Variations in carbonyl mode intensities in inelastic electron tunneling, and multiple reflection absorption infrared spectroscopy Part I: effects due to the lead cover films for selected mono-carboxylic acids on alumina

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Abstract

In the first of a series of three articles, evidence for attenuation of the carbonyl vibrational mode intensity in inelastic electron tunneling spectroscopy (IETS), and multiple reflection absorption infrared spectroscopy (MRAIRS) is presented. The work may have considerable impact on the interpretation of IET and MRAIR spectra of certain polymers adsorbed on alumina of interest in the field of adhesion. For a better comparison between the two techniques, MRAIR spectra are recorded for compounds adsorbed on conventional oxidized aluminum mirror samples and on samples prepared with thin-film lead cover films to form planar aluminum/alumina/compound/lead structures similar to the tunnel junctions used for IETS. The compounds chosen for the study are all carboxylic acids, known to adsorb on alumina by coordinate bonding of the carboxylate anion in acid–base reactions. The acids contain non-bonding carbonyl groups on the carbon backbone of the molecules whose intensities are investigated. When the compounds are constrained by the above sample geometry, similar carbonyl attenuation is observed in both IETS and MRAIRS, but to varying degrees depending on the geometry of the adsorbed molecules. The effect, which disappears in MRAIR spectra for samples without the lead cover films, can be explained by consideration of the deformation of the molecules by the lead cover film, which results in steric hindrance of the carbonyl groups and a corresponding reduction in their activity in accordance with the orientational selection rules for both IETS and MRAIRS. This and further spectroscopic evidence for deformation of the molecules by the lead cover film is discussed. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It is well known that the adhesion of polymers on metals and metal oxides (particularly aluminum oxide) has many diverse commercial applications. These range from the adhesive bonding of aluminum sheets in aircraft construction, to the deposition of polymer coatings on aluminum cans to improve the quality of beverage storage. An understanding of the nature of adhesive bonding at the molecular level is therefore vital. Two spectroscopic techniques, sensitive to the adsorption of polymers on alumina, which can provide valuable information

about the nature of chemical bonding at the molecular level with a high sensitivity, are inelastic electron tunneling spectroscopy (IETS) [1–4] and multiple reflection absorption infrared spectroscopy (MRAIRS) [5–7]. Both of these techniques can detect as little as a fraction of a monolayer of adsorbed material on aluminum oxide. This sensitivity is essential if one is to investigate reactions that truly take place at the interface between the metal oxide and the adsorbed material. IETS is now well established as an excellent experimental technique for the investigation of the vibrational spectra of adsorbates incorporated into metal/insulator/metal tunnel junctions [2,3]. Tunneling electrons, while traversing an insulating barrier, lose energy to the vibrational modes of the insulating layer by inelastic collisions. These give rise to incremental changes in the tunnel current, I, appearing as peaks in the plot of d^2I/dV^2 versus bias voltage, V. The

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vibrational spectrum thus obtained can be analyzed to elicit information regarding the insulating layer.

In the extremely useful MRAIRS technique an IR beam suffers multiple reflections between two plane-parallel metal/metal oxide samples (on glass substrates). Absorption bands due to adsorbed molecular layers can be studied to reveal much information about the layers.

In the past, peaks due to carbonyl modes in IET spectra have been found to be weak or, in some cases, absent [4,5]. This is in marked contrast to infrared spectra where they are extremely strong. Some workers have attributed these differences to inherent limitations of the IETS technique itself, although the reasons were not discussed [5].

The ability of IETS to detect carbonyl-related modes is of central importance in the investigation of many surface reactions, for example, those involving carboxylic acids and various polymers on alumina, which is of significant importance in the field of adhesion. Also, certain ester-based polymers are believed to bond to the alumina surface via reactions involving carbonyl groups [8,9]. Cleavage of ester side-groups of these polymers by acid–base reactions with the alumina substrate are believed to result in their adsorption. This interpretation is based on the disappearance of the associated carbonyl mode and on the appearance of symmetric, and asymmetric vibrations of the carboxylate anion. However, in a previous study comparing MRAIR and IET spectra of certain carbonyl containing polymers, doubts have been raised regarding the ability of IETS to detect carbonyl modes at all [5]. Clearly, resolution of this issue is essential to the interpretation of a large number of IET spectra over the years where surface reactions involving carbonyl

groups are involved [2,3]. In a study of pyruvic acid, we have shown that the attenuation of the carbonyl mode intensity is partly due to the lead cover film, which is an integral part of the IETS sample preparation process [10]. In that work, we compared IET spectra with MRAIR spectra obtained from novel samples prepared with a lead cover film, similar to those used in IETS [10]. This was done to better compare the two techniques. We found that compared to IR samples fabricated without a lead cover film the carbonyl mode is attenuated. The objective of the present article is further investigation of the effect of the lead cover film on the carbonyl and other mode intensities, and to compare these vibrational modes by means of IETS and MRAIRS. Also of particular interest is how this effect correlates with the location and orientation of the carbonyl group within the molecules [11] and the tunnel barrier itself [12]; this is addressed systematically in the two accompanying articles [11,12] for series of mono- and di-carboxylic acids.

The mechanism for the bonding of carboxylic acids to alumina surfaces has been well documented by means of IETS [4,13] and other techniques. The choice of pyruvic acid in our previous study [10] was dictated by the presence of a carbonyl group within the molecule, which is not involved in bonding with the alumina surface, as seen in Table 1(a). We shall refer to carbonyl groups situated along the carbon backbone of the acid molecules as internal carbonyls to distinguish them from the carbonyls of the carboxylic acid end-groups. The internal carbonyl of pyruvic acid was expected to produce a strong peak in the IET spectra. However, the peak was weak. On the other hand, The MRAIR spectra of samples prepared without a lead cover film showed a very

Table 1
Comparison of the carbonyl mode intensities for PA, 2-KBA and 4,6-DOHA obtained using MRAIRS with and without a lead cover film and IETS

	(a) Pyruvic acid	(b) 2-Ketobutyric acid	(c) 4,6-Dioxoheptanoic acid
	CH_3 — $C{=}O$ — C — OH / O	CH_3 — CH_2 — $C{=}O$ — C — OH / O	CH_3 — $C{=}O$ — CH_2 — $C{=}O$ — CH_2 — CH_2 — C — OH / O
MRAIR without lead cover film	Strong	Strong	Very weak
MRAIR with lead cover film	Absent	Weak	Difficult to acsertain
IETS	Absent	Weak	Very weak

intense peak corresponding to this mode. MRAIR spectra obtained from samples with lead cover films did not exhibit this peak, which indicates an interaction of the internal carbonyl group with the top electrode.

Since the activity of the carbonyl mode is affected by the proximity of the lead cover film in IETS and MRAIRS samples, this led to our choice of 2-ketobutyric acid (2-KBA) and 4,6-dioxoheptanoic acid (4,6-DOHA) for the present study. The 2-KBA has an internal carbonyl with the carboxylic functional group and an ethyl group on either side, as shown in Table 1(b). The structure of 2-KBA differs from that of pyruvic acid by a methylene group. The internal carbonyl in the 2-KBA molecule is expected to be further removed from the lead cover film than the internal carbonyl of pyruvic acid when these molecules are incorporated in an IET junctions. The 4,6-DOHA has one internal carbonyl located at the center of the molecule and another situated towards one end, as can be seen from Table 1(c). Both these acids are expected to exhibit carbonyl peaks in the IET spectrum because they both have internal carbonyls somewhat removed from the lead cover film.

2. Experimental method

2.1. IETS

Our sample preparation technique for IETS has been described in detail in a previous publication [10]. Briefly, tunnel junctions of the type aluminum/alumina/carboxylic acid/lead were fabricated by conventional vacuum deposition techniques. Before the deposition of the lead cover film the alumina surfaces were exposed to a dilute solution (2 g/l in ethanol) of the appropriate acid under study and the excess was removed by means of a mechanical spinner. Fig. 1 shows a schematic representation of an IETS sample. For samples prepared in this manner we expect near optimal (monolayer) coverage to result on the alumina surface such that the adsorbed acid molecules pack laterally with their axes perpendicular to the surface. The samples are cooled to 4.2 K in liquid helium, and IET spectra are then recorded by phase-sensitive detection techniques to obtain the second-harmonic signal across the junction. An ac modulation signal of 1.3 mV rms at 50 kHz is used throughout. Details of our spectrometer can be found elsewhere [14].

2.2. MRAIRS

Samples were prepared by the evaporation of aluminum films onto pre-cut glass microscope slides in a manner similar to those used for IETS. They were then exposed to the same acid solutions used for IETS [15] and the excess spun off as before and were then placed in
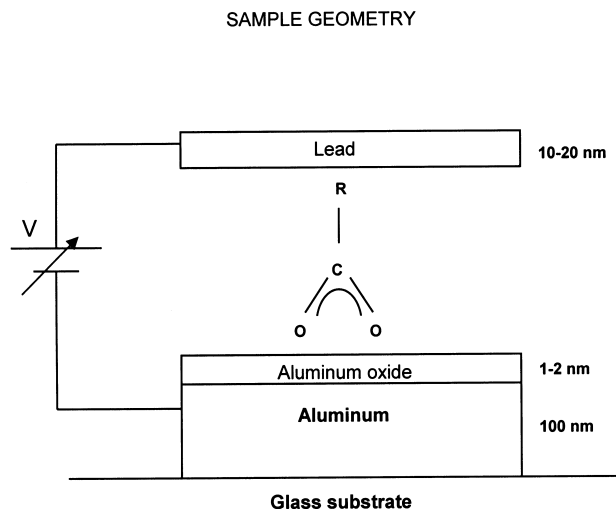

SAMPLE GEOMETRY

Fig. 1. Schematic representation of an IETS and MRAIRS sample. Typical thicknesses of the aluminum, aluminum oxide, and lead layers are indicated. No dc bias is applied in the case of MRAIRS.

the vacuum chamber at approximately 10^{-6} Torr for about 10 min to remove any physisorbed acid/solvent layers. It is important to point out that spectra obtained from samples that were not pumped down after doping were found to exhibit peaks corresponding to the bulk spectrum of the acid and were rejected. One set of samples was not exposed to any acid solution and was used as a reference. Infrared spectra were also obtained for samples prepared similarly to IETS samples (with a lead cover film approximately 20 nm thick) [10]; the structure of these samples is essentially the same as those used for IETS (Fig. 1) except that no dc bias is applied.

MRAIRS measurements were performed with a modified attenuated total reflection accessory manufactured by Specac, Ltd. [16,17]. A Mattson Cygnus 100 model 7020A FTIR spectrometer with a liquid-nitrogen-cooled narrow band MCT detector was used [10].

3. Results and discussion

All IET spectral intensities shown in comparison to MRAIR spectra in the following figures (4 and 6) have been scaled down by a factor of 10^4, and peak positions have been corrected for the lead superconducting energy gap by subtraction of 8 cm^{-1}.

IET spectra obtained for pyruvic acid (PA) and 2-KBA are shown in Figs. 2(a) and (b), respectively. The PA spectrum does not exhibit peaks from the internal carbonyl, which usually appear in the range 1660–1780 cm^{-1} [5,18]. The peak at 1605 cm^{-1} corresponds to the asymmetric carboxylate (CO_2^-) stretching mode, while the symmetric stretching mode appears at 1450 cm^{-1}. The 2-KBA spectrum, however, shows a peak
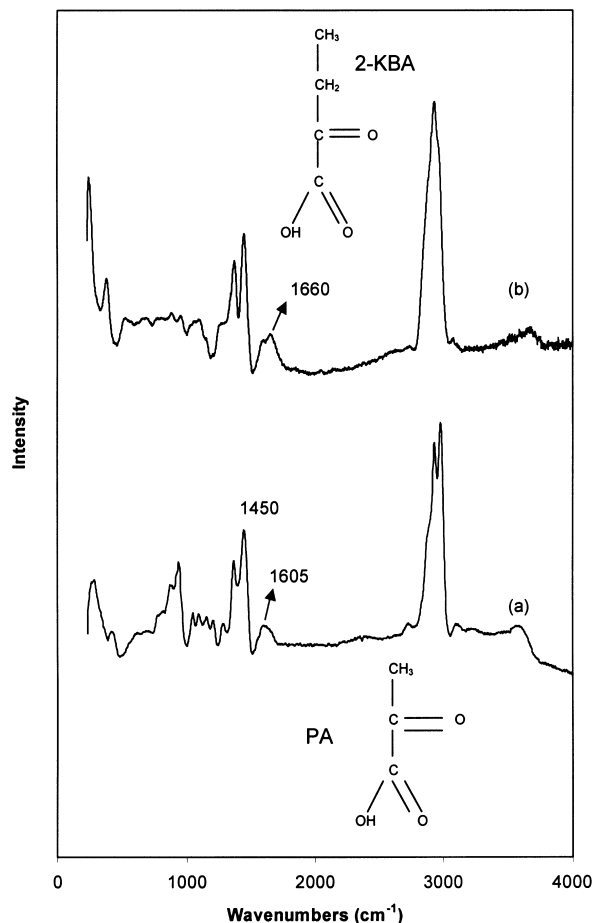
Fig. 2. IET spectra for (a) PA and (b) 2-KBA (2 g/l solution in ethanol). The schematic structures are shown in inset.

Fig. 3. MRAIR spectra for 2-KBA (2 g/l solution in ethanol) for samples prepared with and without a lead cover film.

at 1660 cm^{-1}, which is distinct from the asymmetric carboxylate stretching mode, and is attributed to the internal carbonyl. From the idealized representation of the 2-KBA and PA molecules (inset in Fig. 2), one would expect that for the acids chemisorbed on the alumina surface by the carboxylate anion as shown in Fig. 1, the internal carbonyl for 2-KBA would be, on average, further away from the lead cover film and would interact less strongly with it as compared to the internal carbonyl of the PA sample. Steric hindrance and deformation of the PA layer due to the lead cover film would render the internal carbonyl IETS inactive due to the orientational selection rule (explained later in this section). However, for 2-KBA, the carbonyl mode would be suppressed to a lesser extent, and hence would be expected to appear in the vibrational spectrum. Confirmation of the interaction of the internal carbonyl with the lead cover film is obtained from the comparison of MRAIR spectra obtained for samples prepared with and without a lead cover film. Fig. 3(a) is the MRAIR spectrum for 2-KBA with a lead cover film, while Fig. 3(b) is the one obtained without one. Without a lead cover film, the carbonyl mode exhibits the most intense peak in Fig. 3(a), which appears at
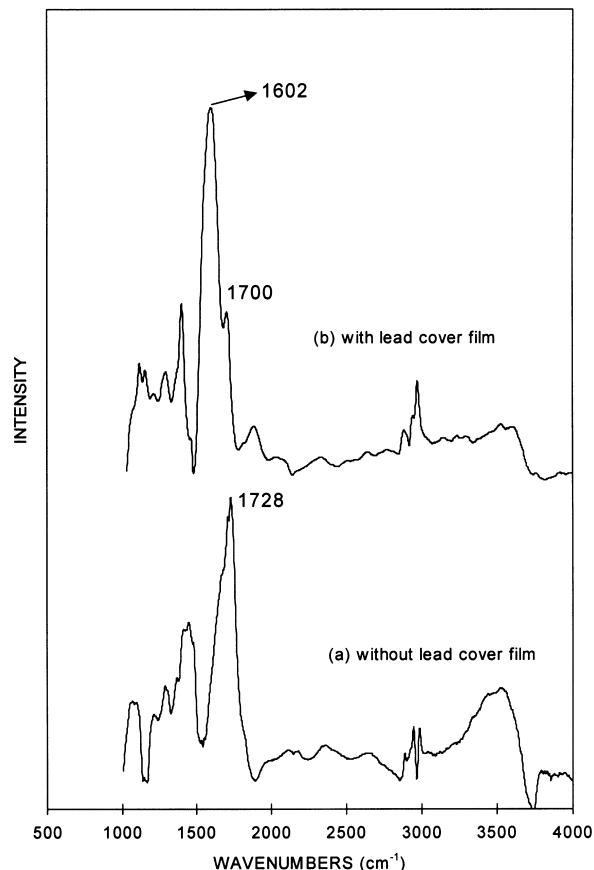
1728 cm^{-1}. Fig. 3(b) however, shows a reduction in the relative intensity of this mode (now at 1700 cm^{-1} due to the presence of the lead cover film.

For comparison, the IET and MRAIR spectra (obtained with samples prepared with a lead cover film) of 2-KBA are shown in Fig. 4. The internal carbonyl absorption is seen at 1700 cm^{-1} in the MRAIR spectrum shown in Fig. 4(a), while in the IET spectrum, Fig. 4(b) this appears at 1660 cm^{-1}. A comparison of Figs. 4(a) and (b) show another interesting feature. The C–H stretches appear as the strongest peaks in the IET spectrum, while they are extremely weak in the MRAIR spectrum. This has been attributed to the different scattering mechanisms involved [19]. Dipole scattering is responsible for the infrared spectrum while both dipole and impact scattering are possible for the IETS. (Similar behavior of the C–H stretches is observed in the comparison of the IET and MRAIR spectra for 4,6-DOHA [Figs. 6(a) and (b).] Figs. 4 and 6 illustrate the sensitivity of IETS for probing hydrocarbon modes).

One might expect the MRAIR spectrum of 4,6-DOHA on alumina to show strong carbonyl absorbances due to the presence of the two internal carbonyls within the
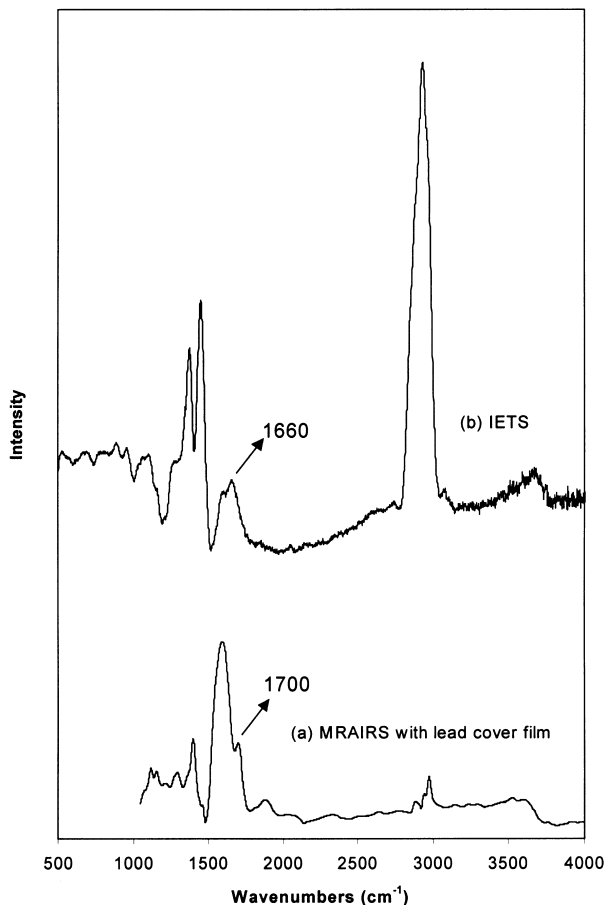
Fig. 4. Comparison of the MRAIR spectrum for sample prepared with a lead cover film with the corresponding IET spectrum for 2-KBA.

Fig. 5. MRAIR spectra obtained for 4,6-DOHA for samples prepared with and without a lead cover film.

molecule. However, as can be seen from Fig. 5(a), there is only one very weak carbonyl peak occurring at $1718 \, \text{cm}^{-1}$ in the spectrum obtained from the sample without a lead cover film. We believe that this may be due to canting or tilting over of the molecule at the surface. This would result in the internal carbonyls (in a *trans* configuration with respect to each other) being approximately parallel to the surface. Rotation of the internal carbonyls about the molecular axis would be hindered by proximity to the alumina surface, such that both groups would remain approximately parallel to the surface. A similar orientational preference exists for IR spectroscopy such that vibrational modes which result in dipole moment changes parallel to the surface would be infrared inactive. Therefore, low intensities would be predicted for the internal carbonyls in this case [20]. Even without a lead cover film the carbonyl mode is very weak in the MRAIR spectrum.

Evidence for the canting of the molecule described above can be obtained by observation of the asymmetric carboxylate (CO_2^-) stretch, which exhibits a very intense peak at $1600 \, \text{cm}^{-1}$. The asymmetric CO_2^- stretch is
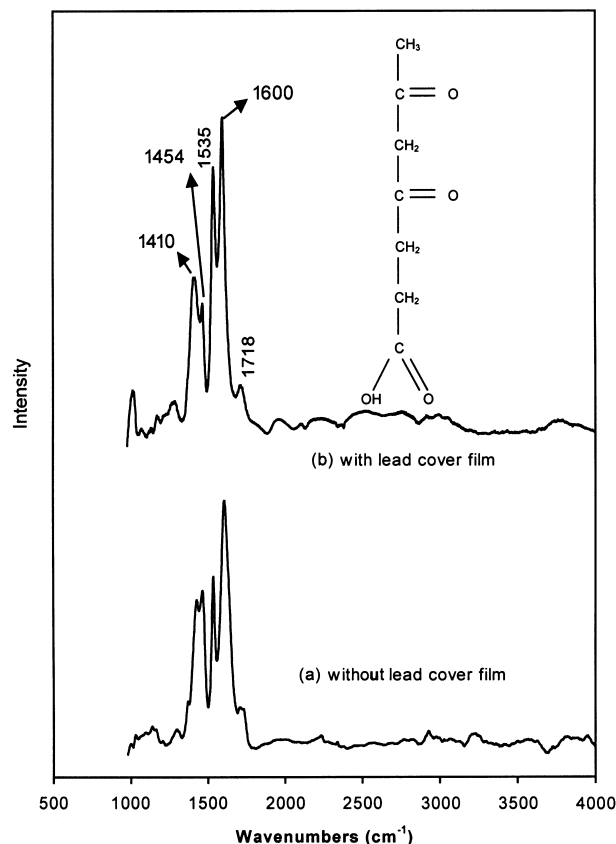
a mode whose dipole moment usually changes parallel to the surface; therefore it is usually weak in MRAIR spectra as compared with the symmetric CO_2^- mode appearing at $1410 \, \text{cm}^{-1}$ (whose dipole moment changes normal to the surface). The high intensity of the asymmetric CO_2^- stretch therefore indicates canting of the molecule at the alumina surface.

Fig. 5(b) shows the MRAIR spectrum of 4,6-DOHA obtained from a sample prepared with a lead cover film; this spectrum is observed to be similar to the spectrum obtained from a sample without one. The effect of the lead cover film on the internal carbonyl peaks is difficult to ascertain; however, its effect can be seen for other peaks in the spectrum. There is a reversal of relative intensity of the peaks at 1410 and $1454 \, \text{cm}^{-1}$ (these peaks are also diminished in intensity as compared to the peak at $1535 \, \text{cm}^{-1}$). The peak at $1454 \, \text{cm}^{-1}$ can be attributed to deformation modes of the methylene group situated in between the two carbonyl groups as shown in Table 1(c). This peak is shifted to higher wavenumbers due to the inductive effect of the two carbonyl groups [5], whereby electron density is drawn away from the C–H bonds of the methylene group, increasing the force constant of the bond and hence its frequency of absorption. The
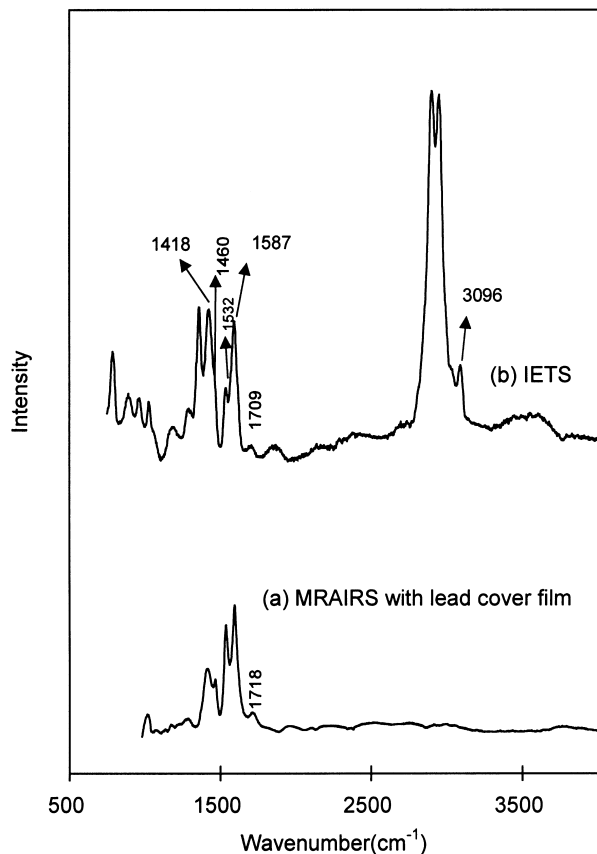
Fig. 6. Comparison of MRAIR spectrum for sample prepared with a lead cover film with the corresponding IET spectrum for 4,6-DOHA.

peak at 1535 cm^{-1} can be attributed to skeletal modes of the molecule or CH_3 deformation modes [5,20]. These are strained by the presence of the lead cover film.

The MRAIR spectrum of 4,6-DOHA (with a lead cover film) in Fig. 6(a) is now compared with the accompanying IET spectrum in Fig. 6(b). The very weak carbonyl absorption appearing at 1709 cm^{-1} and the strong asymmetric CO_2^- stretch absorption at 1587 cm^{-1} in the IET spectrum indicate canting of the molecule at the alumina surface, as indicated earlier with respect to the MRAIR spectra in Fig. 5. The inductive effect of the two carbonyl groups on the methylene group separating them can be seen through the C–H deformation mode at 1460 cm^{-1} (appearing as a shoulder on the symmetric CO_2^- peak at 1418 cm^{-1}) and a C–H stretching mode appearing at 3096 cm^{-1}, both of which are shifted to higher wavenumbers than are usual for alkanes. Once again, the hydrocarbon modes are much stronger in the IET spectrum for reasons described earlier.

Turning to a more generalized discussion, several factors must be considered in the interpretation of the intensities of vibrational modes in IETS. Most interpretations are based on what may be loosely called the orientational selection rule mentioned earlier. This term stems from theoretical predictions that the square of the angle averaged matrix element for inelastic tunneling for dipoles oriented perpendicular and parallel to the plane of the junction is dependent on the dipoles' position within the barrier [4]. For dipoles oriented perpendicular to the plane of the junction, the square of the matrix element is greatest at the edges of the tunnel barrier (next to the metal electrodes), smoothly decreases in magnitude deeper into the barrier, and averages to zero at its center [18]. However, for dipoles oriented parallel to the plane, the result is qualitatively reversed, and the square of the matrix element is greatest at the center of the barrier and averages to zero at the edges. In most experimental situations (as is the case in the present work) the dipoles under investigation are contained within molecular adsorbates on alumina. Under these conditions the dipoles are clearly in close proximity to the top (lead) electrode, and therefore the corresponding inelastic peaks will be strongest for dipoles oriented perpendicular to the plane of the junction, and weakest for those oriented parallel. For small molecules the "orientational selection rule" may be invoked to infer the relative orientation of dipoles within the molecule with some confidence. However, care must be taken in the use of the orientational rule for the interpretation of peak intensities. Other factors, which must be examined, are those due to steric effects, which will become particularly noticeable for larger molecules. For example, interactions between dipoles and the top electrode, inter- and intra-molecular interactions involving the dipoles in question, and fractional surface coverage of the adsorbate will all affect dipole orientation. (We report in the third article in this series [12] the effect of fractional surface coverage, but we note here that a low surface coverage results in a greater range of possible geometrical configurations for adsorbate molecules, and hence a greater range of dipole orientations.)

Returning to the case of 4,6-DOHA, we believe that partial penetration of the top (lead) electrode into the adsorbed 4,6-DOHA molecular layer causes canting of these longer chain molecules such that the orientation of the carbonyl groups renders them relatively inactive in IETS. This explanation is based upon our previous observations on the spectrum of pyruvic acid on alumina [10] and those of other workers [21,22] of the effects of various cover films (lead, aluminum, and tin). Most IETS work is done with lead as the cover film, since lead is relatively inert and has a larger atomic radius; hence, lead does not react with the adsorbed monolayers and will not usually completely penetrate the layers to come into contact with the underlying alumina, unless low surface coverages are employed that leave sufficiently large voids in the monolayers where penetration may occur. These conditions are discussed in detail elsewhere [12].

4. Conclusions

Deformation of the molecular structure due to interactions between the lead cover film and the adsorbed molecular layer in both IETS and similarly prepared MRAIR samples is demonstrated for 2-KBA and 4,6-DOHA. The internal carbonyl of 2-KBA is situated further away from the lead cover film as compared with the internal carbonyl of PA and produces a weak absorption in both MRAIRS and IETS (this carbonyl produces a very strong absorption in MRAIR spectra when no lead cover film is present). For the case of PA, the internal carbonyl absorption is strong in the MRAIR spectrum, when no lead cover film is used, but is absent in the MRAIR spectrum obtained from a sample with a lead cover film. The absorption is also absent in the IET spectrum.

Contrary to expectations, the carbonyl absorption is very weak for 4,6-DOHA in both MRAIR and IET spectra. This can be attributed to canting of this longer chain molecule at the alumina surface. Further evidence for this canting can be found from the strong symmetric and asymmetric CO_2^- absorption peaks, whose relative intensities in the said configuration are in qualitative agreement with the orientation selection rules for IETS and MRAIRS. The results of the present work indicate that the effect of the lead cover film on molecular orientation must be considered in the interpretation of IET and MRAIR spectra of molecules containing carbonyl groups.

The technique of IETS is more sensitive to certain vibrational modes such as the C–H stretching and deformation modes as compared with MRAIRS, whereas the latter technique yields very strong intensities for the carbonyl group as compared with IETS. This is due to the different scattering mechanisms involved in these techniques. Inspite of these differences, data obtained from both techniques must be studied in order to better understand the orientation of molecular adsorbed layers at oxide surfaces.

References

[1] Lambe J, Jaklevic RC. Phys Rev 1967;165:821.
[2] Hansma PK. In: Hansma PK, editor. Tunneling spectroscopy, capabilities, applications, and new techniques. New York: Plenum Press, 1982. p. 1–39.
[3] Gadzuk JW. In: Yates Jr JT, Madey TE, editors. Vibrational spectroscopy of molecules on surfaces. New York: Plenum Press, 1987. p. 49–99.
[4] Walmsley DG, Nelson WJ. In: Hansma PK, editor. Tunneling spectroscopy, capabilities, applications, and new techniques. New York: Plenum Press, 1982. p. 311–57.
[5] Sondag AHM, Raas MC. Appl Spectrosc 1989;43:107.
[6] Silverstein RM, Bassler GC, Morrill TC. Spectrometric identification of organic compounds. New York: Wiley, 1991. p. 91–133.
[7] Banwell CN. Fundamentals of molecular spectroscopy, 2nd. New York: McGraw-Hill, 1972.
[8] Comyn J, Horley CC, Mallik RR, Pritchard RG. Int J Adhesion Adhesives 1986;6:73.
[9] Mallik RR, Pritchard RG, Horley CC, Comyn J. Polymer 1985;26:551.
[10] Devdas S, Mallik RR, Coast R, Henriksen PN. Surf Sci 1995;326:327–34.
[11] Devdas S., Mallik R.R., Paper II, Int J Adhesion Adhesives 2000;20(5):349–53.
[12] Devdas S., Mallik R.R., Paper III, Int. J. Adhesion Adhesives 2000;20(5):355–59.
[13] Korman CS, Coleman RV. Phys Rev B 1977;15:1877.
[14] Wang Y, Mallik RR, Henriksen PN. Rev Sci Instrum 1993;64:890.
[15] Jaklevic RC. In: Hansma PK, editor. Tunneling spectroscopy, capabilities, applications, and new techniques. New York: Plenum Press, 1982. p. 452–3.
[16] P/N 11000-1, Graseby Specac, Inc., 301 Commerce Drive, Fairfield, CT 06003.
[17] Touwslager F.J. Philips Research Laboratory, P. O. Box 80 000, 5600 JA, Eindhoven, The Netherlands, private communication.
[18] Kirtley J, Hall JT. Phys Rev B 1980;22(2):848.
[19] Dubois LH. In: Hansma PK, editor. Tunneling spectroscopy, capabilities, applications, and new techniques. New York: Plenum Press, 1982. p. 168–73.
[20] Lin-Vien D, Colthup NB, Fately WG, Grasselli JG. In: The handbook of infrared and raman characteristic frequencies of organic molecules. New York: Academic Press, 1991. p. 117–42.
[21] Gauvin S, Leblanc RM. Thin Solid Films 1992;210:508.
[22] Sleigh AK, Taylor ME, Adkins CJ, Phillips WA. J. Phys: Condens Matter 1989;1:1107.