Conductivity sensitivity of inelastic scanning tunneling microscopy

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We present some considerations for the inelastic increase in conductivity in scanning tunneling microscopy (STM) by using the dipole approximation for the vibrating molecules. We show that the relative increase in the case of vacuum tunneling can be considerably larger than that obtained in tunneling through oxide layers, even for a single adsorbed molecule. With the present state of STM, such current changes are readily detectable. We further propose an alternative experimental approach unique for STM.

In 1966, Jaklevic and Lambe[1,2] observed that tunneling electrons through oxide layers were able to excite and resolve vibrational modes of molecules adsorbed between one of the metallic plates and the oxide gap. This happens when the applied voltage V between the metal electrodes equals the frequency of the mode. Subsequent theoretical work[3-5] showed that infrared active modes as well as Raman active modes were excited with a change in conductivity $\Delta\sigma$ between 0.1 and 1% of the total conductivity, which is sufficient to detect molecule vibrations. This method is called inelastic tunneling spectroscopy (ITS).

Recently, Binnig, Rohrer, Gerber, and Weibel[6] developed a new experimental technique called scanning tunneling microscopy (STM) by performing the tunneling from a tip of atomic dimensions (≈ 5 Å radius) through a vacuum gap a few angstroms wide (4–15 Å). The great virtue of the STM, apart from bare and well-defined electrode surfaces, is its atomic resolution in real space which should enable ITS with single absorbates. Therefore, it seems interesting to study the sensitivity (change in conductivity) of STM owing to inelastic vibration excitations.

In this Brief Report, we develop a formula for the change in conductivity $\Delta\sigma$ in inelastic scanning tunneling microscopy (ISTM) (for the infrared active modes) by using the dipole approximation (Scalapino and Marcus[3]) and the scattering approach for STM[7,8] thereto. Following Ref. 3, the interaction between electron and molecule can be described by a dipole potential

$$U_{\rm int}(z)=2ep_z z/\epsilon((z^2+R^2))^{3/2}\,, \tag{1}$$

where e is the electron charge, ϵ the dielectric constant of the oxide barrier, p_z the dipole perpendicular to the surface, and $\bar{r}(\bar{R},z)$ the position vector, z being the perpendicular component to the surface. The factor of 2 appears because of the dipole and its image that also cancels to a good approximation the $p_{\bar{R}}$ dipole comments (see Ref. 3 and Hansma's review article, Ref. 8). The dielectric constant ϵ appears since the molecule is in a polarizable medium. In Ref. 3, this is not considered but it has been introduced in further work.[4,8] By using the WKB approximation, for plane metallic electrodes,

$$\Delta\sigma_0^p=N\frac{4\pi me^2}{\phi\epsilon^2\hbar^2}\ln(l/r_0)\sum_i|\langle i|p_z|0\rangle|^2\Theta(V-\hbar\omega_i/e) \tag{2}$$

is found,[3] where l is the distance between electrodes, $r_0\simeq 1$ Å the cutoff parameter, since the dipole diverges for small values of r (this is not important because of the logarithm), $\langle i|p_z|0\rangle$ is the dipole matrix-element excited mode of frequency ω_i, and $\Theta(x)=1$ for $x\geq 0$ and $\theta(x)=0$ for $x<0$. Further, ϕ is the average tunnel-barrier height, and N is the number of molecules per unit area. Equations (1) and (2) immediately show that the sensitivity of an oxide is down by ϵ^2 from that of a vacuum barrier, for otherwise unchanged parameters. However, there are some additional inherent differences when working with oxide barriers and vacuum barriers in general, and the tip configuration in particular. Let us first discuss the planar vacuum barrier. To obtain a tunnel current I sufficiently large to control and stabilize the width of the vacuum gap l_V, say $I\approx 1$ nA, $l_V\approx 5$–10 Å, i.e., $l_V\ll l(\approx 20$–30 Å). Since l enters Eq. (2) only logarithmically, this decreases the sensitivity by at most a factor of 2. However, this can be more than compensated by the image-potential lowering of the average barrier height ϕ (Ref. 9) [see Fig. 1(a)]. Note that this reduction of ϕ is unimportant in oxide barriers for $l>10$ Å, and is reduced by $1/\epsilon$ even at $l<10$ Å. A comparison of $\Delta\sigma$ of planar oxide and vacuum junctions for typical values of the parameters is given in Table I.[10] Thus, a squeezable tunnel junction of the type used by Moreland *et al.*[11] should already be a significant advantage in sensitivity compared to oxide junctions.

We now turn to the tip configuration. The theory of STM[7] in the case of a sharp tip can also be applied to ISTM by a generalization of Eq. (2) in Ref. 8, and again assuming the dipole potential of Eq. (1) (with $\epsilon=1$) for the electron-adsorbate interaction. The tunnel conductivity can be written[8]

$$\sigma\propto R_t e^{-2.14\sqrt{\phi}l_V^t}\,, \tag{3}$$

where R_t is the tip radius and l_V^t the tunnel distance in the tip configuration. A straightforward application following Ref. 3 shows that the increase in conductivity for the tip configurations with the molecules adsorbed on a flat surface is given by

$$\Delta\sigma_V^t=n\frac{4me^2}{\phi_V^t h^2}\ln(L_{\rm eff}/2r_0)\sum_i|\langle i|p_z|0\rangle|^2\Theta(V-\hbar\omega_i/e)\,, \tag{4}$$

where n is now the number of molecules in the surface area illuminated by the tip.[12] This area is given by $\pi L_{\rm eff}^2/4$, where $L_{\rm eff}$ is the effective diameter of the tunnel-current filament (see Ref. 7). To obtain (4), one has to take into account that the integral in the R plane (see Refs. 3 and 8) is between the limits r_0 and $L_{\rm eff}/2$. Also, ϕ_V^t is the average barrier height in the tip configuration. We have found that $L_{\rm eff}$ and ϕ_V^t are strongly affected by image forces and local

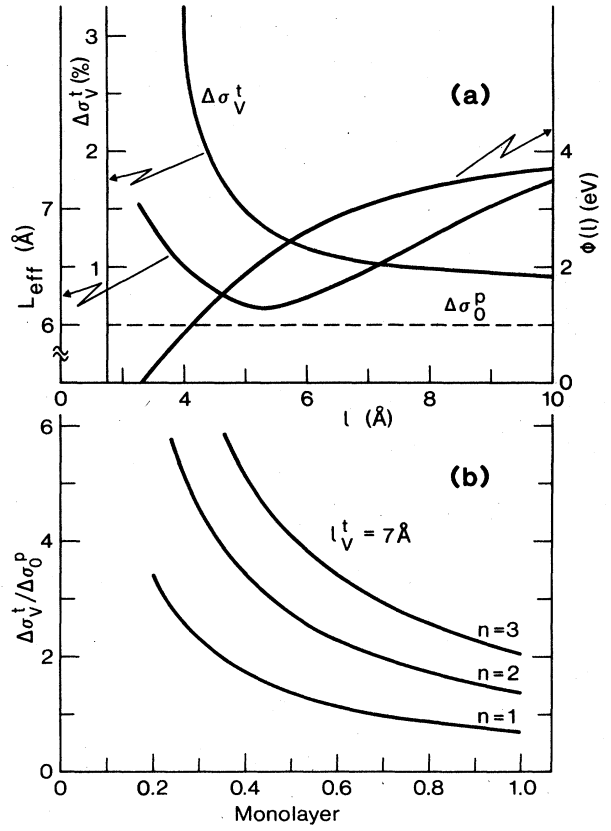

FIG. 1. (a) Variation of ϕ, L_{eff} (after Ref. 9) and $\Delta\sigma\downarrow$ as a function of distance l between jellium edges for $\phi(l\rightarrow\infty)=4.8$ eV and $n=3$. Notice the large increase of $\Delta\sigma\downarrow$ for $l<5$ Å. Also $\Delta\sigma_0^p\approx 0.5\%$ has been drawn for $l_0\approx 30$ Å, $\epsilon=3$, $\phi_0=2$ eV, and $N=10^{15}$ cm^{-2}. (b) Ratio in conductivity increases in ISTM and ITS for $l\downarrow=7$ Å with the same values of the various parameters as in (a), as a function of N. The comparison is made for clusters with $n=1,2$, and 3 adsorbates in the effective tunnel area $\frac{1}{4}\pi L_{\text{eff}}^2$ in ISTM.

polarizations owing to the small dimensions of the tip.[9,13] We have found[9] that the reduction of the barrier height by the image force reads

$$\phi\downarrow[l\downarrow(\text{Å})]=-\frac{9.97}{l\downarrow(\text{Å})-1.4}\ \text{eV}\ . \tag{5}$$

Polarization forces owing to the small dimensions of the tip are more difficult to calculate, but our experiments seem to show that these are also important and contribute to a further reduction of the barrier.

Figure 1(a) shows the variation of $\Delta\sigma\downarrow$ as a function of gap width $l\downarrow$ for a tunnel tip of radius 5 Å considering image potential but not tip polarizations. The latter leads to an additional lowering of $\phi\downarrow$ (Refs. 9 and 13) and a corresponding enhancement of $\Delta\sigma\downarrow$. At large distances, the ϵ^2 gain of a vacuum junction is reduced by a geometrical factor of about 5. At short distances, however, it is enhanced by the reduction in $\phi\downarrow$ [see Eq. (5)]. Thus, $\phi\downarrow$ is at least $\epsilon^2/5$ larger but can be made even much larger than $\Delta\sigma_0^p$ with a monolayer-adsorbate coverage. Of course, the difference increases more rapidly when the coverage is reduced as shown in Fig. 1(b). The comparison is based on a substantially reduced oxide dielectric constant of $\epsilon=3$. Such a reduction by a factor of 4 seems rather large in view of experiments on Josephson junctions[14] which yield bulk values ($\epsilon\approx 30$) down to barrier widths of 25 Å.

TABLE I. Inelastic tunneling sensitivities for various junction configurations for one monolayer coverage $N\simeq 10^{15}$ cm^{-2}.

	ϕ (eV)	l (Å)	ϵ	L_{eff} (Å)	$\Delta\sigma$ (%)
Oxide[a]	2	30	3	···	1.0
Plane vac.[b]	2.5	6	1	···	3.8
Tip vac.[c]	2.5	6	1	6.3	2.4

[a]References 4 and 8.
[b]Equation (2).
[c]Equation (4).

Next, we point out that STM offers an alternative approach to inelastic processes: A type of pumping experiment where the elastic tunnel channel is no longer independent of the inelastic one. Because of the narrow tunnel filament, current densities can easily reach 10^6 A/cm^2 without heating the sample appreciably (in particular when the electrons flow from surface to tip). If sufficient energy is pumped into the adsorbate through the inelastic tunnel channel, the nonequilibrium excitation of the vibrational modes (with respect to the suface) will lead to an outwards relaxation of the absorbate. The relaxation of an adsorbate on a free surface is expected to be much larger than at a metal-oxide interface and always outwards. The corresponding reduction of the width of the tunnel gap increases the elastic part of the tunnel current at a rate 2% per 0.01-Å relaxation at $\phi=4$ eV.

Our final remark concerns the experimental feasibility of ISTM. The limiting factor is the gap-width stability. From Eq. (3), we obtain

$$\Delta l=-\Delta(\ln J)/\sqrt{\phi}-\tfrac{1}{2}l\Delta(\ln\phi)\ , \tag{6}$$

where ϕ is measured in eV and Δl in Å, a current change of 3% corresponds to a gap-width change of 0.02 Å for an l-independent barrier height $\phi=2$ eV. Thus, the smaller ϕ, the larger Δl. Note, however, that for an image-potential lowered barrier,[9] $\Delta l=-\Delta(\ln J)/\sqrt{\phi(l\rightarrow\infty)}$. Using lock-in techniques, current changes of a few percent were readily detected in room-temperature elastic scanning tunneling spectroscopy with the present stability of STM of about 0.05 Å. Further, since operation of STM at cryogenic temperatures does not cause insurmountable problems,[15] we trust that ISTM will become a valuable technique to identify and study single adsorbates.

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[12]In the case of a tip, it does not make any sense to talk about coverage: The tip is on top of a molecule or it is not. Because $L_{\text{eff}} \approx 7$ Å, $n=1$, 2, and 3 (the tip sees a molecule, a dimer or a trimer) corresponding to, roughly speaking, $\frac{1}{3}$, $\frac{2}{3}$, or 1 times 10^{-15} cm^{-2}. L_{eff} enters Eq. (3) because the integral on the R plane has to be cut off at the area illuminated by the tunnel electrons.

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