

# Characterizing molecular junctions through the mechanically controlled break-junction approach

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**Abstract:** Mechanically controlled break-junction techniques, which emerged right after the invention of scanning tunneling microscopy, have enabled substantial progress in characterizing single-molecule junctions toward the ultimate goal of molecular devices. Dramatic advances have been made in design, fabrication, control, and understanding of the measurements of single-molecule junctions over the past decade. In this overview, we present the evolution of some of the recent issues, and an outlook for further developments in mechanically controlled break-junction techniques for characterizing molecular junctions. Topics of recent interest include contact geometry, electrochemical redox experiments, external bias effect, and environmental influences. Each will need further investigation to thoroughly understand the experimental information revealed from a molecular junction.

**Keywords:** mechanically controlled molecular break junction, scanning probe microscopy

## Introduction

The desire to overcome the prediction of Moore's law led researchers to single-molecule-scale devices.<sup>1-3</sup> Molecular junctions emerged from the late 1990s,<sup>4</sup> catalyzed by the invention of scanning tunneling microscopy (STM) and inspired by a paper by Aviram and Ratner describing molecular-sized p-n junctions.<sup>5,6</sup> In the search for effective ways to couple a molecule between electrodes, researchers produced two efficient options: scanning probe microscopy (SPM) using the newly invented STM, and a microfabricated, electromigration piezoelectric three-point arching method. Both techniques provided a reliable platform to conduct measurements at a single-molecule level by utilizing piezoelectric transducers to mechanically open and close a break junction in which a molecule had become bonded. The key feature of each of these methods, and all other mechanically controlled break junctions (MCBJs), is a molecule in contact with two or more electrodes where one of the electrodes is mechanically controlled to allow it to create, break, and reform junctions with the molecule incorporated. In this way, the four main features of study in MCBJs are 1) the electrodes (and the macroscopic system), 2) the electrode-molecule junction, 3) the molecule, and 4) the environment in which the junction takes place. Often, this environment is in solution,<sup>4,7</sup> sometimes in vacuum,<sup>8-10</sup> and sometimes at cryogenic temperatures.<sup>11-13</sup>

MCBJ methods have come a long way since the early stages of the last decades. Experiments using MCBJs to measure the conductance of single molecules began in earnest in the late 1990s, and the first years of experiments resulted in many discrepancies among the measured and simulated results of single-molecule conductance

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from different labs. As the techniques matured, and as more labs took part in the experiments, the reproducibility of MCBJ experiments became more reliable.<sup>14</sup> Today, MCBJ techniques are used in conjunction with other measurement techniques,<sup>15,16</sup> either simultaneously or back to back, to derive still more information about the behavior of molecules at the nanoscopic level.

Some of the more detailed challenges that troubled the field in those early years, such as the strong sensitivity of MCBJs to contact geometry, behaviors relating to redox reactions in molecules in MCBJs, and the phenomenon of negative differential resistance (NDR), as well as other nonlinear current-voltage behaviors of molecular junctions, have been studied at length in the last decade, and we know much more about these issues today. We hope to discuss these advancements here, as well as discuss new directions for the future.

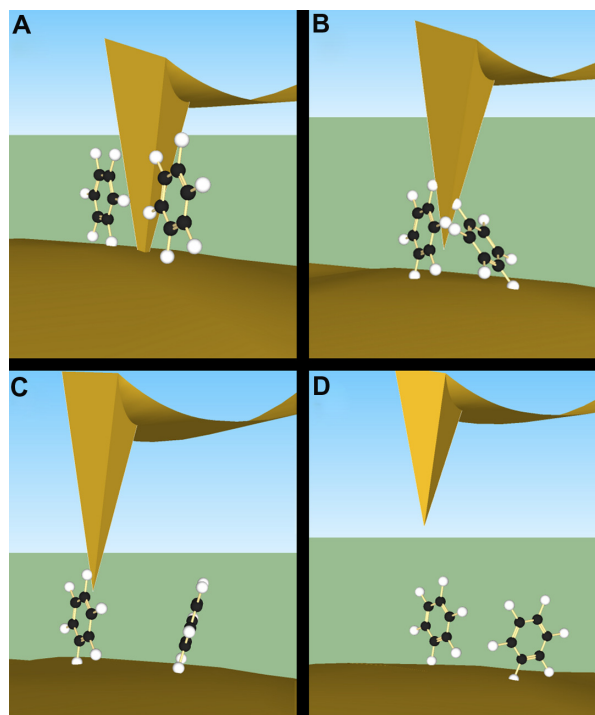
## MCBJ experimental challenges

Before anything resembling single molecular electronics becomes possible, reliable molecule-electrode junctions using chemical bonds are essential. Without these, it had been necessary to rely on approaching the molecule within proximity to the electrodes using increasingly clever ways: using mercury drops as electrodes,<sup>17</sup> using Lorentz force to cross metallic wires,<sup>18</sup> and trapping molecules in a nanopore.<sup>19,20</sup> Other successful techniques involved sandwiching the ends of very robust molecules between layers of electrode material, usually by thermal evaporation, and using lithographic techniques to etch away undesirable quantities of the substrate and electrodes; these techniques worked well for long and strong carbon nanotubes, but were too destructive for smaller molecules.<sup>21</sup> A different method involved crisscrossing nanowires by overlaying layer after layer. This, however, usually only produced large arrays of nanojunction; the single-molecule junction was still out of reach.<sup>22,23</sup> It was still necessary to find ways to bond one end of the molecule to one electrode, and the other end to the second electrode.

Ways to bond the molecule chemically to the electrodes were finally developed using amine and thiol-functionalized molecules, which bond readily to metal electrodes. Thiol-functionalized molecules were used in the crossed-wire technique,<sup>24</sup> and the first attempts to use an STM to probe molecular conductance were attempted by functionalizing one side of the molecule and scanning the other end in a traditional STM or conducting atomic force microscopy (C-AFM) method,<sup>25,26</sup> or with the probe scanning a gold nanoparticle atop the molecule.<sup>27,28</sup> Finally, both ends of the

molecule were functionalized and successfully incorporated into a mechanical break junction. One of the first truly powerful break-junction techniques used a piezoelectric transducer to arch a platform onto which a metallic wire had been anchored.<sup>4</sup> By lithographically etching the metallic wire until it was nanoscopically thin, the arching of the platform allowed complete control of the breaking and reforming of nanojunctions repeatedly with subangstrom control.<sup>29,30</sup> This three-point arching technique provides experimentalists today with a way to perform complementary measurements, such as optical spectroscopy alongside MCBJ-conductance measurements, because the design of the apparatus leaves the top exposed.<sup>31–33</sup>

Another powerful method for creating MCBJs was created by Xu and Tao.<sup>7</sup> This method involved forcing a gold tip into a gold substrate (Figure 1A) starting from a traditional STM setup, where a liquid cell was placed such that the molecule in solution was on top of the gold substrate. When the gold tip was withdrawn, many molecules were incorporated into the gap between the tip and substrate (Figure 1B), but as the tip was withdrawn further, the molecules broke one

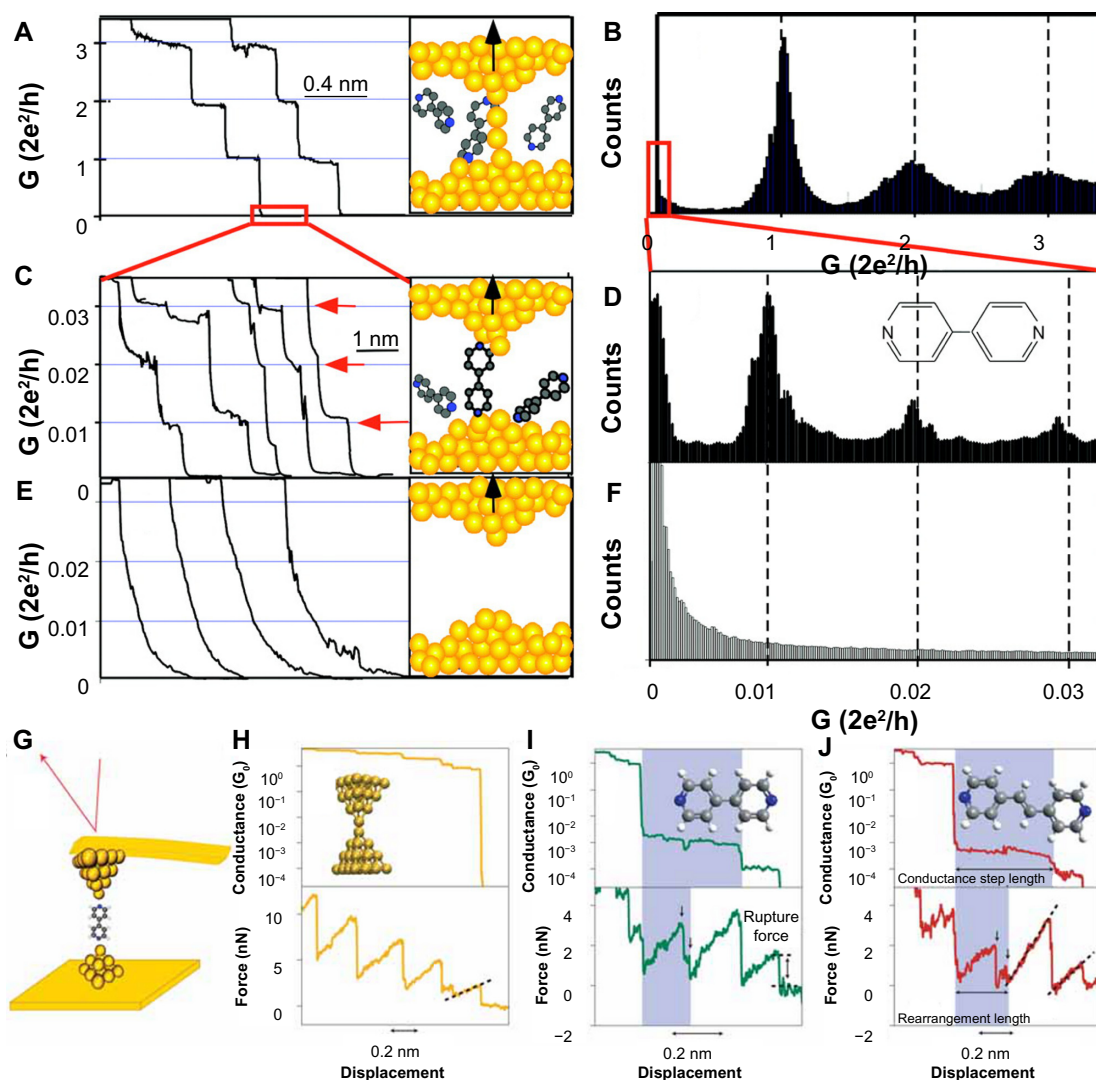


**Figure 1 (A–D)** Time lapse of conductance atomic force microscopy (C-AFM) single-molecule break junction. An identical process occurs with a scanning tunneling microscope tip replacing the C-AFM cantilever. (A) Au-coated C-AFM cantilever collides with Au-coated substrate until a conductance of many conductance quanta are registered, indicating a large contact surface between cantilever and substrate. (B) The cantilever is retracted, leaving multiple molecules in the junction. (C) The cantilever continues to retract until a single molecule is in the junction. (D) The cantilever retracts until the conductance represents the vacuum current, and then the process is repeated.

by one until there was only one left in the break junction (Figure 1C). All the while, a bias was applied between the tip and the substrate, and the current across the junction was recorded. As the molecules broke away, individual steps in the conductance were observed, each step differing from the next by a unique value of conductance. For atomically thin metal junctions, these quantized steps were predicted, and experimentally shown, to have a conductance of  $G_0 = n \times 2e^2/h$ , where  $n$  is an integer,  $e$  is the electronic charge, and  $h$  is Planck's constant.<sup>34</sup> After the last metallic junction, new steps were observed for conductance values much smaller than the conductance quantum of  $G_0$ . These steps corresponded to integer numbers of molecules in the junction. The last

step before the conductance fell to zero (Figure 1D) was the conductance across a single molecule.

Creating strong bonds with the gold electrode at both junctions was a significant improvement upon the previous methods, and created clear data (Figure 2A–D). Proving the molecule, in this case a 4,4'-bipyridine molecule, was indeed present in the junction was the next task. The new scanning probe microscopy (SPM) technique developed by Xu and Tao was very destructive, because it involved forcing the STM tip into the substrate before withdrawing it, and it was necessary to prove that during the withdrawal, a substrate–molecule–tip junction was indeed formed. Because the nitrogen was located at either end of the 4,4'-bipyridine molecule, it



**Figure 2 (A–J)** Representative mechanically controlled break-junction data. **(A)** Au–Au junction-conductance trace with quantized conductance of step  $G_0$ . **(B)** Conductance histogram from Au–Au conductance traces. **(C)** Au–4,4'-bipyridine–Au junction conductance traces with quantized conductance step  $\sim 0.01 G_0$ . **(D)** Conductance histogram from multiple traces. **(E)** Conductance traces without molecule present, with no quantized steps. **(F)** Conductance histogram without peaks. **(G)** Conducting atomic force microscopy (C-AFM) schematic. **(H)** Example Au–Au junction conductance (note semilogarithmic scale for following conductance traces) and force traces resulting from C-AFM. **(I)** Example traces for 4,4'-bipyridine junction. **(J)** Example traces for 1,2-bis(4-pyridyl)ethylene junction.

**Notes:** **(A–F)** Reprinted with permission from Xu B, Tao NJ. Measurement of single-molecule resistance by repeated formation of molecular junctions. *Science*. 2003;301(5637):1221–1223. © 2003 American Association for the Advancement of Science.<sup>7</sup> **(G–J)** Reprinted by permission from Macmillan Publishers Ltd: *Nat Mater*, Aradhya SV, Frei M, Hybertsen MS, Venkataraman L. Van der Waals interactions at metal/organic interfaces at the single-molecule level. 2012;11(10):872–876. Copyright 2012.<sup>65</sup>

was able to bond simultaneously with both electrodes. By conducting the SPM measurement in solution without the molecule present, it was shown that the conductance fell off exponentially, without the presence of the signature steps at the conductance of the molecule (Figure 2E and F). Next, 2,2'-bipyridine was measured in solution. Because the nitrogen in 2,2'-bipyridine is not located at the end of the rod-like aromatic rings, it was not possible for it to bond simultaneously to both electrodes, and the conductance could not be measured, resulting once again with conductance traces that fell off exponentially without steps.

Because there was much thermal noise in measurements of this precision,<sup>35</sup> it was beneficial to create 1-D histograms that revealed the statistical average of single-molecule conductance over thousands of repeated measurements (Figure 2B and D).<sup>36,37</sup> Despite the reliance on statistical methods, this new SPM MCBJ technique resolved many standing debates surrounding MCBJs. SPM MCBJs showed that short strands of deoxyribonucleic acid (DNA) can be described most accurately as a semiconductor.<sup>38</sup> Up until this point, there was much debate surrounding the electronic properties of DNA, with proponents arguing for insulator,<sup>39</sup> large-band-gap semiconductor,<sup>40</sup> conductor,<sup>41,42</sup> and even superconductor.<sup>43</sup> SPM MCBJs showed that DNA acted very much like a semiconductor, especially for short strands heavy in guanine.<sup>38</sup>

Reviews from the field of MCBJ written in the first decade of the twenty-first century all had one concern in common: reproducibility.<sup>14,44,45</sup> The SPM technique resolved yet another debate, by confidently and repeatedly measuring the conductance of simple alkanedithiol chains, molecules that up until that point had discrepancies between different labs and between theory and experiment.<sup>7,46,47</sup> Experiments on the single molecular conductance of octanedithiol conducted at different labs in 2001,<sup>48</sup> 2003,<sup>7</sup> and 2004<sup>49</sup> appeared to have widely ranging results. After closer attention, these discrepancies have been resolved.<sup>14</sup>

As is so common in science, the resolution of one concern often is accompanied by new insight into other concerns. The resolution of the discrepancy in octanedithiol single-molecule conductance provided important information about the significance of contact geometry in MCBJs. It was shown that when the molecule is contacted to a planar crystalline electrode, it is of only minor importance whether it is contacted in a hill or valley of the crystal. Of significantly more importance is a contact geometry in which the molecule contacts a pyramid-shaped crystalline electrode instead of a planar electrode. In the pyramidal case, conductance is greatly decreased when compared to the planar

case. Therefore, if the experimental apparatus has a preference for creating one contact geometry over another, then this can explain why different apparatuses produce different single-molecule conductance values.

## Importance of contact geometry and evolution in MCBJs

At the most basic level, progress in controlling physical and chemical properties of a molecular junction started with the capability of making robust contact to form a single-molecule junction. This proving a difficult task, the role of the contact interfaces was omitted at the initial time point. Experiments without careful control of the contact parts revealed data hard to interpret.<sup>50,51</sup>

It has recently become apparent that electrode geometry and the specific orientation at which the molecule contacts the electrodes has a profound influence on the behavior of MCBJ measurements, and much effort has been devoted to understanding this phenomenon. Detailed quantum chemical studies have even shown allowed and forbidden states, based on phase and symmetry groups, influence molecular conductance.<sup>9,52</sup>

C-AFM (Figure 2G) is especially useful in measuring contact changes and flexibility during MCBJs. C-AFM uses a similar method as SPMBJs, but replaces the STM tip with an AFM cantilever. The result is an MCBJ in which force can be measured alongside conductance (Figure 2H–J).<sup>53</sup> This technique was used to study contact phenomena, such as local heating, where it was predicted that inelastic scattering of electrons caused an increase in the temperature of the molecule.<sup>54,55</sup> It has also been shown that gold contacts in a tetrahedral crystal structure have a quantized length slipping, allowing one, two, and three simultaneous slip events for each of the three tetrahedral faces slipping individually.<sup>56</sup>

Theoretical formalism describes the MCBJ system as a quantum scattering event, with the molecule in the junction performing the scattering much like any dielectric material.<sup>34,57</sup> In this interpretation, the mechanism by which electrons are delivered to the junction via the contacts is of major significance, even when compared to the significance of the molecule in the junction. As stated earlier, the shape of the electrode where it contacts the molecule is of paramount importance. However, an MCBJ is a dynamic event that undergoes mechanical stretching, thermal fluctuations,<sup>58</sup> local current-induced heating,<sup>53,55</sup> and redox reactions.<sup>59</sup> With this in mind, researchers have been focusing much attention on the progression of the MCBJ as it is formed, stretched, and finally broken. Computer simulations have been of



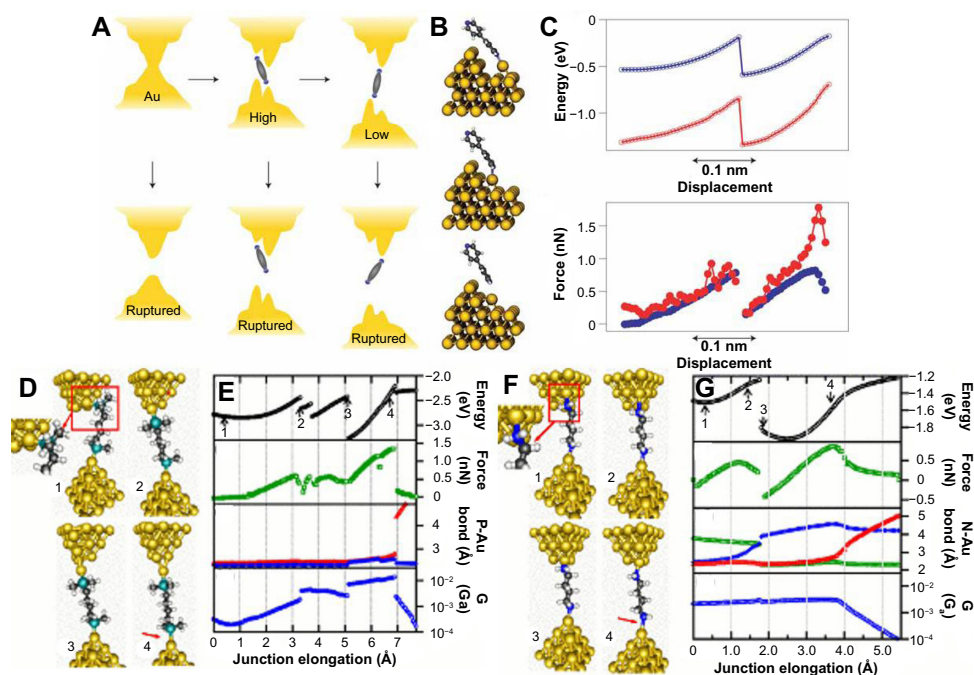
immense help in this area, because as yet direct observation of contact-geometry evolution in experiments has been difficult.<sup>60,61</sup> Simulations reported that with the same molecule bridged between electrodes with different shapes revealed totally different I–V characteristics and asymmetric binding sites of the anchoring group could also influence the resulting electronic properties.<sup>62–64</sup> The same molecule could even have two or more probable orientations within a junction, each with a unique conductance signature (Figure 3A).<sup>65</sup>

Conductance across MCBJs as tunneling electron microscopy images are taken shows that as multiple atoms are individually added to the chain, the conductance oscillates in a consistent manner.<sup>60,66–69</sup> Careful studies of similar chains occurring when a molecule is present in the junction have shown that metal chains of four atoms long can occur before the junction breaks.<sup>70</sup> Other simulation work has shown the effects of slipping gold–gold bonds (Figure 3B and C) and molecule–electrode slipping (Figure 3D and E) and twisting (Figure 3F and G) on conductance in MCBJs.<sup>71,72</sup> Studies like this reveal the molecular MCBJ to be flexible at the electrode junction, and this geometric flexibility has significant influence on molecular conductance as the junction evolves during the process of breaking. Some phenomena predicted for molecular electronics, it has been suggested,

require this flexibility, and more.<sup>73</sup> In cases where the junction is required to stretch still further, carbon nanotubes have been suggested.<sup>74</sup>

## Theoretical advancements in electrochemical redox experiments

Most often, the overarching goal of MCBJ research is to understand and control the alignment of the molecules' Fermi level with the conducting molecular orbitals (MOs) of the electrodes: the highest occupied molecular orbital (HOMO) for hole transfer, and the lowest unoccupied molecular orbital (LUMO) for electron transfer.<sup>75</sup> Electrochemical gating of molecular conductance due to redox reactions is possibly the most powerful method to control this alignment.<sup>76–80</sup> Adding a third terminal to the electrolytic solution within the liquid cell containing the MCBJ allows the experimentalist great control over the local potential at the molecule. For junctions with a large HOMO–LUMO gap, this gating has shown little effect, because the Fermi level of the molecule was never able to reach the conducting MOs.<sup>81</sup> Some molecules exhibited reduction of nitrite groups, and although conductance was significantly increased when negative bias was applied to the gating terminal, the reaction was irreversible. The reaction did have the effect of causing a rectification feature



**Figure 3 (A–G)** Example of geometric adjustments during mechanically controlled break-junction elongation. **(A)** 4,4'-bipyridine orients in two ways during junction elongation, resulting in two separate values for conductance. **(B)** Example slip of Au–Au bond. **(C)** Simulated changes in energy and force due to Au–Au bond slip. **(D)** Example slip of P–Au bond. **(E)** Simulated changes in energy, force, bond length, and conductance due to P–Au bond slip. **(F)** Example N–Au bond twist. **(G)** Simulated changes in energy, force, bond length, and conductance due to N–Au bond twist.

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in the current-bias ( $I$ - $V$ ) relationship of the molecule, and the reaction also caused the negative differential resistance (NDR) phenomenon.<sup>82</sup> Of far greater interest were molecules that experienced reversible redox reactions, thus allowing the molecule to be gated on and off, resulting in ranges of conductance of as much as 15 magnitudes.<sup>83</sup> Cyclic voltammetry revealed that the molecule switched between a low-conductance reduced state to a high-conductance oxidized state.<sup>84</sup> There was great control over this reaction; however, stochastic switching between states was also observed. For most molecules, high bias is required to maintain one state or the other.<sup>14</sup>

Recently, transition voltage spectroscopy (TVS)<sup>85</sup> was used to calculate the energy gap between the molecular Fermi level and the nearest frontier MOs in order to show quantitatively that the solution in which the molecule is immersed contributes to electron transfer, helping resolve questions about the role of solvent in MCBJs.<sup>7,86,87</sup> In conjunction with a simplified model and the electrochemical techniques described in the previous paragraph, TVS was helpful in showing the effects of electrochemical gating on single-molecule conductance.<sup>88</sup> The TVS approach was also helpful in comparing the relative importance of molecular length,<sup>89</sup> contact geometry, energy-level alignment, and contact resistance, and showed that contact resistance is the dominant factor in MCBJ conductance.<sup>90</sup> TVS can discern between the effects of Schottky barriers versus defect barriers at the molecule-electrode junctions.<sup>91</sup> TVS analysis on experimental data, along with density-function theory simulations, identified the MOs, not merely the HOMO and LUMO, responsible for electron transport, and furthermore showed that these MOs can change as the probe-substrate distance is varied.<sup>92</sup> TVS has shown potential to address many questions surrounding MCBJs, even while presenting new questions.<sup>93,94</sup>

## The role of external bias

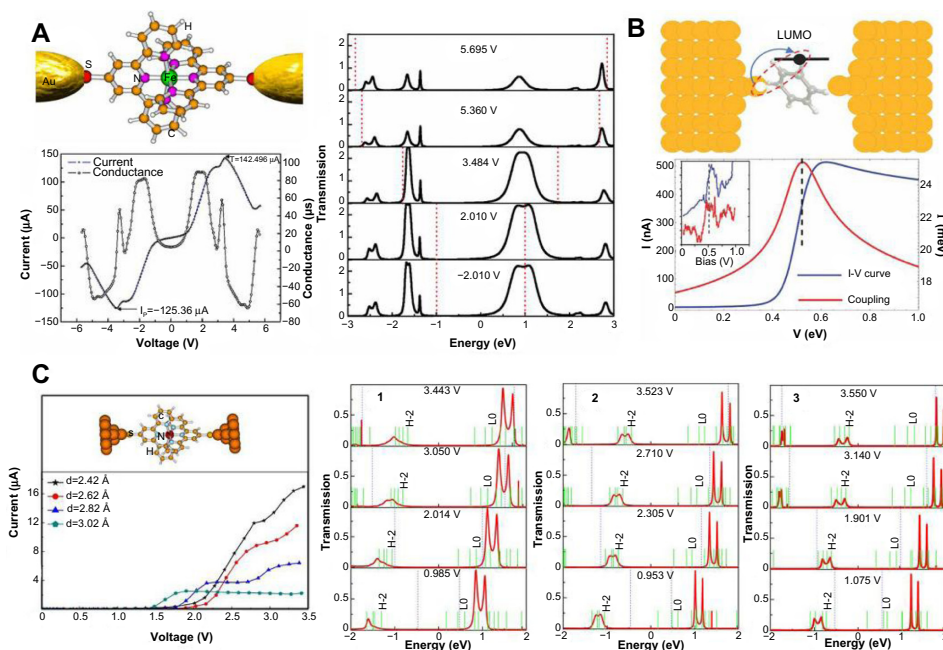
Since the electronic properties of a molecular junction, such as conductance and  $I$ - $V$  characteristics, have to be measured under an external bias applied on one of the electrodes, this bias plays a prominent role in affecting the charge-transport process across the junction. Many studies have emphasized the importance of the explicit inclusion of bias effect in explaining the electrical results of molecular junctions.<sup>62,95,96</sup> Given that the static conductance is usually measured under a fixed bias,  $I$ - $V$  characteristics measured using a bias sweep are the key feature that reflects the influence of external bias. Rectification behavior and NDR have been studied as the main focus of molecular electronics, since the asymmetric

current at the same bias magnitude but opposite bias polarity is the first step to ultimately realizing a molecular diode. To date, in most molecular rectification studies with MCBJ, the switch-on voltage, where rectification ratio starts going beyond unity, is postponed to a certain bias voltage<sup>11,64,97-99</sup> instead of the ideal case for bulk diode, where the switch-on voltage is close to zero. Certain rectifying molecules do show immediate switch-on.<sup>100</sup> Dhungana et al reported an electron-phonon interaction mode perpendicular to the direction of current flow that increased with the increase of external bias, and in turn destroyed part of the electrode-molecule-electrode current.<sup>62</sup> Other simulations<sup>62,101</sup> based on the transmission function suggested that the frontier MOs and the MOs away from the Fermi energy of the electrode respond differently to the applied bias: the transmission peaks may rise, fall, and shift as the bias increases (Figure 4A and C). All the effects induced by external bias were responsible for resulting electrical measurement properties.

NDR, defined as a nonmonotonic dependence of current on the bias voltage (for example, the current decreases with increasing bias), has been observed for various metal-molecule-metal junctions.<sup>19,102-105</sup> However, the sources of this effect are still in controversy. The main sources are discussed to be bias-dependent electron-phonon interaction, potential-drop-induced shifting of MOs, nonlinear bias-dependent effective coupling between MOs and the electrodes (Figure 4B), and even image-charge effects. All possible mechanisms involve the significance of external applied bias.

## Environmental influences

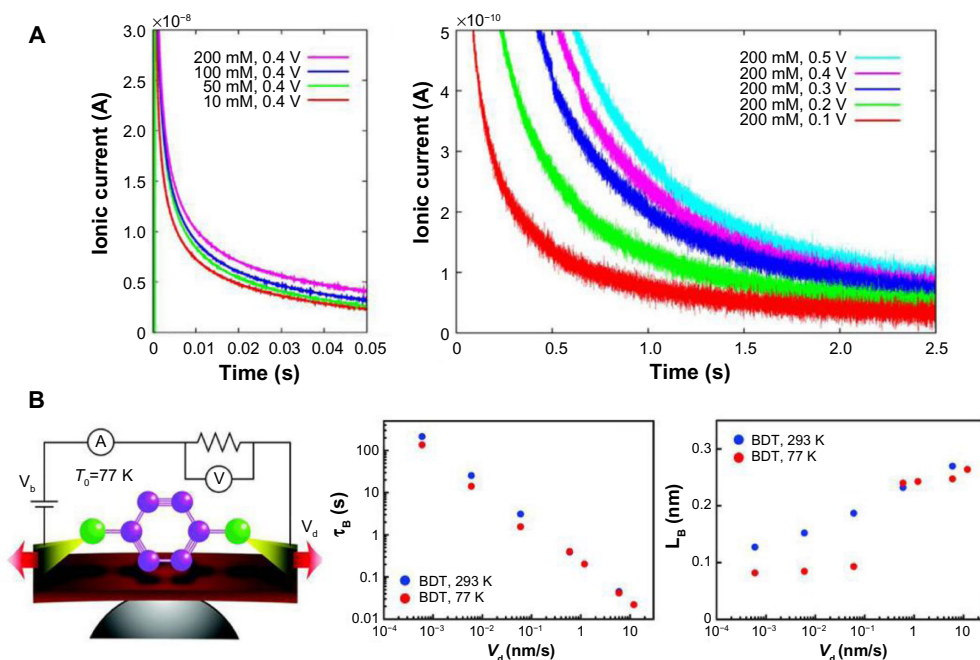
Besides the structure of a molecular junction, effects from the environment surrounding the MCBJ have been of considerable interest as well. To date, the dramatic improvement in design and fabrication of a molecular junction enables more precise measurements, but also begs further investigation into the non-negligible contribution from ionic transport in the solution, especially at room temperature. Recently, Doi et al reported on the transient electrical response of ions in the vicinity of biased electrodes.<sup>106</sup> Their results showed that ions rapidly responded to the strong fields near the electrode surface after turning on an applied voltage that screened the field in the process. Ions subsequently translocated in the weak electric field, and slowly relaxed within the diffusion layer. The ionic current performed as a function of bias voltage and also as a function of ionic concentration (Figure 5A). The interaction between the ions in the solution and the molecule in the junction has been highlighted in studies focusing on DNA molecules.<sup>107-110</sup> The interaction



**Figure 4 (A–C)** Bias-dependent electronic properties of molecular junctions. **(A)** Schematic of the strongly coupled Fe-terpyridine-gold junction (top left); calculated current and conductance as a function of applied bias (bottom-left); bias-dependent transmission as a function of injection energy  $E$  (right). **(B)** Schematic of interface Coulomb interaction (top); current (blue) and effective coupling (red) as a function of the bias voltage for the interface Coulomb interaction (bottom). **(C)** Calculated I-V characteristics for Ru-bis(terpyridine) molecular wires with different junction configurations ("d" refers to the interplanar distance between the sulfur and the nearest gold) (left); bias-dependent transmission as a function of injection energy for interfacial distances of 2.42 Å (1), 2.82 Å (2), and 3.02 Å (3) (right).

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**Abbreviation:** LUMO, lowest unoccupied molecular orbital.



**Figure 5 (A and B)** Environmental influence on molecular junction measurements with mechanically controlled break-junction (MCBJ) approach. **(A)** Transient current response of NaCl solution under an applied potential of 0.4 V for several salt concentrations (left); current response for a concentration of 200 mM NaCl at various voltages (right). **(B)** Schematic illustration of the experimental setup based on MCBJ at 77 K (left), junction lifetime  $\tau_B$  versus junction-stretching rate  $V_d$  (middle), and junction-breakdown length  $L_B$  versus junction-stretching rate  $V_d$  (right) for benzenedithiol (BDT) single-molecule junction. Results acquired at 293 K are also shown for comparison.

**Notes:** **(A)** Reprinted with permission from Doi K, Tsutsui M, Ohshiro T, et al. Nonequilibrium ionic response of biased mechanically controllable break junction (MCBJ) electrodes. *J Phys Chem C Nanomater Interfaces.* 2014;118(7):3758–3765. © 2014 American Chemical Society.<sup>106</sup> **(B)** Reprinted with permission from Tsutsui M, Taniguchi M, Kawai T. Atomistic mechanics and formation mechanism of metal-molecule-metal junctions. *Nano Lett.* 2009;9(6):2433–2439. © 2009 American Chemical Society, reprinted with permission.<sup>13</sup>

mainly consists of a binding between ions and molecules and a doping of ions into the space within the molecule, both of which are experimentally and theoretically expected to impact the charge-transport process. Lowering the temperature to cryogenic levels greatly reduced the influence of thermal fluctuation on conductance, and in turn made the sensitivity to ionic influences more pronounced.

Temperature also has influences on the molecule–electrode junction. Measurements conducted at 77 K revealed the temperature dependence of a benzenedithiol junction lifetime can be explained in terms of gold single-atom contact stability. This suggested that the molecular junction lifetime at 77 K started to become shorter than the lifetime at room temperature under low-strain-rate conditions (Figure 5B), where differences in the effects of thermal fluctuations on gold single-atom contact stability became notable.<sup>13</sup> Otherwise, local heating, a common issue of current-carrying devices, is also observed for molecular junctions. A temperature increase of different degrees due to local heating was revealed for different molecular junctions. Electron–phonon scattering was suggested as the cause of local heating in MCBJs, which emerged at molecule–electrode interfaces and consequentially destabilized the junction.<sup>53,111</sup> Therefore, severe electrical local heating has to be considered when discussing the resulting electronic properties.

## Conclusion and outlook

There is still plenty of room for improvement in the techniques involved in MCBJs. The following suggestions are just some of the potential issues that may be addressed in the near future.

It is now beneficial to incorporate other measurement techniques into multivariate correlation schemes alongside MCBJ conductance. This is already being done with Raman scattering,<sup>15,16,112–115</sup> but there is potential to use multivariate correlation to study magnetic phenomena, such as the Kondo effect.<sup>116,117</sup> Optical manipulation of molecules in MCBJs is already a common practice,<sup>32,33,118</sup> however, further optical manipulation and measurement is also possible using Fourier-transform infrared and further ultraviolet-visible techniques.<sup>22</sup> Force is easily measured alongside conductance using C-AFM in much the same way SPMBJs are performed.<sup>53,119</sup> New methods for analyzing multivariate data sets are just now emerging, with great potential for expansion and development.<sup>120–122</sup> New coupled multivariate measurement techniques will have the ability to measure the behavior of MCBJs at finer resolutions, and

retain the essential time-dependent nature of the evolving junction.<sup>44,123</sup>

Water is an essential part of organic molecule junctions when the molecule must be kept in a natural solution. It has been simulated that water, along with ions in solution, may incorporate into DNA grooves and alter the available conductance channels.<sup>124</sup> However, the effects of water on the conductance of complex molecules have not been studied thoroughly in laboratory experiments.

Along the same lines, electrochemical gating too can have a strong effect on the molecule. Specifically, theoretical investigations into electron transfer and the effects of redox reactions on MO changes are beginning to show promise.<sup>94</sup> The data-analysis method of TVS provides very simplified models, but far more fundamental models are necessary.

Many of the organic molecules researchers study (DNA and proteins) are too large for traditional Hartree–Fock ab initio simulations. In order to fully understand these molecular junctions, simulations are required, but often these simulations must be overly simplified. Better simulation methods for large systems will be required in the future.

For the development of far more stable junctions, it will become necessary to utilize semiconductor electrodes that provide the potential for C–C and Si–C bonds at the molecule–electrode junction.<sup>8,125,126</sup> This will also pave the way for more advanced semiconducting molecular devices.<sup>127</sup> It is also necessary to develop stable dielectric and electrolytic media to stabilize molecular junctions for use in future molecular electronics.<sup>128</sup>

In 1983, when Binnig and Rohrer were concluding the invention of the STM, they described the disadvantage of traditional tunnel junctions available at the time: once a metal–insulator–metal sandwich was manufactured, it was no longer possible to adjust the junction further.<sup>6</sup> The STM they developed solved this problem by using the vacuum barrier between the tip and substrate along with a piezoelectric transducer to allow easy adjustments to the junction. MCBJs are a natural extension of the desire to provide dynamic, easily modified mesoscopic junctions for fundamental physical studies. The STM's ability to scan the local density of states of the molecule is impressive, and when used as a probe to complete a single molecular circuit, it becomes a fundamental tool for physicists and chemists to explore the fundamentals of their fields.

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## Disclosure

The authors report no conflicts of interest in this work.

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