

Recent Advances in Inelastic Electron Tunneling Spectroscopy

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Received January 16, 1978

Inelastic electron tunneling spectroscopy was discovered by Jaklevic and Lambe 12 years ago.¹ It measures the vibrational spectrum of a minute quantity of organic molecules on the insulator of a metal-insulator-metal junction. A vibrational mode of energy $h\nu$ (h is Planck's constant, and ν is the frequency) is detected as a slight change in the electrical characteristics of the junction at a voltage V such that eV , the energy of the most energetic tunneling electrons, equals $h\nu$. Specifically, a tunneling spectrum, d^2V/dI^2 vs. voltage, has a peak corresponding to the vibrational frequency ν at a voltage $V = h\nu/e$. This is shown in the idealized view at the top of Figure 1. The bottom half of Figure 1 shows the actual situation. The metal-insulator-metal junctions are usually fabricated on glass slides. Most commonly an aluminum electrode is evaporated first. It is then oxidized either in a glow discharge or in air to form the necessary insulating layer. Then it is doped, usually with organic molecules. Finally, it is completed with an evaporated top metal electrode, usually Pb. The metal-insulator-metal junctions of the idealized picture are formed at the intersections of the crossed metal electrodes.

Since the typical organic molecule has a large number of vibrational modes, there are a large number of peaks in an actual inelastic tunneling spectra as shown on the right. This particular one is for the dopant molecule, benzoic acid. Spectra are typically obtained by applying a slowly increasing current and a small modulation current to the junction. The bias voltage produced by the slowly increasing current is applied to the x axis of the chart recorder. The second harmonic voltage produced by the small modulation current is applied to the y axis; it is proportional to d^2V/dI^2 . Spectra are generally measured at liquid helium temperatures to increase resolution.

The spectral range of tunneling spectroscopy, 0 to beyond $1/2$ eV (0 to beyond 4000 cm^{-1}), includes all molecular vibrations. There are, however, strong background peaks² below 50 meV (400 cm^{-1}) that must be reduced to reveal the molecular vibrations in this range. One new technique, differential tunneling, is discussed in this Account.

The sensitivity of tunneling spectroscopy is sufficient to detect a fraction of a monolayer in an area of order

1 mm^2 . A recent experiment³ detected one deuterium atom per 1500 \AA in an area less than 0.6 mm^2 . The resolution of tunneling spectroscopy is limited by thermal smearing, $5.4kT$, and modulation voltage broadening, $1.7e\Delta V$, where ΔV is the root mean square modulation voltage. Typical spectra are obtained at temperatures in the range 1 – 4.2 K with modulation voltages in the range 0.5 – 3 mV. Thus the resolution is in the range 1 to 4 meV (8 – 32 cm^{-1}). (It is slightly better than this when superconducting electrodes are used.⁴) Though it is experimentally very difficult to obtain better resolution, there is no known theoretical limit; the best resolution reported to date is of order 0.1 meV (0.8 cm^{-1}).⁵ Fortunately most intrinsic line widths for adsorbed molecules are larger than 1 meV, so that more easily obtainable resolution suffices. Both Raman active and infrared active modes appear in tunneling spectra with comparable magnitudes.⁶ There are, however, orientational selection rules that will be discussed in the theoretical section.

There are two other techniques that are very useful for obtaining the vibrational spectra of adsorbed molecules: infrared spectroscopy and electron energy loss spectroscopy. The pros and cons of various techniques can be easily summarized. (1) Inelastic electron tunneling gives the best spectra, but is severely limited in the systems it can study. (2) Electron energy loss spectroscopy gives relatively poor resolution (≈ 7 meV) spectra over a wide spectral range. It is ideal for use in conjunction with other surface probes on well-characterized metal surfaces. (3) Infrared spectroscopy can study the widest range of surfaces: from actual catalysts of unknown structure to well-characterized single crystals. In general, however, spectral range is limited and sensitivity is a problem.

Since tunneling spectroscopy is so limited in the systems it can study, it will never replace the other techniques. It will be useful to the extent that practical systems can be adequately simulated in tunnel junctions. An example of this simulation is the use of evaporated metal particles on the aluminum oxide insulating layer of a tunnel junction to simulate supported metal catalysts.

It is not our desire in this Account to summarize the theory, experimental techniques, and experimental results for tunneling spectroscopy. That has been done

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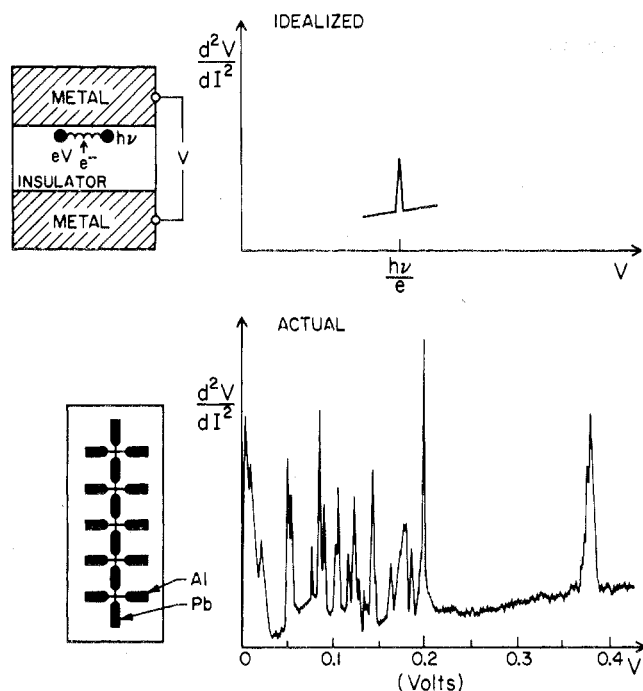


Figure 1. The harmonic oscillator of the idealized picture is one of the vibrational modes of a dopant molecule in the actual junction. Each vibrational mode of the dopant molecule is revealed as a peak in d^2V/dI^2 at a voltage $V = h\nu/e$. The tunneling spectrum can be directly compared to infrared and Raman spectra: 0.1 V corresponds to 806.5 cm^{-1} .

comprehensively elsewhere.⁷ Rather, we want to review some new and exciting developments in each of these three areas. Thus we will include only enough general information to make the context and importance of the new developments clear and refer the interested reader to the comprehensive review for more detailed background information.

Theory: Long, Short, or Both?

A great deal has been learned and will continue to be learned about the structure and bonding of molecules on surfaces from measured peak positions in tunneling spectroscopy. At present, however, it is impossible to predict or interpret peak intensities. Nevertheless, both theory and experiment suggest that the intensities contain orientation information: The orientation of adsorbed molecules could be determined if the intensities could be interpreted. Thus there is practical importance in pursuing the relatively difficult task of understanding intensities.

One of the major questions that has come up lately is: What part of the electron-molecule interaction is most important: the long-range part ($\geq 2 \text{ \AA}$) where the interaction can be well described by a multipole expansion or the short-range part ($\leq 2 \text{ \AA}$) where the exchange correlation potential must be included? In this section we will first discuss a long-range theory developed by Kirtley, Scalapino, and Hansma (KSH)⁸ and then some very recent work by Davenport, Ho, Kirtley, Schrieffer, and Soven on a short-range theory.⁹

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In the KSH treatment the molecule was placed inside a square potential barrier (made up of the metal oxide and dopant molecules) a distance a from one metal surface. The interaction between the tunneling electron and the vibrating molecule was taken to be a sum of dipole potentials localized on the individual atoms in the molecule:

$$V_i(\mathbf{r}, \omega) = - \sum_i e^2 Z_i \delta \mathbf{R}_i \cdot \nabla_i \left(\frac{1}{|\mathbf{R}_i - \mathbf{r}|} \right) \quad (1)$$

where \mathbf{R}_i , $\delta \mathbf{R}_i$, Z_i were the positions, vector displacements, and dipole derivatives, respectively, associated with each atom in the molecule for a given normal mode. The size of the dipole derivatives could be taken as empirical fitting parameters or inferred from infrared data. This assumed Hamiltonian was used as the interaction Hamiltonian in Bardeen's transfer Hamiltonian formalism.¹⁰ Since the method of calculation was discussed in the comprehensive review,⁷ we will not elaborate here.

Approximately correct absolute magnitudes for inelastic intensities were obtained. Further, the theory predicted that: (1) even in the absence of a term in the Hamiltonian corresponding to the interaction of the tunneling electron with the oscillating induced molecular dipole moments, Raman active modes, which do not have net intrinsic oscillating dipole moments, should be nearly as intense as infrared active modes, which do. (2) Normal modes which involve a net oscillating dipole moment normal to the surface should appear more strongly than modes that have an oscillating dipole moment parallel to the surface. (3) Modes that are neither Raman active nor infrared active may be observable.

These predictions appear to be born out by experiment. Tunneling spectra of anthracene,^{6,11} which has a center of symmetry and, therefore, separation of the Raman and infrared active modes, showed that the Raman active modes had intensities comparable to the infrared active modes. Very small intensities were reported for the optically inactive modes.⁶

There has also been some experimental support for the presence of orientation selection rules in tunneling spectra from comparison of intensities of selected modes of adsorbed benzoic acid¹² and more recently several sulfonic acids¹³ with appropriate infrared and Raman spectra. The ratio of intensities for vibrations with oscillating dipole moments normal to the surface to vibrations with oscillating dipole moments parallel to the surface is larger in tunneling spectra than in infrared and Raman spectra.

In addition, however, there has been work on various phenols^{14,15} and a series of substituted ring compounds,^{16,17} which indicated that the absolute intensities

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of all the normal modes of a given molecule could be drastically changed by altering the positions or chemical compositions of ligands on the rings. These experiments seem difficult to explain within the framework of the KSH theory, but there are, at present, uncertainties in molecular orientations, surface densities, and the appropriate dipole derivatives. Thus no quantitative calculations have been done.

Most likely the long-range contribution to tunneling intensities has been treated nearly correctly. However, recent theoretical work by Rath and Wolfram¹⁸ indicates that the electronic charge densities involved in the bond vibrations of ethylene do not necessarily follow the nuclear coordinates, so that some care must be taken in assignment of the vector amplitudes as well as the dipole derivatives used in KSH. There has also been work¹⁹ which suggests that collective effects are important, especially in determining the dependence of intensity on the concentration of dopant molecules. This dependence has been measured only once;²⁰ more experimental data is certainly needed.

There still remains the question of the importance of short range interactions. Recently, one of us (J.K.), in collaboration with Soven, Davenport, Ho, and Schrieffer, used a multiple scattering theory incorporating the $X\alpha$ approximation to the exchange correlation potential^{21,22} to attempt to estimate the relative size of short-range effects. In this formulation the interaction potential between the tunneling electron and the molecule (with fixed nuclear positions) was given by

$$V(\mathbf{r}, \mathbf{R}) = V_N(\mathbf{r}, \mathbf{R}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \quad (2)$$

where V_N was the nuclear attraction with \mathbf{r}, \mathbf{R} being the electron and nuclear coordinates, respectively. The static electron-electron Hartree interaction was given by

$$V_H(\mathbf{r}) = \int \frac{e^2 n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \quad (3)$$

where $n(\mathbf{r})$ was the local electron density. The exchange correlation potential was approximated by

$$V_{xc}(\mathbf{r}) = -3\alpha e^2 \left(\frac{3}{8\pi} n \right)^{1/3} \quad (4)$$

where α was a constant of order 0.7. The potential was approximated further by spherically averaging within nonoverlapping spheres ("muffin tins") surrounding the atoms and outside an outer sphere surrounding the molecule. The intersphere potential was volume averaged.

The molecular potential was constructed by self-consistently calculating molecular wave functions and their resulting potentials and iterating to convergence. Once the molecular potential was constructed, the wave functions for the scattered electron (tunneling at negative energies) was calculated for a set of assumed molecular vibrational normal coordinates. The electronic wave function multiply scattered from the mo-

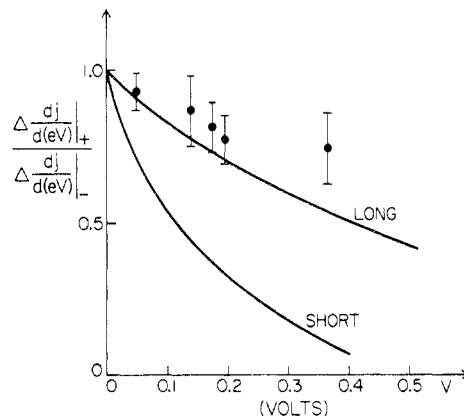


Figure 2. The ratio of the integrated peak intensities for opposite polarities vs. the magnitude of the applied voltage. For positive polarity the electrons tunnel from the electrode in direct contact with the dopant layer (Al positive relative to Pb for standard junctions). The dots are experimental measurements for a benzoate dopant.⁸ The lower curve is the result for the $X\alpha$ calculation (or any other very short-range theory). The upper curve is the result for the KSH theory (a long-range theory). The remaining discrepancy between experiment and theory may be due to tunneling barrier asymmetry.⁸

lecular potential was then matched to initial and final states on opposite sides of the tunneling barrier using Bardeen's transfer Hamiltonian formalism. Finally the inelastic tunneling matrix element was calculated by sandwiching the elastic matrix element (as a function of internuclear spacings) between the ground and first excited vibrational wave functions of the molecule.^{9,23} Inelastic tunneling currents were found by summing over initial and final allowed electron momenta as in KSH.

Since the molecular potential was spherically averaged outside the outer muffin tin region, the dipole contribution to the total potential, which dominates the inelastic potential at distances greater than ~ 2 Å, was neglected. This means that the effective $X\alpha$ interaction potential was extremely short range. However, experiments on the asymmetry in tunneling intensities for opposite bias voltage polarities^{8,24} indicate that the interaction potential is relatively long range. The argument is as follows: When electrons tunnel from Al to Pb in the standard Al- AlO_x -dopant molecules-Pb junction, they tunnel before losing energy to the molecular vibration. In the opposite direction the electrons tunnel after losing energy. More energetic electrons are more likely to tunnel, so one bias voltage direction will have bigger inelastic electron tunneling spectroscopy peaks than the other. If the interaction potential that causes inelastic transitions is very long range, the placement of the molecule in the tunneling region (e.g., on the surface of the oxide in direct contact with one metal electrode) will not matter, and there will be no asymmetry. On the other hand, a very short-range interaction will cause a great deal of asymmetry. Comparisons of the predictions of KSH and the $X\alpha$ approach with experiment (Figure 2) show that the long-range interaction apparently dominates.

This conclusion is supported by calculations of inelastic tunneling cross sections using the $X\alpha$ theory (Figure 3). The value of the $X\alpha$ cross section is highly

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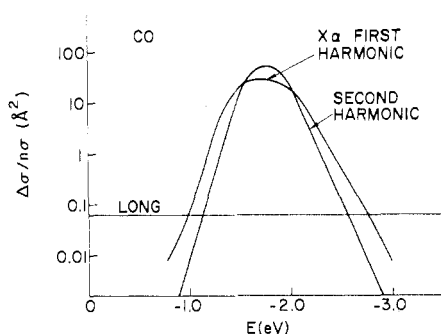


Figure 3. Comparison of the predicted first and second harmonic inelastic cross sections for the $X\alpha$ theory with the prediction of the KSH long range theory, vs. E , the energy of the tunneling electrons (at the Fermi surface of the metal electrode), relative to the molecular levels, for CO. Both first and second harmonic inelastic cross sections become large as a bound state energy at ~ -1.8 eV is approached, but the ratio of second to first harmonic intensities becomes much larger than observed experimentally. We conclude that the tunneling events must occur under conditions where resonant effects are not important.

dependent on the energy of the tunneling electrons relative to the molecular energy levels. As the tunneling energies approach the molecular bound state (5σ) level at ~ -1.8 eV the first harmonic cross section becomes larger than the long-range (KSH) cross section, but the second harmonic intensities grow even faster: the ratio of second to first harmonic intensities becomes much larger than observed experimentally. Since the second harmonic intensities in IETS are small, the short-range contributions must be small also. One guess to explain why this occurs is that the Fermi level of the metal electrode in contact with the molecular impurities is between the highest filled and the lowest empty bound states of the molecule: the molecular valence electrons are in equilibrium with the conduction electrons of the metal, E is ~ 0 , and the short-range contribution to the total inelastic cross section is extremely small.

As should be clear by now, our understanding of the intensities in IETS is far from complete. Nevertheless, progress is being made. In particular, it now appears that the long-range part of the electron-molecule interaction may dominate the short-range part in observed peak intensities. This is fortunate since the long-range part is easier to calculate. The first application of a long-range theory (KSH) to a relatively complex adsorbed species will be discussed in the section on adsorbed sulfonic acids.

New Experimental Techniques

Two major obstacles to the wider use of tunneling spectroscopy are the lack of commercial instrumentation and the difficulties of sample preparation. Thus the improvement of instrumentation and the simplification of sample preparation are important. Fortunately, progress has been made in both areas.

Differential Tunneling Spectrometer. Recently a bridge for measuring differential tunneling spectra has been developed.²⁵ A problem with conventional, single-junction spectra is the presence of structure due to the vibrations (phonons) of the metal electrodes and the insulating layer. This structure obscures the vibrations of adsorbed molecules and makes it difficult to determine peak heights. In addition, variation in the

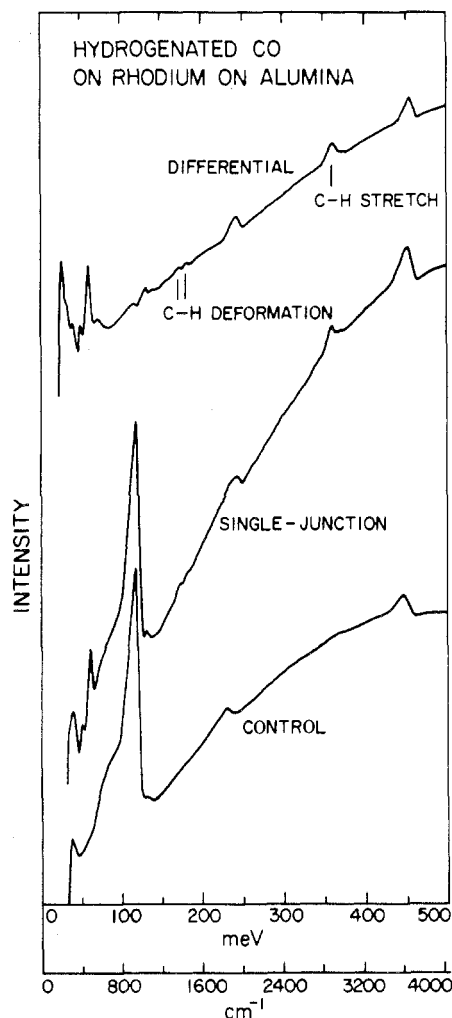


Figure 4. The differential tunneling bridge makes it easier to see the weak bands due to a hydrocarbon that was formed by hydrogenating CO adsorbed on rhodium. These spectra were taken by Richard Kroeker as part of ongoing research with a goal of helping to understand Fischer-Tropsch synthesis.

elastic conductance of the barrier causes a background slope. These problems are minimized in a differential tunneling spectrum, which is a difference spectrum between two junctions—usually a doped junction and an undoped control junction. Perhaps the most important application of differential tunneling spectroscopy will be to the study of low-energy vibrational modes: modes below 400 cm^{-1} . For example, Figure 1 shows a differential tunneling spectrum for benzoic acid adsorbed on alumina. A magnetic field (≥ 700 G) was applied with a small, samarium cobalt permanent magnet below the slide to quench the superconductivity of the lead electrode for this spectrum. Superconducting lead causes structure below 200 cm^{-1} (due to lead phonons) that is too large to be reliably canceled by the bridge.

Differential tunneling spectra are also useful for studying weak peaks. For example, Figure 4 shows single junction and differential spectra for the hydrocarbon that forms upon hydrogenation of CO adsorbed on rhodium particles supported on aluminum oxide.²⁶ Note that the weak hydrocarbon peaks are more clearly resolved in the differential spectrum.

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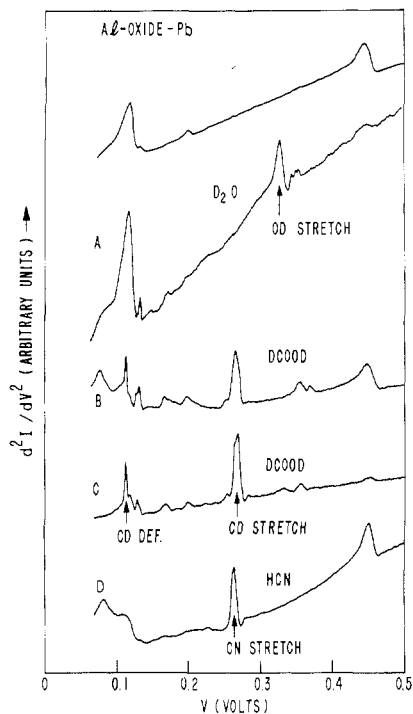


Figure 5. Various compounds can be doped into completed Al_2O_3 -Pb junctions. The top curve shows an undoped junction. The presence of the O-D stretch in curve a, the C-D stretch in curve b, and the C-N stretch in curve d shows conclusively that D_2O , DCOOD , and HCN can be doped in this way. Curve c is a junction doped in the comparison with curve b. Reprinted with permission from ref 27. Copyright 1977 American Physical Society.

We want to emphasize, however, that the bridge is not the only method for obtaining differential tunneling spectra. John Adler (private communication) has begun using a computer to subtract or divide out a stored background spectrum from a measured spectrum. It is too early to predict which technique (or combination of techniques) will turn out to be the most useful.

External Doping. A molecule must be in or near the insulating barrier of a tunnel junction in order for tunneling electrons to have a significant probability for coupling to its vibrations. In general, researchers have accomplished this by doping molecules directly on the insulating barrier and then completing their tunnel junctions with an evaporated top metal electrode. Figure 5 shows recent results for a new type of doping: diffusion doping. All of the spectra were obtained by diffusing the dopants into clean tunnel junctions. Surprisingly large molecules (e.g., methyl alcohol and pyridine) can be doped in this way.^{27,28}

Adsorption of Sulfonic Acids on Aluminum Oxide. A recent series of experiments has shown that sulfonic acids adsorb on aluminum oxide as sulfonate ions.¹³ These experiments give strong evidence that the sulfonate ions are oriented on the oxide in a tripod configuration with the three sulfonate oxygen atoms in nearly equivalent positions.

While the determination of the orientation of the sulfonate ion tripod was interesting as an exercise in the capabilities of tunneling spectroscopy, its real importance may be to help the development of the theory of

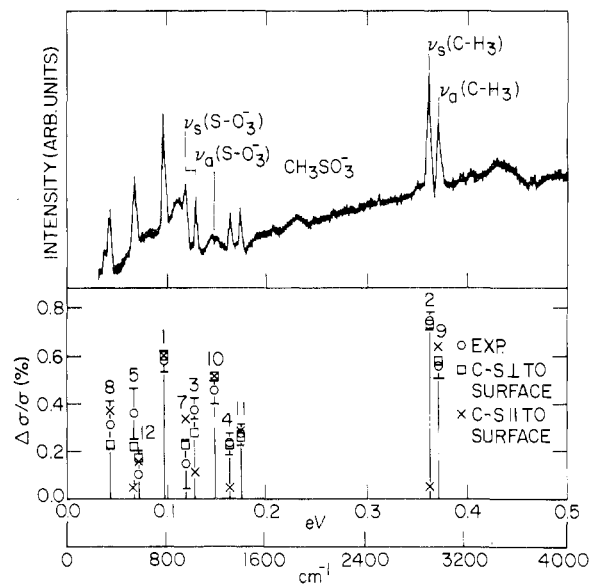


Figure 6. The top curve is the tunneling spectrum of methanesulfonic acid vapor doped onto alumina. The reaction product is a symmetric sulfonate ion. The histogram shows experimental values for absolute intensities (round points) for all of the normal modes (numbered according to identifications in ref 13). The squares are best fit intensities using KSH⁸ assuming an ion orientation with the C-S bond perpendicular to the surface; the crosses assume an orientation parallel to the surface. The much improved fit for C-S_{||}, especially for the asymmetric (net dipole moment perpendicular to the surface) vs. symmetric (net moment parallel) stretch modes, supports the proposed orientation of the ion.

tunneling spectroscopy. There is orientational information in the vibrational mode intensities in tunneling spectroscopy, but so far no one has been able to determine the orientation of a molecule from intensity data alone. In part this is due to the difficulties in developing a good theory for intensity in tunneling spectroscopy as discussed elsewhere in this review, but in part it is also due to the lack of data on oriented systems to check existing theories and guide further theoretical development.

The sulfonic acid data appear to serve this purpose. There is qualitative agreement with the qualitative conclusions of present theories: both Raman active and infrared active modes appear, and modes that involve oscillating dipoles perpendicular to the plane of the oxide are systematically stronger than those involving oscillating dipoles parallel to the oxide. Further, quantitative fits of the dipole derivatives in KSH theory for the observed IETS intensities of methanesulfonic acid on alumina²⁹ (see Figure 6) give reasonable fits (reduced χ^2 values of 3.4) if the molecule is assumed to be oriented with the C-S bond normal to the surface, but give very poor best fits ($\chi^2 \sim 100$) if the C-S bond is taken parallel to the surface. These results support the proposed orientation and represent the first test of any theory of tunneling spectroscopy on any molecule with known orientation.

Furthermore, the sulfonate tripods provide a convenient functional group for orienting other functional groups on aluminum oxide. For example, the sulfonate tripod was used to orient a benzene ring perpendicular to the oxide. It is interesting to note that comparison of the intensities of a pair of modes, an in-plane and

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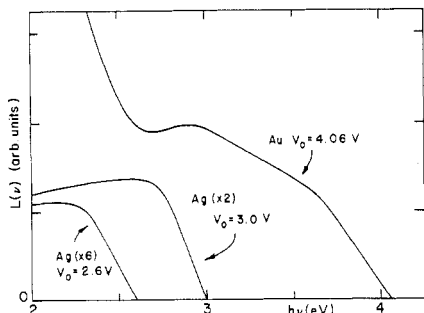


Figure 7. The spectral distribution of the light intensity from AlI-(Ag or Au) junctions with various applied voltages. Note that the junctions emit light up to a photon energy $h\nu = eV_0$. These spectra were taken at 77 K. Reprinted with permission from ref 27. Copyright 1977 American Physical Society.

out-of-plane deformation, with the corresponding modes for the benzene ring anchored with a carboxylate ion to the aluminum oxide suggested that the benzene ring was canted when anchored by the carboxylate ion. Specifically, the ratio of the intensity of the out-of-plane mode relative to the in-plane mode was six times larger when the ring was anchored with the carboxylate ion.¹³ Again we hope that quantitative calculations can be made to follow up this qualitative observation.

Light Emission from Inelastic Electron Tunneling. Almost all experiments on inelastic electron tunneling have involved measurements of the electrical properties of junctions. No one has yet detected the infrared light that may be emitted as vibrationally excited molecules decay to the ground state.

Recently, however, Lambe and McCarthy have detected the visible light emitted by plasmons that were excited by inelastic electron tunneling.^{30,31} They constructed Al_2O_3 -(Au or Ag) tunnel junctions, applied voltages, V_0 , in the range 2–5 V, and observed light that had a broad spectrum with an upper frequency cutoff, ν_{CO} , given by the quantum expression $h\nu_{\text{CO}} = |eV_0|$ as shown in Figure 7. They proposed that the tunneling electrons excited surface plasmons in the Au or Ag films and that these plasmons radiatively decayed. It was necessary, however, for them to roughen the Au or Ag films to allow this radiative decay; the plasmon modes have phase and group velocities very much smaller than that of light; thus there is negligible plasmon-photon

coupling for a smooth film. They accomplished the necessary roughening chemically with etches and by forming the junctions on roughened substrates.

Recently one of us (P.K.H.) has duplicated these experiments and begun experiments using a layer of small Au or Ag particles as the top electrode. The plasmon modes of small particles can radiatively decay, perhaps with higher probability than in roughened films. This research is continuing. It is convenient for experiments that junctions with a gold particle top electrode can be stored and operated at room temperature for weeks. The spectra have shown that the light intensity from these junctions peaks in the red (between 6000 and 7000 Å).³² The light is polarized and emitted preferentially away from the normal to the junction.

A possible name for the general phenomena of light emission from tunnel junctions is tunneluminescence,³³ by analogy to photoluminescence, chemiluminescence, electroluminescence, bioluminescence, and triboluminescence.

New Directions

The application of tunneling spectroscopy to practical problems is beginning. Papers have already appeared on its application to catalysis³⁴ and adhesion.^{35–37} New data on biological molecules^{38,39} may contribute to an understanding of chromatography and possibly even biochemical reactions. Lubrication, corrosion, electrochemistry, and flotation are possible areas for future work. Finally, tunneling electrons can serve as a tunable energy source for inducing light emission.^{30–33} Can they also serve as a tunable energy source for initiating chemical reactions?

We wish to acknowledge support from the Materials Research Division of the National Science Foundation for this work.

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