*). The presence of a similar peak in the spectrum of 3-amino-1-propanol does not support the assignment of this band to CH_3 rocking, since the amino alcohol does not contain CH_3 groups. Accordingly, the peak at 1075 cm^{-1} in the spectrum of 1-propanol is assigned as an alkoxide C–O stretching band. The band at 1060 cm^{-1} in the spectrum of the amino alcohol is probably composed of both C–N and C–O stretching motions and is assigned as such.

The infrared spectra of methanol, ethanol, propanol, and butanol on aluminum oxide (*10, 11, 13, 14*) and tunneling spectra of ethanol on aluminum oxide have been published (*9, 12*). The authors of these studies conclude that at room temperature the above alcohols form alkoxide species on the oxide surface, whereas at high temperatures the formation of carboxylate species is favored. In addition, Brown *et al.* (*9*) suggest that a small amount of ethanol adsorbs as an acetate ion at room temperature. This conclusion is based on the observation of a weak broad band near 1590 cm^{-1}, assigned to the asymmetric stretching mode of the CO_2^- group. This band has also been observed by Weinberg (*12*) in samples exposed to ethanol at, or above, 170°C. The peak in the spectra of 1-propanol (Figs. 4 and 5) near 1590 cm^{-1} is thus tentatively assigned to a carboxylate stretching mode. The intensity of this band increases only slightly with doping temperature up to 300°C.

Carboxylic acids adsorb reactively on aluminum oxide at room temperature to give the corresponding carboxylate ions (*17, 42, 43*). Complete surface oxidation of 1-propanol to propanoic acid would be signaled, therefore, by the observation of similar spectra from both adsorbed compounds. The spectrum of propanoate ion observed by doping tunnel junctions with propanoic acid vapor is presented in Fig. 6, and it agrees with that published by Brown and co-workers (*17*). Table 4 lists the observed bands and their assignments. These assignments are those of Brown *et al.*, as modified by de Cheveigne (*42*).

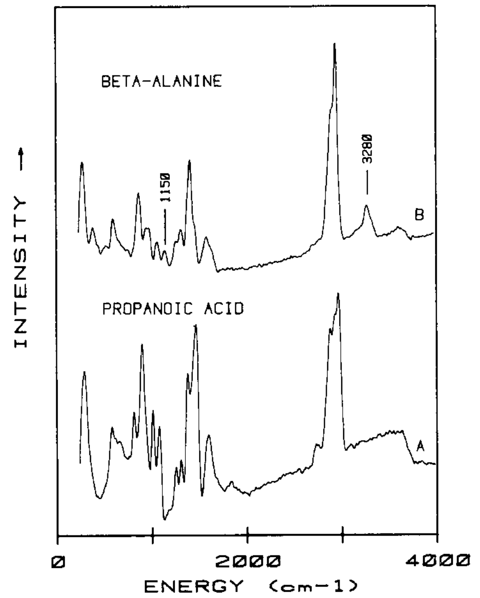

FIG. 6. Spectra of β-alanine and propanoic acid adsorbed on room temperature grown oxides. (B) β-Alanine adsorbed from pH 9 water solution, 13 cm^{-1} resolution. (A) propanoic acid adsorbed from vapor phase at room temperature on a room temperature grown oxide, 15 cm^{-1} resolution.

TABLE 4

Bands Observed in Tunneling Spectra of Propanoic Acid and β-Alanine

Position (cm^{-1})		Assignment
CH_3CH_2COOH	$H_2NCH_2CH_2COOH$	
3640	3625	ν(OH)
	3280	ν(NH)
2970	2960	
2935	2915	ν(CH)
2875		
1595	1580	$\nu_a(CO_2^-)^{a,e}$
1475	1410	$\nu_s(CO_2^-)^{b,c,e}$
1455		$\delta_a(CH_3)^d$
1420	1460	$\delta(CH_2)^{a,c,d,e}$
1305	1305	CH_2 wag, twist^{c,d,e}
1255	1255	$\delta(CH_2)^{c,e}$
	1150	$NH_2{}^c$ twist, see text
1080		$\nu(C{-}C)^d$
	1060	$\nu(C{-}N)^e$
1015		CH_2 wag^d
	980	CH_2 rock^e
	950	ν(Al–O)
	935	$\nu(C{-}C)^e$
905	875	$\nu(C{-}C)^{a,b,e}$
815		CH_2 rock^{a,d}
	745	$\delta(CO_2^-)^{a,b,e,}$
670	655	
580	595	CO_2^- def^{b,e}
	520	
	385	$\delta(N{-}C{-}C)^e$
295	280	$\delta(C{-}C{-}C)^d$ + $Al_{phonon}{}^a$

[a] Ref. (*17*).
[b] Ref. (*42*).
[c] Ref. (*45*).
[d] Ref. (*50*).
[e] Ref. (*40*).

Comparison of the propanoic acid spectrum (Fig. 6) with that of propanol (Fig. 4) shows that they are at best only roughly similar. A spectral feature characteristic of carboxylate formation is the asymmetric COO^- stretching mode near 1600 cm^{-1}. This band is in a region of the spectrum free of other vibrational modes. In the spectrum of propanoic acid this peak is quite prominent, but in the propanol spectrum it is very weak. The COO^- rocking and scissoring bands near 600 and 700 cm^{-1} are also characteristic. These are plainly seen in the propanoic acid spectrum, but are quite weak in the spectrum of 1-propanol. These considerations lead to the conclusion that at 100°C only a small amount of propanol adsorbs as propanoate ion, the remainder being adsorbed as propoxide. Further, diodes prepared by doping with propanol vapor at 300°C yielded spectra whose $\nu_a(CO_2^-)$ peak was only slightly larger than that from junctions doped at 50°. Based on the behavior of alcohols adsorbed on bulk aluminum oxide (*10, 11, 13, 14*) and on thin films (*12*), the amount of propanoate formed and hence the intensity of the peak near 1590 cm^{-1} was expected to increase significantly as the doping temperature was raised. This was not observed.

The close similarity between NH motions of propylamine and amino propanol on the one hand, and the C–O motions of propanol and amino propanol on the other, strongly suggests bidentate coordination for the adsorbed amino propanol. This concept is consistent with the increased adsorption and spectral intensity observed for amino propanol relative to the monofunctional species.

Comparison with a Bifunctional Molecule

3-Amino-1-propanol seems to bond to the aluminum oxide surface via both the amine and alcohol groups. The NH_2 stretching and bending frequencies of the surface complex indicate that the amine end of the molecule is coordinated to an aluminum ion. In this section, the question of how the alcohol end of the molecule is bound to the surface is further addressed. Does the alcohol portion form a surface alkoxide, like propanol, or does it oxidize to form a carboxylate? In order to answer this question the tunneling spectrum of β-alanine (3-aminopropanoic acid) on aluminum oxide was measured. An analysis of the bonding of the amino acid is first presented. The resulting assignments are then contrasted with those for the amino alcohol.

Figure 6 presents the spectrum of β-alanine adsorbed on aluminum oxide from a pH 9 water solution. Table 4 lists the band maxima observed and their assignments. Most of the assignments are based on a normal coordinate analysis of β-alanine (*40*). β-Alanine, like most amino acids, exists in the solid state and in isoelectric solution as a dipolar ion: $^+H_3N\text{–}CH_2CH_2\text{–}COO^-$. Indicative of this structure is a strong broad absorption in the ir extending from 2500 to 3200 cm^{-1} due to RNH_3^+ stretching motions. These are broadened by hydrogen bonding and are so intense that the CH stretching vibrations are completely obscured. In the Raman spectrum the NH_3^+ stretches are weak and are obscured by the CH stretching motions near 2900 cm^{-1}. Other characteristic features in the ir are NH_3^+ deformations near 1650 and 1500 cm^{-1} and the COO^- asymmetric stretch near 1580 cm^{-1}. In addition, two bands near 1150 cm^{-1} have been assigned to NH_3^+ rocking motions (*40*).

In the tunneling spectrum of β-alanine adsorbed from a pH 9 solution, note that the NH stretching vibration at 3280 cm^{-1} is quite strong and distinct (Fig. 6). This frequency is characteristic of coordinated amines (*30–33*), not protonated amines. Also present in this spectrum is a small doublet near 1150 cm^{-1}. This band splits slightly under higher resolution. A band in this region would be expected from NH_3^+ rocking motions if the amine end of the amino acid were protonated on the surface; but, in this case the NH stretching band should be downshifted and broadened from its observed position. This apparent contradiction leads to the following question: Is it not possible to deduce coordination at the amine group from the NH stretching frequency, or is there some other explanation (other than NH_3^+ rocking) for the observed band near 1150 cm^{-1}? Three experiments were performed to address this question. First, the tunneling spectrum of β-alanine was measured as a function of the pH of the doping solution. Second, ir spectra of β-alanine ($H_2NCH_2CH_2COOH$) and deuterated β-alanine ($D_2NCH_2CH_2COOD$) were carefully compared. Third, the ir spectrum of a transition metal complex of β-alanine was measured.

If the 3280 and 1150 cm^{-1} bands in Fig. 6B are both due to motions of an NH_3^+ group, then they should be relatively independent of the adsorption solution pH, until the pH is sufficiently high to deprotonate the amine. At this point the presence of an NH_2 containing species should be apparent in the spectrum. Figure 7 presents the spectrum of β-alanine adsorbed from pH 10, 9, 6, and 4 solutions. Note that the NH stretching intensity decreases uniformly with pH, but that the rest of the spectrum is relatively unchanged. This is interpreted as follows. As the pH of the solution is lowered, the fraction of protonated amine increases. The NH_3^+ stretching modes, however, are completely hidden by the intense CH stretching bands near 2900 cm^{-1}. This is precisely what is observed in the Raman spectrum of β-alanine (*44*). In apparent contradiction, is the occurrence of a band near 1150 cm^{-1} at all pH values. One must, therefore, question the validity of the use of the 1150 cm^{-1} band as an indicator of the presence of NH_3^+.

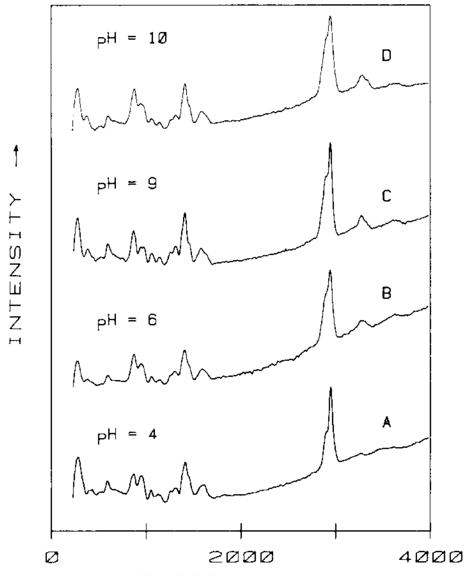

FIG. 7. Tunneling spectra of β-alanine as a function of adsorption solution pH. (A) pH 4, (B) pH 6, (C) pH 9, (D) pH 10.

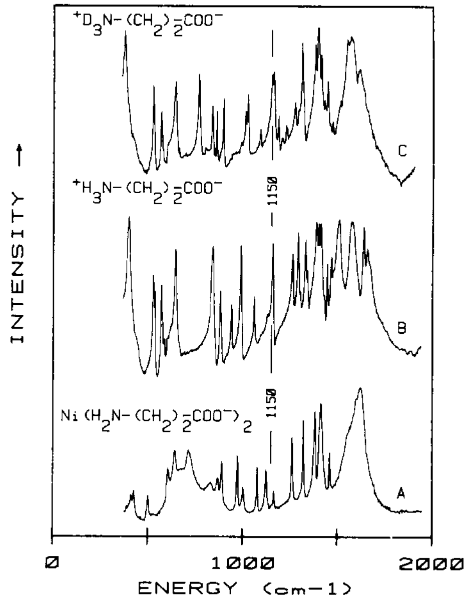

FIG. 8. Infrared spectra of (A) bis-β-alaninatonickel(II), (B) β-alanine, and (C) deuterated β-alanine. Spectra obtained at 20°C (A) and 77°K (B and C).

Figure 8 presents the ir spectra, taken at 77°K, of β-alanine and its deuterated analog. Both isotopic forms of this material have bands in the 1150 cm^{-1} region. Also shown in Fig. 8 is the ir spectrum of bis-β-alaninato nickel(II) dihydrate. In this complex, the amino acid acts as an anionic ligand. The amine group is bonded to nickel and is not protonated. The NH_2 stretching motions of the complex are near 3300 cm^{-1}, as expected (*30–33*). The ir spectrum of the complex shows two peaks near 1150 cm^{-1}; these bands shift to about 810 cm^{-1} in the spectrum of the deuterated material. Bands near these frequencies and showing similar isotopic shifts have been observed for a large number of transition metal complexes of α-alanine (*45*), including bis(DL-α-alaninato)nickel. They have been assigned to NH_2 wagging and twisting motions (*45*). Accordingly, the bands near 1150 cm^{-1} in the spectra of $Ni(H_2NCH_2CH_2COO)_2 \cdot 2H_2O$ are assigned to NH_2

twisting motions. The presence of bands near 1150 cm^{-1} in the free acid as well as in the nickel complex of β-alanine clearly indicates that features in this region are not characteristic of the NH_3^+ group. The pH dependence displayed in Fig. 7 is, therefore, completely consistent with the assignment of the 3280 cm^{-1} band as due to coordinated NH_2 stretching motion. The peak at 1150 cm^{-1} in Fig. 7 is due to NH_2 twisting of coordinated β-alanine at high pH, and to free NH_3^+ rocking at low pH.

It should be pointed out that this picture of the adsorption of β-alanine is not completely consistent with previous studies. Simonsen and Coleman (*16*) have studied the adsorption of several amino acids on alumina by tunneling. They have concluded in general, and for the case of phenylalanine in particular, that the surface species formed by adsorption of amino acids contained free NH_3^+ groups (*16*). The present interpretation of the spectrum of β-alanine is more consistent with the results of Hipps and Mazur (*46*). These authors conclude that, at high pH, glycine does not form a protonated surface complex, although it may at lower values of pH.

It is quite apparent from comparison of Figs. 2 and 6 that 3-amino-1-propanol does not oxidize to form an amino acid like structure when it adsorbs on aluminum oxide. The spectrum of adsorbed 3-amino-1-propanol differs from that of β-alanine in both relative intensities and in the positions of several bands. The NH_2 stretching features, however, are very similar. This similarity is consistent with the aluminum–nitrogen coordination expected for both molecules on the oxide surface.

Surface Structure of 3-Amino-1-Propanol

The preceding considerations lead to the conclusion that both of the reactive groups of 3-amino-1-propanol are involved in bonding to the surface. The alcohol end forms an alkoxide-like species, and the amine group coordinates with aluminum ion. The surface structure of amino propanol, however, is still incompletely characterized. Is the molecule bound to a single aluminum ion, forming a six-membered chelate ring, or is it bridging two adjacent Al ions? The microwave spectrum and gas phase structure of 3-amino-1-propanol indicates that this molecule is intramolecularly hydrogen bonded in the form of a six-membered ring (*47*). This is an ideal shape for forming metal complexes, and indeed, many such complexes are known (*48*). On the other hand, 3-amino-propanol also forms complexes in which it acts as a bridging ligand (*48*). Unfortunately, the present spectroscopic evidence does not distinguish between these two possibilities. The pronounced dehydroxylation of the oxide surface accompanying adsorption of the amino alcohol suggests that whatever the final state is, the adsorption mechanism involves the protonation of a surface hydroxyl group to form water which is subsequently pumped off.

The possibilities for bridged or chelate ring surface species formation may be qualitatively discussed by considering the structure of the oxide surface. γ-Alumina has a defect spinel structure, with 32 approximately close packed O^{2-} ions per unit cell, and 21.33 aluminum ions distributed at random in 16 octahedral and 8 tetrahedral holes (*49*). Since the aluminum lattice is disordered, it is not possible to give exact separations between aluminum *ions*, but it is possible to give approximate distances between aluminum *sites* in the oxygen lattice. Using 2.8 Å as the diameter of the O^{2-} ion (*49*), the distance between an octahedral hole and the next nearest tetrahedral hole is about 4.5 Å. These sites are separated by one anion. If this anion were a hydroxyl ion it could be protonated by the alcohol end of the amino alcohol, and the resulting water would be pumped off. If both cation sites are occupied, this would leave two aluminum ions with one coordination site each available. The O–N distance in the gas phase structure of 3-amino-

1-propanol is very close to the diameter of O_2^- (*47*). Thus the amino alcohol could coordinate with the two available aluminum ions, forming a bridged species.

The formation of a chelate ring species requires the presence of a coordinatively unsaturated aluminum ion on the surface. Such an aluminum ion may be present on a grain boundary or at a defect on the surface. Further, the dehydroxylation of the alumina surface on amino alcohol adsorption suggests that, initially, this ion must also be coordinated to a hydroxyl ion. This hydroxyl group could be protonated by the alcohol and pumped off as water, leaving an aluminum ion with two sites available for chelate ring formation.

It seems plausible that both of these adsorption reactions take place, and the possibility of other reactions leading to either chelate ring or bridged surface complexes cannot be dismissed. In the absence of detailed information about the structure of the oxide surface, it is not possible to estimate the relative probabilities of these reactions.

CONCLUSIONS

1-Propanol and 1-propylamine adsorb on plasma-grown aluminum oxide in very nearly the same orientation. Propanol forms a surface-bound propoxide with little tendency to form propanoate, even at high doping temperatures. The poor conversion yield observed may be due to the short heating times employed in this study. Propylamine forms a surface species that is similar to an amine–metal complex; it is not protonated by the oxide surface. The adsorption of 3-amino-1-propanol appears to proceed by a mechanism that removes OH groups from the surface. This amino alcohol is chemically bound to the oxide surface via both functional groups. One end behaves much like propanol and forms an alkoxide linkage with the surface, the other end coordinates via the nitrogen, as does propylamine. The amino alcohol shows little tendency to form an amino acid-like species on the surface.

During the final preparation of this article, tunneling studies of the chemisorption of 2-amino-1-ethanol and 3-amino-1-propanol were published (*51*). Turner *et al.* conclude that the alcohol end of the alcohol amines studied form an alkoxide bond with the surface. They also assert that no NH_3^+ formation occurs. To this extent, we are in agreement. We differ, however, in interpretation of the NH stretching modes. While the ν(NH) bands observed for the adsorbed species studied are close to the values determined by ir and Raman investigation of the neat liquids, they are significantly lower ($\sim$150 cm^{-1}) than the bands observed in the gas phase spectra of primary amines (*29, 36*). The lowering of ν(NH) in the liquid phase in primary amines, and in all phases in alcohol amines and diamines, is the result of extensive intramolecular and/or intermolecular hydrogen bonding (*29*). These shifts are comparable to those caused by complexation with a metal ion. The position of ν(NH) for "free" surface NH_2 groups, therefore, will depend considerably on the density of these groups on the surface. At low coverage ν(NH) will occur about 150 cm^{-1} higher in energy than in the case of high surface coverage.

As indicated previously, the intensity of a band in IETS is related to surface coverage. Further, because of the vacuum treatment step during top metal deposition, it is doubtful that more than one monolayer was present for any of the systems studied. Because of the weakness of spectra [relative to ν(Al–O)] observed from the alcohol and primary amine, one must conclude that the surface density of primary alcohol or amine is quite low. Relatively large distances, therefore, separate adjacent amines. Since the surface density of NH_2 groups is considerably less than in solution in the case of propylamine, and since no shifts are seen in ν(NH) relative to the other amines studied here, we feel that free NH_2 group frequencies (i.e., gas phase values for amines having no intramolecular hydrogen bonding) are the appropriate ones for comparison with free surface NH_2 groups.

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