is found to be

$$\vec{P} = -eN_0\vec{\xi} + \frac{N_0e^3}{2m^2(\omega_0{}^2-\omega_1{}^2)(\omega_0{}^2-\omega_2{}^2)} \times\{\omega_1(\vec{E}_2\cdot\vec{k}_1)\vec{E}_1+\omega_2(\vec{E}_1\cdot\vec{k}_2)\vec{E}_2\} \times\left[\frac{\sin(\Omega_2+\Omega_1)}{\omega_2+\omega_1}+\frac{\sin(\Omega_2-\Omega_1)}{\omega_2-\omega_1}\right] \qquad (6)$$

up to the second order. Here, we see that one misses the second term if one uses Eq. (4) instead of Eq. (3). If $\vec{k}_1$ and $\vec{k}_2$ are in the same directions, i.e., if we have one incident beam, this term vanishes. For the case of anisotropic oscillators, however, the extra terms in Eq. (3) contribute for one incident beam also, even for the second-harmonic polarization.

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[1] M. Born and E. Wolf, Principles of Optics (Pergamon Press, London, 1965), p. 92.

[2] E. Adler, Phys. Rev. 134, A728 (1963).

[3] R. Kronig and J. I. Boukema, Proc. Koninkl. Ned. Akad. Wetenschap. Ser. B, 66, 8 (1963).

[4] H. Prakash and Vachaspati, to be published.

[5] H. Prakash, thesis, University of Roorkee, 1966 (unpublished), Chap. IV.

THEORY OF INELASTIC ELECTRON-MOLECULE INTERACTIONS IN TUNNEL JUNCTIONS

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The excess tunneling current due to inelastic electron-molecule interactions near the metal-insulator interface is calculated. The expression for the second derivative of this excess current is proportional to the dipole spectral weight function of the molecule.

Recent measurements reported by Jaklevic and Lambe[1] show that vibrational excitations of molecules at the metal-oxide interface of a tunnel junction produce structure in the I-V characteristics. They suggest that this structure is due to the onset of new tunneling channels opened by inelastic electron-molecule interactions. Here we discuss a model which provides a simple theoretical framework for these ideas.

The model is basically a one-electron picture in which we take the dynamics of the electron-molecule interaction into account by including the molecular dipolar field in the potential which the electron sees in the insulating layer of the junction. The expression for the excess current which we derive shows that in the low-temperature limit, the derivative of the conductance is proportional to the dipole spectral weight function of the molecule. The magnitude of the change in conductance induced by this mechanism is in agreement with experiment.[1]

To clarify the model, it is useful to discuss the specific case of H_2O in an Al-Al_2O_3-Pb junction. As discussed in Ref. 1, the junctions are made by evaporating an Al layer and allowing it to oxidize to approximately 30 Å. Hydroxyl groups are bound to the Al_2O_3 surface, probably at exposed Al sites, and H_2O molecules can be physically adsorbed by hydrogen bonding.[2] The junction is completed by a Pb overlay. The exposed hydrogens may form weak hydrogen bonds with the Pb but should be relatively free to vibrate. Figure 1(a) shows a possible configuration of a hydroxyl group near the Al_2O_3-Pb interface.

In the insulating region outside the electron cloud of the hydroxyl, the potential can be written as a sum of the effective Al_2O_3 barrier potential U and the Coulomb potential of the hydroxyl and its images. Using the coordinate system shown in Fig. 1(b), we approximate the Coulomb potential of the hydroxyl and its near image by a single dipole $2p_z\vec{k}$ at the origin.

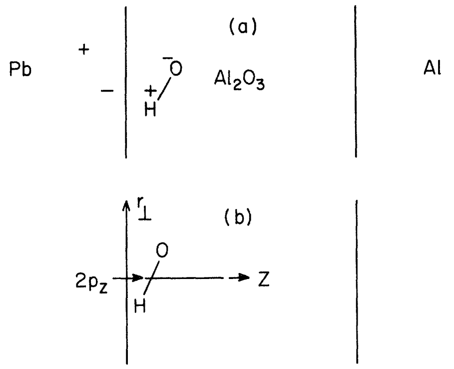

FIG. 1. (a) Hydroxyl group configuration near the Pb-Al_2O_3 interface. The near-image charges in the Pb are shown. (b) The dipole $2p_z$ and the coordinate system used in evaluating the tunneling matrix element.

Here p_z is the component of the OH dipole normal to the junction surface. The transverse components of the OH dipole and its near image effectively cancel at distances greater than their separation and can be neglected. The contribution of the additional images to the structure in the tunneling is negligible when the thickness of the Al_2O_3 layer l is large compared with both the OH bond length and the OH near-image separation. Therefore, the use of the single dipole of strength $2p_z$, normal to the surface, Fig. 1(b), is an adequate approximation at distances greater than the OH near-image separation and less than the oxide thickness l. It is just this region which is important in the inelastic scattering of electrons by the OH.

Using a WKB approximation, the tunneling matrix element for an electron of energy ϵ_k approaching the barrier at a radius $r_\perp$ from the dipole is proportional to[3]

$$\exp\left\{-\int_0^l dz\left[2m\left(U+\frac{2ep_z z}{(z^2+r_\perp^2)^{3/2}}-\epsilon_k\right)\right]^{1/2}\right\}. \qquad (1)$$

In the important region $U-\epsilon_k$ is much larger than the dipole potential so that the dipole part of Eq. (1) can be expanded and the z integral evaluated as

$$\left[1+\left(\frac{2m}{\varphi}\right)^{1/2}\frac{ep_z}{l}g(r_\perp/l)\right]\exp[-(2m\varphi_k)^{1/2}l], \qquad (2)$$

where $\varphi_k=U-\epsilon_k$, $\varphi=U-\epsilon_F$, and

$$g(x)=\frac{1}{x}-\frac{1}{(x^2+1)^{1/2}}. \qquad (3)$$

In the expanded terms we have set ϵ_k equal to its value at the Fermi surface.

If we neglect correlations between the tunneling electrons and the OH molecule, the increase in current density at a distance $r_\perp$ from the molecule due to the second term in (2) is easily evaluated using the "Golden Rule."[4] We find

$$\delta I(r_\perp)=\left(\frac{dI}{dV}\right)_0 g^2(r_\perp/l)\frac{2me^2}{\varphi l^2}\times\int_{-\infty}^{\infty}d\omega_1\int_{-\infty}^{\infty}d\omega_2[f(\omega_1)-f(\omega_2)]\times\tilde{N}_{\rm Pb}(\omega_1)\tilde{N}_{\rm Al}(\omega_2)D(\omega_1-\omega_2+V). \qquad (4)$$

Here $(dI/dV)_0$ is the normal-state junction conductance in the absence of the hydroxyl group. $\tilde{N}_{\rm Pb}(\omega)$ and $\tilde{N}_{\rm Al}(\omega)$ are the effective tunneling densities of states[4] of Pb and Al normalized with respect to the bare single-particle density of states at the Fermi surface, $f(\omega)$ is the Fermi function $(e^{\beta\omega}+1)^{-1}$, and $D(\omega)$ is the dipole spectral weight function of the OH group[5]:

$$D(\omega)=\sum_m|\langle m|p_z|0\rangle|^2\delta(\omega-\omega_{m0}). \qquad (5)$$

Finite-temperature effects on the tunneling electrons have been included but we have used the zero-temperature form of the dipole spectral weight since the vibrational energies are large compared with the temperatures of interest. Note that Eqs. (4) and (5) describe an inelastic process in which an electron of initial energy ω_1+V in metal 1 tunnels to an electron state of energy ω_2 in metal 2, and in the process excites the OH molecule out of its ground state.

The average current density for n impurities per unit area is obtained by integrating Eq. (4) over a unit area and multiplying by n. The integration of g^2 gives

$$2\pi\int_{r_0}^{1}dr_\perp r_\perp g^2(r_\perp/l)\cong 2\pi l^2\ln\left|\frac{l}{r_0}\right|. \qquad (6)$$

This integration has been cut off in the vicinity of the hydroxyl group, where our approximation for the potential begins to fail. Since the cutoff r_0 enters in a logarithm, its exact magnitude is not critical.

The superconducting tunneling density of states in Eq. (4) produces an upward shift and modification of the shape of the structure in δI on a scale of voltages of order of the gap. Neglecting this fine structure, the expression for δI can be reduced to a simple form by replacing the normalized tunneling densities of states in Eq. (4) by unity. Then, in the low-temperature limit, the second derivative of the extra current given by Eq. (4) is

$$\frac{d^2}{dV^2}\delta I = n\frac{4\pi e^2 m}{\varphi}\ln\left|\frac{l}{r_0}\right|\left(\frac{dI}{dV}\right)_0 \times\sum_m |\langle m|p_z|0\rangle|^2\delta(V-\omega_{m0}). \tag{7}$$

Thus, the structure in the second derivative of the tunneling current provides a direct probe of the dipole spectral weight $D(V)$.

Integrating Eq. (7) over an increment of voltage covering a given vibrational band, the change in conductance is

$$n\left(\frac{dI}{dV}\right)_0 \ln\left|\frac{l}{r_0}\right|\frac{4\pi e^2 m}{\varphi}\,\frac{e^2 f_\nu}{2m\omega_\nu}A, \tag{8}$$

where

$$A = \sin^2\theta, \quad \text{bending mode}$$
$$= \cos^2\theta, \quad \text{stretching mode}.$$

Here ω_ν and f_ν are the frequency and oscillator strength of the νth band and θ is the angle between the OH dipole and the normal to the junction surface. Infrared-spectroscopic studies[2] indicate coverage factors of order 10 hydroxyl groups per 100 Å^2 of surface. For the bending mode, $\omega_\nu \sim 0.11$ eV and $f_\nu \sim 10^{-5}$. Taking $l/r_0 = 30$, $\varphi = 2$ eV, and $\sin^2\theta = \frac{1}{2}$, Eq. (8) gives a change in conductance of order 1%. This is consistent with the experimentally reported size of the conductance change.[1]

It is important to recognize that the dipole spectral weight appearing in Eq. (4) is that appropriate to the molecule in its local environment. This includes the influence of the metal-insulator interface and thus provides a direct probe of the surface correlations of a metal. Systematic studies of various metallic overlays, at higher resolution, are of interest. For example, the strength of the hydrogen bonding could be studied as a function of the electron density in the overlay metal.

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[1] R. C. Jaklevic and J. Lambe, Phys. Rev. Letters 17, 1139 (1966).

[2] J. B. Peri and R. B. Hannan, J. Phys. Chem. 64, 1526 (1960).

[3] We use units in which $\hbar = 1$ and voltage is measured in energy units.

[4] See, for example, D. J. Scalapino, J. R. Schrieffer, and J. W. Wilkins, Phys. Rev. 148, 263 (1966), Appendix B.

[5] Note that the structure is associated with the transition-state dipole matrix elements $\langle n|p_z|0\rangle$. The static dipole moment is not directly involved. For small vibrations $p_z = p_z{}^0 + \sum_\nu(\partial p_z{}^0/\partial\zeta^\nu)\zeta^\nu$, where ζ^ν is a normal coordinate. It is the size of $\partial p_z{}^0/\partial\zeta^\nu$ which determines the magnitude of the excess current associated with the electron-molecule interaction. It is just these matrix elements which enter in infrared absorption.