Charge-state dependent vibrational relaxation in a single-molecule junction

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The interplay between nuclear and electronic degrees of freedom strongly influences molecular charge transport. Herein, we report on transport through a porphyrin dimer molecule, weakly coupled to graphene electrodes, that displays sequential tunneling within the Coulomb-blockade regime. The sequential transport is initiated by current-induced phonon absorption and proceeds by rapid sequential transport via a non-equilibrium vibrational distribution. We demonstrate this is possible only when the vibrational dissipation is slow relative to sequential tunneling rates, and obtain a lower bound for the vibrational relaxation time of 8 ns, a value that is dependent on the molecular charge state.

Charge transport through nanostructures, and molecules in particular, is strongly influenced by coupling between electronic and mechanical degrees of freedom[1–6]. Geometric differences between molecular charge states mean that electron transfer steps are accompanied by vibrational transitions, an effect encompassed by the Franck-Condon principle[7]. Typically vibrational transitions are identified as steps in current that are equally spaced in voltage in current-voltage (IV) measurements[3, 5, 6, 8, 9]. Transport behavior that results from coupling to equilibrated vibrations has been extensively studied and well understood. For example, electron-phonon coupling strength and vibrational frequency are precisely extracted from the progression of the current step heights, and low-bias suppression in the strongly coupled condition due to negligible vibrational wavefunction overlap, known as Franck-Condon blockade, has been observed[5, 6, 8]. Conversely, the effects of non-equilibrium vibrational distributions are less well-established. Interesting phenomena such as current-induced molecular heating and dissociation, giant Fano factors, and avalanche tunneling dynamics have been predicted theoretically[7, 10–14] and subsequently observed, primarily in carbon nanotubes devices[3, 6, 8, 15, 16].

Vibrational effects in single-molecule junctions are particularly prominent in the weak molecule-electrode coupling limit, as strong electron-electron interactions lead to Coulomb-blockade (CB) behavior and charge states are well defined. Transport through the molecule occurs either via resonant sequential tunneling outside the CB regime or via off-resonant cotunneling inside the CB regime. Like sequential tunneling processes, cotunneling processes can also excite vibrational states above a bias threshold through inelastic cotunneling[17]. If cotunneling-excited vibrational states can promote sequential tunneling processes, there is a loss of definition of the boundary between resonant and off-resonant tunneling regimes[12, 18]. Depending on the interplay between vibrational relaxation, cotunneling, and sequential tunneling rates, cotunneling-assisted sequential tunneling processes can lead to distinctive features in the transport spectrum, known as absorption sidebands, extending into the CB regime[7].

In this Letter we report the first experimental observation of such sidebands in a single-molecule device and confirm that they originate from a current-driven, non-equilibrium vibrational distribution. We calculate a lower threshold for the molecular vibrational relaxation time of 8 ns, and demonstrate that there is a connection between dissipation rate and molecular charge state, and by extension, its geometry.

The device architecture is displayed in Fig. 1, and has been described previously[19]. A high-κ, 10 nm-thick, HfO2 gate dielectric gives a large electrostatic coupling between the molecular states and the gate potential, \( V_g \) (in this case \( \epsilon_o = 0.5 \text{eV/V} \)). The molecule under study, a fused zinc-porphyrin dimer (FP2, Fig. 1c), has a small charging energy which, combined with the large gate coupling, allows multiple molecular charge states to be studied. FP2 is synthesized by Sonogashira coupling of a dibromo- edge-fused zinc porphyrin dimer[20] with an ethynylpyrene derivative[21][22]. Pyrene groups anchor the molecule to graphene source and drain electrodes through a \( \pi-\pi \) stacking interaction and provide weak molecule-electrode coupling, \( \Gamma \). Electroburnt graphene nanoelectrodes can display transport features prior to molecular deposition and therefore devices were measured before and after deposition to ensure we only study transport features related to FP2[22]. From 98 devices measured at 5 K, the majority displayed resonant tunneling features prior to molecule deposition, in line with previous work[21]. Five displayed clear resonant transport only after deposition and had consistent addition energies with the device studied in detail here. The presented device has the specific combination of molecule-electrode
and gate coupling to allow the experimental study of absorption sidebands. A large $V_g$-range differential conductance map (Fig. 1d) confirms the molecule is weakly coupled to the graphene electrodes. Off-resonant transport is suppressed due to CB and multiple Coulomb diamonds, with addition energies in the range of 150–300 meV, are observed and separated by resonant transport regions. Due to the electron-rich anchor groups and p-doping of graphene by the substrate[23], charge states are assigned to successive oxidized states of FP2, i.e. $N$−5 to $N$, $N$ being the number of electrons on the molecule when it is neutral. The assignment and addition energies are inline with studies on the same family of molecules[9, 24, 25]. We focus on electron-vibration coupling features manifested in the charge transitions at $V_g = -1.25$ V, assigned to the $N$−4/$N$−3 transition (green box), and $V_g = -0.6$ V - $N$−3/$N$−2 (blue box).

Fig. 2a displays high-resolution conductance maps of the $N$−4/$N$−3 transition. The solid slanted lines define the usual resonant transport region separating the $N$−4 and $N$−3 diamonds. Lines of increased conductance running parallel to the diamond edges are caused by additional transport channels to the ground-state to ground-state transition between $N$−4 and $N$−3. The low energy of these excited-state channels, at around 9 meV (dashed/dotted lines), point to a vibrational origin. Vibrational transitions of a similar energy have been observed in a study of a porphyrin monomer[9]. Under weak coupling, resonant transport is dominated by first-order sequential tunneling processes, i.e. $|N, q\rangle$ to $|N', q'\rangle$ where $N' = N \pm 1$, and each additional channel involves either the hopping on/off steps required to transport an electron through the junction to be accompanied by a change in vibrational state, i.e. $\Delta q = q' - q \neq 0$. These steps generate out-of-equilibrium vibrational excitations in the molecule, but if the rate of vibrational relaxation is much faster than sequential electron transfer rates then under steady-state conditions the system can be treated as in equilibrium. Under equilibrium conditions and at low temperature, only the vibrational ground state is appreciably populated, CB is maintained, and sequential tunneling current should be strictly bound within the solid lines defining the ground-state to ground-state resonant tunneling transition. Here, however, more complex behavior is observed, and the additional transport channels at energies of $\hbar \omega_q = 9$ meV (the dashed/dotted lines slanted lines) do not terminate at the boundaries of CB regions but instead extend into the $N$−4 diamond, forming sidebands to the Coulomb peak. The $N$−4 sidebands run parallel to diamond edges, indicating current within them results from sequential tunneling processes. The first sideband corresponds to a transition with $\Delta q = -1$ and thus sequential tunneling must involve at least the first vibrationally excited state of $N$−4. For the second sideband, $\Delta q = -2$ and sequential tunneling must originate from at least the second vibrationally excited state of $N$−4. The sidebands are present at 5 K, despite the absence of thermal population in $|N$−4, 1⟩.

As shown in Fig. 2b, the sidebands do not cross the zero-bias axis. At 5 K the conductance of the first sideband (Fig. 2b, grey) is suppressed below $|eV_{sd}| = \hbar \omega_q$, and the second sideband conductance (pink) is suppressed below $2\hbar \omega_q$. This suggests that the features within the $N$−4 Coulomb diamond are due to cotunneling-assisted sequential tunneling processes[12, 18]. The emergence of the first sideband is shown in Fig. 3a. At low voltages ($|eV_{sd}| < \hbar \omega_q$) cotunneling must be elastic ($q' = q$) and will contribute a small portion of tunneling current (cotunneling is second-order in $\Gamma$). Above $|eV_{sd}| = \hbar \omega_q$ inelastic cotunneling events, which leave the molecule in an excited vibrational state, are energetically allowed (Fig. 3a). Under weak molecule-electrode coupling, inelastic cotunneling processes carry little net current, and we do not observe gate-independent cotunneling lines within the Coulomb diamonds[26]. If the vibrational excitation that results from inelastic cotunneling is slow to relax compared to the sequential tunneling rates, $W_{q,q'}^{N,N'}$ (where $N' = N \pm 1$), specifically $W_{q,q'}^{1,0,N-1,N-3}$, then a sequential tunneling pathway to the ground state of $N$−3 is opened up (Fig. 3a). The $|N$−3, $q = 0\rangle$ state can subsequently undergo sequential tunneling up to the second vibrationally excited state of $N$−4. If electron-phonon coupling, parameterized by the coupling constant: $\lambda_q$, is weak ($\lambda_q < 1$) then the trans-
sition to the $|N-4,q=0\rangle$ is most likely, and the molecule returns to the vibrational ground state until another inelastic cotunneling begins the cycle again. If $\lambda_q > 1$ then transitions to $|N-4,q=1,2\rangle$ out-compete the return to the $N-4$ ground state, and a single inelastic cotunneling event leads to sustained sequential electron tunneling through the molecule, even in the CB region, via vibrationally excited states of $N-4$. Therefore the prominence of the sidebands is enhanced when electron-phonon coupling is strong.

We look to understand these mechanisms quantitatively. Conductance is a sum of the cotunneling and sequential tunneling contributions, i.e., $G_{sd} \approx G_{seq} + G_{cot}$. At low temperature and zero-bias these are given analytically by[27]:

$$G_{seq} = -\frac{2e^2}{h} \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \left[ f'(\epsilon_d) \right] \left[ 1 + f(\epsilon_d) \right] e^{-\lambda^2}$$

(1)

and

$$G_{cot} = \frac{2e^2}{h} \frac{\Gamma_L \Gamma_R}{1 + f(\epsilon_d)} \left[ \frac{1 - f(\epsilon_d)}{\epsilon_d + \lambda^2 \hbar \omega}^2 + \frac{2f(\epsilon_d)}{\epsilon_d - \lambda^2 \hbar \omega}^2 \right]$$

(2)

where $\Gamma_L$ and $\Gamma_R$ are the couplings of the molecule to left and right electrodes, $f(\epsilon_d)$ is the Fermi distribution at the energy of the molecular transition ($\epsilon_d$), and $f'(\epsilon_d)$ is its derivative. We fit zero-bias conductance traces (at 10 K and below) to $\Gamma$ and $\lambda_q$, shown in Fig. 3c ($\Gamma = \Gamma_L \Gamma_R/(\Gamma_L + \Gamma_R)$). The two parameters cannot be determined independently (they are positively covariant[22]), although it is possible to determine the range in which they lie. Sequential tunneling is exponentially suppressed in $\lambda_q$, however cotunneling can still occur via highly excited virtual states of $N-3$, therefore at large $\lambda_q (>2.8)$, and with the corresponding increase in $\Gamma$, there are significant contributions from elastic cotunneling that are not observed experimentally. This sets an upper bound for $\lambda_q$. Simulations (vide infra) of the conductance map show at $\lambda_q < 2$ (corresponding to $\Gamma < 1 \mu$eV) the sidebands become too low in conductance to observe. The lack of sidebands at low values of $\lambda_q$ and $\Gamma$ results from reduced inelastic cotunneling rates that initiate the sidebands, along with the enhanced rates of sequential transfer from excited vibrational states of $|N-3,q\rangle$ to the ground state, $|N-4,q=0\rangle$ due to larger Franck-Condon factors. Therefore, we find pairs of parameters within ranges of 2–3 for $\lambda_q$ and 1–100$\mu$eV for $\Gamma$. Theoretical work predicted that slow vibrational relaxation coupled with values $\lambda_q$ in the range of 2–3 would result in negative differential conductance (NDC) after the conductance peaks of the vibrational sidebands, due to the depopulation of non-equilibrium vibrational distribution to the ground state by sequential transfer as the sidebands enter the bias window[11]. Our experimental observation of NDC (Fig. 2a) and calculated range of $\lambda_q$ are consistent with this prediction. The criteria for the emergence of the first $N-4$ sideband is:

$$1/\tau_{N-4} \leq W_{1,0}^{N-4,N-3}$$

Therefore a calculation of the sequential rate yields a lower bound for the vibrational relaxation time, $\tau_{N-4}$, within the junction. Sequential tunneling rates are given by[27]:

$$W_{q,q';a}^{N-4,N-3} = 2\Gamma_a |M_{q,q'}|^2 f_a(\epsilon + |q' - q| \hbar \omega)$$

(3)
Across the range of $\tau_{\text{osc}}$ values, here $\lambda_q = 2.7$, $\Gamma = 40 \text{meV}$, $1/\tau_{\text{N} - 4} = 100 \times W_1^{-4} N^{-3}$, $1/\tau_{\text{N} - 3} = 1/100 \times W_1^{-4} N^{-3}$; sequential tunneling rates are calculated at the red and grey points respectively.

where $M_{q,q'}$ are the Franck-Condon matrix elements. Across the range of $\lambda_q, \Gamma$, the calculated values of $W_1^{-4} N^{-3}$ are in the narrow range of 56 – 120 MHz,[22] giving a lower bound for the vibrational relaxation time of $\tau_{\text{N} - 4} > 8$ ns. The absence of sidebands within the $N \rightarrow 3$ charge state is an intrinsic part of the system dynamics. If $1/\tau_{\text{N} - 3} > W_1^{-4} N^{-3}$ the sidebands are not present (Fig. 3b) pointing to a charge-state dependence of the vibrational relaxation rates. Using a minor extension to the model developed by Koch et al. to include charge-state dependent relaxation times, $\tau$, we calculate the conductance map (Fig. 3d) using these inequalities[27], which shows good correspondence with the experimental data, reproducing the key features of the transport spectrum.

The temperature dependence of the conductance supports the assignment of the sidebands as cotunneling-assisted sidebands. At zero bias the Coulomb peak and the first sideband follow equilibrium behavior (Fig. 2c). The conductance of the Coulomb peak ($V_{\text{CP}} = -1.08$ V) decays as $G_{\text{max}} \propto 1/k_B T$, due to thermal broadening of the electrode Fermi-Dirac distributions, and the conductance at the point where the first sideband would cross $V_{\text{sd}} = 0$ (from which electron transfer is driven from $q = 1$, red circle, Fig. 2a) can be fitted to the product of thermal broadening and the Bose distribution[8]:

$$G_{\text{max}} \propto \frac{1}{k_B T} \times \exp\left(\frac{1}{\hbar \omega_q/k_B T} - 1\right)$$

with $\hbar \omega_q = 8 \pm 1$ meV. This demonstrates the zero-bias conductance increase is driven thermally by an increasing equilibrium population in $q = 1$. The picture is different at higher bias however (Fig. 2d). At $eV_{\text{sd}} = \hbar \omega_q$ the conductance of the first sideband is already high at 5 K and decreases with increasing temperature, indicating there is a substantial non-equilibrium population at $eV_{\text{sd}} = \hbar \omega_q$ (red square), this state can only arise as the result of two inelastic excitations of the vibrational ground state or due to an inelastic excitation of a thermally-populated $|N - 4, q = 1\rangle$ state. The latter becomes appreciable only at higher temperature. Since the emergence of the second sideband at positive bias is observed only above 10 K, this suggests the second mechanism dominates. A fit to equation 4 gives $\hbar \omega_q = 7.4 \pm 1.5$ meV. The sidebands are stronger at negative bias, likely due to asymmetries resulting from both molecule-electrode coupling, common in single-molecule devices[21], and an asymmetric voltage drop across the junction ($\phi_0 = 0.24$, extracted from the Coulomb diamonds slopes).

The neighboring transition, $N - 3/N - 2$ (blue box on Fig. 1d), as with $N - 4/N - 3$, displays signatures of strong electron-phonon coupling, i.e., Franck-Condon blockade involving a mode of 10 meV[22]. Vibrational modes that couple strongly to the electron transfer process are those that displace atoms along the same vectors that define the nuclear rearrangement. Density functional theory calculations aid our understanding of strong electron-vibrational coupling in the oxidations of FP2[28]. Frequency calculations (B3LYP/6-31G(d) functional/basis set) on FP2 optimized in the N to
of low-energy modes and, combined with the asymmetry induced by the substrate, could expedite intramolecular vibrational relaxation for the $N$ to $N-3$ states\cite{33, 34}.

In summary, we demonstrate that low-energy, torsional motions of a pyrene-porphyrin dimer-pyrene couple strongly to electron transfer and can lead to cotunneling-assisted absorption sidebands. We observe a strong dependence of the vibrational relaxation rate on the charge state of the molecule, and moving beyond the harmonic approximation may be required to fully unravel the tunneling dynamics at play. This study of non-equilibrium vibrational dynamics and dissipation sheds light on heat and energy flow in molecular devices.

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### SUPPLEMENTARY INFORMATION

#### Synthetic details

**FP2.** The dibromo-precursor $\text{Br}_2\text{FP2} (6.88 \text{ mg}, 1.99 \mu\text{mol})$ and 1-ethynyl-3,6,8-tridecoxy-pyrene (7.79 mg, 10 $\mu$mol) were dissolved in toluene (4 mL) and DIPA (1 mL). The solution was degassed by freeze-pump-thaw three times before $[\text{Pd(PPh}_3)_4] (0.23 \text{ mg, } 0.2 \mu\text{mol})$ and CuI (0.04 mg, 0.2 $\mu$mol) were added under a flow of argon. After another freeze-pump-thaw cycle, the mixture was heated to 50 °C for 20 hours. The solvents were removed and the product purified by repeated chromatography (SiO₂, PE/DCM 5:1 followed by size-exclusion, CHCl₃), to give FP2 as a green/brown solid (6.38 mg, yield = 64%). For deposition onto graphene electrodes 2 µl of a 2 µM toluene solution of FP2 was dropcast onto the devices. $^1$H NMR (400 MHz, CDCl₃) δ 8.67 (d, $J = 4.6$ Hz, 4H), 8.50 (d, $J = 9.3$ Hz, 2H), 8.31 (d, $J = 9.3$ Hz, 2H), 8.26 (d, $J = 9.4$ Hz, 2H), 8.18 (d, $J = 9.3$ Hz, 2H), 7.78 (s, 8H), 7.76 (s, 4H), 7.75 (s, 2H), 7.49 (d, $J = 4.5$ Hz, 4H), 7.06 – 7.05 (m, 6H), 4.32 – 4.19 (m, 12H), 2.02 – 1.86 (m, 12H), 1.63 – 1.50 (m, 12H), 1.43 – 1.01 (m, 288H), 0.86 – 0.64 (m, 138H). m/z (MALDI-TOF, dithranol): 4843.6958 ([M]+ calcld. 4860.95).

#### Additional transport data

![Current stability diagrams](before deposition)  ![Current stability diagrams](after FP2 deposition)

**FIG. S1.** Current stability diagrams, measured at 4 K, before and after FP2 deposition.
Determination of ranges of molecule-electrode and electron-phonon coupling

FIG. S2. (a) $R^2$ (blue markers) of fit for zero-bias gate traces from 5 K to 10 K, with different values of $\lambda_q$, the corresponding molecule-electrode coupling is given in red. (b) For each set of $\lambda_q$ and $\tilde{\Gamma}$ the calculated sequential tunneling rate $W_{1,0,L}^{N-4,N-3}$ and cotunneling rates $W_{0,1}^{N-4,N-4}$ at the onset of the first sideband in $N-4$.

Franck-Condon blockade in $N-3/N-2$

FIG. S3. (a) Conductance maps at different temperatures of the $N-3/N-2$ transition (blue box in Fig. 1), showing conductance suppression at low bias and low temperature. (b) Zero-bias gate traces displaying the lifting of the blockade with increasing temperature, consistent with FC blockade, and a fit the temperature-dependence of the Coulomb peak (equation 4) gives the mode energy of $\lambda_q$. 

Franck-Condon blockade in $N-3/N-2$