Introduction.—A fundamental understanding of the nonequilibrium behavior of the atomic degrees of freedom in current-carrying nanoscale junctions is of major importance for the realization of molecule-based electronics. Joule heating arising from the interaction between the electronic charge carriers and the molecular vibrations, has been observed experimentally and poses a serious stability issue in such junctions.

The implications of the electron-vibration (el-vib) interaction on both the current and heating in molecular junctions have been subject of intense theoretical studies and critical effects such as vibrational instabilities and cooling mechanisms have been addressed. In addition, recent developments have demonstrated the existence of nonconservative current-induced forces that can drive the molecular vibrations strongly out of equilibrium and provide further channels for junction destabilization. Efforts to identify vibrational heating and instabilities in, e.g., inelastic-tunneling spectroscopy (IETS) current noise and Raman spectroscopy are still ongoing.

Raman spectroscopy on current-carrying molecular junctions offers a unique diagnostic tool for monitoring the nonequilibrium behavior of the molecular vibrations. Apart from the information about heating encoded in the Stokes/anti-Stokes ratio, Raman spectroscopy provides direct access to the vibrational spectral function of the molecule. Experimentally, this has revealed noticeable frequency shifts and broadenings of the vibrations as a function of bias voltage. Similar effects originating from the electron-phonon interaction are well known from, e.g., Raman spectroscopy on gated graphene and current-carrying nanomechanical carbon-nanotube resonators and provide useful insight into the mechanisms governing vibrational damping and heat dissipation in such systems.

In this work we study these effects in nanoscale atomic/molecular junctions where nonadiabatic (dynamic) effects become important when the electronic and vibrational energy scales are comparable. For this purpose, we formulate a nonequilibrium Green’s function (NEGF) based theory for vibrational frequency renormalization and heating taking into account electronic charging and screening effects on the local junction vibrations. We find that (i) strong bias-dependent frequency renormalization and damping is accompanied by pronounced nonlinear bias-dependent heating, and (ii) the above-mentioned carrier-related mechanisms may explain the voltage dependence of the Raman shifts and linewidths observed in Ref. [4].

![Diagram](attachment:fig1.jpg)

**FIG. 1.** (Color online) (a) Molecular contact with an amine-terminated (NH$_2$) OPV3 molecule sandwiched between the source and drain electrodes. (b) Generic junction description in terms of a single molecular level $\varepsilon_0$ with lead-induced broadening $\Gamma = \Gamma_L + \Gamma_R$ and applied bias voltage $eV = \mu_R - \mu_L$. (c),(d) Processes responsible for the carrier-induced renormalization of vibrational frequencies ($\omega_\lambda \rightarrow \tilde{\omega}_\lambda$) and electron-hole damping ($\gamma_{eh}$). The illustrations correspond to the Feynman diagrams for the self-energies in Eqs. (2) and (3), respectively, describing the dynamic renormalization via virtual electron-hole pairs (screening) (c) and the static renormalization due to (partial) charging of the level (d).
Theory. —To address the effect of carrier-induced renormalization and heating of vibrations in biased nanoscale junctions, we employ the NEGF which treats the dynamics of the electronic and vibrational degrees of freedom on equal footing. In the general case with more than one local junction vibration, the dressed vibrational retarded Green’s function (GF) is given in the matrix form as

$$D^{\tau}(\omega) = \left[ D^{\tau}_0(\omega) \right]^{-1} - \Pi^{\tau}(\omega) \right],$$

where \( D^{\tau}_0(\omega) \) is the bare diagonal GF given by \( D^{\tau}_{0,\alpha,\beta}(\omega) = 2\omega/[(\omega + i\theta)^2 - \omega^2] \) for the vibrational mode \( \lambda \) with frequency \( \omega_{\lambda} \) and the spectral function is given by the imaginary part of the retarded GF as \( A(\omega) = -2\sum_{\lambda} \text{Im} D^{\tau}_{\alpha,\beta}(\omega) \). The vibrational self-energy \( \Pi = \Pi^{(1)} + \Pi^{(2)} \) in general has contributions from both the interaction with electronic charge carriers (\( \Pi^{(1)} \)) and phonon-related effects (\( \Pi^{(2)} \)). The latter, reflecting coupling to environmental phonons as well as anharmonicity, is here described by a phenomenological damping rate \( \gamma_{\text{ph}} \) which does not affect the vibrational frequencies.

For the electronic part of the self-energy, we consider a junction where the transport is dominated by a single electronic level (HOMO or LUMO) with energy \( \varepsilon_0 \) and level broadening \( \Gamma = \Gamma_L + \Gamma_R \) due to the leads (see Fig. 1)). The level is coupled to the local vibrations via linear \( H^{(1)} = n_0 \sum \lambda \lambda' M^{(1)}_{\lambda\lambda'}(a^\dagger_\lambda + a_\lambda) \) and quadratic \( H^{(2)} = \frac{1}{2} \sum \lambda \lambda' \lambda'' \lambda''' M^{(2)}_{\lambda\lambda';\lambda''\lambda'''}(a^\dagger_\lambda + a_\lambda) a^\dagger_{\lambda'} a_{\lambda'} \) el-vib interaction terms where \( n_0 = n_0 + n_0 \) is the level occupancy and \( M^{(1)}_{\lambda\lambda'}(M^{(2)}_{\lambda\lambda';\lambda''\lambda'''}) \) the linear (quadratic) el-vib coupling. The retarded components of the electronic self-energy \( \Pi^{\tau} = \Pi^{(1)} + \Pi^{(2)} \) are, at the lowest (nonzero) order given by the electronic polarizability

$$\Pi^{(1)}_{\lambda\lambda',\tau}(\omega) = -2i \int \frac{d\epsilon}{2\pi} \left[M^{(1)}_{\lambda\lambda'} G^R(\epsilon) M^{(1)}_{\lambda\lambda'} G^< (\epsilon - \omega) + M^{(1)}_{\lambda\lambda'} G^< (\epsilon) M^{(1)}_{\lambda\lambda'} G^R (\epsilon - \omega) \right],$$

and the level occupancy

$$\Pi^{(2)}_{\lambda\lambda',\tau}(\omega) = -2i M^{(2)}_{\lambda\lambda'} \int \frac{d\epsilon}{2\pi} G^< (\epsilon) = \langle n_0 \rangle M^{(2)}_{\lambda\lambda'},$$

respectively, where the factors of 2 account for spin degeneracy. The two self-energies, which are illustrated in Fig. 1c and d) by their respective Feynman diagrams, account for frequency renormalization due to dynamic screening and static (partial) charging, respectively. In addition, the former also accounts for spectral broadening due to damping by electron-hole (eh) pair excitations.

Vibrational heating originates from the linear el-vib interaction and can be quantified in terms of the nonequilibrium occupation \( \hat{n}_\lambda \) of the renormalized vibration. As we here show in detail, the physically relevant (i.e., experimentally verifiable via, e.g., Raman spectroscopy) occupation factor for a renormalized vibration is given by

$$\hat{n}_\lambda = -\frac{1}{2} + \frac{\omega_{\lambda}}{\omega_{\lambda}} \int \frac{d\omega}{2\pi} D^{<}_{\lambda\lambda}(\omega)$$

which for small frequency changes \( \Delta \omega_{\lambda} \ll \omega_{\lambda} \) simplifies to \( \Delta \omega_{\lambda} = \text{Re} \Pi^{<}_{\lambda\lambda}(\omega_{\lambda}) \). In the limit \( \Gamma \gg \omega_{\lambda}, \varepsilon_0, V \) corresponding to the situation in atomic gold wires, the renormalization and damping due to linear el-vib interaction [Eq. 2] scale as \( \Delta \omega_{\lambda}^{(1)} \sim -(M^{(1)}_{\lambda\lambda'} \gamma_{\text{eh}})^2 \) and \( \gamma_{\text{eh}} \sim \omega_{\lambda}(M^{(1)}_{\lambda\lambda'}/\Gamma)^2 \), respectively. Even if the dimensionless coupling constant is small \( (M^{(1)}_{\lambda\lambda'}/\Gamma)^2 \ll 1 \), the frequency renormalization may become appreciable if \( \Gamma \gg \omega_{\lambda} \). In this regime, the omission of the mode-renormalization in Eq. 4 has previously led to disagreements between NEGF and rate equation results for the vibrational occupation (see, e.g., Fig. 2(a) of Ref. 36).

The occupation in Eq. 4 is equivalent to the steady-state solution of the rate equation

$$\dot{n}_\lambda = [\gamma_{\text{emis}} + \gamma_{\text{ph}} N_B(\omega_{\lambda})] (n_\lambda + 1) - [\gamma_{\text{abs}} + \gamma_{\text{ph}} N_B(\omega_{\lambda}) + 1] \hat{n}_\lambda,$$

given by

$$\hat{n}_\lambda = \frac{1}{e^{\hbar \omega_{\lambda}/k_B T_{\text{eff}}} - 1},$$

where we have introduced an effective nonequilibrium mode temperature \( T_{\text{eff}} \) defined by \( e^{\hbar \omega_{\lambda}/k_B T_{\text{eff}}} = [\gamma_{\text{emis}} + \gamma_{\text{ph}} N_B(N_B + 1)]/[\gamma_{\text{emis}} + \gamma_{\text{ph}} N_B] \), \( N_B(\omega) = [e^{\hbar \omega/k_B T} - 1]^{-1} \) is the Bose-Einstein occupation factor of the environmental phonon bath at temperature \( T \), and \( \gamma_{\text{emis}}^\text{eh} \) is the rate for absorption (emission) of vibrational quanta due to intra and interelectrode eh-pair processes [see inset in Fig. 2(b)]. They can be identified from the eh-pair damping rate \( \gamma_{\text{eh}} = -2\frac{\hbar}{\omega} \text{Im} \Pi^{(1)}_{\lambda\lambda}(\omega_{\lambda}) \) as \( \gamma_{\text{eh}} = i\omega_{\lambda} \Pi^{(1)}_{\lambda\lambda}(\omega_{\lambda}) \gg \gamma_{\text{emis}}^\text{eh} - \gamma_{\text{abs}}^\text{eh} \). In equilibrium they are related by the detailed balance \( \gamma_{\text{emis}}^\text{eh} = \gamma_{\text{abs}}^\text{eh} \exp (-\hbar \omega_{\lambda}/k_B T) \) implying \( T_{\text{eff}} = T \). The total damping rate is given by the imaginary part of the full self-energy as

$$\gamma_{\lambda} = -2\frac{\hbar}{\omega} \text{Im} \Pi^{<}_{\lambda\lambda}(\omega_{\lambda}).$$

In the case of independent vibrations, i.e., when mode-mode couplings given by the off-diagonal elements of the self-energy are negligible, the renormalized frequencies are given by the real part of the self-energy as the solution to the equation

$$\omega^2 = \omega_{\lambda}^2 + 2\omega_{\lambda} \text{Re} \Pi^{<}_{\lambda\lambda}(\omega_{\lambda}),$$

which for small frequency changes \( \Delta \omega_{\lambda} \ll \omega_{\lambda} \) simplifies to \( \Delta \omega_{\lambda} = \text{Re} \Pi^{<}_{\lambda\lambda}(\omega_{\lambda}) \). In the limit \( \Gamma \gg \omega_{\lambda}, \varepsilon_0, V \) corresponding to the situation in atomic gold wires, the renormalization and damping due to linear el-vib interaction [Eq. 2] scale as \( \Delta \omega_{\lambda}^{(1)} \sim -(M^{(1)}_{\lambda\lambda'} \gamma_{\text{eh}})^2 \Gamma = -\omega_{\lambda}(M^{(1)}_{\lambda\lambda'}/\Gamma)^2 \gamma_{\text{eh}} \) and \( \gamma_{\text{eh}} \approx \omega_{\lambda}(M^{(1)}_{\lambda\lambda'}/\Gamma)^2 \), respectively. Even if the dimensionless coupling constant is small \( (M^{(1)}_{\lambda\lambda'}/\Gamma)^2 \ll 1 \), the frequency renormalization may become appreciable if \( \Gamma \gg \omega_{\lambda} \). In this regime, the omission of the mode-renormalization in Eq. 4 has previously led to disagreements between NEGF and rate equation results for the vibrational occupation (see, e.g., Fig. 2(a) of Ref. 36).
In the calculations presented below, we assume low temperature \((T = 0)\) and use the bare electronic GFs in the evaluation of the self-energies corresponding to the first Born approximation.

**Generic junction model.**—In order to demonstrate the connection between vibrational frequency renormalization, broadening/damping, and heating in nanoscale junctions, we start by considering a simple junction with an off-resonant electronic level \(\varepsilon_0\) coupled symmetrically to the leads \((\Gamma_L = \Gamma_R)\) and interacting weakly with a local vibration with frequency \(\omega_\lambda\). The significance of the electronic energy scales of the junction is illustrated by considering two cases for the lead-induced level broadening representing junctions with \(\Gamma \lesssim \varepsilon_0, V\) and \(\Gamma \gg \varepsilon_0, V\), respectively (see Fig. 2 for parameters).

In Fig. 2(a) and (b) we plot the bias dependence of the renormalized vibrational frequency \(\tilde{\omega}_\lambda\) obtained from a self-consistent solution of Eq. (7) and the eh-pair damping rate \(\gamma_{eh}\), respectively. The qualitatively different bias dependencies in the two cases stem from different electronic density of states (DOS) of the level. For the largest value of \(\Gamma_{L/R}\) in Fig. 2 corresponding to, e.g., break junctions with small molecules the DOS is low and constant at the scale of the applied bias. The damping is consequently weak \((\gamma_{eh} \lesssim 0.4\) meV\) and both the frequency renormalization and damping show very little bias dependence.

When \(\Gamma \lesssim \varepsilon_0, V\), the electronic resonance can be introduced into the bias window resulting in large changes in the level occupancy and the electronic screening with the applied bias. This situation initially results in a softening of the vibration and increased damping with applied bias. At \(V = 2\varepsilon_0\) where the level becomes resonant with the chemical potential of the source contact, it is partially filled and therefore has a large DOS for eh-pair excitations [see Fig. 2(c)]. As a consequence, the frequency renormalization and eh-pair damping peak close to this bias voltage value. For higher bias the resonance continues to fill up and eh-pair excitations become suppressed by Pauli blocking [see inset of Fig. 2(b)]. This results in a subsequent hardening of the frequency, which at high bias saturates at the value given by the charging-induced renormalization \(\omega_\lambda = \omega_\lambda + n_0 M_\lambda^{(2)}\), and a strongly reduced damping (see also below).

Next, we consider the heating of the vibration. Figure 2(c) and (d) show the bias dependence of the vibrational excitation obtained from Eq. (4) as well as the rate equation result \((\hat{4})\) and the elastic current \(I = -e\Gamma/h \int d\varepsilon \text{Im} G^R (\varepsilon) [f_L - f_R]\) through the junction (inelastic contributions are small corrections). Note that the rate-equation and NEGF results are in perfect agreement as expected. Above the threshold for emission of vibrational quanta at \(eV = h\omega_\lambda\) (given by the renormalized frequency) a qualitatively different behavior of the vibrational excitation is observed for the two \(\Gamma\) values. In the \(\Gamma \gg \varepsilon_0, V\) case, the linear bias dependence of the vibrational excitation is well-known\[39] For \(\Gamma \lesssim \varepsilon_0, V\), the bias dependence of the vibrational excitation is strongly nonlinear and, perhaps counterintuitively, experiences stronger (compared to the large \(\Gamma\) case) heating for \(V \gtrsim 1.1\) V despite the lower current and stronger damping.

To elucidate the physical origin of the pronounced nonlinear heating in the \(\Gamma \lesssim \varepsilon_0, V\) case, we consider the dominant contributions to the eh-pair damping rate from absorption (full lines) and emission (dashed line) processes shown in the inset of Fig. 2(b). At biases \(V > 2\varepsilon_0\), absorption processes with the left lead become Pauli-blocked and transport-induced interelectrode processes become dominant. Furthermore, when the full resonance is contained in the bias window, i.e., \(V \gg \varepsilon_0, \Gamma, \omega_\lambda\), the DOS for absorption and emission processes become comparable implying that \(\gamma_{eh} \approx \gamma_{emis}\) and \(\gamma_{eh} \to 0\). For the steady-state solution \((\hat{6})\) this leads \((\Lambda_B = 0\) at \(T = 0)\) to \(\gamma_\lambda = \gamma_{emis}/\gamma_{ph}\). The bias dependence of the heating thus follows that of the rate for emission processes which is nonlinear due to the Lorentzian broadening of the electronic level and saturates in the high bias limit where the current is carried by the full resonance. This qualitatively explains the pronounced nonlinear heating. It is important to note that the steady-state solution to the rate equation \((\hat{6})\) diverges in the high bias limit \(V \to \infty\) in the absence of the phonon-related damping parameter \(\gamma_{ph}\). This underlines the importance of the \(\gamma_{ph}\) parameter.

![FIG. 2. (Color online) Renormalized frequency \(\tilde{\omega}_\lambda\) (a) and electron-hole damping rate \(\gamma_{eh}\) as a function of bias voltage \(V\) for a vibration interacting with an off-resonant level \((\varepsilon_0 = 0.5\) eV, \(\mu_{L/R} = \pm V/2\), \(\Gamma_L = \Gamma_R\), \(\omega_\lambda = 200\) meV, \(M^{(1)}_\lambda = 50\) meV, \(M^{(2)}_\lambda = -2\) meV, \(\gamma_{ph} = 1\) meV). The inset in (b) depicts the eh-pair processes dominating the damping rate. (c) Nonequilibrium excitation \(\tilde{n}_\lambda\) of the renormalized vibration calculated using Eq. (4) (full lines) and the rate-equation result in Eq. (6) (black dashed lines). (d) Electronic current through the junction.](image-url)
for vibrational heating and instabilities\textsuperscript{617,620} in nanoscale junctions.

**OPV3 junction.**— In the remaining part of the paper, we present first-principles based calculations of the carrier-induced frequency renormalization and vibrational heating in a junction based on the amine-terminated OPV3 molecule [see Fig. 1(a)] where frequency shifts of the order of \(\sim 1\) meV, spectral broadening, and significant heating have been observed experimentally with increasing bias voltage\textsuperscript{6}. The frequency shifts were so far ascribed\textsuperscript{43} to a vibrational Stark effect. However, calculations of ours of the vibrational frequencies in the presence of an electric field do not support this interpretation\textsuperscript{43}. In our model of the OPV3 junction, transport through the LUMO of the OPV3 molecule positioned off-resonant (\(\varepsilon_0 = 0.5\) eV) with respect to the equilibrium chemical potentials of the leads (\(\mu_{L/R} = \pm V/2\)) and coupled symmetrically to the contacts (\(\Gamma_{L/R} = 0.2\) eV) is assumed\textsuperscript{12}. The next molecular level lies \(\sim 1\) eV above the LUMO and can hence be neglected. The vibrations and el-vib interactions have been obtained from first principles for the isolated OPV3 molecule, thus neglecting direct effects from the leads. With few exceptions, the quadratic couplings, which are of the order of \(|M_{\lambda}^{(1)}| \sim 0–10\) meV, are found to be negative corresponding to frequency softening upon charging of the LUMO. This is in good agreement with a recent study of charging-induced frequency shifts in molecular junctions.

Figure 3 shows the bias dependence of the vibrational spectral function \(A(\omega)\) for the OPV3 junction. We focus here on the high-energy vibrations (\(\omega > 140\) meV), but note that the low-energy part of the spectral function shows a similar bias dependence. Overall, the calculated spectral function reproduces the features in the Raman spectra of Fig. 3(b) of Ref. 4. The spectral lines show clear mode softening of up to \(\sim 2\) meV with increasing bias voltage (for HOMO dominated transport, however, many of the spectral lines show mode hardening\textsuperscript{13}). This is a result of partial charging and screening that follows as the chemical potential of the left lead moves into the broadened LUMO resonance. The relative magnitude of the two effects is sensitive to the level alignment and lead broadening in the junction. Here, they contribute comparably to the frequency renormalization.

The eh-pair damping that accompanies screening, gives rise to pronounced broadening of some of the spectral lines. This effect correlates with the strength of the linear el-vib interaction \(M_{\lambda}^{(1)}\) which is indicated in the center panel of Fig. 3 for the modes with the strongest interaction. At zero bias, the spectral peaks for these modes are shifted from the frequencies of the isolated molecule (vertical dashed lines) due to (equilibrium) charging and screening. At large bias voltages, el-vib mediated mode-mode couplings result in a nontrivial bias dependence of some of the closely lying spectral lines.

In Fig. 4 we show the effective nonequilibrium temperature \(T_{\text{eff}}\) from Eq. 6 for the OPV3 modes marked with dashed lines in the center panel of Fig. 3. Above the emission threshold at \(eV = \hbar\omega_N\), the temperature of the vibrations jumps to several hundred Kelvin. For the \(\omega = 201.7\) meV mode, the temperature is in good agreement with the one for the mode with similar energy reported in Fig. 3(a) of Ref. 4. Comparing to Fig. 2(c), the approximate linear increase in the effective temperatures above the emission threshold is seen to correspond to the initial nonlinear increase in the occupation.

**Conclusions.**— In summary, we have studied carrier-induced vibrational frequency renormalization, damping, and heating originating from the microscopic eh-pair excitation processes governing these observables. In junctions characterized by \(\Gamma \lesssim \varepsilon_0, V\) where the effects are most pronounced, a strong correlation with nonlinear vibrational heating and the onset of current results (see Fig. 2). Such heating is inherent to junctions where the current is carried by a full electronic resonance and underlines the importance of eh-pair processes for the damping of vibrational heating. We have further shown that the voltage dependence of the Raman shifts and
line widths observed for an OPV3 molecular junction in Ref. [3] is not consistent with the originally proposed static Stark shift but can be explained by carrier-induced charging and screening effects.

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$$\Pi^{el}(\omega, V) \rightarrow \Pi^{el}(\omega, V) - \Pi^{el}(\omega = 0, V = 0),$$

where $\Pi^{el}(\omega = 0, V = 0)$ is the static zero-bias self-energy, in order not to double count these contributions.
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Note that the cross section for Raman scattering is mode dependent implying that not all spectral lines show up in Raman spectroscopy.
I. JUNCTION HAMILTONIAN

To fix the notation, we start by specifying the Hamiltonian \( H = H_{el} + H_{vib} + H_{int} \) for a junction with an electronic level coupled to left (L) and right (R) leads (\( H_{el} \)) and interacting (\( H_{int} \)) with a set of vibrations (\( H_{vib} \)) through both linear (\( H^{(1)} \)) and quadratic (\( H^{(2)} \)) el-vib interaction, i.e.

\[
H_{el} = \varepsilon_0 d^\dagger d + \sum_{k;\alpha=L,R} \varepsilon_k c^\dagger_{k\alpha} c_{k\alpha} + \sum_{k;\alpha=L,R} (t_{k\alpha} c^\dagger_{k\alpha} d + t^*_{k\alpha} d^\dagger c_{k\alpha}),
\]

\[
H_{vib} = \sum_{\lambda} \frac{p^2_{\lambda}}{2m} + \frac{m \omega^2_{\lambda} x^2_{\lambda}}{2} = \sum_{\lambda} \hbar \omega_{\lambda} a^\dagger_{\lambda} a_{\lambda},
\]

\[
H_{int} = H^{(1)} + H^{(2)},
\]

\[
H^{(1)} = d^\dagger d \sum_{\lambda} M^{(1)}_{\lambda}(a_{\lambda} + a^\dagger_{\lambda}) = d^\dagger d \sum_{\lambda} M^{(1)}_{\lambda} \sqrt{\frac{2m \omega_{\lambda}}{\hbar}} x_{\lambda},
\]

\[
H^{(2)} = \frac{1}{2} d^\dagger d \sum_{\lambda\lambda'} (a_{\lambda} + a^\dagger_{\lambda}) M^{(2)}_{\lambda\lambda'} (a_{\lambda'} + a^\dagger_{\lambda'}).
\]

Here \( \omega_{\lambda} \) denote the unperturbed vibrational frequencies, \( x_{\lambda} = \sqrt{\frac{\hbar}{2m \omega_{\lambda}} (a_{\lambda} + a^\dagger_{\lambda})} \) is the normal mode coordinate, and \( m \) is an effective mass.

II. VIBRATIONAL GREEN’S FUNCTION

We introduce two related vibrational retarded Green’s functions (GFs)

\[
D^r_{x,\lambda\lambda'}(t-t') = \frac{1}{i\hbar} \theta(t-t') \langle [x_{\lambda}(t), x_{\lambda'}(t')] \rangle
\]

and

\[
D^r_{\lambda\lambda'}(t-t') = -i \theta(t-t') \langle [A_{\lambda}(t), A_{\lambda'}(t')] \rangle,
\]

where \( A_{\lambda} = a_{\lambda} + a^\dagger_{\lambda} \) and the latter GF is the one considered in the main part of the paper. The two GFs are related simply by \( D^r_{x,\lambda\lambda'}(t) = D^r_{\lambda\lambda'}(t)/2m \sqrt{\omega_{\lambda} \omega_{\lambda'}} \).

A. Vibrational occupation and frequency renormalization

In this section we discuss the interpretation of the vibrational lesser GF and pinpoints its relation to the occupation of the renormalized vibration as well as problems encountered in the published literature. The main conclusion following our considerations is that for weak el-vib coupling, a rate-equation approach for the occupation of the renormalized vibration is essentially exact and can be recovered via a consistent renormalization scheme for the vibrational GF. For simplicity, we here restrict the discussion to the case of a single vibrational mode coupled linearly to the level occupation.
Using the equations of motion for the oscillator coordinates \( \dot{x}(t) = \frac{i}{\hbar} [x,H](t) = p(t)/m \), \( \dot{p}(t) = \frac{i}{\hbar} [p,H](t) = -m\omega_0^2 x(t) - iM \sqrt{2m\omega_0^3} d^3 d \) we can derive the following exact identities for the retarded GF,

\[
\lim_{t' \to t} D^r_x(t,t') = 0, \\
\lim_{t' \to t} \frac{\partial}{\partial t} D^r_x(t,t') = \frac{1}{i\hbar} \langle [\dot{x}(t),x(t)] \rangle = -\frac{1}{m}.
\]

These identities are exact also for interacting GFs governed by the full Hamiltonian \( H \) (actually, they hold not only for the considered occupation-coordinate coupling but for any interaction term as long as it does not contain the momentum operator \( p \)). Using the above relation between \( D^r_x(t) \) and \( D^r(t) \) together with the transformation to frequency domain, we derive the following exact sum rules for the vibrational spectral function \( A(\omega) \equiv -2\Im D^r(\omega) \)

\[
\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} A(\omega) = 0, \\
\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega A(\omega) = 2\omega_0.
\]

Once more, these identities hold generally also for interacting GFs. Note, that Eq. (10) contains the bare frequency \( \omega_0 \) regardless of the interaction and consequent renormalization of the value of the frequency. This has important implications for the structure of the interacting GFs as we will see shortly. For the free vibrational GF \( D^r_0(\omega) = \frac{1}{\omega - \omega_0 + i\gamma} \frac{1}{\omega + \omega_0 + i\gamma} = \frac{2\omega_0}{(\omega + \omega_0)^2 - \omega_0^2} \) we get the spectral function \( A(\omega) = 2\pi |\delta(\omega - \omega_0) - \delta(\omega + \omega_0)|\) satisfying trivially the above sum rules. When the interaction is included via the polarization operator \( \Pi^{\prime}(\omega) \) (vibrational self-energy) in the Dyson equation \( D^r(\omega)^{-1} = D^r_0(\omega)^{-1} - \Pi^{\prime}(\omega) \) one gets

\[
D^r(\omega) = \frac{2\omega_0}{\omega^2 - \omega_0^2 - 2\omega_0 R\Pi^{\prime}(\omega) - 2i\omega_0 \Im \Pi^{\prime}(\omega)} = \frac{\omega_0}{\Omega(\omega)} \cdot \frac{2\Omega(\omega)}{\omega^2 - \Omega^2(\omega) + i\Omega(\omega) \gamma(\omega)},
\]

with the renormalized frequency (so far being a function of the measurement frequency \( \omega \)) \( \Omega^2(\omega) \equiv \omega_0^2 + 2\omega_0 R\Pi^{\prime}(\omega) \) and the damping function \( \gamma(\omega) \equiv -2\Im \Omega^{\prime}(\omega) \omega_0 / \Omega(\omega) \).

For weak coupling when the linewidth is much smaller than the renormalized frequency \( \gamma(\omega) \ll \Omega(\omega) \), we can approximate Eq. (11) in the vicinity of the renormalized frequency \( \tilde{\omega}_0 \) by (kinetic approximation)

\[
D^r(\omega) \approx \frac{2\omega_0}{\omega^2 - \omega_0^2 + i\omega_0 \gamma} \approx \frac{\omega_0}{\tilde{\omega}_0} \times \left[ \frac{1}{\omega - \tilde{\omega}_0 + i\gamma/2} - \frac{1}{\omega + \tilde{\omega}_0 + i\gamma/2} \right],
\]

where \( \tilde{\omega}_0 \) is determined by the solution of the equation \( \tilde{\omega}_0^2 = \Omega^2_0(\tilde{\omega}_0) = \omega_0^2 + 2\omega_0 R\Pi^{\prime}(\tilde{\omega}_0) \approx \omega_0^2 + 2\omega_0 R\Pi^{\prime}(\omega_0) \) and \( \gamma(\omega) \equiv \gamma(\tilde{\omega}_0) \equiv -2\Im \Omega^{\prime}(\tilde{\omega}_0) \omega_0 / \tilde{\omega}_0 \). The corresponding spectral function is given by two Lorentzians of width \( \gamma \) also the multiplicative factor in front of the square bracket. This factor corresponds to the wave-function renormalization in the quantum-field-theoretic language and is necessary for the satisfaction of the sum rules (10). In order to emphasize its origin in the vibrational case considered here, we shall refer to it as the mode-renormalization factor.

Next, we turn to the vibrational lesser Green’s function \( D^<^{\prime}(\omega) \). It is determined by the Keldysh equation \( D^<^{\prime}(\omega) = D^r(\omega)\Pi^{\prime}(\omega)D^a(\omega) \) giving explicitly

\[
D^<^{\prime}(\omega) = \frac{4\omega_0^2 \Pi^{\prime}(\omega)}{[\omega^2 - \Omega^2(\omega)]^2 + 4\omega_0^2 \Im \Pi^{\prime}(\omega)^2} = -A(\omega) \frac{\Pi^{\prime}(\omega)}{2\Im \Pi^{\prime}(\omega)}.
\]

In the kinetic approximation (12) we can reformulate the above Eq. (13) as

\[
D^<^{\prime}(\omega) \approx -i\frac{\omega_0}{\tilde{\omega}_0} \times \left[ \frac{\gamma}{(\omega - \tilde{\omega}_0)^2 + (\gamma/2)^2} N(\tilde{\omega}_0) + \frac{\gamma}{(\omega + \tilde{\omega}_0)^2 + (\gamma/2)^2} (N(\tilde{\omega}_0) + 1) \right],
\]

with \( N(\tilde{\omega}_0) \equiv \frac{\Pi^{\prime}(\tilde{\omega}_0)}{2\Im \Pi^{\prime}(\tilde{\omega}_0)} \) defining the mean nonequilibrium occupation identical to the rate-equation expression [Eq. (6) of the main paper]. When \( D^<^{\prime}(\omega) \) in Eq. (14) is integrated over the frequency we get

\[
i \int \frac{d\omega}{2\pi} D^<^{\prime}(\omega) = \frac{\omega_0}{\tilde{\omega}_0} (2N(\tilde{\omega}_0) + 1).
\]
Notice that the integral is not simply yielding the expected quantity \( \langle 2a^\dagger a + 1 \rangle \) \( \approx 2N(\tilde{\omega}_0) + 1 \) but the mode-renormalization factor is involved. This together with the omission of the frequency renormalization is behind the reported discrepancies between the NEGF calculations and rate-equation predictions in Ref. 1 as we show in detail below.

From our analysis above, we conclude that the physically relevant occupation factor of the renormalized vibration (i.e., the occupation corresponding to, e.g., the experimental Raman temperature) should be identified from the ratio of lesser and retarded self-energies around the renormalized-frequency peak as in Eq. (14). For a renormalized vibration the integral of the lesser GF has per se no real physical meaning. The reason for this is that the lesser GF contains the sum \( (a + a^\dagger) = \sqrt{2m\omega_0}x_0 \) related to the physical normal mode coordinate \( x_0 \) via the frequency-dependent prefactor. However, the bare frequency \( \omega_0 \) is not the physically relevant true dynamical frequency of the renormalized oscillator. So instead of studying the GFs defined via \( a^\dagger \)s with \( \omega_0 \) we should redefine physical fields \( \tilde{a}, \tilde{a}^\dagger \) related to \( x_0 \) via the renormalized frequency \( \tilde{\omega}_0 \). Then \( D/2m\omega_0 = D_x = D/2m\omega_0 \) relating the GF in terms of renormalized fields \( D \) to the bare one considered everywhere above so far implying \( \tilde{D} = \frac{\omega_0}{\tilde{\omega}_0}D \) and consequently

\[
i \int \frac{d\omega}{2\pi} \tilde{D}^<(\omega) = 2N(\tilde{\omega}_0) + 1 \tag{16}\]

as expected.

"Comparison with results of D. F. Urban et al., Phys. Rev. B 82, 121414(R) (2010)"

We conclude this part by the direct comparison of our findings with those of Ref. 1. There, integral (15) is identified directly with the occupation number, i.e. \( \langle n \rangle = -\frac{1}{2} + \frac{i}{4\pi} \int d\omega D^<(\omega) \) (Ref. 1, p. 3). Rate equation formula gives \( N(\Omega) = \frac{V^2}{\pi \Omega} \) for \( V > \Omega, T = 0 \), and zero external damping \( \eta \) (cf. Eq. (10) in Ref. 1). Inserting the right hand-side of our Eq. (15) in the expression for \( \langle n \rangle \) above results in \( \langle n \rangle \approx \tilde{\omega}_0 \approx 0.19\tilde{\omega}_0 \). Frequency renormalization in the leading order reads in quantities of Ref. 1 (cf. their Eqs. (7)-(9)) \( \Pi \Pi^\dagger(\tilde{\omega}_0) \approx -\frac{\lambda^2}{\pi} \) which implies \( \tilde{\omega}_0 \approx \omega_0 \sqrt{1 - \frac{2\lambda^2}{\pi \omega_0}} \). When plugged into the above expression for \( \langle n \rangle \) we obtain for the parameters of Fig. 2(a) \( V = 5\omega_0, \omega_0/\Gamma = 0.01 \) the following results \( \langle n \rangle = 1.08 \approx 0.97\tilde{\omega}_0 \) for \( \lambda/\Gamma = 0.03 \) and \( \langle n \rangle = 1.26 \approx 0.92\tilde{\omega}_0 \) for \( \lambda/\Gamma = 0.05 \) which perfectly explain the asymptotic values for zero external damping \( \eta \to 0 \) shown in Fig. 2(a) of Ref. 1. It should be noticed that the expected rate equation result also does not coincide with the value \( N = 1 \) mentioned in Ref. 1 where the frequency renormalization was completely omitted. Instead the expected values are \( N(\tilde{\omega}_0) = 1.04, 1.11 \) for \( \lambda/\Gamma = 0.03, 0.05 \), respectively. These values are still different form those calculated for \( \langle n \rangle \) due to the neglect of the mode renormalization factor in Ref. 1.

B. Self-energy for the quadratic el-vib interaction

In the following we derive an expression for the lowest-order self-energy for the quadratic el-vib interaction in Eq. (5). Since the diagrammatic rules for nonequilibrium theory is structurally equivalent to equilibrium theory, it is sufficient to consider the time-ordered Green’s function at \( T = 0^2 \).

The time-ordered vibrational GF is defined as

\[
D_{\lambda\lambda'}(t,t') = -i\langle TA_{\lambda}(t)A_{\lambda'}(t')\rangle, \tag{17}\]

where \( T \) is the time-ordering operator.

In the interaction picture the time evolution of the operators is governed by the \( S \)-matrix

\[
S(t,t') = T \exp \left[ -i \int_t^{t'} dt_1 H_{\text{int}}(t_1) \right] \approx 1 - i \int_t^{t'} dt_1 T[H_{\text{int}}(t_1)] = \text{1-rms} \tag{18}\]

with the last equality giving the lowest-order expansion in the interacting part of the Hamiltonian \( H_{\text{int}} \) (in our case the el-vib interaction). The time-ordered GF can be written in terms of the \( S \)-matrix as

\[
D_{\lambda\lambda'}(t,t') = -i\langle T[A_{\lambda}(t)A_{\lambda'}(t')S(-\infty,\infty)]_0 \rangle / \langle S(-\infty,\infty) \rangle_0 = D_{\lambda\lambda'}^{\text{con}}(t,t') \tag{19}\]
where $\langle \cdot \rangle_0$ denotes the expectation value with respect to the noninteracting part of the Hamiltonian and $D_{\lambda\lambda'}^{\text{con}}(t,t')$ is the sum of connected diagrams in the numerator.

Considering now the quadratic el-vib interaction in Eq. (5) as the interacting part of the Hamiltonian, we insert the lowest-order expansion of the $S$-matrix into the numerator of Eq. (19) and identify the connected diagrams. Using Wick’s theorem on the product of time-ordered operators we get

$$\langle T [A_{\lambda}(t)A_{\lambda'}(t')]S(-\infty, \infty) \rangle_0 = \langle TA_{\lambda}(t)A_{\lambda'}(t') \rangle_0 - \frac{i}{2} \sum_{\lambda_1,\lambda_2} M_{\lambda_1\lambda_2}^{(2)} \int dt_1 \langle TA_{\lambda}(t_1)A_{\lambda_1}(t_1)A_{\lambda_2}(t_1) \rangle_0 (Td^+(t_1^+)d(t_1))_0$$

$$= \langle TA_{\lambda}(t)A_{\lambda'}(t') \rangle_0 - \frac{i}{2} \sum_{\lambda_1,\lambda_2} M_{\lambda_1\lambda_2}^{(2)} \int dt_1 \left[ \langle TA_{\lambda}(t_1)A_{\lambda'}(t_1)A_{\lambda_2}(t_1) \rangle_0 \right]_{\text{disconnected}}$$

$$+ \frac{1}{\delta_{\lambda_1,\lambda_2}} \left[ \langle TA_{\lambda}(t_1)A_{\lambda_1}(t_1)A_{\lambda'}(t') \rangle_0 + \langle TA_{\lambda}(t_1)A_{\lambda_2}(t_1)A_{\lambda'}(t') \rangle_0 \right] (Td^+(t_1^+)d(t_1))_0. \quad (20)$$

For the GF we thus have

$$D_{\lambda\lambda'}(t,t') = D_{\lambda\lambda'}^0(t,t') + \int dt_1 D_{\lambda\lambda'}^0(t,t_1) \left[ -i G(t_1,t_1^+) M_{\lambda\lambda'}^{(2)}(t_1,t') \right] D_{\lambda\lambda'}^0(t_1,t')$$

$$= D_{\lambda\lambda'}^0(t,t') + \int dt_1 \int dt_2 D_{\lambda\lambda'}^0(t,t_1) \Pi_{\lambda\lambda'}^{(2)}(t_1,t_2) D_{\lambda\lambda'}^0(t_2,t'), \quad (21)$$

where $D_{\lambda\lambda'}^0 = \delta_{\lambda\lambda'} D_{\lambda\lambda'}^0$ is the noninteracting GF and $G(t,t') = -i (Td(t)d(t'))$ is the time-ordered electronic GF. In the last equation, we have identified the irreducible lowest-order self-energy for the quadratic el-vib interaction as

$$\Pi_{\lambda\lambda'}^{(2)}(t,t') = -i M_{\lambda\lambda'}^{(2)} \delta(t-t') G(t,t^+)$$

with the retarded and lesser versions given by

$$\Pi_{\lambda\lambda'}^{(2),r}(t-t') = -i M_{\lambda\lambda'}^{(2)} \delta(t-t') G^< (t-t' = 0)$$

$$\Pi_{\lambda\lambda'}^{(2),<}(t-t') = 0. \quad (24)$$

In frequency domain they become

$$\Pi_{\lambda\lambda'}^{(2),r} (\omega) = -i M_{\lambda\lambda'}^{(2)} \int \frac{d\varepsilon}{2\pi} G^< (\varepsilon)$$

$$\Pi_{\lambda\lambda'}^{(2),<} (\omega) = 0. \quad (26)$$

### III. FIRST-PRINCIPLES CALCULATIONS

In this section we present the results of our first-principles calculations of the vibrational Stark shifts and el-vib interactions for the OPV3 molecule. All calculations were performed with the GPAW electronic structure package\textsuperscript{4,5} using the finite-difference method for the calculation of the molecular vibrations and el-vib interactions\textsuperscript{6-7}. The calculations have been carried out on the isolated amine-terminated OPV3 molecule, thus neglecting direct effects of lead electrodes on the calculated quantities.

#### A. Vibrational Stark shifts

In order to clarify the role of the vibrational Stark effect\textsuperscript{8} in the shifts of the Raman lines observed in Ref. 9, we have calculated the vibrational frequencies of the OPV3 molecule in the presence of an electric field along the backbone axis of the molecule. The vibrational Stark shifts have been obtained as the change $\Delta\omega_\lambda$ in the vibrational frequencies in the presence of a potential drop $V$ along the longest axis of the computational unit cell of the isolated molecule ($L \sim 3$ nm) corresponding to a constant electric field $E = V/L$ over the extend of the molecule.

Figure 1 shows the resulting frequency shifts $\Delta\omega_\lambda$ for different values of the potential drop over the molecule. For all modes with $\omega_\lambda > 60$ meV no significant effect of the electric field is observed. We also note that the Stark effect is static and does not produce linewidth broadening. We therefore conclude that the Stark effect is not a likely source of the frequency shifts and linewidth broadening observed in Ref. 9.
B. El-vib interactions

The el-vib interactions in Eqs. (4) and (5) have been obtained following the approach outlined in Ref. 6. Within this approach, the el-vib interactions for the molecular orbital $\psi_0$ of the isolated molecule can be expressed as

$$M^{(1)}_\lambda = \sqrt{\frac{\hbar}{2M\omega_\lambda}} \langle \psi_0 | \hat{e}_\lambda \cdot \nabla H | \psi_0 \rangle,$$

and

$$M^{(2)}_{\lambda\lambda'} = \frac{\hbar}{2M\sqrt{\omega_\lambda \omega_{\lambda'}}} \langle \psi_0 | \hat{e}_\lambda \cdot \nabla \nabla H \cdot \hat{e}_{\lambda'} | \psi_0 \rangle,$$

for the linear and quadratic el-vib interaction, respectively. Here, $M$ is an appropriately defined effective mass, $\hat{e}_\lambda$ is the mass-scaled vibrational normal mode vector normalized according to $\sum_{\alpha} (M_\alpha/M) |\hat{e}_{\lambda\alpha}|^2 = 1$ where $M_\alpha$ is the mass of atom $\alpha$, and the gradient of the Hamiltonian $H$ is with respect to atomic displacements. The expressions (27) and (28) can be understood as the first-order change in the orbital energy $\varepsilon_0$ due to the atomic displacements associated with the vibrational normal modes.

The calculation of the el-vib couplings in Eqs. (27) and (28) have been performed using the finite-difference method$^6$. The implementation for the calculation of the linear el-vib interaction in the GPAW package is outlined in Ref. 7. For the quadratic el-vib interaction, the couplings have been obtained as the second-order derivative of the orbital energy $\varepsilon_0$ with respect to a unit displacements $u_\lambda$ in the normal mode directions,

$$M^{(2)}_{\lambda\lambda'} = \frac{\hbar}{2M\sqrt{\omega_\lambda \omega_{\lambda'}}} \frac{\partial^2 \varepsilon_0}{\partial u_\lambda \partial u_{\lambda'}}.$$

The calculated couplings for the OPV3 molecule are summarized in Fig. 2 which shows the absolute value of the linear (left) and diagonal elements of the quadratic (right) el-vib couplings. For both the linear and quadratic interaction, the couplings to the HOMO and LUMO orbitals are highly mode sensitive. The linear couplings are rather small ($|M^{(1)}_\lambda| < 5$ meV) for many of the modes and therefore hardly have any impact on the corresponding spectral lines (see below). The quadratic couplings are negative ($M^{(2)}_{\lambda\lambda} < 0$) for the majority of modes. This corresponds to frequency softening and hardening for charging of the LUMO and HOMO, respectively (charging of a filled HOMO corresponds to electron removal, implying that the associated frequency shift has the opposite sign of the quadratic coupling). These findings are in good agreement with a recent study of charging-induced frequency shifts in molecular junctions$^{10}$.

IV. OPV3 SPECTRAL FUNCTION

In this section we present the details of the calculation of the vibrational spectral function for the OPV3 junction, as well as results for both HOMO and LUMO dominated transport.
A. Calculational details

The spectral function of the OPV3 junction is obtained from the full non-diagonal GF (cf. Eq. (1) of the main paper)

$$D^r(\omega) = \left[(D_0(\omega))^{-1} - \Pi^r(\omega)\right]^{-1},$$

where carrier-induced mode-mode couplings are accounted for via the off-diagonal elements of the electronic part $\Pi^{el}$ of the total self-energy $\Pi = \Pi^{el} + \Pi^{ph}$. The bare GF $D_0(\omega)$ is here given by that of the isolated neutral molecule with frequencies $\omega_{\lambda}$.

Following our footnote in Ref. 29 of the main paper, effects already included in the frequencies $\omega_{\lambda}$ of the isolated molecule have to be removed from the self-energy in Eq. (30) in order to avoid double counting. Screening effects due to eh-pair excitations are not included in the frequencies $\omega_{\lambda}$ of the isolated molecule (no lead-induced broadening of the electronic levels) and the self-energy of the linear el-vib interaction should therefore not be corrected. On the other hand, charging effects described by the self-energy of the quadratic el-vib interaction, must be measured relative to the level occupations in the neutral molecule. The self-energy is therefore corrected according to

$$\Pi^{el}(\omega) \rightarrow \Pi^{el}(\omega) - \Pi^{el}_{mol}(\omega),$$

where $\Pi^{el}_{mol}$ is the self-energy correction of the neutral isolated molecule given solely by the quadratic self-energy correction as

$$\Pi^{el}_{mol,\lambda\lambda'}(\omega) = \Pi^{(2)}_{\lambda\lambda'}(\omega) = \langle n_i \rangle M^{(2)}_{\lambda\lambda'} = \begin{cases} 2M^{(2)}_{\lambda\alpha}, & i=\text{HOMO} \\ 0, & i=\text{LUMO}. \end{cases}$$

Here the factor of 2 accounts for the spin degeneracy of the HOMO level.

B. Results

The calculated spectral functions for HOMO and LUMO dominated transport are shown in Figs. 3 and 4, respectively. Due to the large variation in the el-vib couplings to the different vibrational modes, carrier-induced shift and broadening of the spectral lines is highly mode dependent. Overall, the quadratic el-vib interaction gives rise frequency softening and hardening for LUMO and HOMO dominated transport, respectively. However, for the high-energy modes with positive quadratic coupling to the HOMO (see Fig. 2) this does not hold. On top of the frequency renormalization given by the quadratic el-vib interaction, the modes with the strongest the linear el-vib
FIG. 3: (Color online) Vibrational spectral function $A(\omega)$ as a function of bias voltage for HOMO-dominated transport in the OPV3 junction (top: full spectral function; bottom: projection onto vibrations with linear coupling $|M_\Lambda^{(1)}| > 5$ meV). Except for the level position, the junction parameters are the same as those used in Fig. 3 of the main paper, i.e. $\varepsilon_0 = -0.5$ eV, $\mu_{L/R} = \pm V/2$, $\Gamma_{L/R} = 0.2$ eV, and $\gamma_{ph} = 1$ meV.

interaction experience additional renormalization and pronounced spectral broadening with increasing bias voltage. The frequency renormalization originating from the linear el-vib interaction corresponds to frequency softening, and thus compensates for (adds to) the renormalization due to the quadratic interaction for HOMO (LUMO) dominated transport. For most of the modes with a significant linear el-vib coupling, the two effects are of the same order of magnitude. As mentioned in the main paper, the relative magnitude of the two effects is sensitive to junction parameters such as the level alignment and lead-induced level broadening. A situation where one effect dominates the other may therefore be realized with a different choice of junction parameters. As a final remark, we note that some of the closely lying spectral lines show complex bias dependencies at high bias which is an indication of carrier-induced mode-mode couplings.
FIG. 4: (Color online) Vibrational spectral function $A(\omega)$ as a function of bias voltage for LUMO-dominated transport in the OPV3 junction (top: full spectral function; bottom: projection onto vibrations with linear coupling $|M_\lambda^{(1)}| > 5$ meV). The junction parameters are the same as those used in Fig. 3 of the main paper, i.e. $\varepsilon_0 = 0.5$ eV, $\mu_{L/R} = \pm V/2$, $\Gamma_{L/R} = 0.2$ eV, and $\gamma_{ph} = 1$ meV.

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