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Bias-polarity-dependent effects on the OH vibrational mode energy in Al–AlO_x–metal tunnel junctions

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Abstract. The shift in position on bias reversal of the 450 meV OH mode in tunnel junctions comprised of aluminium/aluminium oxide/M where M is Pb, Ag and Sn is investigated using inelastic electron tunnelling spectroscopy.

Measurements presented here reveal that the peak shift is independent of M within the experimental error of this work. This is consistent with a simple superposition of the three electric fields acting on the hydroxyl group due to the tunnel barrier, the image charge and the external bias respectively. The implication is that as far as the subtle effect of peak shifts on reverse bias is concerned, the tunnel junction environment of the adsorbed species is essentially benign.

For certain electrode thicknesses and geometries, peak shifts can arise due to finite electrode resistance even when four-point probe conditions pertain. A simple procedure for treating these is presented.

1. Introduction

The technique of inelastic electron tunnelling spectroscopy (IETS) [1–3] allows the vibrational states of molecules located in a tunnel junction, in the energy range 50–500 meV, to be probed.

It is important to realise that incorporated molecules are under the influence of three fields, (i) from the barrier structure, (ii) from the image charges and (iii) from the applied bias.

Using typical values for barrier heights and the distance of the proton in OH from the top electrode together with an expression for image potential [4], the relative orders of magnitude of these three fields are readily shown to be 10^{10} V m⁻¹ for (i) and (ii) and 10^8 V m⁻¹ for (iii). This clearly shows that in the case of the proton of an OH group, both the barrier and image contributions to the resultant field are considerably greater than that arising from the applied bias.

As IETS has progressed and measurements have been refined to the current level (mode energies can now be reproducibly measured to within ± 0.03 meV in 150 meV), subtle effects have emerged. Recent work [5] has highlighted the role of the electric field within the junction, suggesting that it interacts via anharmonic effects to perturb the vibrational frequencies of adsorbed molecules. Other workers have examined the effect of image charges in the metal electrodes of the junction on peak positions [3] and significant peak shifts due to the nature of the metal in the top electrodes have also been

reported [6–8]. It is clear that there is a need to distinguish these effects from the equally important peak shifts associated with the chemical aspects of the adsorption of dopant molecules to the oxide surface [9–11].

It is also important to recognise that the potential barrier associated with the metal oxide work functions produces a significant electric field at a dopant molecule as does the image charge. The net electric field referred to above can be varied in two ways. The first is by alteration of the potential barrier associated with the metal oxide work functions by the use of different metals as counter-electrodes. The second approach is a simple reversal of the applied bias for a given top electrode.

The main aim of this work is to extend previous measurements on reverse-bias peak shifts [5] to include different top-metal electrodes. These data are then used to examine the relative roles of the electric field contributions outlined above.

Measurement of the vibrational modes with the optimum precision requires careful design of the tunnel junction geometry even when four-point-probe measurement techniques are employed [5, 12]. Care must be taken to avoid the finite electrode resistance causing unwanted potential variations along the electrode material forming the actual junction area. As a precursor to the main work, the small shifts in peak position and peak broadening caused by electrode resistance were isolated and a simple correction procedure employed.

2. Experimental details

2.1. Sample preparation

The preparation of tunnel junctions essentially similar to those used in this work have been described in detail [13]. However, as discussed below, modifications to the geometry have been introduced. These facilitate both measurement of the top- and bottom-electrode resistance and simultaneous four-point-probe IETS at 4.2 K.

2.2. Junction fabrication

The procedures referred to in § 2.1. were followed for junctions with lead and tin top electrodes but with silver as a counter-electrode it was necessary to employ different techniques.

Junctions with silver top electrodes proved initially to be very unreliable, exhibiting breakdown below 250 mV, and excessive noise or no OH peak at 450 mV. A subsequent private communication from Professor P K Hansma suggested the use of a lower evaporation rate for the aluminium and thermal oxidation at temperatures higher than ambient (instead of plasma glow discharge) together with thinner top electrodes. The adoption of these procedures resulted in silver junctions having greater reproducibility and reliability.

2.3. Instrumentation and accuracy

The spectrometer used in this work developed by Oxley [13] with improvements by Reynolds and co-workers [14, 15], was recently reviewed by Reynolds [5] where it was shown for the first time that subtle peak shifts of 0.39 meV in the OH mode of the benzoate ion were resolved with an accuracy of ± 0.02 meV.

3. Results and discussion

3.1. Notation

In this paper forward and reverse bias refer to the counter-electrode being biased positively and negatively with respect to the aluminium bottom electrode respectively. The peak shift, ΔV , is the numerical difference between the measured position of a given peak under forward bias and its position under reverse bias.

3.2. Electrode resistance effects

In order to understand fully the conditions under which one may be confident that electrode resistances are not significant, a series of experiments were performed using Al–AlO_x–benzoate–Pb junctions in which the resistance of the Al bottom electrode can be varied in a systematic way by altering its thickness.

These experiments establish clearly that even when four-point-probe measurements are used, it is necessary to be aware of the effects of parasitic potential variations along the electrode material forming the actual junction area. For the reasons outlined in § 2.2, Al–AlO_x–Ag junctions had thin top electrodes. It was thus necessary to perform these initial experiments to establish a criterion by which the spectra obtained from junctions with silver top electrodes could be corrected.

The importance of this is illustrated in figure 1 which presents a detailed examination of the normal mode of the 198.3 meV peak in the benzoate spectrum, where the mode is substantially down-shifted and broadened when the Al electrode is reduced in thickness below the normally used level of 300 nm. A relatively straightforward model given in § 3.3 allows one to establish criteria that allow such effects to be avoided.

3.3. Resistive errors

In the context of § 3.2 above the junctions used for this study are cross shaped, the electrodes being evaporated at right angles to each other. Following the simplification used by Giaever [16] the analysis here uses a linear configuration as a convenient approximation. An examination of figure 2 will show that the currents and voltages along the electrodes will be functions of position. Because the voltmeter and power supply are connected to opposite ends of the electrodes forming the junction, the voltmeter will indicate a measured voltage that is less than that applied. As a consequence of this the vibrational modes will appear to be initiated at apparently lower applied biases and a related commensurate line broadening occurs.

It is convenient to begin with the case where the top electrode is superconducting and of width W and the bottom electrode of length W has resistance R_B . Then a detailed treatment following Giaever shows that the corresponding shift ΔV_p in peak position is given by

$$\Delta V_p = IR_B/2 = (V/2)R_B/R_t$$

where R_t is resistance of the junction. ΔV_p is thus readily obtained from simple measurements of R_B and R_t . Since the intrinsic accuracy of our measurements requires that $\Delta V_p/V < 0.03/200$ a small calculation shows that aluminium electrodes at least 300 nm thick are required.

In the case of two non-superconductors, similar algebra shows that the effects of the individual electrodes are additive—for example, using an aluminium top electrode

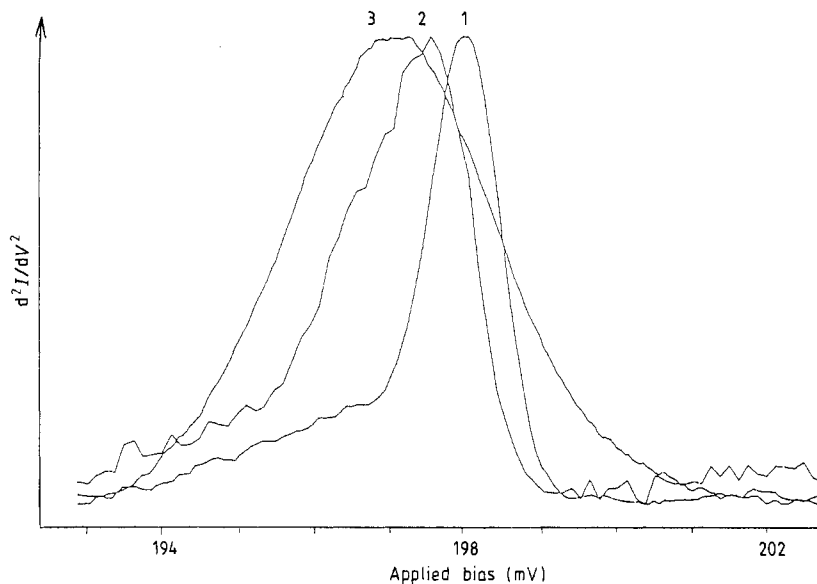


Figure 1. IET spectra of the 198 meV region of the benzoate spectrum, for three thicknesses of the bottom electrode, with the top electrode biased positively. All the spectra were obtained at a junction temperature of 4.2 K, and at a modulation amplitude of 1.0 mV. A smooth background, corresponding to the change in elastic conductance with applied bias voltage, has been subtracted. A downward shift of 2.4 mV occurs when the thickness of the electrode is reduced from 548 nm to 21 nm. Key to peak numbering:

Peak No	Electrode thickness (nm)	Position (mV)
1	548	198.3
2	80	197.7
3	31	196.4

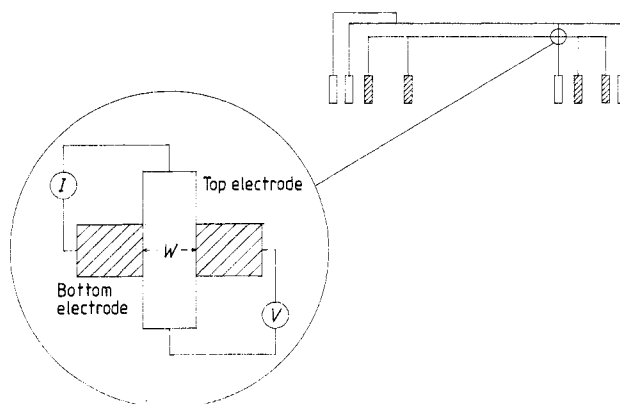


Figure 2. A schematic diagram of an undoped junction (modified mask design). The currents and potentials will be functions of position along the junction when the electrodes are not superconducting.

Table 1. Results for the 450 meV peak. Forward bias and reverse bias refer to the counter-electrode being biased positively and negatively with respect to aluminium. ΔV refers to the numerical difference in peak position, for a given peak, under forward and reverse bias.

Counter-electrode	Forward bias (mV)	Reverse bias (mV)	ΔV (mV)	Kirtley and Hansma (mV)†
Pb	445.6 ± 0.1	447.8 ± 0.1	2.2 ± 0.2	446
Sn	444.3 ± 0.1	446.4 ± 0.1	2.1 ± 0.2	444
Ag‡	435.3 ± 0.5	438.2 ± 0.5	2.9 ± 1.0	438

† Forward bias only.

‡ As seen in § 2.2, the use of silver as a counter-electrode material necessitated adopting different manufacturing procedures for the junctions, which resulted in thinner top electrodes. This has the effect of introducing an error due to the resistance of the electrodes. This is treated using the procedures of § 3.2 and yields $\Delta V_p = 2.7$ mV which when added to the forward-bias result gives 438.0 mV in good agreement with [6], § 3.4.

instead of lead at 4.2 K would double the resistive effect on the peak shift. When using silver as a counter-electrode material thinner films were deposited (§ 2.2). The error due to these thinner electrodes is treated using the procedures outlined above.

It is interesting to note at this juncture that Kirtley and Hansma (KH) [6], using different metals as top electrodes, found a strong correlation between peak position and widths for the OH and OD stretch modes in Al–AlO_x–Pb junctions.

It might be envisaged that this correlation is due to a resistive effect since their results are quoted for electrodes approximately 200 nm thick. However, they found no thickness dependence of the effect they observed, and thus their shifts cannot be explained by the effects discussed in § 3.3. But, for given tunnel junction and bottom electrode materials and thicknesses, it is readily shown that ΔV_p is proportional to W^2 . The electrodes used by KH [6] were 140 μm wide compared with ours which were 500 μm wide. This would indicate that the expected resistive shift of KH would be of the order of a twelfth of those in this study.

This confirms that the resistive effects in the shifts reported by KH would have been outside the resolution of their experiments.

3.4. Top-metal and polarity effects in undoped junctions

Table 1 lists the results from a series of experiments conducted on Al–AlO_x–M tunnel junctions, where M = Pb, Sn, Ag. This table brings together the work of two other groups. KH [6, 7] investigated the effect on the position of the OH peak at 450 mV of using metals other than lead as a top electrode under forward-bias conditions and Reynolds and co-workers [5], revealed a small, polarity-dependent shift on the position of the 144 mV peak in the benzoate spectrum using a lead top electrode, this result being in agreement with similar work on OH at 450 mV by Adkins and Sleigh [4].

By repeating the work of KH and then extending the investigation to incorporate junctions under reverse bias, this study investigates the effect of the metal used as a counter-electrode on the polarity shift of the 450 mV OH peak.

Adkins and Sleigh [4] by assuming, in line with other workers, that the component of the potential of the oscillating system due to the applied field as a linear form, obtained

an expression for the top-electrode shift in terms of the interaction of the molecular system with its electrical image:

$$\Delta\omega/\omega_0 = -(q^2/16\pi\epsilon_r\epsilon_0d^3m\omega_0^2)(1 + \frac{3}{2}d\beta). \quad (1)$$

Here, m is the mass of the proton in the OH group, q is the partial charge on the atom of the adsorbed species, d is the distance from the terminal hydrogen to the top electrode and β is a constant equal to $\omega_0\sqrt{m/2D}$ where D is the dissociation energy and ω_0 is the frequency of the unperturbed system.

A corresponding expression was obtained by KH [6] in their analysis.

Examination of equation (1) shows that because the last term in the second parentheses has a value of approximately eight, this term dominates and thus the frequency shift is seen to have a $1/d^2$ dependence on d . This would have the effect of producing changes of a few per cent in peak position, a result borne out by the present experiments.

Data from the present work are shown in table 1: columns 2 and 5 show that there is a close correlation between the forward-bias results of our work and the data from KH's experiments. Clearly shown is the downward shift in peak position observed when different metals other than lead are used as top electrodes.

The approximation of regarding the electric field acting on a dopant molecule as arising merely from the external bias applied to the junction would appear to be an oversimplification since it is located in a region where one might expect the potential near the edge of the barrier to vary rapidly. The use of different top-metal electrodes should offer a means of modifying this latter contribution. However, if a simple superposition of the three field contributions is assumed one would predict that the peak shift on reversing the applied bias should be relatively insensitive to top-metal material. This is borne out by the results of the present work; examination of column 4 in table 1 shows that the shift due to reverse-bias polarity is insensitive to the metal used to form the top electrode, within the errors of our experimental work.

A comparison of the molecular and image potentials, in this simple one-dimensional model, will show that the spatial variation of the force due to the molecular potential is always much greater than the restoring force due to the image potential. By selecting the dominant terms, Adkins and Sleigh obtained an expression for the polarity shift:

$$\Delta\omega_{\text{polarity}}/\omega_0 = 3q\hbar\beta\gamma/2em\omega S. \quad (2)$$

Here $\gamma = \epsilon_1S/(\epsilon_1S_2 + \epsilon_2S_1)$ is the factor by which the field in the adsorbate exceeds the mean field across the barrier. The permittivities of the oxide and the adsorbate are respectively ϵ_1 and ϵ_2 ; S , S_1 and S_2 are the thicknesses of the tunnel barrier, oxide and the adsorbate respectively and ω is the measured frequency.

By considering equation (2), we see that it is unlikely that any of the parameters other than γ and S could be affected by changing the top metal; ω is determined by experiment and β is a constant from the Morse potential:

$$U_0 = D(1 - e^{-\beta x})^2.$$

Also q is given the value of free OH in this case following Adkins and Sleigh.

The total thickness S is the sum of S_1 and S_2 , and incorporated into S_2 is d , the distance of the top hydrogen to the metal surface. Thus it can be seen that the polarity shift is weakly dependent upon d through γ .

Using observed frequency shifts and assuming a value for d , Adkins and Sleigh calculated a value for q/e . In the case of lead the value selected for d was 200 pm, which corresponds to a figure slightly larger than the radius of a lead atom. The figures $S_1 =$

Table 2. Calculated variations in the peak shift, calculated for three values of the atomic radius.

Top metal	γ	$ \Delta V /(\text{mV})$
Pb	4.7	2.2
Ag	4.99	2.34
Sn	5.04	2.36

2 nm, $S_2 = 0.2$ nm, $\epsilon_1 = 7.6$, $\epsilon_2 = 1$, $h\omega = 450$ meV and $\Delta\omega = 1.1$ meV gave a result of -0.32 for q/e compared with -0.2 in the case of free OH [17].

The radii of tin and silver atoms are smaller, that of tin being 140 pm and that of silver being 144 pm, which raises the question of whether or not using these metals as counter-electrodes would reduce the value of d from that of the lead value and thus change the peak shift by an observable amount.

Handy [18] found that smaller metal atoms gave thinner effective barriers, suggesting that the smaller atoms penetrated further into the oxide. This would have the effect of reducing d in our simple model, which would increase γ and therefore $\Delta\omega$. In this study we have assumed that d would be, in each case, rounded up to a value slightly above the radius of the atoms of the metal used as a counter-electrode in line with the assumption above. The validity of this assumption is, perhaps, questionable but since the whole area of theoretical calculation of charge distribution is somewhat unreliable the assumption is as good a starting point as any to provide order-of-magnitude comparisons.

We substitute values of $d_{\text{Ag}} = 155$ pm and $d_{\text{Sn}} = 150$ pm to give $q/e = -0.28$ for silver and $q/e = -0.27$ for tin. The results compare well with the calculated value of -0.2 cited above but, given the unreliable nature of calculating charge distribution and the low signal-to-noise ratio for the OH mode, it would be naive to draw exact conclusions from these results.

By substituting the values for the radii of the atoms of the various metals used as counter-electrodes, ΔV can be calculated roughly. The results of these calculations are listed in table 2. An examination of column 3 in table 2 shows that the calculated variation in peak shift will not be resolved in this work. A maximum variation between lead and tin of 0.16 mV is calculated, compared with errors of ± 0.2 mV in the experimental results listed in Table 2.

It may prove more advantageous with such small shifts to focus attention onto other, better resolved peaks. The 144 mV peak in the benzoate spectrum, for example, has been shown to exhibit a small shift on polarity change [7]. A detailed study, using different top electrodes, of both the normal and deuterated form of the benzoic acid spectrum, may provide the data that will pinpoint any differences in polarity shift caused by the use of different top-metal electrodes.

4. Conclusion

Examination of the peak shift of the 450 meV OH mode on reversing the applied bias reveals that any dependence on the nature of the top-metal electrode used is too small to be revealed with the accuracy of the present work. This is in accordance with existing

theoretical work and of related interest is the result that we can treat the relatively large and non-uniform barrier and image contributions to the resultant field by superposition with the applied field and show that the effect of the former two upon bias reversal is negligible. Thus, in quite subtle ways, the tunnel junction environment remains benign in so far as the vibrating species are concerned.

Calculations of the ratio q/e for the hydroxyl group on alumina within a tunnel junction performed originally by Adkins and Sleigh for a lead top electrode have been extended to include other electrode materials. The results are again roughly consistent with those obtained for free OH by other workers.

The ratio of width to thickness of the electrodes in IET junctions is shown to influence both the apparent position and breadth of spectral lines. This phenomenon is a result of finite electrode resistance and can be significant even when four-point-probe conditions pertain. A simple treatment after Giaever allows such effects to be corrected for even when they are difficult to avoid experimentally.

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References

- [1] Lambe J and Jaklevic R C 1968 *Phys. Rev.* **165** 821
- [2] Jaklevic R C and Lambe J 1966 *Phys. Rev. Lett.* **17** 1139
- [3] Scalapino D J and Marcus S M 1967 *Phys. Rev. Lett.* **18** 495
- [4] Adkins C J and Sleigh A K 1987 *J. Phys. C: Solid State Phys.* **20** 4037
- [5] Reynolds S, Peasgood A, Oxley D P and Pritchard R G 1987 *J. Phys. C: Solid State Phys.* **20** 4297
- [6] Kirtley J R and Hansma P K 1975 *Phys. Rev. B* **12** 531
- [7] Kirtley R J and Hansma P K 1976 *Phys. Rev. B* **13** 2910
- [8] Lambe J and Jaklevic R C 1968 *Phys. Rev. B* **5** 821
- [9] Hair M L 1967 *Infrared Spectroscopy in Surface Chemistry* (New York: Dekker) p 141
- [10] Bowser W M and Weinberg W H 1977 *Surf. Sci.* **64** 377
- [11] Gundlach K H and Kadlec J 1974 *Chem. Phys. Lett.* **25** 293
- [12] Tunncliffe D L 1983 *PhD Thesis* Leicester Polytechnic
- [13] Oxley D P, Bowles A J, Horley C C, Langley A J, Pritchard R G and Tunncliffe D L 1980 *Surf. Interface Anal.* **2** 31
- [14] Reynolds S 1983 *PhD Thesis* Leicester Polytechnic
- [15] Reynolds S, Gregson L D, Horley C C, Oxley D P and Pritchard R G 1980 *Surf. Interface Anal.* **2** 217
- [16] Giaever I 1969 *Tunnelling Phenomena in Solids* ed. E Burstein and S Lundquist (New York: Plenum) p 27
- [17] Lee T J and Schaefer H F 1985 *J. Chem. Phys.* **83** 1784
- [18] Handy R M 1962 *Phys. Rev.* **126** 1968