High voltage assisted mechanical stabilization of single-molecule junctions

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The realization of molecular-based electronic devices depends to a large extent on the ability to mechanically stabilize the involved molecular bonds, while making use of efficient resonant charge transport through the device. Resonant charge transport can induce vibrational instability of molecular bonds, leading to bond rupture under a bias voltage. In this work, we go beyond the wide-band approximation in order to study the phenomenon of vibrational instability in single molecule junctions and show that the energy-dependence of realistic molecule-leads couplings affects the mechanical stability of the junction. We show that the chemical bonds can be stabilized in the resonant transport regime by increasing the bias voltage on the junction. This research provides guidelines for the design of mechanically stable molecular devices operating in the regime of resonant charge transport.

Chemical bond rupture is a major concern when single molecules are being considered as electronic components in nano-scale devices [1–4]. In single molecule junctions, tunneling electrons temporally dwell on the molecule and therefore induce changes in the molecular charging state. In the deep (or off-resonant) tunneling regime charge fluctuations on the molecule during transport lead to energy exchange between the electronic and the mechanical molecular degrees of freedom [5–8]. These processes have remarkable effect on the molecular junction transport properties, but their influence on the mechanical stability of chemical bonds is considered to be minor. However, resonant tunneling, often associated with relatively high bias voltage, is more relevant for electronics than deep tunneling, since the associated currents are significantly larger. In this regime, changes in the charging state of the molecule are pronounced, and consequently the electronic coupling to molecular vibrations can result in bond rupture either at the molecule or at the molecule-lead contacts. This mechanical instability often limits experiments on single molecule junctions to the off-resonant tunneling regime. In order to combine the desired features of efficient resonant transport at high voltage operation with mechanically stable molecules, one needs to determine which experimentally controlled parameters contribute to the mechanical stability of molecules under non-equilibrium transport conditions.

Charge transport induced bond rupture was observed for physisorbed molecules in scanning tunneling microscope experiments [9–11] as well as in atomic chains [12] and single molecule junctions [3–5,13], where the molecules are chemically bonded to the leads. In particular, the occurrence of bond rupture increased with increasing bias voltage, which points to the increased transport induced charging of the molecule. It is worthwhile to mention in the present context that the possibility to control bond rupture by the molecular junction parameters (e.g., voltage, coupling to the leads, etc.) is relevant not only for the sake of mechanical stability of nano-scale current carrying devices, but also for nano-scale chemical catalysis. It was shown theoretically that (by a proper design) transport induced heating can be directed towards a particular bond [14, 15], suggesting the possibility of mode-selective chemistry in single junction architectures.

Theoretical works on bond dissociation induced by resonant tunneling through molecular junctions consider the effective (anharmonic) mechanical force on the nuclei when the electronic state is a mixture of different charging states [16–18]. This may turn the bond nuclear geometry into a metastable one, leading to bond rupture in the steady state (long-time) limit. Other theoretical approaches restrict the discussion of molecular vibration excitations to the harmonic approximation [14, 15, 18–20]. While bond dissociation cannot be treated explicitly in this case, the occurrence of vibrational instability [18, 22] due to the excess of energy flow into vibrations is considered as the indicator for bond rupture in the anharmonic case.

In this work we address one of the crucial aspects of the realization of single molecule electronic devices: How can the conditions of operation be tuned in order to benefit from efficient resonant charge transport at high voltage through a single molecule junction, and yet to maintain the mechanical stability of the molecule? For this purpose we consider in detail the generic model of vibrational heating in non-equilibrium transport between two Fermionic reservoirs. The onset of vibrational instability is analyzed in the limit of weak molecule-lead and intra-molecular vibronic couplings, where resonant charge transport kinetics is expressed in terms of vibrational heating and cooling processes. We demonstrate cases where increasing the bias voltage favors cooling processes over heating, thus stabilizing the molecular junction at a higher voltage. This result contrasts with the common intuition for resonant transport, which correlates instability with higher voltage. However, it is read-
ily explained by considering realistic, energy-dependent, profiles for the density of states in the leads, beyond the commonly invoked wide-band approximation. Indeed, relative changes in the leads densities of states may favor inelastic transport of low-energy electrons from one lead into high energy states of the other leads, resulting in efficient vibrational cooling. Since the relevant densities of states depend on the bias voltage, this effect can be obtained at relatively high voltages. This analysis provides new guidelines for mechanical stabilization of single molecule junctions under resonant transport conditions.

The minimal model for transport induced vibrational excitation considers a single electronic transport channel through the molecule [23], where a single spin orbital is coupled to a single bond, represented as a quantum mechanical oscillator. In realistic systems vibrational excitation energies exceeding a few (∼10-100) vibration quanta would be typically associated with highly anharmonic parts of the potential energy surface, where bond rupture is likely to occur. However, our purpose is to capture the onset of vibrational instability at low vibration excitation numbers, consistent with the harmonic approximation. Therefore we shall treat explicitly the harmonic part of the potential energy surface. The model Hamiltonian reads, $H = [\hbar \omega_0 + \frac{1}{2}(\tilde{a} + \tilde{a}^\dagger)]^2 + \hbar \Omega \tilde{a}^\dagger \tilde{a}$, where $\hbar \omega_0$ is the charging energy of the single molecular orbital, associated with the Fermionic creation and annihilation operators, $\tilde{a}^\dagger$ and $\tilde{a}$, respectively, and $\tilde{a}^\dagger (\tilde{a})$ are the creation (annihilation) operators for the vibrational degree of freedom with frequency $\Omega$. The vibronic coupling parameter is $\hbar g$. This system Hamiltonian is assumed to be weakly coupled to right and left reservoirs of non-interacting electrons (the baths), $H_{\text{leads}} = \sum_{J= \text{R,L}} \sum_{k \in J} \hbar \omega_k \tilde{c}_k^\dagger \tilde{c}_k$, via the interaction term, $H_{\text{int}} = \tilde{d}^\dagger \sum_{J= \text{R,L}} \sum_{k \in J} \hbar \omega_k \tilde{c}_k^\dagger + \text{h.c.}$. The relevant properties of the baths are encoded in the Fourier transforms of the autocorrelation functions ($J = L, R$), $G_J(\omega) = \sum_{k \in J} J^{\text{FT}}(\omega - \omega_k)\langle \lambda | c_k^\dagger c_k | \lambda \rangle^2 \langle c_k c_k^\dagger \rangle_{T_J} dt = e^{i(\omega - \omega_k) t / k_B T_J} G_J(\omega)$, where $\mu J$ is the lead chemical potential, $k_B$ is the Boltzmann constant and $T_J$ is the lead temperature.

The analysis of this model is simplified by invoking the small polaron transformation [24] which diagonalizes the system Hamiltonian (see supplementary information), $H = \hbar \omega_0 \tilde{d}^\dagger \tilde{d} + \hbar \Omega \tilde{a}^\dagger \tilde{a}$, where $a, a^\dagger$ and $d, d^\dagger$ are transformed system operators, and $\omega_0 = \omega_0 - \frac{\Omega^2}{\hbar g}$. We study the weak vibronic coupling limit of the above model, i.e., $\frac{\Omega^2}{\hbar g} < < 1$, which is realistic for many molecular systems and was associated in earlier works with vibrational instability [18][20]. In this limit, each electron that flows through the junction exchanges either one or zero vibration quanta with the bond oscillator. Our purpose is to capture the onset of vibrational instability at low excitation numbers, as the indicator for bond rupture in realistic anharmonic systems. Therefore, we additionally restrict the following analysis to low excitation numbers, $\frac{\hbar g}{2 \Omega} \sqrt{N} < < 1$, (1)

where $N = \langle a^\dagger a \rangle$ is the average vibrational excitation.

In a typical scenario where the coupling between the molecular junction and the leads is weak, a Markovian master equation is adequate for describing the evolution of $\rho^n_{\text{el}}(\omega)$ which represents the population of the molecular electronic state and the vibrational mode. The superscript 0(1) denotes a neutral (charged) electronic level and $n$ the vibration quantum number. The master equation yields the following equation of motion for the eigenstate populations,

$$\dot{\rho}_n^1 = G(\omega_0)\rho_n^0 - G(\omega_0)\rho_n^1 + \frac{g^2}{4\Omega^2} \left\{ nG(\omega_+ )\rho_{n-1}^0 + (n + 1)G(\omega_- )\rho_{n+1}^0 \right\};$$
$$\dot{\rho}_n^0 = G(\omega_0)\rho_n^1 - G(\omega_0)\rho_n^0 + \frac{g^2}{4\Omega^2} \left\{ nG(\omega_- )\rho_{n-1}^0 + (n + 1)G(\omega_+ )\rho_{n+1}^0 \right\},$$

where $\omega_\pm = \omega_0 \pm \Omega$, and $G(\omega) = \sum_{J \in \{ R, L \}} G_J(\omega)$. Generally, the coupling density to the lead depends on the temperature and the transition frequency, i.e., $G_J(\omega) = \Gamma_J(\omega)(1 - f_J(\omega))$; $f_J(\omega) = \frac{G_J(\omega)}{\Gamma_J(\omega)}$, where $\Gamma_J(\omega)$ is the rate of decay of the electronic occupation on the molecule due to molecule-lead coupling, and $f_J(\omega)$ is the Fermi distribution [28].

Notice that the dynamics of the vibrational mode population is affected by the leads through the electronic charging state. The weak electron-vibration coupling, renders this dynamics slow relatively to the electronic evolution. This can be seen from Eqs. (2), which point to two different time scales: The fast dynamics associated with transfer between the electronic charging states, and the slow dynamics of population transfer between vibrational states, which depends on the small factor, $\frac{\Omega^2}{\hbar g}$. Accounting only for the fast dynamics, one obtains,

$$\dot{\rho}_n^1 = -G(\omega_0)\rho_n^1 + G(\omega_0)\rho_n^0;$$
$$\dot{\rho}_n^0 = -G(\omega_0)\rho_n^0 + G(\omega_0)\rho_n^1;$$

which implies that the electronic populations quickly reach steady state, $\rho_n^{0(1)}(\omega) = \frac{\rho_n(\omega)}{G(\omega_0) + G(\omega_0)}$, where $\rho_n = \rho_n^1 + \rho_n^0$ represents the population of the vibrational state $n$ after the electronic states has reached steady state. Accounting also for the terms proportional to $\frac{\Omega^2}{\hbar g}$, we now derive an equation for $\rho_n$ on the slow time scale, which is the equation of motion for the vibrational state populations,
\[ \dot{\rho}_n = r(n+1)\tilde{\rho}_{n+1} + s n \tilde{\rho}_{n-1} - (s(1+n) + rn)\tilde{\rho}_n, \quad (4) \]

where \( r(s) \) are the cooling (heating) rates,

\[ r = \left( \frac{g}{2\Omega} \right)^2 \frac{G(\omega_+)G(-\omega_0) + G(-\omega_-)G(\omega_0)}{G(\omega_0) + G(-\omega_0)}, \]

\[ s = \left( \frac{g}{2\Omega} \right)^2 \frac{G(\omega_-)G(-\omega_0) + G(-\omega_+)G(\omega_0)}{G(\omega_0) + G(-\omega_0)}. \quad (5) \]

These rates are composed of specific contributions. For example, the product \( G_R(\omega_+)G_L(\omega_0) \) which is included in the first term in \( r \), corresponds to a cooling process in which an electron with energy \( \hbar \omega \) is being absorbed from the left lead, followed by its emission to the right lead at a different energy, \( \hbar(\omega_0 + \Omega) \). The net result is a deexcitation of the vibrational mode by one quantum, i.e., \( \hbar \Omega \).

The equation of motion for the average excitation energy, \( \langle n(t) \rangle \equiv \sum_{n=1}^{\infty} n \rho_n(t) \), can be readily obtained from Eq. (4). \( \langle n(t) \rangle = -r\langle n(t) \rangle + s\langle n(t) \rangle + 1 \), which yields,

\[ \langle n(t) \rangle = \frac{s}{r - s} + \langle n(0) \rangle - \frac{s}{r - s} e^{-(r-s)t}. \]

In the scenario \( r > s \), where the overall cooling rate exceeds the overall heating rate, the vibrational mode reaches a stationary state characterized by the asymptotic average excitation,

\[ \langle n(\infty) \rangle = \frac{s}{r - s}. \quad (6) \]

Recalling that in realistic systems large excitation numbers would be associated with highly anharmonic parts of the potential energy surface, where bond rupture is likely to occur, we set a vibrational excitation threshold level, \( n_{tr} \), beyond which the bond is considered unstable. The condition for bond instability thus reads \( \frac{s}{r - s} > n_{tr} \). Notice that this bounds from above the value of \( r - s \). Hence, large \( r - s \) values imply stable molecules, as suggested by the fact that the overall cooling rates is larger than the overall heating rate. Since the time evolution of \( \langle n(t) \rangle \) is monotonic, it is enough to consider the steady state in order to find out if the vibrational mode population ever crossed the instability threshold. When the overall heating rate exceeds the overall cooling rate one has, \( r < s \). Rather than approaching a steady state, the vibrational excitation level diverges, implying that the junction will be unstable for any \( n_{tr} \). This regime has been previously related with work extraction in the context of heat machines \[27\ 29\].

Let us consider first the wide-band limit for the couplings to the leads. The wide-band approximation implies that the energy-dependence of the coupling densities \( \{G_J(\omega)\} \) is only due to the thermal electronic population in the lead, i.e., \( G_J(\omega) \equiv \Gamma_J(1 - f_J(\omega)) \); \( G_J(\omega) \equiv \Gamma_J f_J(\omega) \), where \( \Gamma_J \) is a frequency-independent decay rate.

\begin{figure}[h]
\centering
\includegraphics[width=\linewidth]{figure1.png}
\caption{Voltage-dependent heating (red) and cooling (blue) processes in the wide-band limit for leads at zero temperature: a) low voltage; b) intermediate voltage and c) high voltage.}
\end{figure}

In the zero temperature limit, \( G_J(\omega) \) can take one of two values, i.e., either zero or \( \Gamma_J \) depending on the chemical potential. Consequently, and for a symmetric junction with \( \Gamma_R = \Gamma_L = \Gamma \), the task of calculating the steady state excitation, \( \langle n(\infty) \rangle \), simplifies to counting the number of non-zero contributions to the heating and cooling rates in Eqs. (4). Fig. 1 depicts schematically the three relevant scenarios, where the chemical potential at the left lead is higher than that at the right lead. A larger bias window, \( \mu_L - \mu_R \), leads to an excess of heating over cooling processes, which is reflected in a larger vibrational excitation number, \( \langle n(\infty) \rangle = 0, \frac{1}{2}, \infty \).

\begin{figure}[h]
\centering
\includegraphics[width=\linewidth]{figure2.png}
\caption{a) Heating and cooling processes at high voltage for low, intermediate and high temperatures (left to right). b) Steady state vibrational excitation, \( \langle n(\infty) \rangle \), as function of the temperature and the voltage in the wide-band limit. Colored areas represent regions of stability in contrast to white areas corresponding to bond instability. The stability regions depends on \( n_{tr} \). The threshold is set to \( n_{tr} = 3 \) on the left and to \( n_{tr} = 10 \) on the right. Notice the different color scale between the two figures. The junction model parameters are: \( \hbar \omega_0 = 0.1 \) eV, \( \hbar \Omega = 0.05 \) eV, \( g = 0.10 \) and \( \Gamma = 0.01 \) eV.}
\end{figure}

The trend in \( \langle n(\infty) \rangle \), within the wide-band approximation, seems to be in accord with recent experiments at finite (non-zero) temperatures \[3\ 13\], in which increas-
The left and right plots in Fig. 2b correspond to the same junction parameters (see figure caption), with \( n_{\text{tr}} = 3 \), and \( n_{\text{tr}} = 10 \), respectively. Associating the bond instability with \( \langle n(\infty) \rangle > n_{\text{tr}} \), the uncolored regions reflect the regions of bond instability, where by definition, a smaller \( n_{\text{tr}} \) corresponds to a larger instability region. Notice in Fig. 2 that, for certain voltages, \( \langle n(\infty) \rangle \) decreases and then increases as a function of temperature. This non-monotonic dependence is due to the fact that the thermal broadening of the Fermi distribution affects differently the heating and the cooling rates. For unstable junctions (see Fig. 2a), a small increase of the temperature permits electron-hole cooling processes and primarily reduces vibrational heating processes. For example, the emission of low energy electrons from the molecule to the right lead is partially blocked in this case, thus reducing the overall vibrational heating rate, and lowering \( \langle n(\infty) \rangle \). A larger increase of the temperature affects also the cooling rate by, among other things, reducing also the emission of high energy electrons, which contributes to a relative increase of \( \langle n(\infty) \rangle \). At infinite temperature, the Fermi distribution approaches the value 1/2 for any frequency and therefore all processes are allowed and have the same rate. Since the numbers of allowed heating and cooling processes are the same, the overall heating and cooling rates become equal, and so \( \langle n(\infty) \rangle = \infty \), destabilizing the junction for any voltage [19].

A much richer voltage-dependence of the vibration instability is expected in realistic systems where the assumption of the wide-band approximation breaks down. While the wide-band approximation is often adequate for describing the decay rates between molecules and metallic leads, this approximation is an over simplification in other cases. For example, graphene electrodes show rich energy-dependence of the molecule-lead coupling, which depend on the particular graphene surface edge coupled to the molecule [30, 31]. Even in the case of metallic leads, covalently bonded adsorbates acting as linkers between the metal and the conducting molecule may induce a pronounced energy-dependence to the molecule-lead coupling. Accounting for the explicit energy-dependence of the decay rates, \( \Gamma_j \to \Gamma_j(h\omega - \mu_j) \), the corresponding coupling densities obtain a non-trivial energy dependence already at zero temperature. Since the latter determine rates of transport-induced vibrational heating and cooling processes on the molecule, the lead chemical potentials control in fact the balance between heating and cooling and thus determine the bond stability in a non-trivial way.

Remarkably, in some realistic cases, an increase in the bias voltage can actually stabilize the bond, in contrast to the intuitive result based on the wide-band approximation. Without loss of generality, let us consider a junction at zero temperature, where one of the leads (the left one) has a flat electronic decay profile, \( \Gamma_L(h\omega - \mu_L) = \Gamma \), and the other (right) lead is also flat, except for an additional Gaussian peak centered at \( \mu_R + h\omega_s \), i.e.,

\[
\Gamma_R(h\omega - \mu_R) = \Gamma \left( 1 + e^{-\frac{(h\omega - \mu_R - h\omega_s)^2}{2\sigma^2}} \right),
\]

as illustrated in Fig. 3a, where the leads Fermi energy is set to zero, and the molecular charging energy is \( h\omega_0 \). The presence of an external bias voltage \( (V) \) on the junction is modeled here in terms of shifts to the single particle energy levels in the non-interacting leads, resulting in shifts of the molecule-lead coupling spectra (marked as vertical arrows in Figs.
where the junction is stable and the white area corresponds to unstable junctions. Below a certain threshold, $2\sigma^2/\langle\Omega^2\rangle \sim 30$, the bond is stabilized by increasing the voltage.

The above example demonstrates a general scenario of high voltage induced mechanical stability, which is facilitated by a non-uniform energy dependence of the electron transport rate between the molecule and the leads. Peaks (and deeps) in the transfer rate profiles which characterize realistic lead structures and/or chemical compositions facilitate such a scenario. For example, employing graphene electrodes or specifically designed molecule–lead linker groups, may be used to design mechanically stable single molecule devices operating at high voltage in the resonance transport regime.

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where $S$ mode. We start by defining new operators that diagonalize their Hamiltonian, which is

$$H = [\hbar \omega + \frac{\hbar g}{2} (\tilde{a} + \tilde{a}^\dagger)] \tilde{d} \tilde{d} + \hbar \Omega \tilde{a} \tilde{a}.$$ (S1)

The new operators are given by

$$\tilde{a} \rightarrow a = U^\dagger \tilde{a} U, \quad \tilde{d} \rightarrow d = U^\dagger \tilde{d} U; \quad U = e^{\frac{\hbar g}{\Omega} (\tilde{a}^\dagger - \tilde{a}) \tilde{d} \tilde{d}}.$$ (S2)

With this new variables, the Hamiltonian is diagonal,

$$H = \hbar \omega_0 d^\dagger d + \hbar \Omega^2 a^\dagger a,$$ (S3)

where $\omega_0 = \omega_0 - \frac{g^2}{\Omega^2}$.

We assume that E is weakly coupled to the leads therefore the reduced dynamics is governed by a Markovian master equation [25, 26, 27]. Furthermore, we analyze the regime where the vibrational mode is weakly coupled to E, $\frac{g}{\Omega} \ll 1$. Under these conditions, $\langle a^\dagger a \rangle \approx \langle \tilde{a}^\dagger \tilde{a} \rangle$, the transformed number operator $\langle a^\dagger a \rangle$ provides a reliable measure of the excitation level of the vibrational mode in the original frame.

In terms of the new operators the transformation is

$$U = U^\dagger U = e^{\frac{\hbar g}{\Omega} (\tilde{a}^\dagger - \tilde{a}) \tilde{d} \tilde{d}} = e^{\frac{\hbar g}{\Omega} (a^\dagger - a) d^\dagger d}$$ (S4)

and

$$\tilde{d}^\dagger = d^\dagger e^{-\frac{\hbar g}{\Omega} (a^\dagger - a)}.$$ (S5)

We continue the derivation of the master equation by transforming the operators of E in the interaction Hamiltonian, $\tilde{d}$ and $\tilde{d}^\dagger$, to the interaction picture:

$$\tilde{d}^\dagger(t) = e^{\frac{i \eta t}{\Omega}} \tilde{d}^\dagger e^{-\frac{i \eta t}{\Omega}} = e^{i \omega_0 t} e^{\frac{\hbar g}{\Omega} (a^\dagger e^{i \omega t} - a e^{-i \omega t})} = d^\dagger e^{i \omega_0 t} + \frac{g}{2 \Omega} (S_1^t e^{i (\omega_0 + \Omega) t} - S_{-1}^t e^{i (\omega_0 - \Omega) t}),$$ (S6)

where $S_1^t = d^t a^\dagger$, $S_{-1}^t = d^t a$. This approximation is strictly valid only for

$$\frac{g}{2 \Omega} \sqrt{\langle a^\dagger a \rangle} < < 1.$$ (S7)

Finally, in the interacitivmo picture the dynamic equations for $\rho$, the density matrix of E + vibrational mode, are

$$\dot{\rho} = \sum_{j = \text{R}, \text{L}} ^{\text{L}, \text{L}} \mathcal{L}_{0, j} + \mathcal{L}_{1, j} + \mathcal{L}_{-1, j},$$ (S8)

where

$$\mathcal{L}_{0, j} \rho = \frac{1}{2} \left\{ G_{j} (\omega_0) \left[ \left[ d \rho, d^\dagger \right] + \left[ d, \rho d^\dagger \right] \right] + G_{j} (-\omega_0) \left[ \left[ d^\dagger \rho, d \right] + \left[ d^\dagger, \rho d \right] \right] \right\} ;$$

$$\mathcal{L}_{q, j} \rho = \frac{1}{2} \left\{ G_{j} (\omega_0 + q \Omega) \left[ \left[ S_q \rho, S_q^\dagger \right] + \left[ S_q, \rho S_q^\dagger \right] \right] + G_{j} (-\omega_0 + q \Omega) \left[ \left[ S_q^\dagger \rho, S_q \right] + \left[ S_q^\dagger, \rho S_q \right] \right] \right\}. $$ (S9)