

## Electronic Transport through Molecular Monolayers

Quantum mechanical tunnelling of electrons through thin inorganic insulators has been thoroughly studied. In contrast, tunnelling through thin *organic* insulators has been studied very little, due primarily to the difficulty of fabricating pinhole-free organic thin films.

New interest in molecular electronic devices is driving efforts to develop a robust understanding of electron transport through these organic systems. Theory and experiment have to date focused on two-terminal devices consisting of a single molecule or a molecular monolayer sandwiched between conducting electrodes. A range of interesting behaviours has been reported, including rectification, negative-differential resistance, switching, and transistor action. Theoretical predictions for molecular device behaviour have relied on standard temperature-independent models of resonant and non-resonant quantum mechanical tunnelling.

We have conducted an investigation of electron transport through a 2.8 nm thick organic insulating film. An exponential temperature dependence and a large low-bias conductance anomaly were observed, in striking contrast to the expected weak temperature dependence and small zero-bias anomaly displayed by an inorganic alumina control sample of matched 3.0 nm thickness. These data imply that tunnelling through organic thin films is very different than the well understood tunnelling through inorganic films. Both the exponential temperature dependence and the large low-bias anomaly suggest a strong electron-phonon interaction may dominate the transport properties in this organic system.

The experiment consisted of current-voltage (I-V) measurements as a function of temperature on two terminal metal/insulator/metal planar junction

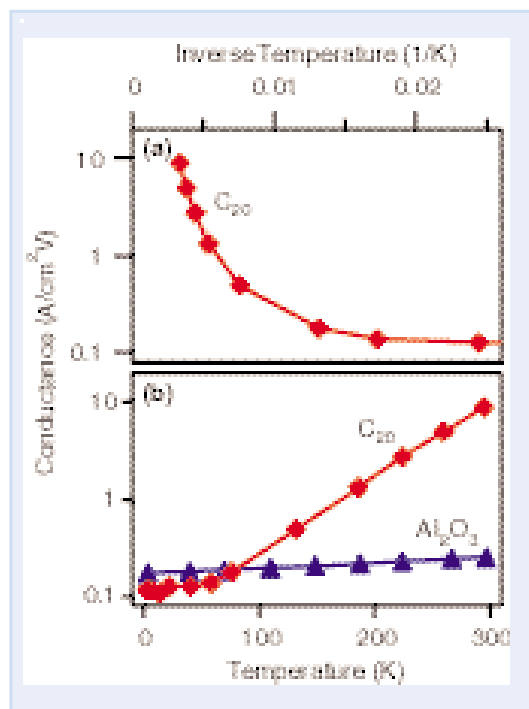


Figure 1. The influence of temperature on electron transport through films

devices. Two different insulating thin films were investigated; a Langmuir-Blodgett (LB) organic molecular monolayer of eicosanoic acid  $C_{19}H_{39}COOH$  ( $C_{20}$ ), and a thin film of plasma-oxidized alumina ( $Al_2O_3$ ). Eicosanoic acid was chosen since it forms physically well characterised, highly ordered LB films and is intrinsically a wide band-gap insulator.  $Al_2O_3$  was selected since it can form high quality, conformal, thin dielectric films, and it has been well characterised in previous studies. Both insulating films were sandwiched between platinum (Pt) electrodes, with active junction areas of  $5\text{-}200\ \mu\text{m}^2$  and thus  $10^7\text{-}10^9$  molecules electrically in parallel at each molecular device junction.

Electronic transport through very thin  $<2$  nm insulators is dominated by temperature-independent tunnelling. Thick films  $>5$  nm display temperature activated hopping or thermionic emission of several flavours; all understood via an inverse temperature Arrhenius plot. The  $C_{20}$  films show a strong temperature dependence, but it is not thermally activated; no straight lines can be found over the  $300\text{ K} - 40\text{ K}$  range of the

Figure 1(a) Arrhenius graph. Surprisingly, when the data are plotted vs. linear temperature in Figure 1(b), over the same temperature range a straight line is immediately evident. The  $C_{20}$  conductance is thus exponential in temperature above  $T_1 \sim 60\text{ K}$ , fitting no known theory. The  $Al_2O_3$ , in contrast, is well behaved with the expected  $\sim 15\%$  change in conductance between  $300\text{ K} - 2\text{ K}$ .

Tunnelling I-V fits using Simmons' tunnelling equation overlay the  $Al_2O_3$  data perfectly. For the  $C_{20}$  however, the data deviated significantly from theory at low bias  $V < 0.2\text{ V}$ . In both cases, tunnel barrier

fit parameters were reasonable, with thicknesses of  $2.6 - 3.2\text{ nm}$  and heights of  $1 - 3\text{ eV}$ .

Vibrational modes of many organic molecules including  $C_{20}$  have been measured by IR and Raman optical spectroscopies, and by inelastic electron tunnelling spectroscopy (IETS). The extensive IETS work has studied electron-vibron interactions in some detail, but sample geometries and techniques prevented temperature dependent studies. Microfabrication of pinhole-free monolayer devices has enabled this additional investigation of organic electron tunnelling. The exponential temperature dependence and large low-bias anomaly observed in the  $C_{20}$  suggest a strong electron-vibron coupling. Theory to explain this intriguing puzzle, however, does not yet exist – and with these difficult-to-characterise organic-inorganic interfaces, experimental unknowns persist. Both serve as a strong incentive for further experiment and theory.

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