INELASTIC TUNELLING SPECTROSCOPY

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Introduction

In 1966, JAKLEVIC and LAMBE illustrate that species doped with the metal-insulator-metal junction absorbed energy from tunneling electrons, marking the beginnings of Inelastic Electron Tunnelling Spectroscopy (IETS)[1]. The transmission of energy from electron to dopant was detected using a second derivative technique to ascertain the small changes that occurred in the electrical properties of the metal-insulator-metal junction. These changes occurred at characteristic voltages which JAKLEVIC and LAMBE were able to relate to vibrational states of the dopant molecule. The term “inelastic” is used to describe tunneling where the electron has given up energy to the dopant species; this is to differentiate this process from the principal electrical current transmission across the barrier which is without energy loss and so described as elastic tunneling. It is from this observation that the technique of Inelastic Electron Tunnelling Spectroscopy (IETS) has evolved.

IETS is a surface spectroscopy which reflects chemical/physical modifications associated with the adsorption process. It has been successfully applied in surface chemistry and catalysis, adhesion and corrosion and molecular vibrational and electronic spectroscopy[2]..

IETS BASICS

The “sample” in IETS is a metal/thin insulator/(adsorbate)/metal sandwich. When a voltage V is maintained across the sandwich, filled states in one metal lie opposite empty states in energy terms in the other metal. Figure 1 is drawn for a typical tunnel junction, something like an Al-Al_2O_3-anthracene-Pb diode[3]. The HOMO and LUMO of anthracene and a few schematic ground vibrational levels are also shown on Figure1. Suppose, as in Figure 1, that a small positive voltage, V, is applied at the top(Pb) electrode. Because the electric field inside a metal must vanish, all the potential drop occurs within the barrier.

Figure 1. energy diagram for a model Al-Al_2O_3-anthracene-Pb tunnel Diode showing elastic and inelastic tunneling channels (top). The hatched Region represents the filled states of the top and bottom metal electrodes.

The area in the center represents the insulator and adsorbate. The HOMO (π) and LUMO(π*) orbitals of an anthracene like adsorbate are shown and a few schematic vibrational levels are indicated. Energy loss (equilibration) for the tunneling electron occurs through a cascade process in the metal electrode. Also shown(bottom) are the *I-V* curve, conductance-*V* curve, and IETS band that would result from an inelastic tunneling channel opening at *eV*=*h*ν.

Because the molecule, X, is closer to Pb than to Al, its potential almost moves with that of Pb. At this point a band of electrons *eV* wide has sufficient energy to tunnel into empty states of the M’(Pb) electrode. If the electrons do so without loss of energy, it is elastic tunneling. Equation 1 approximates the elastic tunneling current at 0 K for small *V*. The average barrier height is ♐🕓☎♐$_{M}$ + ♐$_{M'}$ – eV)/2. For a typical IETS diode, ♐🕓 4 eV and

d 🕓 2 nm. For values of V larger than about 0.7 V the current becomes nonlinear in *V* because of the voltage dependence of the effective barrier height.

$$I = CV \exp(- Ad\ ♐^{1/2}) \qquad (1)$$

In addition to elastic tunneling, there are other tunneling mechanisms which may contribute to the current. IETS is based upon inelastic scattering as is also shown in Figure 1. The moving electronic charge interacts with the time varing molecular dipoles(electronic or vibrational) to induce excitation of the molecule in the barrier with concomitant loss of energy by the electron. If the applied voltage is less than *h*■*/e,* the inelastic channel is closed because the final states are already filled. At *V* = *h*■*/e* the inelastic channel opens. Further increases in *V* result in additional possible final states with an associated increase in current due to this channel. As is depicted in the lower half of Figure 1, there is a break in the *I(V)* curve at *V* = *h*■*/e*. If one measures the conductance, *dI/dV*, the opening of the inelastic channel is signaled by a step, typically of order 1% or more for phonon or electronic excitations, but only 0.1% or less for the majority of molecular excitations. Consequently, it is common for the second derivative of the I-V characteristic to be displayed versus V, that is plotting d^2I/dV^2 versus *V*. This renders the small but steep changes in conductance associated with inelastic events as a series of peaks superimposed on a more gently sloping “elastic background”. Both vibrational and electronic transitions may be observed as peaks in the d^2I/dV^2 versus *V* plots.

EXPERIMENTAL METHODS

Sample Preparation

Basic metal-insulator-metal (MIM) tunnel junctions can be obtained simply by thermal evaporation of metals through a shadow mask onto a glass slide. Because of the high sensitivity of IETS, using scrupulously cleaned and dried substrates with liquid nitrogen traps in diffusion pump vacuum systems to avoid contamination of the insulator surface is required.

Typically, the fabrication procedure is as follows:

1. Evaporation of base electrode film(s) on substrate (often Al on a glass slide).
2. Oxidation step (oxygen plasma discharge, sometimes room oxidation is sufficient).
3. “Doping”- introduction of adsorbate of interest either as a dilute spun-off solution, or as a vapour.
4. Evaporation of top electrode film cross-strip (frequently Pb).

A completed junction is shown in Figure 2.

In practice, four terminal electrical contact is made either through the use of In solder or mechanical contacts to the junction to avoid errors in measuring the junction voltage due to parasitic ohmic volt-drops along the metal films and connecting wires. The resistance of a viable junction will usually in the range 10-1000 ohm.mm^2.

Since the IETS line width depends on temperature and is about 3.5 Tcm^{-1}K^{-1}, vibrational IETS is most often performed below 5 K. To achieve this, the junction is immersed into liquid helium held in a storage dewar. For electronic transitions, liquid nitrogen will suffice.

Comparing to the established technique of making MIM junction, recently there is a new kind of “clean” junction by replacing the oxide layer of MIM junction by an atomically thin gas film. This adjustable oxide-free tunnel junction is called self-assembling tunnel junction (SATJ)[4,5]. The SATJ is formed by pressing together two long, fine metallic wires whose separation is set by an atomically thin inert gas barrier film. The molecules to be studied can either be deposited directly onto the metal surfaces or coadsorbed with the inert gas film. The advantages of having an inert gas instead of an oxide barrier in the junction are (1) the junction is completely adjustable and easily be cleaned and dosed *in situ*; (2) the molecules to be studied are not strongly perturbed by the presence of the inert gas barrier as they would be with an oxide barrier.

INSTRUMENTATION

All IET spectrometers obtain the second derivative of the I-V curve using an ac modulation technique. This evolves lock-in detection of the second harmonic voltage generated by junction nonlinearities in response to a small modulation signal applied to the dc bias. The amplitude of the second-harmonic can be shown by means of a Taylor series expansion to be proportional to the second derivative. The recovered signal is plotted as a function of dc bias voltage (0-30 mV for metal phonons, 30 – 500 mV for molecular modes, 0.5-2.5 V for electronic transitions) in a sweep which may take typically 10-100 minutes. As the second-harmonic signals are small (down to nV levels), minimizing internal noise and external pick-up is very important. Frequently, the scan and signal recovery hardware is computer-controlled and may also include background subtraction/nulling and other more complex features. Figure 3 shows the simplest design appropriate for the vibrational region of the spectrum.

PEAK BROADENING EFFECTS

There are three parameters which affect the width of a peak in addition to the natural width (of order 1 meV FWHM for phonons and molecular vibrations, but typically 100 meV or more for electronic excitations).

1. Thermal broadening – contributing a FWHM of 5.4 kT to a line of zero natural width. This amounts to 2 meV at 4.2 K, 36 meV at 77 K and 140 meV at 300K.
2. A.c. modulation voltage or instrumental broadening – equivalent to a FWHM 1.7 times the rms modulation voltage for a line of zero natural width at 0 K.
3. Superconductivity effects – one or more of the electrodes in a tunnelling junction maybe superconducting at liquid helium temperatures. This improves resolution

by sharpening the quasiparticle DOS, but also shifts and distorts the peak and produces undershoot on narrow features.

ADVANTAGES

1 ultrahigh sensitivity – 0.01 monolayer in a junction of area ○ 1 mm^2 (~ 10^9 molecules) can be detected;

2 wide spectral range –20 to 20000 cm^{-1};

3 good resolution – better than 5 cm^{-1};

4 overtone and combination bands are exceptionally weak – easier to identify fundamentals in IETS than in IR or Raman;

5 optically forbidden transitions may be observed as strong bands;

6 singlet-triplet electronic transitions are allowed.

DRAWBACKS

1. IETS is only applicable to system incorporating a thin, continuous insulating layer sandwiched between two conductors;
2. Resolution is limited by thermal smearing of electron energies at E_F, necessitating the use of liquid helium temperatures in vibrational spectroscopy;
3. Tunnel junctions normally exhibit a rapidly-increasing elastic current followed by breakdown at biases in excess of 2 to 3 volts. This limits the prospects for studying electronic transitions;
4. Studied molecules are buried within the junction in a complex environment that is difficult to characterize.

SELECTION RULES

There are no quantum mechanical selection rules to restrict IETS, with the result that all vibrational modes are active. Furthermore forbidden electronic transition – single-triplet electronic transitions are allowed – probably due to spin exchange between the tunnelling electron and the excited system.

By consideration of image forces, a preference for coupling between tunnelling electrons and dipoles oriented normal, rather than parallel, to the electrode plane is predicted for dipoles close to one electrode. However no detailed theoretical justification has been produced for the orientational selection rule.

APPLICATIONS

There are many instances in which IETS has proved a useful tool in surface analysis. It has been applied in

1. Study of vibrational modes

Since IETS is in general not selection-rule restricted and has the potential to present all non-degenerate vibrational modes, it is useful as an alternative to optical spectroscopies. Recent study of tunnelling spectroscopy of fullerene/Ge multilayer systems[6] is a good case in point. By layering thin, thermally evaporated films of germanium and fullerene molecules, composite multilayer tunnel barriers are formed which appear to produce enhanced IET results. IETS successfully resolved 40 of the 46 C_{60} intramolecular vibrational modes and ~50 of the 122 modes of C_{70}.

2. Study of electronic transitions

Forbidden electronic transitions can also be observed by IETS. The first electronic transition observed by IETS was the singlet to triplet π-π* transition of copper phthalocyanine.

Recently, IETS has been applied to investigate the electron states of a tunneling junction containing both magnetic and nonmagnetic electrodes[7,8], assisting characterization of magnetic tunnel junctions.

3. Study of molecular orientation

By accepting that vibrational modes of bonds parallel to the surface will not normally be observed in the IETS spectrum and by analysing for the presence or omission of vibratoinal modes of molecules, their surface orientation may be inferred. But no theory supports this selection rule.

4. Study of adhesion and corrosion

Aluminum is the most widely studied substrate for adhesive bonding, due to its numerous industrial applications. This is fortunately convenient as alumina is the most common surface oxide studied in IETS tunnel junctions. It therefore seems that IETS is "tailor-made" for the study of adhesion and corrosion through observing surface reactions taking place on a metal oxide surface.

5. STM-IETS

IETS has bee applied to a wide range of systems and has led to a better understanding of molecules in the adsorbed state. However, IETS has a major drawback: Molecules are buried within the junction in a complex environment that is difficult to characterize. Recent development of the STM implementation of IETS extends the IETS method to a single molecule. The STM essentially consists of a tiny tunnel junction, in the form of an atomically-sharp tip suspended about 1 nm above the conducting surface of interest. In this arrangement, the metal-oxide-metal tunnel junction is replaced by the STM tunnel junction: a sharp metal tip, a vacuum gap of several angstroms, and a surface with the adsorbed molecules. The combination of atomic resolution and vibrational spectroscopy allows the creation of atomic-scale spatial images of the inelastic tunneling channel for each vibrational mode rather than solely to "infer" the atoms/molecules under the tip from their relative positions on the surface or from coarse spectroscopic data. Chemical identification would considerable enhance the usefulness of STM, especially on poorly-defined surfaces of technological interest.

Recent study of inelastic electron tunneling spectra for an isolated acetylente(C_2H_2) molecule adsorbed on the copper (100) surface showed an increase in the tunneling conductance at 358 millivolts, resulting from excitation of the C-H stretch mode. An isotopic shift to 266 millivolts was observed for deuterated acetylene (C_2D_2)[9]. Vibrational microscopy from spatial imaging of the inelastic tunneling channels yielded additional data to further distinguish and characterize the two isotopes. Vibrational imaging of the adsorbed molecule was obtained while scanning the tip in constant-current mode to record the surface topography. At each data point, the feedback was turned off and the bias modulation turned on to record dI/dV and d^2I/d^2V. This procedure resulted in three images of the same area.

Figure 4.Background difference d^2I/dV^2 spectra for C_2H_2 (1) And C_2D_2 (2), taken with the same STM tip, show peaks at 358 mV and 266 mV, respectively. The difference spectrum (1-2) yields a more complete background subtraction. For this tip, Δ♦/♦ = 6.2% and 4.5% for C_2H_2 and C_2D_2 respectively.

Figure 4. Spectroscopic spatial imaging of the inelastic channels for C_2H_2 and C_2D_2. (**A**) Regular(constant current) STM image of a C_2H_2 molecule(left) and a C_2D_2 molecule (right). Data are the average of the STM images recorded simultaneously with the vibrational images. The imaged area is 48Å by 48Å. d^2I/dV^2 images of the same area recorded at (**B**) 358 mV, (**C**) 266mV, and (**D**)311mV are the average of four scans of 25 min each with a bias modulation of 10 mV. All images were scanned at 1 nA dc tunneling current. The symmetric, round appearance of the images is attributable to the rotation of the molecule between two equivalent orientations during the experiment.

As expected, no contrast was observed in a constant-current images of both acetylene isotopes (Fig.5A). When the dc bias voltage was fixed at 358 mV, only one of the two molecules was reveled in the image constructed from the d2I/d2V signal. By changing the dc bias voltage to 266 mV, the other molecule was imaged (Fig. 5C). Two small identical depressions observed at 311 mV (Fig. 5D) were attributed to the change in the electronic density of states on the sites of the two molecules, The spatial extent of the inelastic tunneling channels appears to be at least as narrow as the constant-current molecular image. Single-molecule vibrational analysis should lead to better understanding and control of surface chemistry at the atomic level. It may soon be possible to use single-molecule vibrational spectroscopy and microscopy to determine the identity and arrangement of functional groups within a single molecule and to study its chemical transformation.

CONCLUSION

Inelastic tunneling, whether in tunnel junctions or at the STM tip, has a potentially important role to play in surface analysis and as an alternative bulk molecular spectroscopy. Although IETS has drawbacks, its established theory background and variety uses in different surface analysis still make it a useful surface analysis tool and worthy of the notice by chemists. In the later development of IETS, it may be used in the study of chemical sensing, single-crystal/oriented surfaces or electronic transitions in organic semiconductors etc.

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