

## Temperature Effects on the Transport Properties of Molecules

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Recent experiments found an unusual temperature-induced large shift in the resonant-tunneling voltage of certain molecules. We report first-principles calculations showing that such behavior can be caused by the excitation of rotational modes of ligands. These modes have classical characteristics, i.e., the maximum excursion is dominant, while at the same time they have a significant effect on the energy levels responsible for resonant tunneling. The proposed mechanism of ligand rotations is unique to molecules and accounts for the fact that the effect is not seen in semiconductor nanostructures.

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Interest in the transport properties of single molecules is increasing due to their possible use as electronic components [1]. New synthetic reactions allow the realization of new and diverse molecules, resulting in devices with novel and unique properties [2]. For example, molecules have been shown to operate as Coulomb blockade structures [3], diodes [4], or switching devices with high negative differential resistance (NDR) even at room temperature [5,6]. Theoretical investigations have elucidated, e.g., the role of contact chemistry and geometry on the current-voltage characteristics of single molecules [7], molecule-length dependence of the conductance [8], role of the injection energy at the contacts [9], three-terminal device operation [10], and stress-induced modification of transport properties [11].

Molecules are intrinsically different from semiconductor nanostructures, and one expects that some of their transport properties would be unique. The recent report by Chen *et al.* [6] confirms that this is the case with the *temperature dependence* of the resonant-tunneling peak. The molecules studied by Chen *et al.* are chains of three benzene rings with one or more ligands attached to the carbon atoms of the central ring. An unusually sharp peak with an enormous NDR has been observed at very low temperatures [6]. At higher temperatures, the peak broadens, as expected, but it also shifts to substantially lower voltage [6]. The large shift ( $\sim 1$  V) is highly unusual and contrasts sharply with the well-known behavior of resonant tunneling in semiconductor heterostructures where practically no voltage shifts are observed [12,13]. Seminario *et al.* [14] have proposed that the voltage shift is caused by a rotation of the middle carbon ring plus charging of the molecule by single extra electrons. The suggestion was motivated by *ground-state* calculations of the electronic structure of the same molecule and *assumption* that the molecule's lowest-unoccupied molecular orbital (LUMO—in this case referred to as  $\pi^*$  orbital) mediates resonant tunneling. Our recent first-principles calculations [7] of transport in a single benzene ring have shown, however, that *the electronic structure of molecules changes substantially*

*as a function of applied voltage*, making it difficult to infer transport properties from ground-state electronic properties.

In this Letter we report first-principles calculations that explore the role of ligands in determining the transport properties of the benzene-ring family of molecules. The study was motivated by the fact that a three-benzene-ring molecule without ligands has effectively zero conductivity for all voltages (up to about 5 V) and insertion of ligands produces significant differences in the shape of the *I-V* curve [6]. As an additional indication we performed ground-state density-functional calculations [15] on the three-ring molecule which revealed that rotation of the middle ring produces no perceptible change in the electronic structure of the molecule in the vicinity of the highest-occupied molecular orbital (HOMO)-LUMO states, whereas rotation of the ligand does. Our full transport calculations for a single benzene ring with an NO<sub>2</sub> ligand find essentially the same behavior as that exhibited by the three-ring molecule measured by Chen *et al.* [6,16]: rotation of the ligand—activated by temperature—causes a substantial shift in the resonant-tunneling voltage. This large voltage shift is due in part to the rotation properties of the NO<sub>2</sub> group and in part to the different symmetry of the states localized on the NO<sub>2</sub> group with respect to the  $\pi$  orbitals of the carbon ring responsible for transport. In particular, unlike the  $\pi$  orbitals of the carbon ring, the orbitals on the NO<sub>2</sub> group have a nonzero dipole moment: they have a lower symmetry with respect to reflection through a plane bisecting the molecular axis so that they are shifted in energy by a field applied along the axis. The perturbation of the states induced by the external electric field is thus first order. At increasing temperature, these states thus “push” the  $\pi$  orbital to reach the resonant tunneling condition at lower voltages. The results show that, unlike in mesoscopic devices, temperature can produce different effects on resonant tunneling in molecular structures. This must be taken into account in the design of future molecular devices.

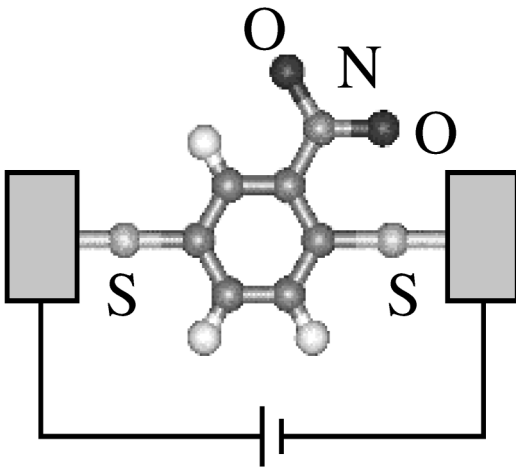


FIG. 1. Scheme of the molecular structure investigated. The structure is the benzene-1,4-dithiolate molecule where a H atom is replaced by a  $\text{NO}_2$  group. All atoms lie on the plane defined by the carbon ring. The sulfurs attach to ideal metallic leads.

The molecule we investigated is depicted in Fig. 1. The two sulfur atoms make contact to gold surfaces that we model with ideal metals (uniform positive background model or jellium model [17]). The interior electron density of the jellium electrodes is taken equal to the value for metallic gold ( $r_s \approx 3$ ). We computed the  $I$ - $V$  characteristic using the method developed in Ref. [18]. 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 the density-functional formalism within the local-density approximation [18]. The current is computed from the wave functions of the electrode-molecule system. At zero temperature, the atoms of the  $\text{NO}_2$  group lie on the same plane defined by the six-carbon ring (see Fig. 1).

We first discuss the  $I$ - $V$  characteristics at zero temperature and then the effect of the rotation of the  $\text{NO}_2$  group. The calculated  $I$ - $V$  characteristic of the molecule is plotted in Fig. 2. The current is effectively zero for voltages up to about 0.5 V. The current then increases almost linearly with external bias until a peak and a valley are visible at about 3.8 and 4.2 V, respectively. This behavior can be understood by looking at the density of states (DOS) for different external voltages. In Fig. 3 we show the calculated DOS of the molecule for three different voltages, namely, 0.01, 3.8, and 4.2 V (the DOS shown is the difference between that of the molecule-electrodes system and that of the electrodes without the molecule). The zero of energy is the left Fermi level so that the right Fermi level is equal to the external bias (in Fig. 3 the labels  $E_{FR}$  correspond to the 3.8 and 4.2 V values of the bias). Contrary to the case of the benzene-1,4-dithiolate molecule (i.e., the same molecule with the  $\text{NO}_2$  group replaced by a H) the  $\pi$  bonding orbital of the carbon ring lies close to the left Fermi level (at about 0.5 eV below the left Fermi level for a bias of 0.01 V—see Fig. 3) [7]. This is due to the presence

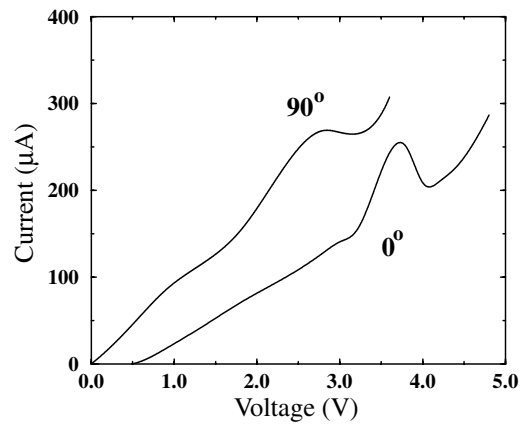


FIG. 2. Theoretical  $I$ - $V$  curve of the molecular structure of Fig. 1 for  $0^\circ$  and  $90^\circ$  of rotation of the  $\text{NO}_2$  group with respect to the carbon-ring plane.

of the hybridized  $p$  orbitals of nitrogen and oxygens that push the  $\pi$  orbital higher in energy. These states lie about 1.7 eV below the  $\pi$  orbital for a 0.01 V bias (indicated as  $\text{NO}_p$  in Fig. 3). Therefore, these states do not contribute directly to transport. Increasing the bias, the  $\pi$  orbital enters in resonance with the left Fermi level and a peak in the current occurs at this resonant tunneling condition. Increasing the bias further, the resonant tunneling condition is no longer satisfied and a valley in the  $I$ - $V$  curve is observed [19]. This is completely different from the case of the molecule without the  $\text{NO}_2$  group where the first resonant tunneling condition is due to  $\pi^*$  antibonding states [7]. We note that the resonant tunneling condition at zero temperature occurs at 3.8 V, i.e., at a higher voltage than in the experiment [6]. We note, however, that in the experiment three carbon rings form the entire molecule. In this case, the  $\pi$  orbitals of the outer rings will push the  $\pi$

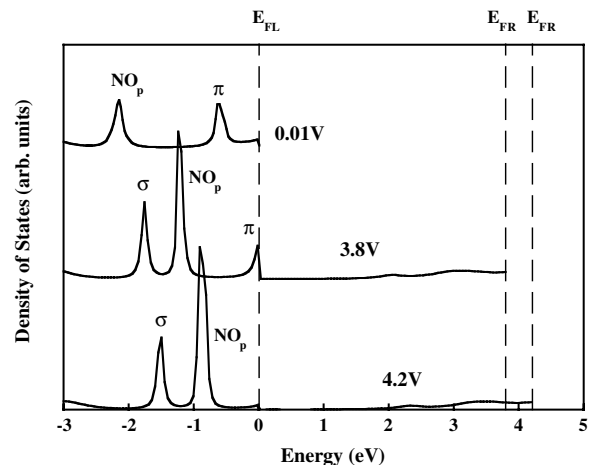


FIG. 3. Difference between the density of states of the two semi-infinite electrodes with and without the molecule of Fig. 1 in between, for three different voltages. The left Fermi level ( $E_{FL}$ ) has been chosen as the zero of energy. The labels  $E_{FR}$  correspond to the energy position of the right Fermi levels. The three curves correspond to the bias voltages indicated.

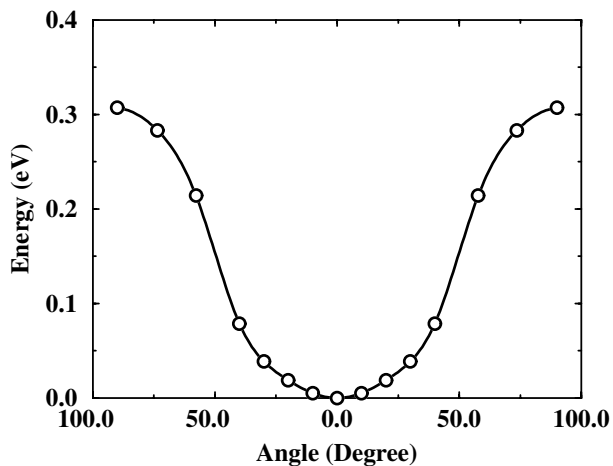


FIG. 4. Total energy of the isolated molecule of Fig. 1 for different angles of rotation of the  $\text{NO}_2$  group with respect to the carbon-ring plane.

orbital of the central ring even closer to the left Fermi level thus allowing resonant tunneling at lower voltage. Overall the molecule behaves as a molecular resonant tunneling device.

Let us now discuss the effects of temperature on the  $I$ - $V$  characteristics. Increasing the temperature, vibrational modes can be excited. However, usual optical-phonon scattering cannot account for the large shift of the current peak observed experimentally [13]. To confirm this, we performed a set of calculations of the current at external voltages close to the resonant tunneling condition where a “frozen phonon” has been allowed in the structure. We considered the highest frequency C-H vibrational mode, and we found that displacements of the H atoms along the C-H bond reduce the current but do not shift the voltage at which resonant tunneling occurs. On the other hand, the rotation of the  $\text{NO}_2$  group with respect to the plane of the carbon ring produces a different effect. This rotational mode can easily be activated by temperature. This is demonstrated in Fig. 4 where we plot the total energy of the free molecule for different rotation angles of the  $\text{NO}_2$  group with respect to the plane of the carbon ring [15]. The total energy difference between  $0^\circ$  and  $90^\circ$  of rotation is about 0.3 eV. An estimate of the energy level separation for this vibrational mode can be obtained by fitting the curve of Fig. 4 to a simple harmonic potential up to about  $50^\circ$  of rotation [20]. The energy levels are thus  $E_n = \hbar\omega(n + 1/2)$ ,  $n = 0, 1, \dots$ , and  $\omega = \sqrt{\kappa/I}$ . Here  $\kappa$  is obtained from a fit to a harmonic potential and  $I = 2M_O(d_{OO}/2)^2$  is the moment of inertia, where  $M_O$  is the mass of the oxygen and  $d_{OO}$  is the distance between the two oxygens of the  $\text{NO}_2$  group. Taking into account all parameters, the energy separation is about 3 meV. The  $\text{NO}_2$  group can thus rotate easily at room temperature, practically as a classical rigid rotator, and the system will spend most of the time at the highest degree of rotation possible at a given temperature. This rotation produces the same effect

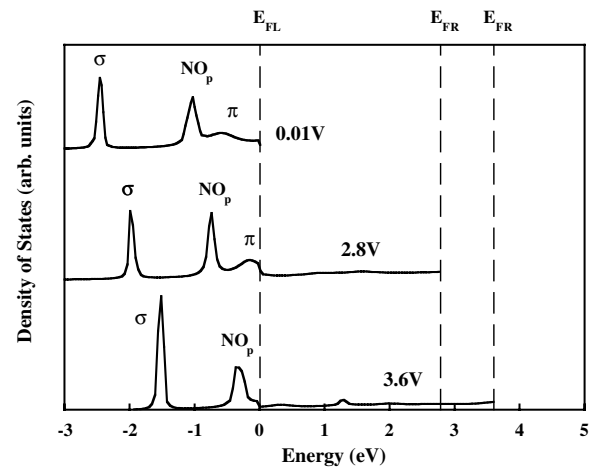


FIG. 5. Density of states for three different voltages for the molecule with the  $\text{NO}_2$  group rotated by  $90^\circ$  with respect to the carbon-ring plane. The same conventions apply as in Fig. 3.

on the  $I$ - $V$  characteristics as observed experimentally. This is shown in Fig. 2 for the  $90^\circ$  rotation. The peak-to-valley ratio is reduced, and the peak occurs at about 1 V less than at zero temperature. The reason for this can be rationalized by looking at the DOS for different external voltages. In Fig. 5 we plot the calculated DOS of the molecule with the  $\text{NO}_2$  group rotated by  $90^\circ$  for three different voltages, namely, 0.01, 2.8, and 3.6 V. The same conventions as in Fig. 3 apply. The rotation of the  $\text{NO}_2$  group pushes the NO-related  $p$  orbitals very close to the ring  $\pi$  orbital (the energy separation is now less than 0.5 eV). Because of symmetry, the dipole moment of the  $\pi$  orbital is zero while the dipole moment of the NO-related  $p$  orbitals is non-vanishing. Therefore, by applying an external electric field the NO-related  $p$  orbitals will be subject to a linear Stark shift while the ring  $\pi$  orbital shows a quadratic Stark shift [21]. Therefore, with increasing bias, the NO  $p$  orbitals get closer to the left Fermi level faster than the  $\pi$  orbital. Since, in the present case, the two orbitals are very close in energy, the  $\pi$  orbital of the benzene ring will be “forced” to reach the resonant tunneling condition at a lower bias due to the presence of the NO  $p$  orbitals. The effect is sizable since at  $90^\circ$  the voltage shift for the peak in the  $I$ - $V$  curve is about 1 V as observed in the experiment [6].

In conclusion, we have shown that thermally excited rotational modes of single molecules, like rotation of ligands, can have dramatic effects on their  $I$ - $V$  characteristics. The result has no counterpart in usual mesoscopic physics and must be taken into account in the design of future molecular devices.

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