Effect of the second metal electrode on vibrational spectra in inelastic-electron-tunneling spectroscopy*

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(Received 24 February 1975)

Inelastic-electron-tunneling-spectroscopy experiments on the peak positions and bandwidths of the hydroxyl and deuteroxyl stretch bands for three different oxides and four different top metals are described. The bandwidths and peak positions depend on the top metal electrodes used. Two possible mechanisms for this effect, hydrogen bonding between the hydroxyl ions and the metal atoms, and an image-dipole model, are discussed. Order-of-magnitude estimates are made for the simple image-dipole model and compared with experiment.

I. INTRODUCTION

Inelastic-electron-tunneling spectroscopy[1-3] (IETS) is rapidly developing into a valuable tool for the vibrational spectroscopy of organic molecules.[4-9] It has been shown that tunneling spectra contain both infrared-active and Raman-active vibrational modes, with comparable intensities.[9] The agreement between the mode energies, as determined by tunneling, and the mode energies, as determined by infrared and Raman spectroscopy, has been, in general, good (e.g., to within 1 meV for all the modes of the benzoate ion on alumina[9]). This agreement is perhaps surprising when one considers that in the tunneling measurement the molecule is covered with an evaporated metal electrode.

In this paper we report the first systematic measurements of vibrational-mode shifts due to the evaporated top metal electrode. We have chosen the stretch modes of the hydroxyl and deuteroxyl ions adsorbed on aluminum and magnesium oxide as our model system, and studied the shifts and broadening due to four different top metal electrodes: The shift through the sequence Pb, Sn, Ag, Au was ≈ 3%, and the broadening was ≈ 50%.

Section II contains our experimental methods and results. Section III contains two possible theoretical explanations for the effect: (i) hydrogen bonding between the hydroxyl ions and the metal atoms, and (ii) an image-dipole model. The predictions of these models are compared with our experimental results.

II. EXPERIMENT

A. Methods

In our sample preparation, all metals used were high purity (at least 99.5%), and all evaporations were done at pressures below 5×10^{-5} Torr. We found that there was sufficient outgassing of water vapor from the vacuum system to supply the dopant for the hydroxyl ions. The deuterium-oxide vapor was introduced into the vacuum system through a leak valve by heating a $\frac{1}{4}$-in. glass tube filled with deuterium-oxide liquid. Film thicknesses were kept around 2000 Å, although no film thickness dependence of our effects was observed.

The samples were prepared using standard techniques. First, the bottom metal electrode was evaporated through an aluminum mask onto a glass slide from an electron-beam-heated source. Then the samples were oxidized either by heating them to 120 °C in an oxygen atmosphere for 10 min or by exposing them to a glow discharge for 20 min at 70-mTorr O_2 pressure. The slides were doped by introducing a saturated atmosphere of deuterium-oxide vapor for 5 min. The junctions were then completed with an evaporated top metal electrode. For the magnesium–magnesium-oxide–metal junctions, the substrates were cooled to liquid-nitrogen temperatures before completing the junctions. This helped to produce samples with resistances high enough to be usable.

Sample resistances ranged from 50 to 200 Ω for junctions 140 μm on a side, corresponding to resistivities of 1–4 Ω mm^2. The metals with large atomic volumes typically produced samples with higher resistances than those with smaller atomic volumes. However, there was sufficient variation in sample resistances that samples with different top metals, but about the same resistances, could be compared. This helped to check that our effects were not merely due to different degrees of resistive heating of the samples while traces were being run.

B. Results

Figure 1 compares the d^2I/dV^2 vs V traces[9] for magnesium–magnesium-oxide–metal junctions with lead versus gold top metal electrodes. Both the OH stretch mode at about 450 meV and the OD stretch mode at about 320 meV are clearly visible. The figure shows that the vibrational frequencies are shifted down and broadened for gold with re-
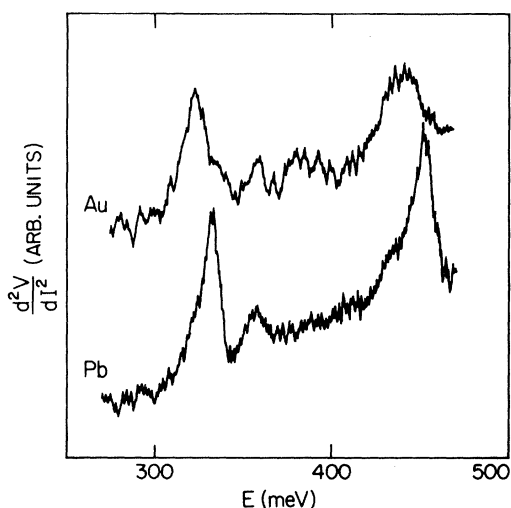
FIG. 1. Comparison of the inelastic electron tunneling spectra for magnesium–magnesium-oxide–metal junctions doped with water vapor and deuterium-oxide vapor, for lead vs gold top metal electrodes. Both the OH stretch mode at ~ 450 meV and the OD stretch mode at ~ 320 meV are visible. The bands are shifted down and broadened in energy for gold with respect to lead top metal electrodes.

spect to lead top metal electrodes.

Since there is as yet no satisfactory theory for the shape of the background curve, we simply drew a smooth curve for the baseline of our peaks. The background was subtracted from the trace by hand. Two parameters of the peaks of interest, the peak bandwidth and energy, were measured. The peak energy corresponded to the voltage at which the trace was highest after the background had been subtracted out. The bandwidth corresponded to the width of the trace where the amplitude was half of its maximum amplitude. The total instrumental broadening[6] was approximately 3 meV: $[(5.4kT)^2 + (1.22 \, eV_{mod})^2]^{1/2}$, where $T = 4.2$ K and $V_{mod} = 2$ mV. This was small compared to the observed bandwidths.

The results of our experiments are summarized in Table I. The standard deviations for the peak energies and bandwidths for the aluminum–aluminum-oxide–metal samples are approximately 3 meV, while those for the magnesium–magnesium oxide–metal sample are approximately 2 meV. The data in the table were compiled from measurements on roughly 50 individual junctions.

In examining our data, some qualitative observations can be made immediately. First, the peak energies depend on the top metal electrode used, the order of dependence being the same for all three classes of junctions. Second, as Fig. 2 shows, there is a strong correlation between the peak energies and bandwidths of our samples, the lower peak energies being associated with larger bandwidths. Third, the OH stretch mode band-

widths are always larger than those for the OD stretch modes.

In their original paper Jaklevic and Lambe[1] identified the band at 450 meV (3600 cm^{-1}) in their Al–Al-oxide–Pb junctions as due to the stretch vibration of hydroxyl ions. They verified this identification by adding deuterium oxide to their samples and noting the appearance of a new band with frequency nearly $1/\sqrt{2}$ of the old, as expected for an OD stretch. Geiger[10] went further and concluded that the band at 450 meV was due to free OH molecules adsorbed on the oxide. Klein[6] similarily concluded that the band near 450 meV for Mg–Mg-oxide–Pb junctions was due to free OH molecules, as opposed to hydroxyl ions implanted in the structure of the barrier oxide. Peri[11] has done computer models of the surface of hydrated γ alumina, and concluded that a structure in which a monolayer of hydroxyl ions occupy empty lattice sites on the surface of the aluminum oxide fits the infrared data.[12] Thus it seems reasonable to assume in our modeling that for both magnesium and aluminum junctions the hydroxyl ions occupy sites directly on the surface of the oxide. Our junctions then take the form of a multilayered sandwich: metal–metal-oxide–hydroxyl-ions–metal.

III. THEORY

A. Hydrogen bonding

With the hydroxyl ions in close proximity to the top metal electrode, two mechanisms for the shift-
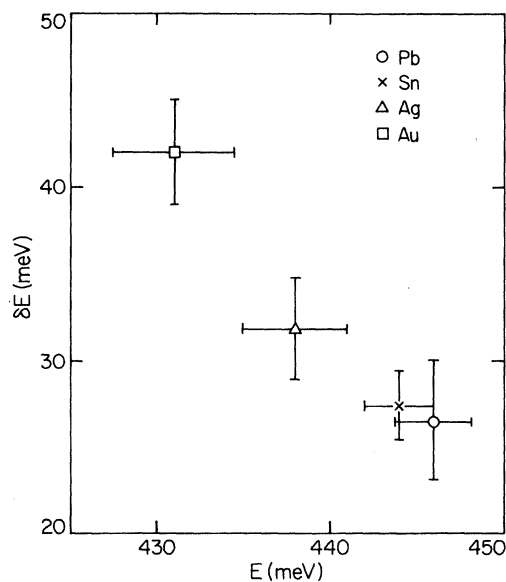

FIG. 2. Plot of peak position vs bandwidth (full width at half-maximum) for the OH stretch mode on aluminum oxide for four different top metal electrodes. Larger frequency shifts (to lower peak energies) are correlated with larger bandwidths.

TABLE I. This is a summary of the data obtained for the peak positions (E) and bandwidths (δE) of the vibrational stretch modes of hydroxyl and deuteroxyl ions doped onto thermal and glow-discharge oxides of aluminum and thermal oxides of magnesium, for four different top metal electrodes, using inelastic-electron-tunneling spectroscopy. (All energies in meV.)

Metal	Al–Al-oxide–metal junctions								Mg–Mg-oxide–metal junctions			
	Thermal oxide				Glow-discharge oxide				Thermal oxide			
	ν_{OH}		ν_{OD}		ν_{OH}		ν_{OD}		ν_{OH}		ν_{OD}	
	E	δE	E	δE	E	δE	E	δE	E	δE	E	δE
Pb	446	26.5	333	14.3	445	33.7	333	16.5	459	16.0	338	10.1
Sn	444	27.3	330	17.5	441	26.5	331	17.5	455	17.3	335	12.9
Ag	438	31.9	327	20.6	435	35.0	326	21.3	451	23.8	331	16.2
Au	433	41.9	322	27.5	431	50.0	319	25.0	445	24.8	328	18.2

ing and broadening of the hydroxyl stretch mode become apparent. The first is hydrogen bonding between the hydroxyl ion and the metal atoms. Such a bond would allow the metal to lower the electron density in the O-H bond, decreasing the bond strength and thus the frequency of the OH stretch mode. Hydrogen bonding has long been associated with a downward shift in the resonance frequencies of the chemical bonds involved in the hydrogen bond, a corresponding increase in the linewidth of these bonds, and an increase in the integrated intensities of their vibrational modes.[14] The good correlation between peak shifts and linewidths for our experiments satisfy the first two conditions. However, we were unable to determine whether the third condition (increased integrated intensity) was met. The difficulty lies in the fact that the amplitude of the spectral line in IETS is not easily related to the tunneling electron-dipole interaction cross section. This amplitude is proportional to the product of the number of impurities in the tunneling region times the cross section for the impurities.[3] But the number of impurities in the tunneling region is difficult to control. Geiger et al.[10] have done a study of the size of the impurity bands in aluminum–aluminum-oxide–metal junctions and found that the size of a band for a given quantity of impurities was directly related to the ionic radius of the top metal atoms. They concluded that smaller metal atoms diffused farther into the oxide, effectively excluding the impurities on the surface of the oxide from the tunneling region.

Further complicating the situation, the adsorbed hydroxyl ions could be expected to partially desorb during the evaporation of the top metal electrode. The combination of size-related impurity exclusions from the tunneling region and thermal desorption made it impossible to test for increased oscillator cross sections due to hydrogen bonding.

As a partial test of the hydrogen bonding hypotheses, however, we can compare the peak shifts and band broadening to the chemical properties of the top metal electrode. The Pauling theory of

metals[15] makes use of resonating valence bonds involving dsp hybrid orbitals. The bonds resonate since there are more nearest neighbors in the lattice than valence electrons. The strength of the bonds is related to the amount of d character they have, stronger bonds having a higher percentage d character. Higher percentage d characters have also been correlated with larger heats of chemisorption for hydrogen and ethane on metals,[16] and higher specific activities for hydrogenolysis on supported metal catalysts.[17] Both of these quantities are a measure of the strength of the interaction of the metal with hydrogen. Therefore we might expect the percentage d character to correlate with our peak energy shifts if they are due to hydrogen bonding between the metal and the hydroxyl group. Figure 3 shows a plot a peak position for the OH stretch mode on aluminum oxide for seven different top metal electrodes vs percentage d character assigned by Pauling.[15] The correlation is fair. While the connection between catalytic activity or heats of adsorption experiments and our measurements is by no means obvious, this correlation is at least suggestive.

B. Image dipole

A second possible mechanism for producing shifts and broadening in the hydroxyl stretching mode is an image-dipole effect. The physical idea is simple: an oscillating charge outside of a plane metal surface induces an image charge inside the metal. The attractive interaction potential between the charge and its image is proportional to $1/d$, where d is the separation between the charge and the surface of the metal. This attractive potential shifts the resonance frequency down. The correlation between peak shifts and broadening can be explained by assuming that the OH⁻ ions occupy inequivalent sites on the surface of the oxide. There is then a distribution in effective d's, with some of the ions being shifted more than others. The top metals that produce larger overall peak shifts can be expected to have larger distributions in peak
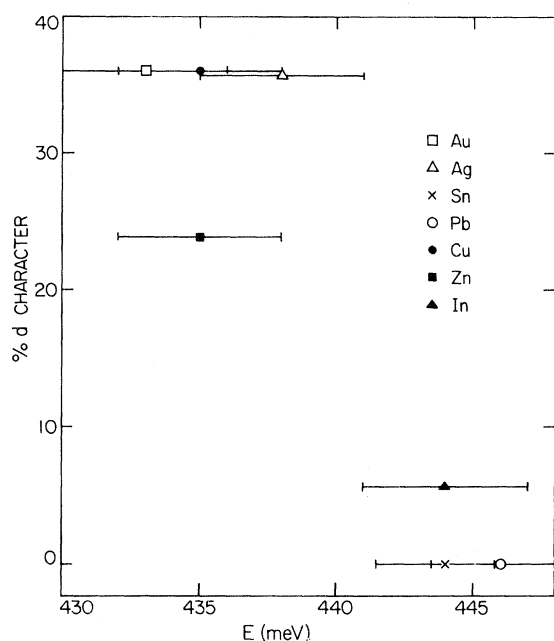
FIG. 3. Plot of percentage of d character in the electronic valence bands in the metal (from Pauling) vs peak position for the OH stretch mode on aluminum oxide for seven different top metal electrodes. Smaller percentage d characters are associated with smaller frequency shifts.

shifts and thus larger bandwidths. It follows that the peak shifts will be about the same size as the bandwidths, as can be seen from Fig. 2.

Although the physical ideas are simple, the detailed calculations are complicated and will not be attempted in this paper. Some order-of-magnitude calculations can, however, be made. Consider the simple model in which the oscillating dipole moment of the hydroxyl ion is replaced by a single charge q of mass M separated by an equilibrium distance d_0 from an infinite metal sheet. We assume that the charge is oscillating in a direction normal to the surface of the metal.[13] The exact orientation of the ion is not critical since the size of the effects calculated from our image-dipole model below fall off only as $\cos^2\theta$, where θ is the angle between the OH axis and the normal to the surface.

The oscillating charge induces an image of itself in the metal. An electrostatic calculation (valid since $\nu_{OH} \sim 10^{14}$ sec^{-1} while plasma frequencies are typically 10^{16} sec^{-1}) gives an interaction potential between the charge and its image of[18]

$$U_{int} = \frac{-q^2}{2d\epsilon_1} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} , \qquad (1)$$

where ϵ_2 is the frequency-dependent real part of the dielectric constant of the metal, and ϵ_1 is the dielectric constant of the oxide.

Motulevich[19] has measured the optical constants of several metals at low temperatures and infrared frequencies. His results show that within our frequency range the dielectric constants of metals are large and negative (on the order of -400). Thus, to a good approximation, Eq. (1) becomes

$$U_{int} = -\frac{q^2}{2\epsilon_1 d} . \qquad (2)$$

To calculate the shift in energy due to the attractive potential of Eq. (2) we approximate the O-H bonding potential with a Morse potential[20]

$$U(r - r_e) = D_e(1 - e^{-\beta|r - r_e|}) . \qquad (3)$$

For the OH$^-$ group $\beta = 1.6 \times 10^8$ cm^{-1} and $D_e = 4.7$ eV.[20] A classical treatment to first order in $r - r_e$ (and in one dimension) gives for the energy shift

$$\Delta E \simeq -\frac{\hbar q^2}{(2M\beta^2 D_e)^{1/2} 2\epsilon_1 d_0^3}(1 + \tfrac{3}{2}\beta d_0) . \qquad (4)$$

Peri, in his study of the hydroxyl bands on γ alumina[12] at high temperatures found a number of bands from 455 to 473 meV, with the exact positions depending on the temperature and degree of dehydration. Schwartz[21] has measured the O-H peak positions and widths on a large number of commercial and specially prepared alumina surfaces. Although there is a good deal of variability, especially on dehydrated surfaces at high temperatures, he states that at room temperature the O-H band is generally centered at 455 ± 3 meV with a width of order 20 meV. Using this estimate (455 meV) for the OH stretch mode peak energy for aluminum oxide in the absence of a top metal electrode ($\Delta E = 0$), we can obtain values for d_0 by fitting Eq. (4) to experiment. Using $M = m_p$, the mass of a proton, estimating $q = $ (dipole moment of OH$^-$ group)/(bond length of OH$^-$ group) $\simeq 0.71e$,[22,23] and taking $\epsilon_1 = 8$, the dielectric constant of γ aluminum oxide,[24] we obtain

$$\Delta E = (5.91/d_0^3)(1 + 2.4\, d_0) \text{ meV} , \qquad (5)$$

where d_0 is measured in angstroms.

Physically, d_0 is a measure of the distance from the proton in the hydroxyl group to the metal surface. Other workers have noted the dependence of junction resistance upon the top metal electrode used.[25] They found that smaller metal atoms correlated with thinner effective barriers, indicating that the top metal electrode was packed in tighter with and penetrated farther into the oxide layer. Our experimental results agree with theirs, and we believe this interpretation is correct. Thus we would expect d_0 to be smaller for metals with smaller atomic radius. Figure 4 shows a plot of d_0, calculated from Eq. (5), vs R, the radius of a
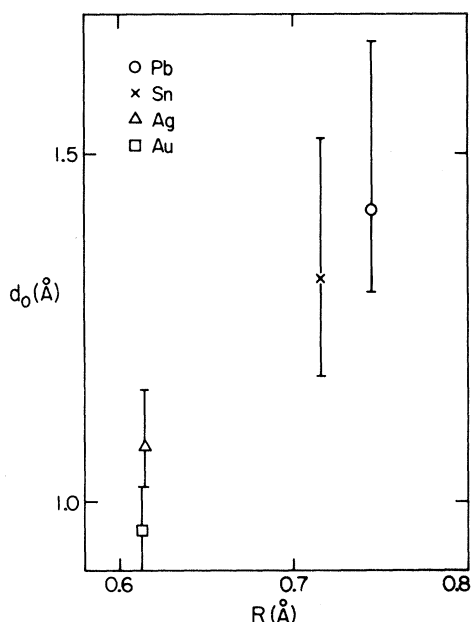
FIG. 4. Plot of d_0, the equivalent distance from the oscillating charge to the metal surface in our simple model, fit to experiment using Eq. (5) as described in the text, vs R, the atomic radius of the metal atoms in the top electrode, for the OH stretch mode on aluminum oxide for four different top metal electrodes.

sphere having the same volume as the atoms in the metallic lattice. This figure shows that the correlation is good, and that spacings of about 1 Å are required to fit Eq. (5) to experiment. Also, Eq. (4) predicts that the peak shifts are proportional to $1/\sqrt{M}$, where M is the reduced mass of the ion. We would expect therefore that the effect of the top metal electrode will be stronger for the hydroxyl than for the deuteroxyl ions. Inspection of Table I shows that this is indeed the case. For example, the peak shift in going from Pb to Au samples for thermally grown aluminum oxide is 13 meV for the OH⁻ ions but only 11 meV for the OD⁻ ions. Also, the bandwidths are always larger for the OH⁻ ions than for the OD⁻ ions, as would be

expected if the bandwidths are tied to the peak shifts through an inequivalent site mechanism, as postulated above.

Finally, the peak broadening due to resistive losses in the induced currents in the metal surface can be estimated. Using the model described above, and relating the bandwidth to the imaginary part of the interaction potential of Eq. (1), we find that the peak broadening due to this mechanism is roughly two orders of magnitude smaller than the observed width. Thus it can be neglected.

Although our simple model allows us to predict some of the general features of the observed effects, it is clear that it is highly oversimplified: (i) the oxide-metal surface is not flat on the scale of a few angstroms as we assume, (ii) the calculation is done classically though the system is microscopic, and (iii) bulk-material parameters are used. We believe that a more careful study of the effect holds the promise of determing some of the properties of the first few angstroms of a metal surface.

IV. DISCUSSION AND SUMMARY

Experiments using IETS to study the OH stretch modes of adsorbed hydroxyl ions for magnesium and aluminum bottom metal oxides indicate that the peak positions and bandwidths depend on the top metal electrode used. Two mechanisms, hydrogen bonding between the hydroxyl ions and the metal atoms, and an image-dipole model, can be used to explain this effect. Although calculations using a simple image dipole indicate that electronic effects in the surface of the top metal electrode may be large enough to account for both peak shifts and widths, hydrogen bonding should not be ruled out.

*Supported by National Science Foundation Grant No. GH-37239.

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