Mechanical Stabilization of Nano-scale Conductors by Plasmon Oscillations

Supplementary Information

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Rate equations for molecular junctions with time-dependent molecule-lead coupling in the presence of vibronic coupling

A. Transient transfer rates in the weak molecule-lead coupling limit

Here we review the rate equation formulation for transport through a molecular junction with time-dependent molecule-lead couplings. This formulation was originally introduced in Ref. 34, and here it is generalized to include vibronic coupling on the molecule. We consider the generic model Hamiltonian for a molecular junction composed of a molecule (M), and two (L and R) leads,

\[
\hat{H} = \hat{H}_M + \hat{H}_R + \hat{H}_L + \left[ \hat{H}_{MR}(t) + \hat{H}_{ML}(t) + \text{h.c.} \right].
\]  

(S1)

The time-dependent molecule-leads couplings read (for \( K \in L, R \)),

\[
\hat{H}_{MK}(t) = g^{(K)}(t)\hat{V}_M^{(K)} \otimes \hat{V}_K^+, 
\]  

(S2)

where, for time-periodic coupling, with a period, \( T = \frac{2\pi}{\omega} \), one has,

\[
g^{(K)}(t) \equiv \sum_{l=-\infty}^\infty e^{il\omega t} g^{(K)}_l; \quad g^{(K)}_l = \frac{1}{T} \int_0^T dt e^{-il\omega t} g^{(K)}(t) 
\]  

(S3)

For weak molecule-lead coupling it is useful to define a zero-order Hamiltonian,

\[\hat{H}_0 = \hat{H}_M + \hat{H}_R + \hat{H}_L,\]

associated with the time evolution operator, \( U_0(t,0) \equiv e^{\frac{-i}{\hbar} \hat{H}_0 t} \), and a time-dependent perturbation, \( \hat{V}(t) = \hat{H}_{MR}(t) + \hat{H}_{ML}(t) + \text{h.c.} \). Transforming the operators into the
interaction representation, \( \hat{O}^j(t) = U^+_0(t,0)\hat{O}(t)U_0(t,0) \), and neglecting terms beyond second order in \( \hat{V}_j(t) \), the exact Liouville-von Neumann equation for the entire system is approximated as [36],

\[
\frac{d}{dt}\hat{\rho}^j(t) \equiv -\frac{i}{\hbar} [\hat{V}^j(t), \hat{\rho}^j(0)] - \frac{1}{\hbar^2} \int_0^t dt' [\hat{V}^j(t), [\hat{V}^j(t'), \hat{\rho}^j(t)]] .
\]  

(S4)

The focus of interest is the projection of the full density operator onto the subspace of molecular degrees of freedom, defined as, \( \hat{\rho}_M(t) \equiv tr_{L,R}[\hat{\rho}(t)] \), where,

\[
\frac{d}{dt}\hat{\rho}_M(t) = -\frac{1}{\hbar^2} \int_0^t dt' tr_{L,R}[\hat{V}^j(t), [\hat{V}^j(t'), \hat{\rho}^j(t)]] .
\]  

(S5)

Following the Redfield approach[35,36], in consistency with the second order accuracy in the molecule-leads coupling in Eq. (S4), the density operator under the time-integral is approximated as \( \hat{\rho}^j(t) \approx \hat{\rho}_L \otimes \hat{\rho}^j_R(t) \). Here \( \hat{\rho}_L \) and \( \hat{\rho}_R \) are the equilibrium densities of the separated leads, corresponding to grand canonical ensembles of non-interacting fermions,

\[
\hat{\rho}_K = \frac{e^{-\hat{H}_K - \mu_K \hat{N}_K}}{tr\{e^{-\hat{H}_K - \mu_K \hat{N}_K}\}} .
\]

The respective chemical potentials are denoted \( \mu_K \) and \( \mu_L \), and \( \hat{N}_K \) is the number operator for the \( K^{th} \) lead. Utilizing the fact that (see below), \( tr_K \{\hat{V}_R \rho_R\} = tr_L \{\hat{V}_L \rho_L\} = 0 \) in Eq.(S5), a closed equation is obtained for the reduced molecular density,

\[
\frac{d}{dt}\hat{\rho}_M(t) = -\frac{i}{\hbar} [\hat{H}_M, \hat{\rho}_M(t)] - \frac{1}{\hbar^2} \int_0^t dt' tr_{L,R}[\hat{V}(t), [U_0(t,t')\hat{V}(t')U_0^+(t,t'), \hat{\rho}_L \otimes \hat{\rho}_R \hat{\rho}_M(t)]] .
\]  

(S6)

The second term in the right hand side accounts for the molecule lead interactions. Using the explicit form of the coupling operators, \( \hat{V}(t) = g^{(R)}(t)\hat{V}^{(R)}_M \otimes \hat{V}^+_R + g^{(L)}(t)\hat{V}^{(L)}_M \otimes \hat{V}^+_L + h.c. \), and the product form of the zero order propagator, \( U_0(t,t') = U_M(t-t') \otimes U_R(t-t') \otimes U_L(t-t') \), Eq. (S6) can be rewritten as,
\[\frac{d}{dt} \hat{\rho}_M(t) = -i\frac{\hbar}{2}\{\hat{H}_M, \hat{\rho}_M(t)\} \]
\[- \sum_{k=L,R} \left[ g^{(K)}(t)\hat{V}_M^{(K)}(t)\hat{\rho}_M(t)\right] - [g^{(K)}(t)\hat{V}_M^{(K)}(t)\hat{\rho}_M(t)\hat{F}_M^{(K)}(t)] + \text{h.c.} \}

(S7)

The molecular space operators, \(\hat{F}_M^{(K)}(t)\) and \(\hat{F}_M^{(K)}(t)\) are defined as,
\[
\hat{F}_M^{(K)}(t) = \frac{1}{\hbar^2} \int_0^t dt' g^{(K)*}(t')\hat{C}_K(t-t')U_M(t-t')\hat{V}_M^{(K)}U_M^+(t-t')
\]
and the lead correlation functions are,
\[
\hat{C}_K(t-t') = \text{tr}_K\{\hat{V}_K^U(t-t')\hat{V}_K^U(t-t')\hat{\rho}_K\}
\]
\[
C_k(t-t') = \text{tr}_K\{\hat{V}_k^U(t-st')\hat{V}_k^U(t-t')\hat{\rho}_K\}
\]

For the analysis of steady-state molecular observables in the weak molecule-leads coupling limit, it is instructive to study Eq.(S7) in the basis of the molecular eigenstates, defined by,
\[\hat{H}_M |n\rangle = E_n |n\rangle\]. Focusing on the eigenstate populations dynamics, and neglecting the coupling to coherences, when the molecule-lead coupling energy is much smaller than the energy gaps between the molecular eigenstates, Eq. (S7) yields,
\[
\frac{d}{dt} [\hat{\rho}_M(t)]_{n,n} = -2\text{Re}\sum_{k=L,R} g^{(K)}(t)\sum_{k',k} [\hat{V}_M^K(n,k)\hat{\hat{F}}_M^{(K)}(t)_{k,k'}[\hat{\rho}_M(t)]_{k',n}]
\]
\[-[\hat{F}_M^{(K)}(t)]_{n,k'}[\hat{\rho}_M(t)]_{k,n} - [\hat{V}_M^K(n,k)\hat{\hat{F}}_M^{(K)}(t)_{k,k'}[\hat{\rho}_M(t)]_{k,n}]
\]+[\hat{\rho}_M(t)]_{n,k'}[\hat{F}_M^{(K)}(t)_{k,k'}[\hat{V}_M^K(n,k')]]
\approx -2\text{Re}\sum_{k=L,R} g^{(K)}(t)\sum_{k} [(\hat{V}_M^K(n,k)\hat{\hat{F}}_M^{(K)}(t)_{k,n}[\hat{\rho}_M(t)]_{n,n}]
\[-[\hat{F}_M^{(K)}(t)]_{n,k}[\hat{\rho}_M(t)]_{k,n} - [\hat{V}_M^K(n,k)\hat{\hat{F}}_M^{(K)}(t)_{k,n}[\hat{\rho}_M(t)]_{n,n}]
\]+[\hat{\rho}_M(t)]_{n,k}[\hat{F}_M^{(K)}(t)_{n,k}[\hat{V}_M^K(n,k)]]
\]

Denoting the eigenstate populations as, \([\hat{\rho}_M(t)]_{n,n} = \rho_n(t)\), and defining transient population transfer rates,
\[ \Gamma_{n \to k}^{(K)}(t) = 2 \text{Re}\{ g_{\ell}^{(K)}(t)[\hat{V}_{M}^{(K)}]_{n,\ell}[\hat{E}_{M}^{(K)}(t)]_{\ell,n} + [\hat{V}_{M}^{(K)}]_{k,\ell}[F_{M}^{(K)}(t)]_{\ell,n} \} \], \quad (S11) \]

Eq. (S10) is rewritten as a quantum master equation,

\[ \frac{d}{dt}\rho_n(t) = -\sum_{K=L,R} \sum_{k} \Gamma_{n \to k}^{(K)}(t)\rho_n(t) + \sum_{K=L,R} \sum_{k} \Gamma_{k \to n}^{(K)}(t)\rho_k(t) \]  

Using the Fourier expansion of the periodic molecule-lead interaction, Eq. (S3), one obtains,

\[ \Gamma_{n \to k}^{(K)}(t) = \frac{2}{\hbar^2} \text{Re}\{ \sum_{\ell,l=0}^{\infty} \bar{g}_{\ell}^{(K)}(\bar{g}_{l}^{(K)})^* e^{i\omega(l-\ell)t} \} \]

\[ (|[\hat{V}_{M}^{(K)}]_{n,\ell}|^2 \int_0^t d\tau \bar{C}_{K}(\tau)e^{i(\xi_{\ell,l} - \xi_{\ell})/\hbar}) + |[\hat{V}_{M}^{(K)}]_{k,\ell}|^2 \int_0^t d\tau C_{K}(\tau)e^{i(\xi_{\ell,l} - \xi_{\ell})/\hbar}) \} \], \quad (S13) \]

**B. The wide band limit**

We now consider explicitly the non-interacting lead Hamiltonians (\( K \in L,R \)), and the molecule-lead coupling operators (in the lead space), defined as,

\[ \hat{H}_K = \sum_{k_x} \xi_{k_x} \hat{b}_{k_x}^{\dagger} \hat{b}_{k_x} \quad ; \quad \hat{V}_K^{\dagger} = \sum_{k_x} \xi_{k_x} \hat{b}_{k_x}^{\dagger} \]

\[ \hat{b}_{k_x}^{\dagger} \text{ is the electron creation operator in the single particle state at the } K \text{ th lead, } \xi_{k_x} \text{ is the corresponding lead orbital energy, and } \xi_{k_x} \text{ is the respective molecule-lead coupling parameter.} \]

For this model, the lead correlation functions (Eq. (S9)) take the explicit forms,

\[ \bar{C}_{K}(\tau) = \sum_k |\xi_{k}|^2 e^{\frac{i\xi_{k}\tau}{\hbar}} f_{K}(\xi_{k}) \quad ; \quad C_{K}(\tau) = \sum_k |\xi_{k}|^2 e^{\frac{i\xi_{k}\tau}{\hbar}} [1 - f_{K}(\xi_{k})] \], \quad (S15) \]

where, \( f_{K}(\xi) \) is the Fermi distribution function, \( f_{K}(\xi) \equiv (1 + e^{\frac{(\xi - \mu_K)}{k_B T}})^{-1} \). For a dense electrode spectrum, the summation can be replaced by an integral over the lead spectral density,

\[ \sum_{k} |\xi_{k}|^2 \rightarrow \frac{1}{2\pi} \int d\xi J_{K}(\xi) \], \text{ where, } J_{K}(\xi) = 2\pi \sum_{k} \delta(\xi_{k} - \xi)|\xi_{k}|^2, \text{ which yields,} \]
The wide-band limit assumes that the electrode band is sufficiently wide, and that $J_k(\varepsilon)$ is a sufficiently smooth function of the energy, such that the time integrals in Eq.(S16) converge for any (field-displaced) molecular transition energy, $\Delta_{n,k,l'} \equiv E_n - E_k - \hbar \omega l'$. While this strictly holds only for an infinite uniform band, it holds approximately also for a finite smooth band, as long as the transition energy, $\Delta_{n,k,l'}$, is within the band, for any $(n,k,l')$. More precisely, this condition translates to, $\varepsilon_{\text{min}} < \Delta_{n,k,l'} < \sim \mu_k$, and $\sim \mu_k < \Delta_{n,k,l'} < \varepsilon_{\text{max}}$, for the first and second contributions to the time integral in Eq.(S16), respectively. Here $\varepsilon_{\text{min}}$ and $\varepsilon_{\text{max}}$ are the band edges, and $\sim \mu_k$ corresponds to the lead chemical potential, with some uncertainty owing to thermal broadening of the Fermi distribution. These conditions can trivially hold when the molecular spectrum is bounded (and therefore $E_n - E_k$ is bounded) and in the absence of a driving field (where, $l'$ is restricted to zero).

Nevertheless, the wide band limit can still hold for a finite band width even in the presence of a driving field and/or an unbounded molecular spectrum, as long as the following conditions are satisfied. First, the driving function, $g^{(K)}(t)$, must be band limited, namely,

$$\hat{g}^{(K)}_{l'}(t) \xrightarrow{t \to \pm \infty} 0.$$  \hfill (S17)

Second, the representation of the molecular coupling operator, $\hat{V}_M^{(K)}$, in the molecular eigenstate basis, must be a band matrix, namely,

$$\hat{V}_M^{(K)}(n,k) \xrightarrow{|n-k| \to \infty} 0.$$  \hfill (S18)
The restrictions, Eqs. (S17,S18), guarantee that contributions associated with diverging values of \( E_n - E_k - \hbar \omega \)' are filtered out from the time integrals in Eq. (S16), such that all the contributing values are confined within a finite energy band. Assuming a uniform spectral density of the electrode within this band, we therefore set,

\[
J_K(\varepsilon) = \Gamma_K \quad ; \quad \varepsilon_{\text{min}} < \varepsilon < \varepsilon_{\text{max}},
\]

The convergence time of the remaining integrals, \( \int_0^t d\tau \int_{\varepsilon_{\text{min}}}^\varepsilon e^{i(\varepsilon - (E_n - E_k - \hbar \omega))\tau}/\hbar \), and, \( \int_0^t d\tau \int_{\varepsilon_{\text{min}}}^\varepsilon e^{i(\varepsilon - (E_n - E_k - \hbar \omega))\tau}/\hbar \), is limited by the shortest oscillation period, and therefore it is set by the band width, namely, \( \tau_d \sim \frac{2\pi\hbar}{|\varepsilon_{\text{max}} - \varepsilon_{\text{min}}|} \). Restricting the following discussion to driving field periods which are much longer than \( \tau_d \), namely, \( \frac{|\varepsilon_{\text{max}} - \varepsilon_{\text{min}}|}{\hbar} \gg \omega \),

the upper limit of the time integrals in Eq. (S16) can be taken to infinity with a negligible effect on the result. The wide band limit of the transfer rates therefore reads,

\[
\Gamma^{(K)}_{n\rightarrow k} (t) \frac{1}{\pi \hbar^2} \Gamma_K \text{Re} \left\{ \sum_{l,l'=\omega}^{\infty} \bar{g}_l^{(K)}(g_l^{(K)})^* e^{i(m-l-\omega)t} \right\}
\]

\[
(|\hat{V}^{(K)}_M| )^2 \int_0^\infty \int_0^\infty d\varepsilon \int d\varepsilon f_K(\varepsilon) e^{i\varepsilon (E_n - E_k - \hbar \omega))/\hbar}
\]

\[
+ |\hat{V}^{(K)}_M| e^{i\varepsilon (E_n - E_k - \hbar \omega))/\hbar}) \}
\]

\[\textit{C. Time-averaged rates}\]

Owing to the explicit driving field oscillations associated with the terms \( e^{i\omega (m-l-\omega)t} \) in Eq. (S21), the transfer rates, \( \Gamma^{(K)}_{n\rightarrow k} (t) \), remain time-dependent even when wide band limit can be applied. However, in many cases of interest, the time-period of the driving field is much
shorter than the typical times for population transfer between the system eigenstates. In such cases, it is instructive to replace the transient rates in the master equation (Eq. (S12)) with their time average over the driving field period. The rate equations become,

$$\frac{d}{dt} \rho_n(t) \equiv - \sum_{K=L,R} \sum_k \Gamma^{(K)}_{n \rightarrow k} \rho_n(t) + \sum_{K=L,R} \sum_k \Gamma^{(K)}_{k \rightarrow n} \rho_k(t), \quad (S22)$$

with the averaged rates defined as,

$$\Gamma^{(K)}_{n \rightarrow k} = \frac{1}{T} \int_0^T dt \, \Gamma^{(K)}_{n \rightarrow k}(t'), \quad (S23)$$

which holds when the field frequency is larger than the transfer rate for any $n$ and $k$,

$$\omega >> \{\Gamma^{(K)}_{n \rightarrow k}\}. \quad (S24)$$

Invoking the wide band result for the transient rates (Eq. (21)), the time-averaged rates read,

$$\Gamma^{(K)}_{n \rightarrow k} = \frac{\Gamma_K}{\hbar} \sum_{l=-\infty}^{\infty} |g^{(K)}_{l}|^2 \{ [\hat{V}_{M}^{(K)}]_{n,k} | \hat{f}_K (E_n - E_k - \hbar \omega l) |^2 + [\hat{V}_{M}^{(K)}]_{k,n} | 1 - \hat{f}_K (E_n - E_k - \hbar \omega l) |^2 \}. \quad (S25)$$

It is instructive to express the time-averaged rate in terms of an averaged (generalized) Fermi distribution function,

$$\bar{f}_K (E_n - E_k) = \sum_{l=-\infty}^{\infty} |g^{(K)}_{l}|^2 \hat{f}_K (E_n - E_k - \hbar \omega l), \quad (S26)$$

where, for, $\sum_{l=-\infty}^{\infty} |g^{(K)}_{l}|^2 = 1$ (see below), we obtain,

$$\Gamma^{(K)}_{n \rightarrow k} = \frac{\Gamma_K}{\hbar} \{ [\hat{V}_{M}^{(K)}]_{n,k} | \bar{f}_K (E_n - E_k) |^2 + [\hat{V}_{M}^{(K)}]_{k,n} | 1 - \bar{f}_K (E_n - E_k) |^2 \}. \quad (S27)$$

**D. Application to the monochromatically driven Holstein model**

We now consider an explicit minimal model for the molecular Hamiltonain, in which a single electronic orbital is coupled to a single harmonic vibrational mode (the Holstein model[21]),


\[ \hat{H}_M = \hat{h}_i a_i^\dagger a_i + \hat{h}_o a_o a_i^\dagger, \]
\[ \hat{h}_o = \hbar \Omega c^\dagger c, \]
\[ \hat{h}_i = \varepsilon_i + \hbar \Omega c^\dagger c + \lambda (c^\dagger + c) / \sqrt{2} \]  

(S28)

\( a_i^\dagger \) creates an electron in the molecular orbital associated with the charging energy, \( \varepsilon_i \), where the vibrational Hamiltonians, \( \hat{h}_o = \hbar \Omega c^\dagger c \), and \( \hat{h}_i = \varepsilon_i + \hbar \Omega c^\dagger c + \lambda (c^\dagger + c) / \sqrt{2} \), correspond to the empty and charged states of the orbital, respectively. \( c^\dagger \) creates a vibration quantum on the molecule at a frequency \( \Omega \), and \( \lambda \) is the vibronic coupling parameter.

The undriven lead Hamiltonians are defined in Eq. (S14). We consider a particular model in which plasmon oscillations drive monochromatically the left lead (only), namely, \( \hat{H}_L \rightarrow \hat{H}_L + \alpha \cos(\omega t) \), where \( \alpha \) and \( \omega \) are the field intensity and frequency, respectively. Performing a unitary transformation[34], the time-dependence is transferred from the leads Hamiltonian to the molecule–lead coupling operators, which take the form,

\[ \hat{H}_{MR} = \hat{a}_i \sum_{k_e} \xi_{k_a} \hat{b}_e^\dagger; \quad \hat{H}_{ML}(t) = e^{i \frac{\alpha}{\hbar} \sin(\omega t)} \hat{a}_i \sum_{k_e} \xi_{k_e} \hat{b}_e^\dagger. \]  

(S29)

where we identify,

\[ \hat{V}_{M}^{(L)} = \hat{V}_{M}^{(R)} = \hat{a}_i. \]  

(S30)

The eigenstates of the molecular Hamiltonians, Eq. (S28), are products, \( |n\rangle \otimes |v_n\rangle \), where \( |n\rangle \) is the electronic orbital occupation state, \( (n \in 0, 1) \) and the vibrational states are defined by,

\[ \hat{h}_n |v_n\rangle = E_{v_n} |v_n\rangle. \]  

(S31)

The matrix elements of the molecular coupling operators, \( \hat{V}_{M}^{(K)} \), therefore obtain the form,

\[ |\left[ \hat{V}_{M}^{(K)} \right]_{(m,v_\lambda),(n,v_n)}|^2 = \delta_{n,m} \delta_{v_\lambda v_n} |\langle v_0 | v_1 \rangle|^2. \]  

(S32)

where \( \langle v_0 | v_1 \rangle \) are Franck Condon overlap integrals between displaced harmonic vibrational eigenfunctions associated with the two charging states of the molecule.
We now notice that the basic requirements for invoking the wide band approximation are fulfilled for the present model. In particular, the FC integrals decay to zero for arbitrarily large differences between the vibrational quantum numbers $\nu_0$, and $\nu_1$, such that Eq. (S18) is satisfied. Additionally, expanding the driving function in Eq. (S29) as Fourier series, one obtains,

$$e^{i\frac{\alpha}{\hbar}\sin(\omega t)} = \sum_{l=-\infty}^{\infty} e^{il\alpha g_l(R)} ; \quad g_l(R) = J_l\left(\frac{\alpha}{\hbar\omega}\right),$$  \hspace{1cm} (S33)

where, $J_l$ is the Bessel function of order $l$, which satisfies, \(J_l\left(\frac{\alpha}{\hbar\omega}\right) \rightarrow 0\), in line with Eq. (S17). Practically, since the wide band limit requires, $\varepsilon_{\min} < E_{\nu_o} - E_{\nu_s} - \hbar\omega l < \varepsilon_{\max}$, and since $\alpha$ sets the range of non vanishing values of $\hbar\omega l$, the wide band limit holds for field intensities satisfying,

$$\alpha << \varepsilon_{\max} - \varepsilon_{\min}.$$  \hspace{1cm} (S34)

The validity of the time-averaged rate equations is restricted to a specific range of driving field frequencies. In particular, the driving frequency should be small in comparison to the electrode band-width frequency, Eq. (S20), but large in comparison to the eigenstate population transfer rates, Eq. (S24). The latter can be expressed in terms of the model parameters. Noticing that each vibronic state of the charged molecule, \(|\nu_1\rangle\), can be mapped uniquely onto a specific state of the uncharged molecule, \(|\mu_0\rangle\) at energy $E_{\mu_0}$, where,

\[|\nu_1\rangle = e^{i\Omega\frac{1}{\hbar}\omega (\nu_1 - \nu_0)} |\mu_0\rangle,\]

and $E_{\nu_1} = \varepsilon_{\nu_1} - \lambda^2 / (\hbar\Omega)^2 + E_{\mu_0} \equiv \bar{\nu} + E_{\mu_0}$, the FC integrals obtain the form,

\[\langle \nu_0 | \nu_1 \rangle = \langle \nu_0 | e^{i\Omega\frac{1}{\hbar}\omega (\nu_1 - \nu_0)} |\mu_0\rangle.\]

In the present work we focus on weak vibronic coupling, $\lambda / (\hbar\Omega) << 1$, which yields, \[\langle \nu_0 | \nu_1 \rangle \approx \delta_{\nu_0,\nu_1} + \frac{\lambda}{\hbar\Omega} \sqrt{\mu_0 + 1} \delta_{\mu_0 + 1,\nu_0} - \frac{\lambda}{\hbar\Omega} \sqrt{\mu_0} \delta_{\mu_0 - 1,\nu_0}.\]

Substitution in Eq. (S27), the non-vanishing state-to-state population transfer rates obtain the form,
\[
\Gamma_{0, v_0 \rightarrow 1, j_0}^{(K)} = \frac{\Gamma^K}{\hbar} \left[ \delta_{v_0, j_0} \bar{f}_K(\bar{\epsilon}) + \delta_{v_0, j_0} \left( \frac{\lambda}{\hbar \Omega} \right)^2 \nu_0 \bar{f}_K(\bar{\epsilon} - \hbar \Omega) \right] + \delta_{j_0, v_0 + 1} \left( \frac{\lambda}{\hbar \Omega} \right)^2 (\nu_0 + 1) \bar{f}_K(\bar{\epsilon} + \hbar \Omega).
\]

\[
\Gamma_{1, v_0 \rightarrow 0, j_0}^{(K)} = \frac{\Gamma^K}{\hbar} \left[ \delta_{v_0, j_0} [1 - \bar{f}_K(\bar{\epsilon})] + \delta_{v_0, j_0} \left( \frac{\lambda}{\hbar \Omega} \right)^2 (\nu_0 + 1)[1 - \bar{f}_K(\bar{\epsilon} - \hbar \Omega)] \right] + \delta_{v_0 - 1, j_0} \left( \frac{\lambda}{\hbar \Omega} \right)^2 \nu_0 [1 - \bar{f}_K(\bar{\epsilon} + \hbar \Omega)].
\]  \hspace{1cm} (S35)

where, \( \bar{\epsilon} = \epsilon_i - \lambda^2 / (\hbar \Omega)^2 \), is the elastic electronic charging energy. These rates are either

\[ \leq \frac{\Gamma^K}{\hbar} \] , for all the vibrationally elastic transitions (associated with \( \delta_{v_0, j_0} \)), or \( \leq \frac{\Gamma^K}{\hbar} \left( \frac{\lambda}{\hbar \Omega} \right)^2 \nu_0 \),

for inelastic transition (from the vibrational level associated with the quantum number, \( \nu_0 \)). Consequently, the time averaged rate equations (Eqs. (S22, S23)) are valid as long as,

\[ \frac{\epsilon_{\text{max}} - \epsilon_{\text{min}}}{\hbar} \gg \omega \gg \max \left( \frac{\Gamma^K}{\hbar} \nu_0 \left( \frac{\lambda}{\hbar \Omega} \right)^2, \frac{\Gamma^K}{\hbar} \right). \]  \hspace{1cm} (S36)

In the numerical simulations presented in the text, \( \left( \frac{\lambda}{\hbar \Omega} \right)^2 = \frac{1}{50} \), where \( 0 < \nu_0 < 60 \), which implies that, \( \nu_0 \left( \frac{\lambda}{\hbar \Omega} \right)^2 \geq 1 \). This implies that the time-averaged quantum master equations are valid as long as the field frequency is small in comparison to a realistic band width (\( \sim 1-10 \) \( eV \)) and large in comparison to \( \Gamma^K \). Restricting \( \Gamma^K \) to the weak molecule-lead coupling limit (\( \Gamma^K < 0.001 \) \( eV \), was considered in the numerical simulations) the time-averaged quantum master equations are capable of approximating the kinetics for a broad frequency range, \( 10^{-3} \leq \omega \leq 1 \) \( eV \).
E. The non-equilibrium vibrational temperature

Restricting again to the weak vibronic coupling limit as discussed above, the non-vanishing electronic transition rates are associated with an exchange of up to a single vibration quantum (Eq. (S35)). Using this result in the time-averaged quantum master equations (Eq. (S22)), obtain the following compact form,

\[
\dot{\rho}_{(0,v_0)} = W^h_0 \rho_{(1,v_0)} - W^e_0 \rho_{(0,v_0)} + \left( \frac{\lambda}{\hbar \Omega} \right)^2 \left[ (v_0)(W^h_{-1}\rho_{(1,v_0-1)} - W^e_{-1}\rho_{(0,v_0-1)}) + (v_0 + 1)(W^h_{1}\rho_{(1,v_0+1)} - W^e_{1}\rho_{(0,v_0+1)}) \right]
\]

\[
\dot{\rho}_{(1,v_0)} = W^e_0 \rho_{(0,v_0)} - W^h_0 \rho_{(1,v_0)} + \left( \frac{\lambda}{\hbar \Omega} \right)^2 \left[ (v_0 + 1)(W^e_{-1}\rho_{(0,v_0-1)} - W^h_{-1}\rho_{(1,v_0-1)}) + (v_0)(W^e_{1}\rho_{(0,v_0+1)} - W^h_{1}\rho_{(1,v_0+1)}) \right]
\]

(S37)

where, \( W^{elh}_p = \frac{1}{\hbar \Omega} \sum_{k-L,R} \Gamma_k \bar{f}_k^{(elh)}(\varepsilon) \rho_{(L,R)} \), are rates of electron(hole) transfer into the molecule in the presence of the driving field. Notice that each transfer event is associated with a gain (loss) of the electronic charging energy, \( \varepsilon = \epsilon_i - \lambda^2 / (\hbar \Omega)^2 \), plus \( v \) vibration quanta, where, \( \bar{f}_k^{(elh)}(\varepsilon) = 1 - \bar{f}_k^{(e)}(\varepsilon) \), and \( \bar{f}_k^{(e)}(\varepsilon) = \bar{f}_k(\varepsilon) \), is the generalizd Fermi distribution function (Eq. (S26)). For elastic transitions, \( p = 0 \), whereas \( p = \pm 1 \) correspond to inelastic transitions involving a single vibration quantum. When the vibrational excitation is restricted to low values (e.g., due to effective stabilization via the plasmon oscillations), we can additionally assume, \( \left( \frac{\lambda}{\hbar \Omega} \right)^2 v_0 \ll 1 \), which implies that the inelastic \( (p = \pm 1) \) contributions in Eq. (S37) are small with respect to the elastic \( (p = 0) \) ones. In this case, the electronic populations, \( \rho_{(L,R)} \) and \( \rho_{(0,v_0)} = \rho_{v_0} - \rho_{(1,v_0)} \), reach a fast steady state per each vibrational state[7],

\[
\rho_{(0,v_0)} = \frac{W^h_0}{W^h_0 + W^e_0} \rho_{v_0} , \text{ and, } \rho_{(1,v_0)} = \frac{W^e_0}{W^h_0 + W^e_0} \rho_{v_0} ,
\]

prior to any inelastic vibronic transition.
Substitution of these steady state values in Eq. (S37), one obtains an effective equation of motion for the molecular oscillator states,

$$\dot{\rho}_{\nu_0} = \nu_0 k_H \rho_{\nu_0+1} + (\nu_0 + 1) k_C \rho_{\nu_0+1} - (\nu_0 k_C + (\nu_0 + 1) k_H) \rho_{\nu_0},$$

(S38)

where, $k_H \equiv \left(\frac{\lambda}{\hbar \Omega}\right)^2 \frac{W_h^0 W_e^0 + W_e^0 W_h^0}{W_h^0 + W_e^0}$ and $k_C \equiv \left(\frac{\lambda}{\hbar \Omega}\right)^2 \frac{W_h^e W_e^h + W_h^e W_e^h}{W_h^e + W_e^e}$ are vibrational heating and cooling rates, respectively, owing to inelastic electronic pathways involving an exchange of a single vibration quantum with the molecule. The steady state solution of this equation ($\dot{\rho}_{\nu_0} = 0$) is readily obtained as[7],

$$\rho_{\nu_0} = \sum_{\nu_0} e^{-\beta \hbar \Omega \nu_0},$$

(S39)

$$\beta \equiv \frac{1}{\hbar \Omega} \ln \left(\frac{k_C}{k_H}\right) = \frac{1}{\hbar \Omega} \ln \left(\frac{W_h^0 W_e^0 + W_e^0 W_h^0}{W_h^e W_e^h + W_h^e W_e^h}\right),$$

(S40)

where $\beta$ is a the non-equilibrium inverse vibrational temperature.