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Inelastic Electron Tunneling Spectroscopy (IETS) of Simple Unsaturated Hydrocarbons Adsorbed on Plasma-Grown Aluminum Oxide

N. M. D. BROWN, W. E. TIMMS, R. J. TURNER, AND D. G. WALMSLEY

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

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The paper reports the inelastic electron tunneling spectra (IETS) of 1-hexene, 1-heptene, 1-octene, 1-hexyne, 3-hexyne, 1-heptyne, cyclohexene, and 1,3,5-cycloheptatriene adsorbed from the vapor onto plasma-grown aluminum oxide. Chemisorption, surface reactions, and adsorbate orientation are discussed. The 1-alkenes appear to undergo a Lewis base interaction with surface aluminum cations; the resultant perturbed double bonds lie parallel to the oxide surface. The alkynes are little altered by adsorption but they too may lie parallel to the surface. Many related species failed to adsorb at all.

INTRODUCTION

It is now clear that inelastic electron tunneling spectroscopy (IETS) can be used, via vibrational mode assignment and identification, to study the adsorption of molecules on barrier oxide films grown on metals. The best spectra are obtained from relatively small molecules such as acids (*1–4*), aldehydes (*1, 4, 5*), acid chlorides (*1, 6*), phenols (*7*), alcohols and amines (*8*), including pyridine (*9*), where chemisorption is clearly involved with or without further surface reaction. Satisfactory tunnel spectra have also been reported for larger species where simple physisorption or surface condensation is important, e.g., amino acids (*10, 11*), proteins (*11*), and other biological materials (*12*).

The details of the IETS method and all but current work have recently been reviewed (*13*). With good practice the technique has sufficient sensitivity to study adsorbates at ~5% monolayer coverage or less (*14*). It also readily covers the usual range (300–4000 cm^{-1}) of molecular vibrational energies without significant interference from bands of the adsorbent oxide itself. These two features, coupled with the fact that the method is free (*15*) of the normal selection rules, give IETS great utility in the investigation of chemisorption processes. In addition, information about the orientation of the adsorbate may be had (*2, 7, 16*) from the observed tunneling band intensities provided band assignments can be made. The adsorbates, (X), on the surface of the barrier metal oxide, I, of the Al–I(X)–Pb tunnel junctions can be considered as being matrix isolated. The effect of the top lead electrode is well understood (*17*) and does not materially affect the interpretation of the resultant junction spectra.

We report here on the behavior of simple unsaturated hydrocarbons, work prompted by our earlier observation (*3*) of the chemisorption of unsaturated acids as carboxylates in which further reaction of the unsaturated moiety is also apparent in certain instances. Mechanistic aspects of the chemisorption of alkenes on bulk aluminas (*18*) and other catalytic surfaces (*19*) have been of interest over a prolonged period and, as such, have prompted much work using conventional infrared (*20, 21*) methods and more recently laser Raman spectroscopy (*22*).

The alkenes, alkynes, and cycloalkenes

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were all adsorbed from the vapor onto plasma-grown aluminum oxide inside the vacuum evaporator used for junction preparation. The IET spectra obtained are, we believe, the first representative spectra of simple unsaturated hydrocarbon adsorbates, although barrier junctions prepared by exposing aluminum metal to a dc ethene plasma rather than the usual oxygen or air have been studied (*23*) elsewhere.

Comparison is made with the vibrational data of the free molecules and with the behavior, where known, of the same species adsorbed on bulk aluminas. However, the relatively poor quality and paucity of the latter data make anything more than a general comparison of the chemisorption properties of the amorphous thin-film plasma-grown aluminum oxide with those of the more crystalline γ-, α-, or δ-alumina difficult at present.

EXPERIMENTAL CONSIDERATIONS

The detailed sample preparation procedure has been described in full previously (*1, 7*). In brief, the aluminum oxide layers used were grown by exposing a glass-supported film of the metal to an oxygen dc plasma ($p_{O_2} \simeq 0.03$ Torr, current ~5 mA) for ~60 s. The adsorbates, which were all carefully redistilled under nitrogen at low pressure immediately before use (purity ≥99.5% by glc), were admitted to the evacuated (10^{-6} Torr) sample preparation chamber as vapor from an external reservoir for adsorption onto the oxide surface at room temperature. From the detailed behavior of several such preparations it was found that, for a given adsorbate, a similar inelastic signal strength, relative to the elastic background slope, is obtained irrespective of how long (always >10 s) the vapor is held in contact with the oxide surface. We therefore believe the oxide surface to be site-saturated with well below (~10%) monolayer coverage resulting. It should be noted that extreme care was taken to ensure that no cross-contamination of junctions arose when changing from one adsorbate to another; clean adsorbate-free Al–Al oxide–Pb junctions were prepared each time before the vapor of a new dopant molecule was admitted to the evaporator system.

The actual measured band positions are reproducible, with an error of $<\pm 5$ cm^{-1}, from junction to junction and between different preparations. Instrumental linewidth is ~10 cm^{-1}.

Completed junctions had resistances in the range 20–200 ohms, and the IET spectra were recorded at ~2 K in a standard double-glass helium cryostat using the detection circuitry described previously (*1, 7*). The spectra are displayed as d^2V/dI^2 vs V(1 meV = 8.065 cm^{-1}), for a given sample, on an X–Y recorder.

The comparison infrared data were recorded on a Perkin–Elmer 457 spectrometer from liquid films between CsI plates. The corresponding Raman data were obtained on an Anaspec 33 laser Raman spectrometer from filtered capillary samples.

RESULTS AND DISCUSSION

The IETS spectra of 1-hexene, 1-heptene, and 1-octene are shown in Figs. 1a, b,

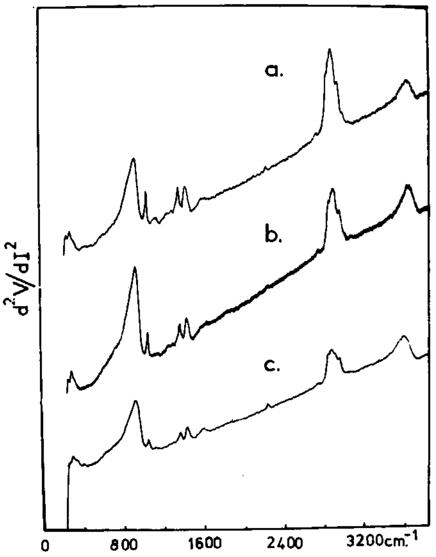

FIG. 1. IET spectra, recorded at 2 K, of (a) 1-hexene, (b) 1-heptene, and (c) 1-octene adsorbed onto plasma-grown aluminum oxide at room temperature.

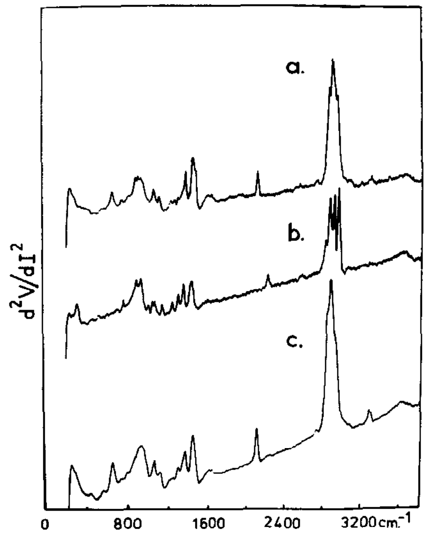

FIG. 2. IET spectra, recorded at 2 K, of (a) 1-hexyne, (b) 3-hexyne, and (c) 1-heptyne adsorbed onto plasma-grown aluminum oxide at room temperature.

and c, respectively. Those of 1-hexyne, 3-hexyne, and 1-heptyne are shown in Figs. 2a, b, and c, and of cyclohexene and cycloheptatriene in Figs. 3a and b, respectively. These various spectra all show the adsorbate bands superimposed on a background characteristic of Al–AlO–M junctions. This background has identifiable features located, in order of decreasing energy, at ~3600, ~940, ~600, and ~300 cm^{-1}. Of these, only that at ~3600 cm^{-1} which is identified (*24*) with ν(O–H) modes has any real sensitivity to surface adsorption or reaction. One can infer (*1, 7*) from its position, after correction (+70 cm^{-1}) for the effect of the top lead electrode (*17*), that the hydroxyl groups[1] of the plasma-grown oxide are rather acidic in type, surrounded by few or possibly no nearest-neighbor oxide ions (*18, 25*). Bands ascribed (*26*) to surface-bound molecular water, at ~3300 and ~1630 cm^{-1}, are never seen in the IET spectra of either doped or undoped junctions. The 940-cm^{-1} band is assigned (*1*) to the longitudinal component of the ν(Al–O) vibration of the thin-film plasma-grown oxide. The corresponding transverse component of the vibration is of much lower intensity and may contribute (*1*) to the low-intensity low-energy tail on the 940-cm^{-1} band, as does the broad δ(Al–O–H) mode at ~600 cm^{-1}. The remaining band, at ~300 cm^{-1}, is due to lattice phonons of the aluminum metal film itself.

1-Hexene, 1-Heptene, and 1-Octene

The IET spectra derived from these three adsorbates on the plasma-grown oxide are shown in Figs. 1a, b, and c. Table 1 lists the corresponding band positions, relative intensities, and band assignments.

Inspection of these spectra obtained following the room-temperature adsorption of the alkenes from the vapor shows all three behave similarly. Apart from some differences in the relative intensities the band positions agree very closely. In detail the major bands observed have been assigned from a general consideration of the liquid alkenes and analogous alkanes. A number of significant points arise. Should the double bonds present in these adsorbates be retained, perturbed, or lost following adsorption, then the details of the tunnel spectra will differ accordingly from the vibrational spectra of the free alkenes. Such differences are apparent.

It is clear in all three cases that the

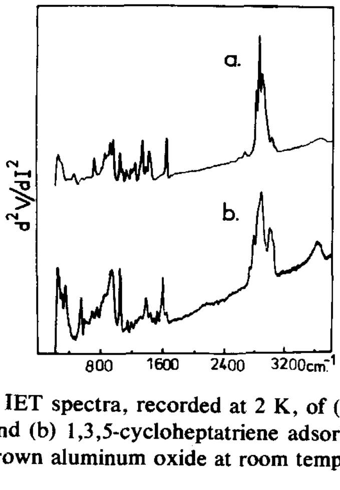

FIG. 3. IET spectra, recorded at 2 K, of (a) cyclohexene and (b) 1,3,5-cycloheptatriene adsorbed onto plasma-grown aluminum oxide at room temperature.

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

TABLE 1

IETS Vibrational Data,[a] Obtained at 2 K, for 1-Hexene, 1-Heptene, and 1-Octene Chemisorbed on Plasma-Grown Aluminum Oxide

1-Hexene	1-Heptene	1-Octene	Assignment
~3640(—)	~3640(—)	~3640(—)	ν(O—H)
2983(0.71)	2998 sh	2988(1.61)	ν(C—H)
2938(2.18)	2948(1.42)	2948(2.13)	
2872(3.73)	2888(2.49)	2877(2.61)	
2827(2.76)	2842(2.04)	2827(2.35)	
2726(0.31)	2731(0.18)	2726(0.17)	
2225(0.20)	2227(0.09)	2222(0.43)	ν(C≡C)[b]
1612(0.27)	1617(0.17)	1597(0.48)	ν(C=C)[c]
1434(1.00)	1436(1.00)	1436(1.00)	CH_2 scissoring
1368(1.00)	1370(0.87)	1367(0.74)	CH_3 deformation
1285(0.15)	1280(0.08)	—	CH_2 wag and twist
1240(0.13)	1240(0.12)	—	
1138(0.27)	1140(0.08)	—	
1052(1.27)	1055(1.04)	1051(0.69)	ν(C—C)/CH_2 rock
940(—)	940(—)	940(—)	ν(Al—O)
294(—)	294(—)	294(—)	Al lattice phonon
255(?)[d]	260(?)[d]	260(?)[d]	

[a] Band positions, in cm^{-1}, are those observed corrected (-8 cm^{-1}) for the effect of the superconducting energy gap of lead; intensities shown in parentheses are scaled w.r.t. the 1436-cm^{-1} band; sh, shoulder.

[b] See text.

[c] Broad, perturbed double bond.

[d] Superimposed on lattice phonon.

ν(C=C) band (strong in the infrared and very strong in the Raman) is broad and of low intensity in the tunnel spectra. It is also shifted by ~30 cm^{-1} from ~1640 to ~1610 cm^{-1}. Here the apparent breadth is indicative of some inhomogeneity of the surface sites where adsorption has occurred. The lack of intensity (in part due to the breadth of the band) suggests, in view of the known (*16*) orientational dependence of inelastic band intensity, that the perturbed double bond interacting with the oxide surface may lie parallel or close to parallel with the surface. In the 3000-cm^{-1} region of the tunnel spectra the ν(C–H) modes of the terminal double bond, if still present, are not resolved; the highest ν(C–H) band position is seen as a shoulder at ~2990 cm^{-1}. After allowance for the known effect of the top lead electrode of the junctions (+ ~40 cm^{-1} at ~3000 cm^{-1}) on the ν(C–H) band positions, the corrected bands are still shifted to lower energy compared to those found in the free alkenes. The rather poor resolution in this region can be attributed to the effects of random orientation of the flexible alkyl chains at the adsorption sites: all localities around a given site type are thus sampled and a smearing of the spectral detail results. The two very strong bands seen in infrared close to 985 and 900 cm^{-1}, associated with C–H deformations perpendicular to the nodal plane of the double bond, are absent from the tunnel spectra, and likewise with the bands, assigned to a twisting of the terminal double bond, seen with moderate intensity at ~635 and ~550 cm^{-1} in the infrared spectra of these alkenes. In the case of the out-of-plane C–H deformations image–dipole considerations (*16*) lead to the conclusion that even if the associated double bond was lying flat (perpendicular to the direction of motion of the tunneling electrons), then these modes should be seen in the tunnel spectra as should the two bands assigned to the twisting of the double bond.

Their absence coupled with the low intensity of the ν(C=C) mode already commented on and the failure to observe olefinic ν(C–H) bands provide strong evidence for either a particular orientation of the double bond at the surface or a reaction there which leads to a structural change in the molecule on adsorption.

Before considering the actual adsorption process it should be noted that the adsorption procedure used (and discussed earlier) was the same for each alkene. The increasing relative strengths of the background ν(Al–O) and ν(O–H) modes at ~940 and ~3600 cm^{-1}, respectively, suggest that the amount of alkene adsorbed decreases in the order $C_6 > C_7 > C_8$, possibly because of increased masking of the oxide surface as the chain length increases. It is also clear that the levels of coverage reached following room-temperature adsorption are substantially less than with other adsorbates of different functionality, i.e., the number of sites on the oxide surface capable of producing a surface-bound adsorbate is lower for the alkenes than for acids, bases, or phenols and the like. Simple physisorption is discounted since this would be non-site specific and lead to higher surface coverage.

Two main adsorption processes need now to be considered. These are (a) protonation (*27*) at the double bond by surface hydroxyl groups of acidity sufficiently high to act as Brønsted acids and (b) a Lewis base interaction of the double bond with Lewis acid sites (*18–22*) such as exposed aluminum cations on the oxide surface. The processes described can clearly operate independently or in concert. Both must clearly be site-limited processes and both may lead to isomerization or further reaction of the adsorbate.

The spectral features listed in Table 1 and discussed above do not allow a clear choice between the two chemisorption processes to be made. If a significant number of the surface acidic hydroxyl groups is involved, then the 3600-cm^{-1} band associated with these should be sensibly altered either in intensity, band shape, or position. In the doped tunnel spectra the hydroxyl band remains unchanged so it seems likely that process (b) involving a Lewis acid–Lewis base interaction between the double bond in the adsorbate and surface aluminum cations is dominant though perhaps not exclusive. Thus the double bond axis is held roughly parallel to the oxide surface. In fact the change in position observed between the $\nu(\mathrm{C{=}C})$ band of free and adsorbed 1-hexene is about half that known (*28*) to occur ($-58\ \mathrm{cm}^{-1}$) when 1-hexene is complexed with aluminum bromide. Therefore it would seem that the plasma-grown oxide behaves at least in terms of its surface acidity rather like bulk aluminas (*18, 19*). We believe hydroxyl interactions between the plasma-grown oxide and the three alkenes dealt with here are not important. Adsorbed carboxyl species (*20, 29*) are not formed nor does isomerization, as noted (*22*) with 1-hexene, take place.

The tunnel spectra derived from all three alkenes we note show a weak band, on replicate junctions, at $\sim 2225\ \mathrm{cm}^{-1}$, close to that identified as the $\nu(\mathrm{C{\equiv}C})$ mode in 3-hexyne, discussed below. At this juncture no explanation is offered for the formation of such a triple bond on the surface following adsorption of the alkenes but we point out that the three alkenes used contain no detectable alkynes and that clean adsorbate-free junctions were prepared with the vacuum evaporator before each was used. The band indicated is therefore not simply contamination. The foregoing discussion is not inconsistent with at least a proportion of the adsorbed alkenes undergoing a chemisorption-promoted reaction of the type: $2\mathrm{R{-}CH_2CH{=}CH_2} \rightarrow \mathrm{R{-}CH_2CH_3} + \mathrm{R{-}C{\equiv}C{-}CH_3}$ with the second product retained on the surface, whereas the first may desorb and be pumped away during junction preparation.

1-Hexyne,3-Hexyne, and 1-Heptyne

The IET spectra of 1-hexyne, 3-hexyne, and 1-heptyne adsorbed on plasma-grown aluminum oxide are shown in Figs. 2a, b, and c, respectively. The corresponding line positions, relative intensities, and likely band assignments are given in Table 2.

Inspection of the tunnel spectra shows that all three are adsorbed with retention of the triple bond present. Overall the correspondence between the IETS data and the observed infrared and Raman band positions of the liquid alkynes is good.

The $\nu(\mathrm{C{\equiv}C})$ modes are seen with moderate intensity at 2110, 2106, and 2232 cm^{-1}, respectively, for 1-hexyne, 1-heptyne, and 3-hexyne. In the 1-hexyne case the acetylenic $\nu(\mathrm{C{-}H})$ band is located at 3294 cm^{-1} and in the 1-heptyne at 3285 cm^{-1}; in both, the identified position is very close to that on the free alkynes. This, together with the narrow bandshape, we take as evidence for lack of involvement of the acetylenic proton in the surface adsorption. In addition the almost completely unperturbed position implies that the same mode is not materially affected by the presence of the lead top electrode. The molecule is therefore probably held on the surface orientated so that

TABLE 2

IETS Vibrational Data,[a] Obtained at 2 K, for 1-Hexyne, 3-Hexyne, and 1-Heptyne Chemisorbed on Plasma-Grown Aluminum Oxide

1-Hexyne	3-Hexyne	1-Heptyne	Assignment
~3640(—)	~3640(—)	~3640(—)	ν(O—H)
3294(0.16)	—	3285(0.25)	ν($\equiv$C—H)
2951(1.84)	2958(3.03)	2931 sh	ν(C—H)
2903(2.63)	2916(2.74)	2889(3.00)	
2866(2.04)	2866(2.64)	2855(2.39)	
—	2830(1.26)	—	
2110(0.53)	2232(0.44)	2106(0.69)	ν(C$\equiv$C)
1636(0.20)[b]	1590(0.12)[b]	1610(0.16)[b]	ν(C=C)
1444(1.00)	1444(1.00)	1441(1.00)	CH_2 scissoring
1378(0.80)	1368(0.94)	1370(0.69)	CH_3 deformation
1304(0.27)	1315(0.63)	1296(0.39)	CH_2 wag and twist
1263(0.24)	1257(0.39)	—	
1230(0.22)	—	—	
1114(0.36)	1159(0.36)	1120(0.27)	
—	1085(0.36)	—	ν(C—C)/CH_2 rock
1058(0.44)	1061(0.41)	1061(0.43)	
—	1025(0.21)	—	
936(0.52)[c]	950(1.11)[c]	935(0.61)[c]	ν(Al—O)
904(0.20)	904(1.06)	—	
881(0.40)	—	—	
748(0.10)	778(0.37)	—	CH_2 rock
655(0.34)	—	654(0.49)	C$\equiv$C—H def.
—	—	562(0.06)	
—	—	551(0.07)	
—	335(0.57)	—	C—C$\equiv$C bend
294(—)	294(—)	294(—)	Al lattice phonon

[a] Band positions, in cm^{-1}, are those observed corrected (-8 cm^{-1}) for the effect of the superconducting energy gap of lead; intensities shown in parentheses are scaled w.r.t. the 1444-cm^{-1} band; sh, shoulder.

[b] Broad, see text.

[c] Unidentified band superimposed on ν(Al—O) mode, possibly CH_2 rock.

the terminal ν(C–H) is at least partially shielded by the rest of the molecule.

On consideration, the observed relative band intensities of the alkyne tunnel spectra, apart from those of the ν(C$\equiv$C) bands, appear to reflect the combined infrared and Raman intensities of the free alkynes. While, in principle, it should be possible (*1, 2, 7, 16*) to define the orientation of relatively small molecules, a specific conclusion is not evident in the case of 1-hexyne, 1-heptyne, and 3-hexyne. Nevertheless, because all three show a less intense ν(C$\equiv$C) band than is perhaps expected it can be inferred that the triple bond is probably held well away from the normal to the oxide surface. Such an orientation is consistent with discussion above of the behavior of the acetylenic ν(C–H) mode. The various other C–H and C–C bands lie where expected. It is worth noting too that the symmetrical and more mechanically rigid 3-hexyne shows greater spectral detail, particularly with the $\nu(CH_2)$ and $\nu(CH_3)$ modes around 2900 cm^{-1}.

It would seem therefore that these three alkynes are adsorbed largely without reaction or major structural change at the oxide surface. In this regard the plasma-grown oxide appears to behave differently from bulk aluminas on which adsorbed 1-alkynes are known, for example, to undergo chemisorption by loss of the acetylenic proton (*30, 31*), as well as self-reduction and polymerization (*31*).

It should be pointed out that all three tunnel spectra show a low-intensity band close to 1600 cm^{-1}, the position and broad ill-defined shape of which matches the band assigned as ν(C=C) in the alkene tunnel spectra. It is therefore reasonable to conclude that there are some sites on the plasma-grown oxide which can produce an apparent partial reduction, possibly by protonation of the triple bond π-electron system in all three alkynes. This proposition is borne out by the reduced intensity of the surface oxide ν(O–H) band in each case. Again the presence of the bands tentatively assigned as ν(C=C) is not due to cross-contamination of alkyne with alkene.

Finally, attempts to adsorb 1,5-hexadiyne and 1-phenylethyne under the same general conditions failed. Upon exposure to vapor the quartz crystal, which monitors deposition, showed a frequency shift similar in magnitude to that observed in successful samples, but as the excess vapor was pumped away the crystal frequency was seen to return to near its original value. Such apparently undoped samples also gave unexpectedly low tunnel barrier resistances. The obvious interpretation is that the sorptive bond is weaker for these species and the adsorbate is pumped away before the top metal film is deposited. Possibly the difficulty may be overcome by cooling the oxide after adsorption and before pumping away the organic dopant vapor prior to junction completion. Such a method has been used successfully in the case of pyridine (*9*).

Cyclohexene and 1,3,5-Cycloheptatriene

The IETS spectra of cyclohexene and 1,3,5-cycloheptatriene are shown in Figs. 3a and b, respectively. The observed line positions, relative intensities, and band assignments are given in Table 3.

Again inspection of the tunnel spectra and comparison with the infrared and Raman band positions show them to be adsorbed with retention of the double bond in the former and the conjugated system in the latter. In the cyclohexene case the ν(C=C) is seen as a moderately intense sharp band at 1643 cm^{-1} with the corresponding olefinic ν(C–H) band now resolved at 3006 cm^{-1}. The latter is some 40 cm^{-1} to lower energy than in cyclohexene itself, a change in position consistent with the known effect (*17*) of the top electrode. Similar arguments apply to the olefinic ν(C–H) band at 3001 cm^{-1} in the cycloheptatriene case, with the major ν(C=C) band at 1603 cm^{-1}.

For both compounds line-by-line agreement between the optical vibrational spectra (*32*, *33*) is good and again the relative intensities of the bands found reflect the corresponding combined infrared and Raman intensities. It can be concluded that cyclohexene and cycloheptatriene are adsorbed on the surface of the plasma-grown oxide without major perturbation, in contrast with the C_6, C_7, and C_8 1-alkenes discussed above. For example, protonation of the double bond in cyclohexene (and in cycloheptatriene) can be discounted because of the positions and relative intensities of the ν(C=C) and olefinic ν(C–H) modes as well as the persistence of the other bands associated with the unreacted species. Formation of the symmetrical $C_7H_7^+$ tropylium (1,3,5-cycloheptatrienylium) cation from the adsorbed cycloheptatriene, should it have arisen, would give a less complex spectrum (*34*) than that observed, with major shifts in some band positions. Similar arguments apply to the oxidation product tropone (2,4,6-cycloheptatriene-1-one) (*35*). However, the presence of minor amounts of these products on the oxide surface cannot be discounted. It is also clear from the observed signal-to-noise ratio and baseline slopes that more cyclohexene is adsorbed than cyclohepta-

TABLE 3

IETS Vibrational Data,[a] Obtained at 2 K, of Cyclohexene and 1,3,5-Cycloheptatriene Chemisorbed on Plasma-Grown Aluminum Oxide

Cyclohexane	1,3,5-Cycloheptatriene	Assignment
~3640(—)	~3640(—)	ν(O—H)
3006(0.39)	3001(1.05)	ν(C—H)
2904(1.69)		
2883(1.97)	2888(1.85)	
2843(2.95)		
2807(1.64)	2793(0.99)	
	2739(0.40)	
2654(0.17)		
1643(1.00)	1651(0.26)	ν(C=C)
	1603(1.00)	
1570(0.10)[b]	1533(0.29)	
	1499(0.13)	CH_2 scissoring
1444 sh	1452(0.24)	
1424(0.73)		CH$_2$ wag and twist; =C—H in-plane deformations
1391(0.34)	1388(0.50)	
1338(0.99)	1327(0.05)	
1313 sh		
1247(0.47)		
1222(0.32)	1254(0.13)	
	1204(0.21)	
1194(0.30)		
1164(0.15)	1157(0.28)	
1139(0.28)		ν(C—C)/CH$_2$ rock
1089(0.30)		ν(Al—O)
1056(0.70)	1061(1.29)	
968(0.99)[c]	960(1.11)[c]	
930(0.89)		
889(0.53)	887(0.56)	skeletal and =C—H out-of-plane deformations
864(0.59)	864(0.53)	
817(0.21)	829(0.35)	
	766(0.27)	
728(0.48)	706(0.23)	
	627(0.16)	
	597(0.32)	
	559(0.84)	
471(0.20)	464(0.08)	
320 sh	363(0.65)	
294(—)	306(?)[d]	Al lattice phonon
	266(?)[d]	

[a] Band positions in cm^{-1}, are those observed corrected (-8 cm^{-1}) for the effect of the superconducting energy gap of lead; intensities in parentheses are scaled w.r.t. the band at 1643-cm^{-1} in the cyclohexene case and 1603 cm^{-1} in cycloheptatriene; sh, shoulder.

[b] Broad, see text.

[c] Unidentified band superimposed on ν(Al–O) mode, possibly CH$_2$ rock.

[d] Superimposed on lattice phonon.

triene under the junction preparation conditions used.

The ν(C═C) bands in both cases are relatively more intense than in the alkenes discussed earlier. Some evidence is seen in the cyclohexene IETS spectrum of a low-intensity broadened band on the low-energy side of the unperturbed 1643-cm^{-1} band. Thus at least for adsorbed cyclohexene some of the adsorbed species show behavior akin to that of the straight-chain alkenes discussed above. The intensity of the main ν(C═C) band may indicate an orientation of the double-bond axis more nearly vertical to the oxide surface than was suggested above for 1-hexene. Thus orientated, coupling of the stretching vibration to electrons tunneling through the barrier oxide is maximized. In the case of the cycloheptatriene, because of the additional conjugated double bonds and associated spectral complexity, the behavior of the adsorbate is less clear.

Just as with the alkenes and alkynes, not all of the unsaturated cyclic systems with which surface adsorption was attempted gave satisfactory and reproducible spectra. In spite of numerous attempts, with a variety of partial pressures in the vacuum preparation chamber, vapor doping with cyclopentene, cycloheptene, cyclooctene, cyclohexadiene, freshly redistilled cyclopentadiene, and indene was unsuccessful. In contrast, for reasons that remain unclear, the adsorption behavior and tunnel spectra of cyclohexene and cycloheptatriene were consistently reproduced. The behavior of cyclopentene, cycloheptene, and cyclooctene compared with that of cyclohexene is remarkable, the more so in view of the behavior of the straight-chain C_6, C_7, and C_8 alkene analogues.

CONCLUSIONS

We have demonstrated that inelastic electron tunneling spectroscopy (IETS) can be used satisfactorily to study the adsorption of a range of simple unsaturated hydrocarbons containing the C═C and C≡C moieties on plasma-grown aluminum oxide. From the data, evidence for the chemisorption processes may be adduced and furthermore some indication of adsorbate orientation ascertained.

It is believed that the IETS data is consistent with the 1-alkenes being involved in a Lewis base interaction with surface aluminum cations acting as Lewis acids and that the resultant perturbed double bonds lie on average in an orientation that is approximately perpendicular to the direction of the tunneling electrons, i.e., parallel to the oxide surface at the adsorption site. Formation of surface carboxy compounds is discounted but all three alkenes may give adsorbate containing a nonterminal C≡C moiety at some surface sites.

In the triple-bond examples (1-hexyne, 1-heptyne, and 3-hexyne) the adsorption appears to take place with little or no perturbation or reaction of the adsorbate. We believe an orientation parallel to the surface of the oxide is likely on the basis of the spectral evidence. It is also clear that the plasma-grown oxide does not interact with alkynes in the manner of bulk aluminas.

Finally, for cyclohexene and 1,3,5-cycloheptatriene, adsorption does not involve major perturbation of the adsorbate though in the cyclohexene case some sites involved seem to give behavior similar to that of the corresponding 1-hexene.

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