Current-Induced Forces in Molecular Wires

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We report first-principles calculations of current-induced forces in molecular wires for which experiments are available. We investigate, as an example, the effect of current-induced forces on a benzene molecule connected to two bulk electrodes via sulfur end groups. We find that the molecule twists around an axis perpendicular to its plane and undergoes a "breathing" oscillation at resonant tunneling via antibonding states. However, current-induced forces do not substantially affect the absolute value of the current for biases as high as 5 V, suggesting that molecular wires can operate at very large electric fields without current-induced breakdown.

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The phenomenon of atom motion due to current flow (electromigration) has been extensively studied in the past both from the fundamental standpoint and for its importance in microelectronics [1–4]. Most recently, a new electronics is emerging that envisions the use of single molecules or molecular wires as fundamental components in electronic devices [5]. For instance, it has been demonstrated that molecules can operate as Coulomb blockade structures [6], transistors [7,8], diodes [9], or switching devices with high negative differential resistance even at room temperature [10–12]. Since electromigration has been a major concern in conventional microelectronics due to current-induced device breakdown, the question arises as to whether current-induced forces may present a severe limitation to the development of molecular electronics.

It was recognized in early theoretical work [1–4] that current-induced forces on a given physical system depend strongly on the microscopic details of the self-consistent electric field that is created upon scattering of the electrons across the region of interest. Self-consistency in the calculation of the local electric field with the correct scattering boundary conditions is thus essential to have meaningful quantitative results on current-induced forces.

In this Letter, we report first-principles calculations that explore the role of current-induced forces on molecular wires, and their role in weakening chemical bonds at the contacts and in the wire. Considering as an example current flow in a benzene molecule connected to two bulk electrodes via sulfur end groups [10], we extract general trends on the stability of molecular wires under current flow. The molecular structure investigated represents a prototype molecular device showing nonlinear transport properties [10]. It has been investigated both experimentally [10] and theoretically [13–16] without, however, addressing the issue of current-induced forces. Since we are interested in the role and magnitude of these forces, and the actual experimental contact geometry and structure of the molecular device are not known, we focus on the molecular structure depicted in Fig. 1. The effect of contact chemistry and geometry in the current has been discussed in Ref. [13]. We find that, under current flow, the molecule twists around an axis perpendicular to its plane and undergoes a "breathing" oscillation at resonant tunneling via antibonding states [17]. However, current-induced forces do not substantially affect the absolute value of the current up to biases as high as 5 V. This is a remarkable result for a molecule of nominal length of only 8 Å. At external voltages larger than 5 V, the contact that is depleted of electrons during current flow weakens considerably with a consequent dramatic reduction of the current. This suggests that molecular wires can operate at very large biases without current-induced breakdown, in contrast to recent findings in atomic gold wires that have been found to break at biases of 1 to 2 V [18,19].

We computed the I-V characteristics of the molecular structure by using the method discussed in Ref. [20]. The two sulfur atoms of the molecule (see Fig. 1) make contact to gold surfaces that we model with ideal metals (jellium model) [20]. The interior electron density of the electrodes is taken equal to the value for metallic gold ($r_s \approx 3$). The electron wave functions are computed by solving the Lippman-Schwinger equation iteratively to self-consistency in steady state. Exchange and correlation are included in

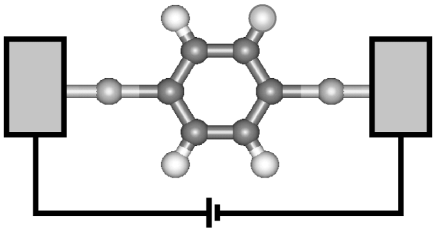

FIG. 1. Scheme of the molecular structure investigated. The structure is the benzene-1,4-dithiolate molecule. All atoms lie on the plane defined by the carbon ring. The sulfurs attach to ideal metallic leads.

the density-functional formalism within the local-density approximation [20]. The current is computed from the wave functions $|\psi\rangle$ of the electrode-molecule system. The force $\mathbf{F}$ acting on a given atom at position $\mathbf{R}$ due to the electron distribution as modified by the external bias is given by the Hellmann-Feynman type of theorem developed in Ref. [21]:

$$\mathbf{F} = \sum_i \left\langle \psi_i \left| \frac{\partial H}{\partial \mathbf{R}} \right| \psi_i \right\rangle + \lim_{\Delta \to 0} \int_\sigma dE \left\langle \psi_\Delta \left| \frac{\partial H}{\partial \mathbf{R}} \right| \psi_\Delta \right\rangle . \quad (1)$$

The sum and integral in Eq. (1) include spin variables also. The first term on the right-hand side of Eq. (1) is the usual Hellmann-Feynman contribution to the force due to localized electronic states $|\psi_i\rangle$. The second term is the contribution to the force due to the continuum of states [21]. It is calculated by constructing, for each energy in the continuum, square-integrable wave functions $|\psi_\Delta\rangle$ in an energy region Δ

$$|\psi_\Delta\rangle = \mathcal{A} \int_\Delta dE\, \psi\, , \quad (2)$$

where $\mathcal{A}$ is a normalization constant and the ψ's are single-particle wave functions in the continuum, solutions of the Lippmann-Schwinger equation [21]. The continuum integration σ covers the part of the spectrum occupied by the electrons at a given bias [22]. Finally, the total force on the atom includes a trivial ion-ion interaction. Starting from a given atomic configuration (e.g., the atoms at the equilibrium experimental atomic positions), we calculate the forces acting on each atom. We then move the atoms according to the gradient of these forces until the force on each atom is zero.

We now discuss the main results obtained using the above theoretical approach. The relaxed configuration of the system at zero bias consists of C-C bond lengths of 1.40 Å, C-H bond lengths of 1.09 Å, C-S bonds of 1.70 Å, and S-jellium surface bond length of 1.00 Å. The latter is in agreement with the equilibrium distance of sulfur adsorption on jellium surfaces [23], and the other bond lengths are in good agreement with the experimental bond lengths in isolated benzene molecules and thiophenol molecules [24].

The I-V characteristic of the molecular structure with and without the effect of current-induced forces is reported in Fig. 2. The first peak in conductance (indicated as a vertical arrow in Fig. 2) occurs at about 2.4 V and is due to resonant tunneling via π^* antibonding states (see also Ref. [13]). The second peak at about 4.4 V (also indicated as a vertical arrow in Fig. 2) is due to resonant tunneling via π bonding states [13]. The electron transport via antibonding states corresponds to a depletion of charge in the central C-C bonds, and an accumulation of charge in the nearest C-C bonds (see Fig. 3a). The total charge depleted with respect to the zero bias condition is about $0.05e$ per bond. This charge is nearly completely recovered in the middle bonds when the resonant tunneling condition is lost. In particular, at 4.4 V—corresponding to resonant-tunneling via π bonding states—the charge is

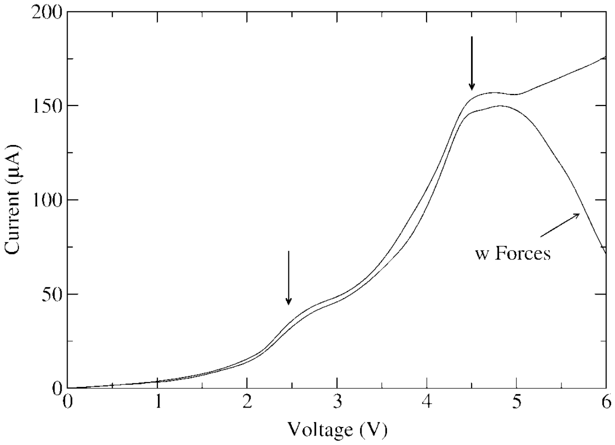

FIG. 2. Theoretical I-V curve of the molecular structure of Fig. 1 with and without the effect of current-induced forces. The vertical arrows indicate the onset of resonant tunneling via antibonding (at ~2.4 V) and bonding (at ~4.4 V) states.

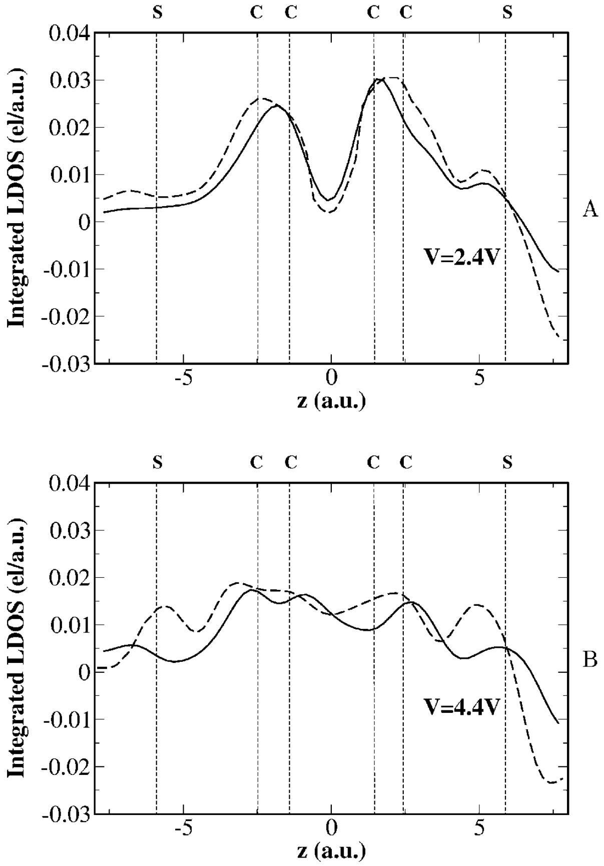

FIG. 3. Local density of states difference between that of the molecule-electrodes system and that of the electrodes without the molecule, integrated between left and right Fermi levels for a bias of 2.4 V (A) and 4.4 V (B). Solid lines correspond to the unrelaxed geometry, dashed lines to the relaxed one. The vertical dotted lines correspond to the unrelaxed atomic positions.

more uniformly distributed across all bonds in the benzene ring (see Fig. 3b).

It is immediately evident from Fig. 2 that current-induced forces do not substantially alter the absolute value of the current for external voltages as high as 5 V. Nonetheless, the molecular structure undergoes some structural transformations (see below).

The bonding and antibonding nature of the states involved in the electron scattering has a dramatic effect on the dynamics of the molecule under current flow. This is illustrated in Fig. 4 for different external biases. The structure at 0 V has been found to be unstable under current flow (see Fig. 4): With increasing bias, the mirror symmetry with respect to a plane perpendicular to both the benzene ring plane and the surface of the electrodes can be easily broken, leading to a slight rotation of the central carbon ring with respect to an axis perpendicular to its plane [17]. At the same time, the S-metal bond on the right electrode weakens due to the transfer of charge from the right to the left electrode (the left electrode is at a positive bias with respect to the right electrode, see Fig. 3a). At about 2.4 V, i.e., when resonant tunneling via antibonding states occurs, some charge depletes from the central C-C bonds, leading to a weakening of these bonds. Consequently, these bonds slightly expand forcing the remaining C-C and C-S bonds to expand. These bonds expand on average 0.05 Å while the C-H bonds are not affected. This can be rationalized by knowing that the π^* states of the molecule are formed only by carbon and sulfur p orbitals that are perpendicular to the ring plane, while the C-H bonds are σ-like. Upon relaxation, some extra charge is depleted from the central C-C bonds with consequent redistribution in the nearby bonds (see Fig. 3a, dashed line).

Increasing the bias further, the resonant-tunneling condition is lost and charge is almost completely recovered in the central C-C bonds (see Fig. 3). The C-C bonds then contract back to almost their length at 0 V. In summary, the molecule undergoes a “breathing” oscillation when the bias is scanned across the first resonant-tunneling condition. This “breathing” oscillation as a function of bias is typical only of resonant-tunneling via antibonding states. Indeed, increasing the bias further, until resonant-tunneling via bonding states is satisfied ($\sim$4.4 V), no bond-length oscillations are observed due to a more uniform distribution of charge across the central C ring (see Fig. 3b). On the other hand, with increasing bias, the central ring continues to twist with respect to an axis perpendicular to its plane, while the S-metal bond on the right electrode weakens (see

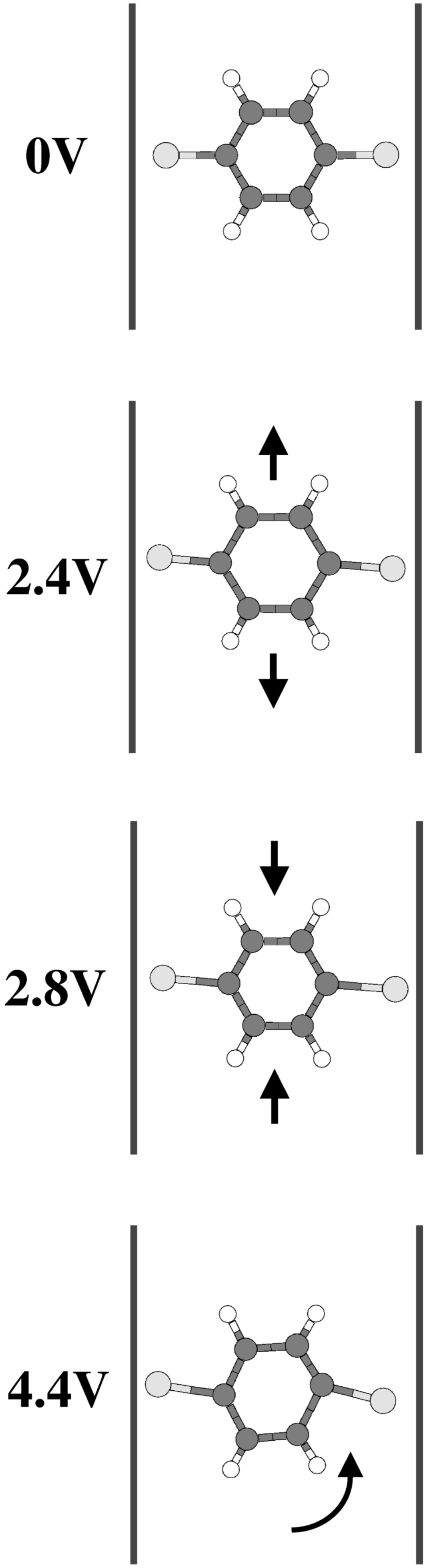

FIG. 4. Structural transformations of the molecule of Fig. 1 for four external biases. At 2.4 V, the C-C bonds of the molecule slightly expand, while at 2.8 V, the same bonds contract, as indicated by the arrows. Upon symmetry breaking, a counterclockwise (or, equivalently, a clockwise) rotation of the central carbon ring with respect to an axis perpendicular to its plane is observed. The left electrode is at a positive bias with respect to the right electrode.

Fig. 3b, dashed line). Remarkably, the absolute value of the current depends only weakly on the dynamical changes of the molecule for voltages up to about 5 V (see Fig. 2). At these high voltages, however, the charge transfer from the right to the left electrode strongly weakens the S-metal bond on the right electrode. This bond expands by more than 0.3 Å for biases larger than 5 V (at 6 V the bond expansion is 0.5 Å), therefore behaving as an extra barrier for electrons to tunnel across the molecular structure. The sign of the current-induced forces on the S atom of this bond coincide with the sign of the electron current [25]. Because of thermal and current fluctuations, and the fact that the S-metal bond has been weakened, the S-metal bond distance can oscillate at these high voltages, giving rise to small oscillations in the conductance [26]. Small conductance oscillations are indeed observed for such high voltages in the present system [10]. It is also worth noticing that complete fracture of this bond can occur at these high voltages if temperature effects are taken into account [19].

In conclusion, we have shown, using first-principles calculations, that current-induced forces in molecular devices can induce unusual dynamical changes in the structure of the molecules. However, we have found that the absolute value of the current is quite unaffected up to external voltages as high as 5 V, in contrast to the case of atomic gold wires that break at smaller biases: The strong σ bonds of the carbon-based molecular structures make them more resistant to current-induced forces than atomic gold wires.

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[26] Because of the large vibrational frequencies of the molecule investigated and its small feature length, we expect in this case that heating effects take place mostly in the electrodes for biases at which breathing occurs. For larger biases, local heating of the molecular region can contribute to the S-metal bond oscillations as well as to steady-state current fluctuations. However, the reduction of the current due to the S-metal bond weakening is large enough for biases greater than 5 V that this effect should be observable even in the presence of current fluctuations.