Heating and cooling mechanisms in single-molecule junctions

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In this work we analyze the role played by molecular resonances on the thermal behavior of single molecule junction. We consider a fullerene molecule on a Cu(110) substrate when current is driven across using an scanning tunnel microscope tip. Calculations based on density-functional theory and nonequilibrium Green's functions have predicted a lowering of molecular temperature whenever a resonance gets close to the injection window. This behavior, due on the interplay of emission and absorption phonon processes, can take place (at $T_0=0$ K) for bias $E_L-\hbar\omega<V<E_L+\hbar\omega$ where E_L and $\hbar\omega$ are the lowest unoccupied molecular orbital (LUMO) and phonon energy, respectively. We further show that the decay channel into electron-hole excitations is very effective in keeping the molecule stable, whereas the direct decay of the vibron into contact phonons gives only a marginal correction. Furthermore, we have investigated the possibility to cool the molecule below the environment temperature. We found that this phenomena is favorite for modes with energy $\hbar\omega<k_bT_0$ and $\hbar\omega<E_L-E_F$.

I. INTRODUCTION

Single molecule electronics[1,2] is still a fascinating concept, attracting the interest of the scientific community thanks to the challenges it poses at experimental as well as fundamental theoretical level. Despite a large number of yet unresolved issues, successful advances have been made in understanding electron-vibration interactions, both in the weak and strong coupling limits.[3,4] In recent years a great interest has been drawn toward the challenging problem of probing the heat dissipated within a molecular junction under bias. Searching for an experimental way to measure, even indirectly, the nonequilibrium vibron population is by itself a fascinating problem, which several research groups are trying to tackle.[5–8] The problem also has practical relevance as molecular stability is crucial for possible device applications.

Several theoretical works have investigated electron-phonon interactions and power dissipation in molecular junctions.[9] In this work our computational approach is applied to understand and discuss heating and stability of a C_{60} molecule sitting on a Cu(110) substrate in which a Cu STM tip is used to drive a current through the junction.[10]

II. THEORY

The single electron Hamiltonian and system geometry are obtained within the density-functional tight-binding (DFTB) method,[11] whereas incoherent electron-vibron scattering, current and power dissipated are obtained using the nonequilibrium Green's function (NEGF) approach.[12] The vibron dynamics is described by a rate equation that balances the quanta emitted and absorbed via electron-vibron interactions,

$$R_q^e = (N_q + 1)E_q - N_qA_q, \tag{1}$$

and the vibrons dissipated via vibron-to-phonon decays[13] into the contact reservoirs,

$$R_q^d = \sum_\alpha J_q^\alpha[N_q - n_q(T_\alpha)]. \tag{2}$$

In Eqs. (1) and (2), α runs over the contact index (L and R contacts in this case), q is the mode label, N_q is the nonequilibrium phonon population, $n_q(T_\alpha)$ is the equilibrium phonon population at temperature T_α, J_q^α are the decay rates of molecular vibrons into the phonon reservoir of contact α. The terms A_q and E_q represents the absorption and emission rates, respectively. The steady state solution is obtained by imposing $R_q^e=R_q^d=R_q$, resulting in the nonequilibrium vibron population,

$$N_q = \frac{R_q}{J_q} + \frac{\sum_\alpha J_q^\alpha n_q^\alpha(T_\alpha)}{J_q} = \frac{\sum_\alpha J_q^\alpha n_q(T_\alpha) + E_q}{J_q + A_q - E_q}, \tag{3}$$

whereas the net emission rate of quanta is given by

$$R_q = \sum_\alpha J_q^\alpha \frac{E_q[n_q(T_\alpha) + 1] - A_q n_q(T_\alpha)}{J_q + A_q - E_q}. \tag{4}$$

In Eqs. (3) and (4) the terms J_q represent the total phonon decay rates, i.e., $J_q=\sum_\alpha J_q^\alpha$. From the previous expression it should be noted that when there is no dissipation ($J_q=0$), the condition $R_q=0$ must be fulfilled; this implies that the heat must be absorbed by the electrons themselves. The phonon-phonon decays give rise to a heat flux going out from the α contact that can be written as

$$P_q^\alpha = \hbar\omega_q J_q^\alpha[N_q - n_q(T_\alpha)], \tag{5}$$

which, by using Eq. (3), becomes

$$P_q^\alpha = \frac{J_q^\alpha \hbar\omega_q \sum_\beta J_q^\beta[n_q(T_\beta) - n_q(T_\alpha)]}{J_q} + \frac{\hbar\omega_q R_q J_q^\alpha}{J_q} \tag{6}$$

The first term in Eq. (6) represents the heat flux originated by the gradients of temperature imposed between different contacts; the second contribution is the power dissipated by the Joule's effect.

The molecular heating is described in terms of an *effective*

temperature, T_m, which is found by setting the equivalence between the total vibrational energy, U, given by the non-equilibrium population, N_q, with the energy obtained imposing an equilibrium Bose-Einstein population at temperature T_m,

$$U = \sum_q \hbar \omega_q N_q = \sum_q \frac{\hbar \omega_q}{\exp\left(\dfrac{\hbar \omega_q}{k_B T_m}\right) - 1}. \qquad (7)$$

The molecular temperature should not be interpreted as a thermodynamical quantity but can be regarded as a parameter mapping the vibrational energy of the molecule. This is established by the monotonic dependence between U and T_m expressed by Eq. (7). The advantage of using T_m is that it does not depend on the size of the system and coincides with the rigorous concept of temperature in the thermodynamical limit.

Let us now analyze in detail the quantities calculated from first principle calculations, i.e., J_q, A_q, and E_q. Heat dissipation is modeled by means of rates (J_q) describing vibron decays into contact phonons. These rates are extracted from the broadening of the spectral peaks of the phonon density of states projected on the molecule.[14] The terms A_q and E_q refer to the absorption and emission process, respectively, and can be expressed as[13]

$$A_q = \frac{2}{h} \int \mathrm{Tr}[\gamma_q G^<(E - \hbar \omega_q) \gamma_q G^>(E)] dE, \qquad (8)$$

$$E_q = \frac{2}{h} \int \mathrm{Tr}[\gamma_q G^<(E + \hbar \omega_q) \gamma_q G^>(E)] dE. \qquad (9)$$

In the above equations γ_q is the electron-phonon coupling and $G^<(E)$, $[G^>(E)]$ are the lesser (greater) nonequilibrium Green's functions. These quantities are computed using a perturbative approach to the electron-phonon coupling within the self-consistent Born approximation (SCBA). The perturbative approach is valid since the electron-phonon coupling is weak compared to the molecule-contact coupling. For the following discussion it is useful to write the explicit expressions for E_q and A_q that can be obtained to lowest order of perturbation theory, assuming $T_L = T_R = 0$ and neglecting the self-energy in the vibron propagators. We introduce the notations

$$A_q^{\alpha,\beta} = \frac{2}{\hbar} \int \mathrm{Tr}[\gamma_q S_\alpha^*(E - \hbar \omega_q) \gamma_q S_\beta(E)]$$
$$\times \Theta(E - \mu_\beta) \Theta(\mu_\alpha - E + \hbar \omega_q) dE, \qquad (10)$$

$$E_q^{\alpha,\beta} = \frac{2}{\hbar} \int \mathrm{Tr}[\gamma_q S_\alpha^*(E + \hbar \omega_q) \gamma_q S_\beta(E)]$$
$$\times \Theta(E - \mu_\beta) \Theta(\mu_\alpha - E - \hbar \omega_q) dE, \qquad (11)$$

where the integration domain runs over the whole real axis, $\Theta(x)$ is the Heaviside step function and μ_α is the electrochemical potential of contact α. Finally, the spectral density matrix for the α contact is given by
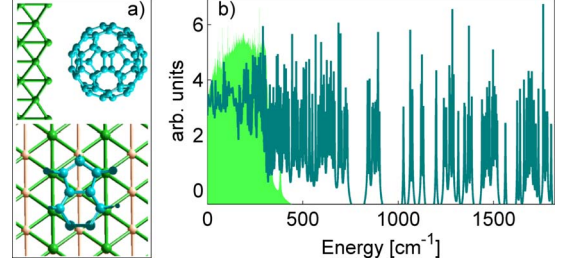

FIG. 1. (Color online) (a) C_{60} fullerene molecule on Cu(110) surface. (b) The phonon DOS of the perturbed molecule. The phonon DOS of the contact is shown in the background.

$$S_\alpha(E) = G^r(E)\Gamma_\alpha(E)G^a(E), \qquad (12)$$

where G^r (G^a) are the retarded (advanced) Green's functions and Γ_α is the imaginary part of the self-energy of contact α. In Eqs. (10) and (11) the labels α and β refer to incoherent processes in which an electron enters the molecule from contact α and is scattered into contact β after absorption or emission of one vibrational quantum. The total absorption and emission can be expressed as $A_q = \sum_{\alpha,\beta \in L,R} A_q^{\alpha,\beta}$ and $E_q = \sum_{\alpha,\beta \in L,R} E_q^{\alpha,\beta}$, respectively. Higher order diagrams involve more vibrons as well as virtual absorption/emission processes, but for the sake of simplicity we present a qualitative analysis of the numerical calculations only considering these dominant first order terms. As the terms A_q and E_q depend nonlinearly on N_q, the nonequilibrium population is computed with a self-consistent loop.

III. RESULTS AND DISCUSSION

The STM tip is modeled as a pyramid of Cu atoms and is positioned at varying distances (D_{tip}) from the closest C atom of the fullerene. The details of the C_{60}/Cu interface geometry, shown in Fig. 1(a), can also be found in Ref. 10.

The vibron decay rates, J_q are computed by coupling the phonon density of states projected on the molecule. This is obtained by introducing in the substrate an open boundary condition for the propagating vibrational waves. The calculation is formally very similar to the Green's function approach used to treat open boundary conditions for the electronic wave functions, in which the Hamiltonian matrix is substituted with the dynamical matrix of the system. This in turn is computed for a finite extended system comprising the molecule, a surface of three atomic layers, a bulk of six atomic layers and an additional buffer of other three atomic layers used to avoid surface effects. The resulting dynamical matrix for this system is partitioned into contact and device regions and the decimation algorithm is applied to compute the self-energy and the local density of states projected on the molecule. The latter is shown in Fig. 1(b). The same figure also shows the phonon spectrum of the Cu substrate as a shaded area, in which the Debye cutoff frequency at about 300 cm^{-1} is quite evident. The values of J_q, extracted from the peak broadenings, range between 10^{10} and 10^{12} Hz for the low energy modes, found within the Cu phonon bandwidth, and progressively decrease to as low as 10^3 Hz for the highest frequency modes ($\cong 1800$ cm^{-1}). These low de-
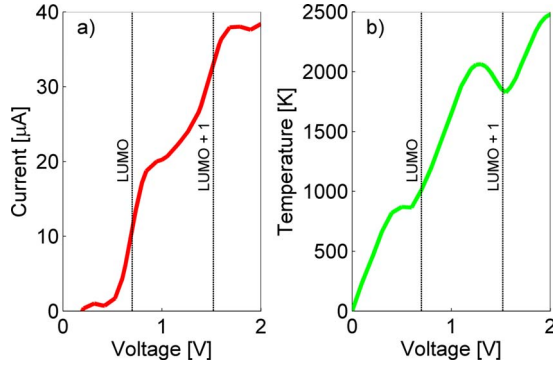
FIG. 2. (Color online) The dashed line is the electronic DOS. (a) Total current vs bias. As expected, the resonance makes the current rises (b) Molecular temperature vs bias. The lowering of the temperature across the resonance is due on the interplay between the emission and absorption processes.

FIG. 3. (Color online) (a) For $0 < eV < E_L - \hbar\omega$ there is one resonant absorption process via $e\text{-}h$ pairs in the substrate and one absorption process via transmission. (b) For $E_L - \hbar\omega < eV < E_L + \hbar\omega$ there are three resonant absorption processes (one into $e\text{-}h$ pairs) and one resonant emission process. (c) For $eV > E_L + \hbar\omega$ there are two absorption and two emission processes via transmission.

cay rates are probably strongly underestimated as anharmonic coupling and one-to-many phonon decays may give a considerable contribution. In order to overcome the limitations of our simplified model we could introduce at this stage phenomenological parameters, however we prefer to avoid the introduction of artificial parameters that are quite uncertain. Furthermore, we will show in the following discussions that already at moderate voltages the emission/absorption rates, E_q and A_q, can be quite large for the high frequency modes, such that we expect $E_q \gg J_q$ and $A_q \gg J_q$ even after higher order corrections are taken into account. As a consequence, J_q should not play a significant role for these modes. We assume that there is no difference of temperature between the two contacts, namely, $T_L = T_R = T_0 = 0$ K which is close to STM experiments carried at $T = 4.2$ K. In this case the contributions E_q^{LL}, E_q^{RR}, and E_q^{RL} vanish because of the Heaviside functions, whereas A_q^{RL} is nonzero only for $eV < \hbar\omega_q$. The terms E_q^{LR} and A_q^{LR} correspond to tunneling between the two contacts with corresponding emission and absorption of phonons. The terms A_q^{LL} and A_q^{RR} correspond to electron reflections after absorption of a phonon and we will refer to them as A_q^{tip} and A_q^{sub}, respectively, assuming the substrate to the right ant the tip to the left. These terms correspond to phonon decays via electron-hole ($e\text{-}h$) excitations in the contacts.

We now assume that a bias, V, is applied to the substrate, while the STM tip is grounded, i.e., $\mu_R = \mu_L - eV$. Under these conditions the unoccupied levels are probed for positive voltages. We further assume that the molecular levels are pinned with the substrate Fermi energy and the whole applied bias drops at the molecule/tip interface. This is an extreme assumption, but it is supported by independent self-consistent DFT/NEGF calculations. The voltage ranges from 0.0 to 2.0 V. As shown in Fig. 2(a) the current steeply rises whenever a resonance enters in the injection window. The molecular resonances, centered at energy $E_1 = 0.7$ eV and $E_2 = 1.5$ eV, will be referred as LUMO and LUMO+1, respectively. Correspondingly, Fig. 2(b) shows that the temperature rises because resonant phonon emission takes over. In the same figure it is possible to observe that just before reaching a resonance, the molecular temperature can even
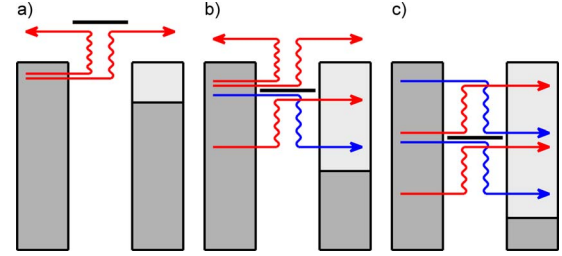
decrease. The effect is especially visible for the LUMO+1.

In the case of metal contacts this can be understood by considering Eqs. (10) and (11), with the help of Fig. 3. The LUMO level entering the bias window has energy E_L and we consider, for simplicity, just one effective vibrational mode of energy $\hbar\omega < E_L$. The equilibrium Fermi energy is assumed at $E_F = 0$. For increasing voltages up to $eV < E_L - \hbar\omega$ the molecular temperature increases since the emission rate prevail. As the molecular level approaches, for a bias in the range $E_L - \hbar\omega < eV < E_L + \hbar\omega$, resonant absorption channels activate and can prevail over the emission, leading to a decrease in temperature. For $eV > E_L + \hbar\omega$ two resonant emission processes become possible and the term E^{LR} rises, whereas A^{tip} become no longer active because no states are available for the reflected electrons. In this regime emission prevails over absorption and the molecule heats up, resulting in the usual increase in temperature with applied bias. A further analysis shows that in the intermediate cooling regime the high energy modes play a major role. The first reason for this is that, thanks to their high energy, these excited modes contribute considerably to the total vibrational energy of the molecule, which is therefore more sensitive to a decrease in their population, N_q. The second reason is because, for energies higher than the Debye frequency, the phonon-phonon decay rates becomes very small [see Fig. 1(b)] and the vibron population becomes more sensitive to the absorption and emission processes, depending only on the ratio $A_q/E_q (J_q \approx 0)$. The last reason is simply because for larger $\hbar\omega_q$ the energy range in which absorption overcomes emission is wider, leading to a more visible effect in terms of applied bias. Our calculations also show that the population of the high energy modes decrease, whereas the population of the low energy modes keep increasing with increasing bias. By observing Fig. 2, it should also be observed that when $T_0 = 0$ there are no excited quanta to absorb when the LUMO resonance approaches the bias window [as in Fig. 3(a)], resulting in a barely visible decrease in temperature. On the other hand, when the second molecular level (e.g., LUMO+1) approaches the bias window, resonant absorption give rise to a much more evident cooling effect, since phonons are removed from an already excited vibronic population. A qualitatively similar effect was also computed in Ref. 15 using a model Hamiltonian.

We observe that in the cooling regime the power dissipated, as given by Eq. (6), keep increasing since it is domi-
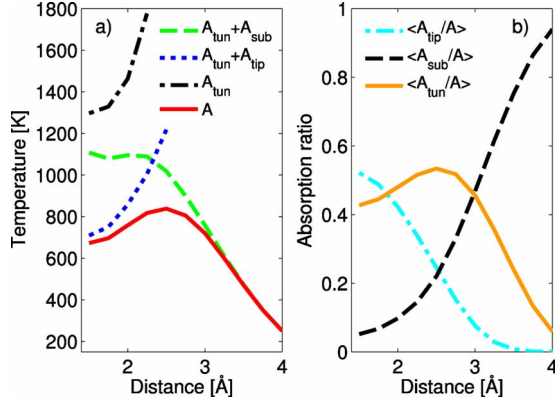
FIG. 4. (Color online) (a) Temperature vs tip distance. The solid line shows the temperature trend taking into account all absorption processes. The dotted line and the dashed line neglects e-h formation into the substrate and the tip, respectively. The dash dotted line corresponds to absorption via tunneling only. (b) Different relative contributions to the total absorption rate via *e-h* in the tip, the substrate and via tunneling.

nated by the values of J_q corresponding to the low frequency modes, which heat up monotonically. In this regime internal energy and power dissipated via phonon-phonon decays have opposite trends.

Phonon decays via *e-h* excitations in the metal contacts provide a crucial cooling mechanism. Indeed, thanks to this decay channel, the molecule can remain stable even at relatively large voltages. To better emphasize this issue, we sweep the distance between tip and molecule keeping the voltage fixed. Figure 4 shows the results for a bias of 0.4 V. This voltage is small, but larger than the higher vibrational energy of the molecule. Consequently we can expect that all modes are excited by electron-phonon scattering. As long as the tip is far from the molecule (tunneling region) the current is low and only A_q^{sub} plays a relevant role.

The crucial point here is to note that in the absence of *e-h* excitations in the substrate the molecule will easily brake. Indeed, when A_q^{sub} is removed from Eq. (8), we find that N_q has no longer physical solutions for $D_{tip} \geq 2.8$ Å. In practice N_q diverges and we understand this results as a thermal instability of the molecule. Furthermore, if we remove both the substrate and the tip contributions and keep only the tunneling absorption mechanisms, the molecular temperature would be much higher (black line).

As shown in Fig. 4 the stability of C_{60} on the metal substrate is guaranteed by the *e-h* decays. Reducing the tip-molecule distance, the term A_{tip} becomes large and we observe two competing effects. On the one hand, as the tip approaches the molecule, the current increases, leading to an increase in heating; on the other hand the tip increases absorption via *e-h* excitations, keeping the molecule cool. These competing effects produce the maximum at $D_{tip} = 2.8$ Å shown in Fig. 4(a).

Figure 4(b) shows the relative magnitude of the absorption processes as a function of tip distance. As expected, when the tip is close both tip and substrate contribute equally, whereas when the tip is far *e-h* pairs can be excited in the substrate only.

The role of dissipation via phonon-phonon decays is only marginal in this system and only effective for low energy modes. Although our lowest order treatment of the one phonon-to-one phonon decay processes may considerably underestimate the decay rates J_q, this can hardly reach the absorption rates necessary to keep the molecule stable, provided by A_q. The average of the A_q^{sub} is 10^{10} Hz and the average of A_q^{tip} range from 10^{11} Hz when the tip is at 2.0 Å to 10^7 Hz when the tip is at 4 Å. The values of J_q are several orders of magnitude smaller.

A natural question that may arise is whether it is possible to cool a molecule below the environment temperature. We assuming that the phonon decays rates are equal for the two contacts, i.e., $J_q^\alpha = J_q/2$. Under this assumption the net rate of phonon emission and their nonequilibrium population can be written as

$$R_q = \frac{J_q}{J_q + A_q - E_q}[(n_q + 1)E_q - n_q A_q], \qquad (13)$$

$$N_q = n_q(T_0) + \frac{R_q}{J_q}. \qquad (14)$$

At $V = 0$ the system reaches thermodynamical equilibrium and $R_q = 0$ [and, consequently, $N_q = n_q(T_0)$] which leads to the equilibrium conditions, $A_q = E_q e^{\hbar\omega_q/k_b T_0}$.

It's straightforward to show that this condition is satisfied thanks to the general relationship $G^<(E) = -e^{E/k_b T_0} G^>(E)$ at $V = 0$, applied to the Eqs. (8) and (9). To the contrary, the relationship $A_q = E_q e^{\hbar\omega_q/k_b T_0}$ is generally not valid under bias.

An inspection to Eq. (13) leads to the conclusion that cooling effect below T_0 may occur for $A_q > E_q e^{\hbar\omega_q/k_b T_0}$. In fact, in this case we have $R_q < 0$, $N_q < n_q(T_0)$ and part of the energy given by the applied bias is used to cool the molecule, like in a Peltier cell. Unfortunately this condition is not easily obtained for a normal molecule with large vibrational energies, $\hbar\omega_q \gg kT$, with the consequence that the molecular temperature is always greater than the environment temperature. The molecule can effectively cool to lower temperatures only when it possesses vibrational modes of low energy, $\hbar\omega_q < kT$. For instance in the case of $T = 300$ K it is sufficient to have $\hbar\omega_q \approx kT/2$ and $A_q \approx 2E_q$ to obtain a phonon population lower than in equilibrium. Fundamental is also the role played by the resonant energy levels of such a molecule, which in equilibrium should be positioned at $E_L > E_F + \hbar\omega_q$ in order to activate the resonant absorption channel before the resonant emission. These conditions could be met for instance by a system of heavy ions (like a CdTe nanoparticle) placed in between Au contacts.

IV. CONCLUSIONS

In summary, we have investigated the thermal behavior of a C_{60} molecule on Cu(110) surface. We have analyzed in detail the interplay between molecular resonances, phonon absorption and emission process. An effective molecular temperature was introduced mapping the internal energy stored in the vibrational degrees of freedom. Given a

resonance with energy E_L we have found a cooling regime in the bias range $E_L - \hbar\omega < V < E_L + \hbar\omega$ in which the nonequilibrium vibronic population and the effective molecular temperature decrease. Furthermore, we have computed the vibron decay rates due to electron-hole excitations in the substrate and in the tip and we have outlined the importance of these contributions in keeping the molecule stable. A tip-induced cooling effect was also discussed. Finally, we have investigated the possibility to cool the molecule below the environment temperature.

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