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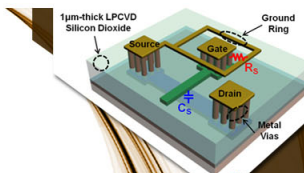
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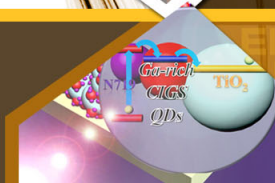
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Admittance of Au/1,4-benzenedithiol/Au single-molecule junctions

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Employing the admittance formula for double-barrier junctions [Fu and Dudley, *Phys. Rev. Lett.* **70**, 65 (1993)], we have estimated an ac susceptance (imaginary part of admittance) of Au/1,4-benzenedithiol/Au single-molecule junctions from their current-voltage characteristics. In the MHz regime, we find that the junction susceptance shows a very small (~ 0.1 aF) capacitive component that can be entirely masked by a larger electrode capacitance. Direct ac signal transmission measurements up to 1 GHz reveal no molecular signals and confirm the smallness of the molecular capacitance in the MHz regime. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4772642>]

Molecular electronics based on the idea of using single molecules as circuitry building blocks¹ have attracted much attention in the past decades. One of the promising and widely studied devices is a molecular field-effect transistor (FET) where a single molecule links a pair of metal electrodes and its conductance is modulated by a gate voltage. For such molecular FETs, understanding of the charge transport through a metal/molecule/metal junction becomes a key issue for designing and optimizing device characteristics. Up to this time, enormous amount of experimental and theoretical studies have been made on carrier transport through molecular junctions. Most of past studies, however, deal with static junction properties measured at dc and low frequencies, and little has been known on characteristics of molecular junctions at high frequencies. For practical applications of molecular FETs, it would be critically important to know how molecular junctions respond to high frequency signals, but no such studies have been made on molecules, except carbon nanotubes whose impedance has been experimentally investigated² and theoretically analyzed³ up to GHz or above. An ac impedance has also been calculated for a straight chain of carbon atoms.^{4,5} In this letter, we point out that the ac admittance of some molecular junctions can be quantitatively estimated from their current-voltage (I - V) characteristics and apply this scheme to evaluate the ac admittance of Au/1,4-benzenedithiol (BDT)/Au single-molecule junctions. The results are compared with experimental admittance obtained from the direct ac signal transmission measurements.

We first start from a single-level model^{6,7} of molecular junctions, where a bridging molecule is represented by a single molecular level coupled to right and left electrodes. In this model, an electronic transport through a junction can be characterized by two parameters, ΔE and Γ , a distance of the molecular level from the electrode Fermi level E_F and a strength of molecule-electrode coupling, respectively. Specifically, an I - V characteristic for nearly symmetric junctions can be expressed as^{6,7}

$$I(V) = \frac{2e}{h} \int_{-\infty}^{+\infty} dE T(E, V) [f_F(E - E_F - eV/2) - f_F(E - E_F + eV/2)]$$

$$T(E, V) = \frac{\Gamma^2}{(E - \Delta E - \eta(eV/2))^2 + \Gamma^2}, \quad (1)$$

where f_F and E_F are the Fermi distribution function and the Fermi energy, respectively, and we assumed a Lorentzian shape with width Γ for the broadening of the molecular level due to the molecule-electrode coupling.⁸ We included in Eq. (1) a parameter η ($-1 < \eta < 1$) that accounts for a bias induced shift of the molecular level and allows for a weak asymmetry in I - V characteristics. Symmetric transport corresponds to $\eta = 0$. The unique advantage of the single-level model lies in the fact that its linear ac response has been theoretically studied by Fu and Dudley,⁹ and an analytical expression has been obtained for a junction admittance. For example, a susceptance of a symmetric junction can be expressed as

$$\text{Im}Y(\omega) = -\frac{G_0}{4\beta} \ln \left[\frac{((\alpha + \beta)^2 + 1)((\alpha - \beta)^2 + 1)}{(\alpha^2 + 1)^2} \right] \quad (2)$$

$$\alpha = \Delta E/\Gamma, \quad \beta = \hbar\omega/\Gamma,$$

where $G_0 \equiv 2e^2/h$ is the conductance quantum unit. This equation allows us to calculate a junction susceptance from two parameters, ΔE and Γ , which can be deduced from the I - V characteristics through Eq. (1). Thus, within a framework of the single-level model and the linear response theory, we can indirectly estimate a junction susceptance from the junction I - V characteristics.

We note that the single-level model has a practical applicability for real molecular junctions, specifically for a group of π -conjugated molecules. In fact, conductance,¹⁰ I - V ,^{11,12} and transient voltage spectroscopy (TVS)¹³ characteristics of various π -conjugated molecular junctions can be well described by the single-level model. We therefore employed in this work a BDT molecule, an archetypal π -conjugated molecule, and constructed Au/BDT/Au junctions for studying their ac susceptance. Direct ac signal

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transmission measurements were also carried out for comparison.

We exploited the mechanically controllable break junction (MCBJ) method to fabricate Au/BDT/Au single-molecule junctions. Details of our MCBJ apparatus have been described elsewhere.¹⁴ A gold wire of 0.1 mm diameter was used as an electrode. After rupturing the wire, we deposited onto a break point a small amount of 0.5 mM BDT solution with ethanol as a solvent. After evacuating the sample chamber and backfilling it with an Ar gas, the junction conductance was monitored under a 0.1 V bias while repeatedly opening and closing the BDT-deposited junction. Care was taken not to heavily crash the electrode surface so that the conductance was kept below $20G_0$ during junction closing. Upon confirming molecular bridging, the junction was held fixed and the I - V characteristics were measured by varying the bias voltage from -1.0 V to $+1.0$ V. A picoammeter (Keithley 6487) was used for measuring both conductance and I - V characteristics. After recording an I - V curve, the measuring circuit was switched to a network analyzer (Rhode and Schwarz ZNC3) through coaxial relays, and the junction transmission characteristics were measured in the frequency range 100 kHz \sim 1 GHz. Some junctions were found broken at the circuit switching but some survived. We could carry out simultaneous I - V and ac transmission measurements on three specimens and acquired on each specimen 10–20 data on their transmission and I - V characteristics.

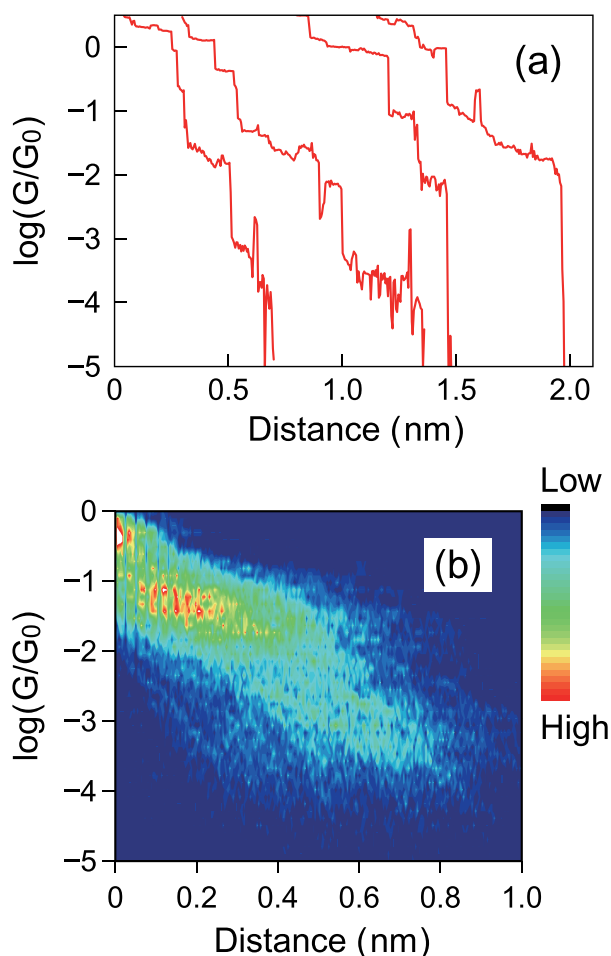


FIG. 1. Typical conductance traces (a) and 2D conductance histogram (b) obtained on Au/BDT/Au junctions.

Figure 1(a) shows examples of conductance traces recorded during the junction opening. The electrode distance was calculated from the opening speed which was calibrated by analyzing the junction current in the tunneling regime. The opening speed was 0.07 nm/s in Fig. 1(a) but found to vary from sample to sample. The conductance traces show plateaus at different conductance values below $1G_0$, and these sub- $1G_0$ plateaus likely correspond to molecular bridging with different configurations. To visualize the distribution of the conductance, we constructed from 1000 conductance traces a two-dimensional (2D) histogram depicted in Fig. 1(b). The conventional histogram shows two broad peaks at $0.04G_0$ and $0.001G_0$, but the 2D histogram reveals that the conductance actually extends over many orders of magnitude as observed in previous experiments.^{11,15–17} This wide spread in conductance is theoretically interpreted as arising from diversities in the bridging geometry of a BDT molecule and in the arrangement of electrode atoms.^{18–20} The 2D histogram also indicates a tendency that the conductance decreases with increasing the electrode distance, in good agreement with recent experiments¹⁷ and theoretical prediction.¹⁹

We show in Fig. 2, two examples of an I - V characteristic observed on Au/BDT/Au junctions. Majority of the I - V curves are similar to the one indicated by filled squares. They exhibit positive nonlinearity and become convex downward in agreement with our previous I - V measurements.¹⁴ We fitted these I - V curves by Eq. (1) and obtained good fitting as illustrated by a solid curve in Fig. 2. Unbridged junctions yield linear I - V curves of tunneling conduction and can be unambiguously discriminated. A small fraction ($\sim 7\%$) of I - V curves show poor fitting to Eq. (1). An example of such curves is represented by open symbols in Fig. 2. These I - V curves result in unusually low voltage minimum in their TVS spectra and presumably correspond to some imperfect bridging configurations. We therefore omitted them from further analyses. The results of our I - V fitting are summarized in Figs. 3(a) and 3(b), where the parameters Γ and ΔE are plotted, respectively, as a function of the junction conductance at 0.1 V. In Fig. 3(a),

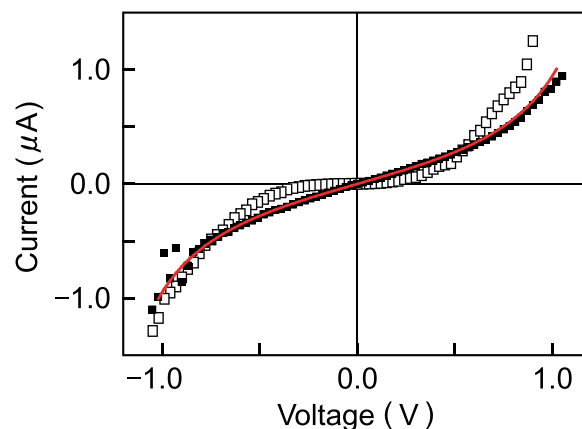


FIG. 2. Examples of the measured I - V characteristics. A curve plotted by filled squares is representative of the majority of the observed I - V curves, and a solid line represents the fitting by Eq. (1). Small fraction of I - V curves are found to poorly conform to Eq. (1), and an example of such curves is indicated by open squares.

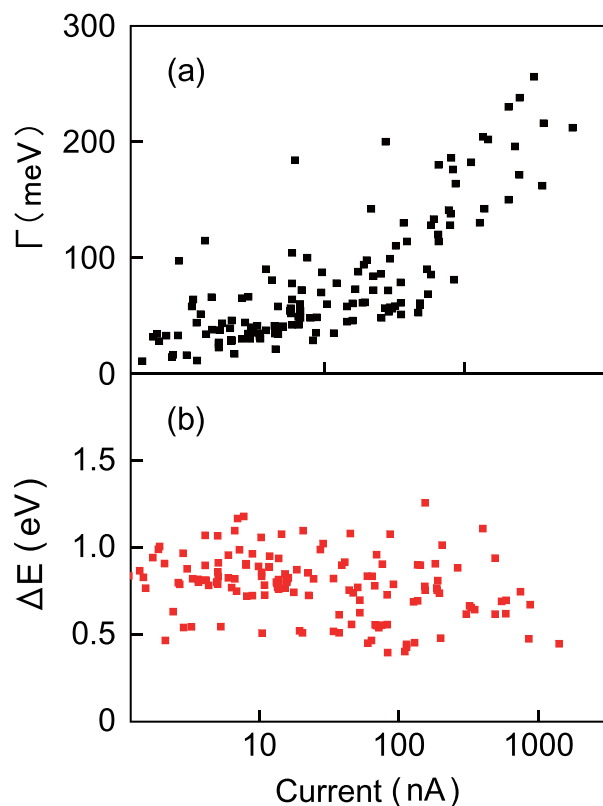


FIG. 3. Panels (a) and (b) show parameters Γ and ΔE , respectively, obtained from the I - V curve fitting to Eq. (1).

Γ tends to increase with the conductance showing a plausible correlation between the conductance and the molecule-electrode coupling strength. On the other hand, ΔE shows little dependence on the conductance and stays 0.4–1.0 eV. We note that our ΔE values are in good agreement with previous theoretical^{19,20} and experimental¹¹ results. Most I - V curves are found nearly symmetric, like the one shown in Fig. 2. As a result, the asymmetric parameter η is nearly zero ($|\eta| < 0.1$), irrespective of the conductance.

It can be seen in Fig. 3(a) that Γ lies in the range 20–120 meV which corresponds to 30–180 THz in frequency. Thus, we have $\beta = \hbar\omega/\Gamma \ll 1$ in Eq. (2) in the MHz range and can therefore replace $\text{Im}Y(\omega)$ by its low-frequency limit $\text{Im}Y(\omega) \sim G_0(\hbar\omega/2\Gamma)[(\alpha^2 - 1)/(\alpha^2 + 1)^2]$. In this limit, $\text{Im}Y(\omega)$ varies linearly with ω and shows a capacitive behavior with a molecular capacitance $C_{mol} = (\hbar G_0/2\Gamma)[(\alpha^2 - 1)/(\alpha^2 + 1)^2]$. The magnitude of this capacitance is very small: if we take $\Delta E \sim 0.8$ eV and $\Gamma \sim (20 - 120)$ meV, for example, we have $C_{mol} \sim 0.2$ aF at the largest. Such a small capacitance is negligible compared to a parasitic capacitance of the junction and would make no substantial contributions to the ac response of the junction. This point can be tested by directly measuring ac signal transmission through molecular junctions. Figure 4 shows experimental $\text{Im}Y(\omega)$ obtained from ac transmission measurements on six junctions. The frequency axis is normalized by Γ of each junction obtained from the I - V curve. Below $\hbar\omega/\Gamma \sim 10^{-5}$ (~ 200 MHz), the measured $\text{Im}Y(\omega)$ shows a capacitive behavior with a junction capacitance $C \sim (10 - 100)$ fF. This capacitance is orders of magnitude larger than C_{mol} estimated above and probably represents a parasitic capacitance of junction

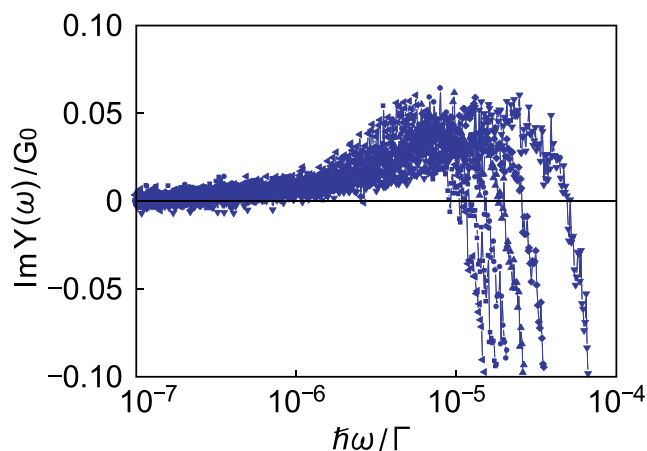


FIG. 4. Experimental susceptance of six Au/BDT/Au junctions obtained from direct ac signal transmission measurements.

electrodes. In fact, we found a linear correlation between $1/C$ and $\ln R$, where R stands for a dc junction resistance. Because $\ln R \propto d$ with d being an electrode gap distance, the observed linear dependence of $1/C$ on $\ln R$ indicates $1/C \propto d$ as expected for an electrode capacitance. Assuming an appropriate work function (~ 0.5 eV) for Au electrodes in ambient conditions,²¹ we can estimate an effective area A of the capacitance from the slope of the $1/C - \ln R$ plot and obtained $A \sim (0.4 - 0.6) (\mu\text{m})^2$. This would be a reasonable value for an apex area of electrodes formed by breaking a 0.1 mm-diameter Au wire. All these results clearly indicate that the ac signal transmission through Au/BDT/Au junctions substantially takes place through the electrode capacitance and contains negligible contribution from the molecular capacitance.

The measured susceptance shown in Fig. 4 exhibits a capacitive-inductive crossover around $\hbar\omega/\Gamma \sim 10^{-5}$. This should not, however, be of molecular origin because the crossover shows no clear correlation with molecular parameters Γ and ΔE . Also, values of these parameters shown in Figs. 3(a) and 3(b) suggest that such a crossover could be expected in the THz range ($\hbar\omega/\Gamma \sim 1$). Presumably, the observed crossover comes from a remnant inductive component of measuring cables. Though we made cancellation of cable contributions before each transmission measurement, some contributions might be left uncanceled. We found that $\text{Im}Y(\omega)$ of blank junctions without BDT molecules shows a similar crossover around 200 MHz. This also indicates the non-molecular origin of the crossover.

In conclusion, we showed that for admittance of molecular junctions can be deduced from the junction I - V characteristics within the frame work of the single-level model. We applied this method to Au/BDT/Au single-molecule junctions and found that their molecular capacitance in the MHz regime is the order of 0.1 aF and negligibly small compared to the parasitic electrode capacitance. Our ac transmission data through Au/BDT/Au junctions bear no molecular signatures and support the smallness of the molecular capacitance. For detecting the genuine molecular admittance, one has to reduce the electrode capacitance comparable to or below C_{mol} or increase the frequency range to THz, where the molecular susceptance is expected to become inductive. We note that junction capacitances lower than 0.5 aF have been

realized in some Coulomb blockade experiments employing sharp metal tips,²² and the incorporation of metallic atom wires into atom-sized transistors has been recently accomplished.²³ Practical application of these atom-sized electrodes would, however, still remain a remote possibility, and foreseeable applications of molecular devices would be limited to those at low frequencies.

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⁸Definition of the level broadening or the electrode-molecule coupling Γ differs by a factor of two among literatures. We have followed in this work the definition employed in Ref. 7 and put $\Gamma = \Gamma_L + \Gamma_R$, where Γ_L

and Γ_R represent the molecular coupling to a left and a right electrode, respectively.

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