

a significant impediment to meaningful electronic structure studies. Although this complication is usually circumvented in other materials by cleaving the sample in vacuum, the dense perovskite structure makes cleaving bulk oxides, let alone superlattices, exceedingly difficult.

Monkman *et al.* leverage the capabilities of both techniques in their integrated MBE–ARPES approach to investigate the interfacial electronic structure in $(\text{LaMnO}_3)_{2n}/(\text{SrMnO}_3)_n$ superlattices as a function of dimensionality, n . The digital superlattice samples are compositionally equivalent to bulk $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$, a canonical metallic ferromagnetic oxide⁷. However, the ordered atomic layers of the superlattices display physical properties that differ dramatically from the random alloy. Previously, electronic transport measurements⁴ demonstrated a metal–insulator transition as a function of n , with insulating behaviour observed when n is larger than three. Although these earlier resistivity measurements^{4,8} already indicated that this insulating state differs from that found in either bulk LaMnO_3 or SrMnO_3 , the electronic structure measurements obtained by ARPES now reveal the origin of the metal–insulator transition. Monkman and colleagues find that as the distance between the $\text{LaMnO}_3/\text{SrMnO}_3$ interfaces increases with larger n ,

the low-energy electronic structure near the Fermi level that originates from the interfaces between the two oxides becomes more two-dimensional. Simultaneously, a substantial redistribution of energy states occurs as n goes from 2 to 3: the states near the Fermi level are largely suppressed and a broad incoherent feature grows below the Fermi energy suggestive of enhanced many-body interactions. The result being that for $n = 3$ the superlattice has a Fermi surface that vanishes despite the metallic band structure persisting. In other words, a pseudogap state is induced by the dimensionality enhanced correlations.

The present work provides unique insight into the metal–insulator transition in manganite superlattices, but more broadly, it illustrates the critical role that an integrated synthesis–ARPES approach (Fig. 1) can play in revealing interface-specific electronic structures. Combined with recent advances in atomically resolved electron spectroscopies⁹ and synchrotron-based photoemission spectroscopy^{10,11}, the experimental capabilities that are now available in the discovery and understanding of novel interfacial electronic phases have expanded the materials explorers' arsenal. The ability to measure the intrinsic electronic structure is essential to building electronic–atomic structure property relationships necessary

to engineer the phases of complex oxides superlattices with correlated electrons. We anticipate rapid actions will be taken in laboratories throughout the world to replicate the unique capabilities of the techniques applied here. The rate at which new electronic phases are discovered will accelerate and the newly acquired data will provide important tests for the theoretical understanding of correlation effects in atomic-scale oxide superlattices. The integration of oxide MBE and ARPES represents a great stride forward in explaining Sir Eddington's 'and'.

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References

1. Dagotto, E. *Science* **309**, 257–262 (2005).
2. Hwang, H. Y. *et al.* *Nature Mater.* **11**, 103–113 (2012).
3. Monkman, E. J. *et al.* *Nature Mater.* **11**, 855–859 (2012).
4. Bhattacharya, A. *et al.* *Phys. Rev. Lett.* **100**, 257203 (2008).
5. Martin, L. W. & Schlom, D. G. *Curr. Opin. Solid State Mater. Sci.* <http://dx.doi.org/10.1016/j.cossms.2012.03.001> (2012).
6. Damascelli, A., Hussain, Z. & Shen, Z.-X. *Rev. Mod. Phys.* **75**, 473–541 (2003).
7. Salamon, M. B. & Jaime, M. *Rev. Mod. Phys.* **73**, 583–628 (2001).
8. Adamo, C. *et al.* *Phys. Rev. B* **79**, 045125 (2009).
9. Botton, G. A. *Mater. Res. Soc. Bull.* **37**, 21–28 (2012).
10. Kaiser, A. M. *et al.* *Phys. Rev. Lett.* **107**, 116402 (2011).
11. Sing, M. *et al.* *Phys. Rev. Lett.* **102**, 176805 (2009).

METAL/MOLECULE INTERFACES

Dispersion forces unveiled

The role of dispersion forces in molecule–metal bonding has often been underestimated or ignored. Two groups now report independent single-molecule experiments that illustrate and quantify the effect of such interactions on bonding strength.

Jan van Ruitenbeek

Research in molecular electronics traditionally relies on cartoons to interpret and communicate experimental results. Typical experiments are aimed at applying two electrical contacts to individual organic molecules and at characterizing electronic transport through the molecular bridges formed. The fact that the molecules are ten times smaller than any structure that can currently be nanofabricated implies that some form of self-assembly needs to be used in the process. This strategy seems to be very effective in that it has

led to a lot of successful experiments, but the inherent difficulty remains that the structures formed can neither be controlled nor imaged. Almost without exception, experimental papers therefore contain some artistic representation of the molecular structure, the bonding configuration and the atomic-scale metal electrodes. Usually these pictures show the molecule suspended straight, bound through its anchoring groups to nicely ordered pyramidal gold electrode tips. Only recently have deviations from this ideal geometry been appreciated^{1,2}.

Writing in *Nature Materials*, Sriharsha Aradhya and colleagues at Columbia University and Brookhaven National Laboratory, USA, now describe experiments and calculations that call for another revision of our simplified model of molecular junctions³. The researchers study two types of molecules between gold electrodes: bipyridine and a longer variant based on the same bonding concept. Their experiment is relatively simple: it makes use of an atomic force microscope with a conductive tip that is periodically driven in and out of contact with a molecule-

covered gold surface. During this process the conductance of the contact and the force between tip and sample are recorded. When the contact is broken in this manner, the conductance decreases in steps. As has become common practice, the last step at low conductance, just before contact is completely lost, is attributed to a junction formed by a bridging molecule. Conventionally, the pictures that accompany the measurements are those described above: the molecule is suspended from its anchoring points, which would in this case be N–Au bonds.

By careful analysis of the force and conductance data, Aradhya *et al.* make two important observations. First, the conductance shows not one, but two steps. Moreover, the breaking force for the higher-conductance configuration is about 25% larger than the breaking force for a clean Au–Au contact. This deviation is inconsistent with the image of a molecule binding to both electrodes with N anchoring groups. The Au–N bond is known to be weaker than the Au–Au bond, and even if it were enhanced for some reason, the maximum breaking force would be given by the force between the Au atoms in the tips of the electrodes.

The researchers therefore propose an explanation that is based on a more complex bonding scheme. It relies on an electrode geometry that allows the molecule to lie flat over part of the tip structure while still bonding chemically at the N sites (Fig. 1), leading to a large contribution from van der Waals forces. Such forces are the result of non-homogeneous charge distributions in the molecule, which can be either static or dynamic (in the case of dispersion forces). The partial charges induce an image potential in the conducting metal electrodes, which in turn leads to an attractive force. According to Aradhya *et al.*, the contribution from these dispersion forces is surprisingly large, increasing the breaking force from 0.85 nN for just Au–N bonding, to 1.88 nN for the longer of the two molecules investigated. The researchers are able to support this picture with computational evidence from density functional theory (DFT) calculations, which include an approximate description for the dispersion forces.

First-principles DFT calculations have only recently been extended to include dispersion forces, and the reliability of these methods remains to be fully tested. A sophisticated experimental approach for investigating this problem on the single-molecule scale was recently offered by Christian Wagner and colleagues of the Forschungszentrum Jülich, Germany⁴.

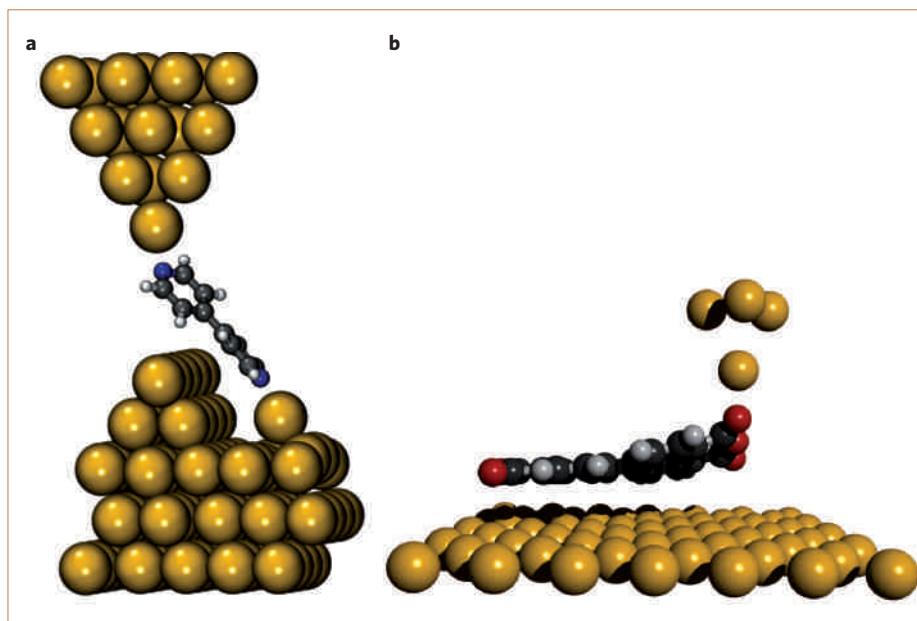


Figure 1 | Single-molecule experiments provide quantitative data on dispersion interactions. **a**, Dispersion interactions between the metal substrate and the lower part of a bipyridine molecule strengthen the metal–molecule bond and lead to an additional stable junction configuration that is reflected in simultaneous measurements of junction conductance and breaking force¹. **b**, Measurements of the junction stiffness provide information on dispersion interactions as a perylene-tetracarboxylic dianhydride molecule is lifted from a metal surface⁴. Gold atoms are shown in yellow, carbon atoms in black, hydrogen in white, nitrogen in blue and oxygen in red. Image courtesy of: **a**, L. Venkataraman; **b**, C. Wagner.

They made use of the capabilities of a low-temperature, ultrahigh-vacuum scanning tunnelling microscope, fitted with a tuning-fork-type force sensor. Such force sensors use a simple piezoelectric tuning fork resonator as the tip mount⁵, by which small changes in stiffness resulting from tip-to-surface forces can be measured through shifts in the resonance frequency. The scanning tunnelling microscope allows the isolation and imaging of individual molecules on freshly prepared atomically flat metal surfaces. Wagner *et al.* succeeded in lowering the microscope tip to one corner of a perylene-tetracarboxylic dianhydride molecule on Au(111), making the molecule bind to the tip, and then gradually peeling it off the surface. By modelling the various components of the metal–molecule interaction with a limited set of parameters and fitting these to the experimental data, they were able to show convincingly that, apart from the chemical bonding at the carboxylic oxygen atoms, an important component of the metal–molecule interaction comes from dispersion forces, which were found to be significantly larger than calculated. The validity of the experimental approach was confirmed by using the same parameter set for a shorter version of the molecule, naphthalene-tetracarboxylic dianhydride.

Without further adjustments, the researchers obtained very good agreement of the calculated and measured force-derivative curves. A further improved version of the DFT calculations that includes dielectric screening in the substrate now seems to be coming close to the observed binding energies⁶.

These results emphasize the important role of dispersion forces at metal/molecule interfaces and will be essential in forming proper images for further exploration of unknown territory in molecular electronics research. There may be great potential in exploiting such forces to achieve stable and well-defined anchoring, which is one of the most important problems to be solved in molecular electronics. □

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References

1. Wu, S. *et al.* *Nature Nanotech.* **3**, 569–574 (2008).
2. Perrin, M. L. *et al.* *Beilstein J. Nanotechnol.* **2**, 714–719 (2011).
3. Aradhya, S. V., Frei, M., Hybertsen, M. S. & Venkataraman, L. *Nature Mater.* **11**, 872–876 (2012).
4. Wagner, C., Fournier, N., Tautz, F. S. & Temirov, R. *Phys. Rev. Lett.* **109**, 076102 (2012).
5. Giessibl, F. J. *Rev. Mod. Phys.* **75**, 949–983 (2003).
6. Ruiz, V. G., Liu, W., Zojer, E., Scheffler, M. & Tkatchenko, A. *Phys. Rev. Lett.* **108**, 146103 (2012).