

Inelastic Electron Tunnelling Spectroscopy of Selected Alcohols and Amines on Plasma-grown Aluminium Oxide

BY NORMAN M. D. BROWN,* ROBERT B. FLOYD, W. JOHN NELSON
AND D. GEORGE WALMSLEY

School of Physical Sciences, New University of Ulster, Coleraine,
Northern Ireland BT52 1SA

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The surface chemical properties of plasma-grown aluminium oxide are explored by inelastic electron tunnelling spectroscopy. Spectra of benzyl alcohol, benzylamine, 2-phenylethylamine, diphenylamine and ethanol, all adsorbed from the vapour onto the oxide at room temperature, are reported. The ethanol gives mainly an ethoxide species upon adsorption and the liberated proton remains on the surface and enhances the surface hydroxyl concentration. Benzyl alcohol behaves differently. Two possible adsorption mechanisms are proposed for it and for benzylamine. Either (a) a Lewis acid–Lewis base coordination of the adsorbed species at a surface aluminium cation, with attendant substantial charge redistribution, leads to strong hydrogen-bond formation involving adjacent surface oxide centres or (b) Brønsted acid protonation of the adsorbate by the surface occurs. Both may lead to broad, downshifted $\nu(\text{OH})$ and $\nu(\text{NH})$ modes like those seen in the spectra. The other two amines, though less readily adsorbed, give confirmation of this behaviour.

Our own work and that of other groups has shown that inelastic electron tunnelling spectroscopy (IETS) can be used for the detailed study of molecular adsorbates on barrier oxide films grown on metals. Both theoretical and practical aspects of the IET method and all but the current work have recently been reviewed.¹

The method is essentially a non-optical vibrational spectroscopy with which the normal $4000\text{--}300\text{ cm}^{-1}$ range is spanned without significant interference from vibrational modes of the adsorbate. It has a sensitivity sufficient to study adsorbates at $\approx 5\%$ monolayer coverage or less. Moreover, IETS is free of the normal optical selection rules. Therefore, provided vibrational mode assignments can be made, tunnel spectra yield specific information about the interactions of an adsorbate with the oxide layer and hence about the surface characteristics of the latter. In principle, information may also be adduced, from the observed tunnelling band intensities, about the surface orientation of the adsorbate. The adsorbed entity, (X), on the barrier oxide, I, of the Al–I(X)–Pb tunnel junctions is best considered as being matrix isolated. The effect of the top lead electrode is well understood and does not materially affect the interpretation of the tunnel spectra of interest.

Here we continue our series of investigations into simple chemical species adsorbed on plasma-grown aluminium oxide, with our attention now focused on selected amines and alcohols. Aspects of this work were prompted by our earlier IET studies of pyridine² and phenols³ with reference to the Brønsted acidity and Lewis acid/base activity of the plasma-grown oxide films compared with the known characteristics of bulk aluminas. The latter have, of course, been exhaustively studied by conventional infrared spectroscopy (and other methods) largely because of their importance as catalysts or catalyst supports.

The amines and alcohols dealt with here were all adsorbed at room temperature from the vapour on to plasma-grown aluminium oxide inside the vacuum evaporator used for junction preparation. The IET spectra obtained are compared with the vibrational data of the free molecules and with the behaviour, where known, of the same or related species adsorbed on bulk aluminas.

EXPERIMENTAL

The sample preparation procedure has been described in detail previously.^{3,4} In short, the aluminium oxide films (≈ 20 Å) are grown on a glass-supported evaporated film of the metal (≈ 1000 Å) by exposing it to an oxygen d.c. plasma ($p_{O_2} \approx 0.03$ Torr, current ≈ 5 mA) for ≈ 60 s. The adsorbates, first dried over molecular sieve and carefully purified ($\geq 99.5\%$ by g.l.c.) by distillation under nitrogen immediately before use, are admitted to the evacuated (10^{-6} Torr) sample preparation chamber (Edwards E12E) as vapour from an external reservoir for adsorption at room temperature onto the freshly grown oxide surface. The reservoir is then closed off and excess organic vapour pumped away. A quartz crystal microbalance monitors each stage of the junction preparation and in the case of reactive adsorbates it is found that a characteristic amount remains on the oxide surface after pumping away the excess. To complete the doped junction the required top lead electrode (≈ 2000 Å) is deposited and only then is the vacuum system let up to atmosphere for removal of the junction from the evaporator.

From the detailed behaviour of several such preparations it has been found that a similar inelastic signal strength, relative to the elastic background slope, is obtained irrespective of how long (usually > 10 s) or at what partial pressure the vapour is in contact with the oxide surface. We believe, therefore, that the oxide surface is site-saturated but with well below monolayer coverage, *i.e.*, for a given adsorbate a characteristic amount remains adsorbed.

Completed junctions have resistances in the range 20 – $200\ \Omega$ and the resultant IET spectra are recorded at ≈ 2 K in a standard double glass helium cryostat using the detection circuit described previously.³ The spectra are displayed as d^2V/dI^2 against V ($1\text{ meV} = 8.065\text{ cm}^{-1}$), on an X – Y recorder of which the X -axis is driven by the d.c. bias applied across the junctions.

RESULTS AND DISCUSSION

The IET spectrum of ethanol is shown in fig. 1(a); that of an undoped Al–AlO–Pb tunnel junction in fig. 1(b). Those of benzyl alcohol and benzylamine are shown in fig. 2(a) and (b), respectively, with fig. 3(a) and (b) showing, respectively, the IET spectrum of 2-phenylethylamine and diphenylamine.

All show adsorbate bands superimposed on a background associated with certain characteristic features of a clean undoped Al–AlO–M junction. These features, seen in fig 1(b), are located, in order of decreasing energy, at ≈ 3600 , ≈ 1900 , ≈ 940 , ≈ 600 and $\approx 300\text{ cm}^{-1}$. That at $\approx 3600\text{ cm}^{-1}$, identified⁵ with $\nu(\text{O}—\text{H})$ modes, is the only one to have any potential sensitivity to surface adsorption or reaction. We may infer^{3,4} from its position after correction ($+70\text{ cm}^{-1}$)⁶ for the effect of the top lead electrode that the hydroxyl groups* of the plasma-grown oxide are rather acidic in type and thus are surrounded⁷ on the surface by few, or possibly no, nearest neighbour oxide ions. The question of their Brønsted acidity is discussed later. Note also that bands ascribed⁸ to surface bound molecular water, at ≈ 3300 and $\approx 1630\text{ cm}^{-1}$, are never seen in the IET spectra of either doped or undoped junctions. The very low intensity band at $\approx 1900\text{ cm}^{-1}$ is an overtone of the more intense longitudinal $\nu(\text{Al}—\text{O})$ mode of the thin-film oxide located^{5,9,10} at $\approx 940\text{ cm}^{-1}$. The corresponding transverse component is of much lower intensity

* It is found to be impossible to grow coherent oxide films under rigorously dry conditions hence the presence of hydroxyl groups.

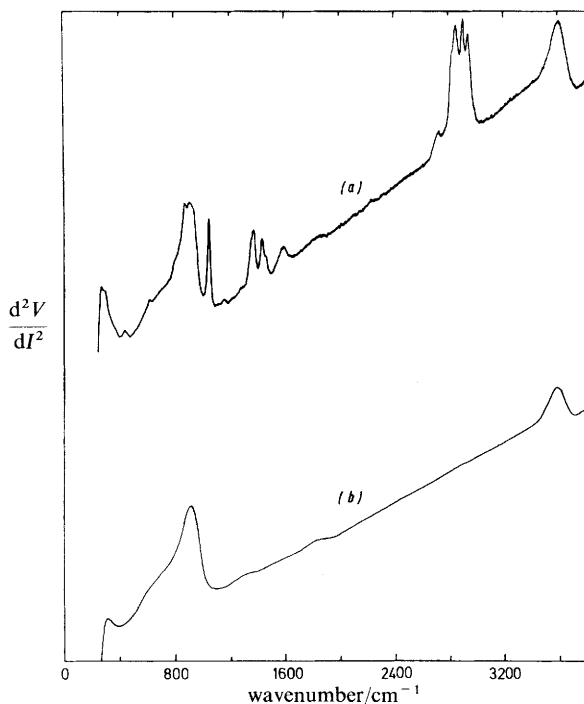


FIG. 1.—Inelastic electron tunnelling spectra, at 2 K, of (a) ethanol adsorbed on the plasma-grown oxide barrier of an Al-aluminium oxide-Pb tunnel junction and of (b) a clean undoped junction.

and may contribute to the low intensity tail of the 940 cm^{-1} band, as does the broad $\delta(\text{Al—O—H})$ mode located at $\approx 600\text{ cm}^{-1}$. The remaining band, at $\approx 300\text{ cm}^{-1}$, is due to lattice phonons of the aluminium metal film.¹¹

ETHANOL

Table 1 lists the corrected* band positions ($1\text{ meV} = 8.065\text{ cm}^{-1}$) and relative band intensities of the IET spectrum of adsorbed ethanol shown in fig. 1(a). For comparison, the positions of the ethanol fundamental modes¹² are also given.

Before considering further the details of the tunnel spectrum it should be noted that the background slope of the experimental d^2V/dI^2 against V plot indicates that coverage of the thin-film aluminium oxide surface is well below a monolayer as do the spectral features themselves; coverage is surface-site limited (see Experimental section).

The relative intensity of the $\nu(\text{OH})$ band shows that the background hydroxyl signal is enhanced following the adsorption of dry ethanol onto the oxide surface. The observed band shape and position are, however, not changed. These observations, plus the apparent absence of the ethanol O—H bending mode (expected at $\approx 1240\text{ cm}^{-1}$) can be interpreted in terms of ethoxide formation at the oxide surface with the loss, following adsorption, of the hydroxylic proton of the ethanol to the oxide surface. In this way one additional surface hydroxyl group is formed for each

* For Al-aluminium oxide-Pb junctions a correction of 8 cm^{-1} is subtracted from the observed line positions to allow for the effect of the superconducting energy gap of the Pb film at the temperatures at which the tunnel spectra are recorded.

TABLE 1.—IETS VIBRATIONAL DATA, OBTAINED AT 2 K, OF ETHANOL CHEMISORBED ON PLASMA-GROWN ALUMINIUM OXIDE

IETS ^a band position, /cm ⁻¹	infrared ^b band position, /cm ⁻¹	assignment
3620 (—) ^c	3662	$\nu(\text{O—H})$
2949 (1.16)	{ 2995	$\nu_a\text{CH}_3$
	{ 2985	$\nu_a\text{CH}_3$
2911 (1.40)	{ 2953	$\nu_a\text{CH}_2$
	{ 2940	$\nu_s\text{CH}_3$
2859 (1.38)	2900	$\nu_s\text{CH}_2$
2731 (0.13)		
1592 (0.20)	—	see text
	1490	CH_2 def.
1466 (sh)	1463	CH_3 asym. def.
1438 (0.46)	{ 1445	CH_3 asym. def.
	{ 1415	CH_2 rocking
1375 (0.61)	1371	CH_3 sym. def.
—	1251	CH_2 torsion
—	1240	OH bend
1158 (0.05)		?
	1092	C—C—O asym. str.
1051 (1.00)	{ 1083	CH_3 rocking
	{ 1025	CH_3 rocking
940 (—) ^c		$\nu(\text{Al—O})$
911 (0.02)		?
876 (0.16)	887	C—C—O sym. str.
801 (sh)	812	CH_2 rocking
618 (0.06)		?
435 (0.08)	417	C—C—O bend
294 (—) ^c	—	Al lattice phonon
264 (?) ^d	264	CH_3 torsion
	211	OH torsion

^a Positions corrected as described in text, relative heights shown as () w.r.t. 1051 cm⁻¹ band; sh—shoulder. ^b Data taken from ref. (12). ^c Discussed in text. ^d Superimposed on aluminium lattice phonon band.

ethanol molecule chemisorbed as ethoxide. Since hydrogen-bonded hydroxyl bands are not seen in the tunnel spectrum it can reasonably be concluded that few if any adjacent hydroxyl pairs or clusters are present either before or after chemisorption. Equally, the additional hydroxyl groups formed are not hydrogen-bonded to the oxygen atom of the surface ethoxide species.

As to the other bands, agreement between the tunnel spectrum and the various non-hydroxyl modes of bulk ethanol is good, the more so if a correction ($\approx +50$ cm⁻¹)⁶ is made to the various $\nu(\text{C—H})$ mode positions to compensate for the known effect of the top lead electrode. Assignments are made in table 1. A number of the observed bands also correspond to those reported for aluminium ethoxide¹³ and to those identified^{14,15} with ethoxide formation on various bulk aluminas.

The low intensity band at ≈ 1590 cm⁻¹, if assigned to the $\nu_a(\text{CO}_2^-)$ of surface bound acetate,⁴ may arise from the presence of some surface acetate produced by

oxidation of the ethanol/ethoxide at the oxide surface as has also been reported for certain bulk aluminas.^{14,16} The corresponding $\nu_s(\text{CO}_2^-)$ mode is not separately identified, although it may be present in the tunnel spectrum along with some other bands associated with surface bound acetate. We believe that it is less likely that the 1592 cm^{-1} band could be derived from a $\nu(\text{C}=\text{C})$ mode by analogy with known behaviour¹⁷ of the bulk oxide with adsorbed alcohols.

BENZYL ALCOHOL AND BENZYLAMINE

Table 2 lists the band positions, relative band intensities and probable band assignments of the IET spectra of adsorbed benzyl alcohol and benzylamine. The spectra are shown in fig. 2(a) and (b), respectively. These are clearly very similar both in band position and relative band intensity. The only marked difference is in the relative intensity of the broad band centred close to 2900 cm^{-1} . This band, the origin of which is discussed later, is of greater width in the spectrum of adsorbed benzylamine, but more intense in the benzyl alcohol case. Most of the remaining bands listed can be readily identified with the expected¹⁸ vibrational fundamentals of a monosubstituted benzene ring.

If the substituent group, $-\text{CH}_2\text{NH}_2$ or $-\text{CH}_2\text{OH}$, is treated as a single unit the adsorbates will each have thirty vibrations characteristic of the phenyl ring. Three of the expected five $\nu(\text{C}-\text{H})$ modes are resolved and are observed in both tunnel spectra close to their expected positions once the correction ($\approx +50\text{ cm}^{-1}$)⁶ for the effect of the top lead electrode is made. The remaining twenty five fundamentals of the phenyl ring lie below 1600 cm^{-1} (where top electrode shifts are no longer significant). Of these, virtually all can be assigned, with reasonable confidence, as indicated.

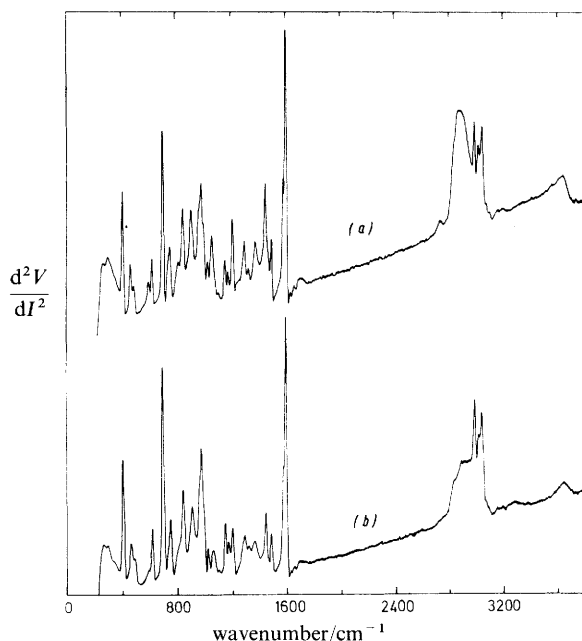


FIG. 2.—Inelastic electron tunnelling spectra, at 2 K, of (a) benzylalcohol and (b) benzylamine adsorbed on the plasma-grown oxide of an Al-aluminium oxide–Pb tunnel junction.

TABLE 2.—IETS^a VIBRATIONAL DATA, OBTAINED AT 2 K, OF BENZYL ALCOHOL AND BENZYLAMINE CHEMISORBED ON PLASMA-GROWN ALUMINIUM OXIDE

benzyl alcohol band position/cm ⁻¹	benzylamine band position/cm ⁻¹	assignment
3620 (—) ^f	3620 (—) ^f	$\nu(\text{O—H})$
	3299 (0.02)	$\nu(\text{N—H})$
3047 (0.67)	3050 (0.41)	aryl $\nu(\text{C—H})$
3027 (0.68)	3025 (0.32)	
2994 (0.75)	2996 (0.49)	
2885 (1.18) ^f	2900 (0.22) ^c	see text
2734 (sh)		
1598 (1.65)	1605 (1.16)	$\nu(\text{C—C})$
1580 (0.93)	1585 (0.47)	$\nu(\text{C—C})$
1492 (0.27)	1496 (0.15)	$\nu(\text{C—C})$
1449 (0.54)	1454 (0.22)	$\nu(\text{C—C})$
1375 (0.23)	1375 (0.09)	CH_2 scissoring
1323 (sh)	1333 (0.09)	$\nu(\text{C—C})$
1295 (0.29)	1301 (0.14)	$\nu(\text{C—H})$
1210 (0.45)	1214 (0.20)	X sensitive/ CH_2 rocking
1175 (0.17)	1184 (0.14)	$\beta(\text{C—H})$
1151 (0.27)	1159 (0.22)	$\beta(\text{C—H})/\text{CH}_2$ twisting
1100 (0.02)	1107 (0.02)	?
1055 (0.61)	1071 (0.09)	$\beta(\text{C—H})$
1025 (0.17)	1032 (0.11)	$\beta(\text{C—H})$
1000 (sh) ^d	1000 (sh) ^{d,e}	α ring
978 (0.58) ^d	988 (0.47) ^d	$\gamma(\text{C—H})$
962 (sh) ^d	960 (sh) ^{d,e}	$\gamma(\text{C—H})$
907 (0.40) ^d	915 (0.17) ^d	$\gamma(\text{C—H})$
844 (0.52)	851 (0.31)	$\gamma(\text{C—H})$
817 (sh)	820 (sh) ^e	X sensitive/ CH_2 rocking
748 (0.35)	758 (0.27)	$\gamma(\text{C—H})$
696 (1.00)	703 (1.00)	$\phi(\text{C—C})$
617 (0.30)	625 (0.29)	$\alpha(\text{C—C—C})$
592 (0.17)	585 (0.06)	?
484 (0.19)	495 (0.11)	X sensitive/ $\phi(\text{C—C})$
458 (0.34)	466 (0.18)	$\phi(\text{C—C})$
401 (0.78)	407 (0.58)	X sensitive/ $\phi(\text{C—C}_1)$
	348 (0.01)	?
294 (—)	294 (—)	lattice phonon
270 (?) ^f	266 (?) ^f	$\beta(\text{C—X})$

^a Positions corrected as described in text, relative heights shown as () w.r.t. band close to 700 cm⁻¹; sh—shoulder. ^b ν , β and $\gamma(\text{C—H})$ are stretching, in-plane and out-of-plane deformation modes, respectively; $\nu(\text{C—C})$ and $\phi(\text{C—C})$ are, respectively, ring stretching modes and out-of-plane deformations, as is $\phi(\text{C—C}_1)$; $\alpha(\text{C—C—C})$ is an in-plane deformation; α ring, the trigonal ring breathing mode; X sensitive modes are associated with motion of the substituent group on the phenyl ring; $\beta(\text{C—X})$ is an out-of-plane substituent-ring deformation. ^c Discussed in text. ^d Superimposed on $\nu(\text{Al—O})$ band. ^e Adduced from band contour. ^f Superimposed on aluminium lattice phonon band.

The remaining vibrational modes may be assigned by treating the phenyl ring (Ph) as a single unit so that the PhCH_2NH_2 system will have fifteen characteristic modes while the PhCH_2OH system will have twelve. The vibrational frequencies of the disubstituted methylene species to be identified are a twisting mode, two rock-

ing modes, a scissoring mode and two stretching modes. Of these, the scissoring mode is reasonably assigned to the 1375 cm^{-1} band but the torsional mode known¹⁹ to arise at $\approx 1150\text{ cm}^{-1}$ is not separately identified and may be coincident with an in-plane phenyl C—H deformation seen at $\approx 1150\text{--}1160\text{ cm}^{-1}$ in the tunnel spectra. Similarly, the CH_2 rocking mode usually seen¹⁹ in the $1200\text{--}1270\text{ cm}^{-1}$ region, in the adsorbate spectra could be coincident with the band at $\approx 1300\text{ cm}^{-1}$, or preferably with that at $\approx 1210\text{ cm}^{-1}$. The band seen as a shoulder at 817 cm^{-1} in the benzyl alcohol case and only just resolved in the benzylamine tunnel spectrum may be assigned, as indicated, to the second rocking mode, in agreement with expectation.^{19,20} The location of the two expected methylene stretching modes in the tunnel spectra requires further consideration as does the identification of the modes of the amino and hydroxyl groups. Detailed examination of the tunnel spectra suggests these two questions are interrelated.

Both spectra show, as already noted, a broad band centred on 2900 cm^{-1} but little, if any, evidence of bands in the region $3100\text{--}3500\text{ cm}^{-1}$ where simple hydrogen bonded $\nu(\text{N—H})$ or $\nu(\text{O—H})$ modes are expected. Moreover, the normal background $\nu(\text{O—H})$ band at $\approx 3620\text{ cm}^{-1}$ associated with surface bound hydroxyl intrinsically present in the plasma-grown aluminium oxide remains unperturbed in position; there is, however, some evidence of a reduction in intensity, in contrast with the behaviour in the case of adsorbed ethanol discussed above. Chemisorption involving hydrogen-bond formation between adsorbate and surface hydroxyl or between adsorbate and exposed surface oxide ions seems insufficient to explain the appearance of the spectra obtained. A significantly stronger adsorbate–adsorbent interaction is therefore likely. We believe this may involve either (a) Lewis acid–Lewis base coordination of the adsorbed species at an exposed surface aluminium cation with substantial charge redistribution to leave the oxygen or nitrogen centres present more positively charged; simultaneously, strong hydrogen-bonds are formed with adjacent oxide centres, or (b) Brønsted acid protonation of the adsorbate by the surface hydroxyl to give a surface bound benzyl oxonium (ROH_2^+) or ammonium species. Examples of both types of chemisorption have been discussed elsewhere^{15,21–23} in relation to the surface acidity of bulk aluminas. In either of the two suggested processes the $\nu(\text{O—H})$ and $\nu(\text{N—H})$ modes are likely to sample a range of surface environments. Hence, as well as showing a substantial shift to lower energy, the bands will be broad. Their resultant position will cause them to overlap with and obscure the symmetric and antisymmetric $\nu(\text{C—H})$ modes of the methylene groups expected¹⁹ at ≈ 2870 and $\approx 2920\text{ cm}^{-1}$, respectively. Similarly shifted $\nu(\text{N—H})$ bands have been reported for amine:aluminium trihalide complexes²⁴ and alkyl ammonium salts²⁵ but comparable data²⁶ for appropriately perturbed or protonated alcohols are less readily available. The fact that the corresponding deformation modes of the perturbed or possibly protonated hydroxyl or amino groups located in the $1200\text{--}1600\text{ cm}^{-1}$ region are not identified can be attributed to the likely bandwidth and a low relative intensity for these modes.

The very low intensity broad band at $\approx 3300\text{ cm}^{-1}$ in the tunnel spectrum of benzylamine we attribute to a very minor amount of physisorbed amine.

2-PHENYLETHYLAMINE AND DIPHENYLAMINE

Table 3 lists the band positions and relative intensities of the IET spectra of adsorbed 2-phenylethylamine and diphenylamine. The corresponding spectra are shown in fig. 3(a) and (b), respectively. The detailed behaviour of these adsorbates

TABLE 3.—IETS VIBRATIONAL DATA,^a OBTAINED AT 2 K, OF 2-PHENYLETHYLAMINE AND DIPHENYLAMINE CHEMISORBED ON PLASMA-GROWN ALUMINIUM OXIDE

2-phenylethylamine		diphenylamine	
band position/ cm ⁻¹	assignment ^b	band position/ cm ⁻¹	assignment ^b
3620 (—) ^c	$\nu(\text{O—H})$	3620 (—) ^c	$\nu(\text{O—H})$
3309 (0.06)	$\nu(\text{N—H})$	—	
3050 (0.76)	aryl $\nu(\text{C—H})$	3034 (0.71)	aryl $\nu(\text{C—H})$
3029 (0.71)		3008 (0.52) sh	
2999 (0.84)			
2916 (0.92)			
2855 (0.65) ^c	methylene $\nu_a(\text{C—H})$	2870 (0.52) ^c	see text
1605 (0.91)	see text	1597 (0.46) sh	$\nu(\text{C—C})$
1585 (0.75)	$\nu(\text{C—C})$	1576 (0.95)	$\nu(\text{C—C})$
1499 (0.22)	$\nu(\text{C—C})/\text{CH}_2$ scissoring	1485 (0.73)	$\nu(\text{C—C})$
1456 (0.30)	$\nu(\text{C—C})$	1451 (0.28)	$\nu(\text{C—C})$
		1419 (0.11)	?
1385 (0.12)	$\nu(\text{C—C})$	1380 (0.14)	$\nu(\text{C—C})$
		1330 (0.12)	$\nu_a(\text{C—N—C})$
1303 (0.24)	$\beta(\text{C—H})/\text{CH}_2$ wagging	1298 (0.33)	$\beta(\text{C—H})$
		1242 (0.24)	$\beta(\text{C—H})/\nu_s(\text{C—N—C})$
1210 (0.23)	X sensitive/ CH_2 rocking	1217 (0.10) sh	X sensitive
1190 (0.18)	$\beta(\text{C—H})$		
1161 (0.25)	$\beta(\text{C—H})/\nu(\text{C—C})/\text{CH}_2$ twisting	1172 (0.10)	$\beta(\text{C—H})$
		1148 (0.32)	$\beta(\text{C—H})/\nu(\text{C—N})$
		1108 (0.07)	
1061 (0.18)	$\beta(\text{C—H})/\nu(\text{C—N})$	1050 (0.49)	$\beta(\text{C—H})$
1036 (0.23)	$\beta(\text{C—H})$	1022 (0.39)	$\beta(\text{C—H})$
980 (0.38) ^d	$\gamma(\text{C—H})$		
945 (0.05) ^d	$\gamma(\text{C—H})$	950 (0.18) ^d	$\gamma(\text{C—H})$
915 (0.30) ^d	$\gamma(\text{C—H})$		
		896 (0.18)	$\gamma(\text{C—H})$
854 (0.60)	$\gamma(\text{C—H})$	871 (0.36)	$\gamma(\text{C—H})$
		829 (0.44)	X sensitive
758 (0.23)	$\gamma(\text{C—H})/\text{CH}_2$ rocking	748 (0.41)	$\gamma(\text{C—H})$
706 (0.63)	$\phi(\text{C—H})$	692 (0.50)	$\phi(\text{C—C})$
627 (0.38)	$\alpha(\text{C—C—C})$	639 (0.08)	?
603 (0.14)	?	611 (0.46)	$\alpha(\text{C—C—C})$
582 (0.13)	?	564 (0.22)	?
502 (0.25)	X sensitive/ $\phi(\text{C—C})$	498 (0.82)	X sensitive/ $\phi(\text{C—C})$
474 (0.18)	$\phi(\text{C—C})$		$\phi(\text{C—C})$
413 (1.00)	X sensitive/ $\phi(\text{C—C})$	407 (1.00)	X sensitive/ $\phi(\text{C—C})$
367 (0.13)	?	329 (0.21)	?
294 (—)	lattice phonon	305 (0.26) ^e	lattice phonon

^a Positions corrected as described in text, relative heights shown as () w.r.t. band close to 410 cm⁻¹; sh—shoulder. ^b For symbols used, see table 2. ^c Discussed in text. ^d Superimposed on $\nu(\text{Al—O})$ band. ^e Superimposed on aluminium lattice phonon band.

during junction preparation suggested that they were adsorbed with more difficulty on to the plasma-grown aluminium oxide than benzylamine. This is borne out by the actual appearance of the tunnel spectra: both show a characteristically poorer signal-to-noise ratio and increased background slope, particularly in the case of

diphenylamine, compared with those of adsorbed benzylamine. Nevertheless, the spectral quality is good.

The observed bands of the tunnel spectrum of 2-phenylethylamine match in close detail those of benzylamine apart from the contributions to the spectrum of a second methylene group. Again the background $\nu(\text{O—H})$ band at $\approx 3620\text{ cm}^{-1}$ is of reduced intensity and the expected methylene $\nu(\text{C—H})$ modes coincide, we believe, with $\nu(\text{N—H})$ modes of an appropriately perturbed or protonated amino group. As with adsorbed benzylamine the corresponding deformation modes are not readily identified and again a low intensity broad band seen at $\approx 3300\text{ cm}^{-1}$ is ascribed to the $\nu(\text{N—H})$ modes of loosely bound adsorbate. The other assignments made follow a general consideration of those expected¹⁸ for a mono-substituted phenyl ring and 2-substituted ethylamines,^{19,27} as indicated in table 3. Similar general arguments²⁸ apply to adsorbed diphenylamine with which, even on prolonged exposure of the oxide surface to the vapour of the adsorbate, less is chemisorbed than with 2-phenylethylamine. It can be concluded that the sterically more crowded and substantially weaker base is capable of interacting with fewer surface sites than the primary amines, a point to which we return again below. As with the primary amines a major broad band is seen in the tunnel spectrum with its centre at 2870 cm^{-1} . Since in this case there are no methylene modes present the indicated band can only be ascribed to $\nu(\text{N—H})$ modes of a highly perturbed or protonated amine. This further substantiates the assignments discussed above in the case of the other two amines. Again, the corresponding deformation modes are not seen.

Though oxidation of diphenylamine to diphenylnitroxide on bulk alumina is known²⁹ to occur, the presence of a relatively intense perturbed $\nu(\text{N—H})$ band argues against significant oxidation of the adsorbate on the surface of the plasma-grown oxide, as does the absence of any intense band which could reasonably be

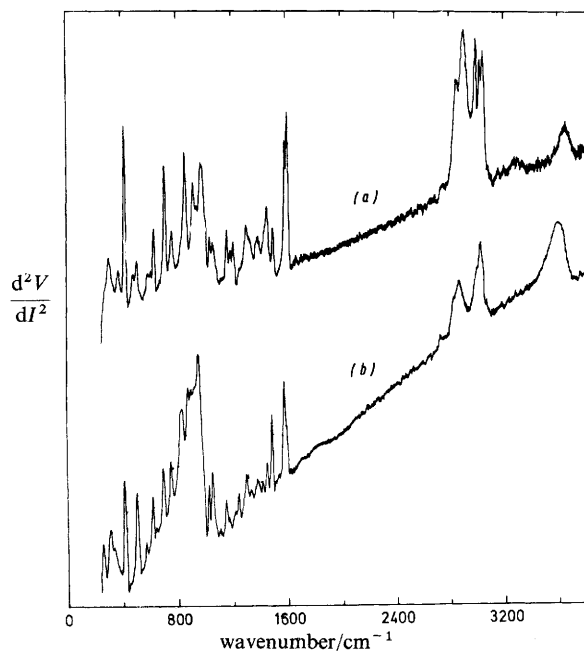


FIG. 3.—Inelastic electron tunnelling spectra, at 2 K, of (a) 2-phenylethylamine and (b) diphenylamine adsorbed on the plasma-grown oxide of an Al-aluminium oxide—Pb tunnel junction.

assigned to a $\nu(\text{N—O})$ mode which is found³⁰ in the free nitroxide at $\approx 1330\text{ cm}^{-1}$. In the case of 2-phenylethylamine, for which disproportionation or deamination at the oxide surface might be expected in view of the known³¹ behaviour of amines including benzylamine on certain bulk aluminas, the number of bands observed and their positions show that only chemisorption without further reaction has occurred. It is clear from the proposed behaviour of the four amines discussed that a self-consistent view of the adsorbate-adsorbant interaction is attainable, with or without actual protonation of the amines. However, without further evidence involving adsorbates deuteriated at the amino group and, or with, pre-deuteriated surface hydroxyl on the plasma-grown aluminium oxide a clear distinction cannot be made between the chemisorption processes (a) and (b) above. It may be that work now in hand will resolve the question or show that both processes occur separately on different surface sites or concurrently on adjacent Lewis acid and Brønsted acid sites.

What is more difficult to rationalise at this stage is the relationship of the two adsorbed alcohol tunnel spectra to each other and to the spectra of the amines. While it is possible to equate the 2859 cm^{-1} band of the adsorbed ethanol with 2885 cm^{-1} band of the adsorbed benzyl alcohol, *i.e.*, as a highly perturbed or protonated hydroxyl group, it seems unlikely that the corresponding hydroxyl deformation band(s) would be unseen in the relatively simple ethanol tunnel spectrum. Hence ethoxide formation is our preferred interpretation. It could also be argued that on adsorption the benzyl alcohol gives a surface bound alkoxide, but if this is so then the two $\nu(\text{C—H})$ modes or the methylene group would be resolved. Also, the intense broad band observed at $\approx 2885\text{ cm}^{-1}$ would be absent and the background $\nu(\text{O—H})$ mode would be correspondingly enhanced. Clearly, for benzyl alcohol the tunnel spectrum is more in keeping with the chemisorption processes (a) and (b) suggested above.

CONCLUSIONS

Chemisorption of ethanol on the plasma-grown aluminium oxide gives mainly surface bound ethoxide and in part, as with ethanol on bulk aluminas, surface acetate. Therefore the reactivity of the plasma-grown oxide towards adsorbed ethanol mirrors that of the bulk oxide.^{14–16} To our knowledge benzyl alcohol has not been studied on bulk aluminas. With both alcohols chemisorption, on equilibration of the adsorbate vapour with the oxide substrate at room temperature, may proceed at surface exposed aluminium cations acting as Lewis sites. In the ethanol case the hydroxylic proton is transferred on, or immediately following, adsorption to an adjacent surface oxide ion and from there to the pool of hydroxyl groups already present on the thin oxide film. For benzyl alcohol initial coordination at an exposed aluminium cation is not followed by reaction but by charge redistribution which weakens the O—H bond of the adsorbate. A significant concurrent involvement of an adjacent surface hydroxyl group (or groups) in the formation of strong hydrogen bonds with the coordinated oxygen atom of the alcohol is proposed. Some of these interactions may lead to actual protonation of the adsorbate hydroxyl group. The differences indicated for ethanol and benzyl alcohol may imply that different surface sites are involved. Ethanol, being sterically less demanding than benzyl alcohol, can react with more reactive sites which most of the adsorbed benzyl alcohol apparently cannot reach.

Should the plasma-grown oxide surface have hydroxyl groups of sufficient acidity to protonate an alcohol then the more basic nitrogen atom of the amines must also

be so protonated with or without involvement of an aluminium cation acting as a Lewis acid site. However, with the amines as with benzyl alcohol we believe Lewis base interactions of the amino nitrogen with Lewis acid aluminium cations occur at the oxide surface.

Brønsted acid protonation of amines²³ and Lewis acid–Lewis base interactions with alcohols²¹ and amines²² have both been characterised on various bulk aluminas. The evidence here suggests that the thin-film plasma-grown aluminium oxide behaves similarly. In contrast, the known²⁹ oxidation of diphenylamine to diphenylnitroxide on bulk alumina does not appear to arise. Neither does disproportionation³¹ of the chemisorbed amines, at least under the ambient temperature conditions of adsorption and junction completion.

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- ¹ P. K. Hansma, *Phys. Rep.* 1977, **30**, 145; P. K. Hansma and J. Kirtley, *Accounts Chem. Res.*, 1978, **11**, 440; W. H. Weinberg, *Ann. Rev. Phys. Chem.*, 1978, **29**, 115; E. L. Wolf, *Reports Progr. Phys.*, 1978, **41**, 1439.
- ² N. M. D. Brown, D. G. Walmsley and R. B. Floyd, *J. Catalysis*, 1978, **52**, 347; P. K. Hansma, D. A. Hickson and J. A. Schwarz, *J. Catalysis*, 1977, **48**, 237.
- ³ I. W. N. McMorris, N. M. D. Brown and D. G. Walmsley, *J. Chem. Phys.*, 1977, **66**, 3952.
- ⁴ N. M. D. Brown, R. B. Floyd and D. G. Walmsley, *J.C.S. Faraday II*, 1979, **75**, 17.
- ⁵ J. Lambe and R. C. Jaklevic, *Phys. Rev.*, 1968, **165**, 821; W. M. Bowser and W. H. Weinberg, *Surface Sci.*, 1977, **64**, 377 and references therein.
- ⁶ P. R. Antoniewicz, *Surface Sci.*, 1975, **52**, 703; J. R. Kirtley and P. K. Hansma, *Phys. Rev. B.*, 1975, **12**, 531; 1976, **13**, 2910.
- ⁷ H. Knözinger and P. Ratnasamy, *Catalysis Rev.*, 1978, **17**, 31 and references therein.
- ⁸ L. H. Little, *Infrared Spectra of Adsorbed Species* (Academic Press, N.Y., 1966), p. 233; J. B. Peri and R. B. Hannan, *J. Phys. Chem.*, 1960, **64**, 1526.
- ⁹ B. F. Lewis, M. Mosesman and W. H. Weinberg, *Surface Sci.*, 1974, **41**, 142; T. Takumura, H. Kihara-Morishita and U. Moriyama, *Thin Solid Films*, 1970, **6**, R17; W. Vedder and D. A. Vermilyea, *Trans. Faraday Soc.*, 1969, **65**, 561.
- ¹⁰ A. J. Maeland, R. Rittenhouse, W. Lahar and P. V. Romano, *Thin Solid Films*, 1974, **21**, 67; J. Chataler, H. H. Claassen, D. M. Green, I. Shaft and R. B. Wright, *Appl. Spectroscopy*, 1975, **29**, 185; A. V. Uvarov, T. V. Antipina and S. P. Tikhomirova, *Russ. J. Phys. Chem.*, 1967, **41**, 1647.
- ¹¹ T. T. Chen and J. G. Adler, *Solid State Comm.*, 1970, **8**, 1965.
- ¹² A. J. Barnes and H. E. Hallam, *Trans. Faraday Soc.*, 1970, **66**, 1932; J. P. Perchard and M. L. Josien, *J. Chim. Phys.*, 1968, **65**, 1834; 1856.
- ¹³ R. C. Wilhoit, J. R. Burton, F.-T. Kuo, S.-R. Huang and A. Viquesnel, *J. Inorg. Nuclear Chem.*, 1962, **24**, 851; C. G. Barraclough, D. C. Bradley, J. Lewis and I. M. Thomas, *J. Chem. Soc.*, 1961, 2601; S. Pinchas, *Spectrochim. Acta*, 1973, **29A**, 853; N. Takesawa and H. Kobayashi, *J. Catalysis*, 1972, **25**, 179.
- ¹⁴ R. G. Greenler, *J. Chem. Phys.*, 1962, **37**, 2094.
- ¹⁵ H. Jeziorowski, H. Knözinger, W. Maye and H. D. Müller, *J.C.S. Faraday I*, 1973, **69**, 1744; R. O. Kagel, *J. Phys. Chem.*, 1967, **73**, 716; R. O. Kagel, *J. Catalysis*, 1970, **16**, 316; H. Knözinger and H. Stolz, *Ber. Bunsenges. phys. Chem.*, 1970, **74**, 1056.
- ¹⁶ H. Knözinger, H. Bühl and E. Ress, *J. Catalysis*, 1968, **12**, 121; W. Hertl and A. M. Cuenca, *J. Phys. Chem.*, 1973, **77**, 1120.
- ¹⁷ H. Pines and J. Manassen, *Adv. Catalysis*, 1966, **16**, 49.
- ¹⁸ D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350; F. R. Dollish, W. G. Fateley and W. F. Bentley, *Characteristic Raman Frequencies of Organic Molecules* (Wiley-Interscience, N.Y., 1974), p. 170; G. Varsanyi, *Vibrational Spectra of Benzene Derivatives* (Academic Press, N.Y., 1969).
- ¹⁹ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. van Nostrand, N.Y., 1966), p. 317; L. J. Bellamy, *Infrared Spectra of Complex Molecules* (Chapman and Hall, London, 1975), p22.
- ²⁰ S. Chattopadhyay, *Indian. J. Phys.*, 1967, **41**, 759; L. Verdonck and G. P. van der Kelen, *Spectrochim. Acta*, 1972, **28A**, 51; 55.

- ²¹ H. Knözinger and B. Stübner, *J. Phys. Chem.*, 1978, **82**, 1526.
- ²² K. Hirota, K. Fueki and T. Sakai, *Bull. Chem. Soc. Japan*, 1962, **35**, 1545; J. Medema, J. J. G. M. Van Bokhoven and A. E. T. Kuiper, *J. Catalysis*, 1972, **25**, 238; T. Morimoto, J. Imai and M. Nagao, *J. Phys. Chem.*, 1974, **78**, 704.
- ²³ M. Tanaka and S. Ogasawara, *J. Catalysis*, 1972, **25**, 111; D. S. MacIver, H. H. Tobin and R. T. Barth, *J. Catalysis*, 1963, **2**, 485.
- ²⁴ H. Sato, Y. Kusumoto, S.-I. Arase, M. Suenaga and S. Kammura, *J. Phys. Chem.*, 1978, **82**, 66; W. Gerrard and E. F. Mooney, *J. Chem. Soc.*, 1960, 4028.
- ²⁵ C. S. Douse and P. B. Tooke, *Canad. J. Spectroscopy*, 1973, **18**, 101; C. Brisette and C. Sandorfy, *Canad. J. Chem.*, 1960, **38**, 34.
- ²⁶ B. Desbat and P. V. Huong, *Spectrochim. Acta*, 1975, **31A**, 1109; M. Fournier and J. Rozière, *Compt. rend. Ser. C.*, 1970, **270**, 729.
- ²⁷ L. A. Gribov, M. P. Noskova and I. N. Krupennikova, *Optics and Spectroscopy*, 1974, **36**, 466.
- ²⁸ H. Levitsky, G. Norwitz and D. E. Chasan, *Appl. Spectroscopy*, 1968, **22**, 493; J. Itier and A. Casadevall, *Bull. Soc. chim. France*, 1970, 168; A. P. Rud'ko, I. N. Chernyuk, Yu. S. Rozum and G. T. Pilyugin, *Ukrain. Khim. Zrur.*, 1968, **34**, 1275.
- ²⁹ B. D. Flockhart, P. A. F. Mollan and R. C. Pink, *J.C.S. Faraday I*, 1975, **71**, 1192.
- ³⁰ M. N. Volkotrub, E. G. Rozantsev and L. A. Skripko, *Izv. Akad. Nauk S.S.S.R. Ser. khim.*, 1967, 179.
- ³¹ J. Koubek, J. Volf and J. Pašek, *J. Catalysis*, 1975, **38**, 385; P. Hogan and J. Pašek, *Coll. Czech. Chem. Comm.* 1973, **38**, 1513; S. Ogasawara, M. Takagawa and K. Takahashi, *J. Catalysis*, 1973, **29**, 67.

(PAPER 9/1863)