Surface Science 155 (1985) 31–45
North-Holland, Amsterdam

CHARACTERIZATION OF A NEW SUBSTRATE FOR TUNNELING SPECTROSCOPY

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Received 31 October 1984; accepted for publication 28 January 1985

An insulating layer is produced on aluminum by glow discharge in CF_4. This substrate, used as the insulator of metal–insulator–metal diodes is characterized by Inelastic Electron Tunneling Spectroscopy as an aluminum trifluoride AlF_3. The adsorption of ammonia, benzylamine, formic and propiolic acid on this substrate is investigated. A comparison between spectra of samples obtained on this insulator and on alumina for the same dopant molecules shows significant differences which are interpreted as revealing an enhanced Lewis acidity of AlF_3 relative to Al_2O_3, determined – at least in part – by an enhanced electronegativity of surface Al^+ cations of AlF_3.

1. Introduction

Inelastic Electron Tunneling Spectroscopy (IETS) has proven to be a valuable technique for investigating the vibrational properties of adsorbates on insulators and on metals supported on insulators [1]. Although this spectroscopy exhibits unique performance in combined sensitivity, spectral range and resolution, its application remains very limited due to the difficulty in obtaining very thin (~ 15 Å) insulating layers of sufficient electrical quality. Most of the tunneling studies of adsorbates to this day have been carried out on alumina and magnesia. Other good barriers have been obtained but they are generally of little interest for adsorption studies.

The aim of this paper is to report a study of a new barrier – obtained on aluminum by a glow discharge in CF_4 – which presents interesting chemical properties. The nature of this substrate is inferred from the analysis of spectra of undoped samples in section 3. Its chemical properties are investigated in section 4. A comparison between spectra of samples obtained on this insulator and on alumina for the same dopant molecules is made to complete this investigation.

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2. Experimental

Our usual sample preparation procedure was followed in this study: an aluminum film is deposited on a clean microscope slide; this film is then oxidized in a plasma of H_2O, CF_4 or O_2 at a pressure of 0.1 Torr, the sample holder being polarized positively relative to an electrode located at about one centimeter below the sample. The resulting oxide is then exposed to the vapor of the chosen dopant. Finally, after reevacuation of the evaporator (10^{-6} Torr), the junction is completed by deposition of a counter-electrode – in the present study Al or Pb. All the dopants used were pure liquids or gases except for ammonia on alumina where the ammonia was dissolved in water.

The spectra are displayed as $\sigma^{-1}d\sigma/dV$ against V (1 meV = 8.065 cm^{-1}), σ being the conductance dI/dV of the junction. They were obtained at 4.2 K with an 8 mV peak-to-peak modulation tension, unless specified; these factors limit the spectral resolution to about 40 cm^{-1}. For the junctions with a lead counter-electrode 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 4.2 K. These energy positions are reported with an estimated error of about ±10 cm^{-1}.

The absolute intensities of the bands are measured in tunneling spectroscopy by the dimensionless quantity $\delta\sigma/\sigma$, where $\delta\sigma$ is the increase of the conductance due to the opening of the inelastic channel responsible for the measured band. Relative intensities can be roughly evaluated by comparing the areas of the bands above the background of the spectrum since the variation of the total conductance of the samples is usually small in the vibrational range (0–4000 cm^{-1}).

3. Nature of the substrate

Figs. 1a and 1b show the spectra for a junction whose insulator has been made by a glow discharge in CF_4. The corresponding peak positions are reported in table 1. Spectra for a junction obtained by a discharge in H_2O (figs. 1c and 1d) are displayed in the same figure for comparison. The complete identification of the structures which appear on these latter spectra has been established in ref. [2] and is also reported in table 1.

Two prominent features are present on both types of spectra (a–b and c–d), near 3600 and 1870 cm^{-1}. Moreover, these peaks exhibit the same behavior for all the spectra when the polarity of the bias applied to the junctions is reversed: the intensities of the bands near 3600 and 1860 cm^{-1} are respectively reduced and enhanced when the aluminum electrode is biased positively instead of negatively.

The peak at 3605 cm^{-1} corresponds, on alumina, to the stretching mode of the hydroxyl groups which are known to be always present at the alumina–lead

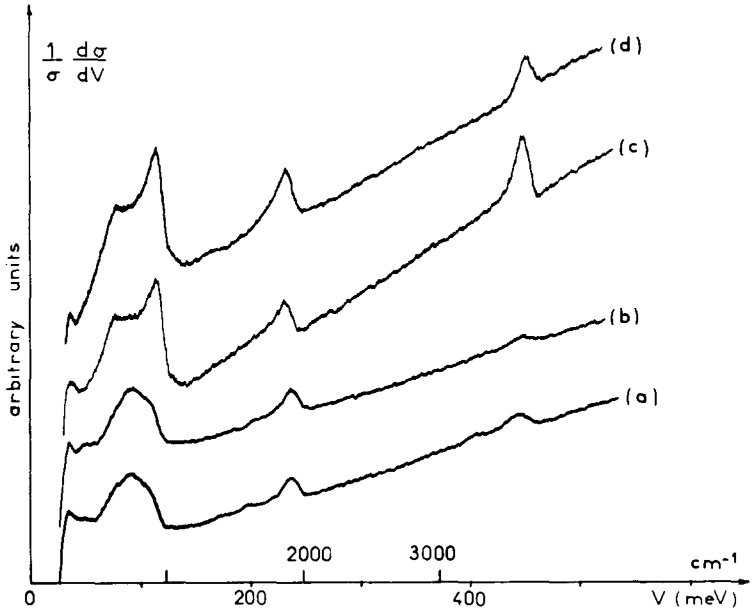

Fig. 1. Spectra for aluminum-insulator-*lead* junctions made in CF_4 (a and b) and H_2O (c and d); a and c (b and d) were traced with the aluminum electrode held negatively (positively).

interface of the tunneling junctions; a detailed analysis of the spectra c and d [2] has led us to attribute the band at 1855 cm^{-1} on alumina to the stretching mode of an Al–H bond belonging to an AlH_x species. This assignment has

Table 1

This table summarizes the attributions for the spectra of figs. 1 and 2; * means that the band mentioned by the line appears on the spectra designated by the column (w, weak; m, medium; s, strong; sh, shoulder)

Energy positions		Figs. 1a, 1b CF_4/Pb	Figs. 1c, 1d H_2O/Pb	Figs. 2a, 2b CF_4/Al	Figs. 2c, 2d H_2O/Al	Assignments
(meV)	(cm^{-1})					
49 w	395	*		*		Phonon AlF_3?
80 sh	645	*		*		δ(Al–H)
75–90 sh	605–726		*		*	
91 s	734	*		*		Phonon AlF_3
110 sh	887	*				δ(O–H)
115 sh	928		*			
117 s	944		*		*	Phonon Al_2O_3
230 ms	1855		*		*	ν(Al–H)
235 ms	1895	*		*		
444 ms	3581	*				ν(O–H)
447 ms	3605		*			

been confirmed independently by Igalson and Adler [3]. Moreover, Al–H bonds have recently been detected during early oxidation of Al(110) surface by HREELS by Thiry et al. [4]. The behavior of the intensity of this peak with the polarity of the applied bias showed that this species should be located at the aluminum–alumina interface [2].

The similarities in both the energy position and the behavior with polarity of these structures on a–b and c–d lead us to make the same assignments for the bands at 3581 cm^{-1} and at 1895 cm^{-1} on spectra a and b. The bending modes are located for OH at about 928 cm^{-1} and for AlH_x in the region of 605–726 cm^{-1} on alumina. The shoulders which appear near 887 and 645 cm^{-1} on the spectra of the junction elaborated in CF_4 are therefore assigned to the same modes.

The intense band at 944 cm^{-1} on spectra c and d characterizes the alumina substrate: it corresponds to a longitudinal optical phonon of bulk alumina. A measurement of the absolute intensities of this peak on c and d and of the broad band centered at 734 cm^{-1} on a and b gives respectively $\delta\sigma/\sigma = 7\ 10^{-3}$ and 10^{-2}. Since these bands have nearly equal areas on both spectra, the intensities can be roughly compared in fig. 1 even between two different spectra simply using the area of the bands. It is then possible to ensure that no peak appears nears 944 cm^{-1} on spectra a and b, and consequently that the substrate grown in CF_4 is not alumina.

The most intense feature appearing on a and b is the broad band near 734 cm^{-1}. The intensity and energy position of this structure suggest its attribution to a phonon of the insulating layer constituting the junction.

In fig. 2, the counter-electrode of the junctions is no longer lead, but aluminum. Aluminum when used as a counter-electrode has been shown [2] to extinguish the tunneling intensities of the modes of species adsorbed at the substrate–counter-electrode interface. A comparison between analogous spectra of figs. 1 and 2 thus permits us to distinguish between species located at this interface and species contributing from the bulk of the insulating layer.

As expected, the features at 3581 and 887 cm^{-1} do not appear on spectra 2a and 2b: they reveal species located at the substrate–counter-electrode interface (hydroxyl groups). The observation of the bands at 1895 and 645 cm^{-1} is coherent with our attribution of these structure to a species located at the electrode–substrate interface. Moreover, the band at 734 cm^{-1} on spectra 2a and 2b remains unaffected as expected of a phonon of the insulating substrate. Finally, one can note that the structure at 395 cm^{-1} is not affected either by the aluminum counter-electrode.

All these observations lead us to attribute the peak(s) at 734 cm^{-1} (and possibly 395 cm^{-1}) to phonon(s) of aluminum fluoride.

The variety of aluminum fluoride which is stable at room temperature is the trifluoride AlF_3. It forms a very stable, essentially ionic lattice containing 6-coordinated δ aluminum [5]. It finds its major use in the industrial produc-

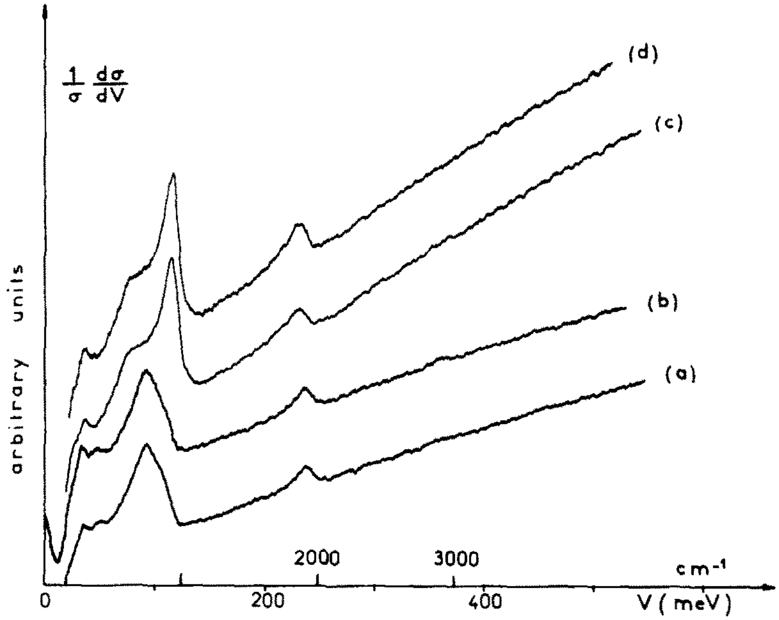

Fig. 2. Spectra for aluminum–insulator–*aluminum* junctions made under the same conditions as for fig. 1.

tion of aluminum but also enters, pure or mixed with alumina into the composition of some catalysts [6]. The chemical property which is primarily involved in these utilizations is its strong Lewis acidity, as for the other aluminum trihalides (the best known of them is $AlCl_3$, the catalyst of the Friedel and Crafts reaction).

As far as we know, no vibrational data are available for this solid. Characteristic frequencies for the stretching of the Al–F bonds in various related molecules in the gas phase are reported in table 2 as an indication. These compare reasonably well with our value of 734 cm^{-1}.

Snelson [9] reported the observation of bands in the region of 400–455

Table 2
Characteristic frequencies for stretching of Al–F bonds

	ν(Al–F) (cm^{-1})
AlF gas [7]	802
AlF_3 gas [8]	945
Al_2F_6 gas [9]	995, 600
$LiAlF_4$ gas [8]	775–783
$NaAlF_4$ gas [8]	853–880

cm^{-1} on the spectrum of Al–F trapped in rare gas matrices. These features were attributed to the formation of polymeric or agglomerate material due to poor conditions of matrix isolation. This could explain our observation of a band at 395 cm^{-1}.

In conclusion:

- The insulator grown on aluminum by glow discharge in CF_4 is mainly an aluminum fluoride, probably AlF_3. It is responsible for bands at 734 cm^{-1} and possibly 395 cm^{-1} on the spectra a and b of figs. 1 and 2. The displayed spectra cannot be interpreted in terms of a mixed oxide AlF_3–Al_2O_3 or of a fluorided alumina (so the system studied here is very different from the fluorided alumina studied by IETS by Hansma et al. [10]). No band appears which could be assigned to alumina. In particular, the shoulder at 887 cm^{-1} does not result from a contribution of an alumina phonon since it disappears when Al is substituted for Pb as the counter-electrode of the junction – confirming our attribution of this band to the bending mode of surfacic hydroxyl groups. However, one cannot exclude the presence of *traces* of alumina in bulk AlF_3.
- This substrate is covered by a layer of hydroxyl groups as attested by the appearance of the 887 and 3581 cm^{-1} features on spectra a and b of fig. 1.

In the following, the adsorption properties of this substrate for some amines and carboxylic acids are investigated.

4. Investigation of the adsorption properties of AlF_3

4.1. Amines

The molecules most widely used to test the Lewis activity of a compound are amines, whose Lewis base character is due to the lone pair electrons of their nitrogen atom. We analyze here the spectra of ammonia NH_3 and benzylamine $C_6H_5CH_2NH_2$ adsorbed on AlF_3.

4.1.1. Ammonia NH_3

Spectra of (a) AlF_3 and (b) Al_2O_3 junctions doped with NH_3 are shown in fig. 3. Bands characteristic of the adsorbate appear at nearly the same positions, namely, 1620 and 3300 cm^{-1} on both of them. Despite the fact that the Al_2O_3 sample was held at 77 K during the doping process (NH_3 did not fix otherwise), these peaks are much stronger on the AlF_3 sample. In particular, the band near 3300 cm^{-1} which is characteristic of the stretching modes of N–H bonds is unusually intense. This enhanced adsorption is first evidence of a stronger acidity of this substrate. The observed peak positions are reported in table 3. Infrared data for coordinately held NH_3, NH_3^+, $-NH_2$ and NH_4^+ adsorbed on alumina are displayed for comparison. An examination of these

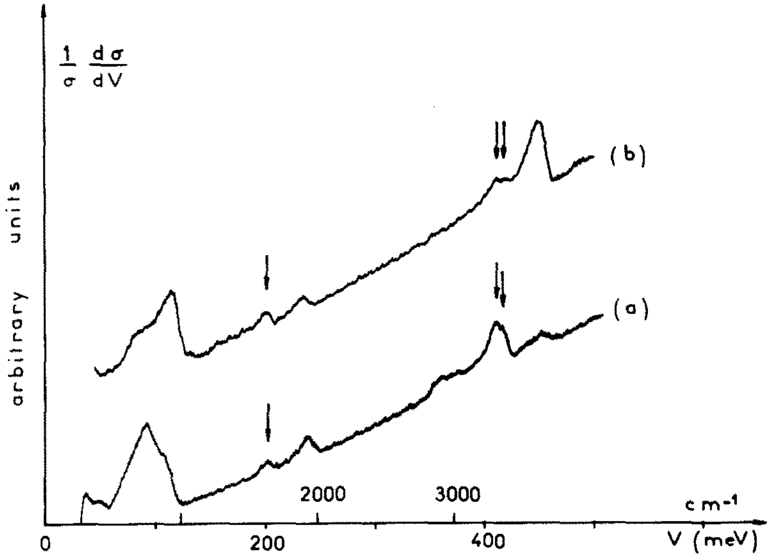

Fig. 3. Spectra of NH_3 adsorbed on (a) AlF_3 and (b) Al_2O_3. The arrows designate the bands assigned to adsorbed NH_3.

results suggests that NH_3 observed in Al_2O_3 junctions is coordinately bound to a Lewis acid site of alumina: the stretching or the bending frequencies reported for the other species (NH_4^+, $-NH_2$ or NH_3^+) are generally too low to account for the observed tunneling spectrum. A similar conclusion was reached by Shklyarevskii et al. [11] in a study by tunneling spectroscopy of the adsorption of NH_3 on alumina thermally activated at 150–200°C (bands at 3260 and 3330 cm^{-1} were reported).

Nearly the same positions are observed on both substrates; this leads us to the conclusion that NH_3 must also be coordinately bound on AlF_3 and on the same type of sites, probably Al^+ cations *. So, as expected, the *Lewis acidity* of AlF_3 is enhanced relative to Al_2O_3.

4.1.2. Benzylamine $C_6H_5CH_2NH_2$

The adsorption of benzylamine on alumina has been investigated by Brown et al. [12]. It was observed that this molecule adsorbs very readily on alumina to give a very intense and structured spectrum. Their conclusion was that this

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* The strong intensity of the ν(O–H) band near 3600 cm^{-1} on the Al_2O_3 sample should not be interpreted as revealing a different mechanism of adsorption on Al_2O_3. It is due to the water in which NH_3 was dissolved for the experiment on Al_2O_3.

Table 3

IETS		Infrared					Assignments
On AlF_3	On Al_2O_3	Gas a)	Adsorbed on γ-Al_2O_3 b)				
			NH_3 coordinated	NH_3^+	$-NH_2$	NH_4^+	
3340 3290	~ 3300	3443 3337	3400 3355	3100	3386 3335	3150 3050	ν(N–H)
1620	~ 1610	1626	1620	–	1510	1680 1410	δ(N–H)

a) From ref. [24].
b) From ref. [25].

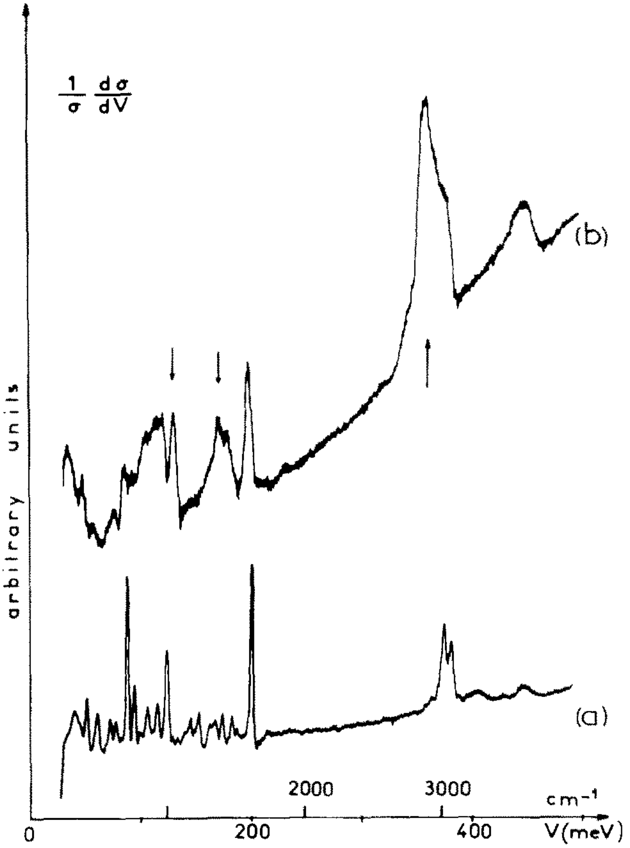


Fig. 4. Spectra of $C_6H_5CH_2NH_2$ adsorbed on (a) AlF_3 and (b) Al_2O_3.

spectrum can be interpreted either as resulting from Lewis acid–Lewis base coordination involving the electronic lone pair of the nitrogen atom of the amine radical or Brönsted acid protonation of the adsorbate by a surface hydroxyl to give a surface bound ammonium species.

We have tried, in collaboration with one of the authors of ref. [12], to reproduce this experiment in our laboratory, but although experimental conditions were very close, it has been impossible to obtain such an intense spectrum (see fig. 4a). It seems that the alumina grown in our evaporator is less reactive towards amines. This illustrates the difficulty in comparing IETS studies made in different laboratories.

The spectrum of benzylamine adsorbed on AlF_3 is displayed in fig. 4b. A comparison with spectrum a – taking the phonon bands as a reference for a rough evaluation of the intensities – shows that the adsorption is much favored on AlF_3.

This spectrum b is very similar in the positions and the relative intensities of the bands to the result of the reference [12]; nevertheless differences appear:

– The broad intense band near 2900 cm^{-1} which appears on Al_2O_3 is not observed on AlF_3. Brown et al. [12] interpreted this band as due to down-shifted OH or NH vibrations. This attribution seems questionable to us. We think this band could reveal the presence on the surface of another adsorbed hydrocarbon: in fact the bands designated by arrows on spectrum b, fig. 4, seem to be correlated in intensity with each other while uncorrelated with the other peaks characteristic of benzylamine. Further studies are under progress to clarify this point. Anyway, it certainly reveals a difference in the chemical nature of both substrates.

– Two weak bands are observed on AlF_3 at 3186 and 3315 cm^{-1} instead of only one at 3299 cm^{-1} on alumina. ν(N–H) modes are expected in this region. But the weakness of these bands makes this difference not really significant.

A measure of the absolute intensities of the ν(O–H) band near 3600 cm^{-1} indicates that the hydroxyl content of an AlF_3 junction doped with benzylamine is essentially the same as for an AlF_3 undoped sample (the agreement is better than 10%). This result suggests that the hydroxyls adsorbed on the substrate are not involved in the adsorption reaction and therefore the amine radical of the dopant molecule must subsist undissociated in the adsorbed species since any removal or addition of hydrogen would affect the intensity of the ν(O–H) band. This conclusion is consistent with the observation of two ν(N–H) bands at 3186 and 3315 cm^{-1}.

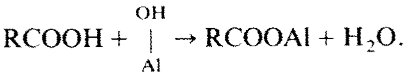
The only sufficiently strong adsorbate–adsorbant interaction which does not dissociate the amine radical is a Lewis acid–Lewis base coordination involving the nitrogen lone pair. We are thus led to the conclusion that the benzylamine is *coordinately bound on Lewis sites* on AlF_3, these sites being likely to be surface aluminum cations.

One may also infer from the energy position of the ν(N–H) bands that the two N–H bonds are not equivalent in the adsorbate. Bellamy and Williams [13] have edicted an empirical rule which states that the frequencies (in cm^{-1}) of the two N–H modes of a primary amine must be approximately related by the relation $\nu_{sym} = 345.63 + 0.876\ \nu_{as}$ if the two N–H bonds have equivalent configurations in the compound (ν_{sym} and ν_{as} stand for the frequency for the symmetric and asymmetric stretching mode of the amine radical respectively). This relation is not satisfied by the observed frequencies for benzylamine on AlF_3 ($\nu_{sym} = 3186\ cm^{-1}$, $\nu_{as} = 3315\ cm^{-1}$): ν_{sym} predicted from ν_{as} differs by 63 cm^{-1} from the observed value.

4.2. Carboxylic acids

Carboxylic acid adsorption on alumina has been widely studied by tunneling spectroscopy [15,16]. The formation of a carboxylate species is observed. A model mechanism for this reaction, based on observations of spectra of acetic acid and formic acid [16] at different coverages has been proposed. It successively involves two types of sites in the sequence:

$$RCOOH + Al^{+} - O^{-} \rightarrow RCOOAl + OH, \qquad (1)$$



$$RCOOH + \underset{Al}{\overset{OH}{|}} \rightarrow RCOOAl + H_2O. \qquad (2)$$

The first step occurs on the Lewis acid–base sites which are expected on the surface of alumina due to the dehydration of the surface under vacuum [14], while the second involves a basic site AlOH. The sequence can be monitored by examining the intensity of the ν(O–H) band which increases with the coverage at low coverage and then decreases with coverage until of the surface is saturated [16].

In this paper, the adsorption of formic acid HCOOH and propiolic acid $HC \equiv CCOOH$ is studied on AlF_3.

4.2.1. Formic acid

Spectra of (a) AlF_3 and (b) Al_2O_3 samples doped with formic acid are shown in fig. 5. Saturation of the substrate was reached in both cases (more dopant did not produce stronger spectra). Under these conditions, the observation of comparable intensities on both spectra implies that the number of the adsorption sites involved is roughly the same for Al_2O_3 and for AlF_3. Energy positions are also very similar on both spectra. This indicates that formic acid adsorbs on AlF_3 as a formate species in the same configuration as on Al_2O_3. The ν(O–H) band on AlF_3 is very weak as expected when the adsorption follows step (2) of the mechanism presented above.

These similarities are not really surprising: in both cases the adsorption of formic acid is essentially determined by reaction with the surface hydroxyl groups of the substrate. However, two slight differences appear:

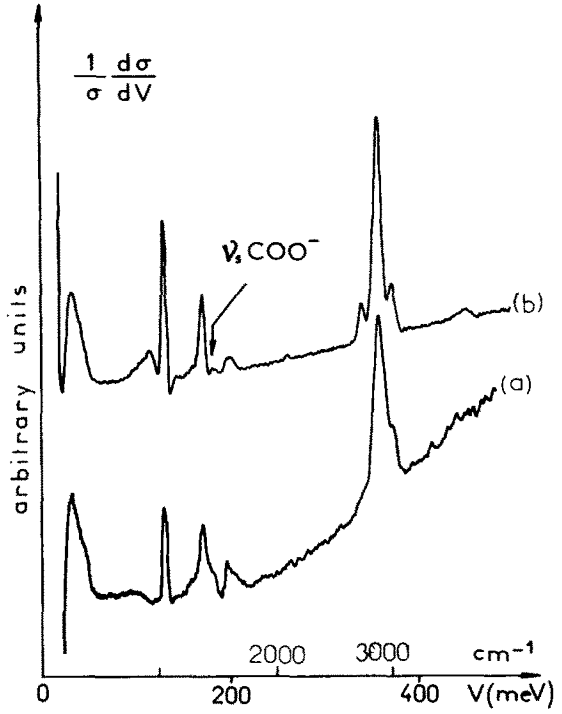


Fig. 5. Spectra of formic acid adsorbed on (a) AlF_3 and (b) Al_2O_3.

- The $\nu_s COO^-$ mode at 1468 cm^{-1} on Al_2O_3 is downshifted on AlF_3. Walmsley et al. [17] have shown, in a comparison of adsorbates on aluminum and magnesium oxides by IETS, the special sensitivity of this band to the adsorption configuration. They interpreted a downshift of its frequency on MgO as an indication of a stronger binding of the adsorbate to the substrate.
- The stretching mode of the C–H bond of the formate near 2900 cm^{-1} has lost its characteristic triplet form on AlF_3. The lower wing of this peak is generally assigned, on alumina, to an overtone of the C–H deformation mode at 1387 cm^{-1} while the upper wing is attributed to a combination of the C–H bending mode at 1387 cm^{-1} with the asymmetric stretching mode at 1620 cm^{-1} or to an overtone of the symmetric elongation mode at 1468 cm^{-1}. These wings are enhanced by Fermi resonance with the main C–H stretching band. The observed difference can then be understood as the result of an attenuation of the resonance due to slight shifts in the energies of the involved modes (especially 1387 cm^{-1}). This phenomenon is also observed by IETS with formate on MgO or modified alumina (for instance HCl pre-treated alumina [18]).

The mechanisms of adsorption on Al_2O_3 or AlF_3 must obviously be different for amines and carboxylic acids. But the final configurations are very similar. In both cases the species (amine or carboxylate ion) behaves as a Lewis base by coordinating on an Al^+ cation. It seems then reasonable to assume that the same type of sites are involved. If this statement is correct, the observed enhancement of Lewis acidity on AlF_3 relative to Al_2O_3 must be a consequence of *an increase of the intrinsic acid strength of the* Al^+ *sites of* AlF_3 and not of a simple increase in the number of these sites since – as shown by the comparable intensities for the saturated spectra of adsorbed formate – this number is the same on both substrates.

The observation of a downshift of the $\nu_s COO^-$ band of the formate on AlF_3 also points to an increased strength of these adsorption sites.

The Lewis acidity of a site is determined by its electron affinity and by other factors such as the geometry of the site and the orientation of the unoccupied orbitals. The results presented here do not permit us to distinguish between both types of influence. However, the strong electronegativity of fluorine – which explains the ionic character of AlF_3 as opposed to the essentially covalent nature of Al_2O_3 – points to an enhanced electronegativity of Al^+ as a consequence of a charge transfer between the cation and the neighboring fluorine anions.

4.2.2. Propiolic acid

The adsorption of propiolic acid on alumina was studied using IETS by Jaklevic and Gaertner [19,20] and by Brown et al. [21]. Jaklevic [20] showed that propiolic acid adsorbs as the corresponding carboxylate which is then slowly converted to an acrylate species by hydrogenation presumably involving the hydroxyl surface groups of alumina. This catalytic reaction is rather slow at room temperature (a few days for complete conversion) and therefore could be easily monitored by tunneling spectroscopy.

Fig. 6 shows spectra obtained with propiolic acid. The spectra a and b correspond to AlF_3 and Al_2O_3 samples traced just after the doping process while the junction c is an Al_2O_3 sample which was heated at 135°C for 20 h to activate the hydrogenation reaction. Evidence for the presence of adsorbed propiolate clearly appears on the spectrum b. The bands near 2105 and 3275 cm^{-1} are typical of stretching modes of C≡C and ≡C–H bonds. Other peaks, particularly at 1620 cm^{-1} ($\nu C{=}C$) and 3080 cm^{-1} (asymmetric $\nu{=}CH_2$) are attributable to an adsorbed acrylate species. A more detailed analysis, based on a comparison with the spectrum of an alumina junction doped with acrylic acid shows that some bands of the spectrum b can be attributed to a saturated carboxylate species, probably a propionate species. So, as pointed out by Brown et al. [21], the hydrogenation reaction proceeded partially during the adsorption. This observation contrasts with the result of Jaklevic [20], whose spectrum taken just after the doping process shows no sign of this further reaction; a major difference which could be responsible for this discrepancy is

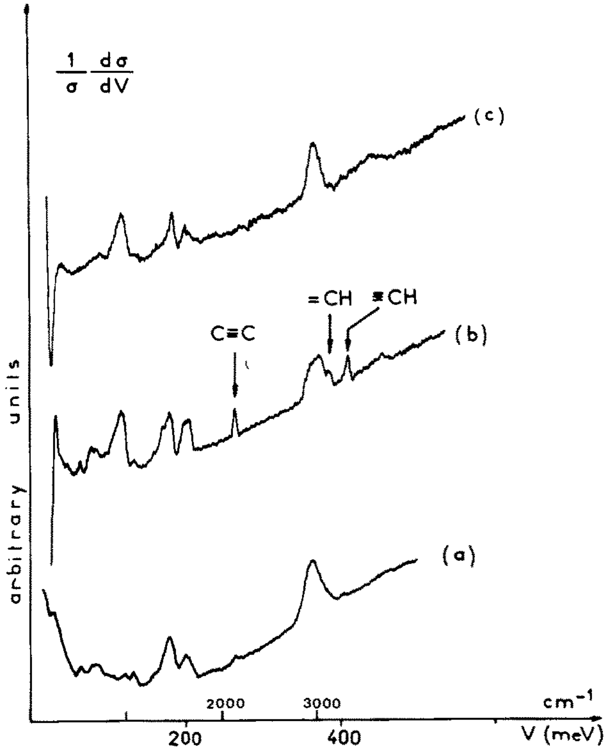


Fig. 6. Spectra of propiolic acid adsorbed on (a) AlF_3, (b) and (c) Al_2O_3. The sample c was heated 20 h at 135°C.

that the spectrum of Jaklevic was obtained with a sample made by a liquid doping technique while Walmsley et al and our group used gas doping.

Anyway, the hydrogenation can be completed by heating the sample as demonstrated on spectrum c: the peaks which characterize the C≡C and C=C bonds have disappeared.

The spectrum a, of propiolic acid-doped AlF_3 sample, is very similar to spectrum c. No sign of a C≡C or C=C bond appears. The hydrogenation reaction was rapidly complete without heating above room temperature.

This observation clearly evidences *an increased hydrogenating power of* AlF_3 *as compared to* Al_2O_3. Could it be related to the preceding observations of this study?

One step in a hydrogenation reaction is the opening of the multiple bond, an eventuality being is the π-coordination of the unsaturated species on a metallic centre. Such species have been observed on γ-Al_2O_3 (for instance propylene [22]) and have been shown to play the role of intermediate in some reactions of hydrogenation of unsaturated hydrocarbons on molecular coordination complexes (for instance hydrogenation of ethylene on $ClRh[P(C_6H_5)_3]_3$ [23]). The hydrogenation of propiolate and acrylate species on Al_2O_3 and AlF_3 could involve π-coordination as an intermediate step. The observed difference in hydrogenating activities of Al_2O_3 and AlF_3 would then appear as a consequence of the increased Lewis acidity of the Al^+ sites demonstrated above.

5. Summary

The insulating layer grown on alumina by glow discharge in CF_4 exhibits good properties for tunneling spectroscopy: it gives high quality, noiseless spectra. The analysis of spectra of undoped samples leads us to characterize this substrate as *aluminum fluoride AlF_3*.

The study of the spectra obtained on Al_2O_3 and AlF_3 from the same dopant molecules evidences the following differences:

- The adsorption of amines (namely NH_3 and $C_6H_5CH_2NH_2$) is favored on AlF_3; they are bound to the substrate by Lewis acid–Lewis base coordination of the nitrogen lone pair.
- Formate is more strongly adsorbed on AlF_3, as attested by the downshift of the symmetric elongation of the COO^- radical.
- The activity of the substrate for the hydrogenation of adsorbed propiolate and acrylate species is stronger with AlF_3, as attested by the absence of the band characterizing the C≡C and C=C bonds on the spectrum of a sample doped with propiolic acid.

These differences can be intepreted as consequences of an enhanced Lewis activity of AlF_3 relative to Al_2O_3 determined at least in part by an enhanced electronegativity of surface Al^+ cations.

Until now, IETS has been limited mainly to Al_2O_3 as substrate. It is important for the development of this spectroscopy to investigate new insulating barriers, with interesting chemical properties such as AlF_3.

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