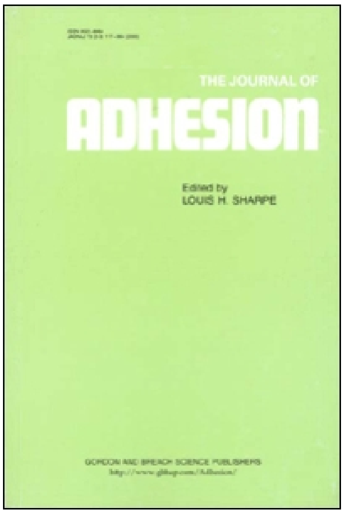

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Inelastic Electron Tunneling Spectroscopy of Some Aminosilane Coupling Agents†

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Inelastic electron tunneling spectra have been obtained for some aminosilanes (3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, the mixed and separated isomers of aminophenyltrimethoxysilane and *N*-2-aminoethyl-3-aminopropyl trimethoxysilane) adsorbed on aluminium oxide. The silanes have been applied from the vapour and from solutions in either benzene, water or acidic aqueous alcohol. Spectra indicate different levels of hydrolysis and condensation for the amines, which depend upon the doping conditions, and that no isotopic exchange occurs when the doping medium is D_2O. The mode of attachment to the oxide surface is different for the three isomers of aminophenyltrimethoxysilane.

KEY WORDS Aminosilanes; inelastic electron tunneling spectroscopy; aluminium oxide; preferential adsorption; hydrolysis; isotopic exchange.

INTRODUCTION

Silane coupling agents can be used as adhesion promoters for glass and metal surfaces prior to adhesive bonding, and the advantages of doing so is that in many instances there is an improvement in environmental resistance.[1]

Inelastic electron tunneling spectroscopy (IETS) is particularly appropriate to the study of adhesives and adhesion promoters since it records the vibrational spectra of molecules adsorbed on a metal oxide. Aluminium is the most widely chosen cathode for IET junctions and aluminium alloys are also the most widely studied metals for adhesive bonding because of their widespread use in the

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aerospace industries. The technique has previously been reported in studies of silane coupling agents on aluminium oxide by Alexander, Gent and Henriksen,[2] Diaz, Hetzler and Kay,[3] Furukawa, Eib, Mittal and Anderson[4,5] and Van Velzen,[6] and in an earlier paper[7] from these laboratories. It has also been used to study a number of adhesives or adhesive-related systems on alumina including epoxides,[8,9,10] polymers containing ester groups[11,12] and phenolics.[13]

The aminosilanes are some of the most important coupling agents because the amine group can react with epoxide groups, and thereby the coupling agent becomes covalently bonded to the adhesive or matrix resin. In a previous paper[7] we reported IET spectra of 3-aminopropyltrimethoxysilane (APMS) doped from the vapour phase on to aluminium oxide. We now report IET spectra of 3-aminopropyltriethoxysilane (APES), *N*-2-aminoethyl-3-aminopropyltrimethoxysilane (AAPMS), and the mixed and separate isomers of aminophenyltrimethoxysilane (APhMS) applied to a surface of aluminium oxide from the vapour, or from solutions in benzene, water, D_2O or acidic aqueous alcohol. Spectral assignments for APES in our earlier paper[7] were based on comparison with infra-red spectra. Present assignments, which we regard as correct, are also based on IET spectra of many simple silanes which we hope to publish later.

Some other spectroscopic techniques have been employed to study aminosilanes adsorbed on metal surfaces. Boerio and his co-workers have used reflection-absorption infra-red spectroscopy to study APES adsorbed on aluminium,[14,15] iron,[14,16] copper[17] and titanium[18] surfaces and have backed up their results by X-ray photoelectron spectroscopy (XPS). Sung, Sung and co-workers[19,20,21] have also examined APES by infra-red but this time adsorbed on sapphire (α-Al_2O_3). Apart from these studies the majority of work on adsorbed aminosilanes has been performed by Koenig[22] and his co-workers on glass and silica substrates. Using mainly Fourier transform infra-red (FTIR) they have demonstrated the complex nature of the amine group and identified several different species formed under different conditions of solvent, surface and film thickness. Koenig[23,24,25] has also used carbon-13 nuclear magnetic resonance spectroscopy to study silanes adsorbed on silica and glass.

EXPERIMENTAL

APES and AAPMS were obtained from Union Carbide Ltd., APMS from Lancaster Synthesis and APhMS mixed isomers from Petrarch Systems Inc. The isomers of APhMS were separated by fractional distillation using a Vigreux column. The first fraction distilled over at 88°C and a pressure of 0.1 torr, the second at 105°C and 1.0 torr and the third at 118°C and 1.5 torr. A gas chromatograph fitted with a Tenax column at 240°C was used to check the purity of the isomers. The chromatogram showed that separation of the 2-isomer was almost complete, with less than 1% of the 3- and 4-isomers remaining. Although retention times were different for the latter isomers (66 s for 3- and 72 s for 4-) the assessment of purity was hindered by the overlap of peaks. It is interesting to note that 2-APhMS has the lowest boiling point and this is possibly caused by intramolecular hydrogen bonding. Proton NMR using $CDCl_3$ was used to check the identity and purity of the fractions.

The theory[26] and experimental details[27] of IETS have been described previously. Briefly, junctions were prepared on glass microscope slides, the metal electrodes being deposited by vacuum evaporation with their geometry controlled by masks. After the aluminium electrode was deposited, the oxide layer was formed simply by venting the apparatus to air. Vapour phase doping was performed by exposing the slides, after the deposition of aluminium, face downwards across the edges of a Petri dish containing a silane. A one litre beaker was used as a cover. As each silane has a different vapour pressure doping times varies between 1 and 20 minutes. Atmospheric moisture was not excluded from the vessel. In liquid doping the slide is held in place on a small spinner by a vacuum chuck. A dilute solution of silane is then poured onto the slide to cover the aluminium electrodes, and after a few seconds the slide is spun at 50 rpm to remove the excess solution.

The choice of solvent is usually restricted to linear and cyclic paraffins (hexane, cyclohexane), simple aromatics (benzene, toluene), simple alcohols (methanol, ethanol) and water. All are relatively inert to the oxide and available in spectroscopic grades. Such solvents were used here and the water was put through a millipore filter. Solutions in organic solvents had concentrations of about 0.1% by volume, but in water and D_2O concentrations of about 0.5% were used to compensate for hydrolysis and reaction with the glass containers. Doping solutions of acidic aqueous alcohol were prepared by adding about 0.5% of silane, 0.5% water and a drop of 1 M hydrochloric acid to either ethanol or methanol. The choice of alcohol had no effect on the spectrum. Doping conditions were selected to give suitable junction resistances and good spectra. The junctions were completed by vacuum deposition of the lead electrodes. The completed slides were inserted into a specimen holder which could be lowered into a dewar of liquid helium and connected to the spectrometer. The spectrometer was housed in a room totally screened with aluminium sheets and containing a filtered mains supply. The apparatus was operated in conjunction with a Digital PDP 11 computer which was used to gather the data and fix peak positions.

Infra-red (IR) spectra were obtained on thin liquid films of silanes spread on KBr discs, employing a Perkin–Elmer 683 IR spectrophotometer.

RESULTS AND DISCUSSION

The assignment of IET spectra largely rests on comparisons with IR and, to a lesser extent Raman, spectra. The experimental data on selection rules for IET spectra suggests that there is no evidence for selection on grounds other than orientation of groups relative to the direction of electron tunneling.[26] This is consistent with theory in that a tunneling electron may interact with both permanent and induced dipoles. It is thus expected that the allowed vibrations appropriate to both IR and Raman are observable by IETS.

In IR spectra of aminosilanes the vibrations of the amine groups occur in well-defined areas. According to Bellamy[28] the stretching modes occur between 3300 and 3500 cm^{-1} with the deformation vibrations at 1590–1650 cm^{-1} and an NH wag at 760–840 cm^{-1}. Within these ranges multiple peaks and peak shifts may occur, depending on the type of amine and the extent of inter- and intramolecular hydrogen bonding. For primary aliphatic amines, two peaks occur at 3381–3398 cm^{-1} and at 3324–3344 cm^{-1} corresponding to the asymmetric and symmetric stretching vibrations respectively. Similarly, for primary aromatic amines, two peaks are observed, but here due to electronic effects they are at a higher frequency and are more widely separated. Secondary amines show only one band in this region.

The deformation vibrations show only one band in the 1590–1650 cm^{-1} region for all amines, which is strong in the IR but weak in Raman spectra. However, interference can occur from vinyl and particularly aromatic C═C stretching vibrations.

Hydrogen bonding weakens the NH bond and this causes an upshift in the deformation modes and a downshift in the stretching modes. This has been noted by Thompson, Nicholson and Short[29] who found that the upshifts in the deformation mode are usually not sufficient to take the δNH_2 peak out of the 1590–1650 cm^{-1} range.

The C—N stretching modes are all strong and are found in the following regions. Primary aromatic amines show two bands at 1180–1280 cm^{-1} and 1250–1360 cm^{-1} of medium intensity, primary aliphatic amines show peaks at about 1079 cm^{-1}, 1040 cm^{-1} and 1030 cm^{-1} for primary, secondary and tertiary α-carbons respectively, and secondary amines have a peak at about 1140 cm^{-1} for a primary α-carbon rising to 1180 cm^{-1} for a secondary α-carbon.

Shih and Koenig[30] have obtained Raman spectra of APES and AAPMS in bulk, aqueous solution and adsorbed on glass fibres. They found that the NH stretching and deformation vibrations occurred in similar positions to IR spectra. However, peaks at about 1400 cm^{-1} are assigned to C—N stretching modes; this region is usually associated with CH deformations.

Doping from the vapour or from non-aqueous solvents

APES IET spectra of junctions doped from the vapour or from non-aqueous solvents provide a baseline for other doping methods. This is particularly so for APES doped from benzene (Figure 1) which shows almost no hydrolysis; this can be seen from the intensity of the Si—O—C modes (1070 and 1096 cm^{-1}). This is, therefore, the spectrum of the unreacted APES molecule. Similar spectra have been obtained from tetrachloromethane and cyclohexane. Other assignments are collected in Table I. In IET spectra the νNH modes are broad and weak and this causes difficulties in accurately measuring their positions.

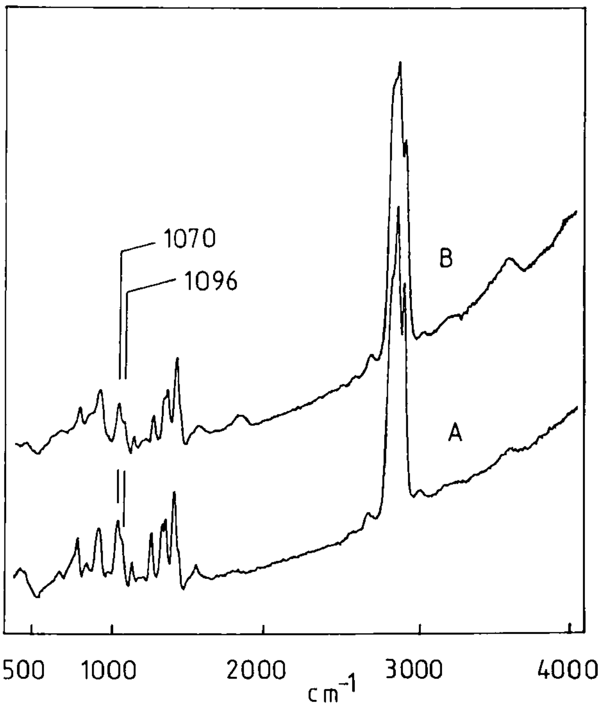

FIGURE 1 IET spectra of APES doped from (A) solution in benzene and (B) vapour. Assignment of spectrum B is in Table II.

APMS The only structural difference between APMS and APES is that the potentially hydrolysable ethoxy groups are replaced by methoxy groups. However, there are some subtle changes in IET spectra. The amine group vibrations in IET and IR spectra are compared in Table II. NH peak shifts do not only occur between APES and APMS but in the case of APMS there are distinct differences in peak positions between vapour and benzene doping (Figure 2). Assignments of the vapour doped spectrum are in Table III. With APMS two νNH peaks are clearly visible in the spectra and they are shifted from their IR positions by about 30 cm^{-1}. The low energy peak is apparently upshifted from its position in the IET spectrum of APES by 20–30 cm^{-1}. The δNH peak has a similar position with both compounds (1590 cm^{-1}) although an extra peak is observed at 1552 cm^{-1} with vapour doping and at 1533 cm^{-1} with benzene doping.

The other interesting feature of APMS spectra is the Si—O—C peak at 1065 cm^{-1}. This is a sharp, intense peak characteristic of methoxy groups and is downshifted from the IR position by about 24 cm^{-1}. The presence of methoxy groups shows a low level of hydrolysis.

APhMS Aminophenyltrimethoxysilane has been previously studied by IETS by Furukawa, Eib, Mittal and Anderson,[4] and it gives different spectra according to

TABLE I
Assignment of peaks in IET spectrum of vapour-doped APES. Spectrum appears in Figure 1

Peak position/cm^{-1}	Intensity	Assignment
421	mw	$RSiO_3$
445	w	
684	w	SiC
785	m sh	ν_{as} SiO_3
807	m	ρ CH_3
868	w	δ NH
946	ms	ν_s Si—O—C
1003	w	CN
1070	s	ν_{as} Si—O—C
1096	ms	
1167	s	$SiOCH_2$
1205	w	δ_s $SiCH_2$ and C—C
1240	w	
1295	m	δ CH_2
1367	ms	δ_s OCH_2
1390	ms	δ_s CH_3
1448	s	δ_{as} OCH_2
1475	m sh	δ_{as} CH_3
1593	w	δ NH
2728	w	combinations
2755	w	combinations
2886	s sh	ν_s CH_3/OCH_2
2918	vs	ν_{as} OCH_2
2962	s	ν_{as} CH_3
3065	w	
3253	vw	ν_{as} NH

In this and other tables the following abbreviations are used; s—strong; m—medium and w—weak; br—broad, sh—shoulder. ν—stretching, δ—deformation, ρ—rocking, ω—wagging. Subscripts s—symmetric, as—asymmetric.

TABLE II
Amine group peak positions (cm^{-1}) for IET and IR spectra of APES and APMS

	APMS			APES		
Mode	IR	IET		IR	IET	
		vapour	benzene		vapour	benzene
ωNH	864	865	862	858	868	
δNH		1552	1553			
	1601	1591	1583	1603	1593	1591
νNH	3210					
		3276	3282	3291	3253	3253
	3310					
	3395			3370		
		3429	3462			

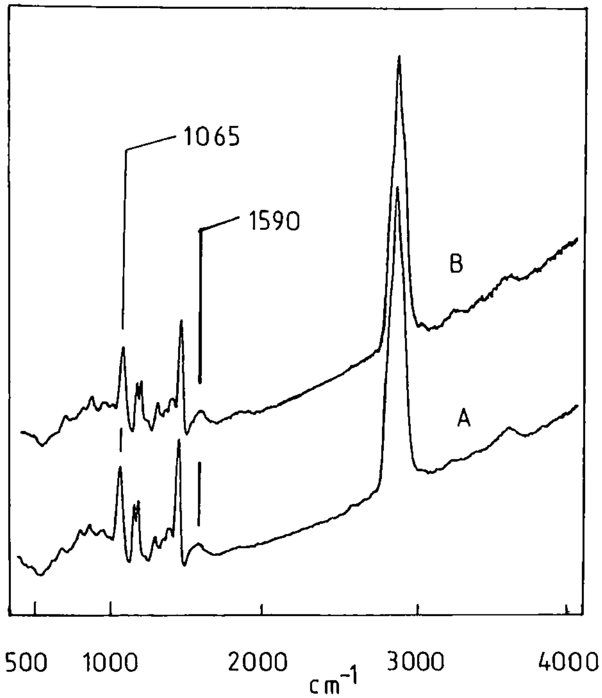

FIGURE 2 IET spectra of APMS doped from (A) solution in benzene and (B) vapour. Assignment of spectrum B is in Table III.

the doping conditions (Figure 3). This is not surprising since all three isomers (2-, 3- and 4-) are present and adsorption could be selective.

The NH stretching mode is found in a similar position (3324 cm^{-1}) in vapour and benzene doped spectra (Figure 3), but this differs from the IR spectrum where three vibrations are observed at 3235, 3367 and 3460 cm^{-1}. Table IV shows assignments of the IET spectrum of the mixed isomers doped from the vapour. The NH deformation mode is obscured by the aromatic C=C stretching vibrations at 1577 cm^{-1}. The major differences in these spectra are attributable to the methoxy groups and they provide evidence for the manner in which molecules of APhMS interact with the surface.

Within the APhMS molecule the methoxy groups are all equivalent and thus it follows that only two methyl stretching vibrations should arise in the IR spectrum. Two peaks occur in the benzene-doped spectrum although there is a small shoulder on the low energy side, but for the vapour doped spectrum there are three peaks. Since the silane contains all three isomers it is possible that preferential adsoption is taking place. To investigate this the IET spectra of the separated isomers were obtained (Figure 4).

They show that in the region below about 1600 cm^{-1} there are a large number of peaks which change in intensity with the isomer. Examples are the peaks at 537

TABLE III
Assignment of peaks in IET spectrum of vapour-doped APMS. Spectrum appears in Figure 2

Peak position/cm^{-1}	Intensity	Assignment
388	w	
472	w	ν RSiO$_3$
572	w	
617	w	
679	w	SiC
700	w	
736	w	
804	w	ρ CH$_3$
865	w	NH
898	w	
954	w	
1003	w	CN
1065	ms	ν Si—O—C
1164	m	
1190	m	ρ CH$_3$
1246	w	δ SiCH$_2$R
1303	mw	
1358	w	δ CH$_2$/CH$_3$
1395	w	
1410	w	CH$_2$N
1454	ms	δ CH$_2$/CH$_3$
1552	w	δ NH
1591	w	
2844	m	ν_s OCH$_3$
2865	ms	ν CH
2901	s	
2936	ms	ν_{as} OCH$_3$
3276	w	ν NH
3429	w br	
3655	w br	νOH (adsorbed water)
3800	w	

and 560 cm^{-1} which appear as strong and weak peaks, respectively, in the 2-isomer but as doublets of similar intensity with 3- and 4-APhMS. This changing pattern is repeated for other peaks and is due to the different substitutions on the aromatic ring. However, there are two significant changes which fall outside this range and affect the CH stretching and the NH deformation modes.

The NH deformation band does not appear in the spectra for the mixed isomers as it is obscured by the aromatic C═C modes. This is also true for 3- and 4-APhMS but in the 2-isomer it is clearly visible as a peak at 1652 cm^{-1}. This is just on the upper limit set by Thompson, Nicholson and Short[29] for the deformation band and it appears here due to intramolecular hydrogen bonding with a methoxy oxygen as is shown in Figure 5.

Other differences occur for the CH stretching modes, centred at about 2900 cm^{-1}, but the additional complication of hydrolysis may play some part in the intensities of these peaks. 2-APhMS shows two aliphatic CH stretching peaks at 2892 and 2948 cm^{-1} plus a small shoulder on the low energy side at 2853 cm^{-1}

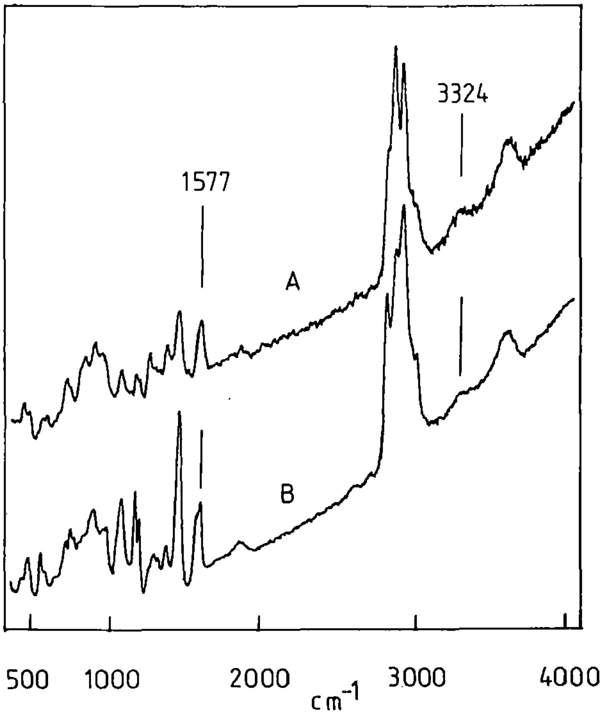

FIGURE 3 IET spectra of APhMS mixed isomers doped from (A) solution in benzene and (B) vapour. Assignment of spectrum B in in Table IV.

similar to the benzene-doped mixed isomers. The intensity of these peaks compared with those of the aromatic CH group is such as to suggest little or no hydrolysis has occurred, which is probably due to a stabilising effect caused by intramolecular hydrogen bonding. In the spectra of both 3- and 4-APhMS three distinct aliphatic CH modes can be seen at 2845, 2893 and 2944 cm^{-1} and here the aromatic peaks are much stronger, suggesting more hydrolysis, particularly for 4-APhMS.

These results support the view that preferential adsorption of one isomer occurs when doping from benzene solution, and further that the surface interactions of the different isomers are as follows. 2-APhMS is attached to the surface, tripod-like, by the three methoxy groups but the amine group is internally hydrogen bonded to a methoxy group. The hydrogen bonded NH group now lies nearly perpendicular to the surface, giving optimum conditions for selection. With the 3- and 4-isomers the amine group and two methoxy groups are attached to the surface. These are illustrated in Figure 5.

AAPMS This compound differs from the previous aminosilanes in that it has both primary and secondary amine groups. The extra NH stretching and deformation modes appear in the spectrum. In fact, with AAPMS the NH peaks

TABLE IV
Assignment of peaks in IET spectrum of vapour-doped APhMS mixed isomers. Spectrum appears in Figure 3

Peak position/cm^{-1}	Intensity	Assignment
402	w	
449	mw	RSiO$_3$
537	mw	
560	w	
626	w	ν_s SiO$_3$
704	mw	CH out of plane
735	mw	CH out of plane
759	mw	
791	mw	
837	mw	
884	m	
919	mw	
949	mw	CH out of plane
971	mw	
1045	w sh	
1070	m	ν Si—O—C
1165	m	
1193	m	ρ CH$_3$
1258	w	NC aromatic
1290	w	
1317	w	
1374	mw	δ_s CH$_3$
1455	s	δ_{as} CH$_3$
1577	m	ν C═C aromatic
1596	m	
1700	w	
2840	s	ν_s CH$_3$
2903	s	CH aliphatic
2949	s	ν_{as} CH$_3$
3006	m	ν CH aromatic
3041	m	
3324	w br	ν NH
3648	m br	ν OH (adsorbed water)

are particularly strong as can be seen in Figure 6 for doping from benzene; assignments are given in Table V. No vapour-doped spectrum is shown since it was identical with the water-doped spectrum (see below).

There are three NH stretching modes appearing at 3296, 3346 and 3416 cm^{-1}, this agrees with the IR spectrum in number but not in position since all three are downshifted. The two vibrations of highest energy are probably due to the primary amine group and the low energy νNH peak to the secondary amine. The two δNH modes can also be treated in the same way; their higher and lower energy modes (1580 and 1539 cm^{-1}) being assigned to the primary and secondary amines, respectively. These are also both downshifted from their IR positions (1593 and 1556 cm^{-1}) which is in the opposite sense to that expected for hydrogen bonding.

The rest of the spectrum, with the exception of the region below 1000 cm^{-1}, is similar to that of APMS as would be expected for a trimethoxysilane.

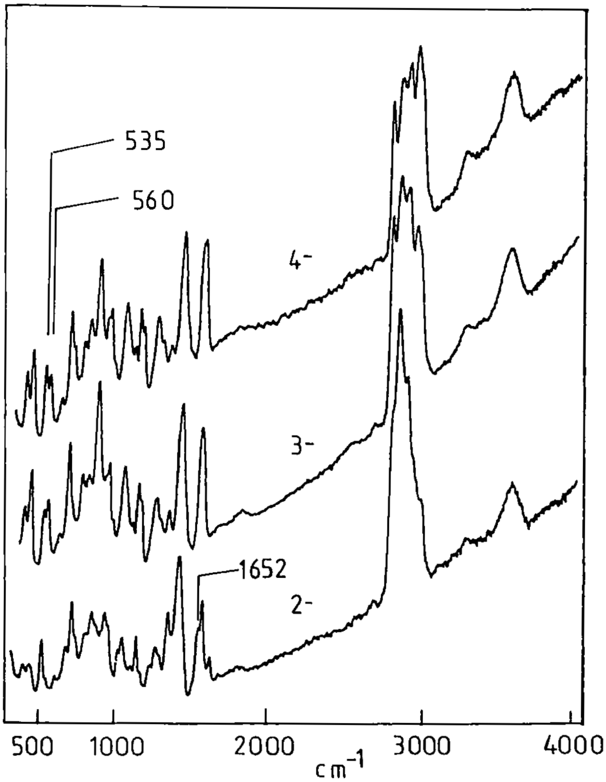

FIGURE 4 IET spectra of the separate isomers of APhMS doped from solution in benzene.

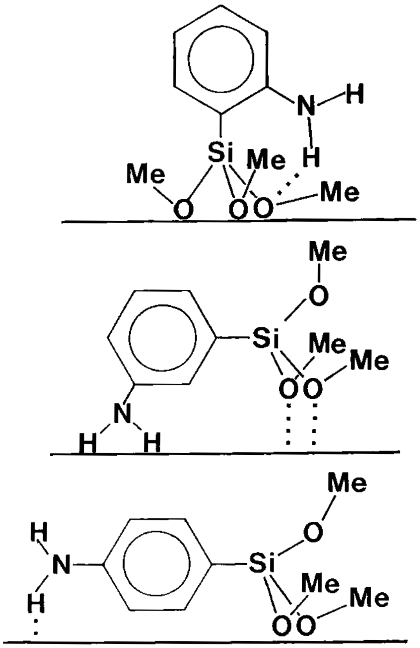

FIGURE 5 Modes of adsorption of the isomers of APhMS.

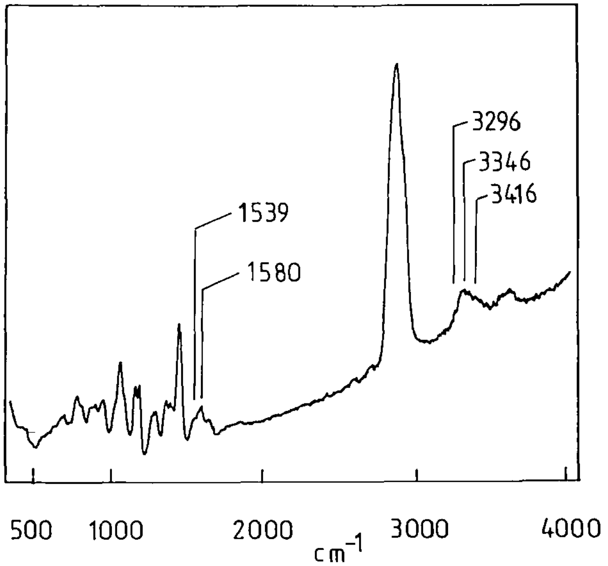

FIGURE 6 IET spectrum of AAPMS doped from solution in benzene. Assignments are in Table V.

TABLE V
Assignment of peaks in IET spectrum of benzene-doped AAPMS. Spectrum appears in Figure 6.

Peak position/cm^{-1}	Intensity	Assignment	
494	w br		skeletal
728	w		secondary NH
815	w	ν_{as}	SiO_3/SiC
880	m		
943	m		
982	mw	ν_s	Si—O—C
1029	mw br		CN
1062	m	ν_{as}	Si—O—C
1164	mw		
1188	mw	ρ	CH_3
1291	mw	ω	CH_2
1374	mw	δ_s	$CH_2/CH_3/CH_2N$
1391	m		
1457	ms	δ_{as}	CH_2/CH_3
1539	mw	δ	secondary NH
1580	mw	δ	primary NH
2860	ms	ν	CH
2873	s		
2910	ms		
3296	m	ν	primary and secondary NH
3346	m		
3416	m sh		
3649	mw br	ν	OH (adsorbed water)

Doping from acidic aqueous alcohol

APES and APMS Doping from acidic aqueous alcohol is a useful method of preparing IET junctions since it gives a completely hydrolysed product and so allows spectra to be studied without interference from the alkoxy groups. Unfortunately, this technique is not so effective for the aminosilanes; this is particularly so for APES and APMS, where the spectra are not unambiguously hydrolysed or reproducible (Figure 7). However, it is possible to discern new peaks one of which is of particular importance. This occurs at 1121 and 1114 cm^{-1} in the spectra of APES and APMS, respectively, and is due to an Si—O—Si stretching vibration. Allied to this are peaks at 926 and 932 cm^{-1} which are possibly due to an SiOH mode. These modes also occur in the spectra doped from water and D_2O (see below). It appears that both APES and APMS hydrolyse and condense to form siloxanes, possibly due to autocatalysis by the amine group.[31]

APhMS Mixed isomers of APhMS give a spectrum (Figure 8) similar to that obtained by Furukawa, Eib, Mittal and Anderson[4] after they infusion-doped water into a vapour-doped junction. The spectrum shows good resolution especially in the CH stretching and deformation regions. The peak at 2894 cm^{-1}

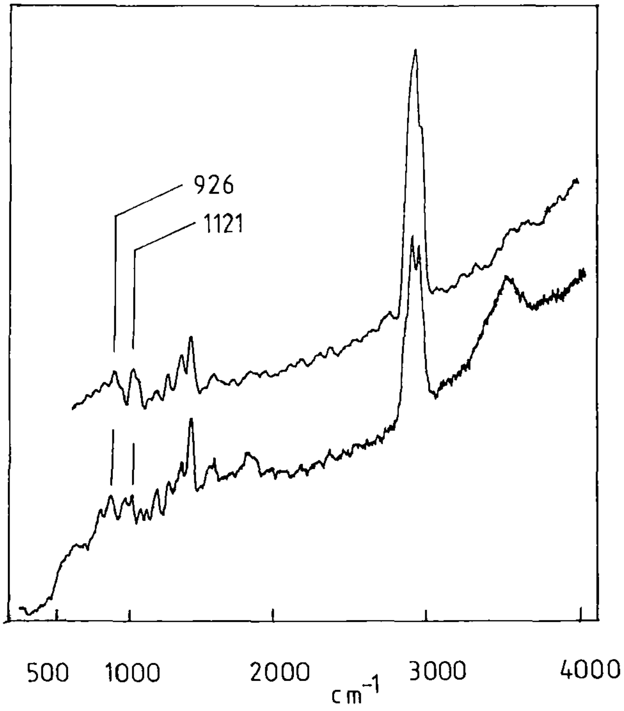

FIGURE 7 IET spectra of APES showing variations obtained by doping from acidic aqueous alcohol.

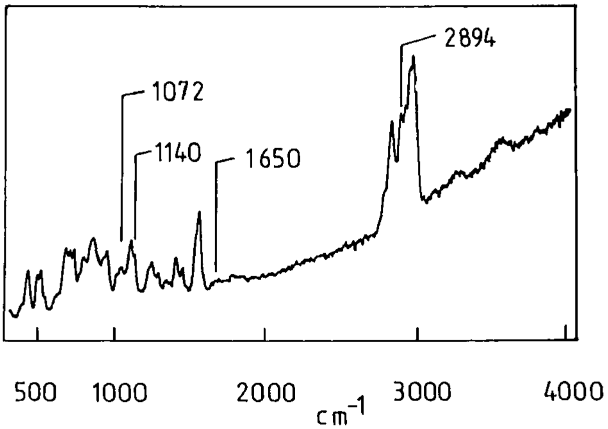

FIGURE 8 IET spectrum of APhMS mixed isomers doped from acidic aqueous alcohol.

may be attributed to 2-APhMS where intramolecular hydrogen bonding could stabilise the methoxy groups against hydrolysis. This will not apply to the other isomers. Further for the presence of this isomer is the small shoulder at about 1650 cm^{-1} due to δNH on the high-energy side of the aromatic C=C peak. This implies that 2-APhMS is preferentially adsorbed, and this may be due to its ability to sit tripod-like by the three oxygen atoms on the surface (Figure 5).

It is presumed that the other isomers contribute to the spectrum and that these are more or less completely hydrolysed. This being the case, bands due to Si—O—Si and SiOH could be expected in the spectrum. Vibrations of the former moiety are assigned to peaks at 1072 and 1140 cm^{-1}. No bands are assigned to the weak SiOH vibrations. Unfortunately, it was not possible in the time available to obtain IET spectra of the separate isomers doped from acidic aqueous alcohol.

AAPMS The diamine AAPMS gives a spectrum (Figure 9) with many interesting features. Perhaps the most interesting are the two νOH vibrations at 3487 and 3665 cm^{-1}. The latter is common to most IET spectra but the former has only been seen by the authors in spectra of silanes doped from water. The conclusion to be drawn is that it is due to the SiOH stretching vibration and this is confirmed by the strong broad feature at 872 cm^{-1}. This latter vibration is the SiOH bending mode which is usually found between 900 and 950 cm^{-1}; thus, it has been downshifted. The other shifted peaks in the spectrum are the amine peaks which have also altered in intensity. The NH stretching mode has become a broad, weak peak downshifted by about 20 cm^{-1} to 3329 cm^{-1} whilst both NH deformation vibrations have been upshifted by approximately the same amount. This is the expected behaviour for hydrogen bonding[29] and an interaction between the amine and surface hydroxyl groups is indicated. One other peak also worth mentioning occurs at 1073 cm^{-1} and may be due to the Si—O—Si stretching vibration.

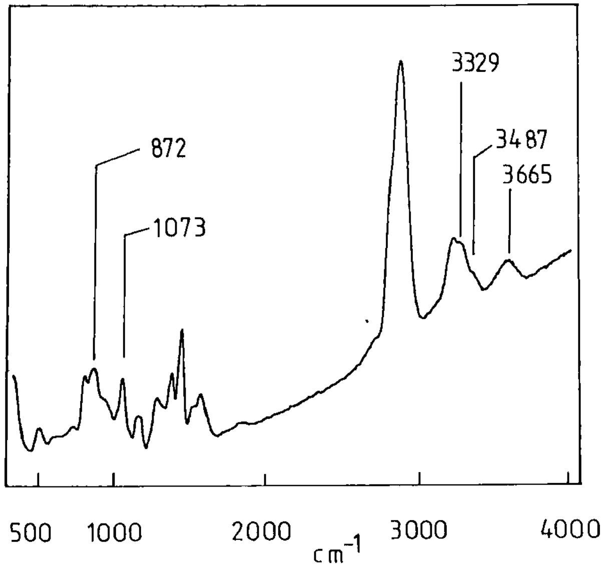

FIGURE 9 IET spectrum of AAPMS doped from acidic aqueous alcohol.

Doping from water and D_2O

This last group of spectra for the aminosilanes is perhaps the most relevant since in industry most silanes are applied from aqueous solutions.

APES and APMS The spectrum of APES doped from water (Figure 10) is much different from the vapour-doped spectrum and the differences can be attributed to hydrolysis and subsequent condensation. It is, however, very similar to that of APMS doped from water (Figure 10).

The NH stretching peaks in both spectra are very weak features centred about 3260 cm^{-1}. Similarly, the NH deformation bands are also weak and appear at about 1600 cm^{-1}. Whilst the stretching modes occur in the same position as in the vapour- and benzene-doped spectra, the deformation vibrations are upshifted by about 10 cm^{-1}. This is consistent with hydrogen bonding but due to the lack of supportive evidence it cannot be confirmed. However, good evidence does exist for the presence of Si—O—Si and SiOH groups.

Peaks due to Si—O—Si vibrations can be seen at about 1060 and 1107 cm^{-1} in both spectra. Modes at similar positions can also be observed in the vapour- and benzene-doped spectra but here their intensities and shapes are quite different. Also, there is a notable absence of CH stretching and deformation vibrations in ethoxy groups. Thus, hydrolysis and condensation has occurred giving rise to Si—O—Si linkages.

Vibrations of SiOH groups occur in two regions of the spectrum, between 3300 and 3600 cm^{-1} and between 900 and 1000 cm^{-1}. In the latter region moderately

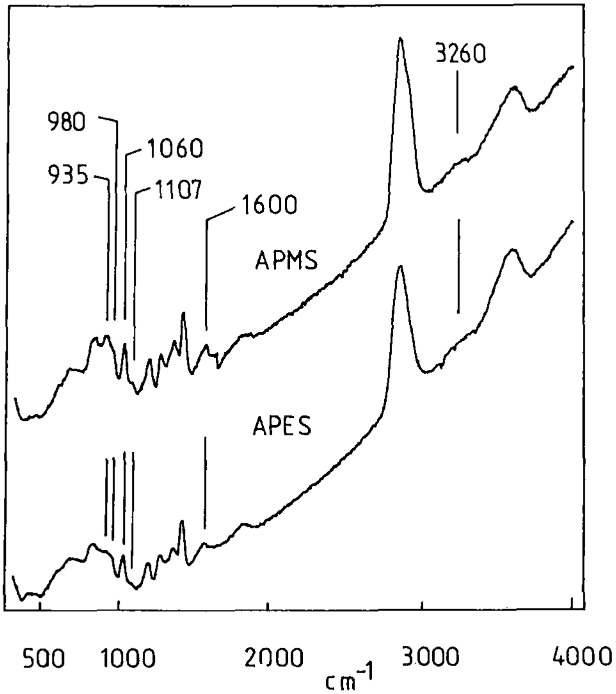

FIGURE 10 IET spectra of APES and APMS doped from water.

intense peaks at 935 and 980 cm^{-1} can be assigned to the deformation of SiOH. Peaks due to the SiOH stretching mode are not clearly observed due to a large background OH band which arises from the water used in doping. Even so, the presence of SiOH modes can be deduced from the angular shape of the OH peak which is normally broad, weak and featureless.

Spectra of APES and APMS doped from D_2O appear in Figure 11. In general, peak positions are very similar but there are some differences in intensity and also some extraneous vibrations which can only be assumed to arise from incomplete hydrolysis. More importantly, however, is the lack of evidence for isotopic exchange between the NH_2 and D_2O to give ND_2 vibrations and also the absence of SiOD modes. Spectra of APES and APMS doped from H_2O and D_2O have, within experimental error, identical peak positions. Differences in peak intensities are probably due to variations in sample preparation.

This lack of deuterium exchange has also been noted by Allen, Hansrani and Wake.[32] They polymerized 3-glycidoxypropyltrimethoxysilane in dilute acid, ground the product to a fine powder and shook it overnight with 99.9% D_2O. No changes were seen in IR transmission spectra. However, the use of multiple internal reflectance IR on a sample which had been exposed for 12 hours indicated the growth of a broad OD peak but without the commensurate reduction in the OH peak. It appears that exchange is restricted to the surface of the sample.

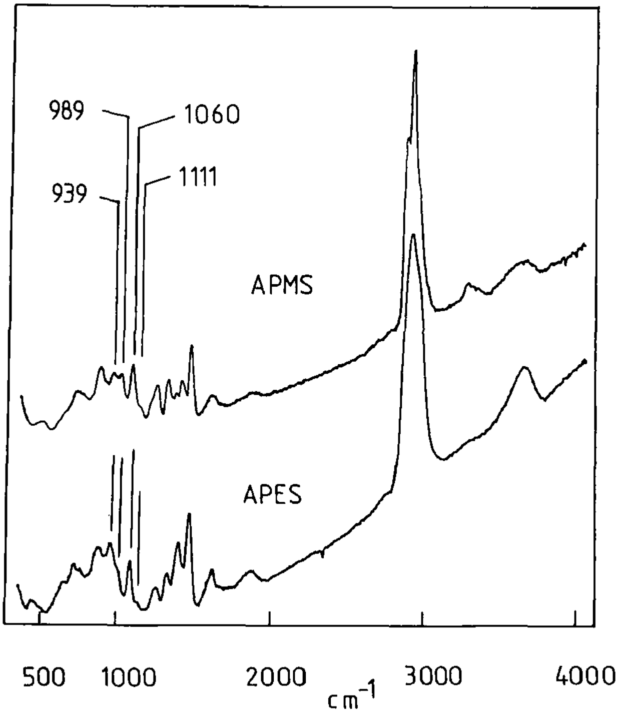

FIGURE 11 IET spectra of APES and APMS doped from D_2O.

The modes that can be positively identified in the spectra are those due to SiOH and Si—O—Si groups. Two vibrations due to SiOH can be seen in both spectra at 935 and 973 cm^{-1} for APES and at 939 and 989 cm^{-1} for APMS. Evidence for Si—O—Si bonds are the peaks at 1061 and 1111 cm^{-1} for APES and 1064 and 1111 cm^{-1}.

The bond angles in Si—O—Si chains are important factors in controlling the orientation of Si—O bonds in IET junctions. From X-ray and electron diffraction data the Si—O—Si angle varies between 130 and 150° [33,34] which would mean that for a siloxane chain lying parallel to the oxide layer, the Si—O bonds make an angle of 15–20° with the surface. From the point of view of the orientational selection rule in IETS the low angle will lead to weak Si—O peaks, even though they may be present in large numbers.

APhMS The spectra of aminophenyltrimethoxysilane doped from water and D_2O (Figure 12) are similar to that of the compound doped from acidic aqueous alcohol. They show that almost total hydrolysis occurs from water but, although the spectrum from D_2O shows a high degree of hydrolysis, there are some extra peaks and some differences in peak intensities. The reasons for this may be preferential adsorption of one isomer combined with a reduced level of hydrolysis.

As with APES and APMS no deuterium exchange was observed.

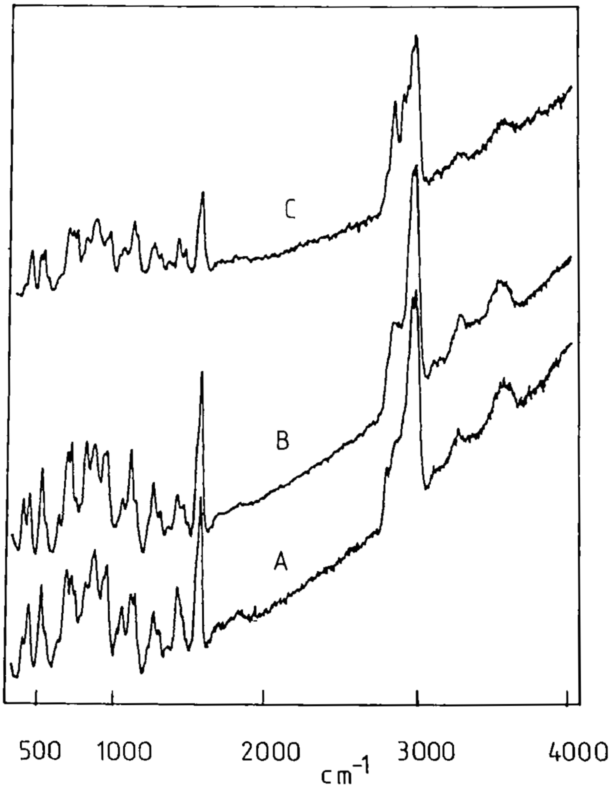

FIGURE 12 IET spectra of APhMS mixed isomers doped from (A) waters (B) D_2O and (C) acidic aqueous alcohol.

AAPMS For the diamine AAPMS the spectra (Figure 13) of the water and D_2O doped spectra are similar. The strongest modes are the CH_2 stretching and deformation peaks at 2937, 2903 and about 1450 cm^{-1}, respectively. However, apart from the mode at 1061 cm^{-1} these are the only similarities. The major difference in the spectra is the almost total absence of any OH modes in the water-doped spectrum. An explanation for this may be a condensation of silanols to a polysiloxane with few silanol groups remaining. The spectrum from D_2O does have large SiOH modes at 3648 and 844 cm^{-1} but these are too high to be due to SiOD. The NH modes at 3287 and 1601 cm^{-1} likewise do not indicate the formation of ND. However, they are shifted, the stretching mode downwards and the deformation mode upwards. This is the correct pattern for hydrogen bonding as described by Thompson, Nicholson and Short,[26] and, in conjunction with the shape of the OH stretching mode, this suggests hydrogen bonding to the surface.

The position of the primary amine modes implies that it does not form ND bonds. If the secondary amine were deuterated the resulting peaks would be masked by other vibrations.

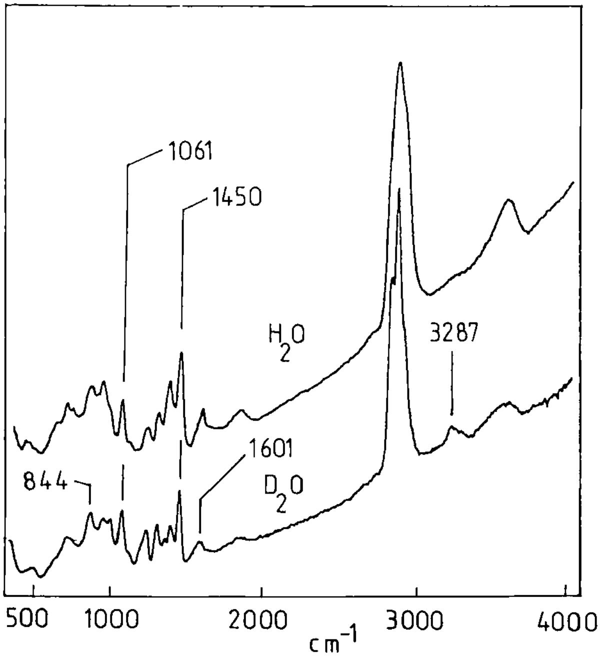

FIGURE 13 IET spectra of AAPMS doped from water and D_2O.

CONCLUSIONS

1) When doped from the vapour or from solution in benzene, the IET spectrum of APES shows no hydrolysis, whilst APMS shows a low level of hydrolysis. In contrast, AAPMS is almost totally hydrolysed in doping from the vapour.

2) In doping the separate isomers of APhMS from benzene, the NH deformation modes of the 3- and 4-isomers are obscured by the aromatic C=C peak at 1577 cm^{-1}. With the 2-isomer, however, intramolecular hydrogen bonding shifts the peak to 1652 cm^{-1} where it can be detected. IET spectra indicate that the three isomers are differently attached to the oxide surface.

3) When adsorbed from water or acidic aqueous alcohol on to IET junctions with aluminium oxide as the substrate, APES and APMS undergo hydrolysis and condensation to form siloxanes.

4) When aminosilanes are doped from D_2O on to IET junctions with aluminium oxide as the substrate, isotopic exchange of the amine hydrogens does not occur.

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