

Charge Transfer through Single Molecules: Effects of IVR and Optical Excitation

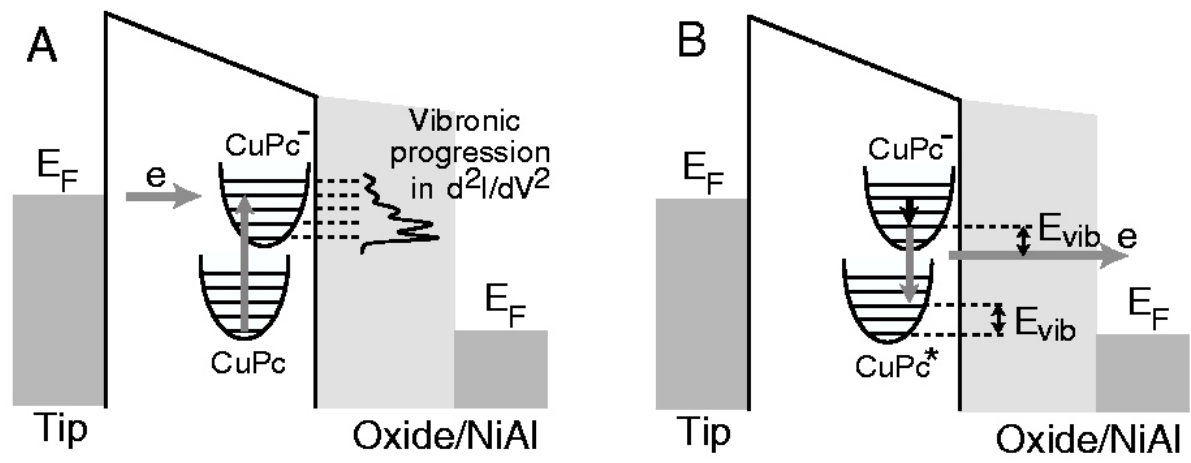
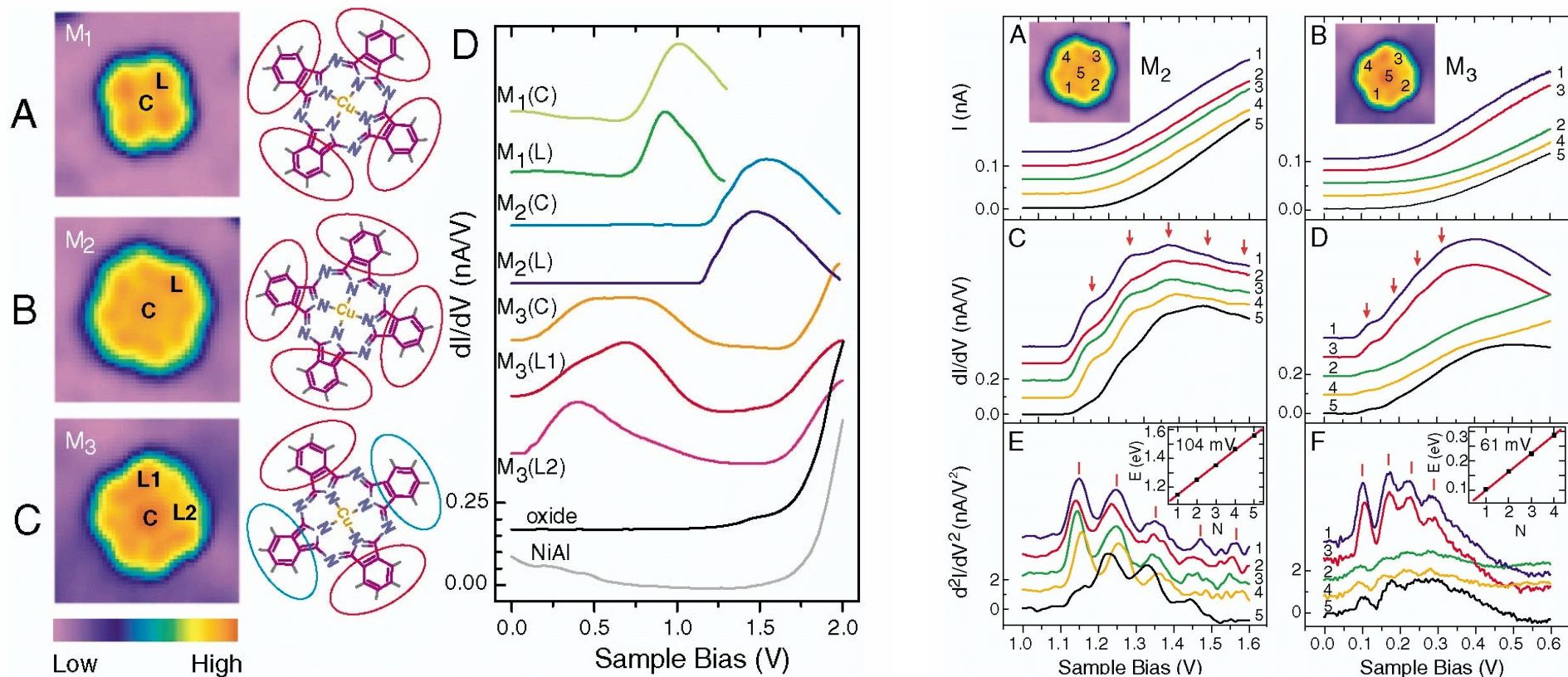
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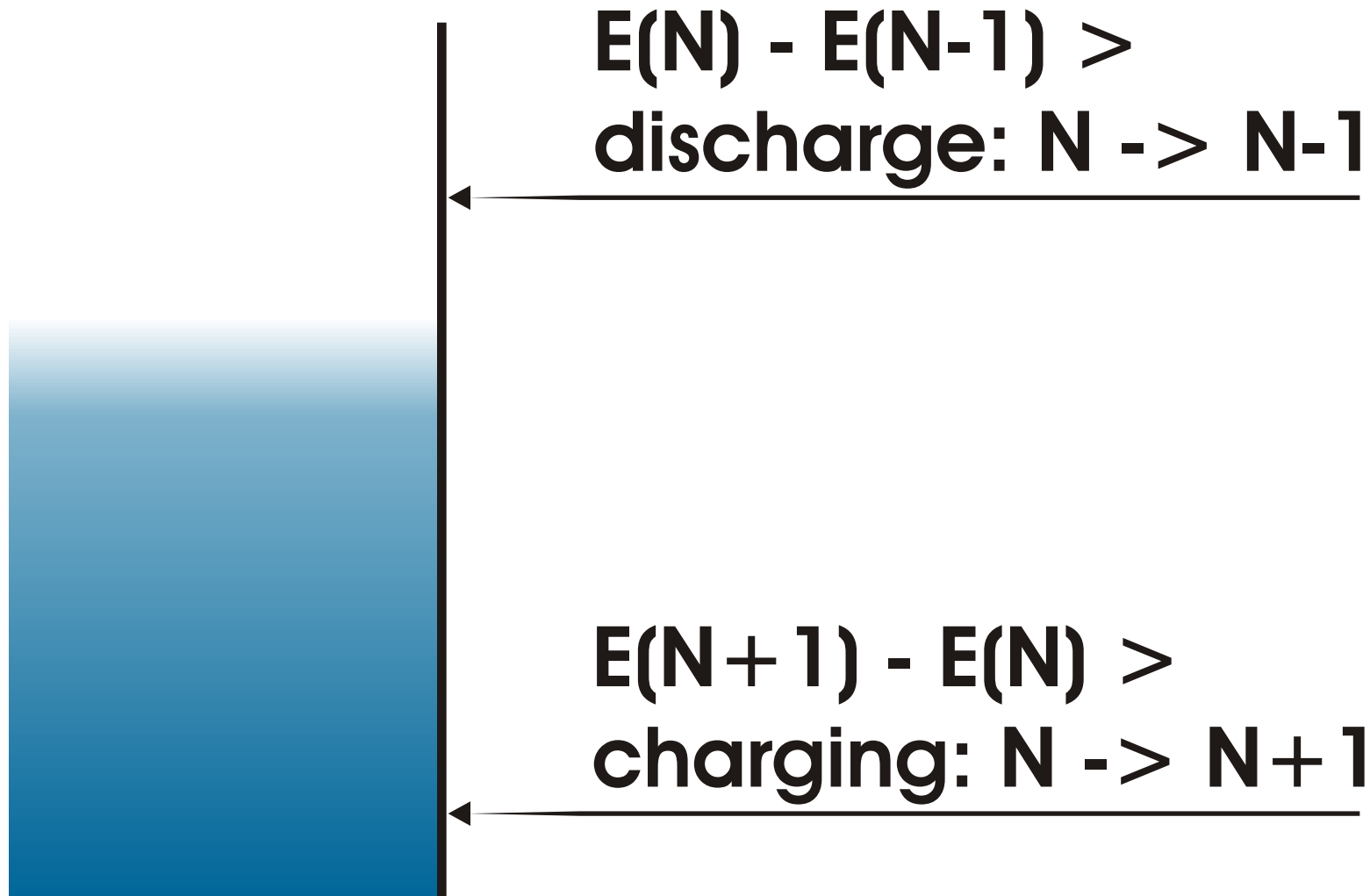
Contents:

- models and basic mechanisms
- small literature overview
- generalized rate equation approach
- nonequilibrium vibrational states - effect of IVR
- control of the current by cw optical excitations

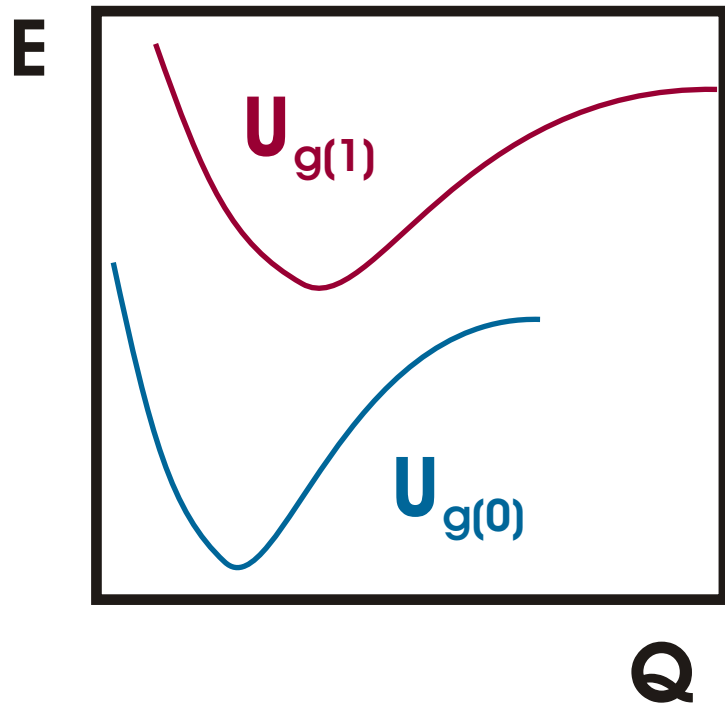
Qui et al. PRL 92, 206102 (2004): Vibronic States in Single Molecule Electron Transport (copper phthalocyanine on NiAl(1 1 0) and Al₂O₃)



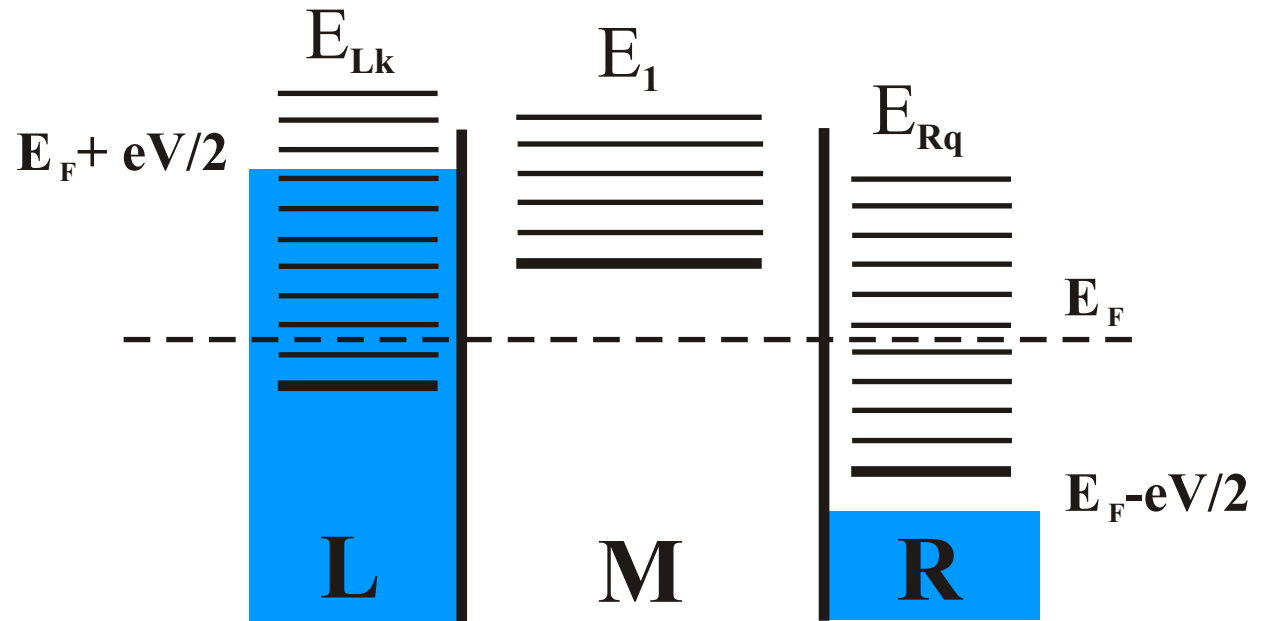
Total Energy of the Molecule and Charging and Discharge



IV Characteristics and the Influence of IVR

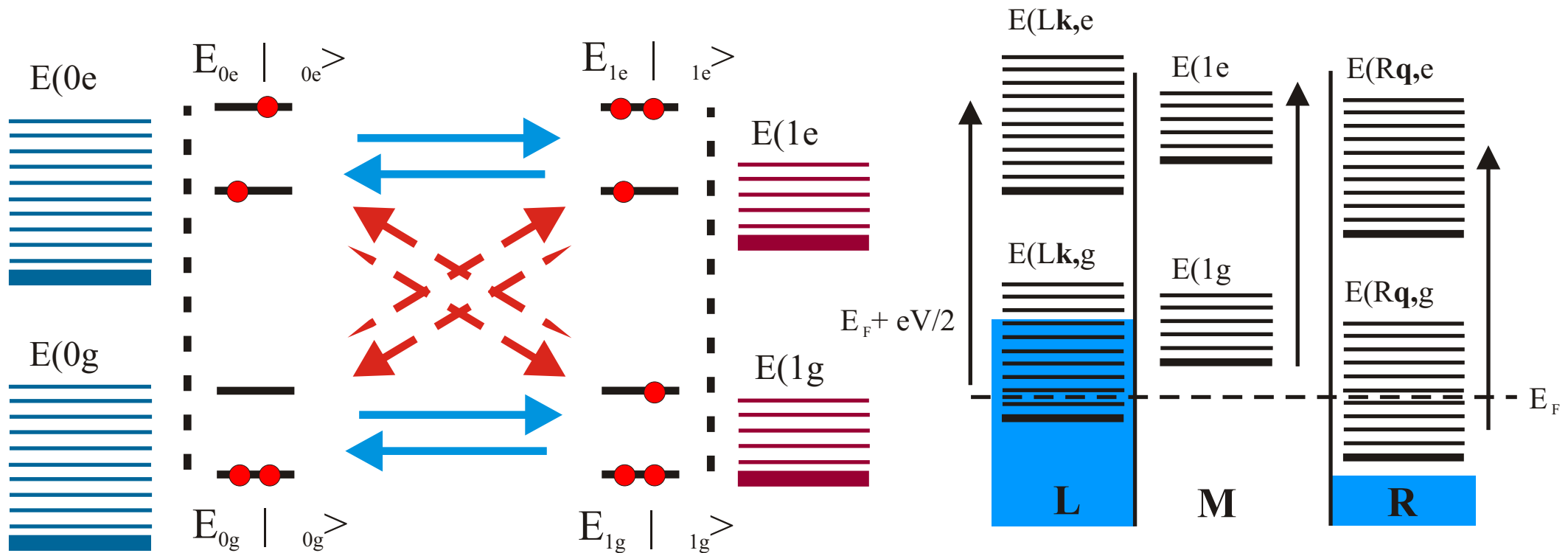


Potential energy surfaces of the neutral and singly charged molecule.



Energy level scheme for charge transmission through a molecule (M) embedded in between a left (L) and right (R) electrode.

IV Characteristics and Optical Excitation



HOMO-LUMO scheme for a molecule in between two leads. Arrows connecting different HOMO and LUMO levels indicate the opening of new transmission channels.

Energy level scheme for a molecule characterized by its ground as well as its first excited electronic state in between two leads.

Inelastic Charge Transmission through Single Molecules

- perturbation theory with respect to the electron vibrational coupling
 - > Lehmann, Hänggi
 - > Nitzan, Galperin
- nonperturbative account of electron vibrational coupling
 - > Petrov, Hänggi
 - > von Oppen
 - > Wegewijs
 - > Thoss, Domcke
- nonequilibrium molecular vibrational states
 - > von Oppen
 - > Wegewijs

FORMULAS FOR THE CURRENT

NGF Expression

$$I = \int \frac{d\omega}{2\pi} \text{tr}_{\text{wire}} \{ \hat{\Sigma}^<(\omega) \hat{G}^>(\omega) - \hat{\Sigma}^>(\omega) \hat{G}^<(\omega) \}$$

Landauer expression including molecular vibrations

$$I_{L \rightarrow R} = 4\pi |e| \int d\Omega d\bar{\Omega} f_{\text{Fermi}}(\hbar\Omega - \mu_L) [1 - f_{\text{Fermi}}(\hbar\bar{\Omega} - \mu_R)] \sum_{M,N} f(\hbar\omega_M) \delta(\bar{\Omega} + \omega_N - \Omega - \omega_M) \\ \times \sum_{a,b,c,d} \Gamma_{ab}^{(L)}(\Omega) \langle \varphi_b \chi_N | \hat{G}^+(\Omega + \omega_M) | \chi_M \varphi_c \rangle \Gamma_{cd}^{(R)}(\bar{\Omega}) \langle \varphi_d \chi_M | \hat{G}(\bar{\Omega} + \omega_N) | \chi_N \varphi_a \rangle$$

ELMAR'S APPROACH – Chem. Phys. 326 (2006) 151

Multi-electron distribution $\mathcal{P}_a = \langle a | \text{tr}_B \{ \hat{\rho}^{(S-B)}(t) \} | a \rangle$

Multi-electron lead-molecule states

$$|a\rangle = \prod_{\mathbf{k},s} |N_{L\mathbf{k}s}\rangle \times |M(N)\rangle \times \prod_{\mathbf{q},s'} |N_{R\mathbf{q}s'}\rangle$$

Balance-like equations $\frac{\partial}{\partial t} \mathcal{P}_a(t) = - \sum_b (\mathcal{K}_{a \rightarrow b} \mathcal{P}_a(t) - \mathcal{K}_{b \rightarrow a} \mathcal{P}_b(t))$

Basic approximation

$$\mathcal{P}_a(t) \sim \prod_{\mathbf{k},s} P(N_{L\mathbf{k}s}, t) \times P(M(N), t) \times \prod_{\mathbf{q},s'} P(N_{R\mathbf{q}s'}, t)$$

Single electron distribution

$$P_{L\mathbf{k}s}(t) = \sum_{N_{L\mathbf{k}s}=0,1} N_{L\mathbf{k}s} P(N_{L\mathbf{k}s}, t)$$

Control of Charge Transmission by External Fields

- strong field modulation of excess electron levels
 - > Lehmann, Hänggi
 - > Kleinekathoefer
- radiative transitions in the charge transmitting molecule
 - > Hettler, Schoeller
 - > Kirczenow
 - > Wegewijs
 - > Nitzan, Galperin
- optical excitation of the charge transmitting molecule
 - > Nitzan, Galperin
- radiative transition in the charge transmitting molecule
 - > Nitzan, Galperin

Generalized Rate Equation Approach

THE MOLECULE-LEAD MODEL

Total Hamiltonian

$$H = H_{\text{mol}} + H_{\text{IVR}} + H_{\text{R}} + H_{\text{field}}(t) + H_{\text{lead}} + H_{\text{mol-lead}}$$

Molecular Electron-Vibrational Part

$$H_{\text{mol}} = \sum_{N,a(N)} (T_{\text{vib}} + U_{a(N)}(Q)) |\phi_{a(N)}\rangle \langle \phi_{a(N)}| = \sum_{\alpha=N,a(N),\nu} \hbar \varepsilon_{\alpha} |\Psi_{\alpha}\rangle \langle \Psi_{\alpha}|$$

Intramolecular Vibrational Energy Redistribution

$$H_{\text{IVR}} = \sum_{N,a(N)} V_{a(N)}^{(\text{IVR})}(Q, Z) |\phi_{a(N)}\rangle \langle \phi_{a(N)}|$$

Coupling to External Time-Dependent Fields

$$H_{\text{field}}(t) = -\mathbf{E}(t) \hat{\mu}$$

Lead Part

$$H_{\text{lead}} = \sum_X \sum_{\mathbf{k},s} E_{X\mathbf{k}s} a_{X\mathbf{k}s}^+ a_{X\mathbf{k}s}$$

Molecule–Lead Coupling 1 – Single Electron Exchange

$$\begin{aligned} & H_{\text{mol–lead}}^{(1)} \\ &= \sum_{N,a(N+1),b(N)} \sum_{X,\mathbf{k},s} V_X(a(N+1), b(N), \mathbf{k}s) a_{X\mathbf{k}s} |\phi_{a(N+1)}\rangle \langle \phi_{b(N)}| \\ &+ \sum_{N,a(N-1),b(N)} \sum_{X,\mathbf{k},s} V_X(a(N-1), b(N), \mathbf{k}s) a_{X\mathbf{k}s}^+ |\phi_{a(N-1)}\rangle \langle \phi_{b(N)}| \end{aligned}$$

Molecule–Lead Coupling 2 – Electron–Hole Pair Excitation

$$H_{\text{mol–lead}}^{(2)} = \sum_{N,a(N),b(N)} \sum_{X,\mathbf{k},\mathbf{q},s} V_X(a(N), b(N), \mathbf{k}, \mathbf{q}s) a_{X\mathbf{k}s}^+ a_{X\mathbf{q}s} |\phi_{a(N)}\rangle \langle \phi_{b(N)}|$$

GENERALIZED RATE EQUATIONS

Population of the Electron–Vibrational States

$$P_\alpha(t) = \text{tr}\{\hat{\Pi}_\alpha \mathcal{P} \hat{W}(t)\}$$

Projection Superoperator

$$\mathcal{P} \dots = \sum_\alpha \hat{W}_{\text{lead}} \hat{R}_R \hat{\Pi}_\alpha \text{tr}\{\hat{\Pi}_\alpha \dots\}$$

Projector on the Electron–Vibrational States

$$\hat{\Pi}_\alpha = |\chi_{\alpha(N)\mu}\rangle |\phi_{\alpha(N)}\rangle \langle \phi_{\alpha(N)}| \langle \chi_{\alpha(N)\mu}| \equiv |\Psi_\alpha\rangle \langle \Psi_\alpha|$$

Generalized Rate Equations

$$\frac{\partial}{\partial t} P_\alpha(t) = - \sum_\beta \int_{t_0}^{\infty} d\bar{t} (K_{\alpha \rightarrow \beta}(t, \bar{t}) P_\alpha(\bar{t}) - K_{\beta \rightarrow \alpha}(t, \bar{t}) P_\beta(\bar{t}))$$

Transition Kernels $\alpha \neq \beta$

$$K_{\alpha \rightarrow \beta}(t, \bar{t}) = -\frac{1}{\hbar^2} \Theta(t - \bar{t}) \text{tr}\{(\hat{\Pi}_\beta, \hat{V}(t))_- \times \mathcal{U}_Q(t, \bar{t})(\hat{V}(\bar{t}), \hat{W}_{\text{lead}} \hat{R}_R \hat{\Pi}_\alpha)_-\}$$

Time–Evolution Superoperator

$$\mathcal{U}_Q(t, \bar{t}) = \mathcal{T} \exp\left(-i \int_{\bar{t}}^t d\tau \mathcal{Q} \mathcal{L}(\tau)\right)$$

Absence of Time–Dependent External Fields

$$\begin{aligned} K_{\beta\alpha}(\omega) &= -\frac{i}{\hbar^2} \text{tr}\{(\hat{\Pi}_\beta, \hat{V})_- \times \mathcal{G}_Q(\omega)(\hat{V}, \hat{W}_{\text{lead}} \hat{R}_R \hat{\Pi}_\alpha)_-\} \\ &= -\delta_{\beta,\alpha} \sum_\gamma K_{\beta \rightarrow \gamma}(\omega) + (1 - \delta_{\beta,\alpha}) K_{\alpha \rightarrow \beta}(\omega) \end{aligned}$$

Rate Expression with the Complete Green's Superoperator

$$L_{\beta\alpha}(\omega) = -\frac{i}{\hbar^2} \text{tr}\{(\hat{\Pi}_\beta, \hat{V}(t))_- \times \mathcal{G}(\omega)(\hat{V}, \hat{W}_{\text{lead}} \hat{R}_R \hat{\Pi}_\alpha)_-\}$$

$$K_{\alpha\beta}(\omega) = L_{\alpha\beta}(\omega) - \frac{i}{\omega + i\epsilon} \sum_\gamma L_{\alpha\gamma}(\omega) K_{\gamma\beta}(\omega) \approx L_{\alpha\beta}^{(2)} + L_{\alpha\beta}^{(4)} - \frac{i}{\omega + i\epsilon} \sum_\gamma L_{\alpha\gamma}^{(2)}(\omega) L_{\gamma\beta}^{(2)}(\omega)$$

THE CURRENT FORMULA

Nonstationary Current through Lead X

$$I_X(t) = -|e| \frac{\partial}{\partial t} \text{tr} \{ \hat{W}(t) \sum_{\mathbf{k},s} a_{X\mathbf{k}s}^+ a_{X\mathbf{k}s} \} = |e| \sum_{\alpha} \int_{t_0}^{\infty} d\bar{t} K_{\alpha \rightarrow X}(t, \bar{t}) P_{\alpha}(\bar{t})$$

Current Kernel

$$K_{\alpha \rightarrow X}(t, \bar{t}) = -\frac{i}{\hbar^2} \Theta(t - \bar{t}) \text{tr} \{ (\sum_{\mathbf{k},s} a_{X\mathbf{k}s}^+ a_{X\mathbf{k}s}, H_{\text{mol-lead}})_- \times \mathcal{U}_{\mathcal{Q}}(t, \bar{t}) (\hat{V}(\bar{t}), \hat{W}_{\text{lead}} \hat{R}_{\text{R}} \hat{\Pi}_{\alpha})_- \}$$

SEQUENTIAL CHARGE TRANSMISSION

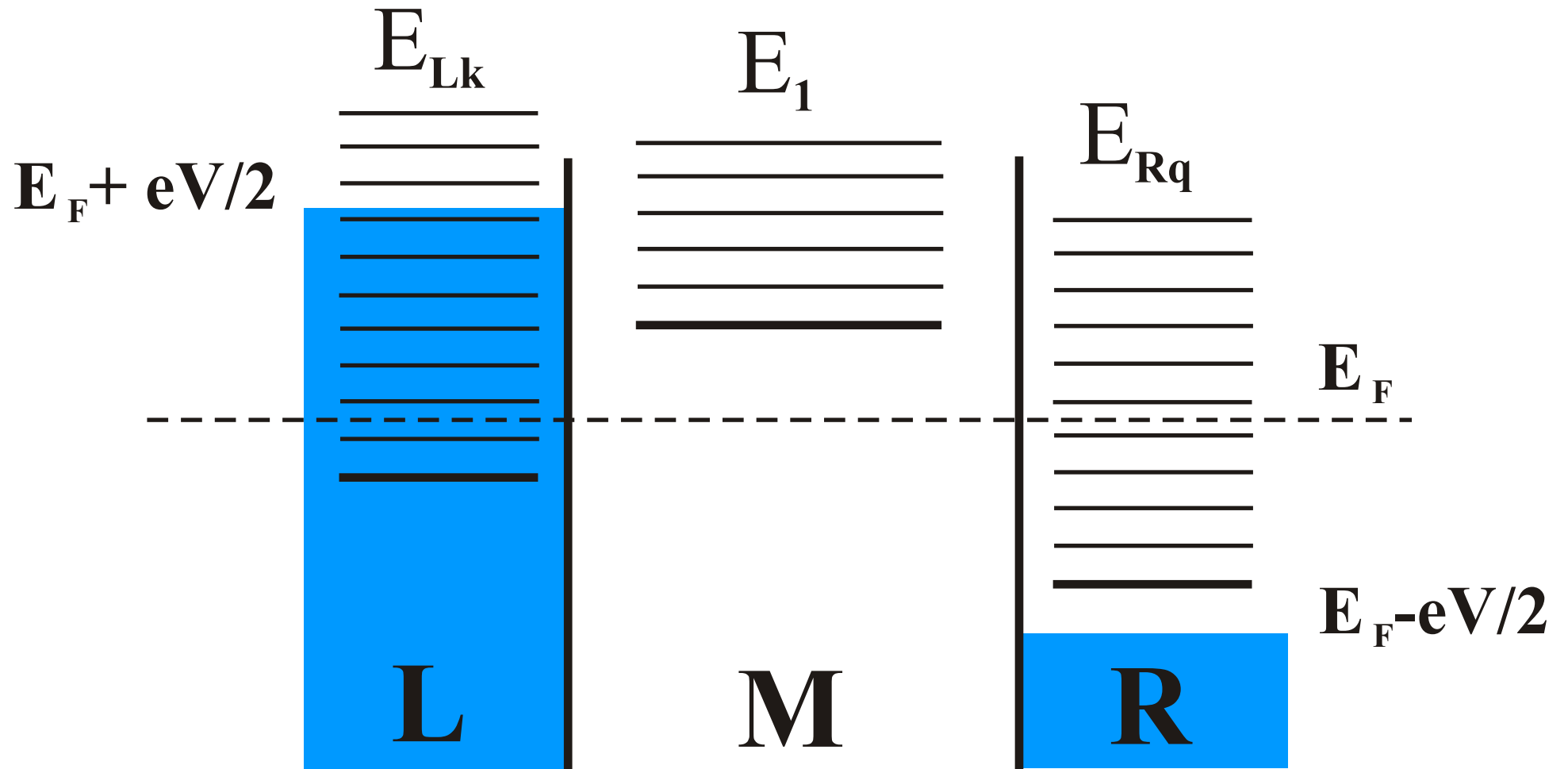
Stationary Current

$$I^{(\text{stat})} = |e| \sum_{\alpha} K_{\alpha \rightarrow X}(\omega = 0) P_{\alpha}^{(\text{stat})}$$

Stationary Limit of the Generalized Rate Equations

$$0 = \sum_{\beta} (K_{\alpha \rightarrow \beta}(\omega = 0) P_{\alpha}^{(\text{stat})} - K_{\beta \rightarrow \alpha}(\omega = 0) P_{\beta}^{(\text{stat})})$$

IV Characteristics and the Influence of IVR



IV CHARACTERISTICS AND THE INFLUENCE OF IVR

single reaction coordinate model

neutral state of the molecule: $P_{0\mu}$

singly charged state of the molecule: $P_{1\nu}$

Stationary Current

$$I \equiv I_L = 2|e| \sum_{\mu,\nu} k_{L, 0\mu \rightarrow 1\nu}^{(\text{mol-lead})} P_{0\mu}(t \rightarrow \infty) - 2|e| \sum_{\mu,\nu} k_{L, 1\nu \rightarrow 0\mu}^{(\text{mol-lead})} P_{1\nu}(t \rightarrow \infty)$$

Molecule-Lead Transfer Rates

$$k_{1\mu \rightarrow 0\nu}^{(\text{mol-lead})} = \frac{4\pi}{\hbar^2} |\langle \chi_{1\mu} | \chi_{0\nu} \rangle|^2 \sum_X \mathcal{N}_X(\varepsilon(1\mu, 0\nu)) |V_X(1, 0, \varepsilon(1\mu, 0\nu))|^2 \times [1 - f_F(\hbar\varepsilon(1\mu, 0\nu) - \mu_X)]$$

Rate of IVR

$$k_{a(N)\mu \rightarrow a(N)\nu}^{(\text{IVR})} = |m(a\mu, a\nu)|^2 ([1 + n(\varepsilon_{a\mu, a\nu})] J_a(\varepsilon_{a\mu, a\nu}) + n(\varepsilon_{a\nu, a\mu}) J_a(\varepsilon_{a\nu, a\mu}))$$

Relaxation Time Approximation

$$\left(\frac{\partial}{\partial t} P_{a\mu}\right)_{\text{IVR}} = -\frac{1}{\tau_{\text{IVR}}} \{P_{a\mu} - f_{\text{th}}(\hbar\omega_{a\mu}) \sum_{\nu} P_{a\nu}\}$$

PARAMETERS

$$\hbar\varepsilon_{10} - \mu_0 = 100 \text{ meV}$$

broad-band approximation

$$\mathcal{N}_\chi(\Omega)/\hbar = \bar{\mathcal{N}}/\hbar = 10/\text{eV} \quad \bar{V} = 10 \text{ meV}$$
$$\Gamma = \pi\bar{\mathcal{N}}|\bar{V}/\hbar|^2 \approx 3 \text{ meV}$$

symmetrically applied voltage

$$\mu_L = \mu_0 + |e|V/2 \text{ and } \mu_R = \mu_0 - |e|V/2$$

PES

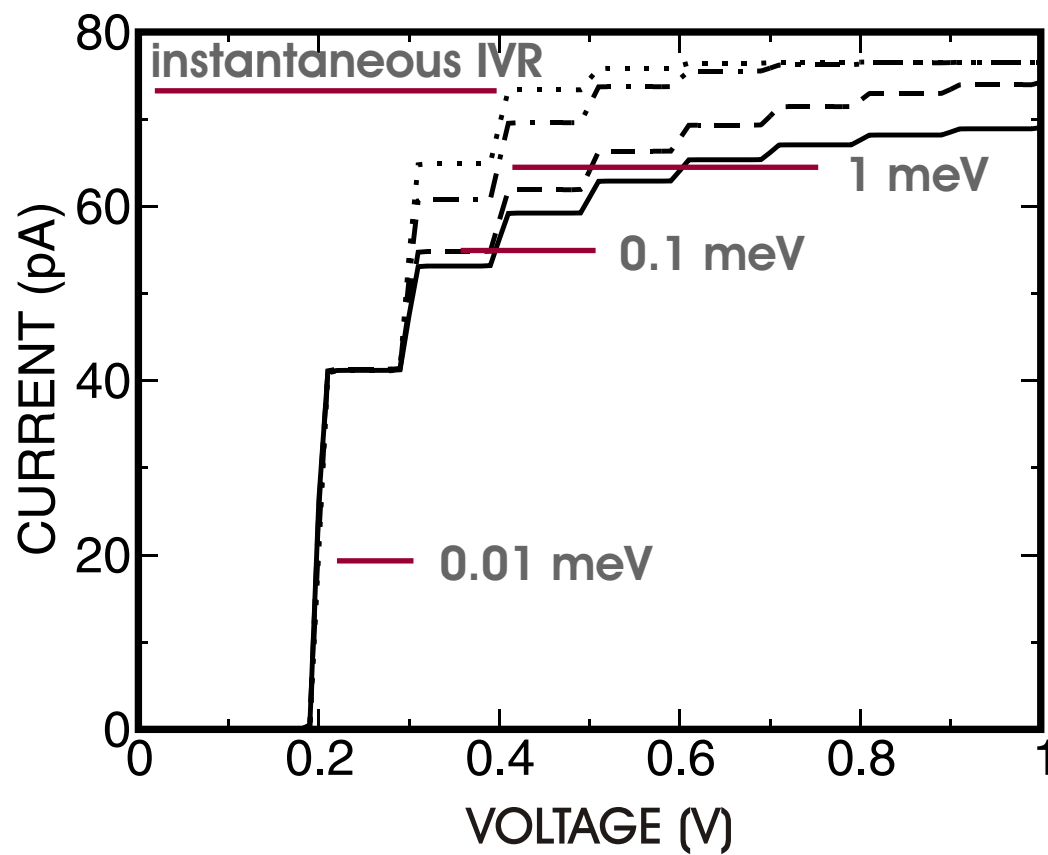
$$U_a(Q) = \hbar\omega_{\text{vib}}(Q + 2g_0)^2/4 \quad \hbar\omega_{\text{vib}} = 50 \text{ meV}$$

Reorganization energy

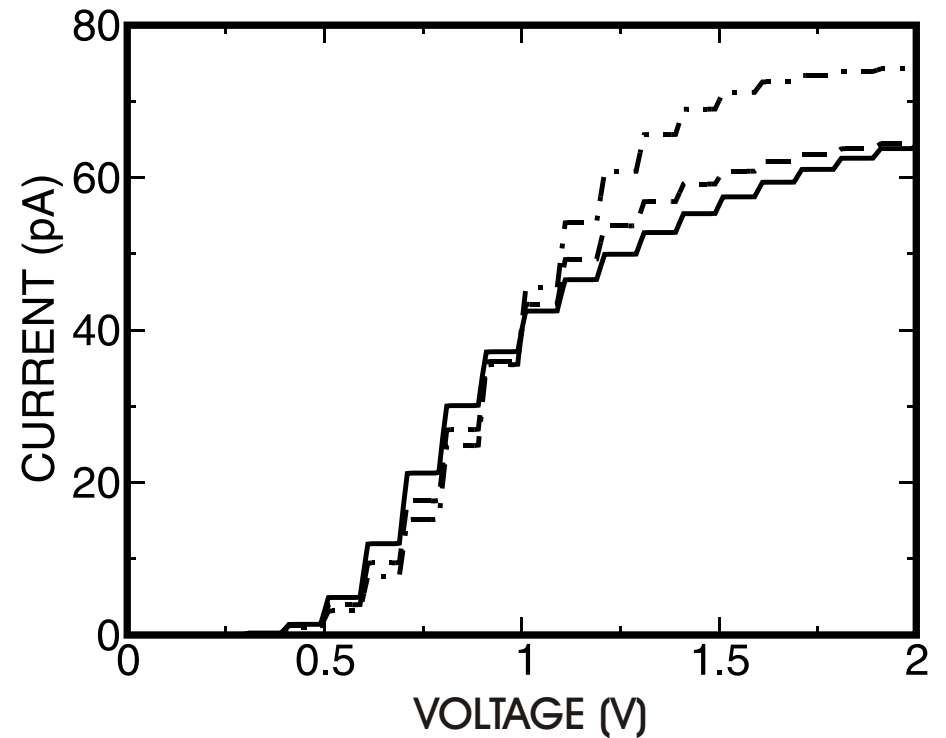
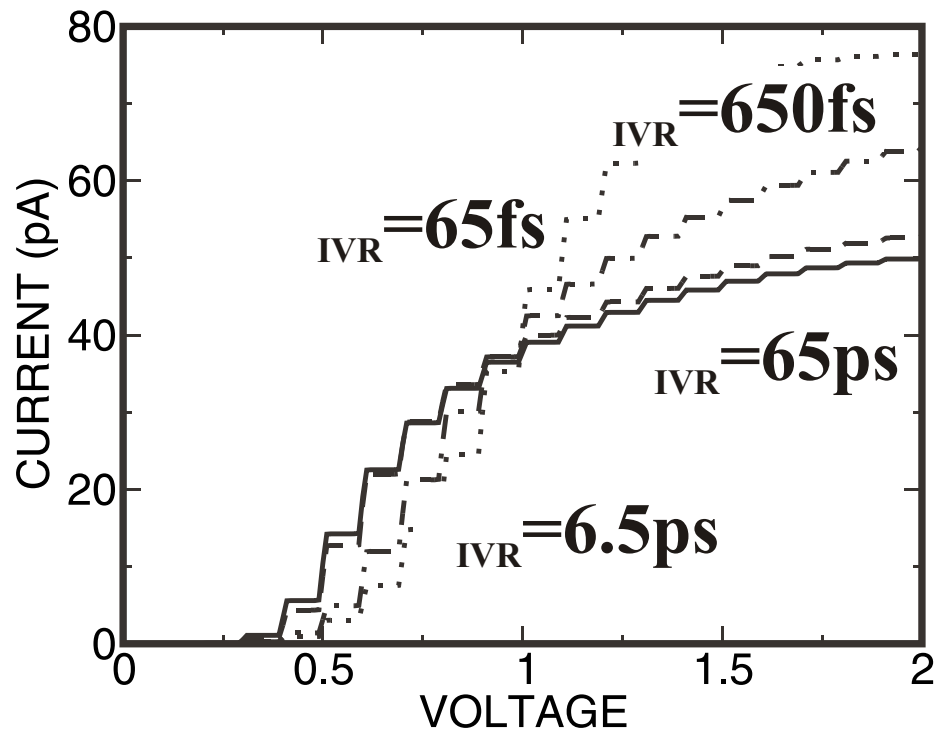
$$E_\lambda = \hbar\omega_{\text{vib}}\Delta g^2$$
$$\Delta g = 1 \implies E_\lambda = 50 \text{ meV}$$
$$\Delta g = 3 \implies E_\lambda = 450 \text{ meV}$$

Rate of IVR

$$k_{a\mu \rightarrow a\nu}^{(\text{IVR})} = \delta_{\nu, \mu+1}(\mu + 1)n(\omega_{\text{vib}})J_a(\omega_{\text{vib}}) + \delta_{\nu, \mu-1}\mu[1 + n(\omega_{\text{vib}})]J_a(\omega_{\text{vib}})$$



IV-characteristics for a bilinear coupling model of IVR and for $E_R = 50$ meV. Variation of J .



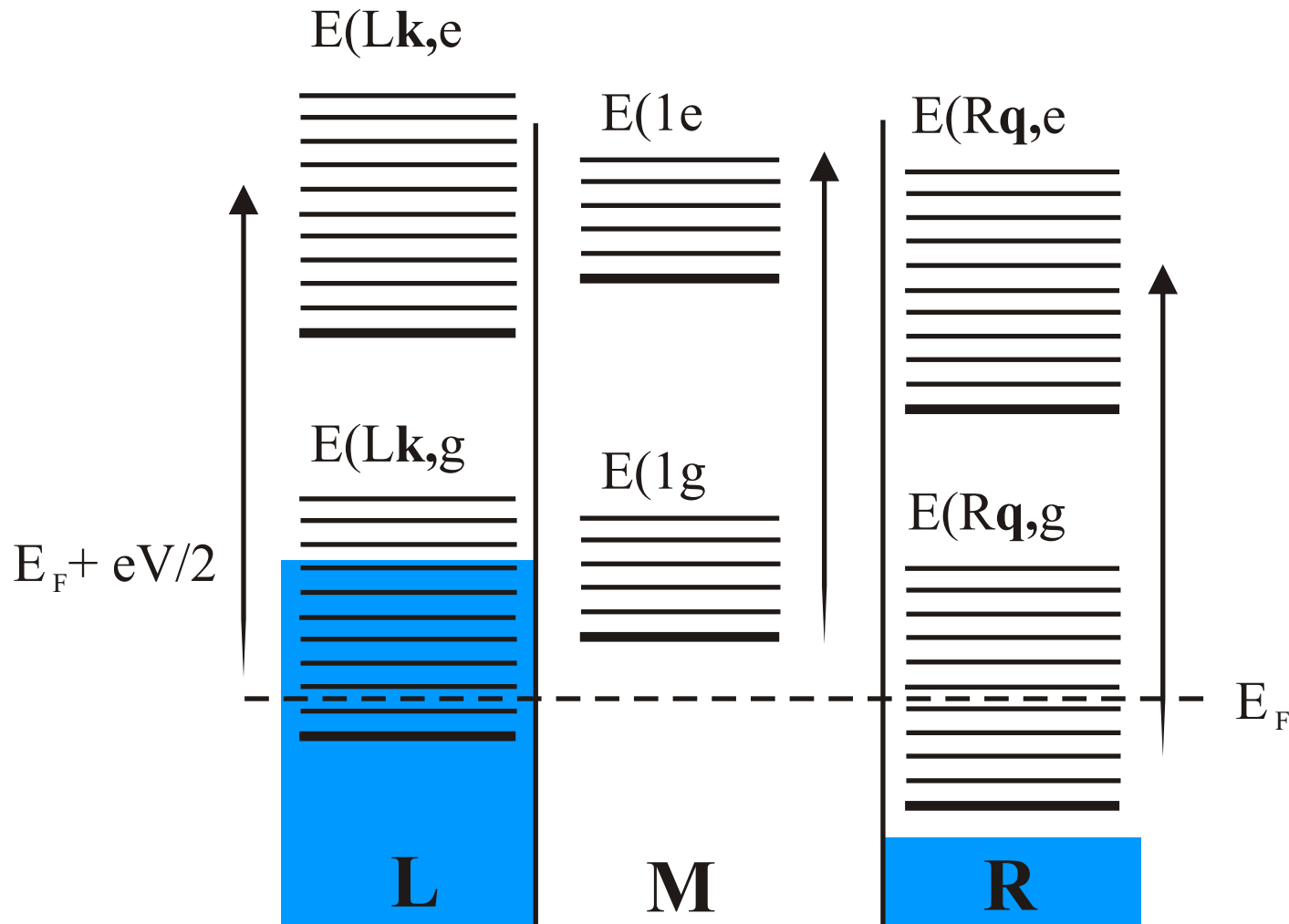
IV-characteristics for a bilinear coupling model of IVR at $k_b T = 1 \text{ meV}$ and for $E = 450 \text{ meV}$ ($g = 3$)

Left panel, dotted line: instantaneous IVR).

Right panel: full line identical with dashed--dotted line of the left panel, other lines: relaxation time approximation with $1/\text{IVR} = J$.

Dashed line: $\hbar J = 1 \text{ meV}$, dashed-dotted line: $\hbar J = 10 \text{ meV}$

IV Characteristics and Optical Excitation



IV CHARACTERISTICS AND OPTICAL EXCITATION

single reaction coordinate model

neutral state of the molecule: $P_{0g\mu}$ and $P_{0e\mu}$

singly charged state of the molecule: $P_{1g\nu}$ and $P_{1e\nu}$

Stationary Current

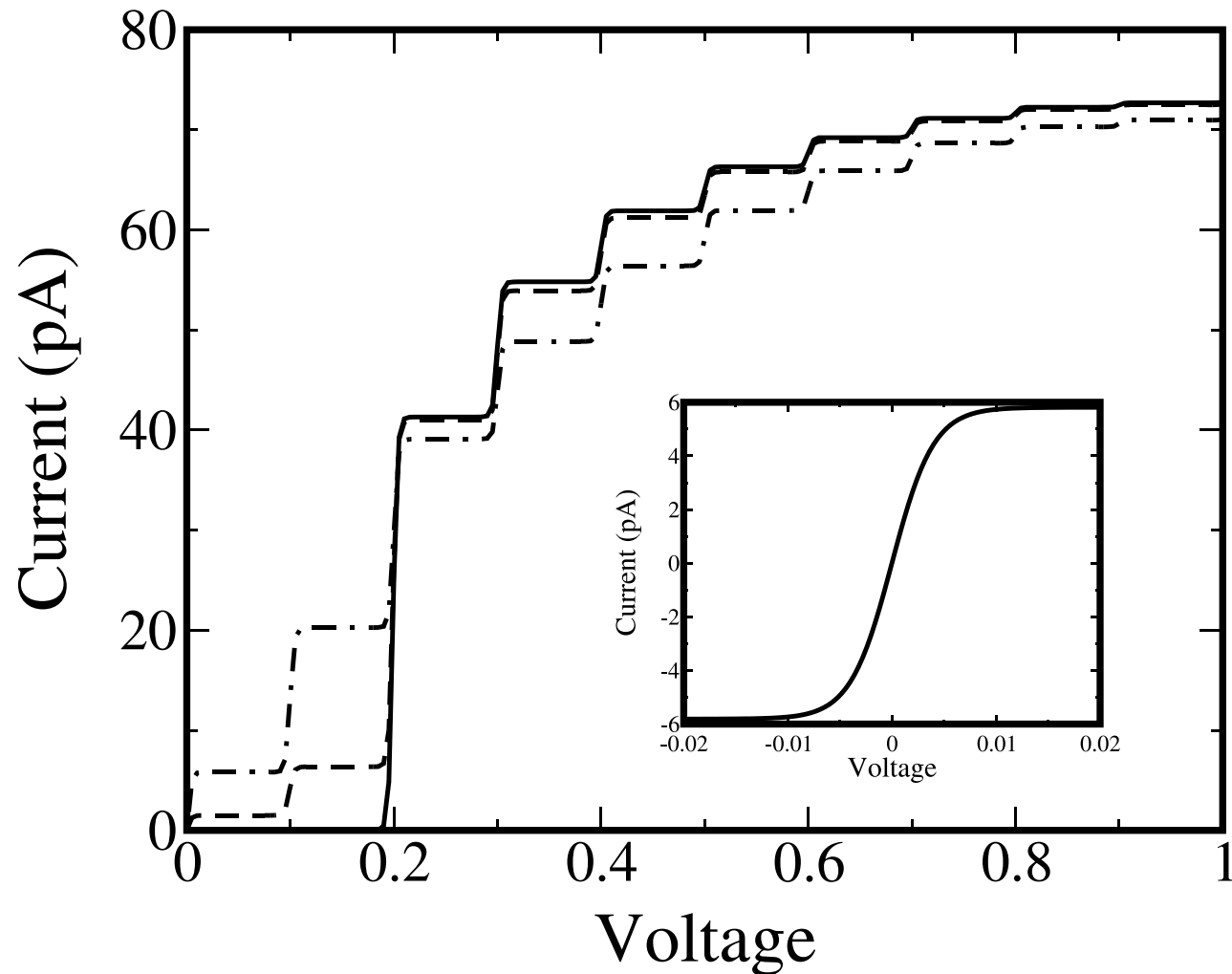
$$I = 2|e| \sum_{\mu,\nu} ([k_{0g\mu \rightarrow 1g\nu}^{(\text{mol-L})} + k_{0g\mu \rightarrow 1e\nu}^{(\text{mol-L})}] P_{0g\mu}(t) + [k_{0e\mu \rightarrow 1g\nu}^{(\text{mol-L})} + k_{0e\mu \rightarrow 1e\nu}^{(\text{mol-L})}] P_{0e\mu}(t) \\ - [k_{1g\nu \rightarrow 0g\mu}^{(\text{mol-L})} + k_{1g\nu \rightarrow 0e\mu}^{(\text{mol-L})}] P_{1g\nu}(t) - [k_{1e\nu \rightarrow 0g\mu}^{(\text{mol-L})} + k_{1e\nu \rightarrow 0e\mu}^{(\text{mol-L})}] P_{1e\nu}(t))$$

Optical Transitions

$$k_{Na\mu \leftrightarrow Nb\nu}^{(\text{opt})} = 2|\Omega_{Na,Nb}|^2 |\langle \chi_{Na\mu} | \chi_{Nb\nu} \rangle|^2 \frac{\gamma_{Na\mu, Nb\nu}}{(\omega_0 - \varepsilon_{Na\mu, Nb\nu})^2 + \gamma_{Na\mu, Nb\nu}^2}$$

Rabi Energy $\hbar\Omega_{Na,Nb} = (1 - \delta_{Na,Nb})\mathbf{d}_{Na,Nb}\mathbf{E}_0$

Decay of Excited States $k_{Ne\mu \rightarrow Ng\nu}^{(\text{lum})} = r_N^{(\text{lum})} |\langle \chi_{Ne\mu} | \chi_{Ng\nu} \rangle|^2$

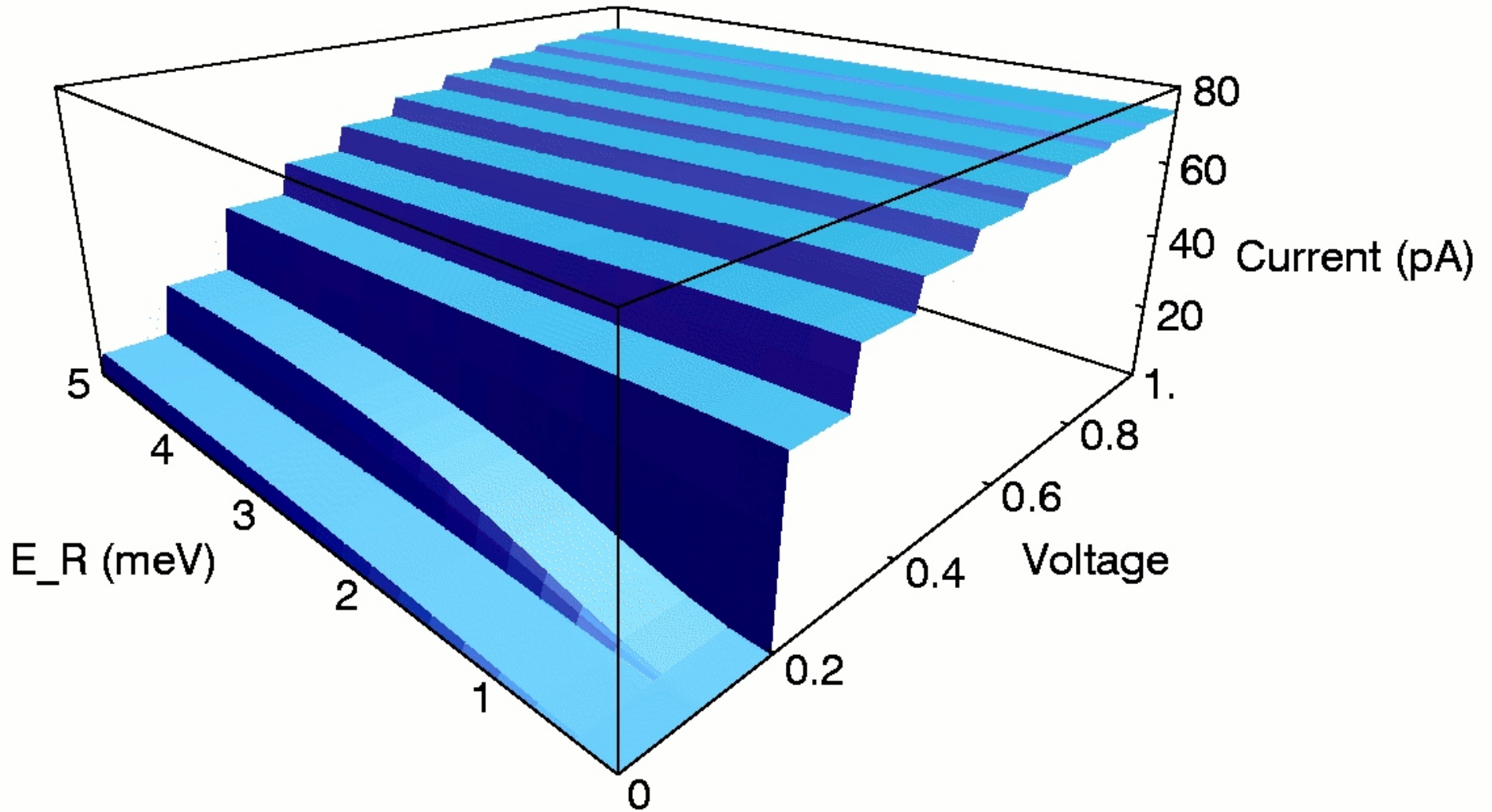


IV-characteristics at a cw-excitation of the molecule. Variation of the excitation intensity (case of small reorganization energy upon charging, excitation in the Franck-Condon transition region, $J = 0.1$ meV). Variation of E_R

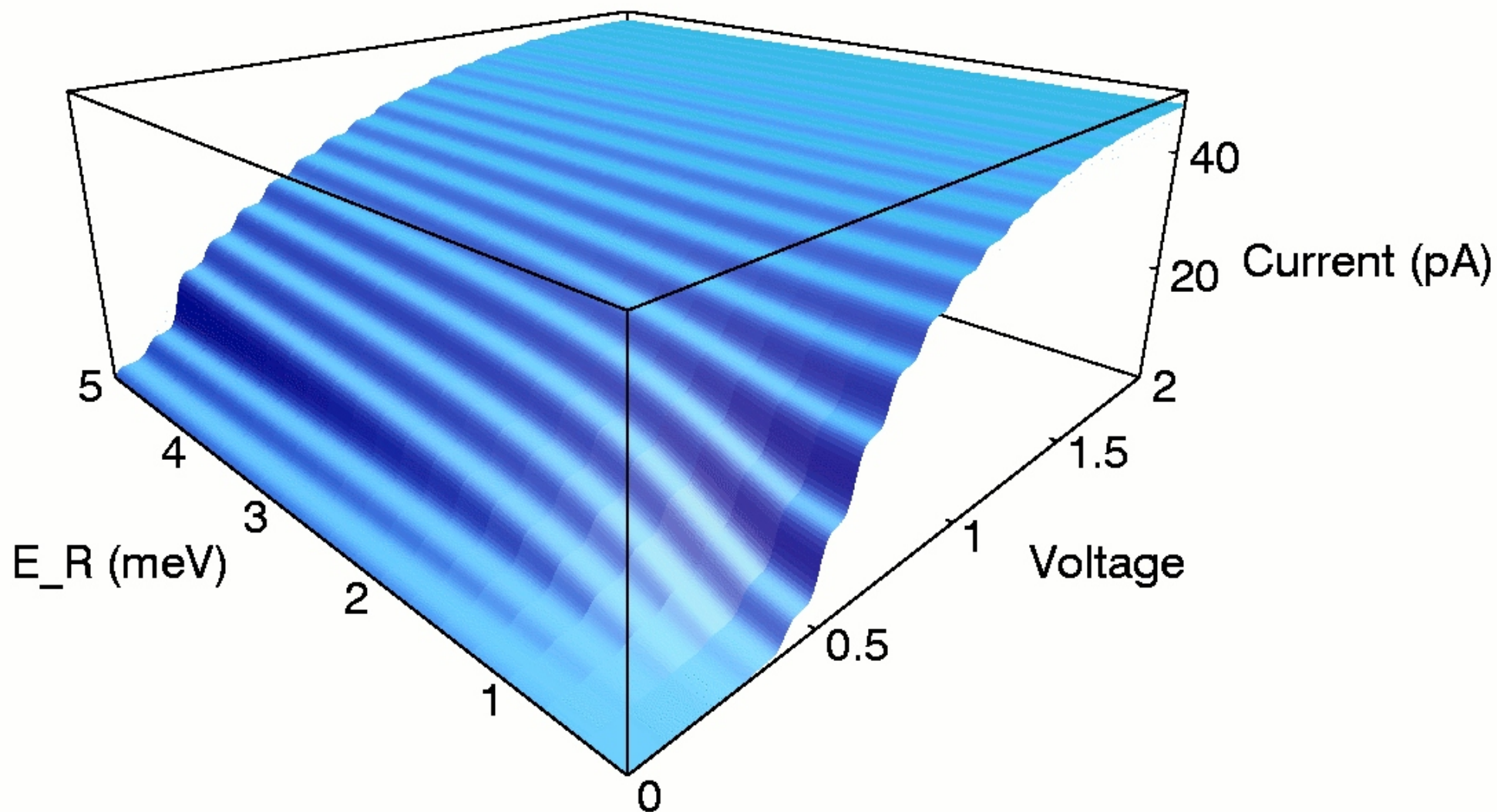
full line: $E^{\wedge}(R)_0 = E^{\wedge}(R)_1 = 0.001$ meV, $r^{\wedge}(\text{lum})_0 = r^{\wedge}(\text{lum})_1 = 0.001$ meV,

dashed line: $E^{\wedge}(R)_0 = E^{\wedge}(R)_1 = 1$ meV, $r^{\wedge}(\text{lum})_0 = r^{\wedge}(\text{lum})_1 = 1$ meV,

dashed-dotted line: $E^{\wedge}(R)_0 = E^{\wedge}(R)_1 = 5$ meV, $r^{\wedge}(\text{lum})_0 = r^{\wedge}(\text{lum})_1 = 2$ meV.



IV-characteristics versus intensity of cw-excitation of the molecule (case of small reorganization energy upon charging) excitation in the Franck-Condon transition region, ($J = 0.1$ meV, $r_0^{(\text{lum})} = r_1^{(\text{lum})} = 0.1$ meV, $T = 0.1$ meV). Optical excitation is characterized by the Rabi energies E_R (identical for the transition in the neutral and singly charged molecule).



IV-characteristics versus intensity of cw-excitation of the molecule (case of large reorganization energy upon charging, excitation in the Franck-Condon transition region, ($J = 0.1$ meV, $r^{(lum)}_0 = r^{(lum)}_1 = 0.1$ meV, $T = 0.5$ meV).

Optical excitation is characterized by the Rabi energies E_R (identical for the transition in the neutral and singly charged molecule),