

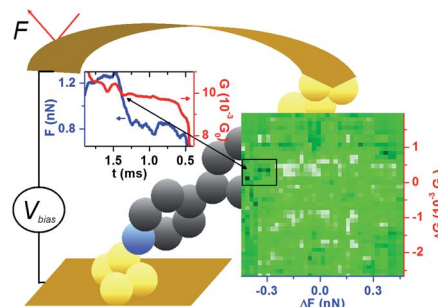
COMMUNICATION

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Force and conductance molecular break junctions with time series crosscorrelation

Joseph M. Hamill, Kun Wang and Bingqian Xu*

A multivariate time series analysis as a toolbox for single molecular junctions is developed. This 2D crosscorrelation method reveals relationships between detailed features of the break junction data which allow the experimentalist to corroborate predictions made by theoretical simulations, allowing both to work in better cooperation and therefore paves the way to the advancement of the field of molecular electronics.



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Force and conductance molecular break junctions with time series crosscorrelation

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Joseph M. Hamill, Kun Wang and Bingqian Xu*

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Force and conductance, measured across 4,4'-bipyridine simultaneously, are crosscorrelated using a two dimensional (2D) histogram method. The result is a 2D multivariate statistical analysis superior to current one dimensional histogram techniques for exploring significant conductance and force modulations within SMBJs. This method is sensitive enough to crosscorrelate signal modulations between force and conductance traces associated with contact geometry perturbations predicted in literature such as Au–molecule contact twisting and slipping during junction elongation.

Nanoelectronic devices will incorporate science derived from single molecular break junctions, but only after the science of molecular–electrode contacts is better understood. Debate surrounds the mechanical and electrical properties of single molecular break junctions (SMBJs); and much of this concerns nonequilibrium contact geometry irregularities.^{1–7} Fluctuations in the plateaus of SMBJs have been attributed to shot noise,⁸ or $1/f$ noise,⁹ but the dynamic nature of break junctions suggests close kinship between force and conductance in break junction measurements. Variable junction trajectories in SMBJs require researchers resort to statistical methods to determine expected values of molecular conductance and forces with standard deviation,¹⁰ despite the observation that the statistics of SMBJs should be treated not as ensemble average measurements, but as time-dependent single molecular spectroscopy measurements.¹¹ Conductance 1D histograms (C-1DH) have been used to study SMBJs to determine most likely molecular conductances.¹² C-1DHs, however, provide limited understanding of the nature of SMBJs because larger trends overwhelm small details, even when displacement is accounted for in analysis.¹³ Kirchhoff's superposition law results in a sum of the relatively large molecular conductance and the relatively small conductance changes due to contact reorientation.¹⁴ Often these small conductance perturbations are less than $0.1 \times$ the magnitude of

the single molecular conductance. The central question in this letter is whether statistical techniques can distinguish significant contact modulations from background noise once the larger molecular conductance is removed. These techniques must preserve details of the time-dependent molecular spectroscopy, but still provide robustness and statistical confidence by averaging numerous individual traces of large data sets.

Time series analysis (TSA) has recently been adapted for SMBJs,^{15,16} and for other force related molecular studies in the past few decades.^{17,18} Autocorrelation, one TSA technique, was applied to SMBJ data creating a conductance two-dimensional autocorrelation histogram (C-2DACH) which revealed correlations between pairs of conductance values from the data set.¹⁹ This is a powerful tool to discover information about the molecule and contact geometry in the break junction. It is suggested that this technique will be useful in investigating room temperature shot-noise.⁸ Autocorrelation is in a class of TSA devoted to single variable measurements, and is a single dimensional analysis. But it is a step towards multivariate TSA. The added dimension of a second variable, along with the TSA tools to analyze such data, provides insights into the nature of SMBJs.

Understanding of relationships between peaks in C-1DHs has improved with recent use of C-2DACH.²⁰ Binning force or conductance *versus* displacement traces into a 2D histogram grid (F-2DH or C-2DH) was also shown to be a useful tool to reveal details about the break point and final conductance in SMBJs.^{13,20–23} This, especially when used in conjunction with the C-2DACH technique, was used in the past to determine a 4,4'-bipyridine (4,4'-bpy) molecule in a SMBJ can be oriented in one of two ways, each with a unique conductance value.²⁰ This phenomenon showed on a C-1DH as separate peaks and on a C-2DACH as an anticorrelated region at the intersection of the two conductances. Expanding the C-2DACH to a multivariate force–conductance two-dimensional crosscorrelation histogram (FC-2DCCH) distinguishes characteristics of force traces which are statistically correlated with characteristics from conductance traces (and *vice versa*).

Single Molecule Study Laboratory, College of Engineering and Nanoscale Science and Engineering Center, University of Georgia, Athens, GA 30602, USA. E-mail: bxu@engr.uga.edu; Fax: +1-706-542-3804; Tel: +1-706-542-0502

Herein, the C-2DACH technique is expanded to its multivariate equivalent, the FC-2DCCH, adding the second dimension of force to a powerful data analysis technique already being applied to conductance. The technique is then applied to a representative data set of about 100 conductance-mode atomic force spectroscopy (CM-AFM) SMBJ measurements of 4,4'-bpy (Fig. 1). This letter provides a proof-of-concept that the calculated correlated magnitudes of detailed modulations in force and conductance plateaus are comparable to *ab initio* investigations focused on trajectories of molecule-Au junctions reported in the literature.^{13,23–25} This suggests that FC-2DCCH has the ability to discern miniature but significant fluctuations in force and conductance traces and allow deductions about sources and causes of those modulations.

A Au-4,4'-bpy-Au break junction, Fig. 1(d), was repeatedly created by approaching and retracting (at a rate of 40 nm s⁻¹) a Au coated AFM tip (with stiffness of 40 N m⁻¹) towards and away from 4,4'-bpy in toluene atop a Au(111) substrate. Labview programs read force and conductance [Fig. 1(b)]. A C-1DH [Fig. 1(c)], with bin size of $8.0 \times 10^{-4} G_0$, confirmed the most prominent conductance, corresponding to the first step in a sample trace when a single molecule was present in the junction, was at $8.65 \times 10^{-3} G_0$. This value is similar to previously published values.^{26,27}

The saw tooth shape of the force traces yielded a poorly defined force 1D histogram (F-1DH). However, by removing the common slope, related to the constant rate of retraction of the cantilever, the saw tooth shape [Fig. 1(b) curve 1] could be

transformed into steps [Fig. 1(b) curve 2] which yielded a clearer histogram [Fig. 1(a)] using the formula $f_i^{\text{new}} [\text{nN}] = f_i^{\text{old}} [\text{nN}] - m [\text{nN s}^{-1}] \times t_i [\text{s}]$, where $m = 40 \text{ nN s}^{-1}$. This emphasized the flat force plateaus coinciding with the conductance plateaus, and had a negligible effect on the magnitude of step height change and modulations because these changes are abrupt and local. The prominent peak in Fig. 1(a) with bin size of 0.087 nN is at 0.68 nN, similar to published values.^{21,28,29} Fig. 2(a) combined these two results in one force-conductance 2D histogram contour plot. The darker regions in Fig. 2(a) corresponded to the intersection of the most common conductance and force for each of the three plateaus. There is a dark region centered on a conductance of $8.65 \times 10^{-3} G_0$, and spanning across the force values associated with the first plateau of the break junction.

4,4'-bpy is exploited for SMBJs because of its rigid structure which orients itself vertically within Au-Au break junctions due to Au-H repulsion.²⁴ This orientation allows conductance to be measured longitudinally across the two benzene rings. Conductance modulations in phenyldithiolate never exceeded $1 \times 10^{-5} G_0$ in Hartree-Fock simulations,³⁰ suggesting that Au contacts will be the most likely source of conductance modulations, and not the aromatic rings of 4,4'-bpy. As a consequence, the conductance modulations studied in this letter are expected to be due to adjustments occurring in the contacts as the junction progresses. Certain reorientations of 4,4'-bpy junctions will not be considered because the large changes involved are comparable to the changes involved when a molecule is removed from the junction entirely, and because they have been discussed elsewhere.³¹

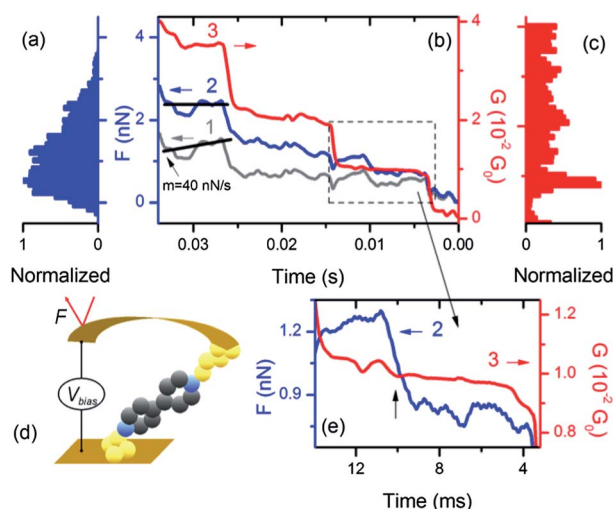


Fig. 1 Example force (F) and conductance (G) traces with 1D histograms from about 30 000 data points. (a) Force 1D histogram from constant-slope-adjusted force traces; first peak at 0.68 nN; bin size is 0.087 nN. (b) Example force (1), constant-slope-adjusted force (2), and conductance (3) traces; thick lines over force traces depict slope of plateau before and after adjustment; square is expanded area in (e). (c) Conductance 1D histogram; first peak at $8.65 \times 10^{-3} G_0$; bin size is $8.0 \times 10^{-4} G_0$. (d) Schematic of experimental apparatus; force and conductance are measured as top electrode is retracted from bottom electrode while bias voltage is applied across 4,4'-bipyridine. (e) Examples of the first plateau correlations of force (2) and conductance (3). Arrow illustrates example location of crosscorrelation.

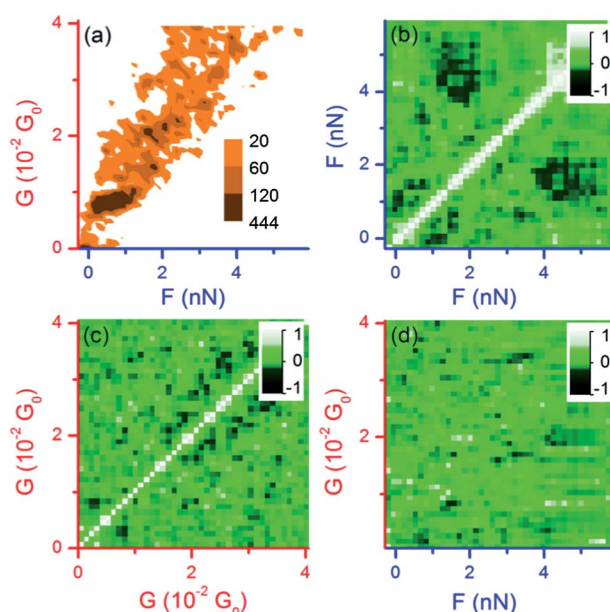


Fig. 2 2D histograms of force and conductance created from about 30 000 data points. (a) Force-conductance 2D histogram contour plot; dark region corresponds to the first plateau region. (b) Force 2D autocorrelation histogram; white is correlation of 1 and black is correlation of -1. (c) Conductance 2D autocorrelation histogram, intensity plot units same as (b). (d) Force-conductance 2D cross-correlation histogram. Bin sizes are the same as those in Fig. 1.

Autocorrelation H calculates the scaled covariance between two elements: (1) bin i of one trace histogram $g_i(l)$ compared with the mean $\langle g_i(l) \rangle_i$ of bin i from all the trace histograms and (2) bin j of the same sample $g_j(l)$ compared with the mean $\langle g_j(l) \rangle_j$ of bin j from all of the samples using eqn (1):²⁰

$$H_g(i, j) = \frac{\langle [g_i(l) - \langle g_i(l) \rangle] [g_j(l) - \langle g_j(l) \rangle] \rangle_l}{\sqrt{\langle [g_i(l) - \langle g_i(l) \rangle]^2 \rangle_l \langle [g_j(l) - \langle g_j(l) \rangle]^2 \rangle_l}} \quad (1)$$

Usually autocorrelation takes a time-varying signal and offsets it in time, so that i and j represent moments in time where j is a time lagged behind (or before when the lag is negative) i , and then calculates the degree with which the signal and its offset are linearly dependent. However, for this analysis, the histograms are being used instead of the signal, and therefore in Fig. 2(c) i and j represent different binned units of conductance where j is lagged, or offset, from i by a certain amount of bins of conductance. The algorithm runs through all possible lags, from a lag of $0G_0$ when $i = j$, to a maximum lag determined by the bin with the largest value of conductance in the histograms. This is why the diagonal of Fig. 2(b) is 1: when the lag is $0G_0$, there is a perfect correlation between each histogram and itself. As stated previously, eqn (1) is essentially a 1D analysis, in terms of the variable g . Eqn (1) was used to calculate Fig. 2(b) and (c), where the intensity plot ranges from -1 (anticorrelated) in black to 1 (correlated) in white. Autocorrelation is a useful tool in discovering repeating patterns in a single signal, or in a multiple samples of a single variable to determine if the signal is noise or information.

Eqn (2) calculates correlation ρ of two variables without a lag, where

$$\rho_{f,g}(i) = \frac{\langle [g_i(l) - \langle g_i(l) \rangle] [f_i(l) - \langle f_i(l) \rangle] \rangle_l}{\sqrt{\langle [g_i(l) - \langle g_i(l) \rangle]^2 \rangle_l \langle [f_i(l) - \langle f_i(l) \rangle]^2 \rangle_l}} \quad (2)$$

Bin i of variable f was only compared with bin i of variable g . Because there is no offset, it is not beneficial to plot this in a 2D grid, although this is now a 2D analysis. Correlation calculates how much two variables depend upon one another at each point.

Finally, crosscorrelation r reintroduces the lag from autocorrelation into the correlation calculation for two variables using eqn (3):

$$r_{f,g}(i, j) = \frac{\langle [g_i(l) - \langle g_i(l) \rangle] [f_j(l) - \langle f_j(l) \rangle] \rangle_l}{\sqrt{\langle [g_i(l) - \langle g_i(l) \rangle]^2 \rangle_l \langle [f_j(l) - \langle f_j(l) \rangle]^2 \rangle_l}} \quad (3)$$

In other words, autocorrelation is the special case when a variable is crosscorrelated with itself, and correlation is the special case when $i = j$ for two variables. For Fig. 2(d), the conductance array was substituted for one of the arrays in the force calculation to result in a FC-2DCCH. The result is a calculation for the correlation (anticorrelation) between a measured value of conductance and a measured value of force. Specifically, this is a crosscorrelation calculation between two variables with the second variable offset by incrementing lag as with autocorrelation. Correlated regions are found at the loci of

the conductance and force values associated with each of the plateaus.

Two dimensional autocorrelation histograms for both force (F-2DACH) and conductance were created [Fig. 2(b) and (c)]. Noticeable features in Fig. 2(b) were the bands of anti-correlation parallel to the center diagonal of width 0.7 nN. This was the average separation between adjacent force plateaus in the constant-slope adjusted-force traces. A similar feature was observed in Fig. 2(c) in which a separation of about $0.01G_0$ was the average.

It is standard procedure in TSA to remove global trends in the data in order to observe behavior on smaller time scales. To this end, Labview subroutines parsed the segment of each force and conductance pair where the conductance trace entered and left a window around $8.65 \times 10^{-3}G_0$. This removed the larger trend related to the decreasing number of molecules in the junction. These segments were then checked to ensure they were of minimum length to exclude any conductance samples which did not have a plateau in that window. Fig. 1(e) shows an example pair of traces clipped down to the first plateau where close relationships between modulations in force and conductance are observed. Finally, the mean of each trace, both

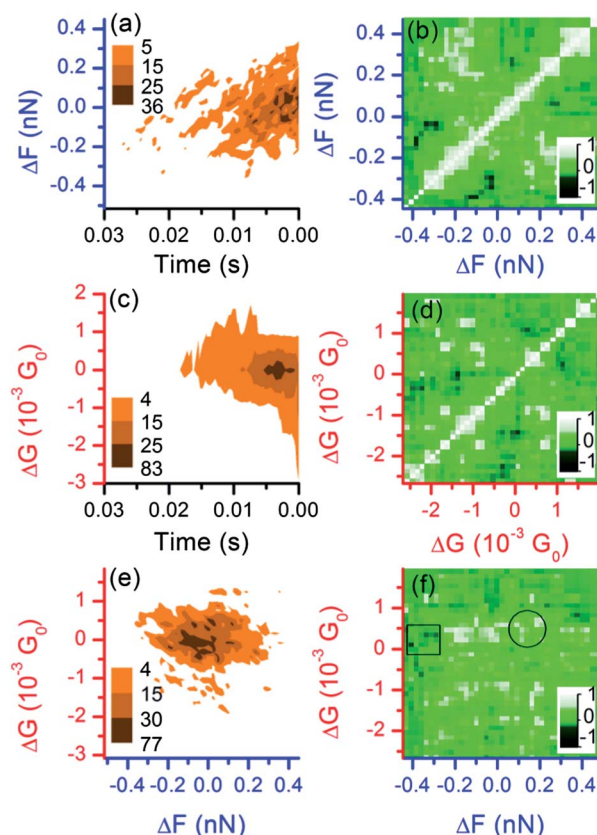


Fig. 3 Histograms for traces clipped to the first plateau from about 10 000 data points. (a) Force 2D histogram. (b) Force 2D autocorrelation histogram. (c) Conductance 2D histogram. (d) Conductance 2D autocorrelation histogram. (e) Force–conductance 2D histogram. (f) Force–conductance 2D crosscorrelation histogram; square and circle highlight (anti)correlated regions. Time bin size is 0.077 ms; force bin size is 0.020 nN; conductance bin size is $1.4 \times 10^{-4}G_0$.

force and conductance, were subtracted to offset each trace to zero. This ensured that when the correlation calculations were conducted, only the force changes ΔF and conductance changes ΔG , measured from the plateau, were compared and not global trends encompassing the entire plateau. These were the segments which were used to create the plots in Fig. 3.

ΔF and ΔG 2DHs [Fig. 3(a), (c) and (e)] were created to emphasize the distribution of values. Bin sizes were 0.077 ms for time, 0.020 nN for force, and $1.4 \times 10^{-4} G_0$ for conductance. Fig. 3(c) revealed no significant trend in ΔG aside from the Gaussian distribution. Fig. 3(a), however, showed a tendency towards a multi-modal behavior in ΔF , an attribute also reflected in the FC-2DH of Fig. 3(e). This multi-modal distribution of ΔF suggested it favored specific magnitudes of change. This is further clarified in the F-2DACH [Fig. 3(b)] and G-2DACH [Fig. 3(d)]. In Fig. 3(b) the change in force of -0.21 nN was correlated to a change in force of 0.29 nN. Similarly, in Fig. 3(d), a ΔG of $-3.8 \times 10^{-5} G_0$ was anti-correlated to a ΔG of $-1.5 \times 10^{-3} G_0$. In both cases, this change was from the average plateau value. The sign not only revealed significant correlations in the changes, but it specified whether those changes result in an increase or a decrease in conductance and force. The correlation (anticorrelation) of pairs of force (conductance) values indicated that within any given trace, there was a strong possibility that when a change of ΔF (ΔG) of one value was observed, so too was the ΔF (ΔG) of the other. Fig. 3(f) indicated that there was a correlation, for example, between a decrease in force of 0.21 nN and an increase in conductance of $5.0 \times 10^{-4} G_0$; but Fig. 3(f) also indicated a correlation between a decrease in force of 0.1 nN and a decrease in conductance of $1.0 \times 10^{-3} G_0$.

The black circle in Fig. 3(f) highlighted the correlated region at the location $(\Delta F, \Delta G) = (0.1 \text{ nN}, 6.0 \times 10^{-4} G_0)$. When a molecule twisted during the initial stages of a break junction there was a corresponding effect on the conductance and force.^{13,23,32} During the relaxation of the twist, when bond distances between the conducting π -orbital of the molecule and the s-orbital of the Au were slowly returning to an overlapped orientation, there were periods of rapid change. One such jump resulted in a rise and fall of force of magnitude 0.08 nN and corresponding increase in conductance of $6 \times 10^{-5} G_0$. High conductance could be achieved either when the molecule was in a perpendicular orientation within the junction and the N-Au bond was minimized, or when the molecule was orientated at a close angle to the substrate, allowing the π^* -LUMO to be more favorably aligned with the s-orbital of the Au. These competing influences on the conductance of the 4,4'-bpy break junction made the conductance highly sensitive to the orientation of the molecule and the contacts, resulting in modulations of the conductance and force when any of these factors changed during elongation. The DFT simulation calculated the predicted changes in force and conductance due to specific orientation changes, and the FC-2DCCH results suggested promising agreement with the predictions, within a reasonable order of magnitude and limitations of the uncertainties as a consequence of discrete bin sizes and resolution.

The second region of interest, marked with a black square in Fig. 3(f), corresponded to $(\Delta F, \Delta G) = (-0.40 \text{ nN}, 1.2 \times 10^{-4} G_0)$.

This pair was similar to the area marked with an arrow in Fig. 1(e). A nitrogen terminated molecule bonding initially to the second tier of the Au contact, before slipping down to the apex under strain, showed similar characteristics in the force and conductance traces.²⁴ During this slip the force quickly changed by -0.6 nN and a rise and fall of conductance of magnitude $4 \times 10^{-4} G_0$ was calculated.¹³ Within an order of magnitude, the simulated results of this precise junction trajectory, and the FC-2DCCH, as calculated from experimental data here, are in agreement.

Au-Au chains formed at the contacts in a 4,4'-bpy SMBJ were predicted to undergo both conductance increase and decrease as the bond angles of the zigzag chain adjusted during junction elongation.²⁵ Oscillations in the conductance of about 20% due to Peierl's distortion were reported when the number of Au atoms in a chain went from odd to even. Au chains as long as four Au atoms were possible when involved in a SMBJ,²⁹ so these oscillations occur more than once as more Au atoms are added to the chain in a single plateau, prior to rupture. Other studies suggested large force changes do not necessarily result in large conductance changes.³³ Various other possible Au junction trajectories have been considered with consequences for the correlated force and conductance modulation.^{24,34,35}

We have shown the FC-2DCCH technique provides the experimentalist with tools not yet available to plumb molecular-electrode interfaces in nonequilibrium junctions. Higher resolution samples of Au-Au junctions will allow for smaller bin sizes and may reveal the types of conductance oscillations referred to in the previous paragraph. Furthermore, dynamic behavior within molecules will also be measurable. Simulation on the unfolding of a molecule shows promising correlation between a force change of 0.044 nN and changes in the transmission function of the molecular junction.³⁶ Other possibilities might include quantum chemistry calculations predicting isomers with transition energies less than 1 eV can be measured with CM-AFM to experimentally establish the transition force and identify the effects this transition has on the orbitals and conductance. Such low transition energies might be associated with a ruptured hydrogen bond, or the disruption of a van der Waal's interaction. Short polymers seem a likely candidate.

In conclusion, by expanding upon recent developments in SMBJ data analysis techniques, and drawing upon established formulations in TSA, a 2D crosscorrelation analysis approach is presented with the ability to allow experiments to compare results to predictions made by first principle simulations for fields including quantum chemistry, molecular force spectroscopy, and molecular electronics. Force and conductance, when measured in unison, were crosscorrelated to compare correlations between modulations of each. Specific changes within conductance plateaus were correlated to modulations within the corresponding force trace, and the magnitude of these modulations found good agreement with break junction trajectories predicted using *ab initio* calculations. This suggested the capacity for TSA to discover many of the subtleties of single molecular conductance still hiding in the data and allow for closer cooperation between experiments and simulations.

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