

General Discussion

Professor Lindsay opened the discussion of Professor Heath's paper: Please comment on the Hewlett-Packard report that switching is seen in systems that do not contain rotaxane molecules.

Professor Heath replied: This is an issue that has gotten a significant amount of attention. The HP group does see molecule-independent switching. When we utilized all-metal electrodes—which is how we began several years ago—we also saw molecule-independent switching. That is why we abandoned metal bottom electrodes and pursued silicon (or carbon nanotube) bottom electrodes.

The HP devices exhibit large amplitude switching that is temperature independent and only weakly (if at all) depends upon the actual molecule within the junction.¹ That group has postulated that a physical mechanism is responsible for the switching—namely the reversible, electrochemical growth of a single conducting filament that bridges the top and bottom electrodes. Indeed, when the HP devices switch from the low-conductance to the high-conductance state, a single 'hot-spot' of high conductance can be imaged, using scanning probe microscopy, on the top electrode surface.² This hot spot apparently correlates to the physical region in which the conducting filament is formed, and it disappears once the junction is electrically switched back to the low-conductance state. The CIT/UCLA devices, on the other hand, are observed to switch based upon a thermally activated process that depends strongly upon the nature of the molecule within the junction.^{3–6} We have proposed a chemical mechanism for this switching, which I have described in my Faraday Discussion paper.

We have investigated this issue in some detail. In one set of experiments, we studied single molecule break junction field-effect transistors.⁷ In those experiments, a single [2]rotaxane molecule was either chemisorbed to either end of the break junction, or physisorbed on one end and chemisorbed to the other end. We found that our device response was highly dependent upon the nature of the molecule/electrode contacts, but almost completely independent of the nature of the [2]rotaxane.

We also found that semiconducting, single-walled carbon nanotubes could be substituted for the silicon bottom electrode, and in those cases we were able to 'see' the molecular properties in the switching response.⁸

The result of all of this is that the electrodes make all of the difference in the world. One possibility is the image charge on the metal surface (which will be significantly greater than that on a semiconductor surface) and how that charge interacts with the electrochemical processes one is trying to realize on the molecular switches. The second possibility is that the metal/molecule contact is simply too ionic—*i.e.* it serves as a sort of Schottky barrier that constitutes the rate-limiting step to charge flow.

In Table 1 I compare the HP and Caltech/UCLA device types.

1. The switching amplitude can be both molecule and temperature dependent. For some rotaxanes investigated, the ground state co-conformation/ metastable state co-conformation (GSCC/MSCC) ratio is temperature dependent in acetonitrile solution. For those same molecules, the switching amplitude within an MSTJ is also temperature dependent.

2. The lifetime of the high-conductance state is both molecule and temperature dependent.

3. The sharp voltages at which the switch opens or closes are observed to shift to high magnitude bias with increased cycling of the device.

4. A current–voltage response similar to what is reported for the HP devices can be observed for the CIT/UCLA devices if those devices are operated at high voltages ($> |3\text{ V}|$). SWNT-based MSTJs were demonstrated for [2]catenanes only.

5. Controls have included **Rblock**⁴⁺, the dumbbell components of bistable [2]rotaxanes, degenerate [2]catenanes, and linear amphiphiles, such as eicosanoic acid.

6. Controls have included the dumbbell components of bistable [2]rotaxanes and linear amphiphiles, such as eicosanoic acid.

1 D. R. Stewart, D. A. A. Ohlberg, P. A. Beck, Y. Chen, R. S. Williams, J. O. Jeppesen, K. A. Nielsen and J. F. Stoddart, *Nano Lett.*, 2004, **4**, 133–136.

Table 1 A comparison of the differences of [2]rotaxane (and [2]catenane) containing devices reported by the HP groups and the CIT/UCLA groups

Property/ Device	Switching amplitude	High cond. state lifetime	Therm. activated?	Stable write voltages	# cycles	Bottom electrodes	Controls switch?
CIT/UCLA	3–10 ¹	10 min–1 h ²	YES	Yes	10 ¹ –10 ³	Si with native SiO ₂ or SWNTs ⁴	NO ⁵
HP	10 ² –10 ⁵	> 125 days	NO	NO ⁴	> 10 ⁶	Metal (Pt)	YES ⁶

- 2 C. N. Lau, D. R. Stewart, R. S. Williams and M. Bockrath, *Nano Lett.*, 2004, **4**, 569–572.
- 3 C. P. Collier, G. Mattersteig, Y. Li, E. W. Wong, K. Beverly, J. Sampaio, F. Raymo, J. F. Stoddart and J. R. Heath, *Science*, 2000, **289**, 1172–75.
- 4 D. W. Steuerman, H.-R. Tseng, A. J. Peters, A. H. Flood, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart and J. R. Heath, *Angew. Chem., Int. Ed.*, 2004, **43**, 2–7.
- 5 A. H. Flood, J. F. Stoddart, D. W. Steuerman and J. R. Heath, *Science*, 2004, **306**, 2055–2056.
- 6 J. W. Choi, A. Flood, D. W. Steuerman, S. Nygaard, A. Braunschweig, N. N. P. Moonen, B. W. Laursen, Y. Luo, E. DeIonno, A. J. Peters, Jan O. Jeppesen, J. F. Stoddart and J. R. Heath, *Chem. – Eur. J.*, DOI: 10.1002/chem.200500934.
- 7 H. Yu, K. Beverly, H.-R. Tseng, J. F. Stoddart and J. R. Heath, *Angew. Chem., Int. Ed.*, 2003, **42**, 5706–5711.
- 8 M. R. Diehl, D. S. Steuerman, H.-R. Tseng, S. A. Vignon, A. Star, P. C. Celestre, J. F. Stoddart and J. R. Heath, *ChemPhysChem*, 2003, **4**, 1335–1339.

Professor Lindsay asked: The molecule contains polar groups—how do you know that no counterions are carried with it when the films are prepared?

Professor Heath replied: We don't know that and, in fact, it is very likely that the counterions are carried with the molecules—we see some evidence of that with XPS, *etc.* The molecules aren't just polar, they have a tetracationic group (the +4 charged cyclophane rings) and that group is accompanied by four PF₆[−] anions. Whether there is some exchange of these counteranions with OH[−] or not (from the aqueous subphase), I don't know—that is a hard question to answer. However, the electrochemical process itself doesn't really need counterions—the electrode materials themselves provide an image charge that is, in effect, a counterion. We reported evidence of that in our very first paper on reconfigurable switching—*i.e.* we showed that as the silicon electrode was cooled (and hence became less polarizable), the voltage required to cycle the device between the high and low conductance states shifted by nearly 1 V.¹ This would not be observed with metal electrodes, since the polarizability of a metal electrode is not really temperature dependent.

- 1 C. P. Collier, G. Mattersteig, Y. Li, E. W. Wong, K. Beverly, J. Sampaio, F. Raymo, J. F. Stoddart and J. R. Heath, *Science*, 2000, **289**, 1172–1175.

Professor McCreery commented: I agree that an image charge can act as a “counterion” in a device, as we have direct spectroscopic evidence for reduction of a molecule to an anion which is stabilised by a positive image charge in a gold counter electrode. Stated differently, a high imposed electric field can cause a redox reaction, analogous to that occurring in an electrochemical double layer.

Professor Heath said: Yes, I of course agree. It think that we made a pretty good case for this in our first paper on a reconfigurable switch.¹

- 1 C. P. Collier, G. Mattersteig, Y. Li, E. W. Wong, K. Beverly, J. Sampaio, F. Raymo, J. F. Stoddart and J. R. Heath, *Science*, 2000, **289**, 1172–1175.

Professor Calvo asked: How many cycles have you tested your molecular devices before it fails?

Professor Heath replied: A good device will cycle for about 1000 times. Most devices will cycle for far fewer times. This is not something that we have worked hard on improving, although we will likely be thinking hard about this issue within the near future.

Dr Schuster asked: What are the differences between the switch and hysteresis of switch?

Professor Heath answered: A switch can be bistable—moving between a high and low conductance state upon the application of a stimulus. However, once the stimulus is removed, it may revert back to its original state (or ground state). A hysteretic response implies that a negative stimulus must be applied to switch the molecule back to the original state—similar to how a ferromagnetic bit responds to the application of a magnetic field. Typically that implies that there is some sort of activation barrier involved in cycling between the two states. For our devices, the high-amplitude molecular mechanical motion provides that activation barrier—typically about 22 kcal mol⁻¹ or so within a device.¹

1. J. W. Choi, A. Flood, D. W. Steuerman, S. Nygaard, A. Braunschweig, N. N. P. Moonen, B. W. Laursen, Y. Luo, E. DeIonno, A. J. Peters, Jan O. Jeppesen, J. F. Stoddart and J. R. Heath, *Chem. – Eur. J.*, DOI: 10.1002/chem.200500934.

Professor Larsson asked: What makes you decide to use a particular molecule in your circuits? For example I recognise the molecule TTF on one of your pictures. This is a well-known molecule in conducting molecular crystals, but since you use a single TTF molecule, you are probably interested in other than conduction properties in this case?

Professor Heath replied: The TTF (tetrathiafulvalene) group is not the key part—the structure of the molecules that we use as switches is what matters most. TTF molecular crystals are good conductors, but that is also not the point. What we mostly care about are good switches—which means that we care about molecules that can change their conductance when they are electrochemically switched and the electrochemical switching process has a significant hysteresis.

The class of molecules that we use (and which contain TTF groups) are bistable, donor–acceptor, electrochemically switchable [2]catenanes and [2]rotaxanes. Our molecules are designed to do a number of things. First, they have to be amphiphilic so that they will orient at an air/water interface. It is from this interface (a Langmuir–Blodgett film) that we fabricate our devices. Second, the molecules should be bistable and electrochemically switchable between the two isomers (co-conformers). The TTF group, which is readily oxidized, does play an important role here. The third issue is that we need to control the potential energy surface that describes the bistability of the molecules, and we do that through the molecular structure of the switches.¹ I believe that all of this is pretty well-described in the Faraday Discussion paper that I have written.

1. J. W. Choi, A. Flood, D. W. Steuerman, S. Nygaard, A. Braunschweig, N. N. P. Moonen, B. W. Laursen, Y. Luo, E. DeIonno, A. J. Peters, Jan O. Jeppesen, J. F. Stoddart, J. R. Heath, *Chem. – Eur. J.*, DOI: 10.1002/chem.200500934.

Professor Weber asked: Is the switching in a solid state device happening under constant volume conditions or constant pressure? Is this important for the thermodynamic picture you presented?

Professor Heath answered: Typically constant volume and constant pressure conditions are most important for gas phase processes. Solution phase and other condensed phase processes are almost always assumed to be at constant volume or constant pressure (which is the case for our systems). Thus, I don't think it is important. Constant temperature is important, and yes, we only varied temperature where it is specifically noted that we did.

Professor Weber asked: When the molecular film changes its structure during switching, would you consider the top layer–substrate distance as unchanged?

Professor Heath replied: Yes, I think that is probably the case. Thomas Bjørnholm's group has done some measurements (work in press to *Angewandte Chemie*, I think) that can speak to just this issue, although a truly direct quantitation has not been done. In addition, Goddard's group has calculated the structure of the ground state and metastable state co-conformers when they are

sandwiched as a Langmuir monolayer between two electrodes.¹ Those results are, I believe, consistent with what Bjørnholm's group has observed.

1. S. S. Jang, Y. H. Jang, Y.-H. Kim, W. A. Goddard, III, A. H. Flood, B. W. Laursen, H.-R. Tseng, J. F. Stoddart, J. W. Choi, D. W. Steuerman, E. DeLonno, J. R. Heath, *J. Am. Chem. Soc.*, 2005, **127**, 1563–1575.

Professor Weaver said: The architectures proposed seem to be driven by the inadequacy of conventional lithography. As modern lithographic pattern definition can define structures to 23 nm period, does this have any impact on the methodology proposed? (using a periodically defined electrode array).

Professor Heath replied: Sure, but I have yet to see any sort of general lithographic method (*i.e.* can fabricate any arbitrary pattern) that can come close to a 20 nm pitch. Our SNAP process can exceed 20 nm pitch—we have demonstrated 16 nm,¹ and, as you have seen, it produces very high quality nanowires, including Si nanowires. I haven't seen any patterning method that can come close to this sort of perfection in fabrication. In fact, our colleagues at Hewlett Packard have repeatedly challenged several excellent groups who specialize in doing state-of-the-art electron-beam lithography to prepare patterns for them that could be utilized to fabricate crossbar memory circuits (out of metals, not silicon (silicon is tougher)) at pitches narrower than 60 nm. No one has yet been successful in meeting their challenge.

1. N. Melosh, A. Boukai, F. Diana, B. Geradot, A. Badolato, P. Petroff and J. R. Heath, *Science*, 2003, **300**, 112.

Dr Higgins communicated: Please could you outline briefly your evidence for the “innocence” of Ti deposition in these systems? Given DFT and experimental evidence for Al reactivity with conjugated organic materials in organic LED top contacts *etc.*, I find it very surprising that Ti does not affect these complex (and quite oxygen-rich) molecules.

Professor Heath communicated in reply: There is a growing body of literature indicating that Ti deposition can form a film that serves as a good electrical interface that is also largely non-destructive for certain molecules, although much depends on the nature of the molecular film and on the nature of the Ti deposition process. For low-density films such as certain SAMs assembled onto Au surfaces, Ti deposition is apparently destructive.¹ This is likely due to the much greater area per molecule for those SAMs. For example, a SAM formed from one of our [2]rotaxanes occupies just under 400 Å² molecule⁻¹, while a typical amphiphilic [2]rotaxane, compressed to $\pi = 30 \text{ mN m}^{-1}$ on a Langmuir trough (a typical transfer pressure for incorporating into a device) occupies 90–130 Å² molecule⁻¹.^{2,3} Most of the molecular structure within a low-density [2]rotaxane SAM would be exposed to an incident flux of Ti, and thus destroyed by reactions with those atoms.

Highly compressed Langmuir monolayers, however, do apparently survive the deposition of Ti. Allara's group published some early work in which they carried out a series of X-ray photoelectron (XPS) studies on organic monolayers before and after Ti had been evaporated.⁴ More recently Chang and co-workers published a reflectance-absorption infrared (RAIR) spectroscopic study of a molecular monolayer both before and after evaporation of 2 nm Ti.⁵ Both groups found evidence that much of the molecular monolayer survived the deposition process. The most thorough study to date has been carried out by McCreery's group.⁶ They investigated the nature of 1–3 nm thick Ti films evaporated on top of a thin nitroazobenzene (NAB) film (thickness controlled from a submonolayer to 4.5 nm) through the use of Raman spectroscopy. While much of the Raman spectrum of the 4.5 nm NAB film remained intact upon deposition of the Ti, they did find evidence for reaction between the Ti and the terminal NO₂ group, although those Raman signatures significantly recovered over a period of several days. For submonolayer films, the changes observed in the Raman spectrum were more significant, as would be expected from the above discussion of SAMs. Equally interesting is that no new spectral features were observed after Ti deposition on azobenzene. McCreery's group concluded that the reaction between Ti and the nitro group appears to prevent short circuits that can form from the inclusion of Ti into the molecular film, and that the Ti forms a covalent bond between the electrode and the molecular film. We have begun to carry out

similar measurements on our [2]rotaxane and [2]catenane monolayers, and our results are so far consistent with what McCreery's group observed. We definitely observe that most of the RAIR spectral signatures of the molecular monolayer survives the deposition process, but we are still working out the details of what we believe happens.

We have reported that the titanium adhesion layer may be replaced with chromium,⁷ although the resultant performance characteristics of MSTJs are inferior. Cr, like Ti, can react rapidly to form a Cr-C interface.⁸ McCreery has investigated Cu, and many groups have investigated Au and other materials for different class of molecular electronic devices.

- 1 B. de Boer, M. M. Frank, Y. J. Chabal, W. Jiang, E. Garfunkel and Z. Bao, *Langmuir*, 2004, **20**, 1539–1542.
- 2 S. S. Jang, Y. H. Jang, Y.-H. Kim, W. A. Goddard, III, A. H. Flood, B. W. Laursen, H.-R. Tseng, J. F. Stoddart, J. W. Choi, D. W. Steuerman, E. DeIonno, J. R. Heath, *J. Am. Chem. Soc.*, 2005, **127**, 1563–1575.
- 3 S. S. Jang, Y. H. Jang, Y.-H. Kim, W. A. Goddard III, J. W. Choi, J. R. Heath, B. W. Laursen, A. H. Flood, J. F. Stoddart, K. Norgaard and T. Bjørnholm, "Molecular Dynamics Simulation of Amphiphilic Bistable [2]Rotaxane Langmuir Monolayer at the Air/Water Interface," *J. Am. Chem. Soc.*, in press, 9/2005.
- 4 K. Konstadinidis, P. Zhang, R. L. Opila and D. L. Allara, *Surf. Sci.*, 1995, **338**, 300.
- 5 S.-C. Chang, Z. Li, C. N. Lau, B. Larade and R. S. Williams, *App. Phys. Lett.*, 2003, **83**, 3198.
- 6 A. M. Nowak and R. L. McCreery, *Anal. Chem.*, 2004, **76**, 1089–1097.
- 7 C. P. Collier, G. Mattersteig, Y. Li, E. W. Wong, K. Beverly, J. Sampaio, F. Raymo, J. F. Stoddart and J. R. Heath, *Science*, 2000, **289**, 1172–75.
- 8 D. R. Jung and A. W. Czandema, *Crit. Rev. Solid State Mater. Sci.*, 1994, **19**, 1–54.

Professor Naaman opened the discussion of the papers by Professor Ashwell and Professor McCreery: There is an organization induced charge transfer when SAM is formed. Hence the dipole moment of the adsorbed molecule is not the same as that of the isolated one.

Professor: McCreery commented: Indeed, we have to keep in mind that these are not isolated molecules, and that their dipoles and/or molecular orbitals will be affected by both orientation and interactions with the contacts and each other. Our approach to this question is to use *in situ* spectroscopy when possible to probe electronic structure in completed junctions.

Professor Ashwell added: I agree but there are many possible structural forms and, when connected to the substrate *via* a flexible $S-C_nH_{2n}$ bridge, overlap of the donor and acceptor groups of adjacent molecules is feasible if there is sufficient tilt. However, the direction of electron flow at forward bias from all reported rectifying SAMs is consistent with that predicted by Aviram and Ratner with rectification in opposite quadrants of the $I-V$ plot when molecules are linked *via* the donor or acceptor end: $Au-S-C_nH_{2n}-D-\pi-A$ and $Au-S-C_nH_{2n}-A-\pi-D$. It suggests the molecular origin of the rectification and, where protonation disrupts the donor-acceptor combination, it is also verified by the rectifying behaviour being respectively suppressed and restored upon exposure to acid and base.

Professor Lindsay said: Professor Naaman's comment about charge-transfer in response to accumulations of a surface dipole does not seem to be consistent with electric force microscopy results that show that in alkanethiol tethered systems, the change in dipole per unit area measured correlates precisely with the change in dipole of the head group.

Professor Naaman responded: It is important to realize that the cooperative effect I described is a result of not having contacts to the molecules on both sides. Namely, it is a result of the dipole layer having to hold a very large electrostatic energy. When a second contact is made, the polarization of the metal contact reduces the effect of the dipole. The cooperative effect is manifested clearly in the fact that the change of the work function as a result of the dipole layer is by far lower than expected based on the dipole layer of the isolated molecule. In addition it is important to realize that in the electric force microscopy studies a very large field is applied locally on the molecular system. This field perturbed the system so that one does not expect a relative weak cooperative effect to be expressed in these studies.

Dr Rampi addressed Professor Ashwell: Polar molecules organise in SAM with a tilt angle that depends on the polarity and tend to neutralise the dipole.

Professor Ashwell replied: It applies to all types of organised molecular films and in LB monolayers of the extensively studied zwitterion, C₁₆H₃₃-Q3CNQ, the molecules adopt three different structural forms dependent upon the conditions of formation. They exhibit different spectra with absorption maxima at 565 nm for an SHG-active purple form and at 610 and 670 nm for SHG-inactive turquoise forms. Only the non-centrosymmetric purple form exhibits rectifying behaviour.

Professor Heath asked Professor McCreery: Your Raman result showed that your molecule junctions are compromised by +3 V. Is this true for all top electrode materials? Is this a field or a voltage effect?

Professor McCreery replied: I would not use the word “compromised” as that implies degradation. We have observed redox activity with TiO_x and AlO_x top contact materials, some of which is reversible. With Cu or Au, the electron transport through the molecule is much faster, and apparently too fast for oxidation or reduction to occur. The oxides prevent rapid electron transport, and presumably a large electric field is developed across the molecule. We speculate that the redox reactions result from the electric field rather than the applied potential, since there is no reference electrode to establish the applied voltage relative to some vacuum reference level. The electric field across the molecule is in the region of 10⁶ V cm⁻¹, which is certainly comparable to the electrochemical double layer that drives electrochemical oxidations and reductions. However, without having a reference potential, it is difficult to determine where the PPF potential lies relative to the redox level or LUMO of the adjacent molecule.

Professor Weber addressed Professor Ashwell: You showed *I*-*V* plots up to ±1 V, which were flat at positive bias and had a steep slope at ~-0.8 V. What happens at higher voltage? Is the rectification still there or is only the threshold asymmetric?

Professor Ashwell replied: The current-voltage plot characteristics were investigated from -1 V to +1 V. We have investigated other films to higher voltages and the rectification persists.

Dr Nichols asked: One may expect that the rectification ratio would depend strongly on tunnelling parameters (tip-surface distance in particular). Did you measure *I*-*V* curves at different tip-sample distances and did you see a dependence? Coupling at large tip-surface distance to the molecular state would be expected to be very weak.

Professor Ashwell replied: We have routinely investigated the tip-surface distance of a number of samples, both inherently rectifying and inherently non-rectifying. There are small variations in the behaviour and it is possible to induce slight electrical asymmetry but such variations are insignificant compared with the high rectification ratios now obtained.

Professor Hush said: The molecule displaying rectification has an aliphatic tail. Although this is shorter than in previous similarly described structures, it nevertheless introduces marked asymmetry. Theoretical considerations suggest that this feature will contribute to rectifying behaviour. What is known about the relative importance of this and a charge-transfer mechanism?

Professor Ashwell replied: The length of the aliphatic tail appears to have little or no effect on the rectification ratio for typical lengths used in organised molecular films. We have investigated the dependence for various Au-S-C_{*n*}H_{2*n*}-D-π-A and Au-S-C_{*n*}H_{2*n*}-A-π-D structures where 3 ≤ *n* ≤ 12 and have found no significant change. The rectifying properties of these films may be suppressed by protonation, which disrupts the donor-acceptor combination, and then restored upon exposure to base. The *I*-*V* curves of the protonated form are symmetrical despite the aliphatic tail and thus, it is difficult to accept the recent theoretical considerations.

Professor Schiffrin commented: Asymmetry can easily result from the presence of an ionic junction (see for example, Fig. 7 of the paper). This could give rise to a large surface potential drop across the ionic junction. The current rectification ratio in Fig. 8 of the paper could simply result from a shift in surface potential of ~200 mV. What is the evidence that the properties measured in this case are due to the molecule and not to the ionic distribution within the junction?

Professor Ashwell replied: The cationic dye is aligned by an anionic surface: $\text{Au-S-C}_3\text{H}_6\text{-SO}_3^-$ $\text{A}^+-\pi$ -D. Extended studies, as yet unreported, show the rectification ratio to be dependent upon the $\text{A}^+-\pi$ -D moiety being sterically hindered and therefore non-planar to maintain the integrity of the acceptor and donor. Ratios as high as 500 at ± 1 V have been achieved for a sterically hindered cationic dye and significantly, non-polar cations exhibit symmetrical I - V curves when coupled in this way. The unreported data remove the ambiguity.

Dr Nichols asked: Have you considered whether reversible bias voltage induced changes in orientation could (in part) give rise to rectification of your molecular junctions. Could these play a role in the systems you present here or is this rather unlikely? I would imagine that the *in situ* Raman spectroscopic technique of Professor McCreery would be suitable for studying such molecular changes with bias voltage in your system.

Professor Ashwell replied: Bias induced changes of the molecular orientation are feasible for LB structures where molecules are untethered but, except for minor changes in tilt, unlikely for SAMs where they are chemisorbed. They could play a significant role but only for isolated or loosely packed molecules that are physisorbed, as close packing is likely to suppress molecular flipping as the bias is reversed.

Professor Kornyshev asked: What happens with the structure of the LB-film when you move along the rectification axis? Is there tilting or even corresponding reorientations of the molecules? It seems that you don't have any independent experimental characterisation of the structural changes on the film with potential bias. For theoretical interpretations of your rectification curve it would be very important to have such data.

Professor Ashwell replied: There is no independent experimental characterisation of the structural changes with potential bias but significantly, similar I - V characteristics have been obtained for multiple scans on the same spot. It suggests that the alignment is stable. Molecular diodes are still in their infancy and, at this stage, I believe that it is far more important to identify the criteria for rectification and experimentally enhance the rectification ratio. Our recent work has resulted in a ratio of 3000 at ± 1 V, which is higher than many reported values for oxide-induced Schottky barriers. Theoretical interpretations will follow.

Dr Nichols asked Professors Ashwell and McCreery: Could you use a Raman spectroscopic probe, as applied by McCreery, to analyze V_{bias} -induced orientational switching?

Professor Ashwell replied: The majority of self-assembled structures investigated at Cranfield exhibit stable I - V characteristics for multiple scans on the same spot and there appears to be no significant bias-induced orientational switching.

Professor McCreery added: In principle, Raman can determine orientation on surfaces, as we have reported in a past publication,¹ and as many authors have described in the SERS literature. The requirements are that the molecule in question have a sufficiently large Raman cross section and number density to detect adequate signal. Without electromagnetic field enhancement (*i.e.* SERS), only resonance enhanced Raman scatterers are likely to meet these requirements. So I would say it is possible that Raman could be used in Langmuir-Blodgett and SAM structures, but it would be challenging. An example of applications to "switching" in carbon/nitroazobenzene/TiO_x/Au junctions in our lab has appeared recently.²

1 J. Zhao and R. L. McCreery, *Langmuir*, 1995, **11**, 4036.

2 A. M. Nowak and R. L. McCreery *J. Am. Chem. Soc.*, 2004, **126**, 16621-16631.

Professor Rovira asked: Can the change in the metal of the phthalocyanine affect the rectification behaviour due to the change in the redox behaviour? Could the huge rectification observed be due to a redox process in the phthalocyanine?

Professor Ashwell replied: It is too early to tell. The rectification ratio of 3000 at ± 1 V was achieved about two months ago and the preliminary study has focused upon modifications to the cationic D- π -A dye rather than its copper phthalocyanine-3,4',4'',4'''-tetrasulfonate anion.

Dr Nichols asked: Can you comment on the influence of other dipole barriers (*e.g.* surface dipole, water films on tip) on the recorded I - V response?

Professor Ashwell replied: These appear to have minimal effect on the shape of the I - V curve and rectification ratio. For example, isomeric D- π -A dyes with the self-assembling substituent located at different ends exhibit similar properties but with rectification in opposite quadrants of the I - V plot. Furthermore, the electrical asymmetry may be switched off and on by protonating and deprotonating the film, this reversible chemical switching confirming that the D- π -A chromophore dictates the properties.

Professor Fitzmaurice addressed Professor McCreery: How are the NAB molecules anchored on the carbon substrate?

Professor McCreery replied: By electrochemical reduction of a diazonium derivative of NAB, using the procedure originally described by Delamar *et al.*¹ We have studied this reaction extensively, as have several other groups, and characterized the resulting surface with Raman, XPS, AFM, *etc.* The bonding between the NAB and the carbon is most likely a phenyl-phenyl bond, and the coverage is very high due to the reactive nature of the phenyl radical generated by reduction of the diazonium reagent.

1 M. Delamar, R. Hitmi, J. Pinson and J. M. Saveant, *J. Am. Chem. Soc.*, 1992, **114**, 5883.

Professor Fitzmaurice asked: Should the model of the systems discussed explicitly include the two interfacial layers?

Professor McCreery answered: We strongly agree that the electronic response of the junction is dependent on the properties of both the contacts and the molecule. Strictly speaking, any model should consider the junction to be a single electronic system, with possibly strong interactions between the molecules and the conductors across the respective interfaces. Both the bonding and the electronic coupling across the various interfaces may have significant effects on junction behaviour, in addition to the structure of the molecule itself.

Professor Calvo said: My question refers to the interfaces in your experiments. The PPF surface seems to be pretty flat, though not as flat as HOPG since you have evidence of C-C bonds at the ring edges. The upper interface is produced by evaporation on e-beam definition. I wonder if you have evidence of the metal or oxide crystal size for the film making contact with the molecular layer. Can you compare the contact to the nanoparticle-molecule (in Professor Lindsay's paper) or to the Hg drop-molecule (in Professor Rampi's paper) interfaces?

Is there any evidence of Au evaporation penetrating the porous contact layer and making direct contact to the molecules?

Professor McCreery replied:

1. PPF resembles glassy carbon: it consists of "ribbons" of sp^2 carbon which form a disordered tangle of graphitic regions with crystallite sizes of ~ 50 Å. AFM shows that the PPF surface has an rms roughness of < 5 Å, presumably due to the slow pyrolysis which forms the surface. This is not atomically flat like HOPG basal plane, but the disorder of PPF provides both higher conductivity normal to the carbon surface and many sites for the molecule to attach. Modification of HOPG basal plane by the same route produces "mushrooms" due to nucleation at defects and low basal plane reactivity.

2. We have no direct evidence for the structure of the electron-beam deposited layers. We do have evidence (XPS) for bonding of Ti or Cu to nitro-containing monolayers such as NAB. Lindsay's case is a Au-S bond, while Hg presumably forms a physisorbed contact. We presume that the

electron-beam metals form physisorbed contacts unless there is the possibility for a covalent interaction.

3. We have made PPF/NAB/Cu and PPF/NAB/Au junctions, so we know that direct metal contact with NAB produces much higher conductance and qualitatively different behaviour from the TiO_x or AlO_x junctions. So if Au were penetrating the oxide, we would expect electronic behaviour like these junctions, and that is not the case. Furthermore, we have also made PPF/ AlO_x /Au and PPF/ TiO_2 /Au junctions, and these show high resistance. So there is no evidence for Au penetration through the oxide.

Professor Heath commented: We have made few-nanometre-wide trenches as model pinholes. We have found that it is very difficult to deposit metals like Ti into those pinholes—it typically forms a bridge over the pinhole, perhaps extending down 1 nm or less, even for 10 nm deep pinholes. We physically looked at the penetration of the metal using electron microscopy imaging of the side of the pinhole.

Professor Barbero addressed Professor Ashwell: It would make sense from the point of view of SHG, *i.e.* how the field will develop in the multilayer. A related question is: if metal nanoparticles could be assembled, would be possible to create nearly macroscopic contacts by self-assembly?

Professor Ashwell replied: It is possible to self-assemble nanoparticles on the surface as long as the molecule has an appropriate functional group to chemisorb the metal.

Professor Bjørnholm addressed Professors Ashwell and McCreery: What is the independent structural evidence you have that allows you to relate the molecular structures known from, say, NMR, to the I - V characteristics you measure in your devices?

Professor Ashwell responded: The orientation of D- π -A molecules is controlled by locating a thiol or thioacetate substituent on the donor or acceptor side for chemisorption on gold and similarly, a hydrophobic substituent for alignment and orientation in LB films with deposition on the upstroke resulting in the chromophore being adjacent to the substrate as long as the latter is sufficiently hydrophilic. The orientation is then simply indicated by the wetting contact angle and the forward bias direction of electron flow, in each case, is from the electrode to LUMO of the acceptor on one side of the device and from the HOMO of the donor to electrode on the other. Significantly, LB monolayers of differently oriented isomers in which a hexadecyl tail is attached on the acceptor side in one (D- π -A- $\text{C}_{16}\text{H}_{33}$) and on the donor side in the other ($\text{C}_{16}\text{H}_{33}$ -D- π -A) exhibit rectification in opposite quadrants of the I - V plot. The direction of electron flow is as predicted by the Aviram and Ratner model.

Professor McCreery responded: NMR is exceedingly difficult on ~ 20 Å thick molecular layers on carbon, although we routinely use NMR to verify the structures of our precursors and diazonium reagents. For our modified PPF, we have used XPS, Raman, AFM, and FTIR to characterize molecular structure after surface bonding, and other groups have used these techniques plus STM and SIMS. Recent experiments with FTIR permit the orientation of the NAB to be determined on the PPF surface, and it has an average tilt angle of 31° relative to the surface normal. All these techniques confirm covalent bonding to primarily edge sites, with nearly perpendicular orientation, and with a thickness verified with AFM.

Dr Dryfe asked: Given that the nitroazobenzene reduction is chemically irreversible, does this irreversibility manifest itself as a change in the current-voltage response, *e.g.* if the sample bias were repeatedly cycled? Would there be a difference between this case and the non-nitro-substituted case?

Professor McCreery replied: As is apparent in Fig. 3B, the azobenzene junction does not differ significantly from that of the NAB junction. We did this experiment to determine if the nitro group was a primary determinant of junction conductance, and at least at first consideration it is not. However, we have not examined the I/V behaviour of NAB junctions following the irreversible reduction of the nitro group. The I/V curves do not differ dramatically from those

observed with a fresh NAB junction, although there is a $\sim 30\%$ decrease in the current observed above +1 V.¹

1 A. Pullen, PhD thesis, Ohio State University, Columbus, OH, 2004, p. 116.

Dr Dryfe asked: Could *in situ* EPR spectroscopy be used to detect radical anions formed in the outside junction cases?

Professor McCreery replied: EPR may have sufficient sensitivity, but I am unaware of its application to flat surfaces. Remember that disordered carbon materials often have a significant population of unpaired electrons, which show up as a broad EPR signal. So I think it would be hard to see a monolayer on top of a several micrometre thick PPF layer.

Professor Lindsay opened the discussion of Professor Remacle's paper: Just to clarify—you mean that the simulations do not meet the McConnell model, and not that there is real charge localization on the molecule?

Professor Remacle replied: The short answer is that whether the system is or is not in the McConnell super-exchange limit is, in our approach, not only a property of the system but is also determined by the particular experimental conditions. The primary variable of interest is the source–drain voltage. The higher it is the more likely is that the transferred charge is actually transmitted *via* the molecular backbone.

Let me elaborate. To determine the temporal history of the charge migration we start our time-dependent simulations with a non-stationary initial electronic state that is localized on one side of the contact. That is, the initial state is localized on those gold atoms that are directly coupled to the bulk electrodes and to the molecule. A non-stationary initial state must have a finite width in energy. The point is how large is that width in energy of the initial state.

When the non-stationary initial state is so broad in energy that it does span several MO's, our simulations show real charge localization on the molecule, as the electron (or hole) migrates between the two electrodes.

However, the superexchange limit can be realized if the initial state can be both localized and yet be not too broad in energy. Such is the case of saturated alkanes. A narrow in energy yet localized state spans only the two highest occupied MO's that are quasi-degenerate at zero field and localized at the two Au–S interface without significant charge density on the bridge (see Fig. 9 of our paper). In this case and when the source–drain voltage is low, so that only these two orbitals fall within the Fermi window, the population transfer will occur without any significant charge localized on the bridge. BUT, even for alkanes, if the initial state is broader in energy then, as we show in Fig. 4 of our paper, there will be charge localized on the bridge.

In conclusion. If a given junction is or is not in the superexchange limit depends also on how many and on the nature of the states that can be brought into the Fermi window.

Professor Lindsay then asked: Small molecules are in disagreement with Landauer-type calculations—Ghosh has calculated effects of electron–electron interactions, and concludes that they suppress transmission in small molecules—have you looked at many-body effects?

Professor Remacle responded: We have not looked yet at many-body effects on molecular transport. We however compute the electronic structure at DFT level which includes some of the electron–electron correlation in the exchange functional but amounts to treating electron–electron interactions as a self-consistent field.

Note however that we always compute the current in the same way, using the DFT functional B3LYP to determine the one electron molecular electronic structure. Yet when compared with experimental results, for some molecules, our computed current can be too low by one to three orders of magnitude while it can be too high by the same factor for others. It is therefore not clear that many-body effects can account for the discrepancies between computed and measured currents.

On the other hand, we have looked at many-body effects on the insulator to metal transition induced by mechanical compression in small arrays of self-assembled colloidal Ag quantum dots (QD)^{1–3} as studied by Professor Heath and his group.^{4–6} For these systems, we compute the many-electron electronic structure by a full-CI diagonalization of a semi-empirical Pariser–Parr–Pople electronic Hamiltonian which includes both on site and intersite Coulombic repulsion. We also include in the electronic Hamiltonian the fluctuations in the dot energies induced by the size dispersion of the dots. At short interdot separation, the exchange coupling is strong enough to overcome both the many-body Coulombic effects and the effects of the fluctuations in the site energies induced by the size dispersion of the dots. As a result, the array is metallic. At large interdot separation, the exchange coupling is not strong enough and the wave function is localized. The array becomes an insulator. Depending on which effect is the strongest, the fluctuation in the dot energies or the Coulomb blockade, the metal to insulator transition is of an Anderson type or of a Mott type. When the metal to insulator transition is of a Mott type, the current is suppressed by many-body effects.

- 1 F. Remacle and R. D. Levine, *J. Am. Chem. Soc.*, 2000, **122**, 4084.
- 2 F. Remacle and R. D. Levine, *ChemPhysChem*, 2001, **2**, 20.
- 3 K. C. Beverly, J. L. Sample, J. F. Sampaio, F. Remacle, J. R. Heath and R. D. Levine, *Proc. Natl. Acad. Sci., USA*, 2002, **99**, 6456.
- 4 C. P. Collier, R. J. Saykally, J. J. Shiang, S. E. Henrichs and J. R. Heath, *Science*, 1997, **277**, 1978.
- 5 S. Henrichs, C. P. Collier, R. J. Saykally, Y. R. Shen and J. R. Heath, *J. Am. Chem. Soc.*, 2000, **122**, 4077.
- 6 G. Markovich, C. P. Collier, S. E. Henrichs, F. Remacle, R. D. Levine and J. R. Heath, *Acc. Chem. Res.*, 1999, **32**, 415.

Professor Larsson asked a general question: What do you mean by superexchange?

Professor Remacle replied: Superexchange is a longer-range charge transfer mediated by a non-resonant bridge between the donating and accepting states. This limit is realized when the effective donor/molecular bridge and acceptor/molecular bridge couplings are small, but the donor and acceptor sites are energetically quasi-degenerate so that they are effectively coupled by higher order terms in perturbation theory.^{1,2} When such is the case, the charge is transferred from the donor site to the acceptor site without significant population of the bridge. We have shown³ that this limit was realized in self-assembled arrays of Ag colloidal QD's in the intermediate mechanical compression regime, which was later confirmed experimentally.⁴ As we discussed in our paper and in our answer to Professor Lindsay's opening question, the superexchange mechanism is not only a property of the molecular system but also depends on the width in energy of the initial non-stationary state created by the transfer of an electron from the bulk electrode to the extended system.

For dithio molecular wires tethered between two small gold clusters, the effective coupling at the Au–S–C interface is typically too strong for the superexchange limit to be realized, except for saturated bridges when the Fermi window is narrow enough so that only the two highest occupied MO's localized at the interface at each end of the bridge participate in conduction.

- 1 H. M. McConnell, *J. Chem. Phys.*, 1961, **35**, 508.
- 2 G. C. Schatz and M. A. Ratner, *Quantum Mechanics in Chemistry*, Prentice-Hall, New York, 1993.
- 3 F. Remacle and R. D. Levine, *J. Phys. Chem. B*, 2001, **105**, 2153.
- 4 J. L. Sample, K. C. Beverly, P. R. Chaudhari, F. Remacle, J. R. Heath and R. D. Levine, *Adv. Mater.*, 2002, **14**, 124.

Professor Kornyshev asked: How is the difference between hopping and superexchange manifested in the nonlinear current–voltage plots?

Professor Remacle responded: The nonlinearities in the current–voltage plots arise when molecular levels with different conducting character are brought in the Fermi window by varying the source–drain or the gate voltage. As such, they will arise in the I – V_{sd} curves both for conduction by hopping or superexchange. The main difference in the I – V_{sd} curves will be in the magnitude of the current. The superexchange limit is realized for conducting levels localized at the junction when the coupling at the junction is very weak, so that the magnitude of the current is very low,

picoamperes in our simulations for saturated alkane dithiols (see Fig. 15 of our paper). On the other hand, the computed current is in the nanoampere to microampere regime when the hopping mechanism operates (see Fig. 12 of our paper for the $I-V_{sd}$ curves computed for dithiolbutadiene). Note that the $I-V_{sd}$ curves will be linear (Ohmic) in strong coupling limit.

The difference between the hopping and the superexchange mechanism should clearly appear if time-resolved current measurements were available. We show in our paper that the matrix element of the transition operator can be related by a Fourier transform relation to the crosscorrelation of the initial state created at the interface by the electron transfer from the electrode, see eqn. (16) of our paper. This was our motivation to compute the time-dependent charge transfer along the chain.

Dr Geskin asked: In superexchange there is exponential decay of conductance with distance. Is this dependence conserved in the sequential mechanism you find?

On the one hand, weak coupling leads to superexchange. On the other hand, weak coupling can lead to incoherent hopping or Coulomb blockade. Is it possible to predict which of these possibilities will be realized?

Professor Remacle replied:

1. As I discuss in my answer to Professor Lindsay's opening question, for a given molecule, superexchange or sequential mechanism depends on the width in energy of the localized non-stationary initial state that is created by the transfer of an electron from the bulk electrode to the gold atoms at the one side of the extended system.

The sequential mechanism operates when the width of the non-stationary initial state is broad enough to span several conducting MO's, and is accompanied by charge localization on the molecular backbone.

The superexchange limit is realized for a non-stationary initial state narrow in energy, and for conducting MO's localized on the gold atoms that are coupled to the electrodes. This is the case for saturated alkanes when the Fermi window is narrow enough so that the two states that participate in charge transport are the two highest occupied MO's, localized each at a given end of the extended system.

We have analyzed the length dependence of the current computed for dithiopropane, -hexane and -nonane in a previous paper,¹ and as can be seen from Fig. 1, in the low voltage limit where the superexchange mechanism operates, we recover an exponential decrease of the current with the length of the wire. Note however, that, as also found experimentally,^{2,3} the value of the decay constant, β , decreases when the voltage increases. We get a value of $\beta = 1.05 \text{ \AA}^{-1}$ at $V_{sd} = -0.4$ Volt. When V_{sd} increases further, more states participate to conduction and the $I-V_{sd}$ curves exhibit nonlinearities. The mechanism for transport becomes sequential and because of the nonlinearities (see Fig. 1), it is no longer possible to define a value for β .

2. The temperature dependence of the current should be different in the two limits. We have shown in our work on transport properties of self-assembled arrays of QD's⁴⁻⁶ that in the superexchange coupling limit the conductivity rises with temperature as $\exp(-(T_0/T)^{-1/2})$. In the Ohmic, activated regime, the dependence is $\exp(-T_{act}/T)$. In the limit of incoherent hopping, the current should decrease when increasing temperature.

- 1 F. Remacle, I. Willner and R. D. Levine, *J. Phys. Chem. B*, 2004, **108**, 18129.
- 2 W. Y. Wang, T. Lee and M. A. Reed, *Phys. Rev. B*, 2003, **68**, 035416.
- 3 X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, L. A. Nagahara and S. M. Lindsay, *J. Phys. Chem. B*, 2002, **106**, 8609.
- 4 F. Remacle, K. C. Beverly, J. R. Heath and R. D. Levine, *J. Phys. Chem. B*, 2002, **106**, 4116.
- 5 F. Remacle, *J. Chem. Phys.*, 2003, **119**, 4550.
- 6 F. Remacle, K. C. Beverly, J. R. Heath and R. D. Levine, *J. Phys. Chem. B*, 2003, **107**, 13892.

Professor Naaman asked:

1. How is the conduction affected by the fact that only a small gold cluster is included in the calculation?

2. Band structure has been observed in two photon photoemission from monolayers of alkylthiols. How does this observation coincide with the calculations?

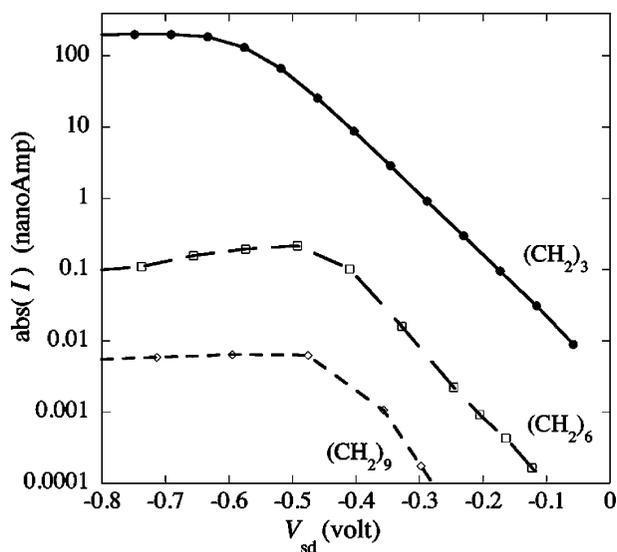


Fig. 1 Absolute value of the current (in nanoamperes on a log scale) vs. applied source–drain negative bias computed for dithiopropane, -hexane and -nonane tethered between two Au_3 clusters. Note how for $V_{\text{sd}} > -0.6$, the I - V_{sd} curves become nonlinear. For positive bias (not shown), the nonlinearities appear at lower values of V_{sd} .

Professor Remacle replied:

1. Including a small gold cluster on the left and on the right of the dithio molecule allows us to take into account the effect of the Au–S interface on the electronic structure of the molecule. For conjugated dithio molecules, we find that the highest occupied and lowest unoccupied MO's are well delocalized over the entire Au_3 –S–molecule–S– Au_3 system while for saturated ones, the two highest MO's are localized at the Au–S–C interface. In that case, current flow is possible *via* a super-exchange mechanism because these two highest occupied MO's are coupled by the field induced by the source–drain bias.

When the cluster size increases sufficiently, the density of electronic states of the extended system increases into a quasi continuum of states but remains discrete: In addition to MO's localized at the interface or delocalized over the entire system, there are also MO's localized only on gold atoms, as was shown by Weber *et al.*¹ who investigated the electronic structure of conjugated aromatic dithio molecules bound to the left and to the right to a Au_{29} cluster. They found that conduction occurs through the HOMO, that is close in energy to the gold Fermi level and delocalized over the gold atoms and the molecule, which is similar to what we find with a smaller cluster size. In addition, their results show that the lowest unoccupied MO's above the HOMO are localized entirely on the gold cluster.

For the current to flow, whether the size of the gold cluster is big or small, one needs to couple the extended system to the continuum of the electrodes on the left and on the right. In our computation, we included this coupling in the weak coupling limit. When the coupling to the electrodes is strong, one needs to add a self-energy term to the electronic Hamiltonian. This term will both shift the position of the conducting levels and broaden them into Lorentzians. We expect that more than the size of the cluster, this term can induce significant changes in the conduction properties of the molecular wire. These effects are discussed in a Comment below.

2. This question is partially answered above. This observation suggests that the coupling to the electrodes is not weak. There are indeed others who say the same. In that case, one needs to include this coupling into the electronic Hamiltonian as a self-energy term. We discuss how to do so and the effect of a strong coupling to the electrodes in the following communication.

1. H. B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs and H. v. Lhoneyesen, *Chem. Phys.*, 2002, **281**, 113.

Professor Remacle communicated: In this comment, we discuss the possible effects of a strong coupling between the extended system and continuous states of the electrodes and we derive the expression of the matrix elements of the transition operator for this case. In so far that in the contact between the extended system and the bulk electrode, the gold cluster is in physical contact with the gold metal without any protective ligands, that the coupling is strong is to be expected.

As shown in Fig. 2 of our paper, the entire junction can be divided into three subsystems, the left electrode, the right electrode and the extended system, which comprises the molecule itself tethered between two small gold clusters. The total Hamiltonian is:

$$H = H_0 + V \quad (1)$$

where the zero order Hamiltonian is $H_0 = H_{\text{left elec}} + H_{\text{ext}} + H_{\text{right elec}}$. V in eqn. (1) is the sum of the two coupling terms between the extended molecule and the right and the left electrode.

The expression for the current is given by (see eqn. (6) of our paper):

$$I = 2e \frac{d\langle P \rangle}{dt} = \frac{2e}{h} \int d\varepsilon g(\varepsilon, V_{sd}, T) \langle F | T(E^-) | I \rangle \delta(E_I - E_F) \langle I | T(E^+) | F \rangle \quad (2)$$

where $|I\rangle$ and $|F\rangle$ are the initial and final many electron states (see eqn. (5) of our paper). The transition operator $T(E^\pm)$ is given by

$$T(E^\pm) = V + VG(E^\pm)V \quad (3)$$

V is a one-electron operator that transfers an electron from the electrode to extended system or *vice-versa*. In our paper, we make the approximation of a weak coupling to the electrodes, so that $G(E^\pm)$ can be replaced by $G_0(E^\pm)$ in eqn. (3). We discuss here the situation when this weak coupling limit is not realized.

To do so, as in our paper, we use the partitioning technique¹ in a one electron description of the electronic structure to evaluate the matrix elements of the transition operator, $T(E^\pm)$. The two orthogonal subspaces are the subspace \mathbf{P} of the one electron continuous states of the electrodes and the subspace \mathbf{Q} of the one electron discrete states of the Hamiltonian of the extended system, H_{ext} . Applying the partitioning technique leads for the matrix elements of $T(E^\pm)$ between the two electrodes to:

$$PT(E^+)P = PVQG(E^+)QVP, \\ QG(E^+)Q = (E^+ - QHQ)^{-1} = [E^+ - (QH_{\text{ext}}Q + QVP(E^+ - PH_{\text{elec}}P)^{-1}PVQ)]^{-1} \quad (4)$$

where we have taken into account that the subspaces \mathbf{Q} and \mathbf{P} are orthogonal and that V cannot induce transitions within these two subspaces.

The term, $QVP(E^+ - PH_{\text{elec}}P)^{-1}PVQ$, in eqn. (4) is the self-energy term that describes exactly the effect of the coupling to the continua of the electrodes on the discrete levels of the extended system, $QH_{\text{ext}}Q$. It has a real part, given by the principal value of $QVP(E^+ - PH_{\text{elec}}P)^{-1}PVQ$, that shifts the energies of the levels of $QH_{\text{ext}}Q$ and an imaginary part, $-i\pi QVP\delta(E^+ - PH_{\text{elec}}P)PVQ$, which broadens the levels of $QH_{\text{ext}}Q$ into a Lorentzian shape. QHQ in eqn. (4) is the effective Hamiltonian. It is a complex symmetric matrix that can be diagonalized self-consistently,^{2,3} see also in another context refs. 4 and 5 or by an orthogonal transformation.⁶ Its eigenvalues are complex and correspond to the energies of the extended system coupled to the continuum states of the electrodes.

As discussed in our paper, it is possible to include in the self-consistent diagonalization of the one electron Hamiltonian of the extended system, $QH_{\text{ext}}Q = Q(H_{\text{Au}_n} + H_{\text{mol}} + H_{\text{Au}_n} + V_{\text{Au-S}} - \mathbf{E} \cdot \mathbf{r})Q$, the effects of two major perturbations, the coupling at the interface, $V_{\text{Au-S}}$, and the fields' effects (included as a dipolar term, see ref. 7) induced by the gating and the source-drain bias. Both lead to energy shifts of the MO's of the extended system and distortion of their charge densities.

When the coupling to the electrodes is included in the expression of the transition operator, each conducting state in the transmission function, eqn. (14) of our paper, is endowed with a finite width. The transmission function becomes a weighted sum of Lorentzian peaks and is no longer a weighted density of discrete conducting states. In other words, the conducting states contributing to the

current are intrinsically broadened by the coupling to the continua of the electrodes. This intrinsic broadening comes in addition to the broadening by the Fermi window induced by the thermal averaging, see eqn. (13) of our paper. Its main effect will be to lead to smoother I - V curves with less pronounced non-linearities.

At 0 K, the Fermi window is a square function of the energy with a width equal to eV_{sd} and its wings are broadened as the temperature increases. Therefore, to significantly affect the current, the strength of the coupling to the continua of the electrodes must be of the order of eV_{sd} . Recent experimental and theoretical results suggest that it could indeed be so.

In the same way that we used to analyze the effect of the coupling V_{Au-S} at the interface in FD 131/4, we can define an effective coupling parameter, $V_{ext-elec}/\Delta E$, where $V_{ext-elec}$ is the strength of the coupling between the extended system and the electrodes, given by the matrix elements of QVP (eqn. (4)) and ΔE is the spacing between the MO's of the extended system.

If the matrix elements QVP are smaller than the energy spacings, ΔE , between the MO's of the extended system, one can use the Fermi Golden rule approximation⁸ and just add an imaginary part, $-\pi|\langle\lambda|V|\varepsilon\rangle|^2\delta(E - E_\lambda)$ to the discrete energy E_λ of the MO's. This is the limit known as that of isolated resonances. It could be realized for conjugated alkenes, since as shown in Fig. 10 of our paper, the molecular orbitals are about or more than one electronvolt apart and almost unshifted in energy by field effects.

On the other hand, when the matrix elements of QVP are not small with respect to the spacings, ΔE , transitions between the MO's of the extended system can be induced by their interaction with the continua of the electrodes. This will be the case when the MO's of the extended molecule are not well separated in energy. This situation is known as that of overlapping resonances. It may for example be realized when the external electric field effects induce avoided crossings between the MO's (see Figs. 13 and 16 of our paper). When such is the case, the coupling to the electrodes could modify significantly the transmission function and therefore the I - V curves. However, as discussed above, unless the strength of the source-drain bias is very small, these effects will be further thermally averaged by the Fermi window.

Note that when the subspace Q is written in the one electron eigenstates of the extended system, including the effects of the coupling at the interface and of external fields effects, one can in first approximation neglect the effects of the level shift operator in eqn. (4) because they are expected to be small compared to the shifts induced by the coupling at the interface and the external fields. The self-energy is then purely imaginary. In the absence of threshold effects for the continua, this approximation can be insured if the matrix elements of the coupling operator QVP do not vary with energy in which case the principal value part vanishes.

- 1 R. D. Levine, *Quantum Mechanics of Molecular Rate Processes*, New York, Dover, 1999.
- 2 Y. Q. Xue, S. Datta and M. A. Ratner, *Chem. Phys.*, 2002, **281**, 151.
- 3 M. Brandbyge, J.-L. Mozos, P. Ordejon, J. Taylor and K. Stokbro, *Phys. Rev. B*, 2002, **65**, 165401.
- 4 E. Brandas and P. Froelich, *Phys. Rev. A*, 1977, **16**, 2207.
- 5 Y. K. Ho, *Phys. Rep.*, 1983, **99**, 1.
- 6 F. Remacle and R. D. Levine, *Mol. Phys.*, 1996, **87**, 899.
- 7 F. Remacle, I. Willner and R. D. Levine, *J. Phys. Chem. B*, 2004, **108**, 18129.
- 8 G. C. Schatz and M. A. Ratner, *Quantum Mechanics in Chemistry*, Prentice-Hall, New York, 1993.

Professor Weber asked: Would the voltage dependence change if you consider only two pieces of gold without the molecule? In my opinion, the "HOMO" in such a finite system is representing electrons in the gold cluster and is unrelated to the HOMO of the molecule.

Professor Remacle agreed. The voltage dependence would certainly change for the case of conjugated wires, because as you also showed in your 2002 paper,¹ the HOMO involved in the conduction is delocalized over the entire system, that is, both on the gold atoms and on the atoms of the molecular wire.

For saturated dithioalkanes, we find that the two highest occupied MO's involved in conduction at low voltages are localized at the interface, with almost no electron density on the molecular backbone. In that case, conduction occurs *via* a superexchange mechanism and the molecular bridge is not accessed during the charge transfer. However, the energy of the two quasi degenerate MO's

localized at the interface is lower by ≈ 0.4 eV than the Fermi level of bulk gold. So there is a threshold value of the V_{sd} below which conduction is exponentially small while there should not be any in the case of conduction between two pieces of bulk gold. Another difference that will arise in the voltage dependence is that even if the molecular bridge is not directly involved, it provides a dielectric medium for the charge transport.

1. H. B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs and H. v. Lhoneyesen, *Chem. Phys.*, 2002, **281**, 113.

Mr Adisa asked:

1. How does varying the metal relate to the coupling and thus the superexchange properties *i.e.* if a different metal is used rather than Au, how does this affect the superexchange?
2. What specific properties of Au have interested you in using this metal for your studies?

Professor Remacle replied:

1. The superexchange mechanism is realized when the interface is very weakly coupled to the molecular backbone, so that the highest MO's involved in conduction are localized at the junction, with almost no electron density on the molecular backbone. In other words, this mechanism operates when the junction has a local ionization potential lower than the molecular backbone itself. It is therefore very much dependent on the value of the Fermi energy of the metal and on the characteristics of the bonding at the junction.

We did not investigate interfaces with another metal than gold but we looked at the effect of replacing the S atom by a O atom. We found that the interface Au–O has very similar properties to the Au–S one.

Ag and Au have similar Fermi energies (≈ 5.5 eV) and one would expect that the Ag–S interface behaves similarly to the Au–S one. Note however that the 4d orbitals of Ag are spatially less extended than the 5d orbitals of Au which leads to weaker bonds.¹

2. We investigate the properties of the Au–S interface because it is widely used in experimental and in theoretical studies and therefore allows us to compared our results with those of others.

- 1 E. S. Kryachko and F. Remacle, *Chem. Phys. Lett.*, 2005, **404**, 142.

Dr Nichols asked: What effect does changing from single coordination geometry to multi-coordination geometry have?

Professor Remacle replied: We did not investigate the effect on the transport properties of the coordination geometry of gold at the interface in detail but experimental and theoretical studies show that it can be significant, with the intensity varying by more than an order of magnitude depending upon the coordination of the gold atom at the interface.

Professor McCreery opened the discussion of Professor Kuznetsov's paper: If tunnelling is not coherent, and involves a vibrational transition as a redox process, will it still occur at 0 K?

Professor Kuznetsov responded: In principle electron tunneling can occur at 0 K due to tunneling along the nuclear coordinates (the probability of which is small). If tunneling of nuclei is neglected, the electron tunneling can take place only if the electron energy level is shifted (by the application of the overpotential or by the variation of the bias voltage) to the activationless position, *i.e.* to the energy window region between the Fermi levels. Then many electrons can tunnel through this energy level while the latter relaxes towards the equilibrium position for the reduced state in the adiabatic limit. However, this will produce a pulse of the tunnel current. The final equilibrium position of the energy level must be located also within the energy window for a steady state tunnel current to flow.

Professor Lindsay asked: The timescale for inelastic tunnelling is presumably \hbar/Δ where Δ is the electron–phonon coupling and not the phonon period, correct?

Professor Kuznetsov replied: There are several characteristic times for inelastic tunneling: \hbar/Δ (where Δ is the coupling of the electron with the electrodes), \hbar/γ_{Bv} (where γ_{Bv} is the electron–phonon coupling constant) and $1/W_{\text{exc}}$ (where W_{exc} is the probability per unit time for the tunneling with the excitation of the phonon). The latter is the most characteristic time for the whole process of inelastic tunneling.

Dr Haiss asked: Are the tunnelling time and the coupling constant equivalent parameters in relation to the probability of the excitation of phonons?

Professor Kuznetsov replied: No. The probability of tunneling with the excitation of phonons depends on both the tunneling time $\tau_{\text{tunn}} \sim \hbar/\Delta$ and the coupling constant γ_{Bv} which characterizes the interaction of the electron with vibrational modes.

Professor Kornyshev asked: What could enhance the visibility of the effect of phonon-assisted tunnelling in the three-terminal geometry?

Professor Kuznetsov answered: The higher is the frequency of the local mode, the better. Some conditions are conflicting. The resonances are sharper, the smaller is coupling of the electron states in the groups B and C with the electrodes, *i.e.* the smaller are Δ_B and Δ_C . However this results in smaller values of the currents.

The other conditions are as follows:

$$U_{12} > \Delta_B, U_{13} \text{ is small, } \varepsilon_{F3} - \varepsilon_B \gg \Delta_{(1)}, \varepsilon_C - \varepsilon_{F1} > V_{BC}.$$

The last two inequalities are the conditions for the elastic current to the third electrode to be small. The best possibility would be a variation of the position of ε_C at fixed potentials. However this is possible only using different systems which would make it impossible to compare the results.

Professor Kornyshev said: What are the temperatures that would make it impossible to see this effect?

Professor Kuznetsov responded: The effect of re-absorption of vibrational quanta is most pronounced at not very high temperatures when $k_B T < \hbar\Omega$ where Ω is the frequency of the local mode. If opposite inequality is fulfilled, the thermal population of the vibrational quanta will interfere with the effect although the current to the third electrode due to the absorptive tunneling will be even greater.

Professor Kornyshev asked: I guess your experiment cannot be realized in electrochemical set-up where the phonon spectrum would be quasi-continuous. Am I right?

Professor Kuznetsov replied: Yes, you are right. It is difficult to observe this effect in the presence of a strong interaction with classical phonons (polarization of the solvent) since usually the lifetime of the excited state of local vibrational mode is rather short. In this case the interaction with the classical vibrational modes will destroy the effect.

Professor Kornyshev commented: We are not speaking about temperature-excited phonons. In the Kuznetsov “setup” one phonon is emitted by electron tunnelling in one channel, and that very phonon helps to excite another electron to higher energies to tunnel in another channel. The effect will be strong if the latter cannot happen without phonon absorption.

Professor Kuznetsov agreed. The electron energy levels are arranged in such a way that the resonance elastic tunneling through the energy level of the group C to the third electrode is impossible. A current due to off-resonant tunneling is small and its dependence on the overpotential and bias voltage is rather weak and quite different from a resonance-like dependence of the current due to the effect of re-absorption of vibrational quanta excited by the electron tunneling in the different channel.

Dr Nichols asked: These effects should be most apparent for high frequency vibrational modes which are not strongly coupled to other modes. Is it likely that low frequency modes are too strongly coupled (with other modes and the environment) to produce a sharp resonance?

Professor Kuznetsov replied: It depends on the system. In a polar medium the interaction of the electron with the medium polarization (low frequency modes) itself is sufficiently strong to destroy the effect even without the interaction of the polarization with the high-frequency local mode. In vacuum or low polar medium the interaction of the medium with the electron and with the local mode may be rather weak and the effect could be observed.

Professor Barbero opened the discussion of Professor Larsson's paper: You compare polyacetylene, a $-(\text{CH})_n-$ chain, with polysulfurnitride, a $-(\text{SN})_n-$ chain, showing that the latter could have high conductivity, of metallic nature. Could you comment on the fact that metallic conductivity has been measured on polyaniline, a $-(\text{N}=\text{C}-\text{C}=\text{C}-\text{C}=\text{N})-$ chain?

Professor Larsson replied: Polyacetylene, polyaniline, and polyphenylene are all insulators with a large band gap without doping. If electrons or holes are introduced into the chain, polaronic states are formed with some activation energy, no matter if we have oligomers or polymers. $(\text{SN})_x$ is 3/4 filled and very different, since there is a near degeneracy that cannot be lifted by Jahn–Teller (or Peierls) effects.

Professor Kornyshev asked: Is there any way to detect experimentally the crossover from the spin-density (SDW) to charge-density waves (CDW)?

Professor Larsson answered: One example is ordinary crystallographic methods. In AgF_2 there are two phases with a complicated SDW structures at a low temperature and a very different CDW phase at a high temperature, with a well-defined transition temperature. Jérôme discussed extensively the TTF-TCNQ system in his review (ref. 2 of our paper). Conductivity drops, X-ray diffuse scattering, elastic neutron scattering, and STM suggest CDW structures at low temperature. SDW is not seen, but SDW becomes a paramagnet above the Néel temperature anyway. Normally crossovers are not expected.

Professor Kornyshev said: This is just to summarize a few questions general to the area, in which all the three speakers, as well as many of us work, which have not been touched in depth in the previous discussion.

1. What is the effect of V_{sol} and V_{g} on transmission coefficients and coupling constants?
2. What is the role of classical bridge fluctuation?
3. What are the generic temperature effects on conductivity and rectification?

Professor Remacle replied:

1. We show in our paper that the V_{sd} and V_{g} can modify the electronic structure of the extended system, by shifting the position in energy of the conducting levels and also by distorting the spatial extension of their electronic density. These effects on the electronic structure lead in turn to changes in the transmission coefficients and affect the I – V_{sd} curves.

Conjugated π systems respond differently to external fields than saturated ones. Because of their symmetry, the π orbitals of conjugated system are very resilient to field effects, while the σ orbitals are strongly affected: small to medium applied voltage strengths shift their position in energy and distort their electronic density, leading to significant changes in the I – V curves.

2. We show that coherent ballistic transport occurs on a femtosecond time scale and therefore it is not very likely that it is strongly affected by bridge fluctuation. However, in cases where the molecular bridge is redox active, bridge fluctuations are expected to play a crucial role.

3. For coherent ballistic transport, the effect of temperature is to broaden the Fermi window and therefore to allow more conducting states to contribute to the current. Typically, the current increases with increasing temperature. When the states brought in the Fermi by increasing the

temperature conduct through a different mechanism, increasing the temperature can also lead to a switch in the temperature dependence of the I - V curves. We have shown in our work on transport properties of self-assembled arrays of Ag QD's¹⁻³ that at low temperatures, the mechanism for conduction is *via* superexchange (also known as variable range hopping, VRH), and characterized by a $\exp(-T_{\text{VRH}}/T)^{-1/2}$ temperature dependence while at higher temperatures, conduction is through an activated mechanism and follows a $\exp(-T_{\text{act}}/T)$ law.

1 F. Rémacle, K. C. Beverly, J. R. Heath and R. D. Levine, *J. Phys. Chem. B*, 2002, **106**, 4116.

2 F. Rémacle and R. D. Levine, *Appl. Phys. Lett.*, 2003, **82**, 4543.

3 F. Rémacle, K. C. Beverly, J. R. Heath and R. D. Levine, *J. Phys. Chem. B*, 2003, **107**, 13892.

Professor Kuznetsov replied:

1. I do not think that the bias voltage and overpotential (gate voltage) can produce a significant effect on electron-phonon and electron-electrode coupling constants. However they affect significantly the transmission function, first of all due to the shift of the positions of the electron energy levels.

2. Classical fluctuations in the bridge are of great importance and should be investigated in more details. They may change the geometry of the bridge and the properties of its contacts with the electrodes. They may produce large variations of the positions of the electron energy levels. The latter is crucial for the transmission function. In the case of the bridge with a redox group they result, in particular, in red-ox transformations.

3. There is no unique answer to this question. It depends on the system and the type of conductivity. For example, the temperature results in a decrease of conductivity if the band mechanism operates. Conversely, the conductivity increases with the temperature in the case of hopping mechanism.

Professor Lindsay addressed Professor Rémacle: You use an initial state based on a small gold cluster, but had you used infinite slabs of metal, then the initial and final states are just plane waves on the left and right electrodes, is that not so?

Professor Rémacle replied: There are plane waves on the left and on the right electrodes as long as the electrodes remain uncoupled to the molecule. On the other hand, the initial state created by the transfer of an electron from the bulk electrode to the extended system is non stationary. We describe this non stationary electronic initial state as the projection of the superposition of plane waves that describes the electron in the bulk electrode on the gold atoms of the extended system that are directly coupled to it. In other words, the initial state is the non stationary state localized at the interface of the extended system, that is created by the transfer of an electron from the bulk electrode. In our paper, see eqns. (16) and (17), we show how the matrix elements of the transition operator are related by a Fourier transform relation to the cross correlation function of that initial state.

Dr Macdonald asked a general question: Is there a difference in electron density along the bridge in the case of long-range electron transfer in DNA when compared with electron transfer in alkane or conjugated molecules?

Professor Larsson replied: Either you have tunnelling or you have conductivity with electrons located on the bridge. Probably in DNA and certainly in alkane bridges you have just tunnelling. Simulation of wave packet motion shows that the wave packet disappears on the donor and appears on the acceptor without visiting the bridge. In a conjugated bridge it happens frequently that the electron first transfers to the bridge and later to the acceptor.